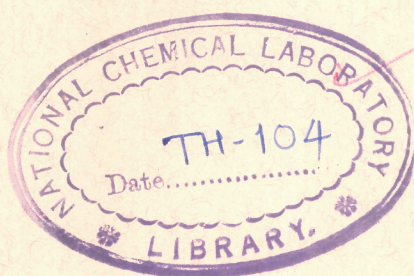


cc/ *hali* ✓

COMPUTERISED



STUDIES IN SYNTHETIC DYES - REACTIVE DY
CONTAINING AMINO GROUPS

A THESIS
PRESENTED TO
UNIVERSITY OF SOVIET
CENTRE DEPT. OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY

COMPUTERISED

N. V. BADANI

1983 & 1984

NATIONAL CHEMICAL LABORATORY

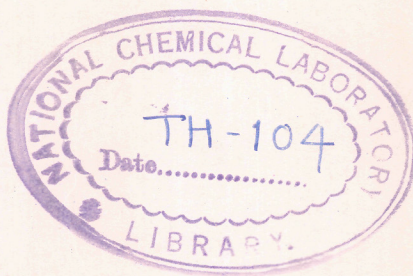
POONA 411 008 (India)

APRIL 1985

STUDIES IN SYNTHETIC DYES - REACTIVE DYES CONTAINING AZIDO GROUPS

A THESIS
SUBMITTED TO THE
UNIVERSITY OF BOMBAY
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

By
N. V. BADAMI
B. Sc.; B. Sc. (Tech.)



668-811 (043)
BAD

NATIONAL CHEMICAL LABORATORY
POONA 411 008 (India)

APRIL 1974

ATATEMENT REQUIRED TO BE SUBMITTED UNDER RULE 0.413 OF
THE UNIVERSITY OF BOMBAY

COMPUTERISED

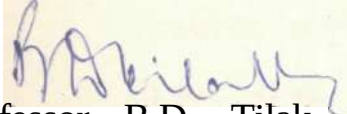
No part of this work has been submitted for a degree or diplome or other academic award. The literature concerning the problem investigated has been surveyed, and all the necessary references are given. The experimental work has been carried out entirely by me. In accordance with the usual practice, due acknowledgement has been made whenever the work presented, is based on the results of other workers.

Poona,
March

1974

(N.V.


Badami)
Candidate


Professor B.D. Tilak,
Research Cuide

C O N T E N T S

	<u>Pages</u>
CHPTER-I: Introduction	
Invention and development of reactive dyes	1
Chemical constitution and fastness properties of disperse dyes	24
Properties of azides	37
References	42
CHAPTER-II: Synthesis of Rresctive disperse Dyes	
Introduction	47
Dyes containing sulphonylazido group	54
Dyes containing carbonyl azido group	77
Dyes containing arylazido group	81
Dyes containing azidoacetamido group	85
References	95
CHAPTER-III: Application of Reactive Disperse Dyes to Synthetic fibres	
Introduction	97
Present work	101
Discussion	106
Shade Cards	120
References	137

CONTENTS (Continued)

	Pages
CHAPTER-IV : Spectral Studies	
a) Mass spectral study of intermediates and dyes containing azido group	
Introduction	.. 138
Present work - Arylazides	.. 148
Derivatives containing Azidoacetamido group	.. 162
Sulphonyl azides	.. 168
Experimental	.. 175
b) IR Spectroscopy	.. 178
c) UV Spectroscopy	.. 183
References	.. 191
SUMMARY OF THE THESIS	.. 193
ACKNOWLEDGEMENTS	.. 200

CHAPTER - I

INTRODUCTION

This thesis deals mainly with the preparation and application of reactive disperse dyes to polyester and other synthetic fibres. The dyes contain azido groups as the reactive systems.

There is hardly any literature available on reactive disperse dyes applicable to cellulose acetate and polyester. Effort has been made here to review the historical development of reactive dyes applicable to cotton and polyamide fibres and also the developments in the disperse dyes. The introduction has been subdivided into three parts.

(a) Invention and development of reactive dyes.

(b) Chemical constitution and fastness properties of disperse dyes.

(c) Synthesis and reactions of organic azides.

(a) Invention and development of reactive dyes

Since dyes are generally graded in terms of their fastness properties, it has been the aim of all dyestuff chemists to develop new dyes with better fastness properties, ultimately leading to a dye which is as permanent as the life of the fibre itself. This aim has led to many developments which are milestones in history of synthetic dyes. The first one is the Perkin's discovery of Mauveine in 1856, which gave a great impetus to the development of synthetic dyes leading to the present

state of the dyestuff industry. Then came the introduction of direct dyes, first of these being Congo Red by Bottiger in 1884. Discovery of the method of azoic dyeing and vat dyes were of great importance for getting fast dyeings on cotton. But the dream of getting a dye which can give a dyeing whose life is as long as the life of fibre itself still remained unfulfilled. This in short means to get a dye moiety which forms a chemical part of the fibre. In other words the dye is covalently linked with the fibre.

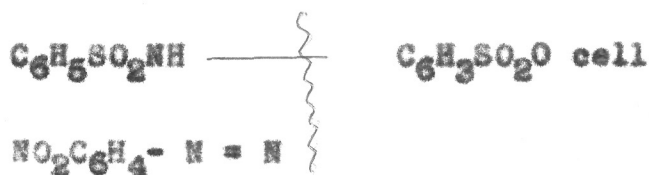
The need for the development of reactive dyes was felt for two reasons.

1. Though direct dyes were applied by simple dyeing operations they did not possess adequate wash fastness.
2. Though azoic colours and vat dyes had good light and wash fastness properties on cotton, the method of application was cumbersome. There was thus a great need for the development of dyes which could be applied to cotton by simple dyeing operations and which possessed the high fastness properties of azoics and vats. Increasing labour cost in Europe further intensified the search for such dyes.

The search for reactive dyes has extended over the last 75 years. The first of such efforts was made by Cross and Bevan¹ who benzoylated the soda cellulose,

nitrated, reduced the nitro compound of cellulose, diazotized and coupled with amines and phenols to obtain yellow to red coloured fibres.

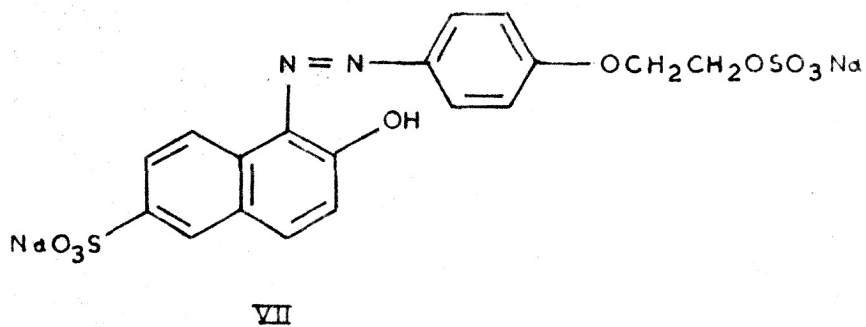
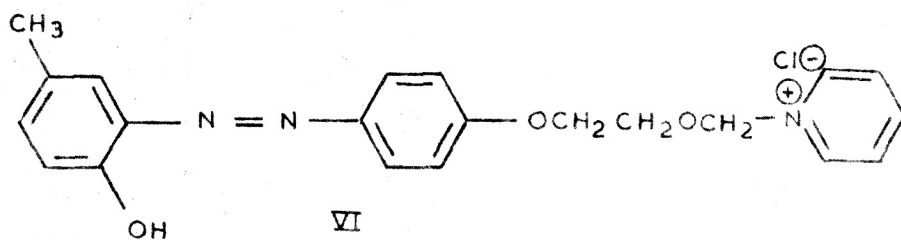
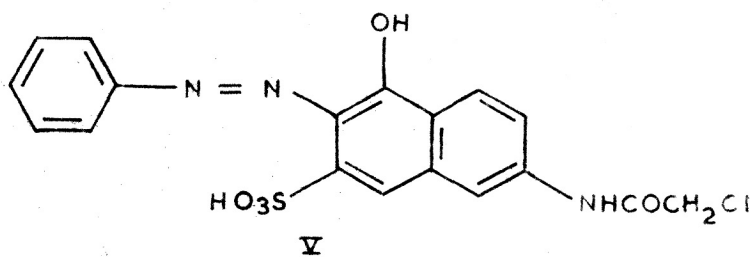
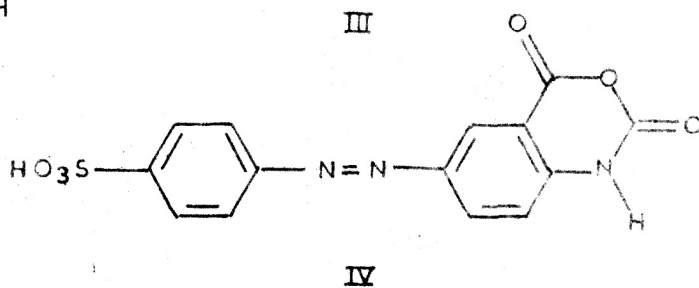
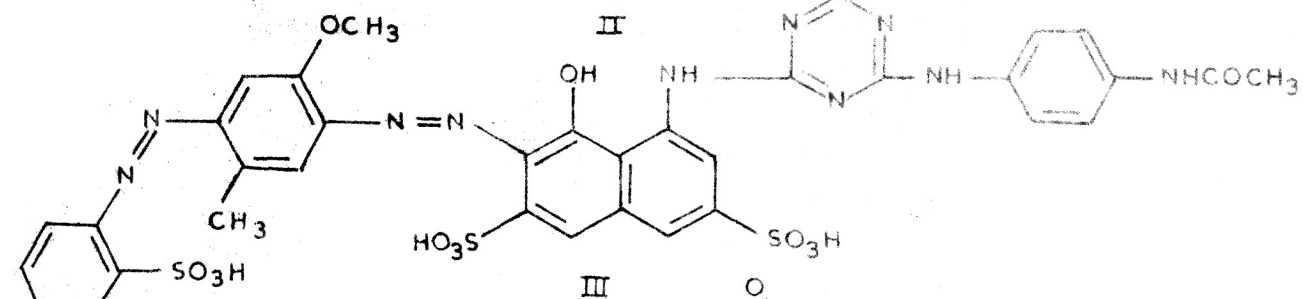
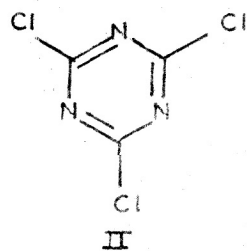
Shroeter² in 1906 treated cotton with p-benzene sulphonylamino benzene sulphonyl chloride. It was then treated with p-nitrobenzene diazonium salts to form yellow coloured fibre. The coloured cellulose was shown to have the doubtful structure (I)



(I)

During 1923³ CIBA patented the dyes derived from cyanuric chloride (II). It was used as a bridging group for intramolecular blue-yellow chromophoric combination to produce green dyes of the Chlorantine series. Even though cyanuric chloride gave increased substantivity, it was mainly used as "chromophoric bridge" and the third chlorine atom in cyanuric chloride was usually replaced by groups such as amino or anilino. Several dyes of the series had an unreplaced chlorine atom, e.g. Chlorantine Light Blue SG (III), but their capacity to dye cellulose reactively was not recognised at that time.

CHART - I



Gunther⁴ in 1925 prepared the coloured derivatives of isatoic anhydride (IV) which were capable of reacting with cellulose in alkaline medium to form ester type bonds.

Peacock⁵ in 1926 employed quaternary ammonium salts such as p-nitrobenzylphenyldimethylammonium chloride, to prepare a cellulose nitrobenzyl ester by treating cotton in presence of sodium carbonate. Such derivatives of cellulose were subjected to reduction, diazotisation and coupling to form azo dyes.

In 1930 IG marketed⁶ Supramine Orange R (V) which formed a covalent bond with wool. The reactive function was the labile chlorine atom of the chloro-acetyl group.

Even though the reactivity of such dyes with wool was not realised, these dyes were claimed to have very high wet fastness. It is now established that reaction occurs under acid dyeing conditions.

Haller and Heckendorn⁷ of CIBA in 1930-32 tried to acylate the cellulose with cyanuric chloride using the stepwise replacement of chlorine atoms. They treated soda cellulose with cyanuric chloride in organic solvents, then reacting the other chlorine atom with dyes containing amino group or intermediates capable of forming dyes. This was closest approach to put a reactive dyes on the

market. This effort did not result in marketing a range of reactive dyes because of two reasons:-

(1) the process of reacting cyanuric chloride with soda cellulose and then with dye was too lengthy for textile dyeing operations and (2) employment of organic solvent medium for reacting cyanuric chloride with soda cellulose was impractical.

Grenacher⁸ during 1928-30 tried etherification of cellulose by treating anhydrous cellulose with p-nitrobenzoyl chloride or dinitrobenzohalogenobenzenes. Reduction gave diazotisable fibres.

In 1937 ICI⁹ patented water soluble anthraquinone dyes containing a reactive halogen e.g. 4-bromo-1-aminanthraquinone-2-sulfonic acid ("Bromanine acid") for dyeing of wool. In 1940 ICI realised the reactivity of dyes containing chloroacetyl groups [Supramine Orange R (V)] with wool which results in very high wet fastness. They worked on dyes containing the chloroacetyl group with a view to produce a commercial range of reactive dyes for wool.

CIBA¹¹ patented the dyes containing the quaternary ammonium salt of the type VI. Some dyes of this class gave dyeings of very high fastness to washing when cotton was padded with such dyes and then subjected to baking.

Solodkov and Kursanov¹² described the formation of ether linkage with cellulose when it was treated with *m*-nitrobenzylloxymethyl pyridinium chloride and sodium acetate. Chemical fixation was brought about by heating at 125°C for 10 minutes. Guthrie¹³ in 1952 made an important effort aimed at forming an ether linkage with cellulose by treating with sulphate esters of dyes containing alcoholic groups. This was another close approach to the type of reactive dyes which are now on the market.

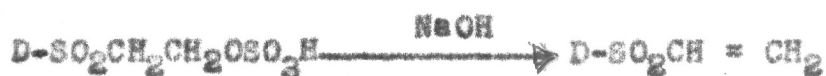
Guthrie produced fast dyeings by impregnating cotton with sodium hydroxide solutions of the dye (VII) and subsequently baking the fibre at 100-110° for 1 hr. or longer. The disadvantages of these dyes were low reactivity, necessity of high alkali concentration longer time and the high temperature used for fixation.

McLaughlin and Mutton¹⁴ investigated the etherification of cellulose with *p*-amino-2,2'-chloroacetophenone. They washed soda cellulose (prepared by treating with 20% sodium hydroxide solution) with ethenol and then treated it with *p*-amino-*m*-chloroacetophenone in boiling ethanol to obtain cellulose containing a diazotisable amino group. Diazotization and coupling gave a coloured cellulose derivatives.

CIBA¹⁵ in 1944 patented dyes containing β -sulphatoethyl sulphonyl groups (VIII).

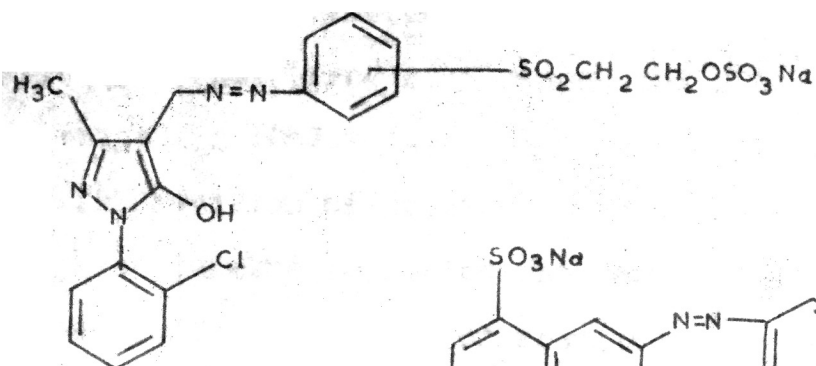
These dyes included no nuclear sulphonie acid groups and were mainly described for application on cellulose acetate and polyamide fibres. Their capacity to form ether linkage with cellulose was not realised at that time.

Hoechst did research on vinyl sulphones and β -sulphatoethyl sulphones during 1948-52 and marketed Remalan range of reactive dyes applicable to wool, silk and polyamide fibres. The precursor sulphate ester

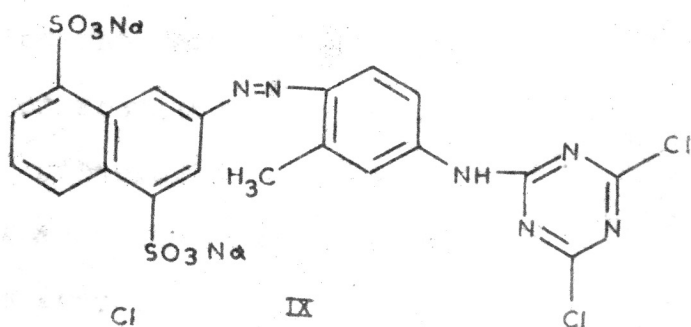


group was hydrolysed to vinyl sulphone which then formed covalent bond with free amino and hydroxyl groups in the fibre¹⁶. In 1957, dyes containing the same reactive groups were marketed as Remazols. Rattee and Stephen of ICI in 1950 investigated the use of dichlorotriazinyl derivatives for reactive dyeing of wool. Following publication of work by Warren, Reid and Hamalainen¹⁷ in 1952 on reaction of soda cellulose with cyanuric chloride, they visualised use of cyanuric chloride as a reactive group in dyeing of cellulose. Further efforts on methods of application and storage of dyes containing dichlorotriazine groups by use of buffers¹⁸ led to the marketing of the Procion range of reactive dyes for cellulose. Three dyes Procion

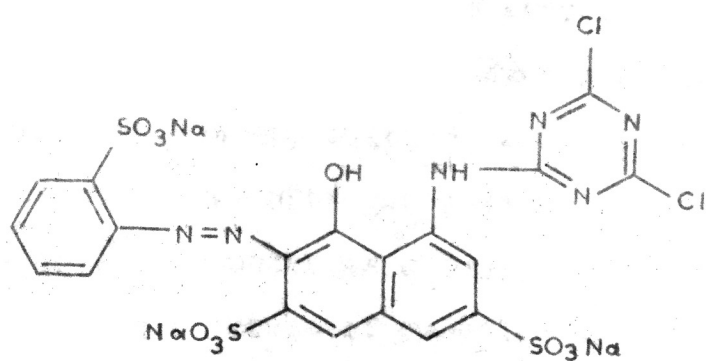
CHART - 2



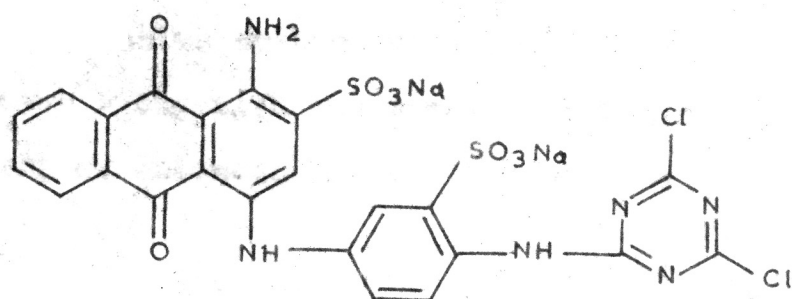
VIII



IX



X



XI

Yellow R (IX), Brilliant Red 2B (X) and Blue 3G (XI) were all dichlorotriazine^s capable of application to cellulose under cold dyeing conditions (20-40°). Dyes containing monochloro triazine group were introduced simultaneously by ICI (Procion H range) and CIBA (Cibacron range) in 1957.

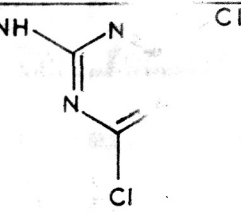
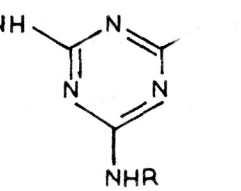
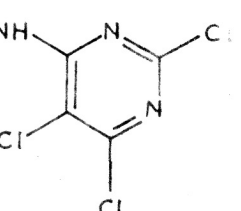
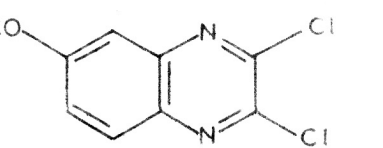
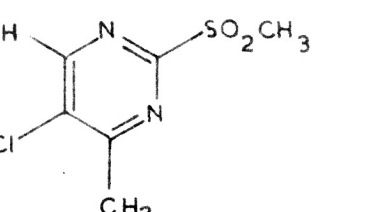
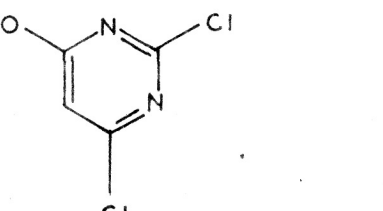
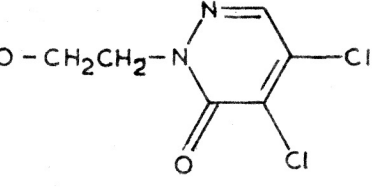
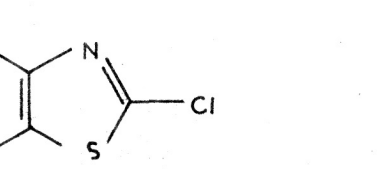
The introduction of procion range of reactive dyes gave great impetus to the search for new reactive systems. The following ranges of reactive dyes were introduced by different firms. Cibacron dyes (CIBA), Reactone dyes (Geigy), Drimaren dyes (Sandoz), Remazol dyes (Hoechst) and Levafix dyes (Bayer).

Once the versatility of cyanuric chloride as a reactive group was appreciated, efforts were directed towards finding new nitrogen heterocyclic systems containing labile chlorine atoms. Reactone (Geigy) and Drimaren (Sandoz) range of reactive dyes contain 2,4,6-trichloropyrimidine and 2,4,5,6-tetrachloropyrimidine groups as the reactive systems.

The different reactive systems used in different range of reactive dyes along with their commercial brand names, firms and year of introduction are listed in Table 1.

TABLE - I

11

STRUCTURE	COMMERCIAL BRAND NAME	FIRM	YEAR OF INTRODUCTION
$(\text{DYE})-\text{NH}-\text{N}=\text{N}-\text{Cl}$ 	PROCION	ICI	1956
$(\text{DYE})-\text{NH}-\text{N}=\text{N}-\text{NHR}$ 	PROCION H CIBACRON	ICI CIBA	1957 1957
$(\text{DYE})-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$	REMAZOL	HOECHST	1958
$(\text{DYE})-\text{NH}-\text{N}=\text{N}-\text{Cl}$ 	REACTON DRIMAREN	GEIGY SANDOZ	1959 1959
$(\text{DYE})-\text{NHCO}-$ 	LEVAFIX E	BAYER	1961
$(\text{DYE})-\text{NH}-\text{N}=\text{N}-\text{SO}_2\text{CH}_3$ 	LEVAFIX P	BAYER	1966
$(\text{DYE})-\text{NHCO}-$ 	REACTOFIL	GEIGY	1968
$(\text{DYE})-\text{NHCO}-\text{CH}_2\text{CH}_2-\text{N}=\text{N}-\text{Cl}$ 	PRIMAZIN P	BASF	1964
$(\text{DYE})-$ 	ELISIANE	FRANCOLOR	1963
$(\text{DYE})-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{OSO}_3\text{Na}$	LEVAFIX	BAYER	1958
$(\text{DYE})-\text{NHCOCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5$	SOLIDAZOL	CASSELLA	1964

Reactive Dyes for Synthetic fibres

The progress made in the reactive dyes for synthetic fibres after the introduction of reactive dyes for cellulosic fibres in 1956 is slow. This can be fully appreciated when one considers the chemical and physical properties of synthetic fibres. Except for polyamide fiber, there is no reactive site in the case of other synthetic and regenerative fibres such as, polyester, cellulose triacetate and polypropylene fibres. Added to this lack of reactive sites is the hydrophobic nature of these fibres which prohibits the use of water soluble reactive dyes. Thus a good reactive dye for synthetic fibre should possess the properties of a good disperse dye in addition to a reactive group capable of forming covalent bonds with the particular fibre.

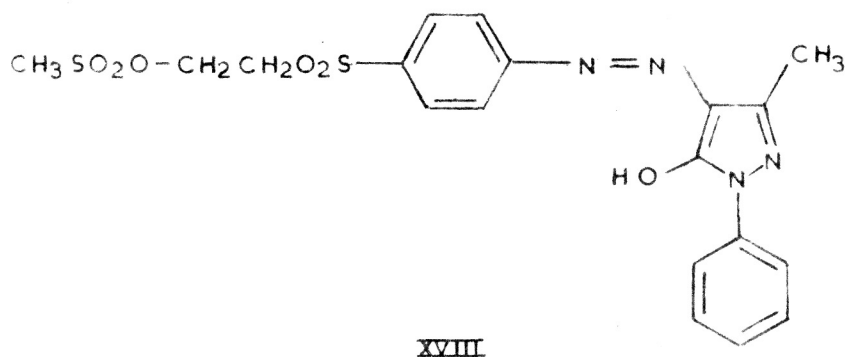
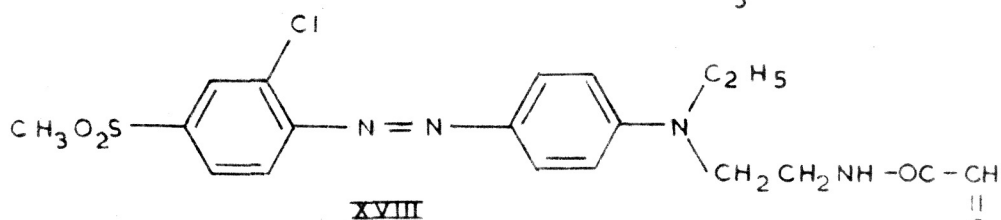
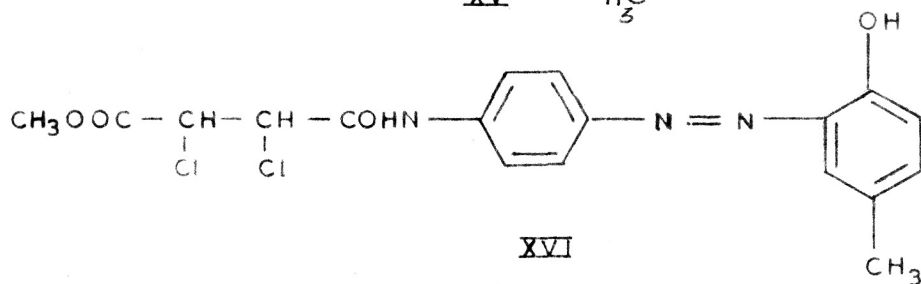
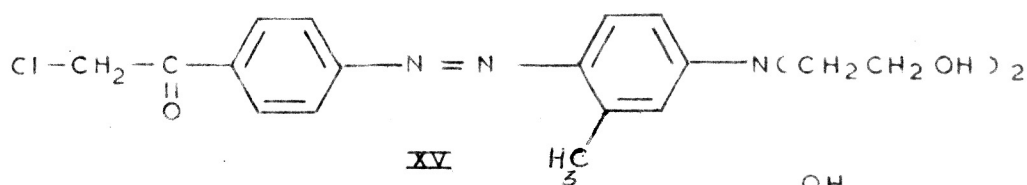
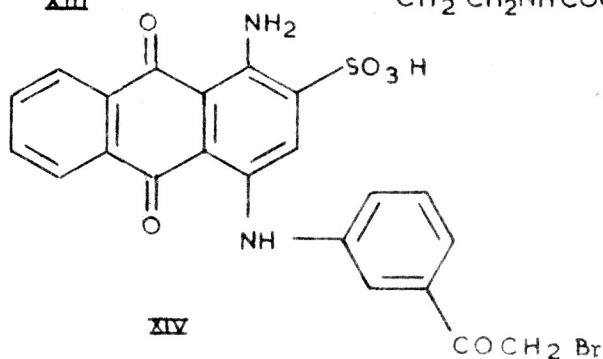
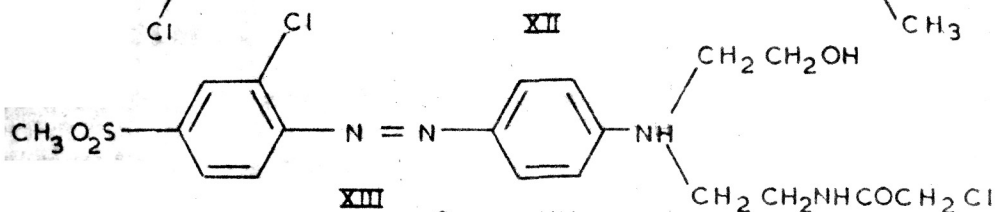
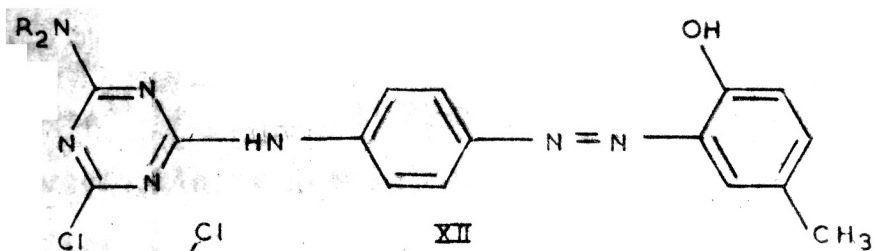
ICI in 1959 marketed procinyl range of reactive dyes for polyamide fibres. These are water insoluble disperse dyes containing a reactive group capable of forming covalent bonds with the amino functions in the polyamide substrate under alkaline conditions. The dyes are applied first as normal disperse dyes under neutral condition. Once the exhaustion is achieved the dye-bath is made alkaline to bring about the reaction with the fibre²⁰.

The reactive systems are so chosen that no reaction occurs under the neutral condition. This is a primary requirement for producing level dyeings. Procynyl range of reactive disperse dyes contain different reactive systems such as monochlorotriazinyl^{21,22} β -chloroethylsulphamoyl²³, epoxy, γ -chloro- β -hydroxypropyl halogeno^{24,25} pyridimine groups²⁶. The yellow dye (XII) is a representative of monochlorotriazinyl dyes in which R may be β -hydroxy ethyl group.

There are no known reactive dyes for polyester, polypropylene and cellulose acetate fibres. The known reactive disperse dyes have been mainly developed for the dyeing of polyamide fibres.

Substituted acetamides

Reactive disperse dyes containing the chloroacetyl group for polyamide fibres are mentioned in patents. These are prepared either by acylation of dyes containing amino or sulphonamido groups with chloroacetyl chloride or by Tscherniac-Einhorn reaction in which chloroacetylaminomethylene group is introduced into a dye containing aromatic nuclei by the action of N-methylol-chloroacetamide in 96% sulfuric acid²⁷. Chloroacetyl groups are also introduced into aliphatic side chains (XIII)²⁸.



Substituted aliphatic ketones

Sandoz²⁹ has patented dyes (XIV) containing chloro- and bromo-acetophenone groups for dyeing of wool and polyamide fibres.

Dyes (XV) containing halomethyl ketone groups are also mentioned as reactive disperse dyes for polyamide fibres³⁰.

Use of alkane dicarboxamides as reactive group in disperse reactive dyes for polyamide fibres are developed such as Dyes (XVI) containing dichloro-succinomethyl ester chloride group have been reported³¹.

Acrylamides

The dyes such as (XVII) containing haloacrylamides have been mentioned for polyamide and cellulosic fibres but they have not achieved technical importance³².

β -substituted sulphonic esters

The dyes such as (XVIII) containing β -sulphonic ester groups were first introduced by CIBA³³ as reactive dyes for wool. ICI³⁴ have used the same group in reactive disperse dyes for polyamide fibres.

β -acyloxy groups

ICI³⁵ have also reported the use of β -acyloxy group in reactive dyeing of polyamide fibres as in (XIX).



(XIX)

Substituted vinyl sulphones

Water insoluble dyes (XX) containing vinyl sulfone system are claimed as reactive disperse dyes for polyamide³⁶.

β -Haloethylamines

Blue disperse reactive dyes (e.g. XXI) containing the β -haloethylamino group are important in wash fast dyeing of polyamide fibres³⁷.

Fixation agents of the type ^(XXII) have been patented ^{for} reactive dyeing of polyamide fibres along with water insoluble dyes containing the amino groups³⁸.

β -Haloethyl sulfonamides

ICI in 1940 patented dyes containing β -haloethyl-sulphonamides ^{for} reactive dyeing of wool³⁹.

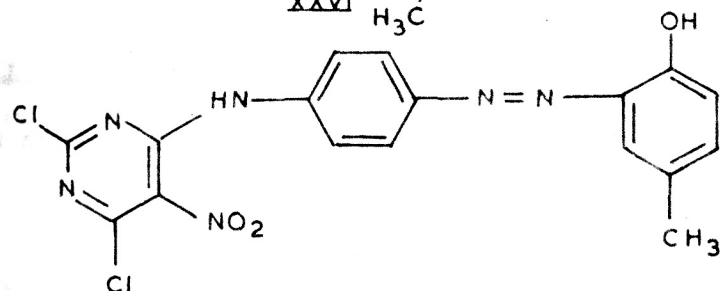
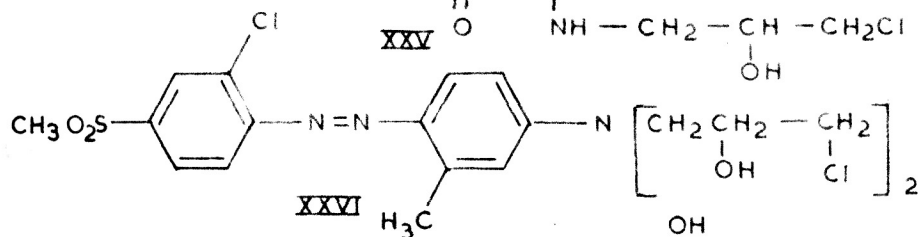
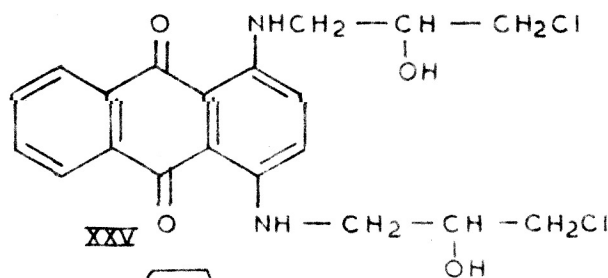
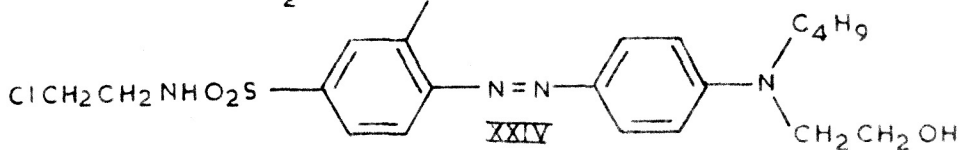
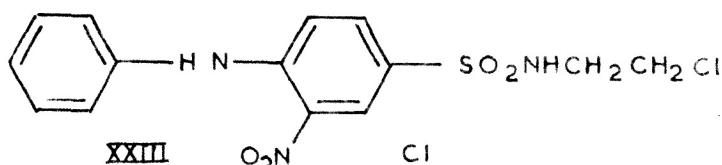
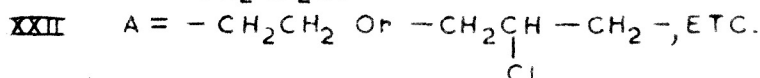
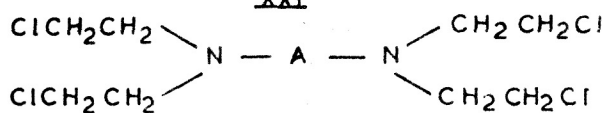
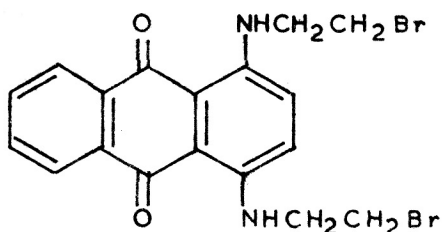
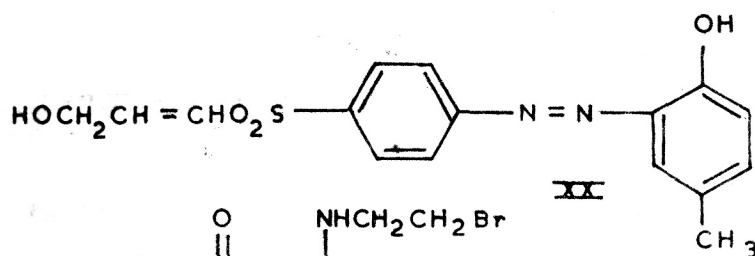
ICI recognised their importance in reactive dyeing of polyamide fibres and patented disperse dyes of the type (XXIII) and (XXIV) which contained the p-chloro-ethylsulphonamido group⁴⁰.

The above structural ^{al} feature has been used in the Procinyl range (ICI) of reactive disperse dyes for polyamide fibres.

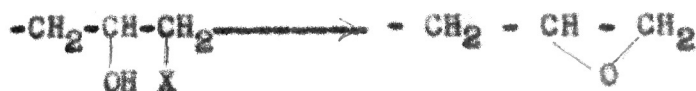
Epoxyde derivatives

Procinyl range of reactive dyes for polyamide fibres also contain dyes in which an epoxyde precursor is present.

CHART - 4.



The latter, under the alkaline conditions, gives the epoxide:



These dyes have attained technical importance because of their stability during dyeing. The reactivity of epoxide group is better with the more basic amino groups of the polyamide substrate as compared to hydroxy groups in cellulose⁴¹. Examples are (XXV) and (XXVI)⁴³.

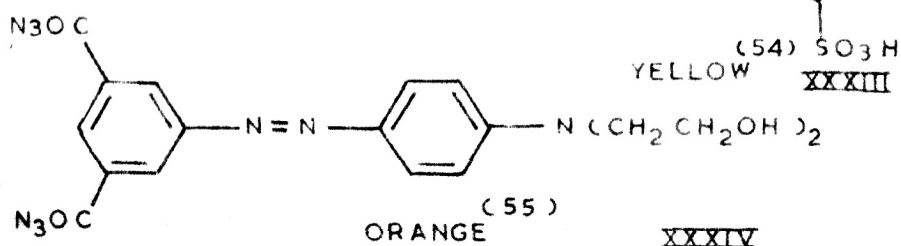
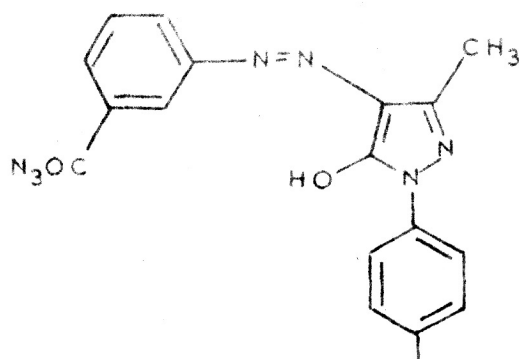
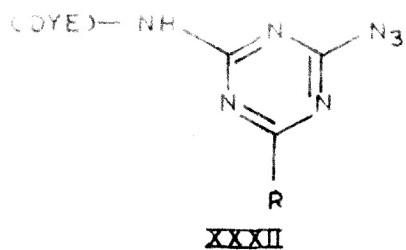
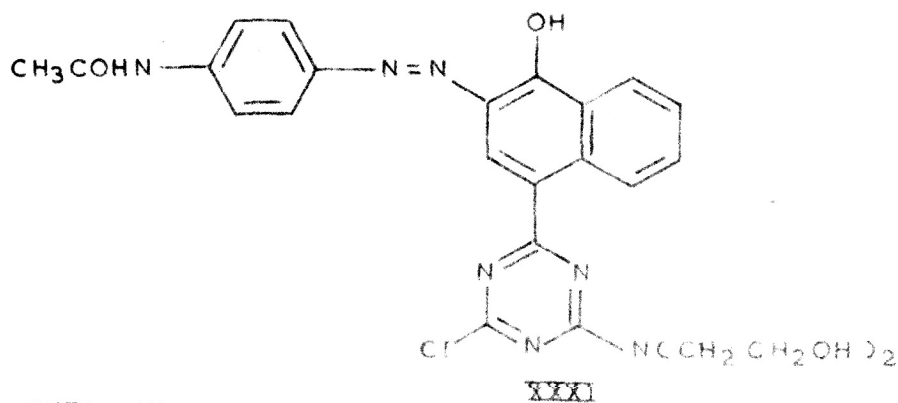
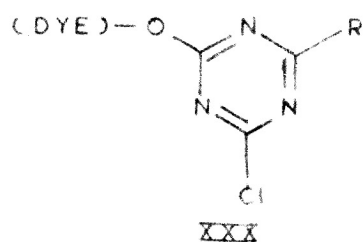
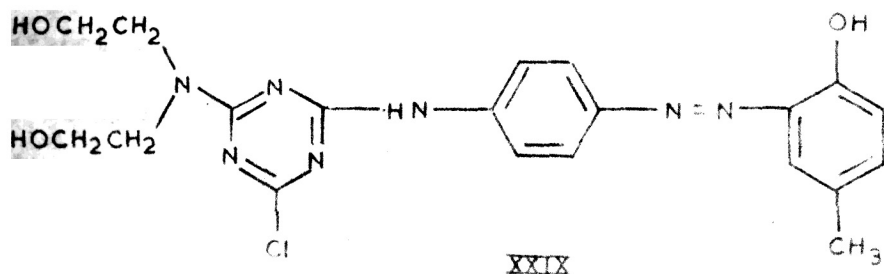
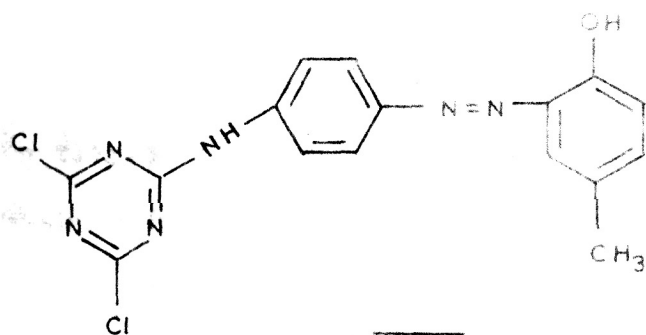
Chloropyrimidine and triazine derivatives

Sandoz⁴⁴ and ICI⁴⁵ have reported disperse dyes containing chloropyrimidylamino groups. These disperse dyes (XXVII) are reactive towards polyamide fibres.

Even though ICI was first to recognize the suitability of water-soluble dichloro-S-triazinylamino (Procion) dyestuffs in dyeing of polyamide fibres, it was Sandoz⁴⁷, which first patented disperse reactive dyes (XXVIII) for polyamide fibres.

Acs⁴⁸ described similar dyes for the dyeing of modified (basic) polypropylene^{yl} fibres. Monochlorotriazine was one of the various groups which was claimed as useful in dyeing wool reactively e.g. (XXIX; Procinyl Yellow G.S.)⁴⁹

The monochlorotriazine derivatives of the type (XXX), obtained by treating a water-insoluble dye containing an acylable hydroxy group with cyanuric chloride have been



described by Sandoz⁵⁰ as reactive disperse dyes for polyamide fibres. Cyanuric chloride has been condensed with naphthols and phenols under Friedel-Crafts conditions to give the corresponding cyanurated derivatives which were then used as coupling components to yield reactive disperse dyes (XXXI) for polyamide⁵¹. Azide as a leaving group in S-triazine derivatives of the type (XXXII) have been mentioned⁵². They are obtained by treating dichloro triazine dyestuffs with sodium azide. But they have no commercial importance.

Isothiocyanates

Dyestuffs containing isothiocyanate groups ($-N = C = S$) have been mentioned as reactive dyes for wool and polyamide fibres. The wet-fastness properties are increased by adjusting the pH of the dye bath to 6.5 - 8.5 with ammonia or hexamethylenetetramine⁵³.

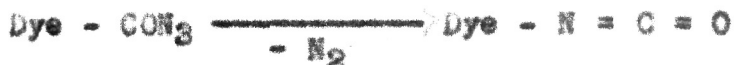
Azides

Azides have been mentioned as a potential reactive system for cellulosic and polyamide fibres. Dyes of the type (XXXIII and XXXIV) were prepared by diazotization of the corresponding aminobenzoic hydrazide with excess sodium-nitrite to get the diazonium compound of the carbazide which on coupling gives the relevant dyes.

When cotton and polyamide fibres are dyed in the alkaline bath, nucleophilic displacement of the azide group takes place as follows:



When applied under thermal conditions the carboxyazides form urethane type stable bonds.



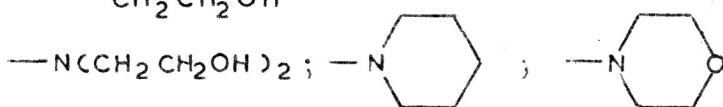
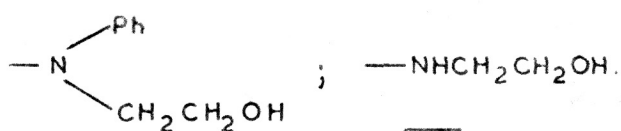
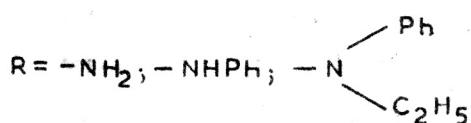
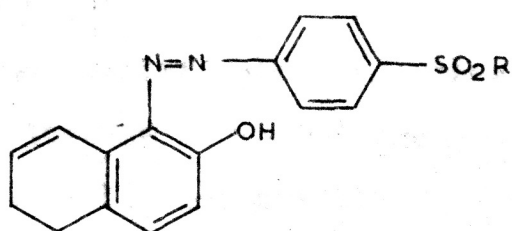
The dyes containing sulfonylazides have also been reported⁵⁶ which are either prepared by diazotization of ~~max~~ p-aminobenzenesulfonyl hydrazide and coupling, or by chlorosulfonation of dyes and then treating with sodium azide. They react with cellulose under the alkaline conditions by formation of bonds of the type:



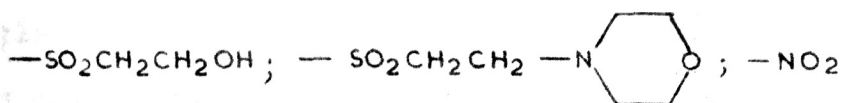
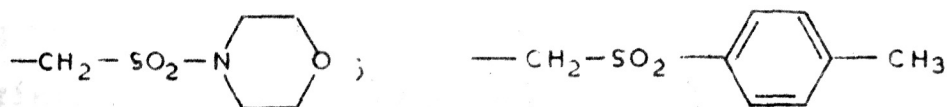
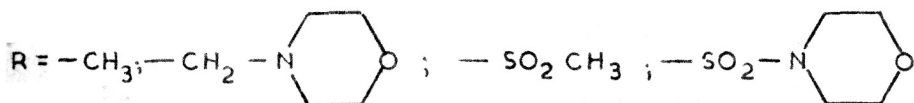
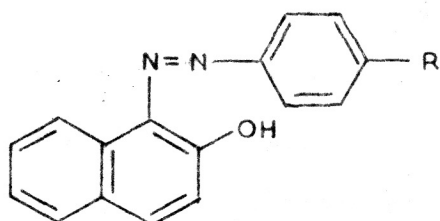
The authors have also discussed the formation of similar bonds with terminal amino groups of polyamide fibres. These water insoluble dyes containing sulfonylazides groups are dyed under alkaline conditions.

The work on disperse dyes containing sulfonamido groups was started in this laboratory in the sixties when dyes of the type (XXXV) were reported. The affinity (K Cal/mole) and the saturation values (g/kg of dry fibre at 95°) of the dyes for polyester, cellulose triacetate, polyacrylic acid-polyamide fibres were determined. It was concluded from the point of view of affinity that in case

CHART - 6



XXXV



XXXVI

of polyester fibres, the introduction of sulphonmorpholide and sulphon piperidide offer maximum advantage whereas, for other synthetic fibres sulphon diethanol amide group offers maximum advantage⁵⁷.

Introduction of sulfonmorpholide group increases the affinity of these dyes for polyester fibre but the tinctorial strength of such dyes is considerably reduced. Kulwant Singh and Tilak then prepared dyes containing sulphon morpholide group which was attached to the chromophore through an insulating group⁵⁸ as in (XXXVI).

As a consequence to the work on dyes containing sulfonmorpholide groups, the synthesis of disperse dyes containing the sulfonazido group was started in 1970. The main object in the synthesis of these dyes was the development of dyes which could be reactively applied to different^e synthetic fibres such as polyester, polyamide, cellulose acetate and polypropylene. Application (reaction) of these dyes to these fibres by thermolysis could be anticipated to occur through intermediate formation of a nitrene. Apart from the synthesis of disperse dyes containing the sulphonazido group, the present work also describes the synthesis of dyes containing carbonyl azido, arylazido and azidocacetamido groups. The dyeing properties and fastness of the dyeing on synthetic fibres was studied as in the case of earlier dyes⁵⁹.

Kamatsu et al.⁶⁰ Griffiths⁶¹ and Sunthanker and Patkar⁶² have independently studied the application of the dyes containing sulfonazido group on different synthetic fibres and reactive fixation under thermal conditions.

(b) Chemical constitution and fastness properties of Disperse dyes

History

Definition of disperse dyes as given by Society of Dyers and Colourists is "a class of water-insoluble dyes originally introduced for dyeing cellulose acetate and usually applied from fine aqueous suspensions"⁶³.

The need of satisfactory dyes for cellulose acetate resulted in the development of disperse dyes. When cellulose acetate was introduced after the first World War, conventional water soluble acid, basic and direct dyes were of no use for this hydrophobic fibre.

Precursors to disperse dyes, the "lonamines" were introduced by Green and Saunders⁶⁴ of British Dyestuffs Corporation Ltd.⁶⁴ These were solubilized disperse dyes. The water insoluble azo and anthraquinone dyes containing primary or secondary amino groups were treated with formaldehyde bisulfite whereby the N-methane sulfonic acid derivatives were obtained. These dyes though soluble in water are slowly hydrolyzed to the parent amino

compounds during dyeing which were then absorbed by the cellulose acetate fibre. A typical example is (XXXVII). The main drawbacks of the ionamine class of dyes were (a) The necessity to make the water insoluble dyes into water soluble ones. (b) The different rates of hydrolysis possessed by different dyes posed problems during dyeing with mixtures of dyes.

From the experience with "Ionamines" it was realised that suitable dyes for cellulose acetate should be (a) basic in character and (b) have relatively simple structure in addition to low solubility in water. This meant a break in the accepted principle that dyes must be soluble or capable of being made soluble before dyeing⁶⁵.

In 1923 Holland Ellis⁶⁶ of British Celanese Ltd. discovered the 'disperse technique' to solve the problem of dyeing cellulose acetate with water insoluble dyes. He prepared fine aqueous suspensions of a group of water insoluble azo and diphenylamine dyes with 'sulphofatty acids' e.g. sulphoricinoleic acid and its alkali-metal salts. These dispersions were marketed under the brand name SRA colours. Within a period of few months Baddiley and Shepherdson⁶⁷ of British Dyestuffs Corporation Ltd. dispersed aminoanthraquinones by grinding or dissolving in solvents and reprecipitating in presence of soap or

Turkey red oil. These were marketed under the name 'Duranols' A.J. Hall⁶⁸ dyed cellulose acetate with aqueous suspensions of nitrodiphenylamines containing Turkey Red oil or soap.

The "disperse technique" was a very important development in the dyeing of synthetic fibres. The importance of particle size in dyeing and printing of cellulose acetate was conclusively established by Vickerstaff⁶⁹ and Daruwalla and Turner⁷⁰.

After the dyeing of cellulose acetate was achieved by the 'disperse technique', efforts of dyestuff chemists were directed towards improving different fastness properties towards various agencies like washing, light, gases, sublimation and fading due to ozone. Dyes were tested not only on cellulose acetate but also on polyester, polyamide, polyacrylonitrile fibres which were introduced later. Thus some basic relationship between fastness properties and chemical constitution have now been established.

The relationship between fastness properties and the chemical constitution is complex. To a large extent the fastness properties also depend on the fibre substrate. Thus the same dye may have different fastness properties on different fibres. The more important structural features of disperse dyes are:-

- (a) Molecular size, shape and complexity
- (b) Hydrophobic- hydrophilic balance
- (c) Hydrogen bonding groups
- (d) Polar and non-polar forces interaction

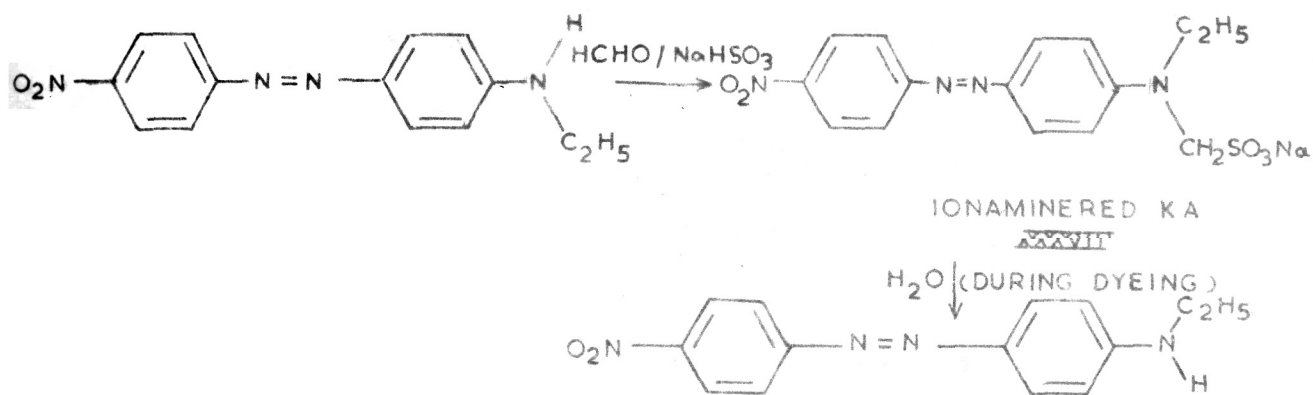
These requirements put a severe limitation on the structural modifications to be made in the synthesis of disperse dyes. Often a structural change made to improve fastness to one agency results in lowering of fastness to some other agency and hence a balancing compromise has to be made to get a dye of satisfactory fastness properties to all the agencies⁷¹.

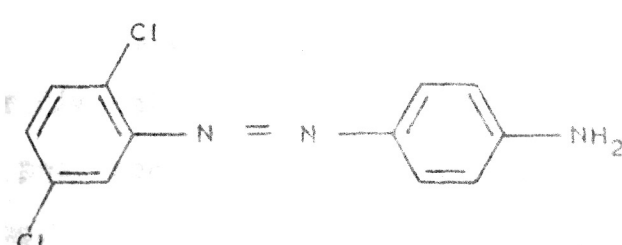
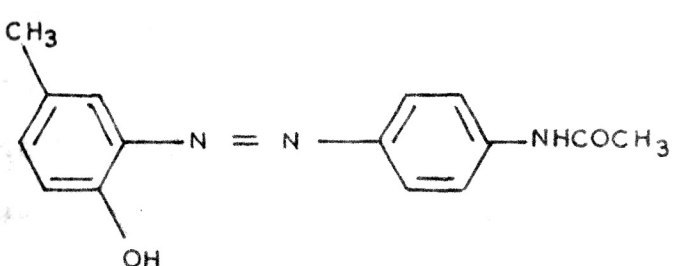
Fastness to light

The effect of light on the dyed fibres is not clearly understood⁷². The light fastness is influenced by several factors such as chemical constitution of dye, physical structure of the fibre, physical state of the absorbed dye, the method of dyeing employed, the nature of the bonds holding the dyestuff and the fibre together and the after-treatment given to the fabric⁷².

The dye molecule on absorption of light goes to the excited state which undergoes two types of changes (a) phototropism- a reversible change in colour when exposed to light, the original colour being restored on storage in darkness and (b) Fading- an irreversible change or loss in the original colour⁷³.

CHART - 7



STRUCTURE	PHOTOTROPISM
	PHOTOTROPIC
	NONPHOTOTROPIC
	NONPHOTOTROPIC

Phototropism

It is assumed to involve cis-trans rearrangement mainly observed in yellow and orange dyes of the aminoazobenzene series. Introduction of strong electron withdrawing groups such as nitro, cyano, acetyl in the 4'-portion of the aminoazobenzene dye or by acetylating the amino group inhibits phototropism⁷⁴ (see Table 2).

Schroeder and Boyd⁷⁴ have observed that the best dyes on polyesters are those having stable aromatic structures with minimum of photosensitive groups (Table 3).

The light fastness of aminanthraquinones has been investigated by numerous workers. Schroeder and Boyd⁷⁴ have observed that an electron withdrawing group either directly attached to the amino group or in the ortho position improves light fastness. The results are shown in Table 4.

Dickey⁷⁵ has found that introduction of the trifluoromethyl group ortho to the amino group in anthraquinones improved fastness to light and gas fading.

Ko Nsiki⁷⁶ has observed in a series of aminanthraquinone dyes that electron withdrawing N-substituent, such as β -chloroethoxy carbonyl group increase light fastness and an electron releasing group, such as β -hydroxyethyl group, decreases it.

TABLE - 3

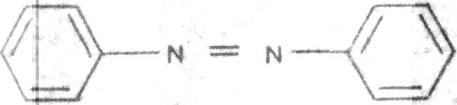
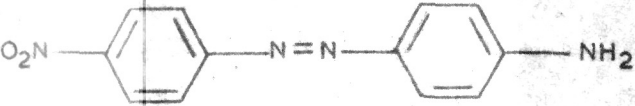
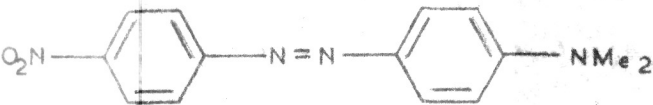
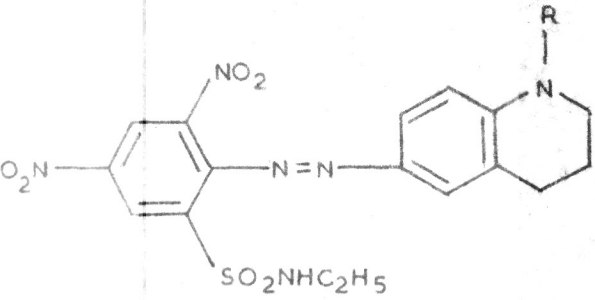
STRUCTURE	LIGHT FASTNESS ON POLYESTER
	EXCELLENT
	GOOD
	FAIR
	POOR

TABLE - 4

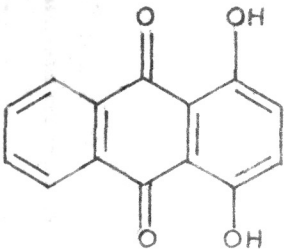
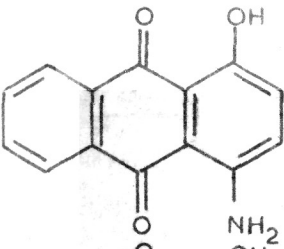
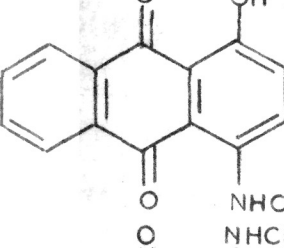
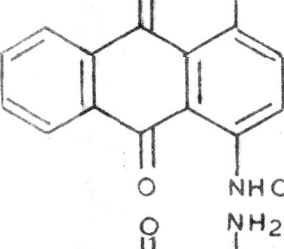
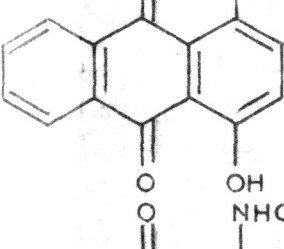
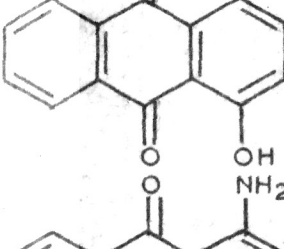
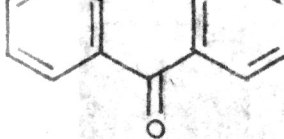
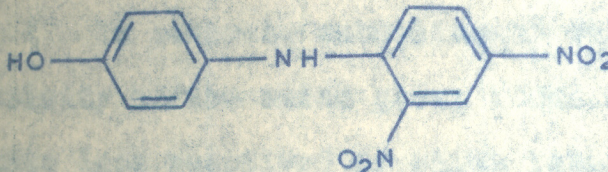
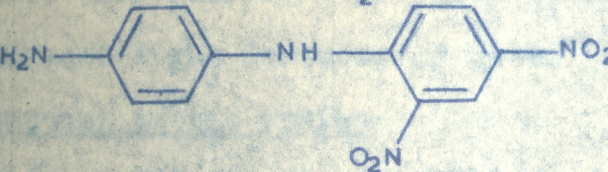
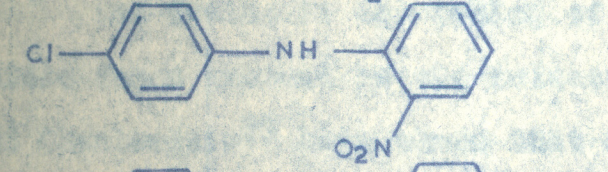
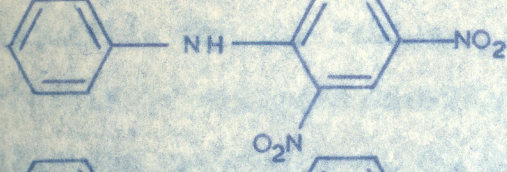
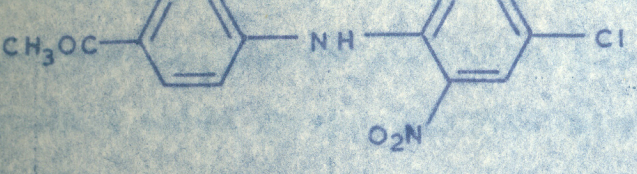
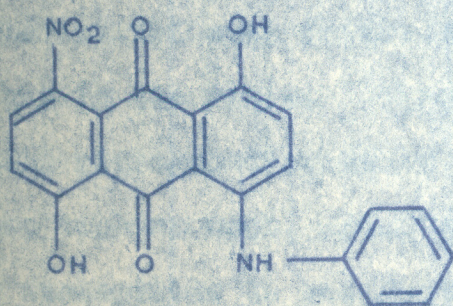
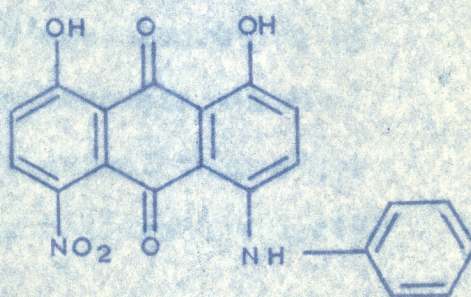
STURCTURE	LIGHT FASTNESS ON POLYESTER (IN HOURS)
	160
	60
	20
	10
	160
	160
	160

TABLE — 5

STRUCTURE	LIGHT FASTNESS
	MODERATE
	MODERATE
	EXCELLENT
	MODERATE
	EXCELLENT



XXXVIII



XXXIX

In case of diphenylamine dyes, the p-nitro group tends to reduce light fastness, otherwise they have excellent light fastness⁷⁷. o-Nitro derivatives are particularly stable as there is possibility of hydrogen bonding in these dyes. Table 5 shows the light fastness of some diphenylamine dyes.

In general, substituents which decrease the basicity of the amino group (thus making the excited state less reactive) or which favour hydrogen bonding increase light fastness of dyes.

Fastness to gas fading

Gas-fading is the fading of dyed fabrics by the acidic fumes present in the industrial atmosphere. Rowe and Chamberlain⁷⁸ have shown that oxides of nitrogen were responsible for gas fading. Salvin et al.⁷⁹ have proved that it is nitrogen dioxide which is mainly responsible for gas-fading. The reactions that are proposed to explain gas fading are diazotization of the primary amino group, nitrosation of the secondary amino group and oxidation.

Gas fading depends also on the type of the fibre as the initial step in the process is the absorption of the gas by the fibre. Thus cellulose acetate which absorbs nitrogen-dioxide to a greater extent than other fibres such as wool, nylon and cotton renders the dyeing more susceptible to gas fading⁷⁹.

The dyes which are vulnerable to gas-fading are blue and violet dyes of the anthraquinone series and reds in the azo series which contain basic amino groups. Salvin⁸⁰ has observed that the dyes having low fastness to gas fading on cellulose acetate also have low fastness to light on polyester. From this it is clear that the basic amino group which makes a dye susceptible to gas fading on cellulose acetate is also responsible for the low-light fastness of the dyes on the polyester. This observation is of practical importance since the earlier search for dyes having high fastness to gas-fading on cellulose acetate proved valuable also in the development of fast dyes for polyester fibres.

There are two methods of improving the fastness to gas-fading:-

(a) Certain basic inhibitors like melamine and triethanolamine are applied to the fibre in finishing treatments. These compounds react preferentially with nitrogen dioxide thus leaving the dye unaffected, (b) by modifying the chemical constitution of 1,4-dialkylamino anthraquinones in such a way that the basicity of the amino group is reduced by incorporating electron withdrawing groups in the ortho position to the amino group, or by preparing blue dyes of anthraquinone series devoid of amino or alkyl amino groups⁸⁰. Thus 1,5-dihydroxy-4-arylamino-8-

nitroanthraquinone (XXXVIII) and 1,8-dihydroxy-4-arylamino-5-nitroanthraquinone (XXXIX) have good fastness to light and gases and also possess good affinity to polyester fibres.

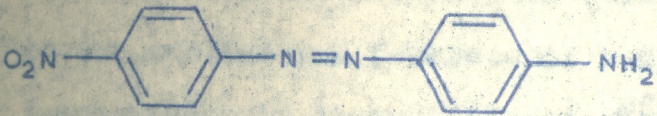
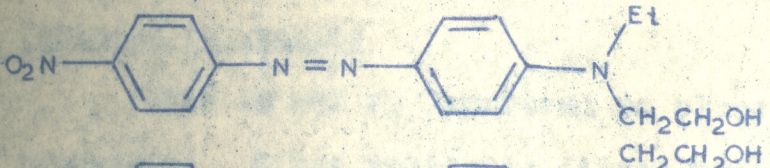
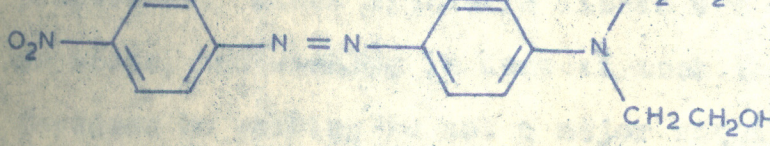
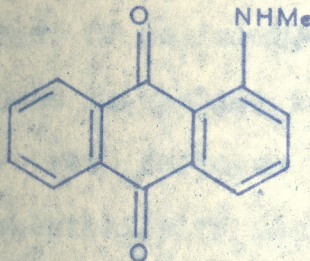
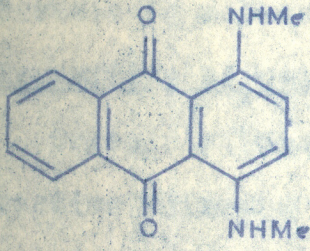
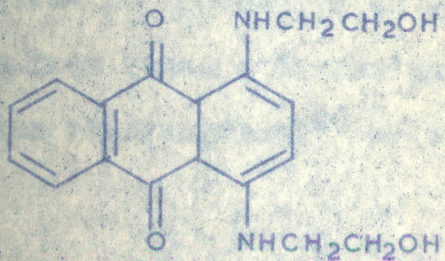
Fading due to ozone

Ozone present in the atmosphere to the extent of 0.25 to 0.26 parts per hundred million causes fading of the dyeings which is called O-Fading⁸¹. O-Fading is mainly observed in the country side. Ozone fading is more severe since ozone is a stronger electrophile than nitrogen dioxide and it reacts with weakly basic amines also. Thus the weakly basic blue dyes of anthraquinone series which are fast to nitrogen dioxide are affected by ozone.

Fastness to sublimation

Synthetic fibres are often subject to heat treatments such as in permanent pleating, thermosol dyeing and hot iron pressing. Temperatures upto 200° are used in such operations. Disperse dyes which are simply constituted to permit adequate permiscibility and are devoid of ionic solubilizing groups exhibit high vapour pressures and sublime when exposed to high temperature in the heat treatments mentioned above. This causes staining in permanent pleating and loss in Colour during pressing.

TABLE - 6

STRUCTURE	SUBLIMATION FASTNESS
	3
	4
	5
	3
	5
	5

Vapour pressure of the dyes is inversely proportional to the mass and polarity⁷⁴. This defect mainly observed in yellow to red dyes of the azo series is overcome by introducing polar groups (Table 6).

Similarly amide group and sulfonamide group also increase the fastness to sublimation. An increase in the sublimation fastness of a dye permits higher temperatures in thermal fixation⁸².

Fastness to washing

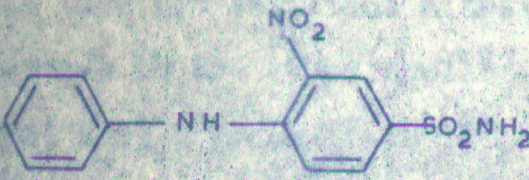
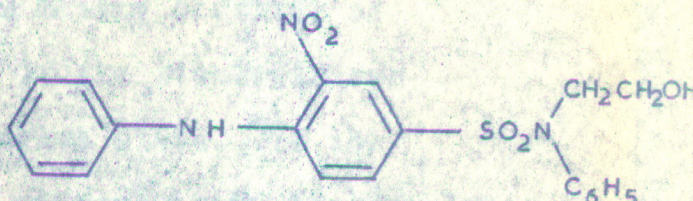
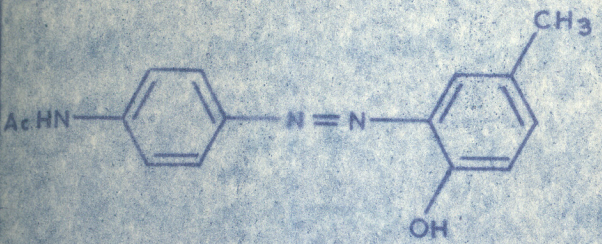
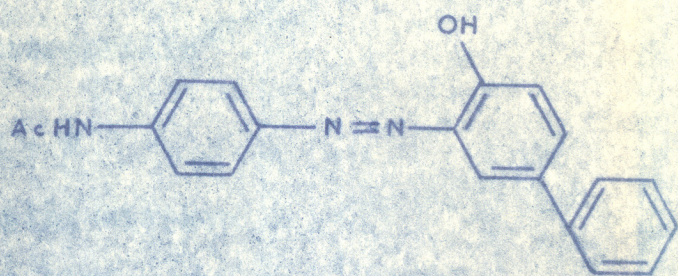
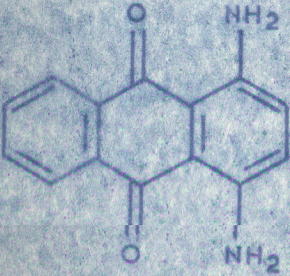
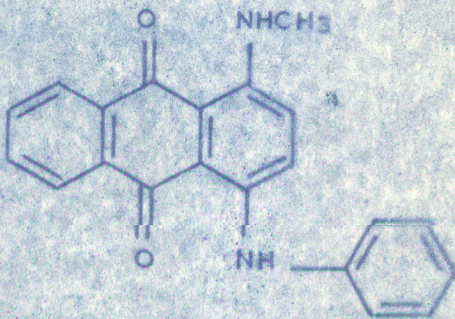
This is not as important as other fastness properties. Since synthetic fibres are dyed at 100° or above, and washing is done at much lower temperature, fastness to washing is not a major requirement. But in the case of cellulose acetate which is dyed at 50-80° fastness to washing is important.

Wash fastness increases with molecular size⁷⁴ but substantivity decreases. Table 7 shows the effect of increase in molecular size on wash fastness.

(c) Properties of azides

Organic azides are precursors for the generation of reactive "Nitrene" intermediates. Peter Griess⁸³ was first to synthesize an organic azide namely phenyl azide from benzene diazonium perbromide and ammonia¹. Curtius rearrangement⁸⁴ of acyl azides to isocyanates

TABLE - 7
EFFECT OF MOLECULAR SIZE ON WASH - FASTNESS

LESS FAST	MORE FAST
	
	
	

generated great interest in organic azides.



Organic azides undergo decomposition under thermal or photolytic conditions to generate "nitrenes". Nitrene is an electron deficient nitrogen having a sextet of electrons in the outer shell⁸⁵. If the electrons are paired then nitrene is in the singlet state. If the electrons are unpaired, then the nitrene is in the triplet diradical state. In the singlet state the electron deficient nitrogen is highly electrophilic⁸⁵.



Triplet nitrene



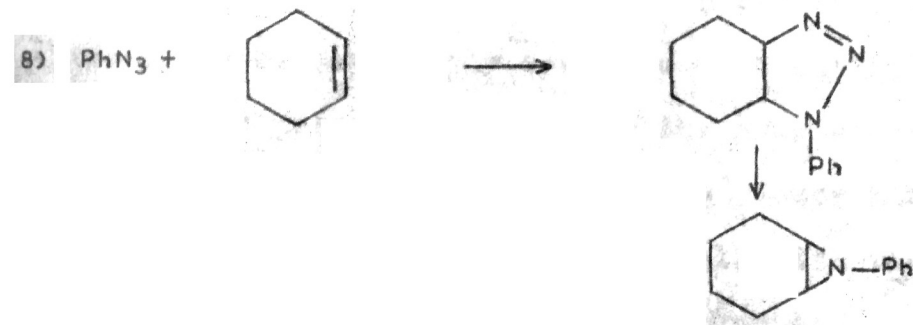
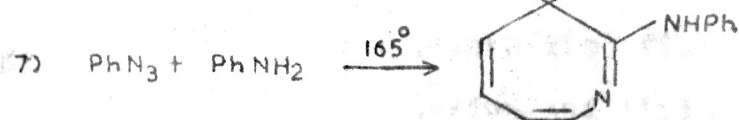
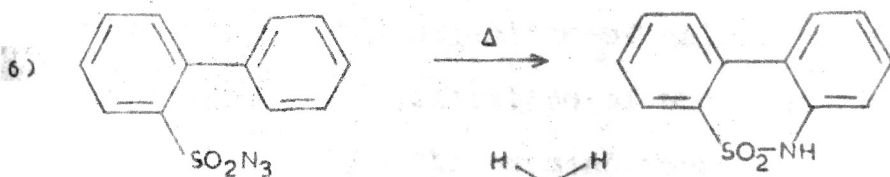
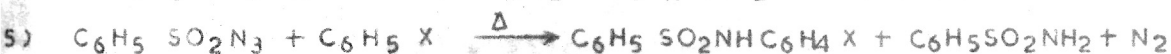
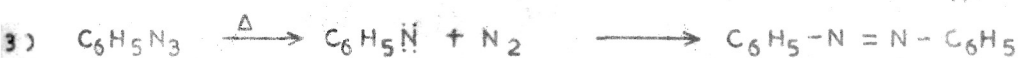
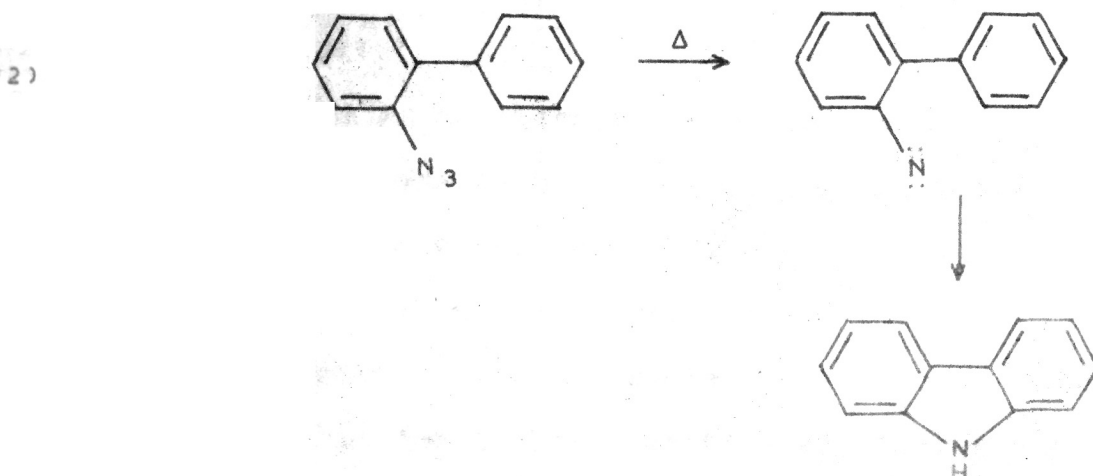
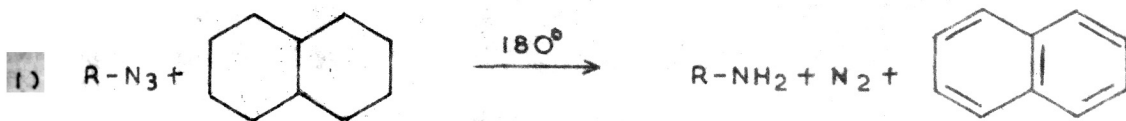
Singlet nitrene

Nitrenes are also known as imenes, azenes, imidogens, imido intermediates and azacarbene. The name nitrene itself is parallel to "carbene" which is neutral bivalent carbon intermediate.



The ground state of nitrenes is the triplet state. The nitrene generated by the thermal process is always in the singlet state⁸⁶ whereas the results from photolysis

TABLE - 8



of the azides have been interpreted in terms of a triplet representation for the nitrene at the ground level. Nitrenes undergo a variety of reactions which include hydrogen abstraction, insertion into aliphatic and aromatic hydrocarbons addition to olefinic double bonds, cyclization and dimerization^{85,87-93} as shown in Table 8.

Cyclization of nitrenes leads to a variety of heterocyclic systems such as, carbazole, carboline, phenazine, benzimidazole, indazole, aziridine etc. A typical reaction of triplet nitrene generated by photolysis is hydrogen abstraction from saturated carbon atoms whereas C-H insertion is the typical reaction of singlet nitrene generated by thermolysis⁹⁴.

Nitrenes can be generated by (a) decomposition of azides (b) the deoxygenation of nitro and nitroso compounds and (c) oxidation of amines⁸⁵. Of the three methods only the generation of nitrenes by thermolysis was considered in the present work since thermolytic treatment of dyed (synthetic) fibres is routinely carried out in commercial dyeing and finishing. In addition, thermolysis would lead to insertion of the dye which would therefore be reactively combined with the fibre substrate.

The general methods for the preparation of organic compounds containing various azido groups have been discussed in Chapter II, which deals with the synthesis of dyes containing various azido groups.

REFERENCES

1. Cross, C.F. and Bevan, E.J., Researches on Cellulose (1895-1900) pp. 34-9.
2. Schroeter G., Ber. 39 (1906), 1559.
3. B.P., 209, 723 (CIBA).
4. B.P. 259, 634; USP 1,567,731 (BASF)
5. Peacock, D.H., J.Soc.Dyers. Colour 42 (1926), 53.
6. B.P., 341, 461 (IC).
7. B.P., 363 897 (CIBA); USP, 1,886,480.
8. B.P. 346, 385; 347,117; 347,263.
9. B.P., 499, 868 (IG).
10. Dawson, T.L., Fern, A.S. and Preston, C., J.Soc.Dyers. Colour, 76, 210 (1960).
11. B.P., 533,073 (CIBA).
12. Solodkov, P.A. and Kursanov, D.N. Zh.prik. Khim (USSR) 16, (1943), 351.
13. Guthrie, J.D., Amer.Dyestuff Reprtr. 41, 13 (1952) USP, 2,741,532.
14. McLaughlin, R.R. and Mutton, D.B. Can.J.Chem. 33 (1955), 647.
15. USP 2,424,493 (CIBA); B.P. 587, 467 (CIBA).
16. Heyna, J. in "Chemistry of Natural and Synthetic Coloring Matters and Related Fields" Ed. Gore, T.S. et al. (1962), Academic Press, p. 473.
17. Warren, J. Reid, J.D. and Hamalainen, C.G., Text. Res. J. 22 584 (1952).
18. Stephen, W.D. Chimia, 19, 261 (1965).
19. Siegel, E. in "The Chemistry of Synthetic Dyes", Vol. VI, Ed. K. Venkataraman (1972) Academic Press (Inc. New York) p. 2.

20. Scot, D.F. and Vickerstaff, T. J.Soc.Dyers Colour 76, 104 (1960).
21. Siegel, E., Chimia Supplement, Synthesis and Reaction Mechanism in Colour Chemistry 1968, 100.
22. B.P. 833, 396 (ICI); USP 3,042,477 (ICI)
Fr. P. 1,177, 851 (ICI).
23. B.P. 862,269 (ICI).
24. Belg. P. 571, 739; 571,740; 571, 742 (ICI);
B.P. 840, 903 (ICI); Fr. P. 1,212,297; 1212, 298 (ICI).
25. Stam, O.A., J.Soc. Dyers Colour, 80 416 (1964)
26. B.P. 822, 948 (ICI).
27. CIBA, Be. P. 598, 707; S.Be P.604, 093.
28. ICI, B.P. 877,667.
29. S.Be P 608, 149; 609, 090.
30. ICI, B.P. 879,263; S. Be.P 597, 309.
31. MCI, S.P. 6833/62; J.P. 26,740/63; 20,236/63.
32. S., Be P 594, 910.
33. CIBA, 1,001, 437.
34. ICI, B.P. 869,100; 877,250.
35. ICI, F.P. 1,279,731.
36. ICI, B.P. 880,886.
37. ICI, B.P. 836,671.
38. S. SP 362,051; F.W . B.P. 922,683; F.P., 1,292,454.
39. IG, DRP 743,766.
40. ICI, BP 821,963; ICI BeP 571, 743.
41. Siegel, E.in "Chemistry of Synthetic Dyes" Vol. VI,
Ed. K. Venkatsaraman, Academic Press, Inc.
New York (1972) p. 74.
42. ICI, Be. P. 571,739; B.P., 875, 105;
F.P. 1,465,924.

43. ICI, BeP 571,740; 571,742; B.P., 868, 468
B.P., 875, 451.
44. S, Be.P., 585, 384.
45. ICI, B.P. 822, 948.
46. ICI, B.P. 826, 375.
47. S, SP. 340, 927.
48. Aena, Be. 666,229.
49. ICI, F.P. 1,177,851; B.P. 802, 935
B.P. 558, 433.
50. S., Be.P. 596,341.
51. ICI, B.P. 1029,212.
52. MCI, J.P. 12082/64; ICI, F.P. 1,419,946.
53. CIBA, SP 356,225; BeP 578, 416.
F.Bye, BeP 598,651; 611,423; 611, 424.
54. Manake, O. Konishi, H., Urakato, T., Hameo, T.,
and Miyama, H., Yuki Goseikagaku Kyokai Shi 20
935-39 (1962), Abstract J.Soc.Dyers Colour 79,
331 (1963).
55. F.By., Be.P. 611, 823 (1960).
56. Manake, O. Konishi, H. Urakato, T., Hameo, T.,
and Hyama, H., Yuki Gosei Kagaku Kyokai Shi 20
940-946 (1962).
57. Kalyan Raman, S. (B.D. Tilak) Ph.D. Tech.Thesis,
Bombay University (1969).
58. Kulwant Singh (B.D. Tilak) Ph.D. Tech. Thesis,
Bombay University (1973).
59. Ayyengar, N.R., Badami, N.V., B.M. Tilak, B.D.
Lugade, A.G. & Daruwala, E.H. Colourage XX, 33 (1973).
60. Kanatsu, Kiroku Tamura, Shuji, Kuroki,
Nobuhiko, Kogyo Kagaku Zasshi, 74 2503-7 (1971).
61. Griffiths, J. F.P. 2,033, 686.

62. Sunthanker, S.V. and Patkar, G.O., Indian J.Chem., 11, 402 (1973).
63. J.Soc. Dyers Colour, 69, 121 (1953).
64. B.D.C. Green and Saunders, B.P. 197, 809; 200, 873; 212, 029; 212, 030.
65. Fourness, R.K., J.Soc.Dyer Colour 72, 513 (1956).
66. British Celanese and Eltis, B.P., 219, 349.
67. British Dyestuffs Corporation, Baddeley and Shepherdson, B.P., 211,720.
68. The Silver Springs Bleaching and Dyeing Co.Ltd. and Hall, A.J., B.P., 222,001.
69. Vickerstaff T. "The Physical Chemistry of Dyeing" Oliver and Boyd, London, 2nd Edition, (1954) p.335.
70. Daruwalla, S.H. and Turner, H.A. J.Soc.Dyer. Colour 69, 240 (1953).
71. Sunthanker, S.V. in 'Chemistry of Natural and Synthetic Colouring Matters' Ed. Gore T.S. et al. Academic Press, New York, (1962) p. 517.
72. Giles, C.H., J.Soc. Dyers Colour, 73, 127 (1957).
73. Knight, A.H. J.Soc.Dyers Colour, 66, 169 (1950).
74. Schroeder, H.E. and Boyd, S.N., Textile Research J., 27, 275 (1957).
75. Dickey, J.B., Ind.Eng.Chem., 48 209 (1956).
76. Ko Naik, Sen-Gakkaischi, 15, 203 (1959).
[c.f. CA 53,9675 (1959)]
77. Salvin, V.S. and Adams, J.R., Amer.Dyestuff Reporter, 48, 43 (1959).
78. Rowe, F.U. Chamberlain, K.A., J.Soc. Dyers Colour, 63, 263 (1937).
79. Salvin, V.S., Peist, W.D. and Myles, W.J., Amer. Dyestuffs Repr., 41, 297 (1952).
80. Salvin, V.S. and Walker, R.A., Amer.Dyestuffs Repr., 48, 35 (1959).

81. Salvin, V.S. and Walker, R.A., Textile Research J. 30, 381 (1960).
82. Salvin, V.S. Amer. Dyestuffs Repr. 55, 48 (1966).
83. Griess, P., Trans. Roy. Soc. London 13, 377 (1964).
Ann. chem. 135, 131 (1865); Ann. Chem., 137, 39 (1866);
Ber., 2, 370 (1869).
84. Curtius, T. Ber., 23, 3023 (1890); J. Prakt. Chem.,
60, 275 (1894).
85. Abramovitch, R.A. and Davis, B.A., Chem. Rev., 64
149 (1964).
86. Smolinsky, G., Wassermann, E. and Yager, W.A.,
J. Am. Chem. Soc., 84, 3220 (1962).
87. Horner, L. and Christmann, A., Angew. Chem. Intern. Ed.,
2, 592 (1963).
88. L' Abbe, O. Chem. Rev. 69, 345 (1969).
89. "Nitrenes" Ed. Lwowski W. (1970) Interscience
Publishers, New York.
90. "Carbenes, Nitrenes and Aryenes" Gilchrist, J.L.
and Rees, C.W., (1969), Appleton-Century-Crafts,
New York.
91. "The Chemistry of the azido group" Ed. Patai, S. (1971)
Interscience Publishers, New York.
92. Smalley, R.K. Buschitzky, H., Chem. and Ind.,
1970, 1338.
93. Abramovitch, R.A. and Sutherland, R.G.,
Fortsch. Chem. Forsch., 16, 1 (1970).
94. Breslow, D.S., Sloan, M.F., Newburg, N.R.,
Renfrow, N.B., J. Am. Chem. Soc., 91, 2273 (1969).

CHAPTER - II

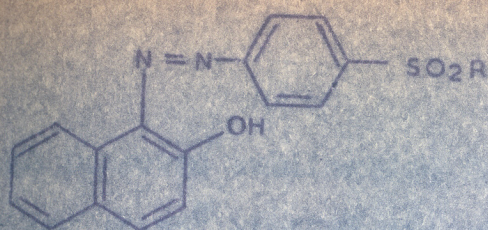
Synthesis of Reactive Disperse Dyes

INTRODUCTION

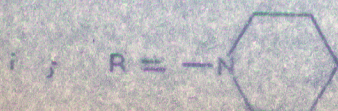
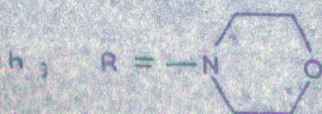
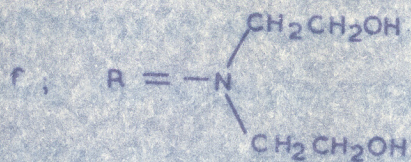
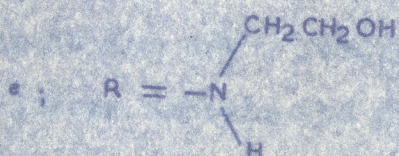
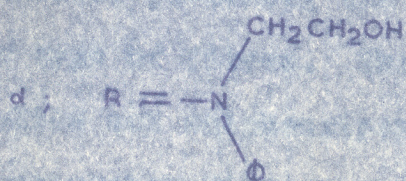
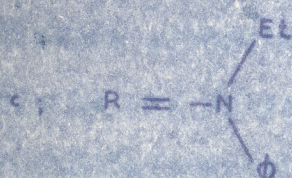
Sublimation fastness is one of the most important requirements of disperse dyes. In yellow to red range of disperse dyes which are mostly simple azo dyes, the sublimation fastness is generally not very satisfactory. Although these dyes have very good dyeing properties, the lack of high sublimation fastness limits their use. Sublimation fastness is even more important in the case of a highly hydrophobic fibre like the polyester which is usually dyed at high temperatures by "thermosol process" and is subjected to thermo-setting treatment.

Introduction of polar substituents resulted in improved sublimation fastness. Thus dyes containing β -hydroxyalkylamino, sulphonamido groups had good sublimation fastness. However, even though dyes containing sulphanamido groups have improved sublimation fastness, they exhibit lower substantivity for the fibre substrate¹.

The effect of introduction of sulphonamide groups in disperse dyes on their fastness and dyeing properties have received considerable attention in recent years. Stead and Murray² have observed that replacement of the nitro group in 4-amino-4'-nitroazobenzene by sulphonyl or sulphonamide group resulted in dyes with enhanced



I

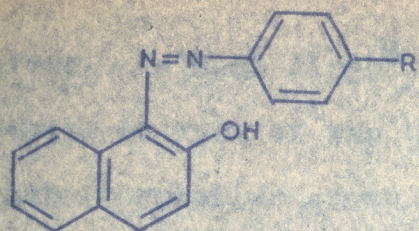


brilliance and improved sublimation fastness.

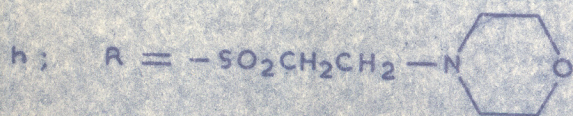
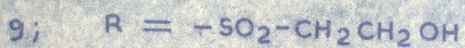
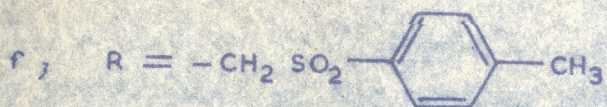
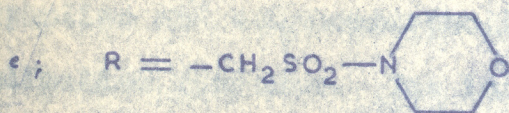
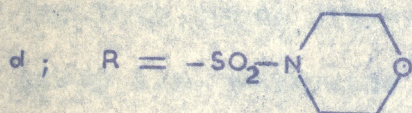
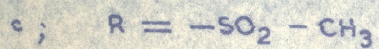
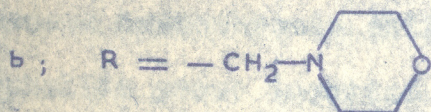
Salvin and Adams³ studied the effect of introducing sulphonamido group in nitrodiphenylamine dyes on their dyeing properties with respect to triacetate and polyester fibres.

Kalyanaraman⁴ in this laboratory has studied the effect of introducing sulphonamido and sulphon-morpholide groups in Acid Orange II (I) as regards their dyeing and fastness properties with respect to cellulose acetate, polyamide and polyester fibres. They concluded that the hydrophobic/hydrophilic balance of the dyes is an important factor governing the affinity of these dyes for the above type of fibres. The introduction of sulphonmorpholide and sulphonpiperidide groups favoured affinity for polyester fibre whereas the more polar sulphon-diethanolamide group favoured the affinity for secondary cellulose acetate and polyamide.

From the work of Kalyanaraman⁴ it was observed that, whereas the affinity of the dyes containing sulphon-morpholide group for polyester fibre increased compared to dyes containing other sulphonamido groups, the tinctorial strength of the dyes was considerably reduced. It was thought that this reduction in tinctorial strength might be due to the hypsochromic effect of the sulphon-



II



morpholide group. Kulwant Singh⁵ from this laboratory prepared a series of dyes of the type (II) which contained sulphonmorpholide group which was attached to the chromophore through an insulating group such as the methylene (-CH₂-) with the view to improve their tinctorial power. These studies revealed that:-

(a) sulphone group when directly attached to the chromophore causes hypsochromic shift, (b) introduction of sulphonmorpholide group imparted greater substantivity to all synthetic fibres whereas introduction of only the morpholide group increased substantivity for cellulose acetate but decreased it towards polyester. Introduction of the sulphone group by itself reduced substantivity for both these fibres, (c) introduction of insulating group i.e. methylene bridge, increased substantivity for polyester fibre and (d) introduction of sulphone, morpholino and sulphonmorpholide groups lead to higher sublimation fastness. The insulating group did not influence sublimation fastness.

Present work

6 From the examination of the earlier work, it was thought that maximum sublimation fastness along with improved light fastness in case of simple monazo disperse yellow dyes in the/to red range could be realised if a co-valent bond is formed between dye and fibre as in case of

reactive dyes for cellulose and polyamide fibres. We concentrated on polyester fibres which had not been reactively dyed because of lack of reactive sites such as hydroxy and amino groups in these fibres. A non-conventional approach in development of reactive dyes for polyester fibres was therefore necessary.

Survey of literature for various reactive systems led us to the preparation of dyes containing the "azido groups". Azides generate "nitrenes" under thermal and photolytic conditions, and the nitrenes react with a variety of organic compounds by insertion into aliphatic and aromatic hydrocarbons, addition to olefinic double bonds, cyclization and dimerization.

We therefore synthesized a series of dyes derived from azo and anthraquinone chromophores containing the azido groups. The synthesis of dyes containing sulphonylazido, carbonyl azido, arylazido and azidoscetamido groups is discussed in the succeeding paragraphs. The dyes were applied as conventional disperse dyes. On polyester they were dyed by "high temperature dyeing" method and on polyamide and secondary cellulose acetate by exhaust dyeing at 100° . These dyes were stable during dyeing, but probably generated 'nitrenes' when the dyeings were subjected to heat treatment in the range of $150-200^{\circ}$.

Nitrenes then reacted with the fibre substrates forming covalent bonds between the dye and the fibre substrate. The details of the dyeing and fixation are discussed in Chapter III which deals with application of dyes containing the azido groups.

Synthesis of Reactive Disperse Dyes

This Chapter is subdivided into four sections:

1. Sulfonyl azides
2. Carbonyl azides
3. Aryl azides
4. Azido acetamido derivatives

Section I

Dyes containing sulfonazido groups

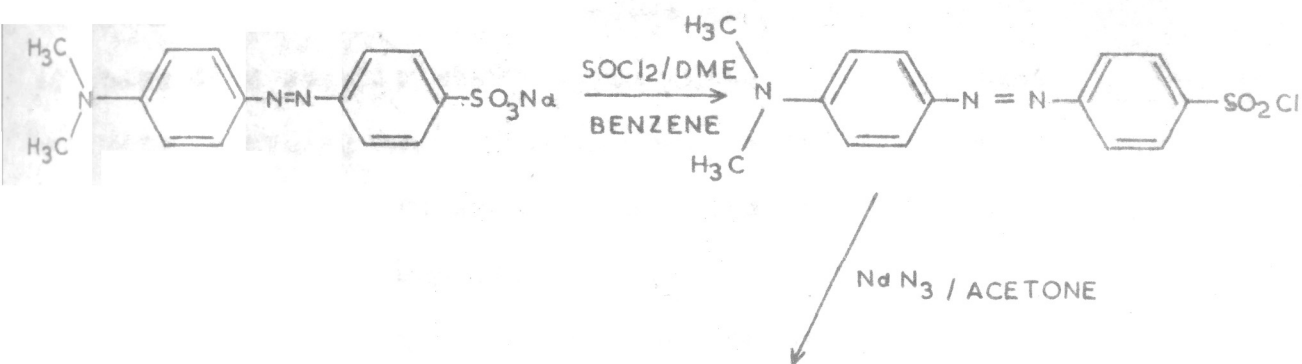
The dyes containing the sulfonazido group were prepared by two methods: the reactive sulphonazido group as introduced in the preformed α azo dye or by using an arylamine containing a sulphonazido group.

a) Dyes containing the sulfonic acid groups were converted into the corresponding sulfonyl chlorides by treatment with thionyl chloride and dimethyl formamide in solvents like benzene, chlorobenzene and the resultant sulfonyl chlorides were treated with sodium azide in solvents like acetone and alcohol (Scheme 1).

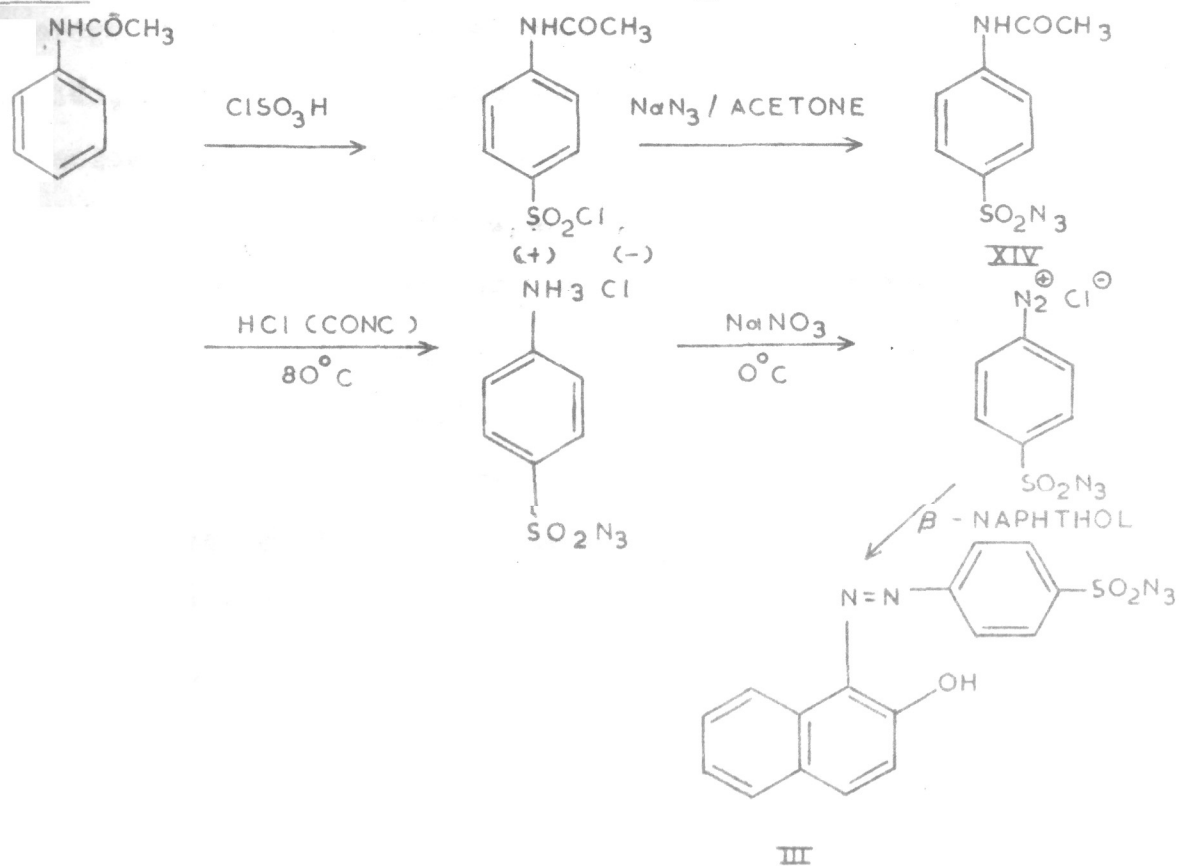
b) Acetanilide and substituted acetanilides were chlorosulfonated with chlorosulfonic acid to obtain the sulfonyl chloride derivatives which were then treated with sodium azide in acetone. The resultant p-sulfonyl azido-acetanilides were hydrolysed with concentrated hydrochloric acid and the resulting amine diazotized and coupled with various coupling components to yield the relevant dyes which contained sulphonazido groups (Scheme 2).

CHART - I

SCHEME -1



SCHEME -2



EXPERIMENTAL

Note: Whereas the synthesis of the various dyes containing azido group is described below, properties of these dyes such as crystalline shape, melting point and data regarding solvent used for crystallisation, IR data and elementary analysis are recorded in tables at the end of this Chapter.

All the melting points are uncorrected. The melting points above 150° are due to the decomposition as the azides are known to decompose between $120-150^{\circ}$. Many dyes show low values for nitrogen due to high percentage of nitrogen in the dyes. Dye containing arylazido, azidoacetamido groups do not analyse satisfactorily for nitrogen. However, the carbon and hydrogen analysis of all the dyes were satisfactory. Wherever possible the structure was confirmed by recording mass-spectra. All the dyes give distinct IR spectra which show characteristic absorption band for the azido group between $2100-2140\text{ cm}^{-1}$ and for the sulphonyl or carbonyl groups attached to the azido group at $1310-1400\text{ cm}^{-1}$ and $1670-1690\text{ cm}^{-1}$ respectively. All IR spectra were recorded as Nujol mulls.

(a) Synthesis of dyes containing sulfonyl azido group from corresponding dyes containing sulfonic acid groups:

Refer Scheme 1 in Chart 1.

4'-Sulphonsazido)phenylazo-2-naphthol (III)

Dye (III) was prepared from Acid Orange II (CI15510).

Sulfanilic acid 19.5 g (0.1 mole) was diazotized with sodium nitrite and hydrochloric acid⁶ and coupled with β -naphthol 14.4 gm (0.1 mole) dissolved in 100 ml of 10% sodium hydroxide solution. Temperature during coupling was maintained between 0-5°. After 2-3 hours stirring the orange-red-dye was filtered redissolved in minimum amount boiling water and reprecipitated by adding rectified spirit after cooling. The pure dye was filtered and dried.

Pure Acid Orange II (17.5 g; 0.05 mole) prepared above was suspended in chlorobenzene (150 ml). Initially chlorobenzene (50 ml) was distilled off to remove last traces of water. The mixture was then cooled down to 30° and thionyl chloride 4.2 ml (0.051 mole) and dimethyl formamide (1 ml, catalytic amount) were added slowly. The temperature was raised to 60° and stirred for 1 hour. The temperature was then raised to 95° and the mixture stirred for one hour more. The completion of the formation of sulphonyl chloride was observed by testing

the solubility of the reaction mixture in water. The aqueous phase should not turn coloured when made alkaline, if the reaction is complete. The reaction mixture was cooled to room temperature and the separated sulphonyl chloride crystals were collected and washed with little petroleum ether (60-80° b.p.) and ice-cold water.

The sulphonyl chloride obtained was dissolved in minimum volume of acetone (about 200 ml) and stirred at room temperature. Sodium azide (3.6 g; 0.051 mole) dissolved in 20 ml of distilled water was added slowly. The mixture was stirred for 1/2 hr. at room temperature and then at 50° for 1 hour. On dilution with water (about 200 ml) the sulphonylazide (III) separated out. The dye (III) was collected, washed with water and dried at 45-50° (Yield 15 g).

Further purification of (III) was achieved by chromatography on a silica gel column using benzene as eluent. The dye (III) finally yielded shining orange red crystalline plates from benzene.

1-Phenylazo-6-sulphoneazido-2-naphthol (IV)

Dye (IV) was prepared from Acid Orange 12 (CI 15970) (1-phenylazo-2-naphthol)-6-sodium sulphonate).

Acid Orange 12 was prepared⁷ by coupling benzene diazonium chloride [prepared by diazotization of

(9.3 g; 0.1 mole) of aniline⁷ with Shaeffer's salt at 0-5° (24.6 g; 0.1 mole) dissolved in 100 ml of 10% sodium hydroxide solution. During the coupling the temperature was maintained at 0-10°. The orange red dye (28 g) was isolated by salting out. The dye was dissolved in minimum amount of boiling water, cooled and then rectified spirit was added to reprecipitate the dye which was filtered and dried.

Acid orange 12 (17.5 g; 0.05 mole) prepared above was suspended in chlorobenzene (150 ml). Initially 50 ml of chlorobenzene was distilled out to remove last traces of water. After cooling to room temperature thionyl chloride (4.2 ml; 0.051 mole) and dimethyl formamide (1 ml) were added. Temperature was then raised to 60° and maintained for 1 hr. and mixture further heated to 95° and maintained for 1 hour more. Completion of the reaction was checked as mentioned above. The reaction mixture was cooled to room temperature and the sulphonyl chloride was filtered, washed with petroleum ether and then with ice cold water.

The dye-sulphonyl-chloride obtained above was dissolved in acetone (about 200 ml). A solution of sodium azide (3.6 g; 0.051 mole) in water (20 ml) was then added slowly. The reaction mixture was stirred at room

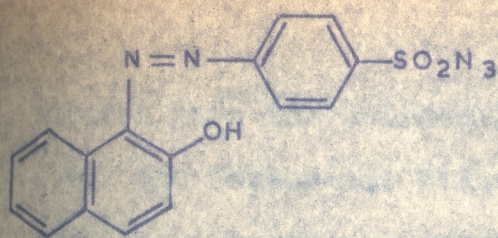
temperature for 1/2 hour and then at 50° for 1 hour. The separation of dye-sulphonyl-azide was brought about by diluting the mixture with water. The dye (IV), obtained in quantitative yield (16.5 g), was further purified by chromatography on silica gel column using benzene as eluent and finally by crystallisation.

4-Dimethylanilino-(4'-sulphonazido)azobenzene (V)

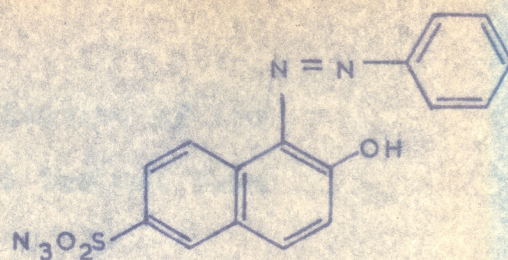
Dye (V) was prepared from Acid Orange III (Acid Orange 52, CI, 13025) (4-Dimethylaminodisobenzene-4-sodium sulphonate).

Acid Orange (III) was prepared⁸ by known methods by diazotizing (19.5 g; 0.1 mol) of sulfanilic acid with sodium nitrite and hydrochloric acid at 0-5° and then coupling under acid conditions with (12.1 g; 0.1 mole) of N,N-dimethylaniline at 0-5°. After stirring the reaction mixture overnight, the dye was salted out and filtered. The crude dye was purified by the method mentioned earlier.

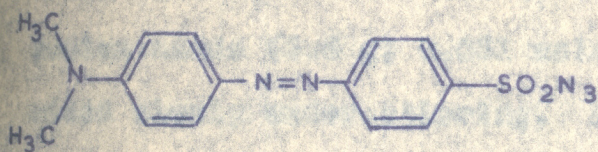
16.35 g (0.05 mole) of the purified dye was suspended in benzene (150 ml). After removal of some benzene (50 ml) by distillation to remove traces of water, the reaction mixture was cooled to room temperature. Thionyl chloride (4.2 ml; 0.051 mole) and dimethyl formamide (1 ml) were added and the mixture heated under reflux for 1.5 hours. On cooling to room temperature the



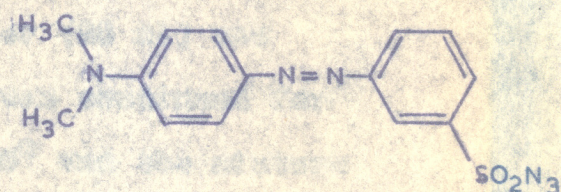
III



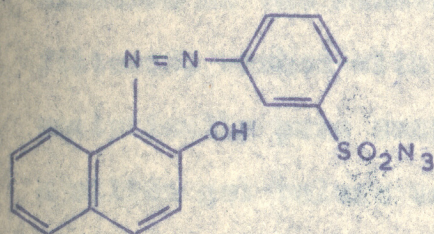
IV



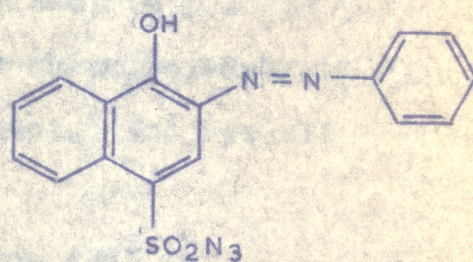
V



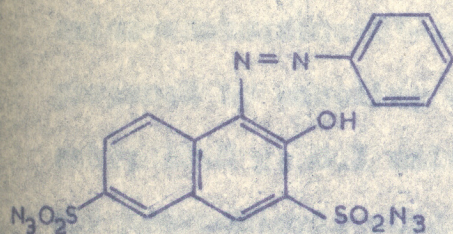
VI



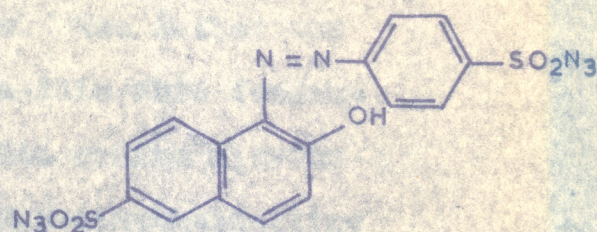
VII



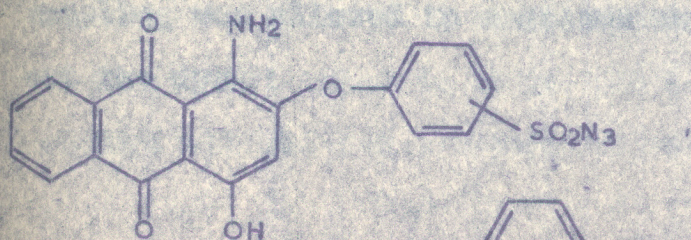
VIII



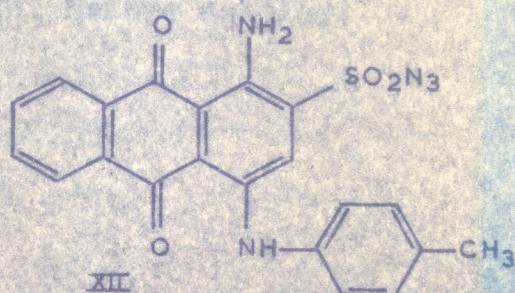
IX



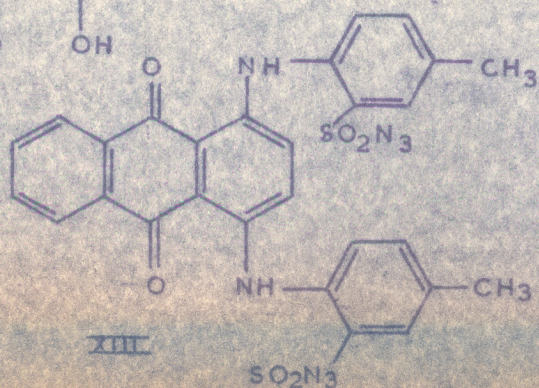
X



XI



XII



XIII

mixture gave the sulphonyl chloride derivative of the dye. The latter was filtered washed and the wet cake used for subsequent reaction.

The above sulphonyl chloride was dissolved in minimum volume of acetone (150 ml) and a solution of sodium azide (3.6 g; 0.051 mole) in water (20 ml) was added slowly under stirring. Stirring was continued for 1/2 hr. and the temperature raised to 50° and the mixture stirred for 1 hour more. Dye (V) separated out by dilution of the reactive mixture with water. The dye was filtered, washed with water and dried (yield, 14 g). An analytically pure sample was obtained by chromatography on a silica gel column using benzene as eluent. The dye was finally crystallized from benzene.

4-Dimethylamino-3'-sulphonazido-azobenzene (VI)

Dye (VI) was prepared from the acid dye, 4-dimethylamino-azobenzene-3'-sodium sulphonate. The latter was prepared by coupling diazotized methanilic acid (sodium salt; 19.5 g; 0.1 mole) diazotized with sodium nitrite and hydrochloric acid at 0-5°) with N,N-dimethylaniline (12.1 g; 0.1 mole) at 0-5° under acidic conditions. The coupling was allowed to continue overnight before salting out the dye.

The method of preparation of sulphonyl azide from the above acid dye was exactly same as for the dye from Acid Orange III.

1-(3'-Sulphonazido)phenylazo-2-naphthol (VII)

Dye (VII) was prepared from the acid dye, 1-phenylazo-2-naphthol-3'-sodium sulphonate.

Sodium metanilate (19.5 g; 0.1 mole) was diazotized with sodium nitrite and hydrochloric acid and coupled with β -naphthol (14.4 g; 0.1 mole). The acid dye was salted out, filtered and purified as in Acid Orange II.

17.5 g (0.05 mole) of the dry acid dye was suspended in chlorobenzene (150 ml), 50 ml of chlorobenzene was distilled off to remove traces of water present. The reaction mixture was cooled to room temperature and thionyl chloride (4.2 ml; 0.051 mole) and dimethyl formamide (1 ml) were added. The temperature was then raised to 60° and the mixture stirred for 1 hour. Temperature was further raised to 95° and the mixture heated for 1 hour more. The reaction mixture on cooling to room temperature gave the sulphonyl chloride.

The dye-sulphonyl-chloride was dissolved in minimum amount of acetone (200 ml). A solution of sodium azide and (3.6 g; 0.051 mole) in water (20 ml) was added to the mixture stirred for 1/2 hour at room temperature and

then at 50° for 1 hour. Dye (VII) was then precipitated by dilution with water. Chromatography over silica gel column gave the pure dye (VII).

2-Phenylazo-4-sulphonazido-naphthol (VIII)

Dye (VIII) was prepared from the acid dye, sodium-azo-2-phenyl-1-naphthol sulphonate.

The latter was prepared by diazotizing aniline (9.3 g; 0.1 mol) and coupling with N.W. acid (1-naphthol-1-sulphonate). The acid dye was then converted to the sulphonyl azide as in the case of the preceding dyes.

1-Phenylazo-3,6-disulphonazido-2-naphthol (IX)

Dye (IX) was synthesised from Acid Orange-14 (CI-16100) (1-phenylazo-2-hydroxynaphthalene-3,6-di-sulphonic acid disodium salt).

Aniline (9.3 g; 0.1 mole) was diazotized with sodium nitrite and hydrochloric acid at 0-5° and the diazo solution coupled with R-salt (2-hydroxynaphthalene-3,6-disulfonic acid disodium salt) (34.8 g; 0.1 mole) under alkaline conditions at 0-10°. Dye was salted out, filtered and purified by dissolving and reprecipitation with rectified spirit.

The above acid dye (22.6 g; 0.05 mole) was suspended in toluene (200 ml). 50 ml of toluene was distilled off to remove traces of moisture. After cooling to room temperature, thionyl chloride (9 ml;

0.12 mole) and dimethylformamide, (2 ml) were added slowly. The mixture was heated to reflux and further heated for two hours. After removal of 75 ml of toluene (to remove excess thionyl chloride and dimethylformamide), the mixture was cooled to room temperature. A solution of sodium azide (7.8 g; 0.12 mole) in distilled water (15-20 ml) was ~~tanxx~~ then added slowly under stirring. The disulphonylazide started forming slowly. Stirring was continued over-night to complete the formation of the diazide. Dye (IX) formed was filtered and washed with water and the crude dye (18 g) was crystallised from benzene.

1-(4'-Sulphonazido)phenylazo-6-sulphonazido-2-naphthol (X)

Dye X was prepared as above starting from Food Yellow 3 (CI 15985) (the corresponding disodium disulphonate) which was prepared by coupling diazotized sulphanilic acid with Shaeffer salt.

1-Amino-4-hydroxy-2-sulphonazidophenoxy-anthraquinone (XI)

Dye (XI) was prepared starting from 1-amino-2-bromo-4-hydroxyanthraquinone by interaction with phenol in alkali followed by chlorosulfonation of the phenoxy derivative and final treatment with sodium azide.

Preparation of 1-amino-2-bromo-4-hydroxyanthraquinone

(BIO3, 1484,5)

1-Aminoanthraquinone (7 g) was taken in 250 ml glacial acetic acid and heated on water bath (100°C) under stirring. Bromine (25.8 g; 8.6 mole) in 50 ml of glacial acetic acid was added dropwise during 1 hour. Heating and stirring continued for 5 hrs. Kept overnight. The separated brominated compound was collected, washed with water and then with 2% sodiumbisulfate solution and again with water. Yield - 11 gms. Melting point 220-2° (from ODCB).

Boric acid (8.3 g) was dissolved in 250 g 3.5% oleum at 50-60°, 25 g 1-amino-2,4-dibromoanthraquinone was added and the charge heated slowly at 100° and kept there for 1 hour. The temperature is then taken up quickly to 20° and maintained there for 5 hrs. when no bromine or hydrobromic acid is given off, the charge was cooled to 60° and 175 ml water added when the temperature rose to 100°. After cooling to 70° the charge was filtered and washed. Yield 18.9 g.

1-Amino-2-bromo-4-hydroxyanthraquinone (18.9 g) was taken in (100 ml) of 10% sodium hydroxide solution at room temperature. 5.2 g phenol was added and temperature was raised to 140-150° and maintained under stirring for 16 hrs. It was then cooled, neutralised and filtered to

get 1-amino-2-phenoxy-4-hydroxy anthraquinone.

1-Amino-2-phenoxy-4-hydroxy anthraquinone (6.62 g; 0.02 mole) was stirred in 60 ml chlorosulfonic acid at 20-5° and kept for 1/2 hr. It was then poured on ice and filtered. The moist residue was immediately taken in acetone (200 ml) and treated with sodium azide (1.56 g; 0.022 mole) dissolved in 10 ml water. After stirring for 1 hr. it was warmed on waterbath. The dye was precipitated by adding water and filtered. Yield 6.2 g crude. Purification was done by crystallisation from methanol/benzene.

1-Amino-4-anilinoanthraquinone-2-sulphonazide (XII)

Dye XII is prepared from Alizarin Saphirol A (CI Acid Blue 25, CI 62055, 1-amino-4-anilinoanthraquinone-2-sulphonic acid).

Alizarin saphirol A is prepared from bromanine acid (1-amino-4-bromoanthraquinone-2-sulphonic acid). Bromanine acid (38.2 g; 0.1 mole) was taken in water (200 ml) water and to it were added toluidine (21.4 g; 0.2 mole), sodium carbonate (10.7 g; 0.1 mole), sodium bicarbonate (10.4 g; 0.1 mole) and copper chloride (CuCl_2) 2 g (catalytic amount) in hydrochloric acid. The temperature was raised to 65° in 1 hr and then it was raised to 95° in 3 hrs. The temperature was maintained at 95° for 1/2 hr. and then it was slowly cooled to 50°. The dye was filtered.

The press cake was redissolved and treated with sodium carbonate, charcoal and Keiselguhr to remove excess toluidine. Then it was filtered and dye was salted out from the filtrate and dried. Yield of the dye (35 g).

The acid dye, Alizarin Saphirol A (20.4 g; 0.05 mole) was taken in phosphorus oxychloride (POCl_3) 300 ml and then 10.3 g (0.052 mole) of phosphorus pentachloride was added. The reaction mixture was refluxed under stirring for 1.5 hrs. Then it was poured in ice-water slowly and the acid chloride separated was filtered and washed with ice-water to free it from acid.

The sulphonyl chloride of the dye was taken in 200 ml of acetone and kept under stirring. Sodium azide (3.7 g; 0.052 mole) dissolved in (10 ml) of water was added slowly. It was stirred at room temperature for 1 hr, then at 50° for one more hour. Stirring was continued overnight at room temperature. The dye-sulphonyl azide was then filtered, washed with water and dried at 45°C . Yield of the crude dye was (18 g).

1,4-Di-p-toluidinoanthraquinone-3'-3''-sulphon azide (XIII)

This was prepared from 1,4-Di-p-toluidinoanthraquinone by chlorosulphonation and then treatment with sodium azide.

1,4-Di-p-toluidinoanthraquinone was prepared according to Fierz-David¹⁰ by heating quinizarin with excess of p-toluidine in presence of boric acid and stannous

chloride. The dye was free from unreacted p-toluidine by extraction with ethanol and boiling with aqueous dilute hydrochloric acid.

Chlorosulphonation¹¹ of 1,4-Di-p-toluidinoanthraquinone

A mixture of 1,4-Di-p-toluidino anthraquinone (8.36 g, 0.02 mole) and chlorosulphonic acid (100 ml) was stirred at 70-80° for 4 hrs. After cooling to 30°, the mixture was poured in ice-water (800 g) under stirring. The dark blue sulphonyl chloride which precipitated was filtered and washed free of acid with ice water.

The wet cake was then taken in acetone 150 ml and treated with sodium azide 3.25 g (0.05 mole) in 10 ml of water. It was refluxed in acetone for 2 hrs. then diluted with water and filtered to collect the pure dye. Yield (9 g).

(b) Synthesis of dyes containing sulphonylazido groups from the intermediates containing sulphonyl azido groups

Scheme 2 in Chart I: The intermediate like p-sulphonylazidoacetanilide or 2-methoxy-5-sulphonylazido acetanilide are prepared by chlorosulphonation of the corresponding acetanilides. Resultant sulphonyl chloride is treated with sodium azide in acetone. Sulphonyl azido derivatives of acetanilides are hydrolysed, diazotized and coupled with various coupling components to obtain the dyes.

This process is very flexible as far as the synthesis of the dyes is concerned. Any coupling component or a dye having a free coupling position can be used. The sulphonyl azido acetanilides are stable and hydrolyse easily to the amines.

Synthesis of p-sulphonyl azido acetanilide (XIV)

Chlorosulphonation of p-aminoacetanilide was done according to the method described in the literature¹².

Chlorosulphonic acid (165 ml) was taken in a three necked flask fitted with thermometer and condenser. The flask was placed in an ice bath and the chlorosulphonic acid was cooled down to 15°. Acetanilide (67.5 g; 0.5 mol) was added slowly in 1/2 hr. During the addition the temperature was maintained at 15° by external cooling. The temperature was then slowly raised to 70° and maintained for 2 hrs. Then the reaction mixture was cooled down to room temperature and then drowned slowly into ice-water under vigorous stirring. Sulphonyl chloride of acetanilide separated as white powder. It was filtered and washed free of acid with ice-water.

p-Sulphonylazidoacetanilide was prepared from the corresponding sulphonylchloride according to Ashley and Buchanan¹³. The resultant cake from the chlorosulphonation was dissolved in 1500 ml acetone and

treated with sodium azide (33 g; 0.5 mole) dissolved in water (150 ml). The mixture formed two layers. Homogeneous mixture was made by adding further amount of water (350 ml) and acetone (150 ml). It was stirred for 3 hrs. at room temperature and then diluted with 10 litres of water. The product was filtered. Yield of the crude product (85 g). It was recrystallised from benzene m.p. 113-114°.

1-(4'-Sulphonazido)benzeneazo-2-naphthol (XV)

p-Sulphonylazido acetanilide (4.8 g; 0.02 mole) was hydrolysed to the corresponding amino compound by heating with 25 ml of concentrated hydrochloric acid on water-bath for 1 hr.

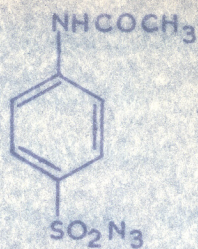
The amine was then diazotized with sodium nitrite (1.51 g; 0.021 mole) at 0° without isolation.

β -Naphthol (2.88 g) was dissolved in 100 ml of 5% sodium hydroxide and cooled down to 5°. The diazo was then added and pH was maintained at 8.5 - 9 by addition of 10% sodium carbonate solution. It was stirred for 3-4 hours, filtered and washed with water.

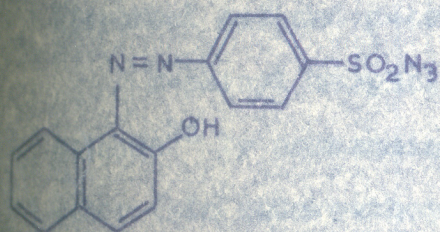
The dye was chromatographed on silica gel column and recrystallised from benzene.

Synthesis of 4-N-phenylmorpholino-4'-sulphonazido-benzene (XVI); 1-(4'-sulphon azido) phenyl azo-2-hydroxy-3-carboxy naphthmorpholide (XVII); 1-(4'-sulphonazido)

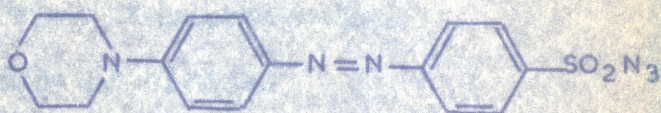
THE DYES PREPARED FROM



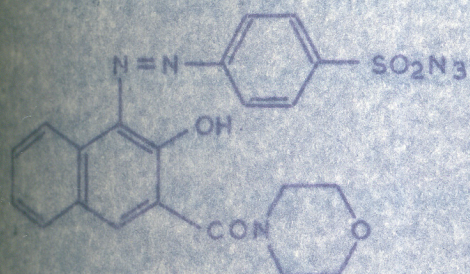
XIV



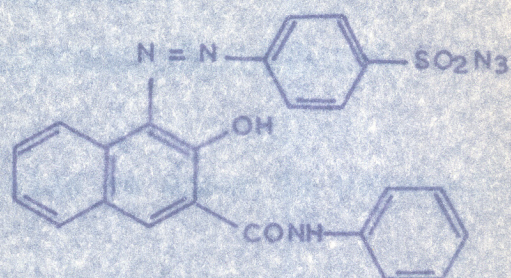
XV



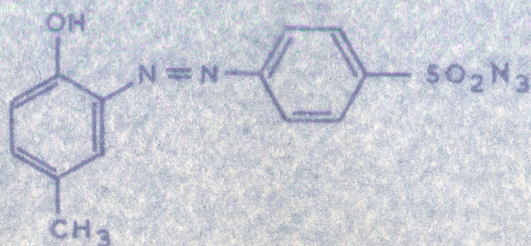
XVI



XVII



XVIII



XIX

phenylazo-2-hydroxy 3-carboxynaphthanilide (XVIII) and
2-(4'-sulphonazido) phenylazo-p-cresol (XIX)

These dyes were prepared by hydrolysing the p-sulphonyl azido acetenilide, diazotizing, and coupling as described in the preparation of XV. The coupling components used were N-phenyl morpholine, 2-hydroxy-3-carboxy naphth morpholide, 2-hydroxy-3-carboxynaphthanilide (Naphthol AS) and p-cresol respectively.

N-phenyl morpholine was prepared from the known methods¹⁴ by condensing aniline with dichlorodiethyl ether (bis chloroether) in presence of alkali.

2-Hydroxy-3-carboxy naphthamorpholide was prepared from 2-hydroxy-3-carboxy naphthalene (BON-acid) by converting it to acid chloride by heating with thionyl chloride and dimethyl formamide in toluene and then condensing the acid chloride with morpholine.

Synthesis of 1-acetylamino-2-methoxy-benzene-5-sulphonyl
azide (XX)

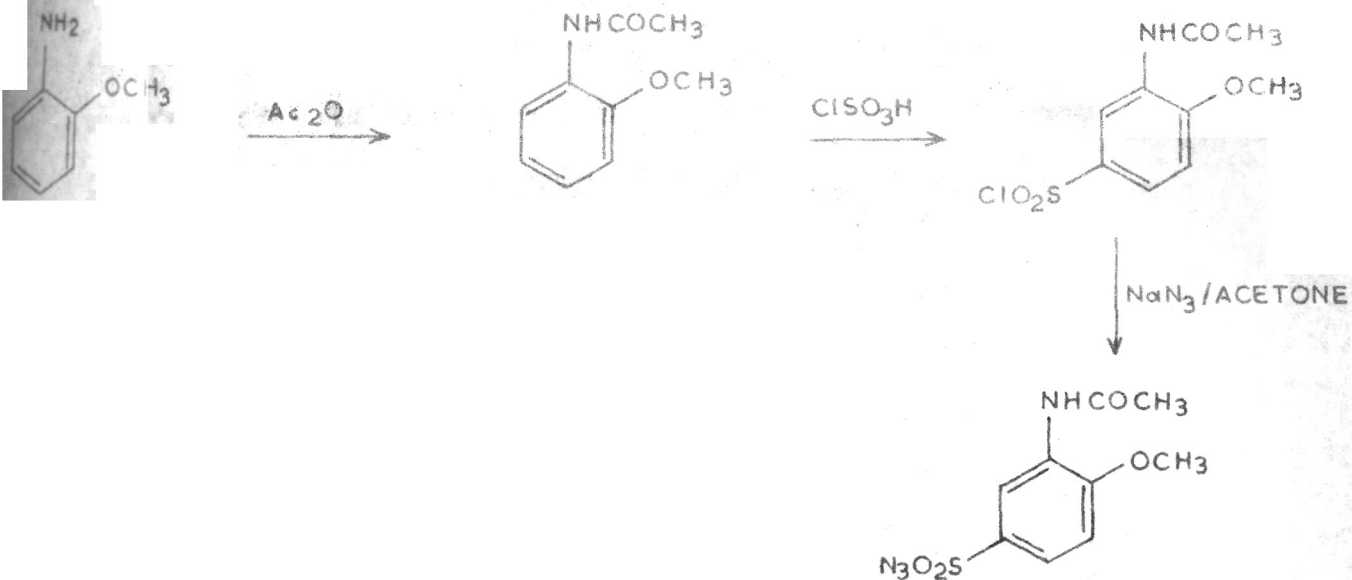
This was prepared from o-anisidine as shown in Scheme 3 in the Chart 4.

N-Acetyl-o-anisidine

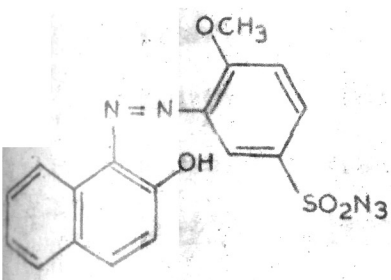
o-Anisidine was acetylated with acetic anhydride as described in literature¹⁵.

CHART - 4

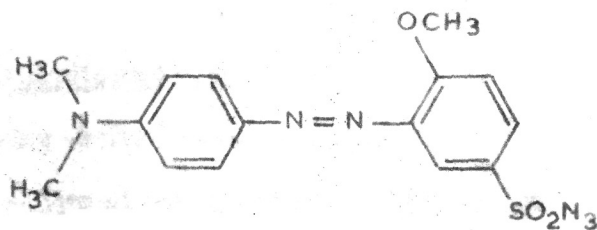
SCHEME - 3



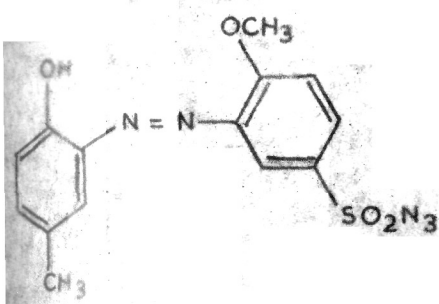
XX



XXI



XXII



XXIII

Chlorosulphonation of N-acetyl-o-anisidine

The compound was treated with chlorosulphonic acid as described in literature¹⁶. The compound was filtered ^{was free} of acid and immediately used in the next step.

Condensation of 1-acetylamino-2-methoxy-benzene-5-sulphonyl chloride with sodium azide

The resultant sulphonyl chloride from N-acetyl-o-anisidine (123 g; 0.75 mol) was dissolved in acetone, (100 ml) and kept under stirring at room temperature. Sodium azide (59 g; 0.87 mole) dissolved in 200 ml water was added slowly. The mixture was stirred for 3-4 hrs. at room temperature. It was then diluted with 5 litres of water. The sulphonyl azide (XI) was filtered and washed with water yield (155 g). It was crystallised from benzene m.p.

Synthesis of dyes 1-(2'-methoxy-5'-sulphon azido)phenylazo xixangix -2-naphthol (XXI); 4-Dimethyl anilino-2'-methoxy 5'-sulphonazido azobenzene (XXII) and 2-(2'-methoxy-5'- sulphon azido) phenyl azo-p-cresol (XXIII) from 1-acetyl- amino-2-methoxy benzene-5-sulphonazide

1-Acetylamino-2-methoxy-benzene-5-sulphonyl azide (5.4 g; 0.02 mole) was hydrolysed by heating with 30 ml of concentrated hydrochloric acid on waterbath for one hour. The resultant amine was diazotized with sodium nitrite (1.52 g; 0.022 mole) at 0°. The diazo was then

added to a solution of 2.9 g (0.02 mole) of β -naphthol dissolved in 100 ml of 10% sodium hydroxide solution at 0-5°. The solution was stirred for 3-4 hrs. to complete the coupling. The water insoluble dye (XXI) was filtered, washed with water and air dried on suction. Yield (6.5 g). The dye was purified by chromatography on silica gel column and crystallised from ~~benzene~~ benzene. The dyes (XXII) and (XXIII) were similarly prepared by coupling with N,N-dimethyl aniline and p-cresol respectively.

Discussion

The two synthetic routes available for the synthesis of sulphonyl azides have been shown in Chart 1 (Schemes 1 and 2).

By Scheme 1 the commercial acid dyes of the azo and anthraquinone series can be converted into the reactive dyes containing sulphonyl azido group. Whereas the synthesis of intermediates (XIV) and (IX) is very useful in the synthesis of azo dyes containing sulphonyl azido groups. It provides great flexibility in the sense that variety of coupling components of the benzene and naphthalene series can be used to build up a range of azo reactive dyes with the same diazo component.

Section II Carbonyl-azides

The preparation of carbonylazides or acyl azides are well known in literature since these compounds undergo the Curtius rearrangement to give isocyanates, Eq. 1.



The dyes containing the carbonyl azido group have been prepared by two methods.

(a) Starting from dyes containing a free carboxylic acid group by converting to the carboxyazide through the acid chloride.

(b) By diazobization of p-aminobenzoyl hydrazide followed by coupling with coupling components. During diazotization the carbonylhydrazide gets converted into the corresponding carbonylazido group.

(a) From the dyes containing a free carboxylic acid group

1-(4'-carboxylazido)-2-naphthol (XXIV) (Scheme 4, Chart 5)

The dye (XXIV) was prepared from acid dye 1-phenyl-azo-(4'-carboxy)-2-hydroxynaphthalene. The acid dye was prepared by diazotizing (6.85 g; 0.05 mole) of p-aminobenzoic acid with sodium nitrite (4.15 g; 0.052 mole) and concentrated hydrochloric acid at 0° and coupling with β-naphthol (7.2 g; 0.05 mole), dissolved in 100 ml

of 10% sodium hydroxide solution, at 0-10°. The dye was salted, filtered and dried.

The acid dye (6.28 g; 0.02 mole) was taken in 150 ml benzene. Benzene (50 ml) was distilled off to remove the last traces of water. The reaction mixture was cooled to room temperature and thionyl chloride (2.65 g; 0.022 mole) was added followed by 2-3 drops of DMF. The reaction mixture was raised to reflux under stirring and maintained for two hours. Benzene (50 ml) was again distilled off to remove the excess thionyl chloride. The reaction mixture was then cooled to room temperature. The separated acid chloride of the dye was filtered and used in the next step.

The acid chloride was dissolved in 100 ml of acetone and kept under stirring at room temperature. Sodium azide (156 g; 0.022 mole) dissolved in 10 ml water was slowly added to the solution of acid chloride and stirred for 1 hour at room temperature and 50° for 1 hour. Then it was diluted with water to precipitate the dye which was filtered and washed with water. Yield (4.5 g).

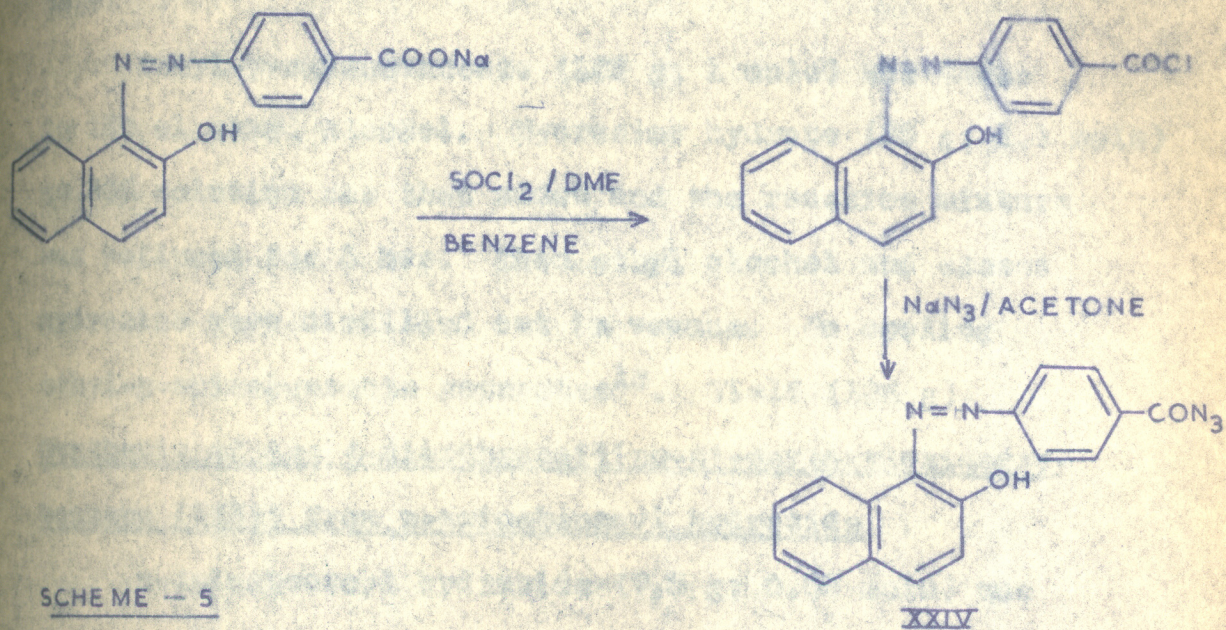
It was purified by chromatography on silica gel column and crystallised from benzene.

Synthesis of p-aminobenzoyl hydrazide (XXV)

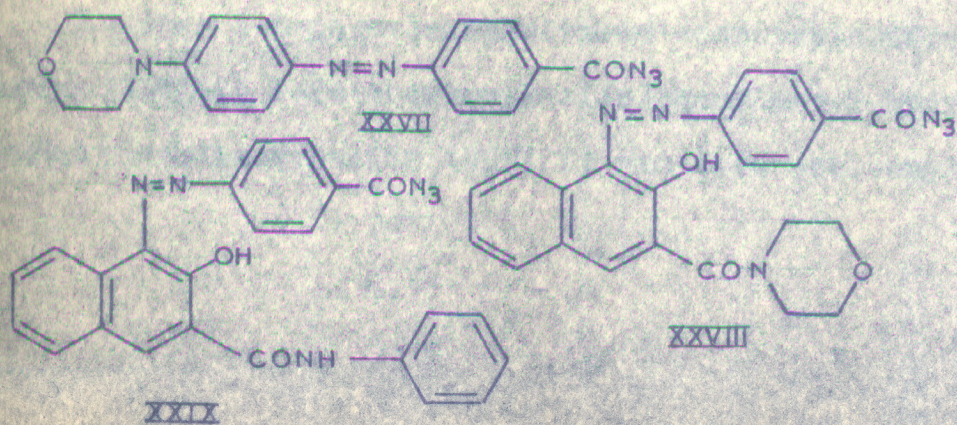
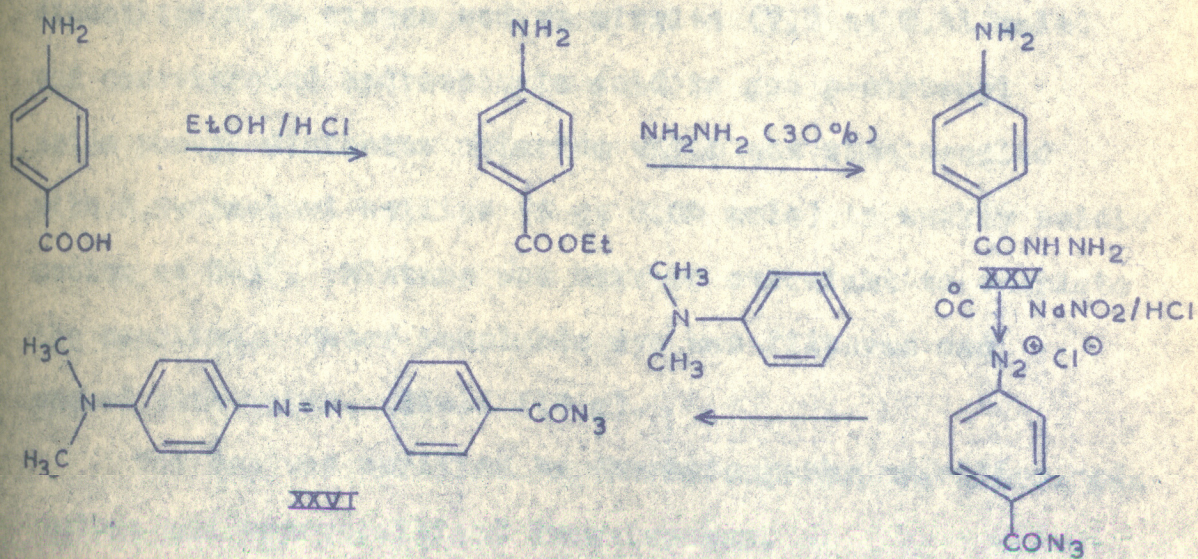
This compound was prepared from p-amino benzoic acid by esterification with ethyl alcohol and then treatment

CHART - 5

SCHEME - 4



SCHEME - 5



with hydrazine hydrate as in Schem 5 (Chart 5).

Ethyl-p-aminobenzoate was prepared according to Vogel¹⁷.

Ethyl-p-aminobenzoate (165 g; 1 mole) was taken in 150 ml ethyl alcohol. Hydrazine hydrate (35 g; 1.1 mole) as 50% solution was then added and the reaction mixture was refluxed for 5 hrs. Then ethyl alcohol and excess hydrazine were distilled out in vacuum. On cooling ethyl-p-aminobenzoate separates¹⁸. Yield (136 g).

Synthesis of dye 4-dimethylaniline-4'-carboxylazidoazo-benzene (XXVI) from p-aminobenzoyl hydrazide

p-Aminobenzoyl hydrazide (7.5 g; 0.05 mole) was diazotized with excess sodium nitrite (7.6 g; 0.11 mole) and concentrated hydrochloric acid to get p-carbonyl azido phenyl diazonium chloride which was then coupled with N,N-dimethyl aniline (6 g; 0.05 mole) in weakly acidic medium at 0-5°. Mixture was stirred overnight to complete the coupling. Water insoluble dye was filtered and washed with water. Yield (13 g).

The dye was purified by chromatography on silica gel column and recrystallised from benzene.

The dyes 4-N-phenylmorpholino-4'-carboxylazidoazo benzene (XXVII); 1-(4'-carbonylazido)phenylazo-2-hydroxy-3-carboxynaphthmorpholide (XXVIII) and 1-(4'-carbonylazido)-

phenylazo-2-hydroxy-3-carboxynaphthanilide (XXIX) were similarly prepared by coupling the p-carbonyl azidophenyl diazonium chloride with N-phenyl-morpholine, 2-hydroxy-3-carboxynaphthamorpholide and 2-hydroxy-3-carboxy naphthanilide respectively.

Discussion

The two different routes for the synthesis of carboxyl azides have been schematically represented in Chart 5 (Scheme 4 and 5). In the case of Scheme 4 the individual dyes were prepared first and then they were converted to the carbonylazides. The preparation of dyes containing carbonyl azides from the intermediate p-aminobenzoylhydrazide is very versatile since different coupling components can be used with the same diazonium component to produce the dyes of different colours. Since the intermediate p-aminobenzoylhydrazide can be prepared easily the Scheme 5 has obvious advantages.

Section III

Synthesis of aryl azides

Synthesis of aryl azides is the easiest of the synthesis compared to all the above azides. Arylazides were prepared by the diazotization of dyes containing a free amino group and treatment of the diazonium salt with sodium azide in the acid medium whereby the diazo group is replaced by the azido group (see Chart 6)¹⁹.

Synthesis of dye 4-azido-azobenzene (XXX)

This is prepared from the dye p-aminoazobenzene (commercially available).

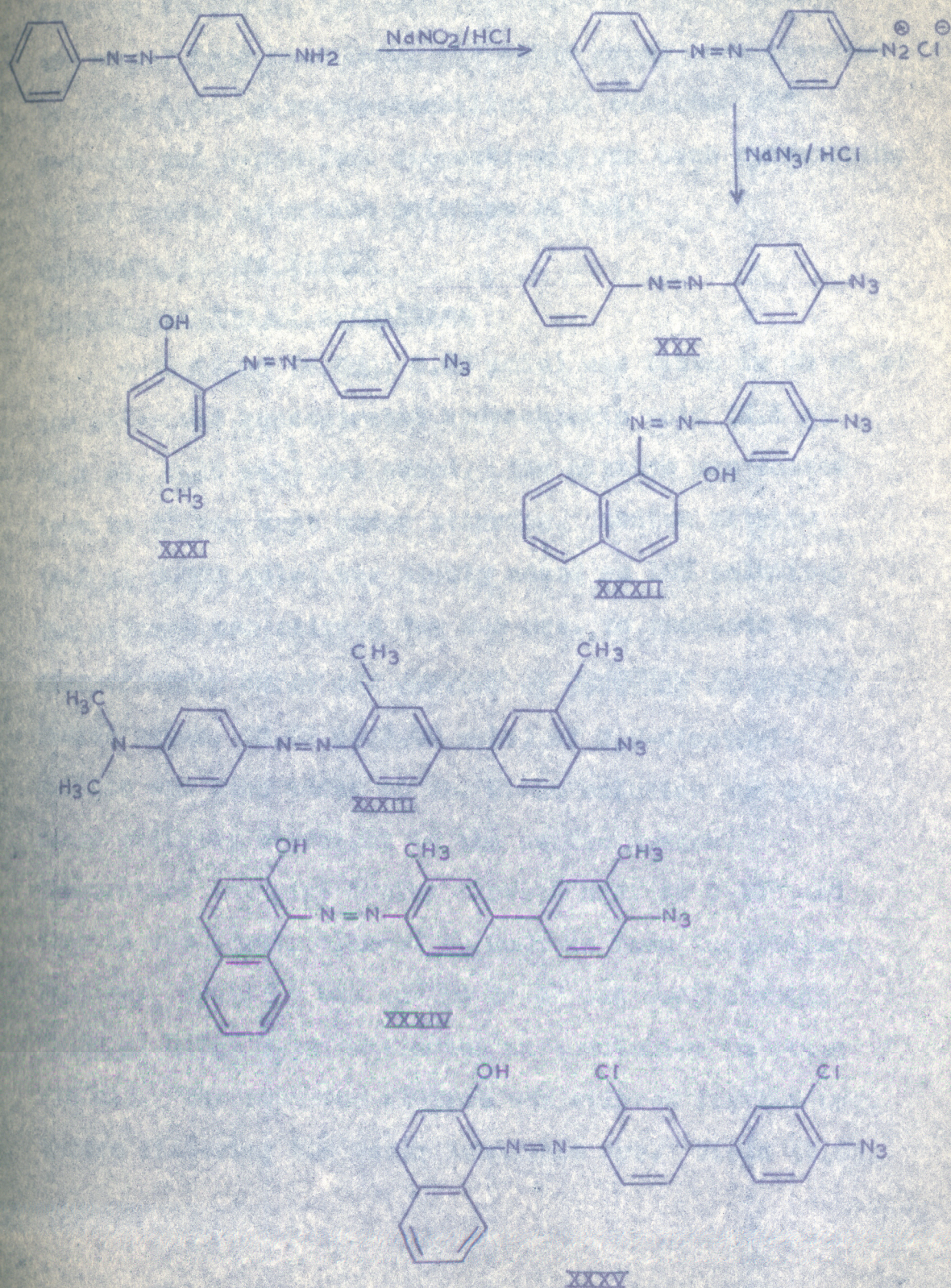
The commercial sample of p-aminoazobenzene was purified by crystallisation in benzene.

The purified p-aminoazobenzene (3.94 g; 0.02 moles) was taken in water (50 ml) and cooled down to 0°. Concentrated hydrochloric acid (30%) (6.1 ml; 0.05 mole) was added and stirred for 10 minutes. Sodium nitrite (1.6 kg; 0.024 mole) was added as 10% solution slowly and stirred for 1 hour. The completion of diazotylation was checked on starch iodide paper. After the completion of the diazotization, sodium azide (1.44 g; 0.022 mole) was dissolved in 10 ml water and was added slowly. Frothing takes place due to liberation of nitrogen gas and the addition must be controlled at such a rate that excess frothing does not take place. The temperature was maintained at 0° throughout and acid was added to maintain the solution at a pH 2-3. After the addition of sodium azide solution, the reaction mixture was stirred for 1 hr. The water insoluble dye was filtered and washed free of acid by water.

The compound was purified by chromatography over silica gel column and was recrystallised from benzene.

CHART - 6

SCHEME - 6



The dyes 2-(4'-azido)phenylazo-p-cresol (XXXI) and 1(4'-azido) phenylazo-2-naphthol (XXXII) were prepared following the same procedure as given above. The parent dyes containing the amino group were prepared by diazotizing p-aminoacetanilide and coupling with p-cresol and β -naphthol respectively and then hydrolysing in 20% sodium hydroxide solution at boil.

Synthesis of Dye XXXIII

Tetrazotization of o-tolidine

o-Tolidine (6.36g; 0.03 mole) was taken in 50 ml of ice water and concentrated hydrochloric acid (5.5 g; 18.1 ml; 0.15 mol) was added. The mixture was cooled down to 0° and kept under stirring. Sodium nitrite (4.3 g; 0.066 mole) was slowly added as 10% solution. The mixture was stirred for 2-3 hrs. to complete the diazotization which was checked by spotting on starch iodide paper. (3.63 g; 0.03 mole) of N,N-dimethylaniline was then added to the diazo solution and kept under stirring overnight in the acidic medium. Temperature was kept during first 5 hrs. at 0-10° and then it was slowly allowed to come to room temperature. Next day, again it was cooled to 0° and sodium azide (2.35 g; 0.036 mole) was added as a solution in water (15 ml). The reaction mixture was stirred for 3-4 hrs. before filtering the water insoluble dye. Yield (2.5).

The dye XXXIV and XXXVI were similarly prepared by coupling the tetrazolized o-tolidine and 3,3'-dichlorobenzidine with 1 mole of β -naphthol and then treating the other uncoupled diazo group with sodium azide.

Discussion

The above examples prove our earlier observation that aryl azide as a functional group in dyes is the easiest to prepare as compared to the other azido functional groups. Benzidine and the derivatives of benzidine are very useful in the one step synthesis of aryl azides since the two diazo groups possess stepwise reactivity. Thus the tetrazotized benzidine or its derivatives can be coupled on one side with a coupling component and on the other side an azido group can be introduced by treatment with sodium azide.

Section IV

Synthesis of dyes containing an azidoacetamido group

Dyes containing an azido-acetamido group were prepared according to the scheme shown in Chart 7 for the dye XXVI. The dye containing a free amino group was treated with chloroacetyl chloride in acetone in presence of an acid binding agent. The resulting chloro derivative was treated with sodium azide in isopropanol or tert-butyl alcohol to obtain dye containing the

azido-acetamido group.

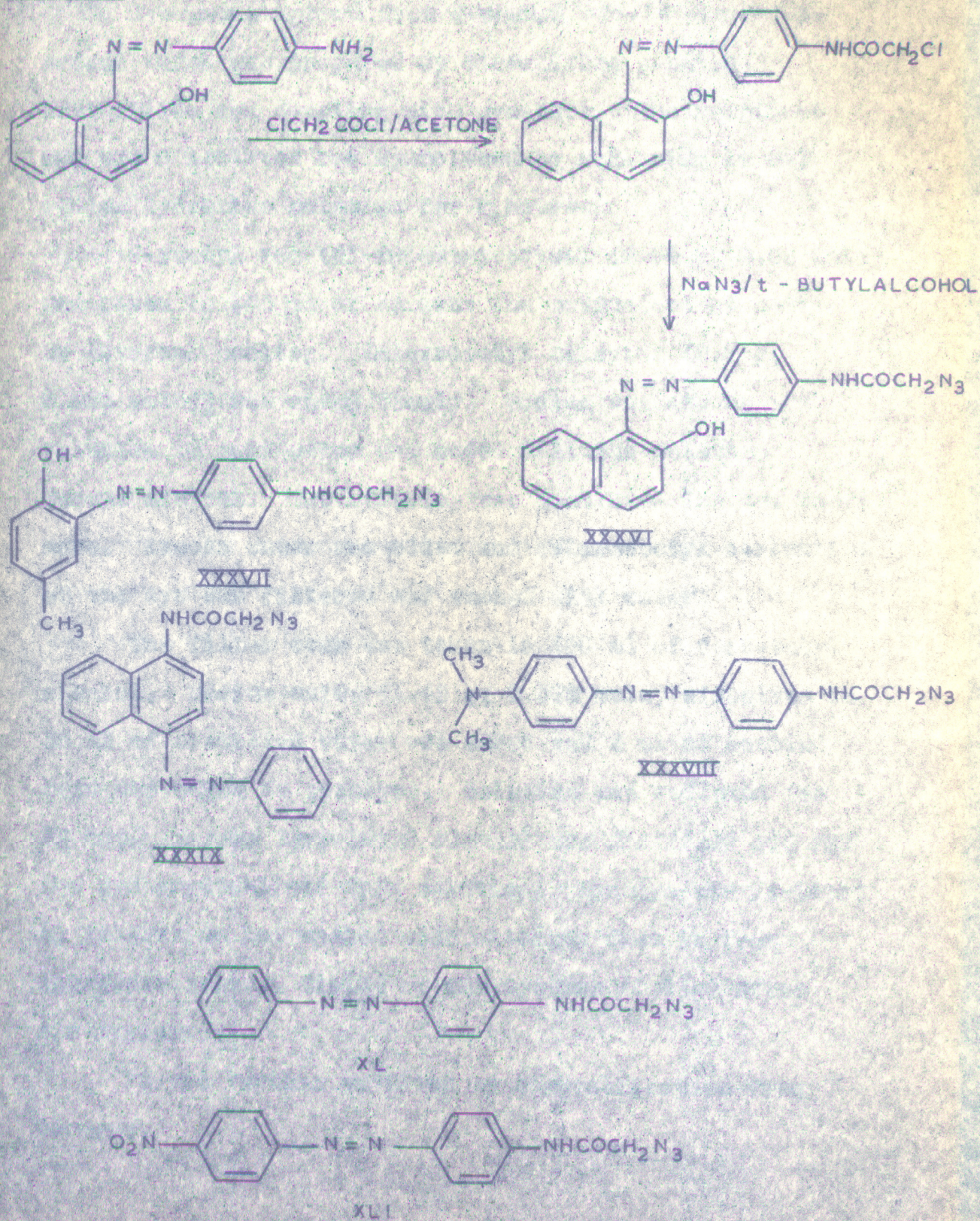
Synthesis of Dye 1-(4'-azidoacetamido)benzene azo-2-naphthol (XXXVI)

The dye XXXVI was prepared from 1-phenyl-azo-(4'-amino)-2-naphthol, which was obtained by diazotizing p-amino acetanilide and coupling with β -naphthol and the resultant dye was hydrolysed in 20% aqueous sodium hydroxide solution at boil for 2 hrs.

1-Phenylazo (4'-amino)-2-naphthol (5.28 g; 0.02 moles) was dissolved in 100 ml of acetone and maintained between 0-5° by external cooling chloroacetyl chloride (2.6 g; 0.022 moles) was added slowly. Sodium acetate dissolved in ice water (10% solution) was added till the solution became neutral. The stirring was continued for 2 hours more. The chloroacetyl derivative of the dye was isolated by filtration and precipitate was washed with cold water. It was then taken in 150 ml of tert-butyl alcohol. Sodium azide (1.43 g; 0.022 mole) dissolved in 15 ml of distilled water was added and 2 ml of acetic acid was added as catalyst²⁰. Solution was refluxed for 36 hrs. Excess t-butyl alcohol was distilled out and the dye crystallised from the solution. The dye was isolated by filtration and washed with water free of inorganic salts and air dried to give 5.7 g of dye XXXVI. The dye was crystallised from benzene.

CHART - 7

SCHEME - 7



Synthesis of dye 2-(4'-azidoacetamido)benzenesazo-
p-cresol (XXXVII)

Dye was prepared from 2-phenyl azo-(4'-amino)-p-cresol which was prepared by diazotizing p-amino-acetanilide and coupling with p-cresol. The resultant dye was isolated and hydrolysed by refluxing in 20% sodium hydroxide solution for 2 hours.

2-Phenyl azo (4'-amino)-p-cresol (4.54 g; 0.02 mole) was taken in 100 ml of acetone and maintained at 0-5° by external cooling. Chloroacetyl chloride (2.5 g; 0.022 moles) was added slowly. Sodium acetate as 10% solution in cold water was added till the solution became neutral. The stirring was continued for two hours more. Excess water was added and chloroacetyl derivative of the dye was filtered and washed with water.

The filter cake was taken in 150 ml of tert-butyl alcohol. Sodium azide (1.43 g; 0.022 mole) dissolved in 15 ml of distilled water was added and 2 ml of acetic acid was added as catalyst. Solution was refluxed for 36 hrs. Excess tert-butyl alcohol was distilled out and the dye crystallised from solution. The dye was isolated by filtration and washed with water to free it from inorganic salts. Yield of the dye was (5.5 g) after air drying.

It was further purified by crystallisation from benzene.

The dyes 4-dimethylanilino-4'-azidoacetamido-azobenzene (XXXVIII); 4-phenylazo-1-azidoacetamido-naphthalene (XXXIX); 4-azidoacetamido-azobenzene (XL) and 4-nitro-4'-azido acetamidazoazobenzene (XLI) were similarly prepared from the dyes containing the free amino group.

The starting material for the dye XL p-amino-azobenzene is commercially available. The Bayer's product was recrystallised from benzene and used in the synthesis.

Starting material for XXXVIII was prepared by diazotizing p-aminoacetanilide and coupling with dimethylaniline and hydrolysing the resultant dye by refluxing ⁱⁿ 20% aqueous sodiumhydroxide solution. The starting material for XXXIX was prepared by diazotizing aniline and coupling with α -naphthylamine.

The starting material for XLI was prepared as mentioned in literature²¹ by diazotizing p-nitro-aniline with aniline.

Discussion

The condensation of the dye containing free amino group with chloroacetyl chloride was very smooth and quantitative. In place of sodium acetate a solution of sodium carbonate can also be used as an acid binding agent.

The reaction could also be carried out by suspending the dye containing the free amino group in water, but in all our experiments acetone was used as solvent, where the reactants were in a homogeneous phase.

The replacement of the chlorine from chloroacetyl-derivative of the dye by azido group requires prolonged heating in high boiling solvents. The same reaction was tried in acetone but the results were not very satisfactory. tert-Butyl alcohol was preferred as a solvent in view of its low reactivity.

Dye Sl.No.	Molecular formula and mol.wt.	Physical Nature	M.P., °C	IR Data Group & Absp. in cm ⁻¹	Analysed			Analysis Obtained		
					C	H	N	C	H	N
III	C ₁₆ H ₁₁ N ₅ O ₃ 353	Red plates (B)	177-8	-N ₃ - 2110 -SO ₂ -1379 -OH 3600	54.4	3.1	19.8	55.0	3.6	19.5
IV	C ₁₆ H ₁₁ N ₅ O ₃ 353	Red needles (B)	171-2	-N ₃ - 2100 -SO ₂ -1360 -OH 3600	54.4	3.1	19.8	55.2	13.7	18.82
V	C ₁₄ H ₁₄ N ₆ O ₂ S 330	Orange needles (B)	149-50	-N ₃ 2110 -SO ₂ 1350	50.9	4.2	25.5	51.1	4.5	24.8
VI	C ₁₄ H ₁₄ N ₆ O ₂ S 330	Red Cubes (B)	120	-N ₃ - 2120 -SO ₂ -1360	50.9	4.2	25.5	51.6	4.3	24.6
VII	C ₁₆ H ₁₁ N ₅ O ₃ 353	Orange red needles (B)	135	-N ₃ - 2120 -SO ₂ -1330 -OH -3600	54.4	3.1	19.8	55.4	2.6	19.5
VIII	C ₁₆ H ₁₁ N ₅ O ₃ 353	Red powder (B)	136-39	-N ₃ 2110 -SO ₂ 1350	54.4	3.1	19.8	54.1	2.9	-
IX	C ₁₆ H ₁₀ N ₈ O ₅ S ₂ 458	Red powder (B)	165 (decomp.)	-N ₃ 2110 -SO ₂ -1360 -OH 3600	42.0	2.2	24.5	42.8	2.1	23.6
X	C ₁₆ H ₁₀ N ₈ O ₅ S ₂ 458	Red powder (B)	155 (decomp.)	-N ₃ 2110 -SO ₂ -1360	42.0	2.2	24.5	42.1	2.1	23.4

Sl. No.	Formula and mol. wt.	Physical Nature	M.P., °C	IR Data Group & Absp. in cm-1	Analysis Required			Analysis Obtained		
					C	H	N	C	H	N
XI	$C_{20}H_{12}N_4O_5$ 436	Pink powder (E)	above 250	-N ₃ 2110 -C=O 1620 -SO ₂ 1360	56.1	2.8		56.7	3.2	
XII	$C_{21}H_{15}N_5O_4$ 433	Blue powder (E)	above 250	-N ₃ 2130 -SO ₂ 1379 -C=O 1650 -NH ₂ 3400	58.1	3.5	14.8	60.4	3.7	14.1
XIII	$C_{28}H_{20}N_8O_5$ 628	Blue powder (E)	143-5	-N ₃ 2110 -SO ₂ 1360 -C=O 1620	53.9	3.2	13.8	54.9	4.0	16.9
XIV	$C_8H_8N_4O_3$ 240	White cubes (B)	113-4	-N ₃ 2140 -SO ₂ -1370 C=O 1690	40.0	3.3	23.3	40.5	3.7	22.9
XV	$C_{16}H_{11}N_5O_3$ 353	Red plates (B)	177-8	-N ₃ 2110 -SO ₂ -1370	54.4	3.1	19.8	55.0	3.6	14.5
XVI	$C_{16}H_{16}N_6O_3$ 372	Yellow shining cubes (B)	175	-N ₃ 2120 -SO ₂ -1360	51.6	4.3	22.6	52.0	4.4	21.8
XVII	$C_{21}H_{18}N_6O_5$ 468	Red cubes (B)	70 (decomp.)	-N ₃ 2120 -C=O 1620 -SO ₃ -1360	54.1	3.9	18.0	52.2 ⁴	3.8	17.7
XVIII	$C_{23}H_{16}N_6O_4$ 472	Red needles (B)	176-77	-N ₃ 2130 -SO ₂ -1370 -C=O 1670	58.5	3.4	17.8	60.8	3.9	16.5
XIX	$Cl_3H_{11}N_5O_3$ 317	Orange needles (B)	99-100	-N ₃ 2120 -SO ₂ -1370	49.1	3.5	22.1	48.5	3.22	21.8

Dye Sl.No.	Molecular formula and mol.wt.	Physical Nature	M.P., °C	IR Data Group & Absp. in cm-1	Analysis Required			Analysis Obtained		
					C	H	N	C	H	N
XX	C ₉ H ₁₀ N ₄ O ₄ S 270	White plates (B)	104°	-N ₃ - -SO ₂ - -C=O	40.0	3.7	20.7	40.2	3.2	20.4
XXI	C ₁₇ H ₁₃ N ₅ O ₄ S 383	Red needles (B)	179-80	-N ₃ ; -SO ₂ ;	53.5	3.4	18.1	53.5	3.0	17.0
XXII	C ₁₅ H ₁₆ N ₆ O ₃ S 360	Red clusters (B)	110-12	-N ₃ ; -SO ₂ ;	50.0	4.5	23.3	49.5	4.3	23.1
XXIII	C ₁₄ H ₁₃ N ₅ O ₄ S 347 324 347	Red needles (B)	142-44	-N ₃ ; -SO ₂ -	48.4	3.7	20.1	47.8	3.4	19.4
XXIV	C ₁₇ H ₁₁ N ₅ O ₂ 317	Red x cubes (B)	150	-N ₃ -C=O	64.4	3.5	22.1	65.07	3.9	18.9
XXV	C ₇ H ₉ N ₃ O 151	White plates (B)	226	-	55.9	6.0	27.9	56.4	6.8	28.9
XXVI	C ₁₅ H ₁₄ N ₆ O 294	Yellow brown plates (B)	Softens at 120° No sharp M.P.-OH; 3500	-N ₃ ; 2110 -C=O; 1670	61.3	4.8	28.6	62.4	4.5	27.9
XXVII	C ₁₇ H ₁₆ N ₆ O ₂ 336	Yellow brown cubes (B)	135-37	-N ₃ ; 2100 -C=O; 1690	60.8	4.7	25.0	60.5	4.5	-
XXVIII	C ₂₂ H ₁₇ N ₆ O ₄ 429	Red powder (B)	169-70 (decomp.)	-N ₃ ; 2110	61.9	4.0	19.6	60.9	3.5	-
XXIX	C ₂₄ H ₁₈ N ₆ O ₃ 436	Red powder (B)	243-50	-N ₃ ; 2120 -C=O; 1680 -OH; 3300	66.1	3.7	19.1	65.8	3.4	-
XXX	C ₁₂ H ₉ N ₅ 223	Yellow plates (B)	84-6	-N ₃ ; 2100	64.8	4.0	31.4	65.4	4.6	30.7
XXXI	C ₁₃ H ₁₁ N ₅ O 253	Brownish yellow needles (B)	142	-N ₃ ; 2100	61.6	4.4	28.8	61.2	4.03	23.4

Dye Sl. No.	Molecular Formula and Sol. wt.	Physical Nature	M.p., °C	IR Data Group & Absp. in cm ⁻¹	Analysis Required			Analysis Obtained		
					C	H	N	C	H	N
XXXII	C ₁₆ H ₁₁ N ₅ O ₂ 284	Violet needles (B)	168-70 (decomp.)	-N ₃ ; 2100	66.5	3.8	24.2	66.8	3.8	22.5
XXXIII	C ₂₂ H ₂₂ N ₆ 370	Orange powder (B)	108-110	-N ₃ ; 2100	71.1	5.9	22.6	70.0	5.9	23.2
XXXIV	C ₂₄ H ₁₉ N ₅ O ₂ 393	Reddish violet powder (B)	above 250	-N ₃ ; 2110	73.1	4.9	17.8	72.8	4.3	-
XXXV	C ₂₂ H ₁₃ N ₅ Cl ₂ O ₂ 434	Reddish violet powder (B)	above 250	-N ₃ ; 2100 -OH; 3200	60.9	3.0	16.2	60.2	2.9	-
XXXVI	C ₁₈ H ₁₄ N ₄ O ₂ 366	Red powder (A)	206-208	-N ₃ ; 2100 -C=O; 1660 -OH; 3300	62.8	4.1	24.2	63.3	4.3	-
XXXVII	C ₁₅ H ₁₄ N ₆ C ₂ 310	Yellow powder (A)	134-36	-N ₃ ; 2100 -OH; 3300 -C=O; 1650	58.0	4.5	27.2	57.8	4.3	-
XXXVIII	C ₁₆ H ₁₇ N ₇ O 323	Yellow powder (A)	160 (decomp.)	-N ₃ ; 2100 -C=O; 1650	59.5	5.3	30.4	58.2	4.8	-
XXXIX	C ₁₈ H ₁₄ N ₆ O 330	Red powder (A)	90-95	-N ₃ ; 2100 -C=O; 1660	65.5	4.3	25.4	65.1	3.9	-
XL	C ₁₄ H ₁₂ N ₆ O 280	Yellow powder (A)	118-19	-N ₃ ; 2100 -C=O; 1650	60.0	4.3	30.0	61.4	4.6	26.1
XLI	C ₁₄ H ₁₁ N ₇ O ₃ 325	Yellow powder (A)	100 (decomp.)	-N ₃ ; 2100 -CO; 1650	51.8	3.4	30.1	50.9	4.0	-

Solvents used for crystallisation - B - Benzene; E - Ethanol; A - Acetone

REFERENCES

1. Schroeder, H.E. Boyd, S.N., Textile Res. J. **27**, 275 (1957),
2. Stead, E. and Murray, A., J.Soc.Dyer Col. **68**, 15 (1962)
3. Salvin, V.S. and Adams, J.R., Amer.Dyestuffs Repr. **48**, 43 (1959).
4. Kalyanaraman, S., Ph.D.(Tech.) Thesis, Bombay University (1969).
5. Kulwant Singh, Ph.D.(Tech.) Thesis, Bombay University (1973).
6. BIOS 961, 44; FIAT 764, Orange II "F" "Practical Organic Chemistry", Vogel 3rd. Edn. (1964), Longmans, p. 625.
7. FIAT 764, Grocein Orang G., Ponceau 4 GBL.
8. BIOS 1548, 44; 961, 43; FIAT 764 - Methyl orange; "Practical Organic Chemistry", Vogel, 3rd Edn., Longmans, 624.
9. BIOS, 1484, 41; "Fundamental Process of Dye Chemistry" Fierz-David and Blangey (1949) Interscience Publishers Inc., New York, Table 19, Ger.Pat. 280646 (Fr. 12, 453).
10. "Fundamental Processes of Dye Chemistry" Fierz-David and Blangey (1949), Interscience Publishers Inc., New York, 317-8.
11. Kalyanaram, S., Ph.D.(Tech) Thesis, 1969, University of Bombay, p. 135.
12. Organic Synthesis Coll. Vol. I (1932), John Wiley and Sons, New York, p. 8.
13. Ashley, J.N. and Buchanan, G.L., J.Chem.Soc. 1947, 60.
14. Kamm, O. and Waldo, J.H., J.Am.Chem.Soc. **43**, 2225 (1921); Cretcher, L.H. and Pittenger, W.H., J.Am.Chem.Soc. **47**, 163 (1925).
15. FIAT 1313, Vol.(I), p. 15.

16. BIOS F.R. 1149, p. 24
17. "Practical Organic Chemistry", Vogel, 3rd Edition, Longmans, p. 1000 (1964).
18. Beilstein, 14, 570; J.Pharm. & Pharmacol. 6, 127 (1954).
19. "Organic Functional Group Preparations", Sandler, S.R. and Karo, W., (1971) Academic Press, New York, Chapter 13.
20. Boyer, J.H. and Straw, D., J.Amer.Chem.Soc. 75, 1642 (1953).
21. BIOS 961, 77; BIOS 1548, 199.

CHAPTER - III

**Application of Reactive Disperse Dyes to
Synthetic Fibres**

Dyeing of synthetic fibres with reactive disperse dyes containing the azido group

Introduction

So far, polyester and cellulose acetate have not been dyed with reactive dyes. Amongst the synthetic fibres only polyamide has been dyed with reactive dyes. Procinyl range¹ of reactive dyes for polyamides were introduced by ICI in 1959. In view of hydrophobic nature and low porosity of synthetic fibres the dye molecule has to be carefully designed to ensure penetration, level dyeing and good fastness properties. Procinyl range of dyes resemble normal disperse dyes in being devoid of water solubilizing ionic groups but have a group which is capable of forming covalent bonds with polyamide fibres. In procinyl range of reactive dyes the reactive systems are different in different dyes. They are applied as normal disperse dyes from ^wweakly acidic dye-bath. After the exhaustion the dye bath is made alkaline to bring about the chemical reaction between dye and the fibre.

"Verofix"² is another range of reactive dyes introduced by Bayer for dyeing of wool and polyamides fibres. "Verofix" dyes are water soluble dyes containing a reactive system based on fluoropyrimidine ring.

Evidence for the existence of a co-valent bond between procinyl dyes and polyamide fibre

Following proofs were given by Scott and Vickerstaff³ for the existence of covalent bond between dyes and ^{nylon (a).} nylon dyed with conventional disperse, azoic or acid dyes can be stripped by boiling with solvents such as chlorobenzene, propanol or aqueous pyridine. Although these solvents easily dissolve Procinyl dyes, the dyed fabric cannot be stripped by them. This suggests that some force other than adsorption, mechanical retention of salt linkage, is holding the dye on the fibre.

(b) If nylon fibre dyed with disperse dyes is dissolved in o-chlorophenol and the resulting solution is poured into propanol, to precipitate dissolved nylon, the dye appears in the liquid phase. When similar treatment is given to nylon dyed with a Procinyl dye the colour is retained by the precipitate.

(c) The colour of Procinyl Scarlet G is due to the presence of an azo group. Consequently the dye can be reduced on the fibre with sodium sulphonylate^xformaldehyde and formic acid to the amine containing end products. If the dye has reacted with the fibre, one of the products should remain firmly attached to the fibre and should resist extraction with hydrochloric acid. Such a "discharged" fibre can, in fact, be diazotized and coupled with a phenol

to produce a new dye. If nylon is dyed with the unreactive analogue of Procinyl Scarlet G and treated in a similar manner, no colour is developed.

Elöd and Einsele⁴ gave further evidence of chemical combination by applying chromatography and diffusion methods. They showed that, if the dye is mechanically held or adsorbed on the fibre it can be chromatographically separated from the fibre; if on the other hand, the dye has reacted with the fibre, the latter migrates slowly along with the dye as a single molecule.

The reactive disperse dyes described in the thesis were applied as normal disperse dyes for the synthetic fibres by usual dyeing procedures which are discussed in experimental section. A few dyes were applied to polyester fibre by high temperature dyeing method. All other dyes were applied by carrier dyeing method at boil. All the dyes were applied at neutral pH on polyamide and cellulose acetate by exhaust dyeing method.

Fastness properties (1) Sublimation fastness

The effect of dry heat on disperse dyeings is of great importance in case of synthetic fibres, as the dyeings are often subjected to a heat setting, curing of

resinfinishes and permanent process treatment at high temperature⁵. The colour changes that may occur in dry heat are due to oxidation or reduction of the dyestuff caused by the auxiliary chemicals present. More often, the changes in appearance are due to change in the optical properties of the fibre, discolouration of the fibre, deeper penetration of the dye, fibre shrinkage, aggregation or crystallisation. The loss or transfer of dye within the fibre when exposed to dry heat is called sublimation fastness. The dyes with low molecular weight vaporise and condense on adjacent fibre when exposed to high temperatures or during hot pressing.

The dyed material is stitched on both sides with undyed x cloth and such sandwiched sample is kept between two hot plates maintained at desired temperature. The temperature ranges in standard test are - (a) 150° for 30 secs., (b) 180° for 30 secs. and (c) 210° for 30 secs. in the increasing order of severity. The dyeings are then examined for,

- a) change in tone
- b) change in depth
- c) staining of the undyed cloth

Grading is given in terms of numbers ranging from 1 to 5 at particular temperatures. Fastness 1 represents the lowest value and 5 the highest.

The sublimation fastness given in the thesis are determined at 210° for 30 secs. (severe conditions).

(2) Light fastness

The test consists in exposing one part of the dyed fabric (the other portion is covered by a metal shield) along with standards, under the standard conditions of temperature, relative humidity and for specified time period to an intense source of light produced by a Xenon arc discharged lamp (Xenotest light fastness machine). The loss in depth of shade or change in tone is compared with the covered portion of the dyeing. The fastness is expressed in terms of numbers ranging from 1-8 scale of increasing light fastness.

Another method of determining the light fastness is by exposing the samples along with standards to the sunlight for specified time period. The light fastness is evaluated as mentioned above. The light fastness of dyeings given in the thesis are day light fastnesses.

Present work

All the dyeings were carried out by exhaust dyeing methods in case of polyamide and cellulose acetate fibres. Except a few dyeings, which were done by high temperature dyeing methods, all other dyeings of polyester were carried out by exhaust dyeing with trichlorobenzene as carrier. Trichlorobenzene, being comparatively least reactive

of all the known carriers towards azido compounds was preferred as carrier for dyeing azido reactive dyes.

Preparation of dispersion

500 mg of dye and 500 mg of Tammol NNO were taken in a glass tube containing steel rods. Little water was added and the tube rolled over on dye electric rollers for 48 hours to grind the dye into a dispersed state. The dye paste was then diluted with water to 250 ml. The standard 0.2% solution was used for dyeing.

Dyeing of polyamide and cellulose acetate fibres⁶

Dye-bath was prepared for 2% shade keeping the material:liquor ratio at 1:50. 500 mg of Tammol NNO was added. The fibres were inserted in the cold and the temperature slowly raised to 90-95° in one hour. Dyeing was continued at 90-5° for 1/2 hr. more. The fabric was then washed, soaped and dried.

Dyeing of polyester fabrics - Carrier Dyeing

Dyeing method is same as for polyamide and cellulose acetate except that 2 g/litre of trichlorobenzene was used as carrier.

High temperature (HT) dyeing method⁷

When dyeing is carried out under high temperature conditions, the addition of carrier is not usually required except in the case of heavy shades, where small amounts

of carrier offer advantage. The dyebath is set with 0.5 - 1 g/lit of a heat resistant leveling agent and about 1 g/lit. of a special dispersing agent which remains stable under HT conditions. Dyeing is started at 40°, the temperature of dyebath is increased in 30 minutes to boil and then in a further 30 minutes to the final temperature of 125°. The dyeing is completed in 1-2 hours.

Thermolysis

All the dyeings were exposed to dry heat of 170° for 5 minutes in a laboratory oven.

Pad-Dry-Cure method

10 gms/litre dispersion was padded on polyester, polyamide, cellulose acetate and on a 67:33 polyester/cotton blend on a padding mangle. Padded samples were dried and then exposed to heat at 170° for 5 minutes in hot-air blown curing chamber.

Printing

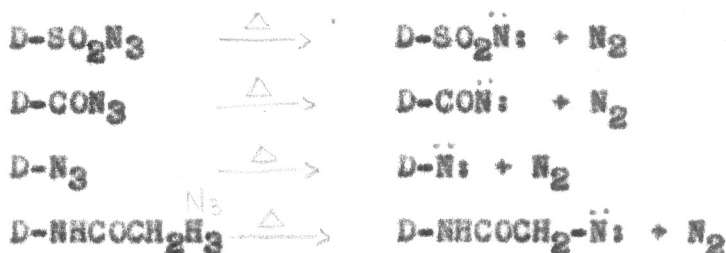
Polyester, cellulose acetate and polyester/cotton blends were printed with a paste prepared by adding 10 gm/litre dispersion to kerosene emulsion thickener. This paste was used for printing. The printed cloth was exposed to dry heat in hot air blown curing chamber at 170° for 5 minutes.

Mechanism of dye fixation

From the literature surveyed in Chapter 1 it is clear that when organic azido compounds are heated

to decompose yielding active "nitrene" intermediates which then undergo various reactions such as, insertion, abstraction and other reactions described earlier in Chapter I.

The dyes containing azido groups presently prepared may be expected to yield the following "nitrenes":



Since the nitrenes generated by the thermal process are in the singlet state⁸ a typical reaction which may be expected is stereospecific insertion in a C-H bond¹⁵.

Thus, when the above dyes are reactively combined with polyester, polyamide and cellulose acetate fibres by thermofixation the following Dye-fibre bonds may be expected:-

- (a) D-SO₂NH-F
- (b) D-NH-F
- (c) D-NHCOCH₂NH-F
- (d) D-CONH-F

D - indicates dye molecule

F - indicates fibre molecule

The dye which is not reactively combined will also undergo change through hydrogen abstraction or dimerization

and other side reactions typical of nitrenes.

Evidence for the existence of chemical bonding between the azido dyes and fibres

1. Polyester, polyamide and cellulose acetate dyed with dyes containing azido groups were thermolysed as mentioned before. The thermolysed pieces were extracted with boiling isopropanol. Dyeings retain colour even after severe boiling treatment (at 82° for 10 minutes).
2. Thermolysed samples of polyester dyed with azido dyes were extracted with chlorobenzene. The fibre was found to retain the dyes even after extract^{ing} at 132° for 10 minutes.
3. Thermolysed dyeings of polyamide and cellulose acetate fabrics were extracted with 25% aqueous pyridine solution at room temperature for 24 hours. The dyeings retained colour.
4. When similar extraction experiments were performed on fabrics dyed with similar disperse dyes which did not contain the azido group, the dyes were completely stripped off from the fibres.
5. The thermolysed dyeing on cellulose acetate polyamide and polyester were dissolved in boiling acetone, meta-cresol and nitrobenzene respectively. They were reprecipitated by adding the solutions to water, isopropanol

and petroleum ether respectively. The precipitated fibre was found to retain colour, thus showing the existence of co-valent bond between dye and fibres. In the case of dyeings with conventional disperse dyes the precipitated fibre did not retain colour.

Discussion: The light fastness listed in the Tables 1-6 are day light fastness.

Sublimation fastness was determined by stitching the undyed cloth on both the sides of the fabric and then heating the piece between two heated plates at 210° for 30 secs. Change in tone and staining of adjacent fabrics have been recorded in the Tables.

Sulphonylazido Dyes

The dyes containing sulphonyl azido groups listed in Tables 1 and ² were compared for their fastness properties with the azo dye (XLII)¹⁶⁻⁹, which does not contain an azido group. The dyes (III), (XV) [the dye was prepared by two alternative routes as described in Chapter (II)] and (VII) show a definite improvement in fastness to staining of the adjacent fabrics as compared with (XLII) which shows very poor fastness to staining. Many of the dyes containing sulphonylazido group e.g. (III), (XV), (IV), (V), (XVI) changed to deeper on-tone thermolysis.

The deepening of tone following thermolysis of the dyeing of sulphonazido dye on polyester may be due to the chemical combination of the dye with the aryl ring of the polyester polymer through sulphonamido linkage.



The UV and visible spectra of the dyes (I), (II) and (III) were compared and given in Table 7.

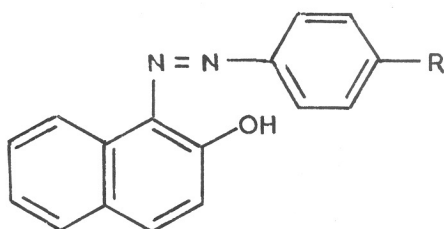


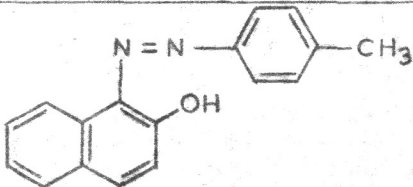
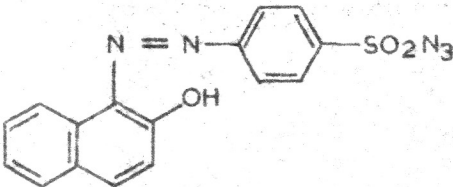
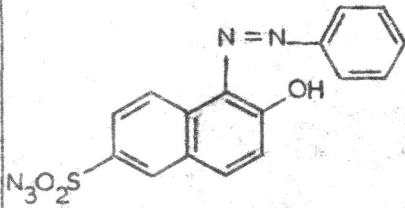
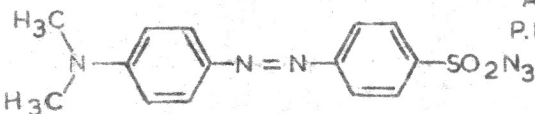
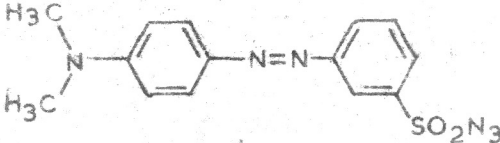
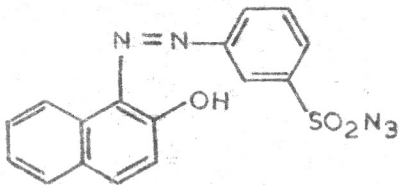
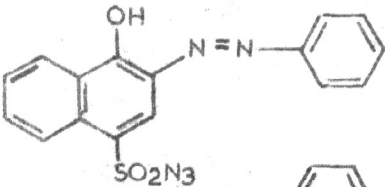
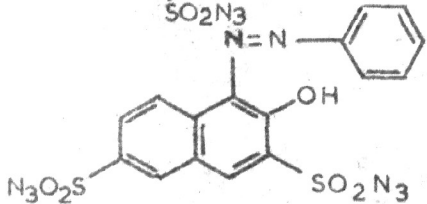
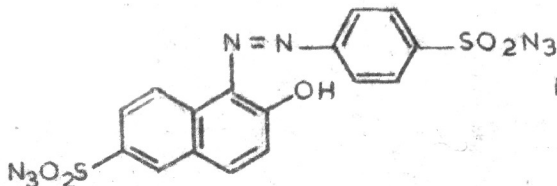
Table 7

No.	R	UV		Visible	
		$\lambda_{\text{max}}(\text{nm})$	ϵ -Molar	$\lambda_{\text{max}}(\text{nm})$	ϵ -Molar
1)	$-\text{SO}_2\text{NH}_2$	302	758	475	3340
11)	$-\text{SO}_2\text{N}_3$	310	1670	465	3710
111)	$-\text{SO}_2\text{NHPh}$	266	21700	480	37000
		310	24300		

TABLE - I

108

108

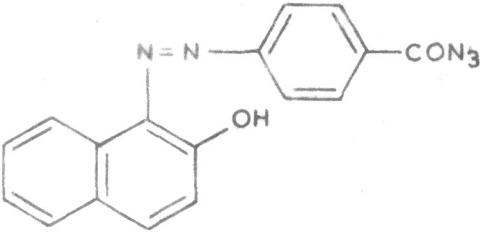
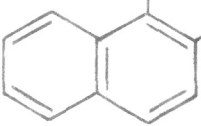
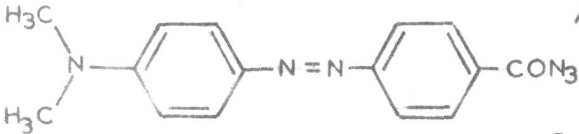
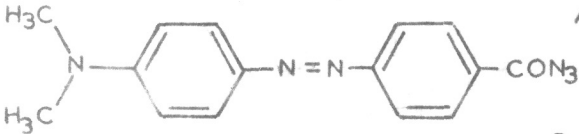
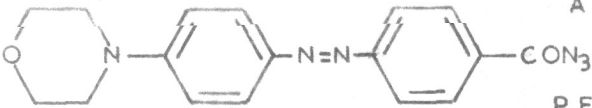
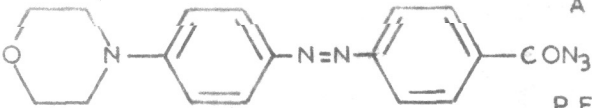
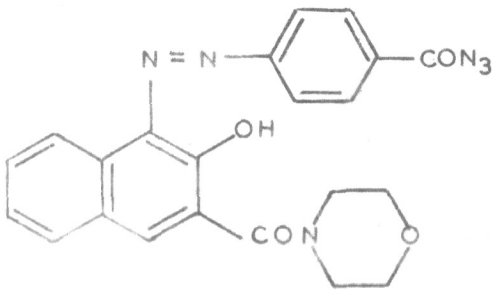
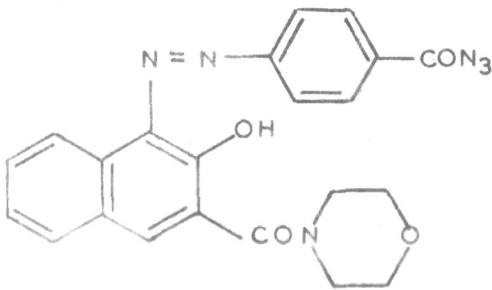
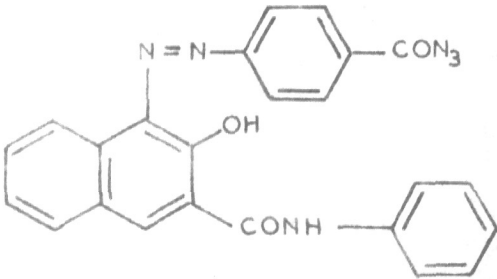
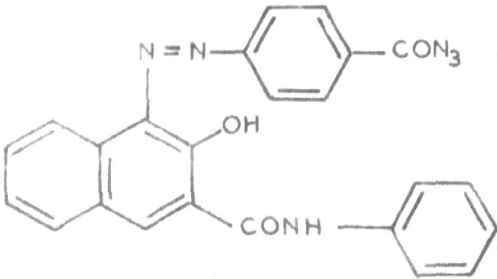
DYENO	STRUCTURE		DAYLIGHT FASTNESS	SUBLIMATION FASTNESS	
				CHANGE IN TONE	STAINING OF ADJ. FABRICS
XLII		P.E.	1	1	1
III, XV		A	1-2	1	3-4
		P.E.	3-4	1	2-3
IV		A	1-2	2-3	1-2
		P.E.	3-4	4-5	2
V		A	2-3	3-4	2-3
		P.E.	3	3	2
VI		A	4-5	4	4
		P.E.	3	4	3
VII		A	1	4	4
		P.E.	2-3	4	4
VIII		A	1-2	4	4-5
		P.E.	2	4	4-5
IX		A	1	—	—
		P.E.	2-3	—	—
X		A	1	—	—
		P.E.	2-3	—	—

A = ON CELLULOSE ACETATE

P.E. = ON POLYESTER

DYE NO	STRUCTURE	DAYLIGHT FASTNESS	SUBLIMATION FASTNESS	
			CHANGE IN TONE	STAINING OF ADJ. FABRICS
XI		A	—	—
		P.E.	5-6	4-5
XII		A	3-4	4-5
		P.E.	4-5	4-5
XIII		A	—	—
		P.E.	—	4-5
XVI		A	4	3-4
		P.E.	3	3
XVII		A	1	4
		P.E.	2-3	4
XVIII		A	1	4
		P.E.	2-3	4-5
XXI		A	1	4
		P.E.	2-3	4
XXII		A	—	4
		P.E.	3	3-4
XXIII		A	2	4-5
		P.E.	2-3	4

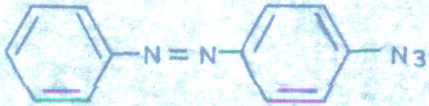
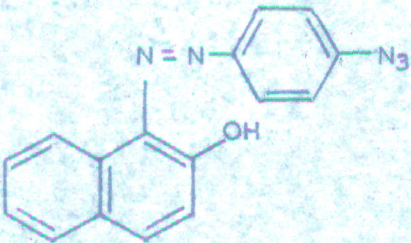
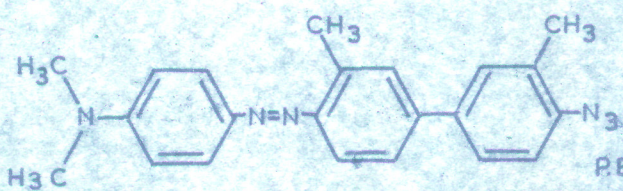
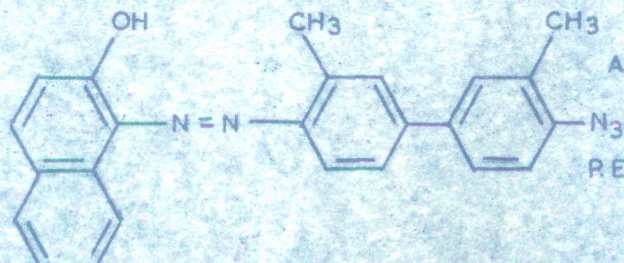
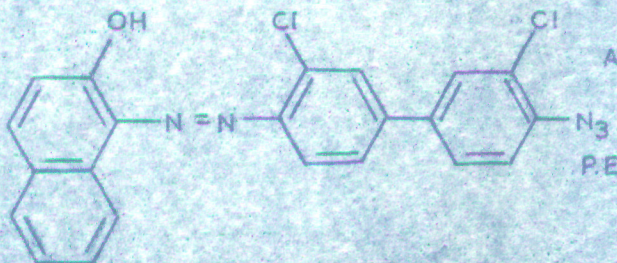
TABLE - 3

DYE NO	STRUCTURE	DAYLIGHT FASTNESS	SUBLIMATION FASTNESS	
			CHANGE IN TONE	STAINING OF ADJ. FABRICS
XXIV		A	4-5	4-5
		P.E.	4-5	3
XXVI		A	4	4
		P.E.	3-4	3
XXVII		A	4	4-5
		P.E.	3	4
XXVIII		A	4-5	4-5
		P.E.	4-5	4-5
XXIX		A	4	4-5
		P.E.	4	4

A = ON CELLULOSE ACETATE
P.E. = ON POLYESTER

STRUCTURE AND FASTNESS PROPERTIES OF DYES
CONTAINING THE AZIDO GROUP

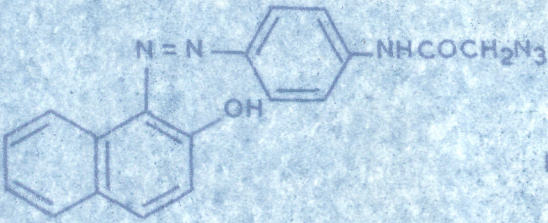
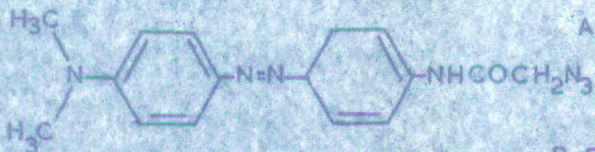
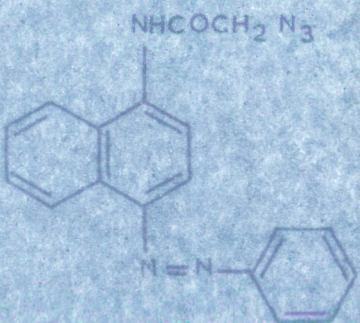
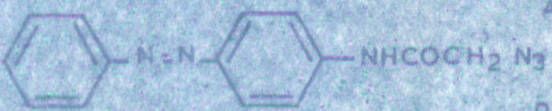
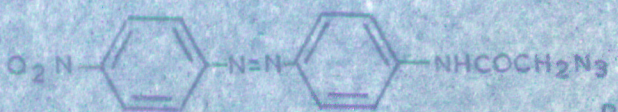
TABLE - 4

DYE NO	STRUCTURE	DAYLIGHT FASTNESS	SUBLIMATION FASTNESS	
			CHANGE IN TONE	STAINING OF ADJ. FABRICS
XXX		A	4	4
		P.E.	3	2
XXXII		A	3-4	3
		P.E.	3	3
XXXIII		A	2	4
		P.E.	3	4
XXXIV		A	1	4
		P.E.	1-2	4
XXXV		A	—	4
		P.E.	2	4

A = ON CELLULOSE ACETATE
P.E. = ON POLYESTER

STRUCTURE AND FASTNESS PROPERTIES OF DYES CONTAINING THE AZIDO GROUP

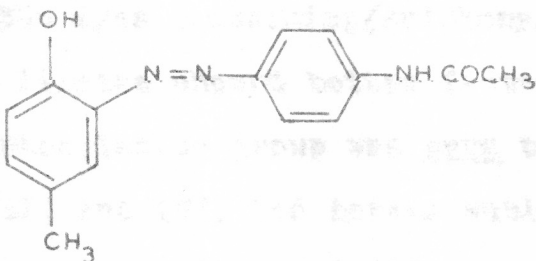
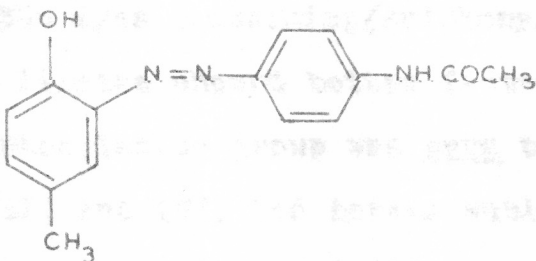
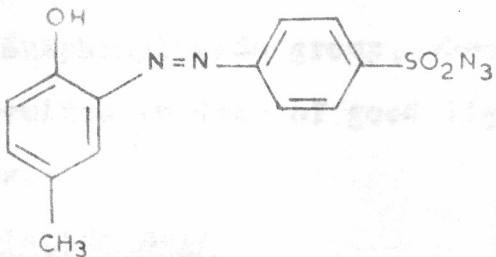
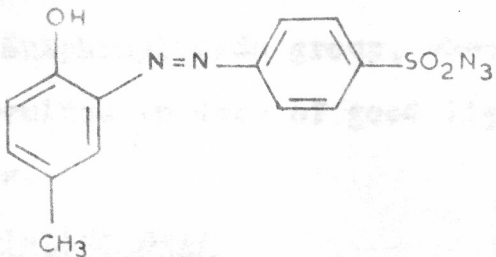
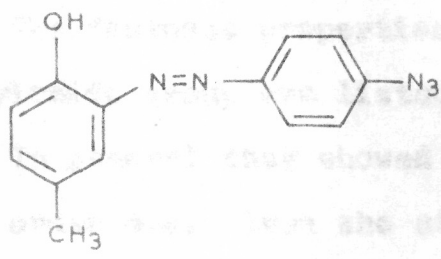
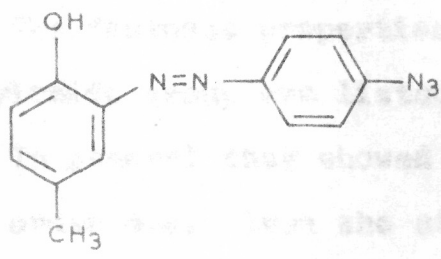
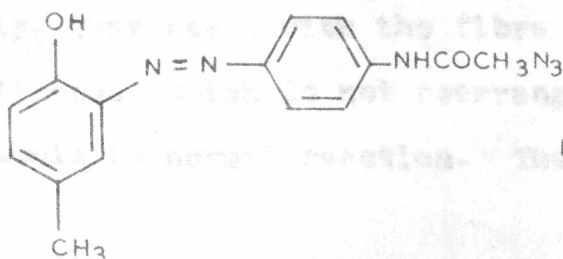
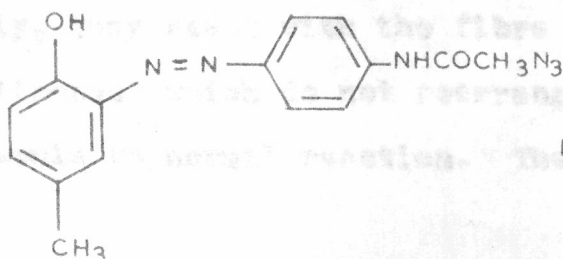
TABLE - 5

DYE NO	STRUCTURE	DAYLIGHT FASTNESS	SUBLIMATION FASTNESS	
			CHANGE IN TONE	STAINING OF ADJ. FABRICS
XXXVI		A	4	4
		P.E.	4	3-4
XXXVIII		A	4-5	5
		P.E.	4	4-5
XXXIX		A	4	3
		P.E.	3-4	1-2
XL		A	4-5	4-5
		P.E.	4	4
XLI		A	4	4
		P.E.	4	4

A = ON CELLULOSE ACETATE
P.E. = ON POLYESTER

COMPARATIVE STUDY OF FASTNESS PROPERTIES OF DYES CONTAINING SAME CHROMOPHORIC SYSTEM BUT DIFFERENT AZIDO GROUPS WITH A DYE WITHOUT AZIDO GROUP.

TABLE -6

DYE NO	STRUCTURE	DAYLIGHT FASTNESS	SUBLIMATION FASTNESS	
			CHANGE IN TONE	STAINING OF ADJ FABRICS
XLIII		A 4-5	3	3
		PE 4-5	3	3
XIX		A 2-3	4	4
		PE 3-4	4	3-4
XXXI		A 4	3-4	4
		PE 3-4	3-4	2
XXXVII		A 4	4	4
		PE 3	3-4	4

A = ON CELLULOSE ACETATE
PE = ON POLYESTER

It is clear from the Table 7 that the introduction arylsulphonamido linkage is accompanied by a considerable (tenfold) increase in the intensity of absorption maxima both in UV and visible regions. Similar effect is probably responsible for the deepening of the tone on thermolysis as mentioned above. This is particularly the case when the sulphonazido substituent is in the para-position to the azo linkage.

The dyes containing ^{the} sulphonylazido group meta to the azo linkage showed better fastness than those where the sulphonylazido group was para to the azo group. Thus dyes (VII) and (VI) had better sublimation fastness properties than (III) and (V).

Sulphonylazido group, when introduced in anthraquinone dyes resulted in dyes of good light and sublimation fastness.

Carbonylazido Dyes

The fastness properties of the dyes containing carbonylazido group are listed in Table 3.

In general they showed good sublimation fastness of the order 4-5. Even the simple structures like (XXVI) and (XXVII) showed sublimation fastness of the order 4 and 5. Probably, they react with the fibre substrates through the "nitrenes" which do not rearrange to the isocyanates which would be normal reaction. The carbonylazido dyes

therefore may be forming carbonylamide bonds with the fibre substrate.



Another interesting feature of carbonylazido dyes was that they do not change in tone on thermolysis. The dye (XXIV), however, behaved peculiarly during dyeing. Thus normal dyeing expected from this dye was deep red but instead it gave a deep violet shade on polyamide, cellulose acetate and polyester. The latter dyeings were resistant to stripping in boiling isopropanol and chlorobenzene. The colour of the parent dye is red but dye bath slowly changes in colour during dyeing and finally it becomes deep violet. The dyeings show very good sublimation fastness as can be seen from Table 3.

Arylazido Dyes

Dye containing arylazido groups again show good sublimation fastness. The fastness properties are listed in Table 4. The sublimation fastness 4, obtained in the case of the simple dye (XXX) on cellulose acetate is proof of the existence of a co-valent linkage between dye and fibre.

Dyes containing the azidoacetamido group

The fastness properties of dyes containing the azidoacetamido group are listed in Table 5. All the dyes

show good sublimation fastness of the order of 4-5. As compared to other azido dyes, they show improved light fastness. Comparison of the sublimation fastness of the dye (XLI) on polyester viz. 4,4 (change in tone and staining of adjacent fabrics respectively) with CI Disperse Orange 3 [4-nitro(4'-aminoazobenzene)] which has sublimation fastness of 4-5 and 3 respectively shows the improvement achieved by the introduction of the azido group.

Comparison of the fastness properties of the dyes (III), (VII), (XXIV), (XXXII)^(xxxvi) and (XLII)⁹ indicate the following points.

1) On cellulose acetate the dye containing the carbonylazido group shows optimum sublimation fastness followed by dyes having sulphonylazide group in the meta position to azo group and az finally dyes containing the azidoacetamido group. Dyes where the sulphonylazido group was para position to the azo group and dyes which containing arylazido group showed moderate sublimation fastness. However, on polyester, dyes containing sulphonylazido group in the meta position to the azo group showed best sublimation fastness followed by dyes containing azidoacetamido and carbonylazido groups. All the listed azido dyes have better sublimation fastness compared to (XLII) which does not contain this group.

Table 6 shows the results of a comparative study of fastness properties of dyes which contained the same chromophoric system but which had different azido groups with a dye not containing an azido group. The dyeing and thermolysis was carried out under identical conditions in the case of all the dyes.

The dye without the azido group (XLIII) (CI Disperse 3) shows good light fastness but low sublimation fastness. Improved sublimation fastness is obtained by introduction of the azido group as will be seen from the fastness listed for the dyes (XXIX), (XXXI) and (XXXVII).

To study the extent of covalent bonding of the dyes to fibre substrates the dyes were stripped by boiling with isopropanol, chlorobenzene and ^{by treatment with} 25% aqueous pyridine at room temperature for 24 hrs. These results are shown in the shade card. Whereas the dye (XLIII) was completely stripped by all the above solvents, dyes (XIX), (XXXI) and (XXXVII) showed much greater resistance to stripping. Dyes (XIX), (XXXI) and (XXXVII) applied to cellulose acetate, polyamide and polyester were practically not stripped at all in boiling isopropanol, but some stripping was observed when the dyeings on polyester were stripped with chlorobenzene. The dyes (XXXI) and (XXXVII) showed more resistance to

stripping in boiling chlorobenzene when they were applied to polyester fabrics.

No stripping is observed with polyamide and cellulose acetate in the case of dyes (XX), (XIX), (XXXI) and (XXXVII) when they were subjected to the action of 25% aqueous pyridine for 24 hrs. as against dyeings of these fibres by the dye (XLIII) which were stripped considerably under similar conditions. The light fastness in case of all dyes containing the azido groups was low indicating that the formation of co-valent bond has no favourable influence on light fastness. No correlation between the position of the azido group in the dye molecular and light fastness of the dyes on the various substrates was apparent. However, dyes (VI) (on cellulose acetate), (XI) (on polyester), (XII) (on polyester), (XVI) (on cellulose acetate), (XXVI) (on cellulose acetate and polyester) showed good light fastness.

Conclusions

Following conclusions may be drawn from the fastness properties listed in Tables ¹⁻⁶ 5.

1. Dyes containing azido group applied to above synthetic fibres by thermolysis show higher sublimation ^{do} fastness than dyes which ^{do} did not contain the azido group.

2. Among dyes containing different azido groups, ^{containing} dyes _^ carbonylazido group showed best sublimation fastness on cellulose acetate.

3. Most of the dyes containing azido groups showed good sublimation fastness on polyester fabrics.

4. Among the dyes containing sulphonylazido groups those having sulphonylazido group in the meta position to azo linkage showed better sublimation fastness as compared ^{to} _^ dyes where sulphonylazido group was ⁱⁿ _^ the para position to the azo group.

5. Dyes containing azido group in general show lower light fastness. Thus covalent linkage of the above disperse dyes containing azido groups with synthetic fibre substrates offers no advantages as regards light fastness.

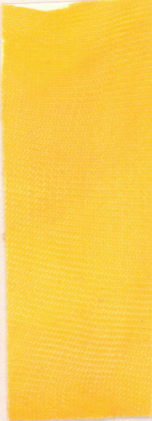
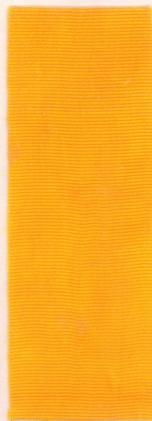
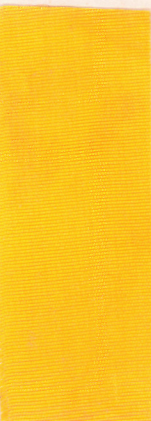
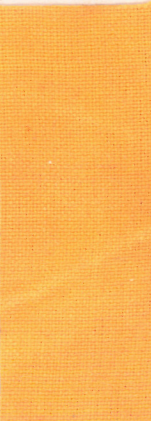
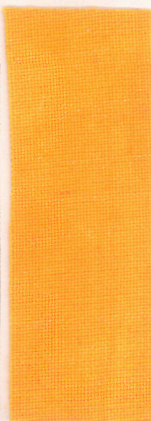
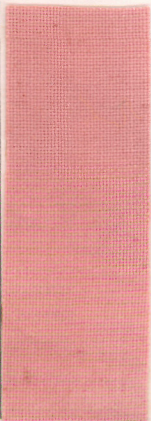
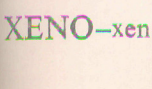
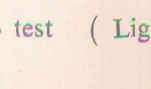
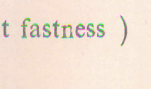
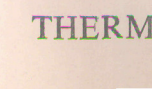
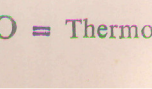
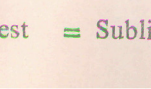
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						1-2	3-4
						3-4	2-3
						1-2	1-2
						3-4	2
						2-3	2-3
						3	2

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

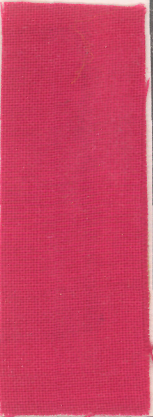
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						4-5	4
						3	3
						1	4
						2-3	4
						1-2	4-5
						2	4-5

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

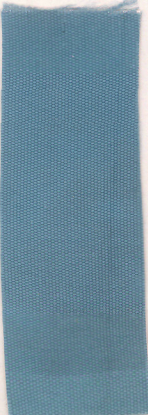
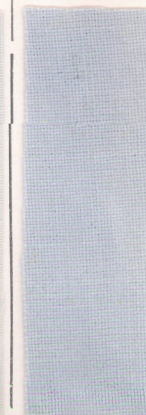
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						1	-
						2-3	-
						1	-
						2-3	-
						-	-
						5-6	4-5

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						3-4	4-5
						4-5	4-5
						-	-
						-	4-5
						4	3-4
						3	3

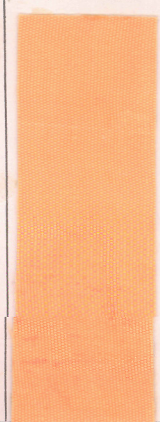
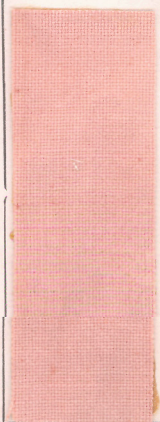
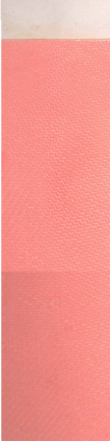
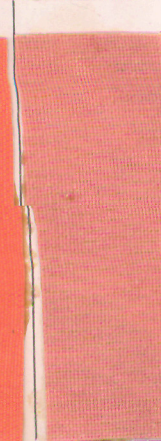
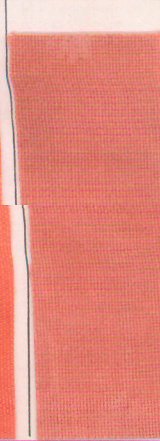
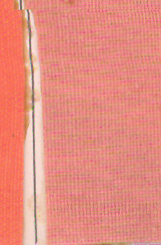
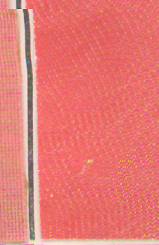
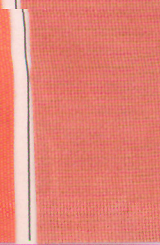
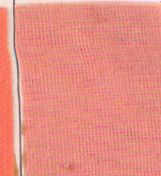
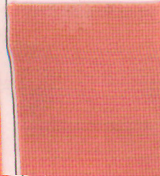
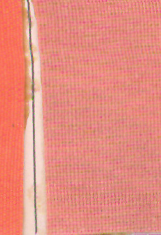
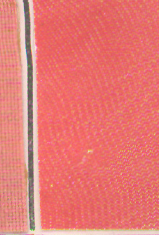
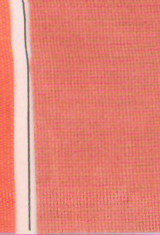
XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

124

124

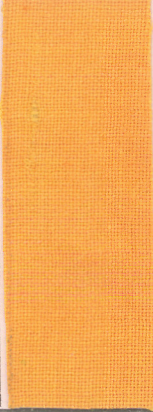
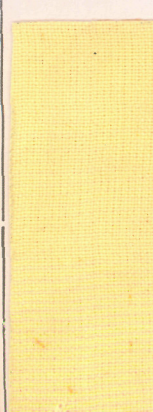
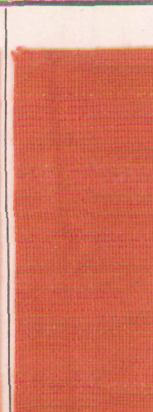
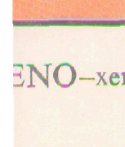
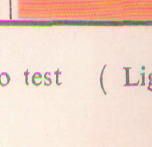
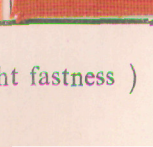
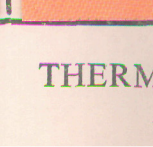
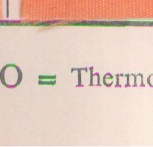
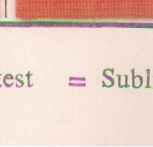
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						1	4
						2-3	4
						1	4
						2-3	4-5
						1	4
						2-3	4

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

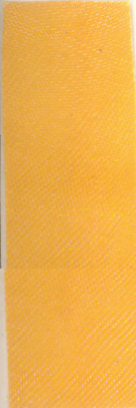
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						-	4
						3	3-4
						2	4-5
						2-3	4
						-	4
						-	4-5

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

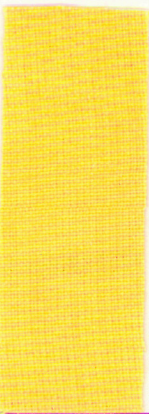
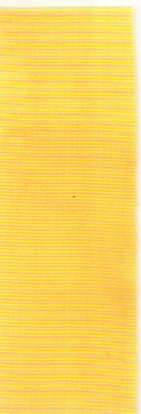
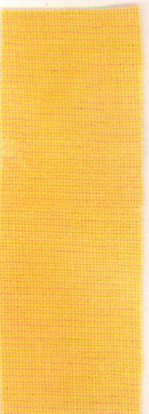
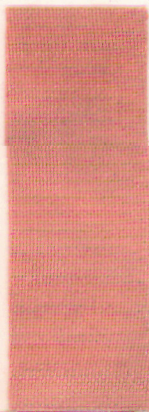
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						4	4
						4	3
						-	2-3
						-	4-5
						-	4-5
						-	4-5

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

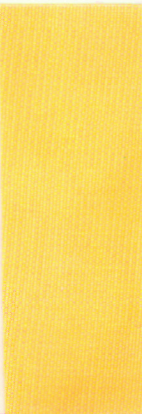
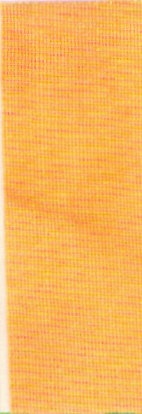
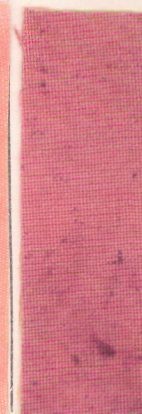
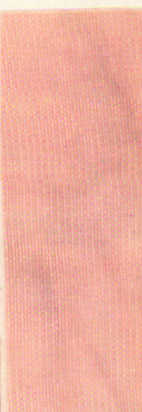
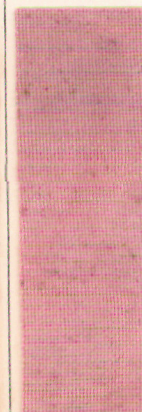
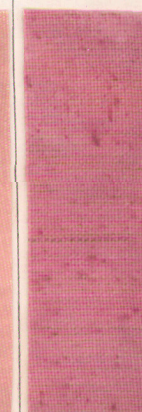
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						2-3	4-5
						3	4
						4	4
						3	2
						1	3
						2	3

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						2	4
						3	4
						1	4
						1-2	4
						-	4
						2	4

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

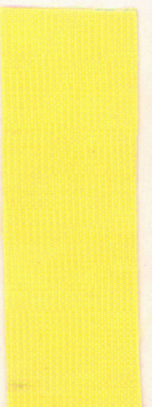
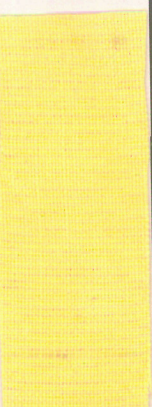
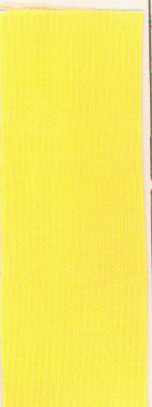
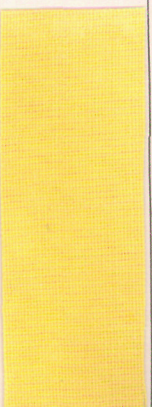
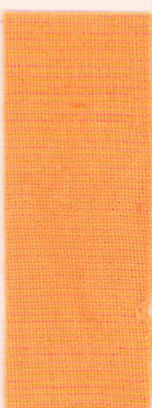
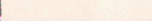
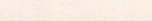
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						1	4
						2	3-4
						3-4	5
						2-3	4-5
						3-4	3
						3	1-2

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

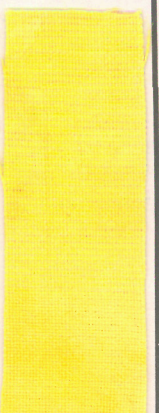
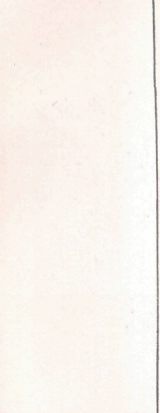
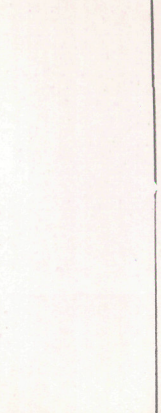
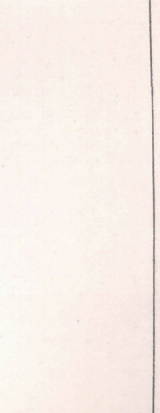
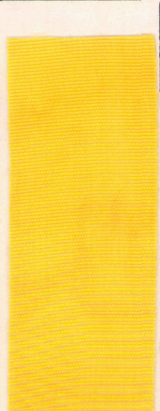
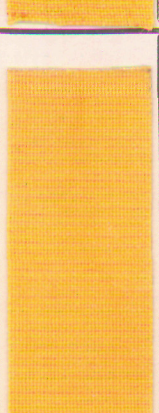
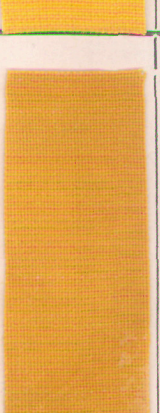
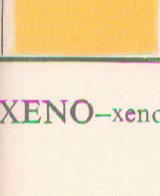
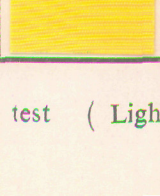
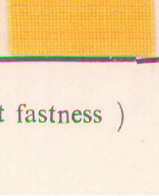
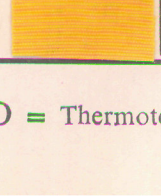
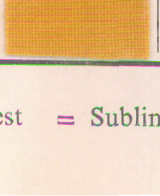
Shade Card (2% Shades)

Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater	-	4-5
						-	4
						5-6	4
						3-4	4
							

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

Shade Card (2% Shades)

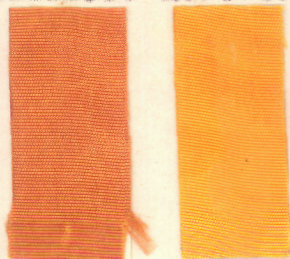
Before Thermolysis			After Thermolysis			XENO	THERMO
Polyamide	Sec. call Acetate	Polycater	Polyamide	Sec. call Acetate	Poly cater		
						4-5	3
						4-5	3
						2-3	4
						3-4	3-4
						4	4
						3-4	2

XENO-xeno test (Light fastness)

THERMO = Thermotest = Sublimation fastness

Dyes III(XV) and V applied by Pad-Dry-Cure method on Cellulose Acetate, polyamide, polyester and polyester-cotton blend (67:33%). Curing temperature 170° for 5 minutes.

Cellulose Acetate



III

V

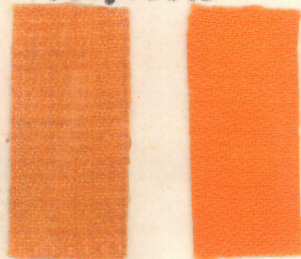
Polyamide



III

V

Polyester



III

V

Polyester-Cotton



III

V

Dye V printed on Cellulose Acetate,
Polyester and Polyester-Cotton blend (67:33%).

Cellulose Acetate



Polyester



Polyester Cotton



Stripping Solvent
and Conditions

25% Aqueous
Pyridine for
24 hrs.

Boiling Iso-
propanol for
10 minutes

Boiling chloro-
benzene for
10 minutes

C.A. Cellulose acetate

C.A.

P.A.

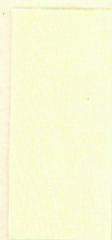
C.A.

P.A.

P.E.

P.E.

XLIII



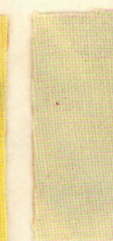
XIX



XXI



XXVII



P.E. Polyester

P.A. Polyamide

Results of the stripping experiments done
one dyeings of dye XXIX

Stripping solvent
and conditions

25% Aqueous Pyridine
for 24 hours

C.A.

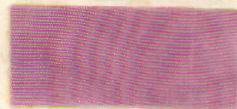


P.A.



Boiling isopropanol
for 10 minutes

C.A.



P.A.



P.E.



Boiling chlorobenzene
for 10 minutes

P.E.



C.A. - Cellulose Acetate P.A. - Polyamide

P.E. - Polyester

REFERENCES

1. Beech, W.F., "Fibre-Reactive Dyes" (1970) Logos Press Ltd., London, pp. 269.
2. F. By., Be P. 706, 987.
3. Scott, D.F. and Vickerstaff, T., J. Soc. Dyers Colour 76, 104, (1960).
4. Elod, E. and Einsele, U., Melliand Textilber. 41, 1377 (1960).
5. Salvin, V.S., Amer. Dyestuff Reprtr. 55, 490 (1966) (1966).
6. Cheetham, R.C., "Dyeing Fibre Blends", D. Van Nostrand Co. Ltd., London. (1966)
7. Schmidlin, H.U., "Preparation and Dyeing of Synthetic Fibres" (1963), Chapman and Hall Ltd., London, pp. 264.
8. Abramovitch, R.A. and Sutherland, R.G., Fortsch. Chem. Forsch. 16, 1, (1970).
9. Kulwant Singh, Ph.D. (Tech.) Thesis, 1973.

CHAPTER - IV

Spectral Studies

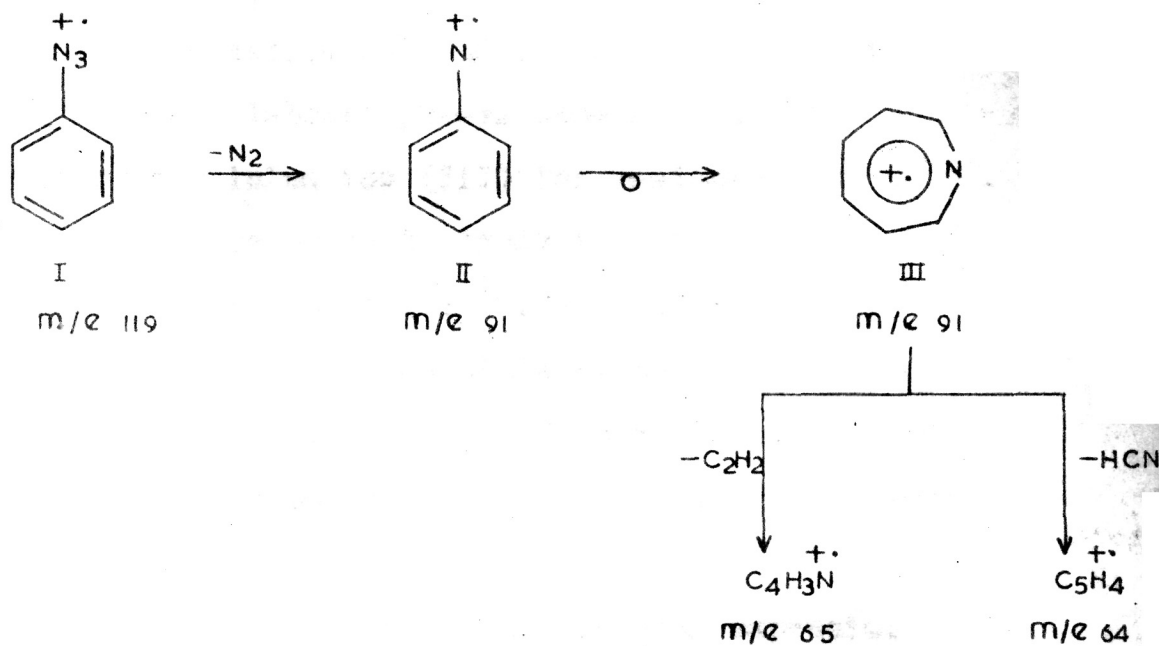
Mass spectral study of various intermediates and dyes

Introduction

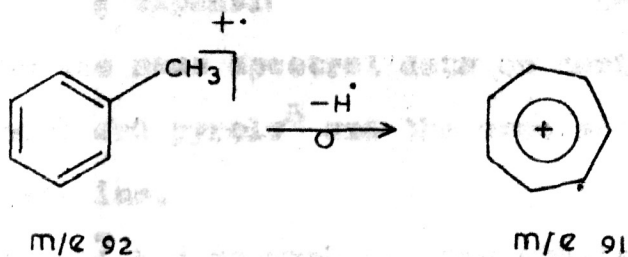
In the previous chapters we have discussed the synthesis and application of reactive disperse dyes containing the azido group. The reactive fixation of the dyes on synthetic fibres by thermolysis is explained by first elimination of molecular nitrogen to form "nitrene" intermediate which inserts into the fibre molecule forming a covalent bond between the dye and the fibre substrate. It was therefore of interest to study the decomposition of organic azides under electron impact. The aim in the present study was to study the pattern of decomposition under the influence of electron impact and to find out if it bears any relationship with thermal or photolytic decomposition. Mass spectral studies of some substituted arylazides and benzenesulphonazide have been reported in recent years. Mass spectral studies of diazides and compounds containing azido acetamido groups have not been reported so far. Mass spectral study of the dyes containing azido groups are also not reported so far.

Crow and Wentrup¹ have reported the mass spectrum of phenylazide which has a base peak at m/e 91 corresponding to loss of molecular nitrogen (N_2) from the parent ion. This is followed by the loss of HCN and C_2H_2 according

SCHEME - I (a)



SCHEME - I (b)



scheme 1(a).

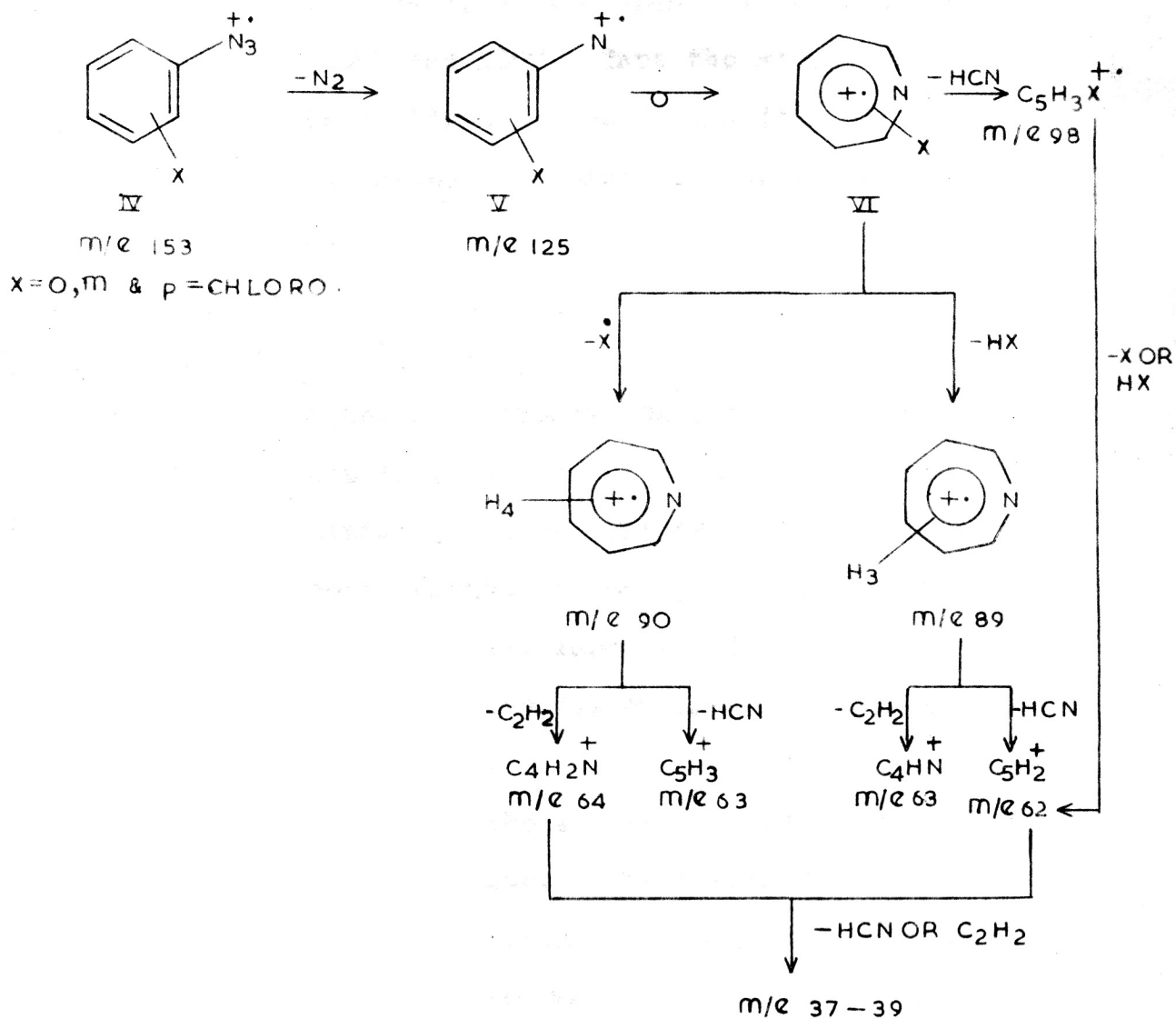
The nitrenium ion, $C_6H_5N^+$ (II) from phenylazide rearranges to give H_5 -azepinium ion (III) prior to elimination of C_2H_2/HCN . The possibility of ring expansion was investigated² and examination of mass spectrum of 1- C^{13} labeled phenylazide showed the formation of azepinium ion (III) for randomization of C-1 throughout the ring prior to expulsion of HCN. About one-half to five-sixth of (II) rearranged to (III). Kingston and Henion³ have established by deuterium labeling that the nitrenium ion (II) formed from phenylazide has its hydrogen atoms randomized before the loss of HCN and C_2H_2 .

The behaviour is similar to the ring expansion pathway suggested for the $(M-H)^+$ ion (m/e 91) from toluene⁴, where it is best represented by a tropylium ion structure (scheme 1b).

Similar ring expansion pathways have been proposed to rationalize the mass spectral data on derivatives of quinoline, indol and pyrrole⁵ and the even electron ion $C_6H_8N^{+6}$ from aniline.

Abramovitch⁷ and co-workers have studied the electron impact induced decomposition of a series of ortho, meta and para-substituted aryl azides to investigate the

SCHEME - 2



possibility of ring expansion.

Fraser⁶ and co-workers have also investigated the electron impact decomposition of ortho, meta and para substituted arylazides and a few disubstituted arylazides.

Abramovitch⁷ and co-workers have shown that the fragmentation pattern remains same when the temperature is varied between 165° and 250°. Thus the major fragmentation is from nitrenium ion (II) and it does not matter whether (II) arises from electron-impact ionisation or from thermolysis.

Present work

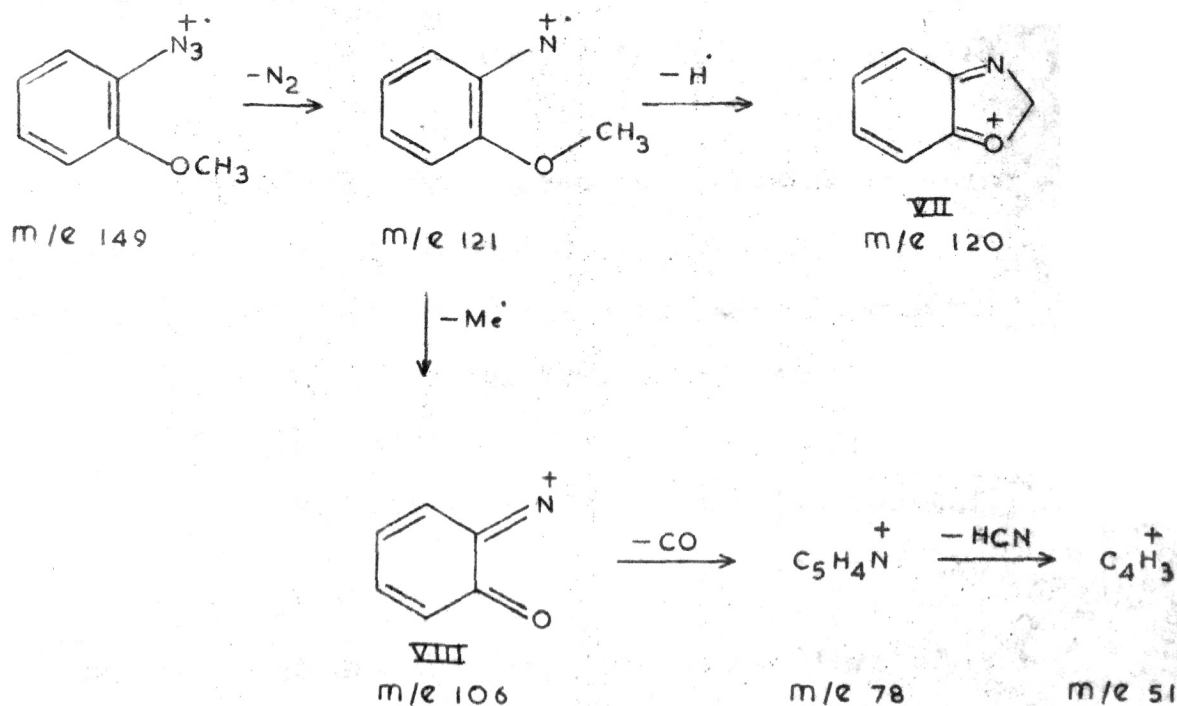
(a) Aryl azides

As mentioned before, Abramovitch⁷, et al. have studied the fragmentation pattern of *o*, *m* and *p*-mono-substituted phenylazides, the substituents being chloro, cyano, nitro, methoxy, phenyl and methyl groups.

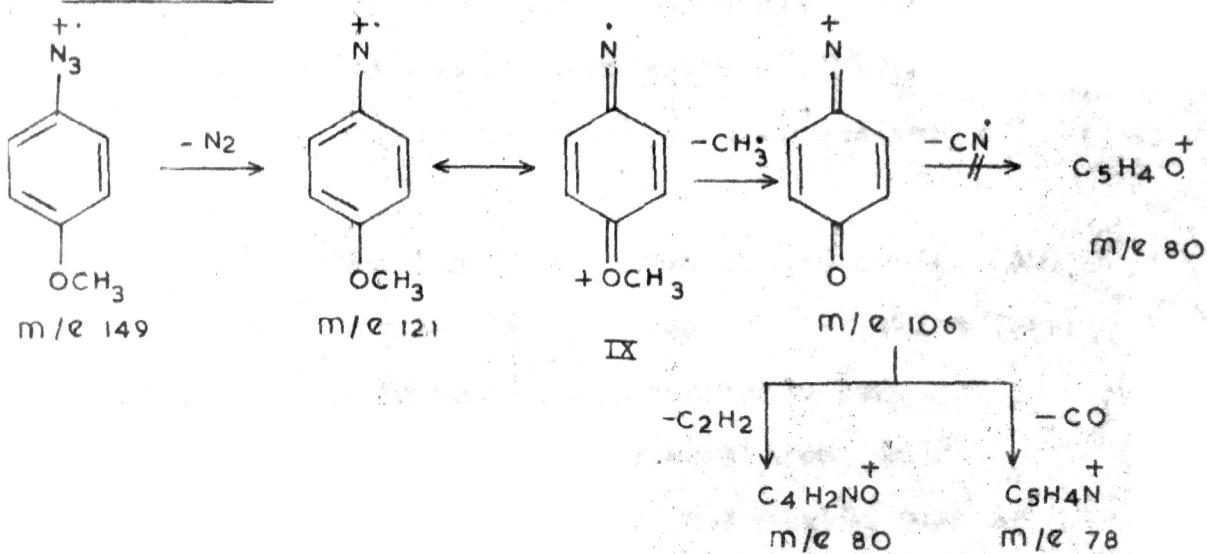
In the case of *o*, *m*, *p*-chloro substituted phenylazides they have suggested the following general pattern of fragmentation (Scheme 2).

We have also studied the spectra of the *o*, *m* and *p* chloro substituted phenylazides. The fragmentation pattern is similar to that given by Abramovitch et al. We have studied, *o*, *m* and *p*-methoxyphenylazide and they also show similar fragmentation pattern as described by Abramovitch et al.⁷ The results can be summarised by

SCHEME — 3



SCHEME — 4



The Schemes 3 and 4 as given in literature⁷.

In case of the meta-isomer the peak at (m/e 121) shows the formation of methoxyazepinium ion, which may then lose a methyl radical to give the azepinone ion (m/e 106). Loss of CO and then HCN gives the other two major peaks in the spectrum, viz. (m/e 78) and (51) respectively.

The fragmentation of p-methoxyphenylazide has been summarised according to (Scheme 4).

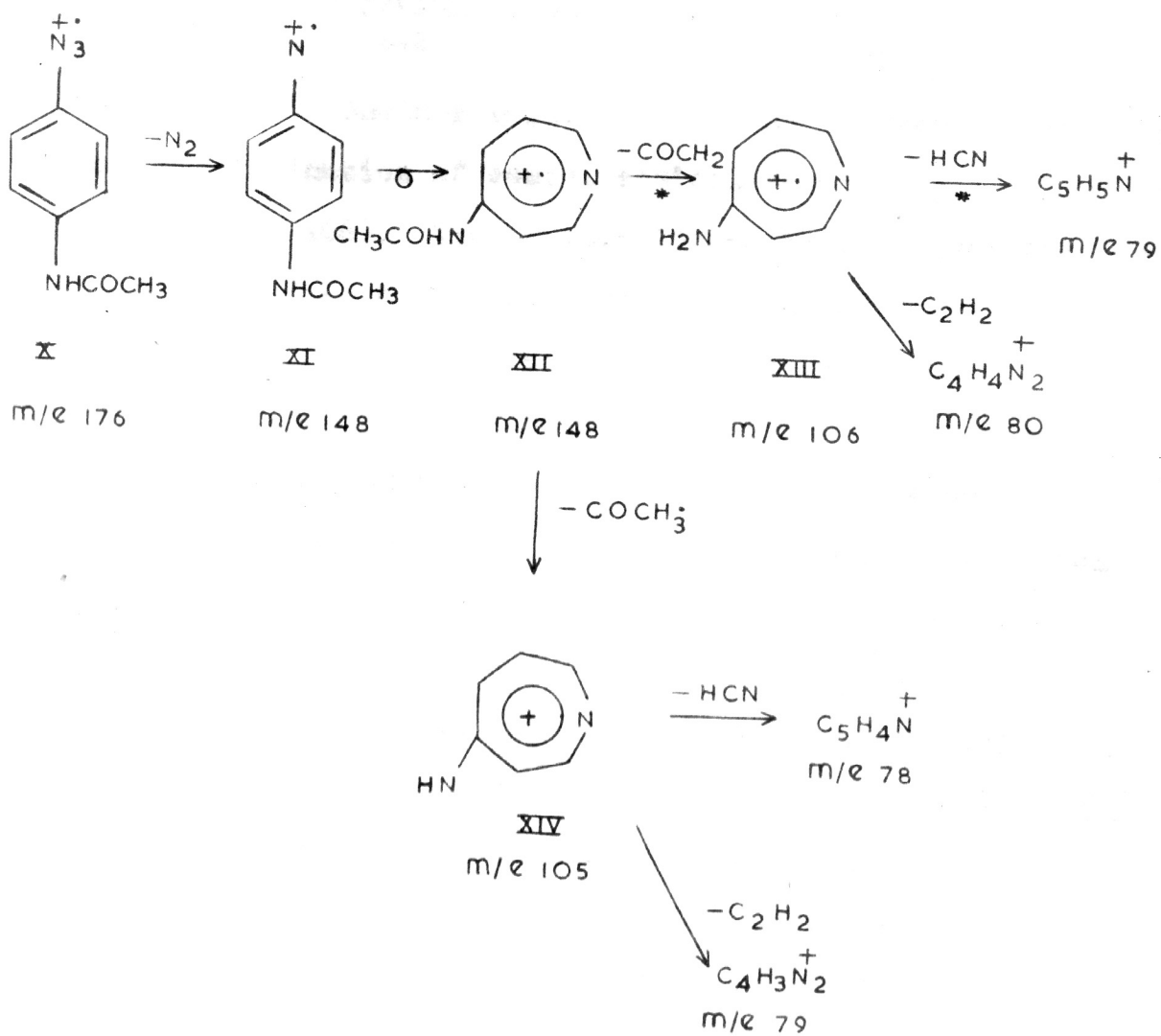
In the mass spectrum of the para isomer two major peaks are seen at (m/e 80) and (52) which are not seen in the spectra of ortho and meta isomers. This may be explained on the basis of resonance stabilized nitrinium ion (IX).

p-Acetamidophenylazide

We have examined the fragmentation pattern of p-acetamidophenylazide which can be used as an intermediate in the synthesis of dyes containing aryl azido group. The fragmentation modes of this molecule resemble the behaviour of phenylazide as well as acetanilide.

Initial expulsion of $-N_2$ from the molecular ion gives a peak at m/e 148 ($M-N_2$) (Scheme - 5) which further eliminates $-COCH_3$ in one step (metastable peak at m/e 75.9) as in the case of acetanilide, to give the base peak at (m/e 106). Metastable peak is

SCHEME - 5



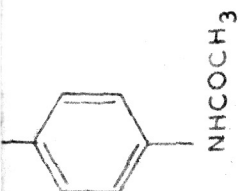
calculated from the formula

$$m^* = \frac{m_2^2}{m_1} \text{ in this case XII} \rightarrow \text{XIII}$$

$$m^* = \frac{(106)^2}{148} = 75.9$$

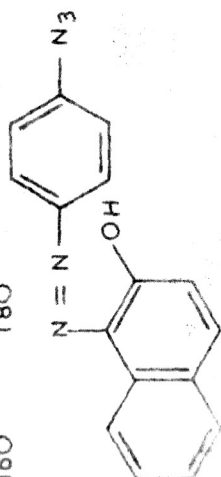
(M-N₂-COCH₂•). Another major peak in the spectrum comes from the elimination of acetyl radical from (M-N₂) fragment (m/e 105). The further fragmentations show the elimination of -HCN and -C₂H₂ which can be explained conveniently by assuming the substituted azepinium structure for the m/e 148 peak (XII). The elimination of HCN from m/e 106 peak is a one step process as shown by a metastable peak at m/e 58.8. Except for the elimination of -COCH₂ and -COCH₃, the mass spectrum is similar to that of phenylazide.

Two dyes, 1-(4'-azido)phenylazo-2-naphthol (XV) and p-azido-azobenzene were then selected as typical cases for the mass spectral study of the dyes containing the azido group. In the case of 1-(4'-azido)phenylazo-2-naphthol XV, the base peak is found at m/e 261, representing loss of -N₂ from the molecular ion (289). Loss of acetylene from (M-N₂) results in the peak at m/e 235. The loss of -HCN from the (M-N₂) is a minor process, whereas the loss of -CHO and CO, the typical



(m)
176

NHCOCH₃

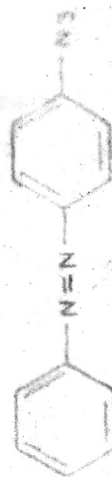


m/e

261

232

289



(m)
223

194

168

77

63

51

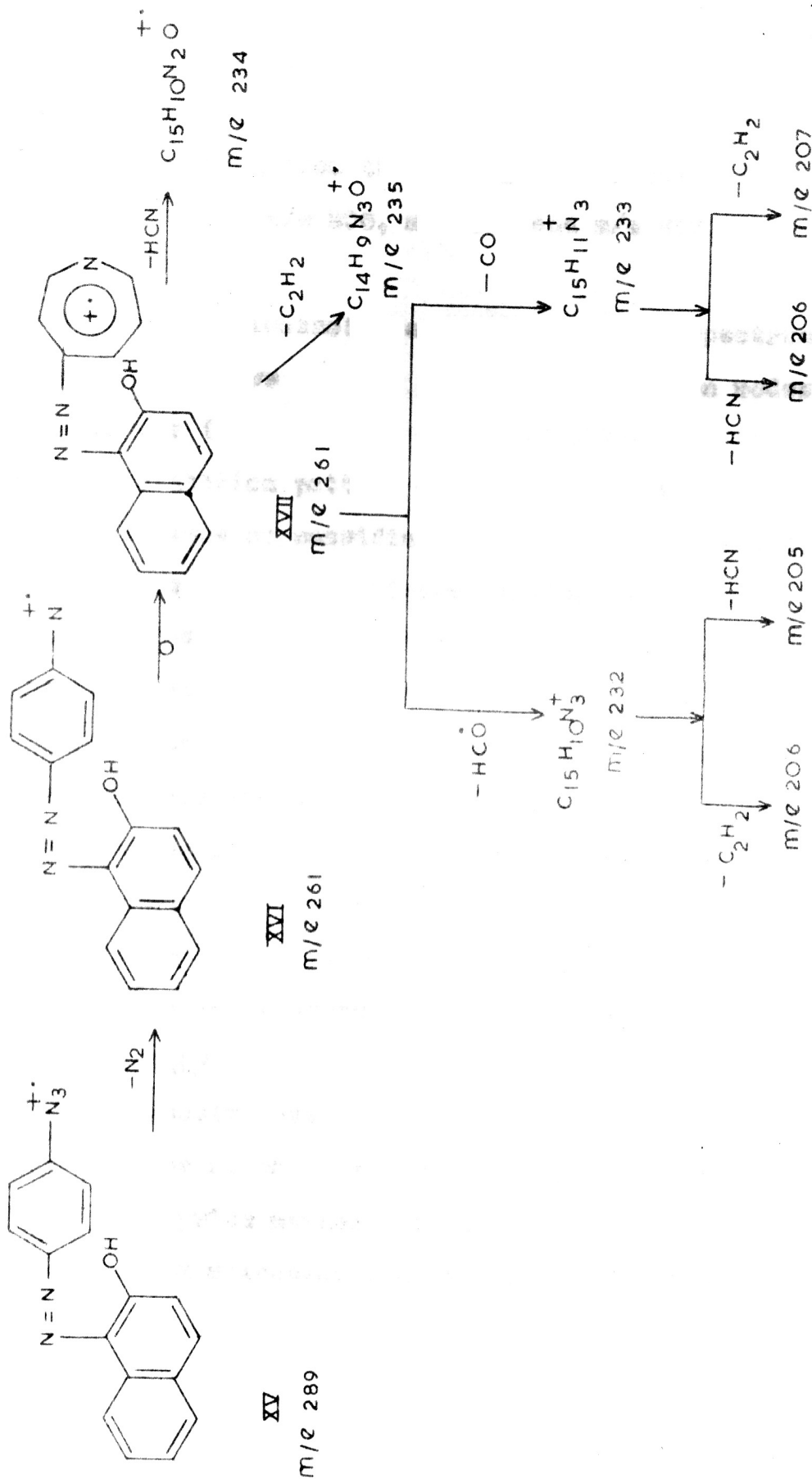
RELATIVE INTENSITY
0.40 0.20 0.40 0.60 0.80 1.00

RELATIVE INTENSITY
0.40 0.20 0.40 0.60 0.80 1.00

RELATIVE INTENSITY
0.40 0.20 0.40 0.60 0.80 1.00

m/e

m/e



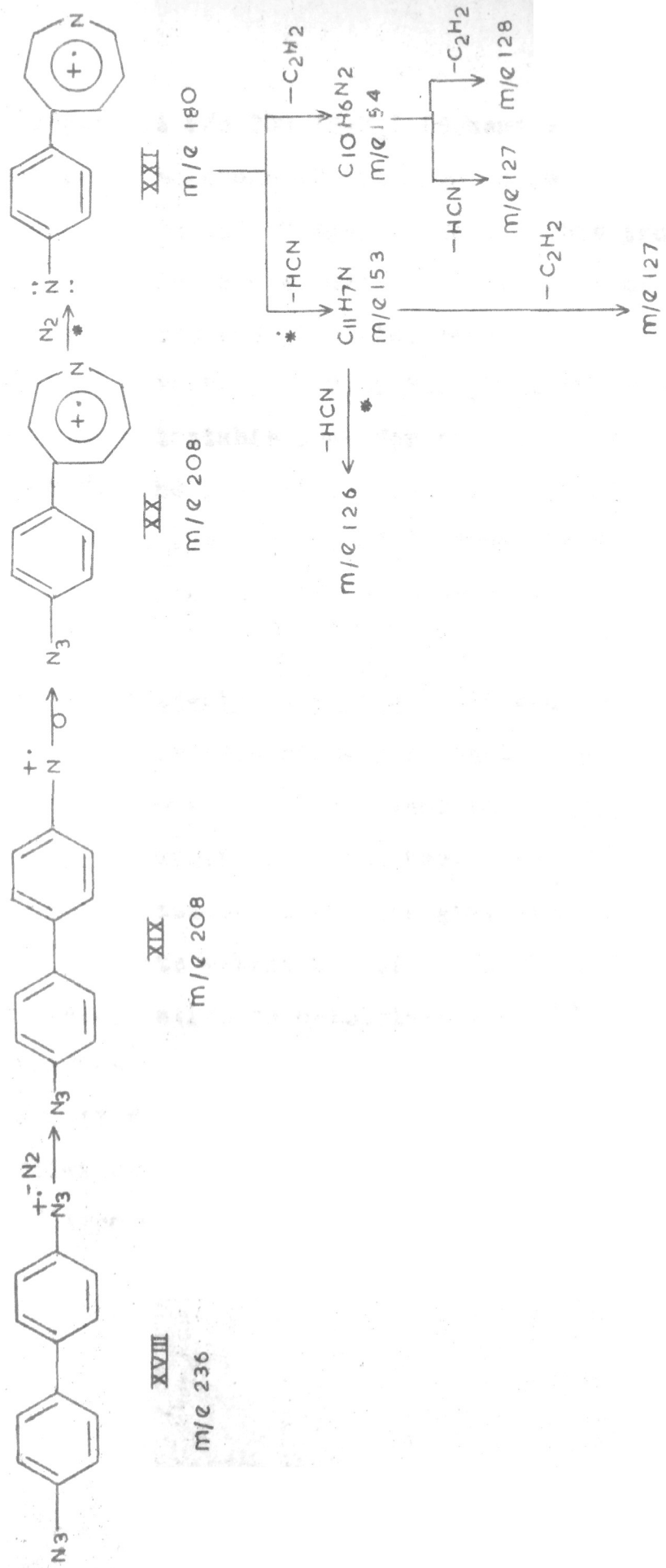
fragmentation of phenols gain importance and give large peaks at m/e 232 and m/e 233 respectively. The loss of $-HCN$ and $-C_2H_2$ from these fragments results in the peaks at m/e 205, m/e 206, m/e 206 and m/e 207 respectively.

In case of p-azidoazobenzene only the mass spectrum is given since it shows similar azide fragmentation modes as in case of dye (XV).

The fragmentation pattern of the diazides derived from benzene or benzidine is so far not reported. The diazides were prepared by tetrazotizing benzidine, o-tolidine, 3,3'-dichlorobenzidine and 3,3'-dimethoxybenzidine and then replacing both the diazo groups by azido groups by treatment with sodium azide. Of the benzene series only diazides from p-phenylenediamine and m-phenylenediamine could be prepared but we could obtain mass spectrum only in case of m-phenylenediamine as the para isomer did not have enough vapour pressure below the decomposition temperature to record the spectrum.

4,4'-Diazidobiphenyl

4,4'-Diazidobiphenyl shows similar fragmentation pattern as in case of phenylazide but fragmentation proceeds in a stepwise manner. A molecule of nitrogen is eliminated from molecular ion (m/e 236) (XVIII)



to give a peak at m/e 208 ($M-N_2$) (Scheme 7) which further loses a molecule of nitrogen in one step to give a peak at m/e 180 ($M-N_2-N_2$) (XXI). This process shows a metastable peak at m/e 153. The loss of HCN from the ion at m/e 180 gives the base peak at m/e 153 ($M-N_2-N_2-HCN$). Further loss of HCN gives the peak at m/e 126. The metastable peak for this process is found at m/e 102.3. The peak at m/e 154, m/e 127 and m/e 128 are explained by the loss of $-C_2H_2$ from the fragments at m/e 180, m/e 153 and m/e 154 respectively as shown in Scheme 7.

3,3'-Dimethyl-4,4'-diazidobiphenyl - Scheme 9

3,3'-Dimethyl-4,4'-diazidobiphenyl is a very interesting compound as it can lead to two types of ring expansions. Abramovitch et al.⁷ have studied the mass spectra of tolylazides which also give rise to two ring expansion products scheme 8 (a,b). By the help of further investigation on o-tolyazide $\alpha-C^{13}$ they have shown that the ring-expanded species (XXIV) or (XXV) and (XXVI) are not important in explaining the facile elimination of C_2H_2 and HCN but the ortho-quinonoid type of structure (XXVII).



The mass spectrum of 3,3'-dimethyl-4,4'-diazidobiphenyl resembles the spectrum of o-tolylazide. The elimination of H_2 from $(M-N_2)$ ion does not take place till the other azido group fragmentation takes place. This behaviour is similar to that observed in case of 4,4'-diazidobiphenyl.

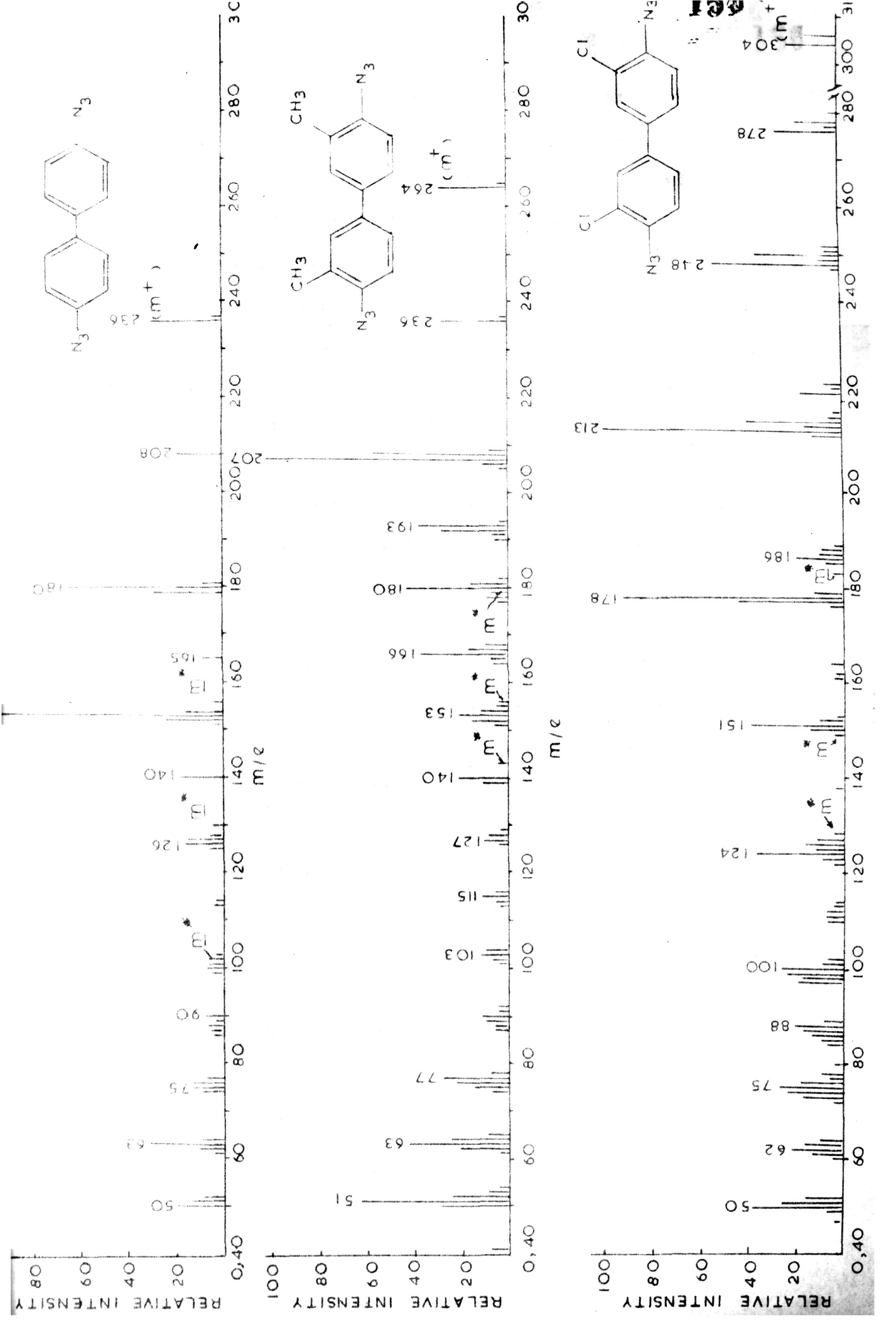
Thus mass spectrum of 3,3'-dimethyl-4,4'-diazidobiphenyl shows a fairly intense molecular ion peak at m/e 264. The elimination of $-N_2$ from this gives a peak at m/e 236 which further eliminates a molecule of $-N_2$ to give a peak at m/e 208 ($M-N_2-N_2$) Scheme 9.

Elimination of H_2 from the peak at m/e 208 gives the base peak for the spectrum at m/e 207 ($M-N_2-N_2-H$)(XXXII) which further eliminates a H^+ to give a peak at m/e 206.

Another interesting feature of the spectrum is the elimination of the $-CH_3$ from the ring expanded species of m/e 208. This behaviour is similar to the expulsion of a methyl group from xylenes⁹. This one step elimination of methyl group shows a fairly intense peak (37%) at m/e 193 and the process also shows a metastable peak at m/e 179.5. The peak at m/e 192 can arise from the fragment at m/e 207 by the elimination of a methyl group. A weak peak at m/e 178 indicates the elimination of another methyl group from m/e 193 ion.

SCHEME - 9

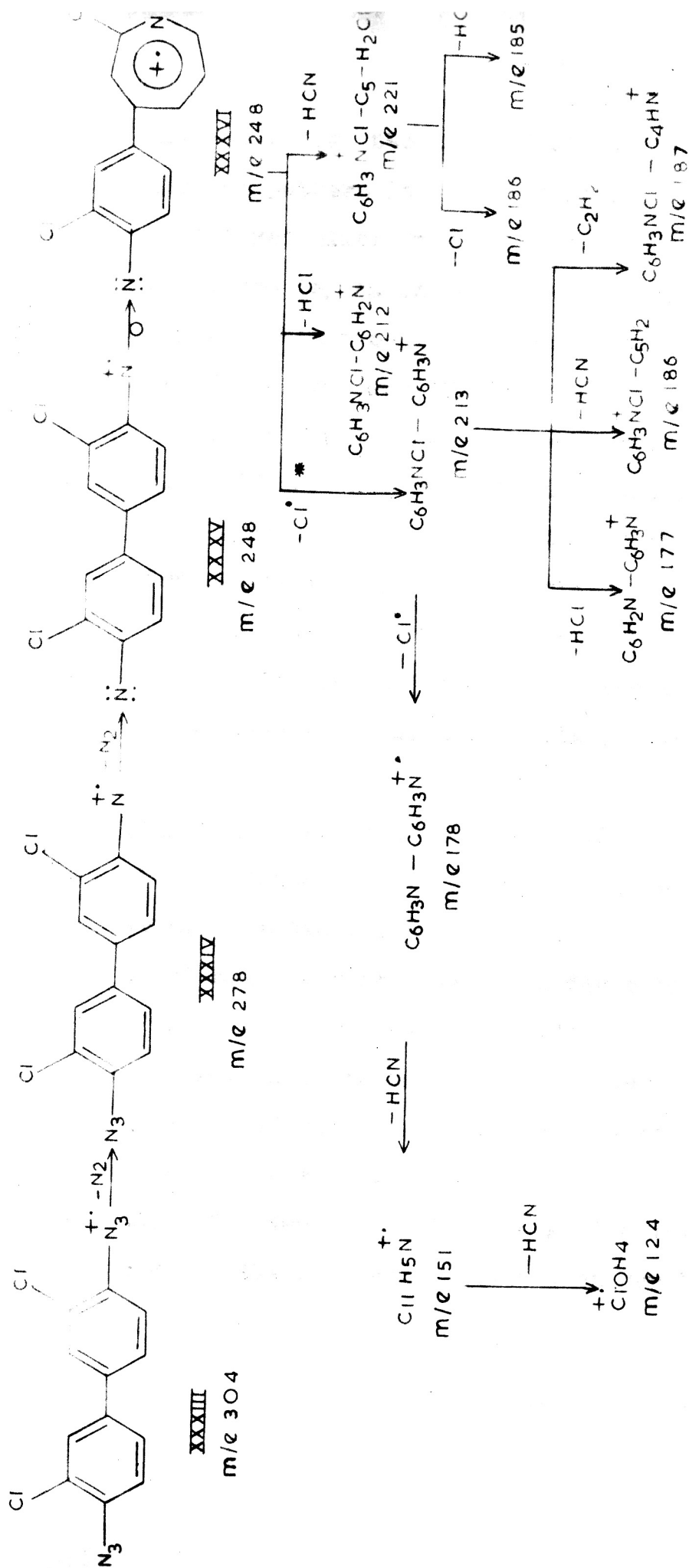




The intense peak at m/e 181 and m/e 180 arise from the ion m/e 207 by the elimination of $-C_2H_2$ and $-HCN$ respectively. The latter process shows a metastable peak at m/e 156. The fragment at m/e 180 can further eliminate $-C_2H_2$ and HCN to give peaks at m/e 154 and m/e 153 respectively. The peak at m/e 152 can arise from the elimination of H_2CN from m/e 180 fragment. Another interesting feature is the elimination of HCN from the ion at m/e 193 in one step giving a fragment at m/e 193 ¹⁶⁶ in one step giving a fragment at m/e 166. The process shows meta stable peak at m/e 142. Similar elimination takes place from the ion at m/e 178. Loss of C_2H_2 gives peaks at m/e 167 and 152 respectively.

3,3'-Dichloro-4,4'-diazidobiphenyl - Scheme 10

3,3'-Dichloro-4,4'-diazidobiphenyl behaves in an analogous manner of 2-chlorophenylazide⁷ and 2-bromophenylazide⁸. The elimination of two nitrogen molecules from the molecular ion at m/e 304 proceeds in stepwise manner giving peaks at m/e 276 ($M-N_2$) and m/e 248 ($M-N_2-N_2$). Further fragmentation is explained by assuming the structure (XXXVI) for the ion at m/e 248 (Scheme 10). Elimination of $-Cl$ gives the base peak at m/e 213. This is a one step process showing a meta stable peak at m/e 183. The spectrum also shows the peaks at



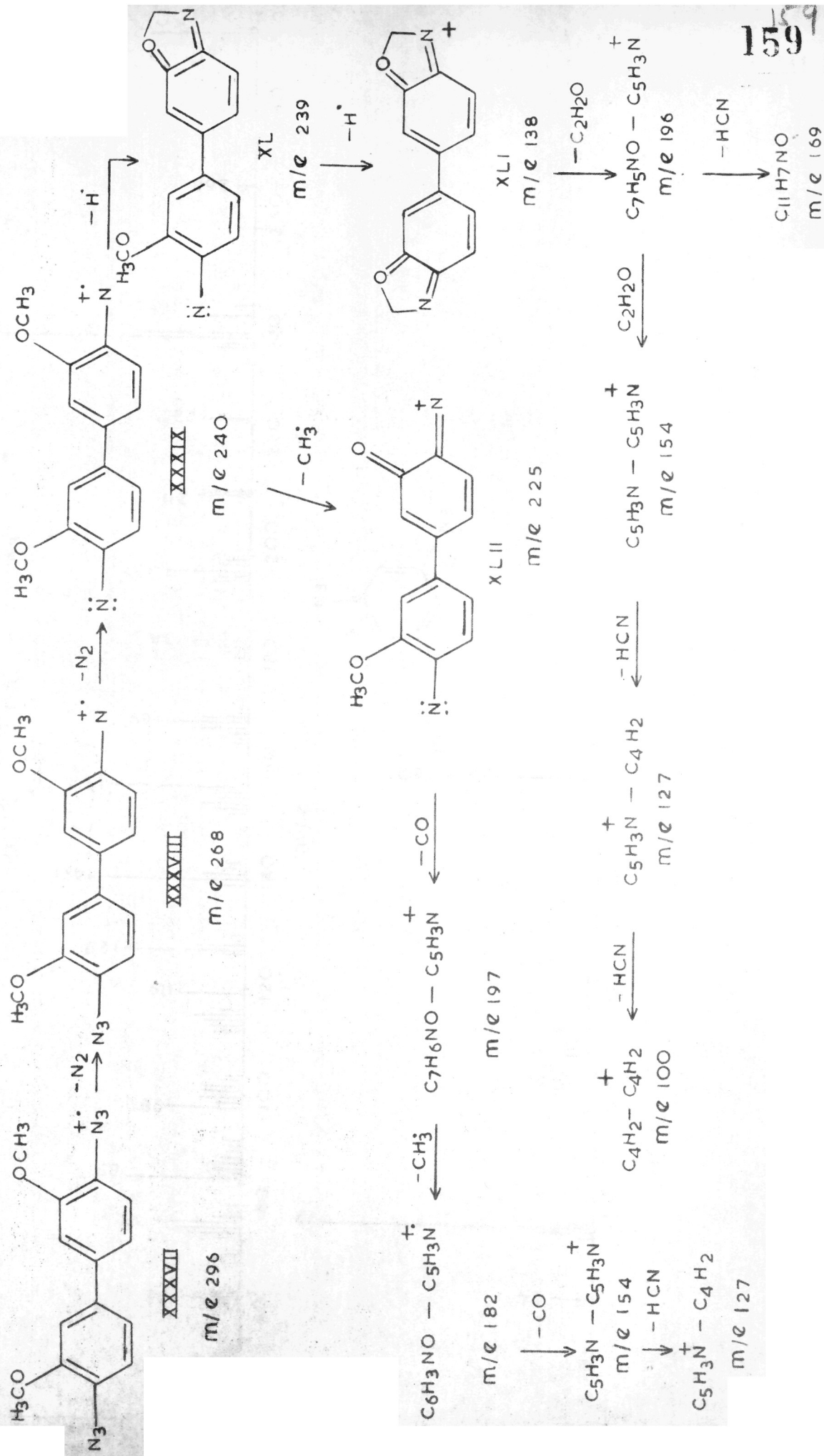
m/e 221 and m/e 212 indicating the loss of HCN and -HCl. Characteristic chlorine pattern is seen. Further elimination of a -Cl takes place from the ion at m/e 213 in one step process, showing an intense peak at m/e 178. The metastable peak for this process is seen at m/e 149. Again the peaks at m/e 186 and m/e 177 indicate the loss of -HCN and -HCl from the ion at m/e 213. Weaker peaks are also seen at m/e 222 and m/e 187 indicating the loss of -C₂H₂ from the ions at m/e 248 and m/e 213. This is another typical feature of the spectrum of phenylazide derivatives. The elimination of hydrogen cyanide from the ion at m/e 178 goes in one step process giving a peak at m/e 151. The metastable peak for this process is seen at m/e 128.5.

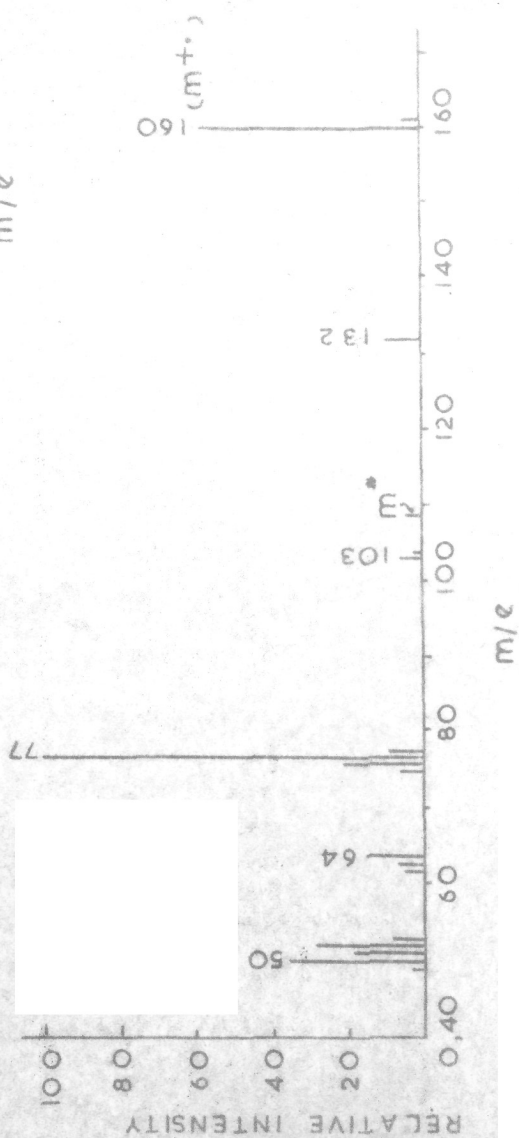
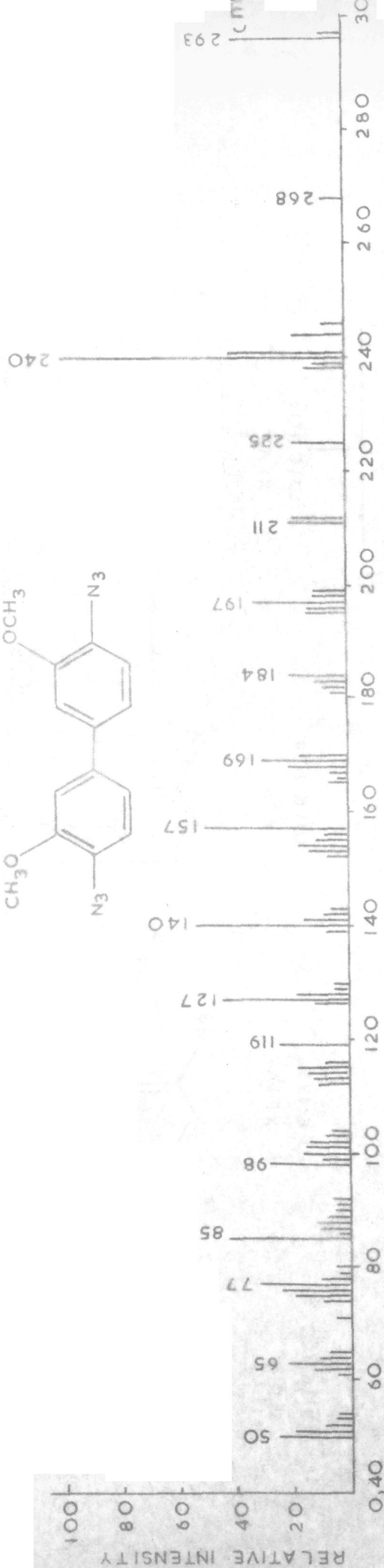
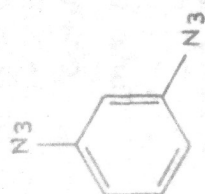
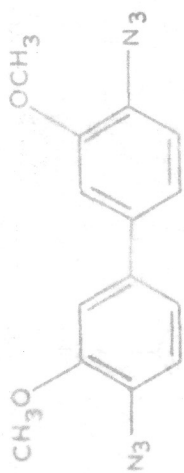
3,3-Dimethoxy-4,4'-diazidobiphenyl - Scheme - 11

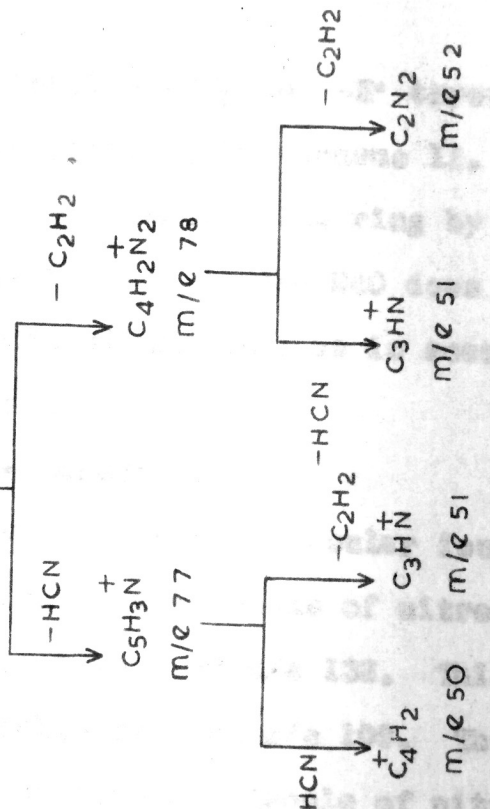
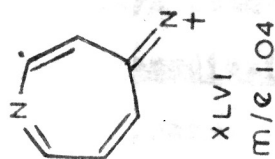
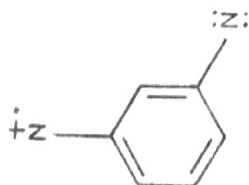
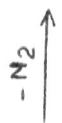
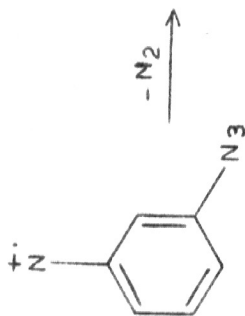
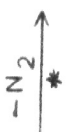
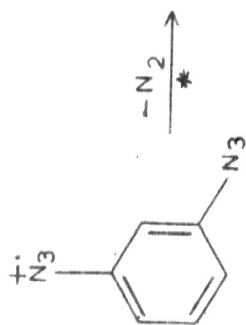
Lastly we have examined the fragmentation behaviour of 3,3'-dimethoxy-4,4'-diazidobiphenyl. This differs from the fragmentation of o-methoxyphenylazide as described in Scheme - 3 in which the base peak is at m/e 120, representing the formation of benzofurazan species.

The molecular ion of 3,3'-dimethoxy, 4,4'-diazido-biphenyl eliminates two molecules of nitrogen in stepwise manner (Scheme 11). The second elimination giving the base peak at m/e 240. The further fragmentation can be

SCHEME - II







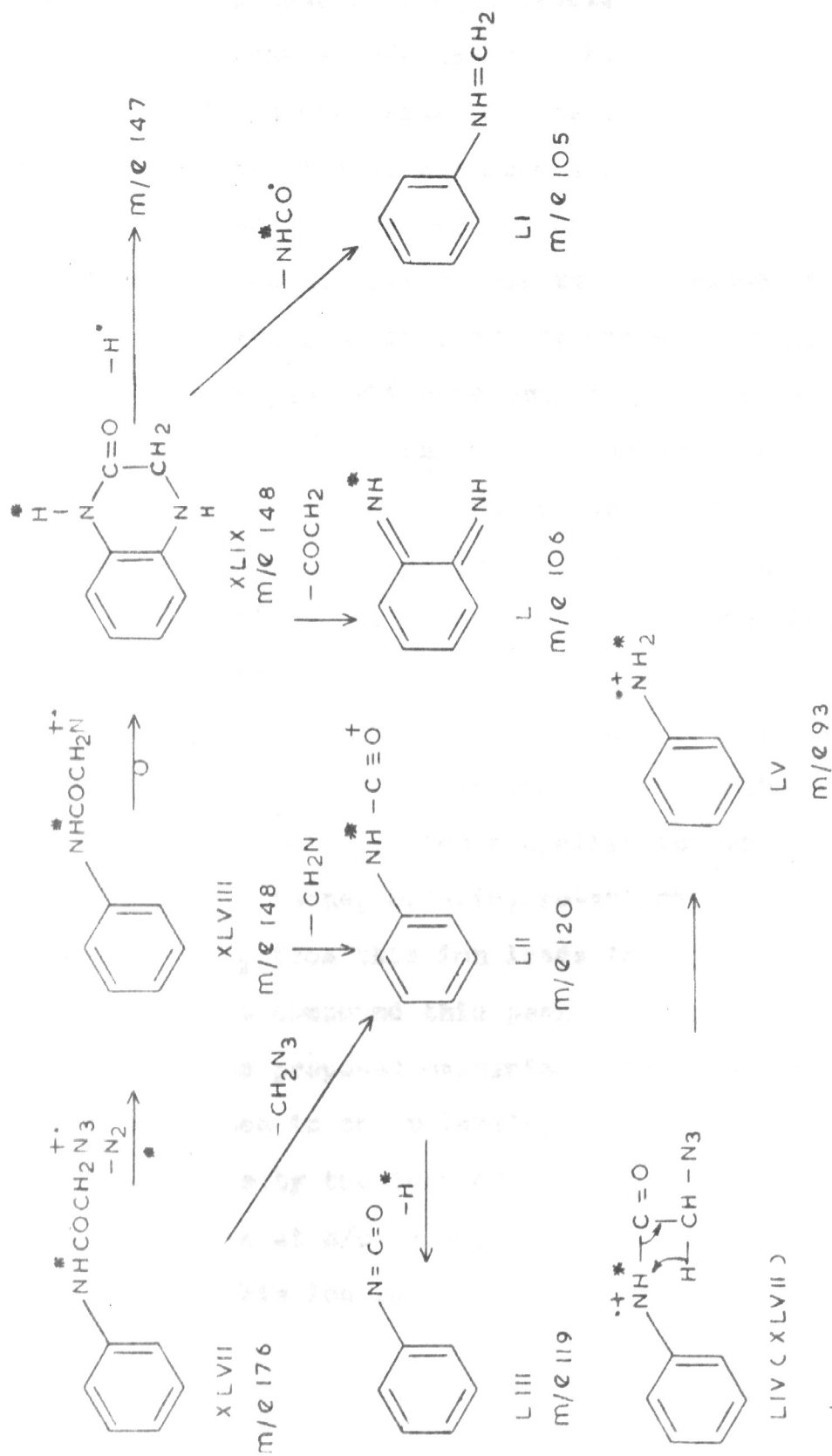
explained both by elimination $-CH_3$ and $-H^{\bullet}$ through benzoxazole ring XLI as given in the Scheme 11. In this case, the formation of benzoxazole ring by elimination of $-H^{\bullet}$ from the ion at m/e 240 does not predominate over the $-CH_3$ elimination as is seen in case of *o*-methoxy phenyl azide.

meta-Phenylenediazide - Scheme - 12

The spectrum shows an intense molecular ion peak at m/e 160, which eliminates a molecule of nitrogen in one step process to give a peak at m/e 132. This process shows a meta stable peak at m/e 109. The ion at m/e 132, further eliminates a molecule of nitrogen to give a peak at m/e 104. Elimination of $H^{\bullet}$ from this gives the peak at m/e 103. The base peak for the spectrum comes from the elimination of $-HCN$ from azepanium ion (XLVI) at m/e 77. Elimination of acetylene ($-C_2H_2$) from ion at m/e 104 gives the peak at m/e 78. The peaks at m/e 52, 51 and 50 arise by elimination of $-HCN$ and $-C_2H_2$ from the ions at m/e 73 and 77 as shown in Scheme 12.

Azidoacetanilide - Scheme - 13

The spectrum of this compound was studied in detail with the aid of corresponding N-deuterated compound. As in the case of phenylazide the primary fragmentation



* H — INDICATES THE HYDROGEN ATOM THAT WAS REPLACED BY DEUTERIUM IN THE LABELED COMPOUND.

process is the loss of a N_2 -molecule (m/e 148) showing a metastable peak at m/e 122.5. This ion loses a hydrogen atom to give rise to a peak at m/e 147. The spectrum of the labeled compound shows that the amide hydrogen is retained by the product. Hence the hydrogen atom that is lost may arise from the methylene group or one of the ortho positions of the aromatic ring.

The base peak which is observed at m/e 120 can result by the loss of $-CH_2N$ from $(M-N_2)$ ion or by the direct loss of $-CH_2N_3$ from the molecular ion. Loss of a hydrogen atom from this gives rise to a phenyl isocyanate ion at m/e 119. Labelling data shows that the amide hydrogen is lost during this reaction.

The peaks at m/e 105, 106 result from skeletal rearrangement processes. As shown in the scheme 13, $M-N_2$ ion (XLVIII) can undergo a cyclisation process to form 2-(1R)-quinoxalinone, 3,4-dihydro-quinoxaline XLIX. Loss of $-COCH_2$ from this ion leads to a peak at m/e 106. In the labeled compound this peak was found at m/e 107, supporting the proposed mechanism. The peak at m/e 105 was not shifted in the δ labeled compound. Hence, it probably arises by the loss of $-NHCO$ from the cyclised ion.

The peak at m/e 93 may have the ionised aniline structure. This ionised aniline is characteristic of

acetanilides. It arises by transfer of a hydrogen atom from the methyl group to the amide nitrogen by a four centre process, followed by the rupture of the amide ring (LIV $\rightarrow$ LV). A simple cleavage of the amide linkage results in the peak at m/e 92.

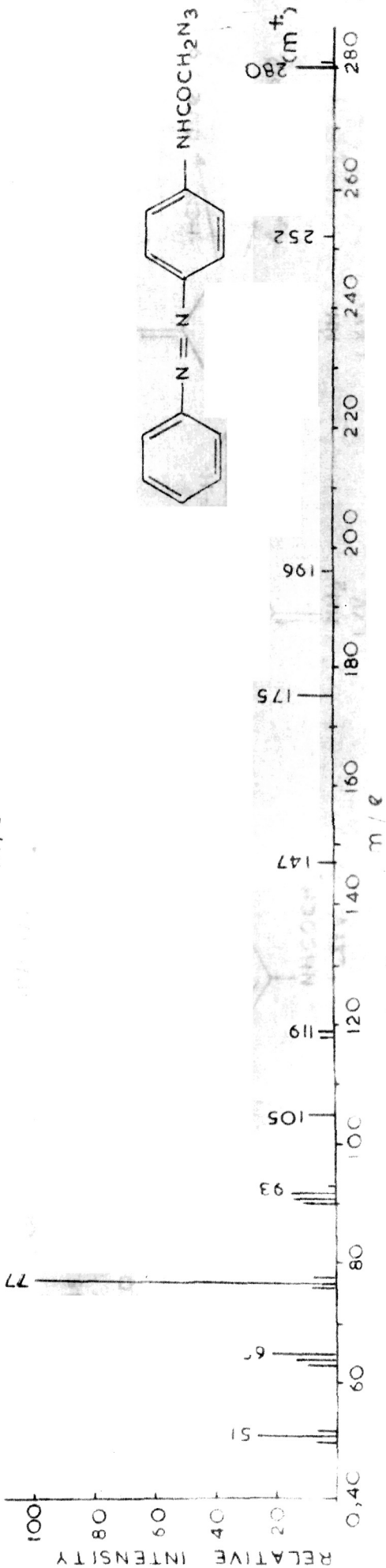
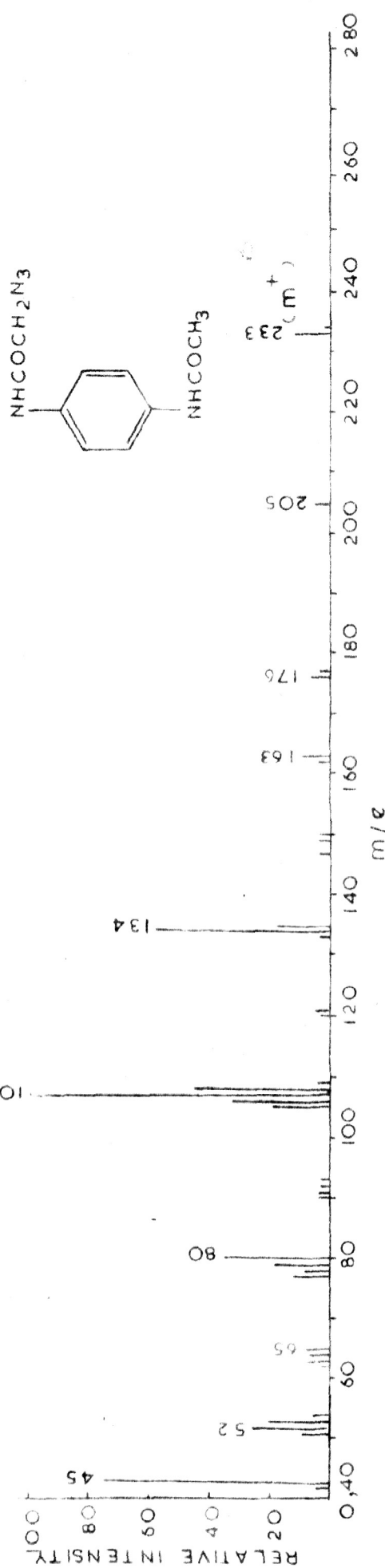
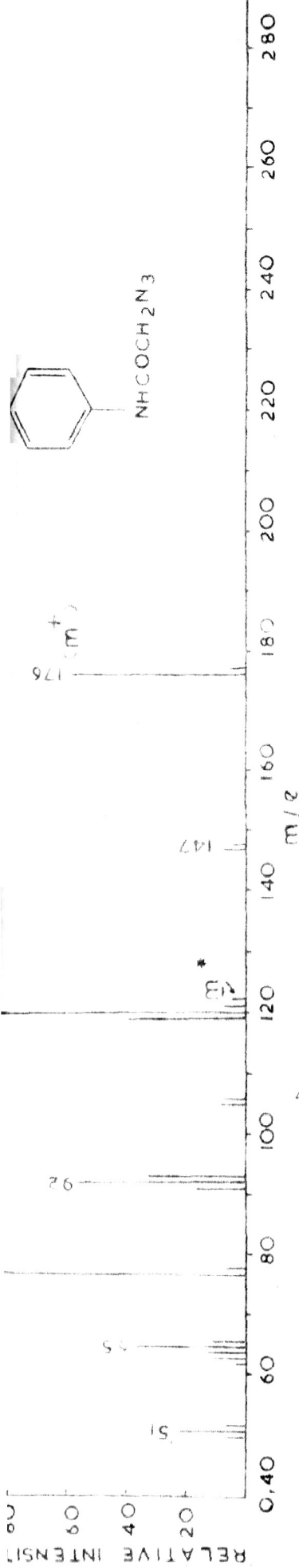
p-Acetamido-azidoacetanilide (Scheme - 14)

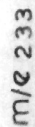
This spectrum also shows the similar fragmentation pattern as seen in case of azidoacetanilide but complexities arise due to the presence of the acetamido group. Fragmentation pattern for the important peaks seen in the spectrum is given in Scheme 14. Here also, the peaks due to the skeletal rearranged product can be seen along with fragments arising from the elimination of $-CH_2N$ from the ion at m/e 205 (LVIII).

An important feature is the elimination of 84 mass units representing the loss of $-COCH_2N_3$ from molecular ion peak LVII $\rightarrow$ LXIV. The ion at m/e 149 further loses $-COCH_2$ to give a peak at m/e 107 which gives rise to peaks at m/e 106, 80 and 79 by elimination of $-H$, $-C_2H_2$ and $-HCN$ as shown in the Scheme.

p-Azidoacetamidazobenzene

In case of this dye, the skeletal rearrangement process is absent as no peaks are seen at m/e 209 and





m/e 210 representing the loss of -NHCO and -COCH_2 from the $(\text{M}-\text{N}_2)$ peak at m/e 252. However, the peak due to elimination of $\text{-CH}_2\text{N}$ from $(\text{M}-\text{N}_2)$ ion is seen at m/e 224, which eliminates $\text{-H}^\bullet$ to give a peak at m/e 223. A peak is also seen at m/e 196 representing the loss of $\text{-COCH}_2\text{N}_3$ from molecular ion m/e 280. Only spectrum is given in this case.

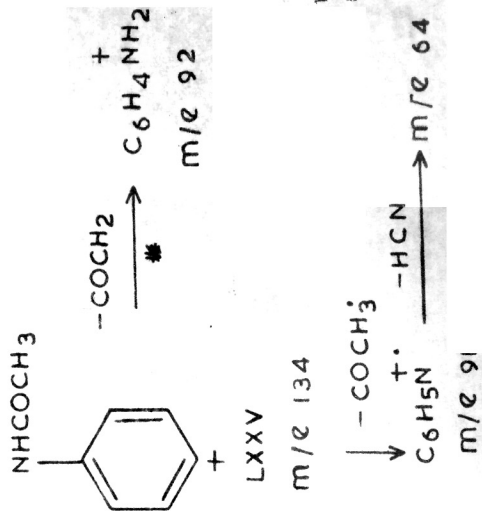
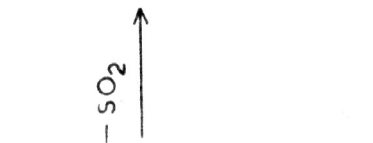
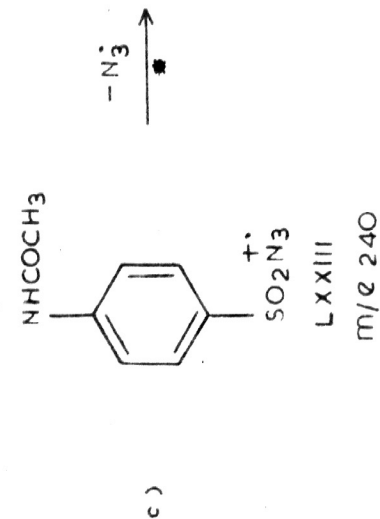
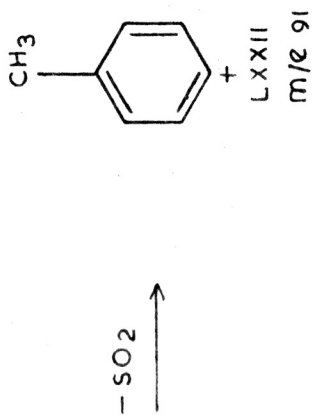
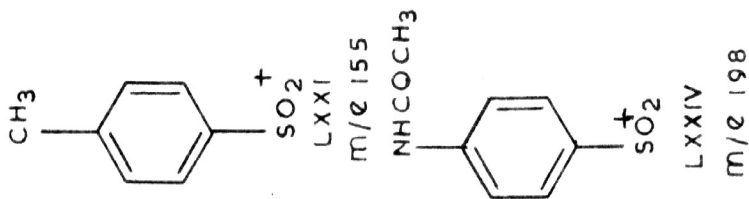
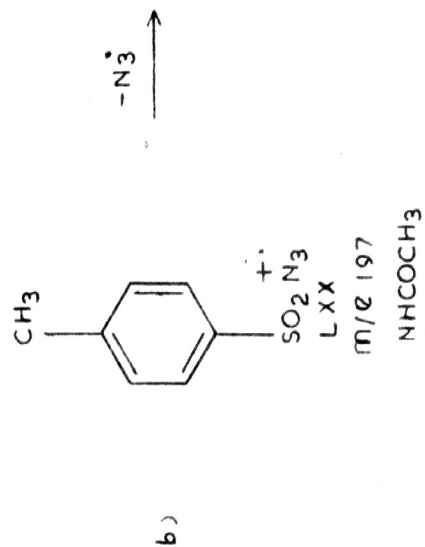
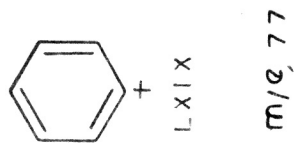
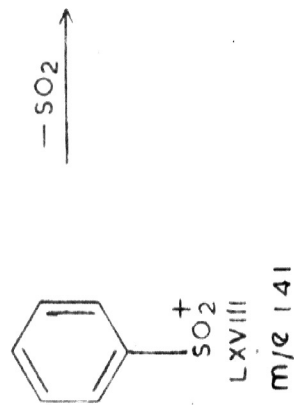
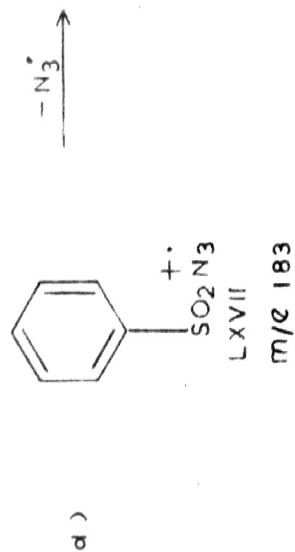
Sulfonylazides

Campbell and Dunn¹⁰ in their short communication on mass spectra of sulfonylazides have given M^+ , M-28, M-42 and M-43 peaks in case of benzenesulfonylazide and p-toluenesulfonylazide.

We have re-examined the mass spectrum of benzenesulfonylazide, p-toluenesulfonylazide along with p-acetamidobenzenesulfonylazide, 3-acetamido-4-methoxybenzenesulfonylazide and the dye, 4'-N,N-dimethylaminoazobenzene-4-sulfonylazide.

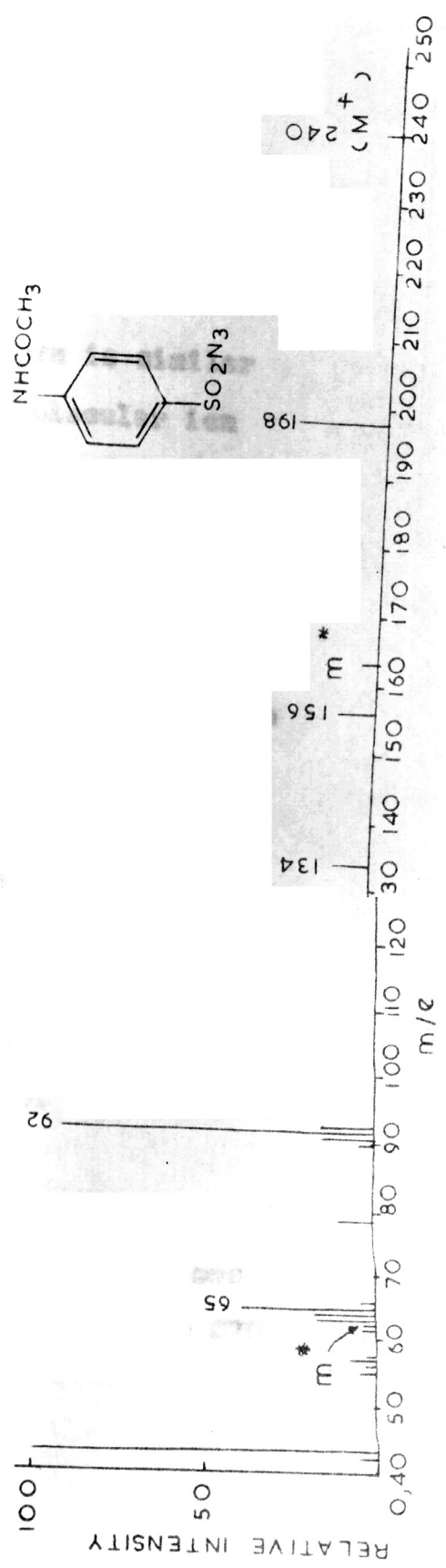
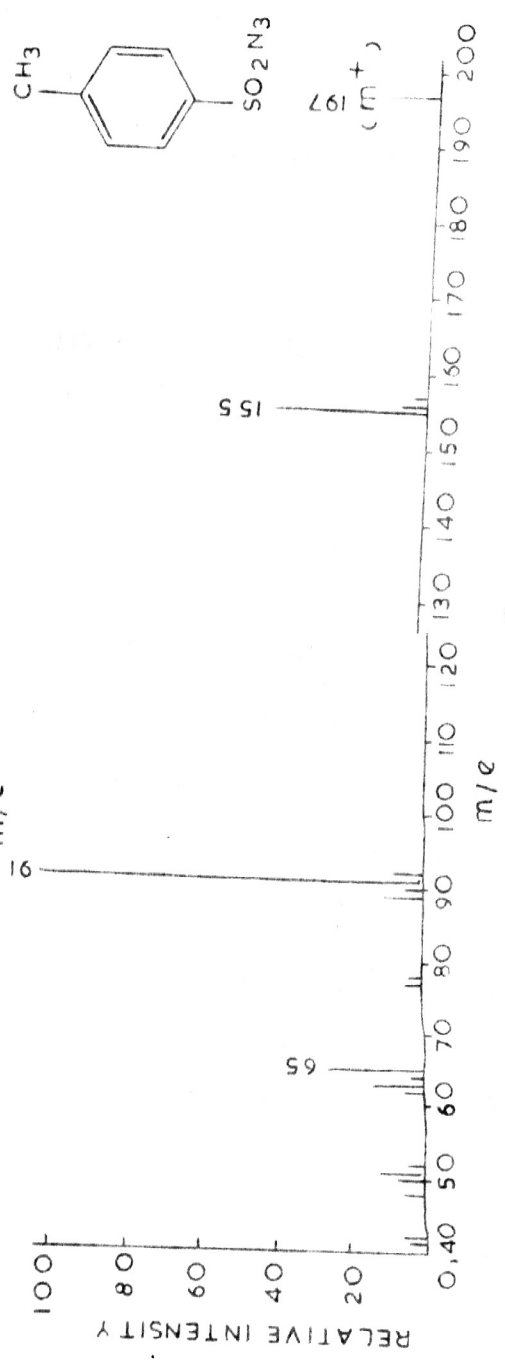
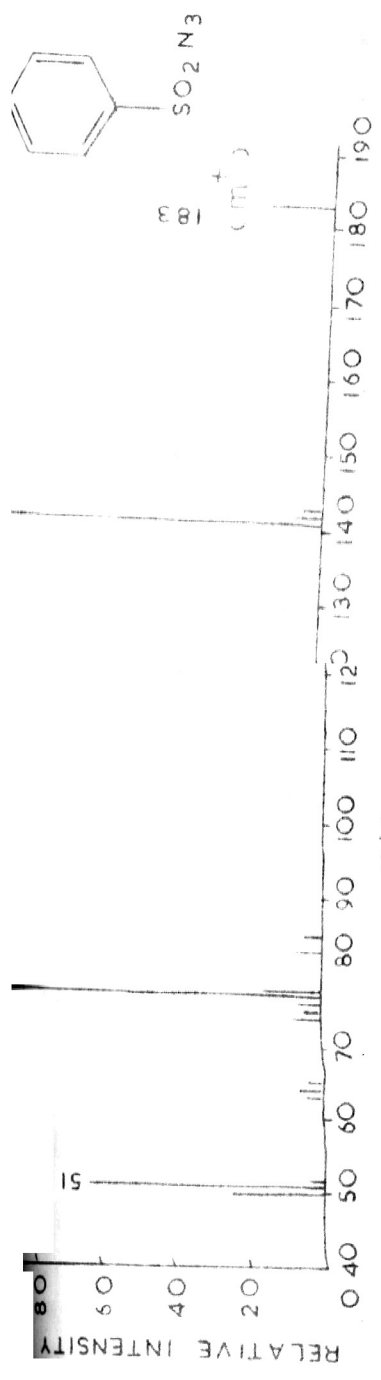
Benzene sulfonylazide (Scheme 15a)

There is no elimination of a molecule of nitrogen from the molecular ion as observed in thermal decomposition of sulphonyl azides giving "nitrene" intermediate. Instead there is an intense peak at m/e 141 showing the elimination of -N_3 ($\text{M} - \text{N}_3$) from the ~~xxxxxxxxxx~~



170

170



molecular ion (LXVII $\rightarrow$ LXVIII). The next intense peak, which is also base peak of the spectrum is at m/e 77 showing the loss of $-SO_2$ from $(M-N_3)$ ion (Scheme -15a). The peaks below m/e 77 arise from the fragmentation of benzene ring.

p-Toluene sulfonylazide

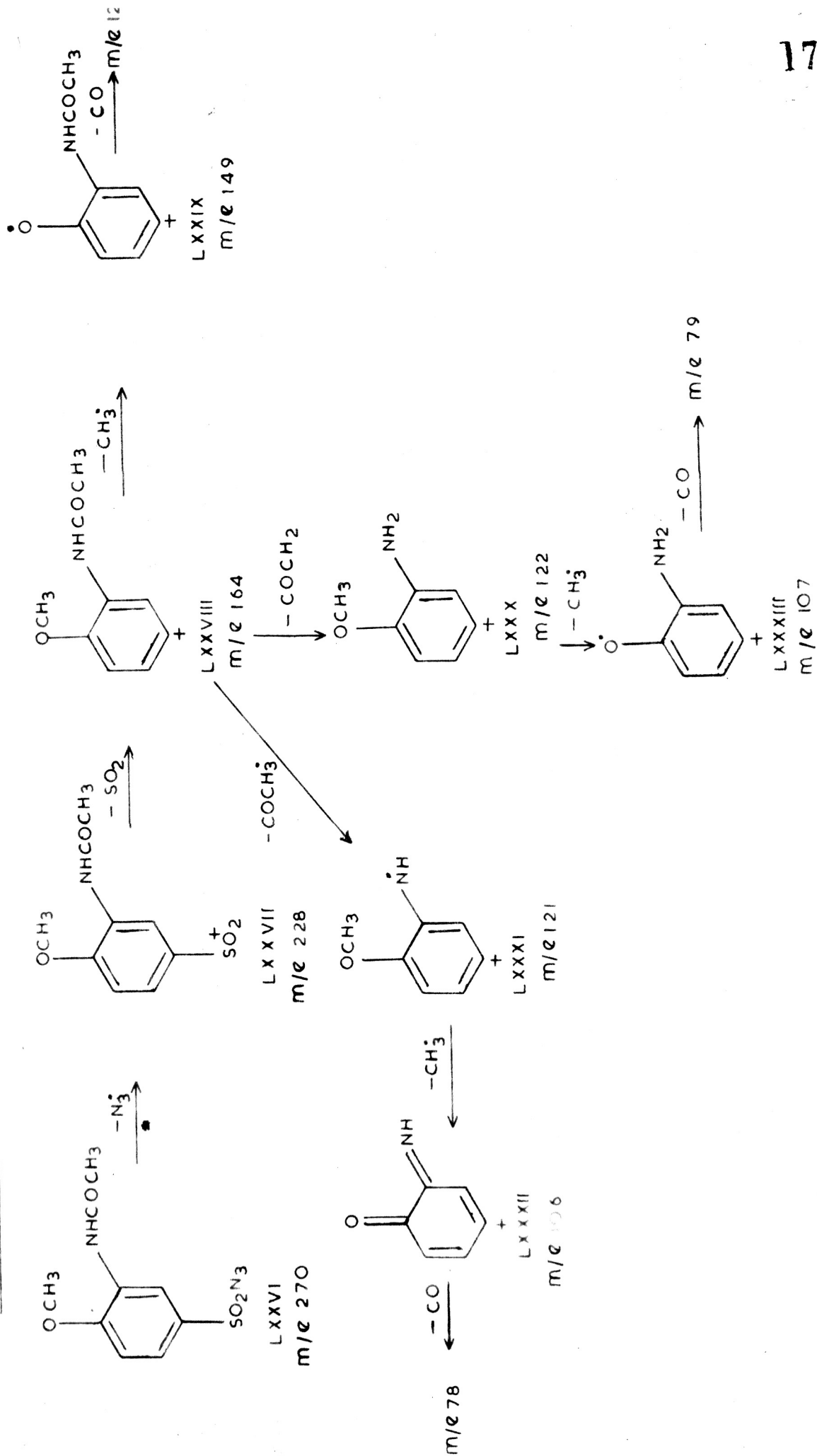
Here again, the fragmentation pattern is similar to that of benzene sulfonylazide. From molecular ion $-N_3$ is eliminated giving an intense peak at m/e 155. Then, $-SO_2$ is eliminated from $(M-N_3)$ ion giving the base peak at m/e 91 (Scheme 15b).

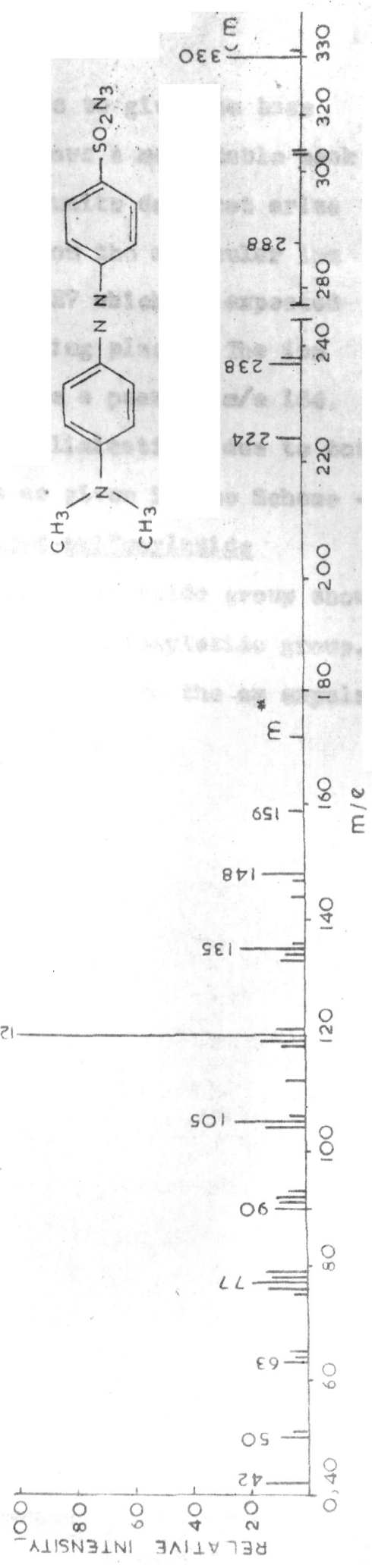
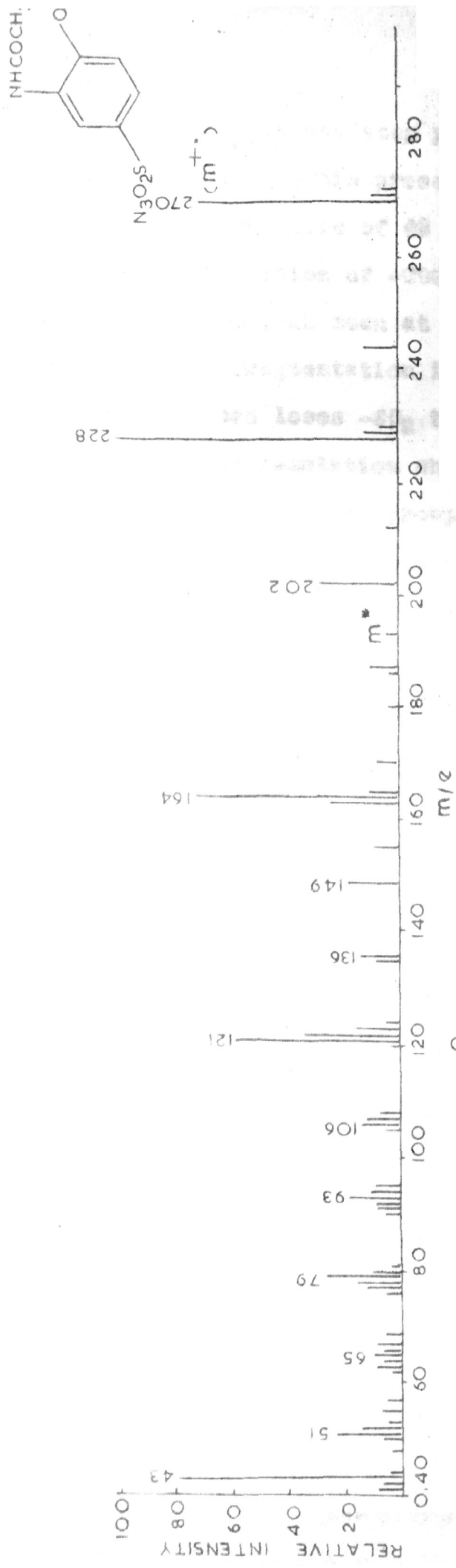
4-Acetamidobenzene sulfonylazide

The compound shows the fragmentation expected from both sulfonylazide and acetamido groups. The molecular ion loses $-N_3$ in one step process to give a peak at m/e 198. The metastable peak for this process is seen at m/e 183. The ion $(M-N_3)$ further loses $-SO_2$ to give a peak at m/e 134. Further fragmentation is due to the acetanilide resulting from the earlier fragmentation as shown in Scheme 15(c). The base peak of the spectrum is seen at m/e 43.

3-Acetamido-4-methoxybenzenesulfonylazide

This compound initially shows the fragmentations due to sulfonyl-azido group. The molecular ion m/e 270





eliminates $-N_3$ in one step process to give the base peak at m/e 228. This process shows a metastable peak at m/e 193. The loss of 42 mass units does not arise from the elimination of $-COCH_3$ from the molecular ion as there is no peak seen at m/e 227 which is expected if acetamide fragmentation is taking place. The ion $(M-N_3)$ ion then loses $-SO_2$ to give a peak at m/e 164. The further fragmentation shows eliminations due to both methoxy and acetanilide groups as given in the Scheme - 16.

4'-N,N-Dimethylamino azobenzene-4-sulfonylazide

This dye containing the sulfonyl azido group shows the fragmentations expected from a sulfonylazido group. The expected fragmentation pattern due to the α -expulsion of N_3 and SO_2 is seen in the spectrum.

EXPERIMENTAL

Preparation of p-acetamidophenyl azide

3 gms (0.02 mole) of p-aminoacetanilide was pasted with 10 ml concentrated hydrochloric acid 50 ml water was added and solution was cooled to 0° under stirring. 1.5 g (0.022 mole) of sodium nitrite was dissolved in water and added slowly. Completion of diazotization was checked on starch iodide paper. Excess nitrite was removed by adding sulfinic acid 1.43 g (0.022 mole) of sodium azide dissolved in 10 ml water was added dropwise maintaining the temperature at 0°. Solution was stirred for 1 hr. Crude p-acetamidophenylazide was isolated by filtration. It was recrystallised from benzene. M.p. 108-10°.

Preparation of diazides

4,4'-Diazidobiphenyl, 3,3'-dimethyl-4,4'-diazidobiphenyl, 3,3' dimethoxy-4,4'-diazidobiphenyl, 3,3'-dichloro-4,4'-diazidobiphenyl and metaphenylenediazide were prepared by following the above method from the corresponding diamines of benzidines and metaphenylenediamine. Only m-phenylene diazide is liquid which was isolated by extraction with chloroform from aqueous solution. Further it was purified by distillation under

vacuum at $70^{\circ}/4$ mm on a low flame.

The remaining diazides were purified by crystallisation from benzene. Melting points of the biphenyl diazides are $122-4^{\circ}$; $88-89^{\circ}$, $90-91^{\circ}$ and $155-7^{\circ}$ respectively.

The preparation of dyes containing aryl azido group is mentioned in Chapter II.

Benzene azidoacetamide

9.3 (0.1 mole) aniline was taken in 50 ml acetone and kept under stirring at $0-10^{\circ}$ 12.4 gms (0.11 mole) of chloro acetyl chloride was added. 20% Sodium acetate solution was added till the solution becomes neutral. It was stirred for $1/2$ hr. at $0-10^{\circ}$ and then at room temperature for one more hour. The chloro derivative was isolated by filtration. It was then dissolved in 100 ml tert-butyl alcohol. 7.17 (0.11 mole) Sodium azide dissolved in 20 ml water was added and solution was refluxed for 48 hrs. Excess tert-butyl alcohol was removed by distillation and compound was filtered. It was purified by recrystallisation from benzene m.p. $79-80^{\circ}$.

p-Acetamido benzene azido acetamide was prepared by the above method from p-aminosacetanilide; m.p. 210° .

Synthesis of dye containing azido acetamido group is given in Chapter II.

Preparation of sulphonylazides

Benzene sulphonylazide

It was prepared from benzene sulphonyl chloride by treating with sodium azide in acetone. Benzene sulphonyl chloride ^{was prepared} according to Vogel (pp. 822) treating 17.6 ml benzene with chlorosulphonic acid 40 ml at 20-25°. After the addition of benzene the mixture was stirred for 1 hour. Then poured on crushed ice and oily layer was extracted quickly with carbon tetrachloride. Benzene sulphonyl chloride was isolated by removing carbon tetrachloride. It was then taken in 100 ml of acetone; 14.3 gms (0.22 mole) of sodium azide dissolved in 20 ^{ml} cc of water was added slowly. Stirring was continued for 1 hr. Enough water was added to separate the layers. Oily layer was extracted with benzene and benzene sulphonyl azide was isolated by removing benzene. It was further purified by vacuum distillation at 75°/4 mm.

p-Toluene sulphonyl azide

It was prepared from commercial p-toluene sulphonyl chloride by treating with sodium azide as described above.

p-Toluene sulphonyl azide was purified by vacuum distillation.

The preparation of p-acetamido benzene sulphonyl azide, 1-acetamido-2-methoxy-5-benzene sulphonyl azide

and the dye containing sulphonazido group has been given in the Chapter II.

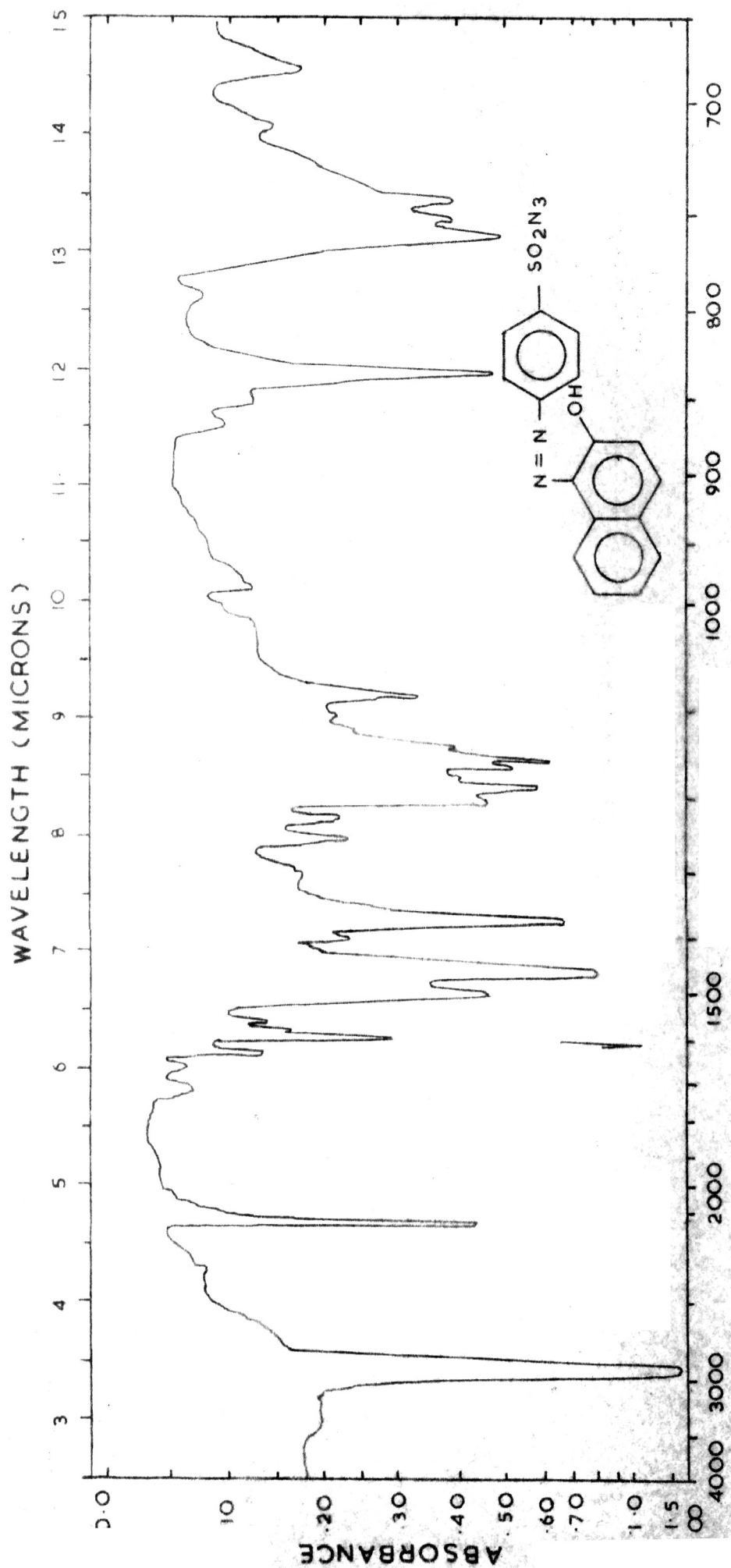
Structures of all the intermediates containing the azido group was confirmed from IR.

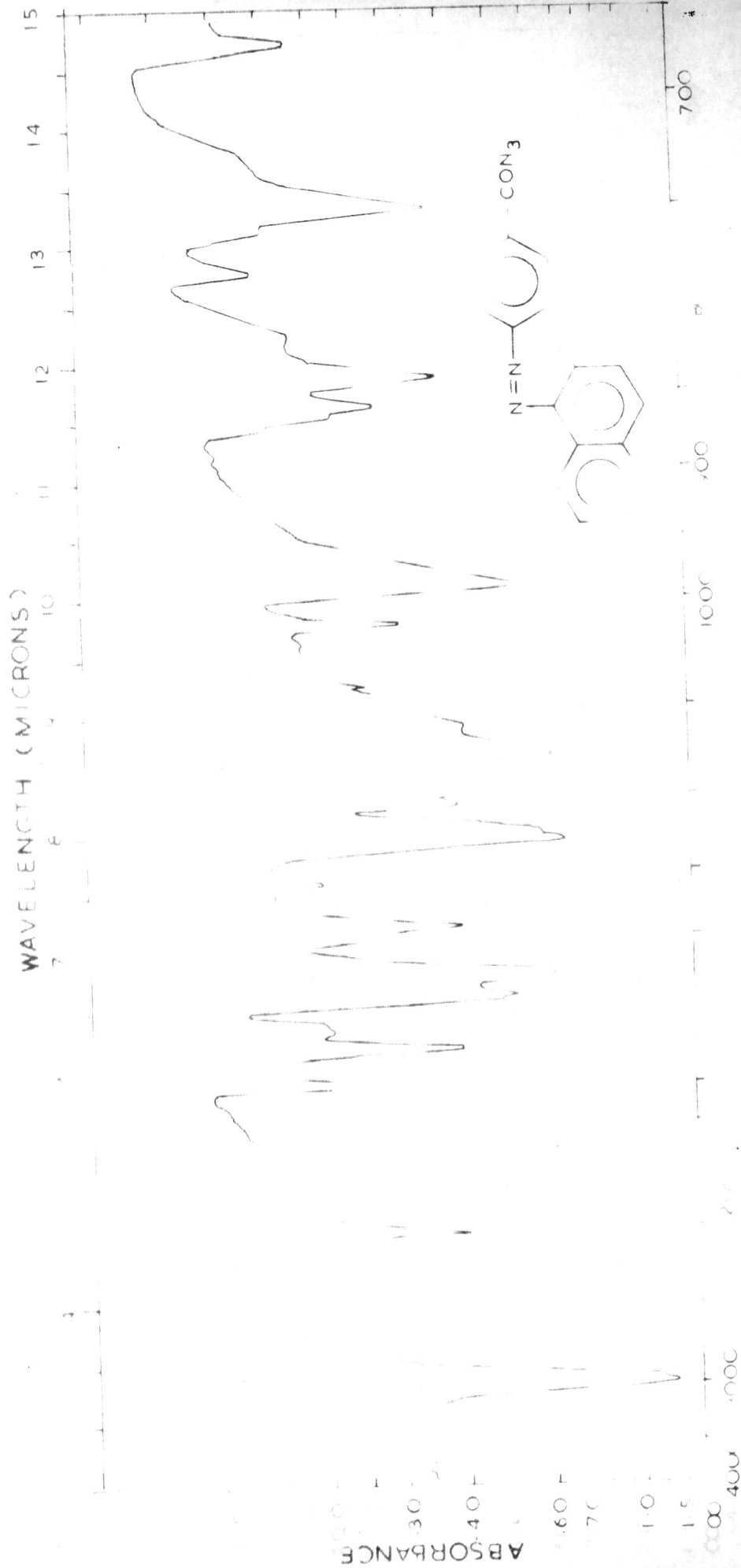
Mass spectra were recorded on CEC-21-110B mass-spectrometer, using the direct inlet system at 70 e.v. The source temperature ranging between 70-180° was used during these measurements.

IR spectroscopy

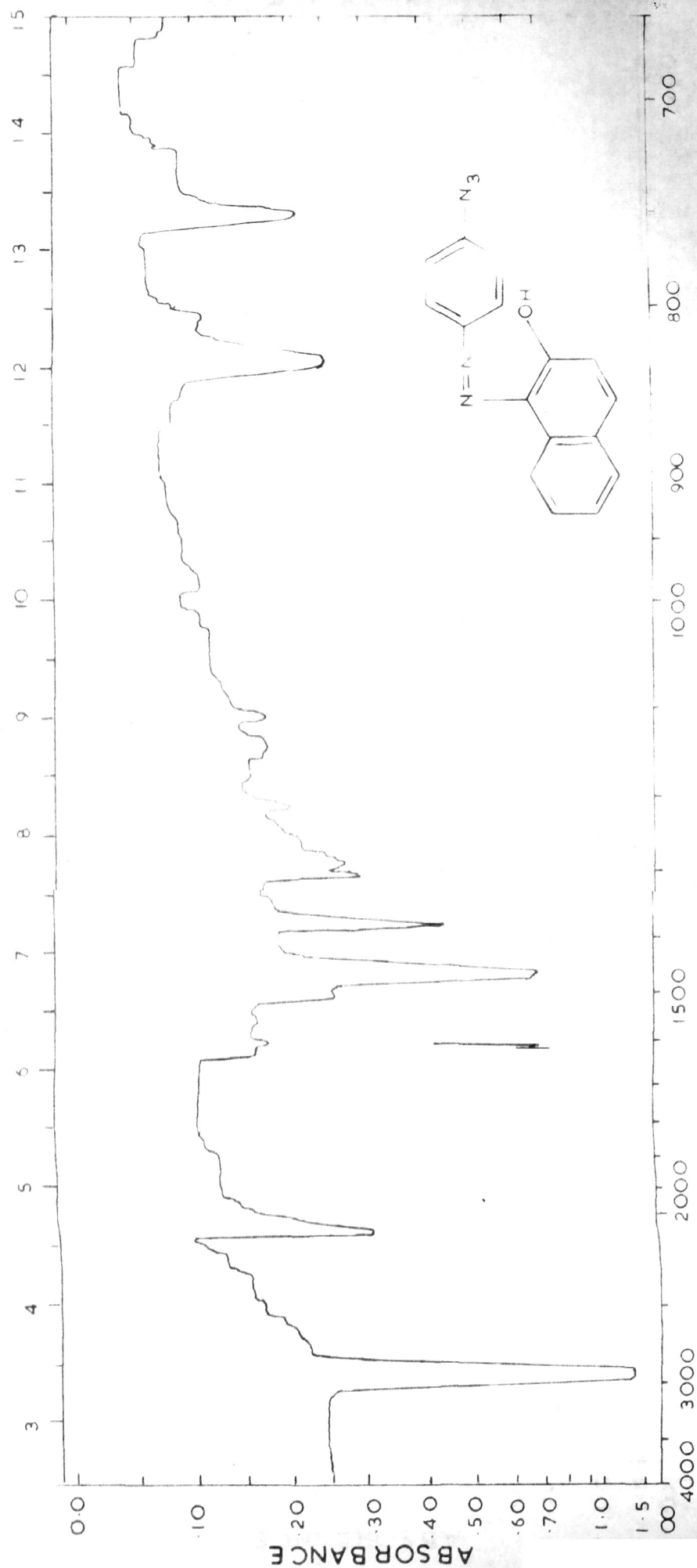
Several extensive reports have been published regarding the infrared spectra of organic azides¹¹⁻¹⁴. All these reports arise at the same conclusion that a strong assymetric stretching frequency in the region 2160-2090 cm^{-1} can be attributed to the azido group. It is slightly influenced by substituents, and highly characteristic of the azido group. Symmetric stretching of the azido group occurs in the region 1340-1180 cm^{-1} and bending at about 680 cm^{-1} .

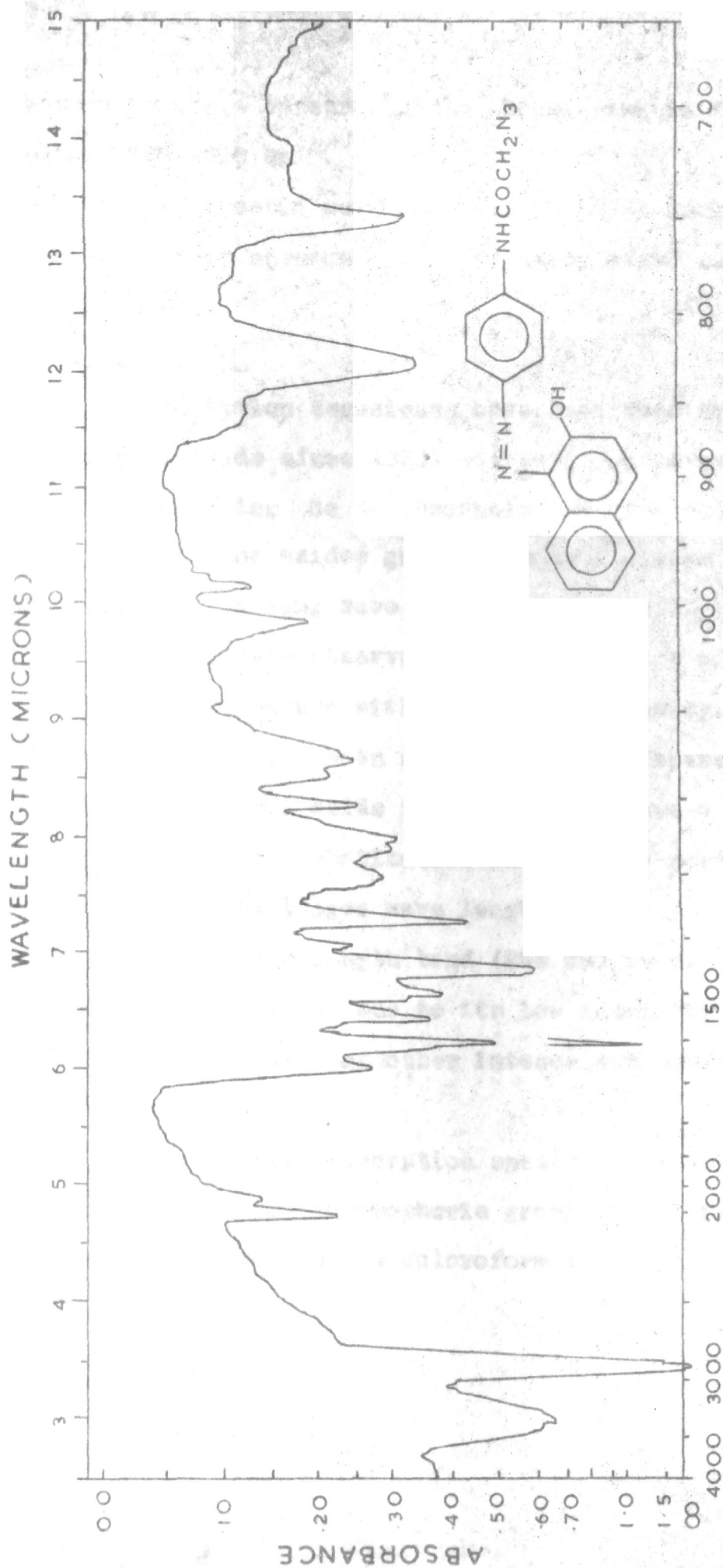
We have only used the IR spectroscopy to confirm the presence of the azido group in the dyes. IR spectroscopy serves as a useful and quick tool in the identification of dyes containing the azido groups. Few spectre of the compounds containing different types of the azido group with the same chromophoric group are given. The main





WAVELENGTH (MICRONS)





feature in these spectra is the strong peak in the region $2160-2090\text{ cm}^{-1}$.

The IR spectra were recorded on 127-E Perkin-Elmer-infracord spectrophotometer using Nujol mulls of the compounds.

UV spectroscopy

UV absorption techniques have been used to study the organic azide since 1930. Several papers have appeared reporting the UV absorption of aryl-azides¹⁵. The effect of the azides group is π to increase the intensity of the long wave length bands substantially. Reiser, et al. have observed that a red shift of the entire spectrum occurs with increased intensity. Aryl azides (ArCON_3) have been studied by some Japanese workers¹⁶. Benzoyl azide is reported to have a maximum at 245.5 nm while substitution in the para position causes a shift to longer wave length.

The long wave length band (285 nm) is not found in sulfonyl azides¹¹. Due to its low intensity it is hidden under the tail of other intense but shorter wave length absorptions.

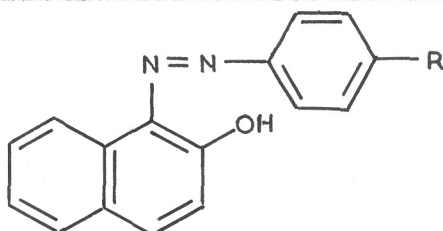
UV and visible absorption spectra of a series of dyes containing the same chromophoric group but different azido linkages were recorded in chloroform solution. The

results are given in Tables 1 and 2.

These spectra were recorded on Perkin-Elmer-350 UV (visible) spectrophotometer.

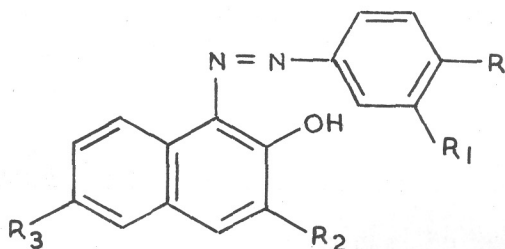
Table 1

Absorption spectra of dyes in chloroform solution



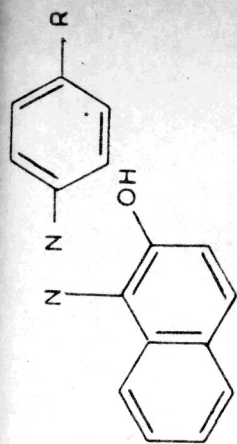
S.No.	R	UV		Visible	
		λ_{max} in nm	ϵ -Molar	λ_{max} in nm	ϵ -Molar
1	$-\text{SO}_2\text{NH}_2$	302	758	475	3340
2	$-\text{SO}_2\text{NHPh}^*$	266 310	21700 24300	480	37000
3	$-\text{SO}_2\text{N}_3$	310	1670	465	3710
4	$-\text{CON}_3$	322	1180	485	2210
5	$-\text{N}_3$	-	-	465	4850
6	$-\text{NHCOCH}_2\text{N}_3$	308	742	475	2340

*Spectra is not given but only the values are given.

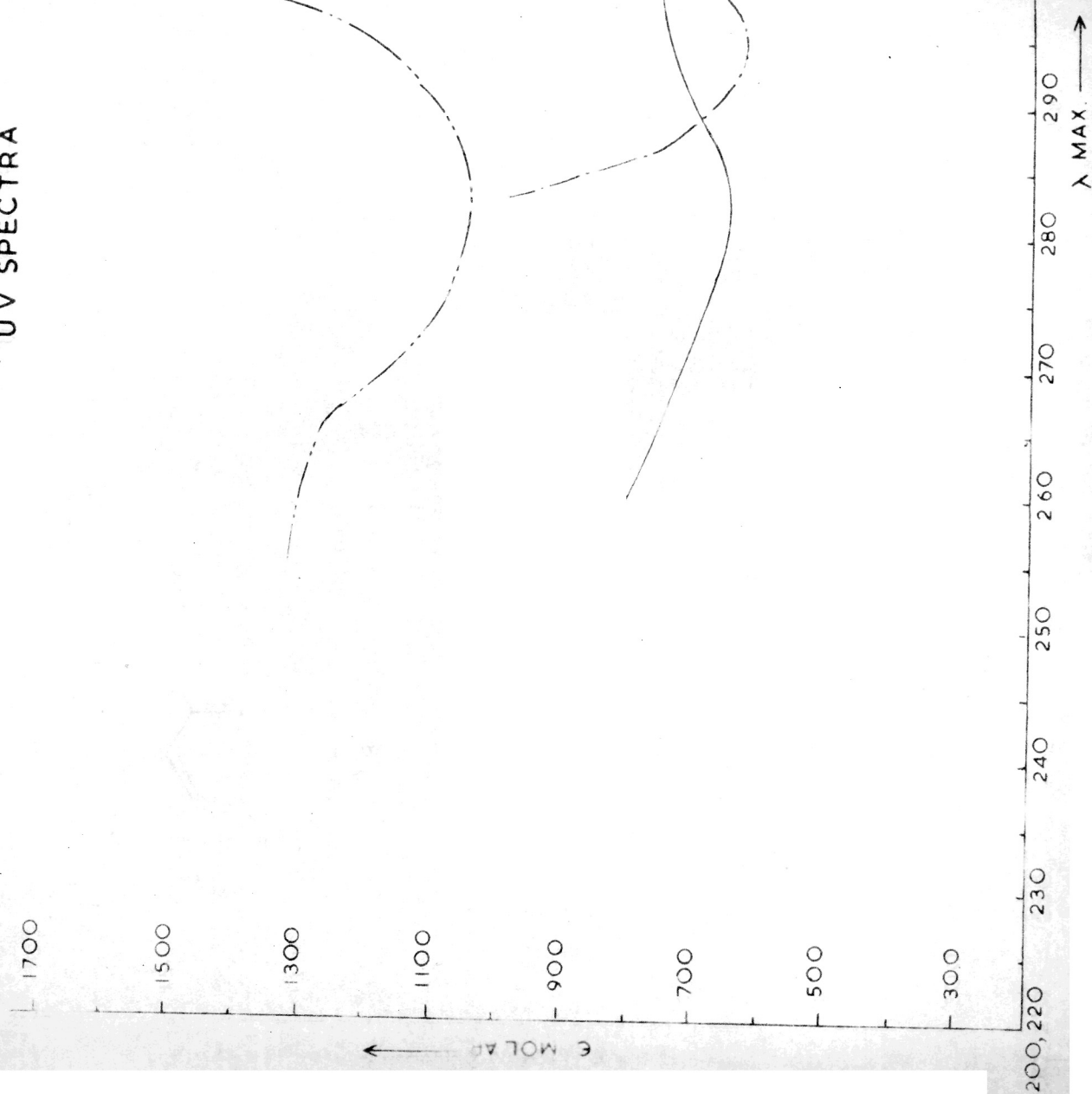
Table 2Absorption spectra of dyes in chloroform solution

S.No. Substitution	<u>UV</u>		<u>Visible</u>	
	λ_{max} in nm	ϵ -Molar	λ_{max} in nm	ϵ -Molar
1 $R = -SO_2NH_3$ $R_1 = R_2 = R_3 = H$	310	1670	465	3710
2 $R_1 = -SO_2NH_3$ $R = R_2 = R_3 = H$	302	1002	445	1770
3 $R_3 = -SO_2NH_3$ $R = R_1 = R_2 = H$	302	1836	465	1805
4 $R_2 = R_3 = -SO_2NH_3$ 1)	336	16,500	490	4610
$R = R_1 = H$ 11)	298	14,100		

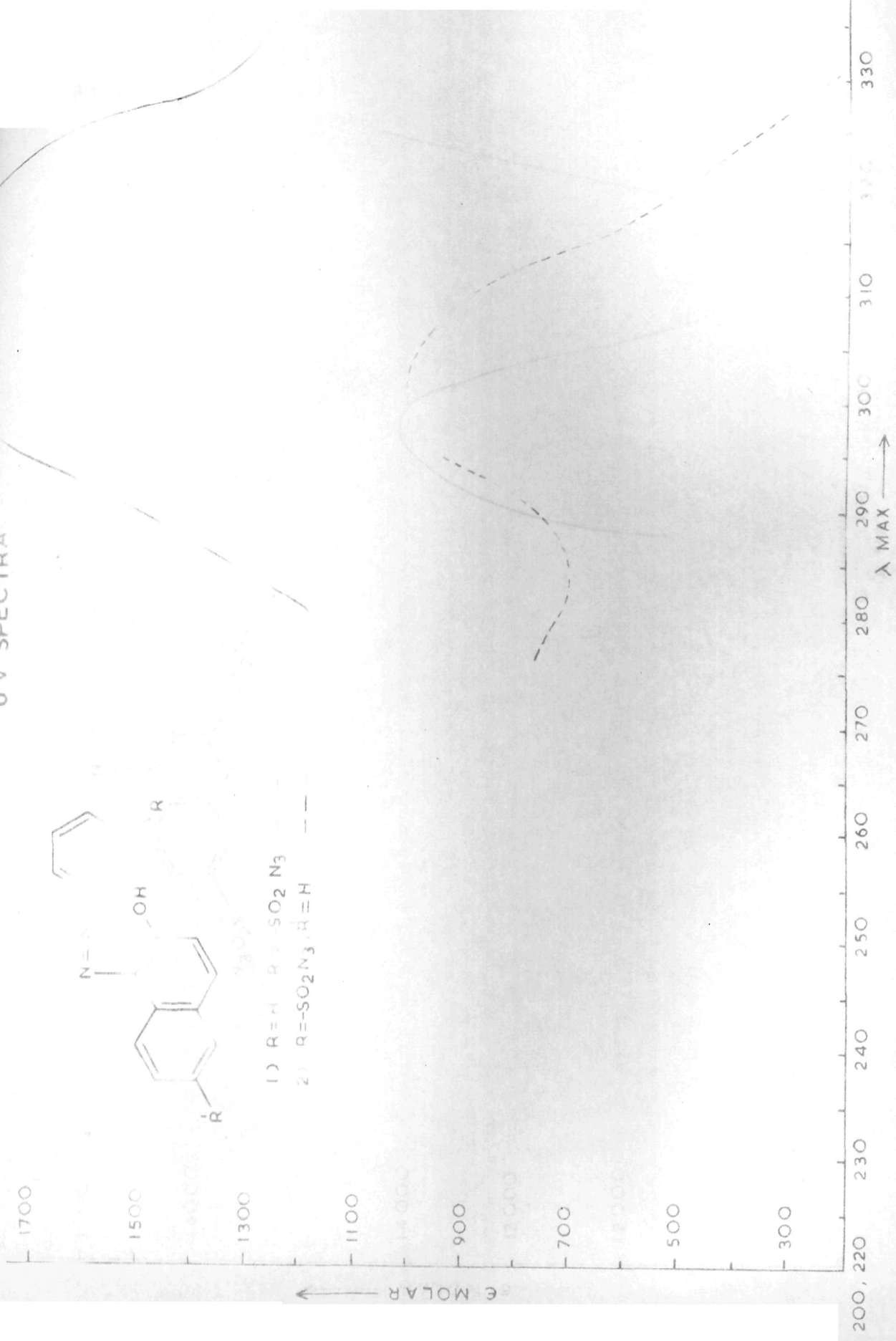
UV SPECTRA



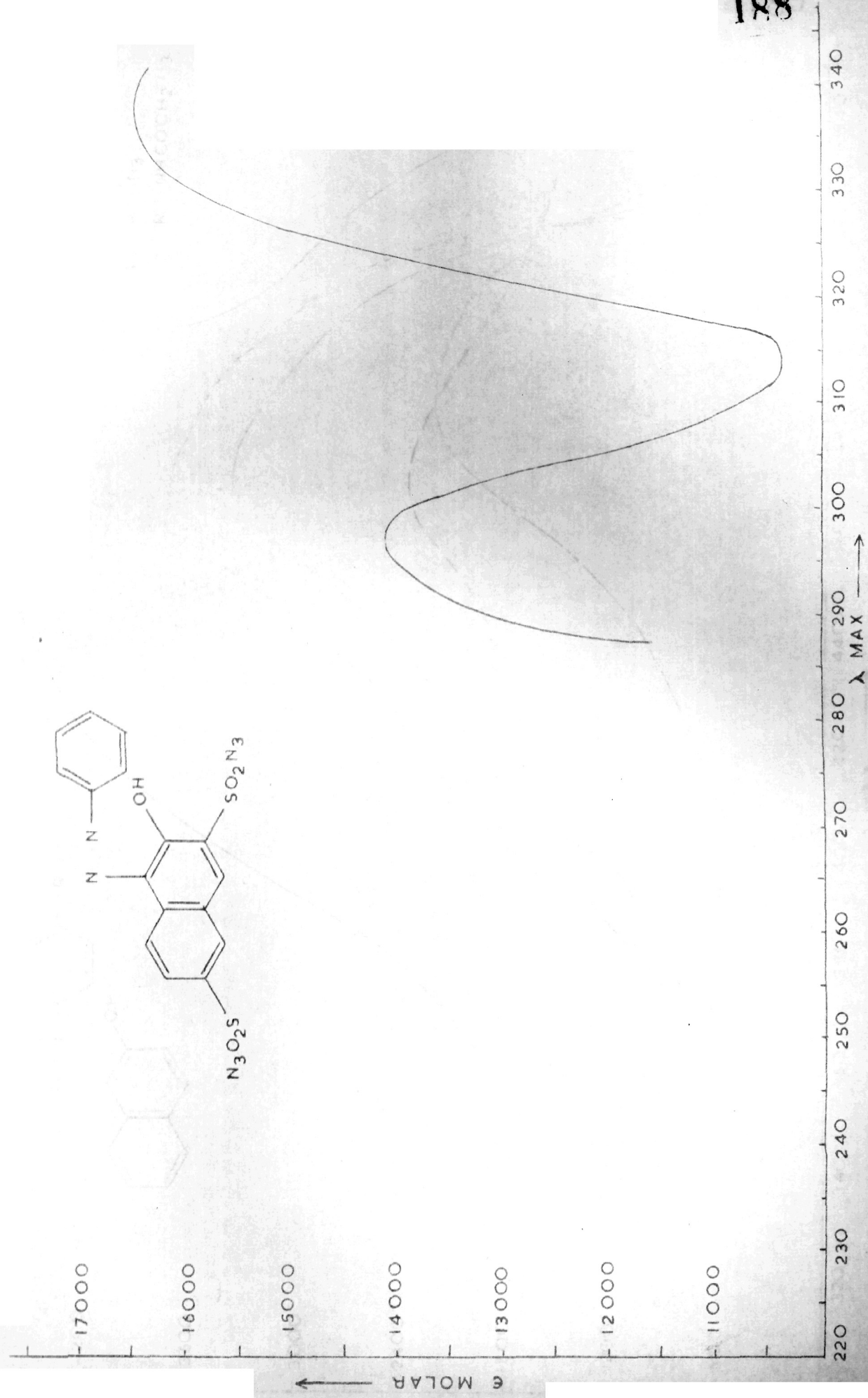
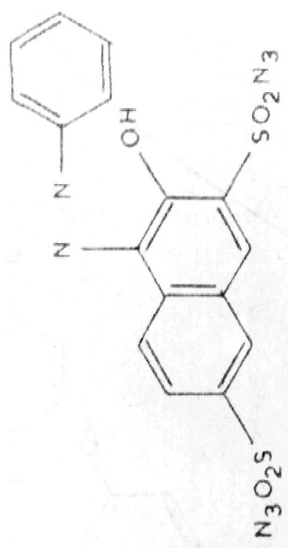
- 1) R = SO₂NH₂
 2) R = SO₂N₃
 3) R = CON₃
 4) R = NHCOCH₂N₃

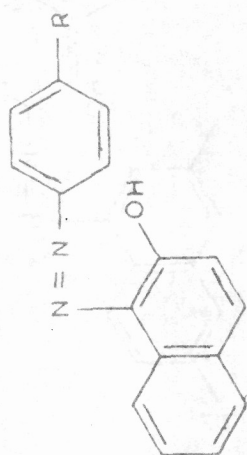


UV SPECTRA



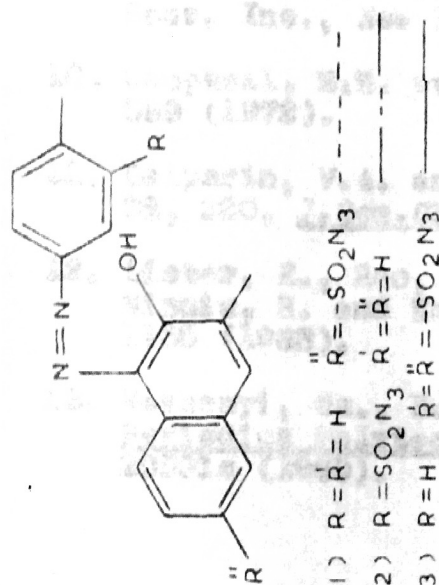
UV SPECTRA





- 1) $R = SO_2 NH_2$
- 2) $R = SO_2 N_3$
- 3) $R = CON_3$
- 4) $R = N_3$
- 5) $R = NHCOCH_2 H_3$





← MOLAR E

λ MAX →

REFERENCES

1. Crow, W.D. and Wentrup, C., Tetrahedron Lett., 4379 (1967).
2. Woodgate, P.D. and Djerassi, C., ibid., 1875 (1970).
3. Kingston, D.G.I. and Henion, J.D. Org.Mass.Spectrum, 3, 413 (1970).
4. (a) Grubb, H.M. and Meyerson, S. "Mass Spectrometry of Organic Compounds", F.W. McLafferty, Ed., Academic Press, New York, N.Y. (1963) p. 516-519.
(b) Rinehart, K.L., Jr., Buchholz, A.C., Van Lear, G.E., and Cantrill, H.C., J.Amer.Chem.Soc. 90, 2933 (1968).
5. H. Marx and C. Djerassi, J.Amer.Chem.Soc., 90, 678 (1968).
6. Rinehart, K.L., Jr. Buchholz, A.C. and Van Lear, G.E., J.Amer.Chem.Soc., 90, 1073 (1968).
7. Abramovitch, R.A., Kyba, E.P. and Scriven, E.F.V., J.Org.Chem. 36, 3796 (1971).
8. Fraser, ^RF.T.M., Paul, N.C. and Bagley, M.J., Org.Mass spectrum 7, 63 (1973).
9. Silverstein, ¹⁷²R.M. and Bessler, G.L. "Spectrometric Identification of Organic Compounds", John Wiley and Sons, Inc., New York (1963), p. 16.
10. Campbell, M.M. and Dunn, A.D., Org.Mass Spectrum 6, 599 (1972).
11. Galperin, V.A. and Balabanov, G.P., Zh.Obshch.Khim., 38, 926, J.Gen.Chem. USSR, 38, 889 (1968).
12. Lieber, E., Rao, C.N.R. Thomas, A.E., Oftedahl, E., Minnis, R. and Nemburg, C.V.N., Spectrochim Acta., 19, 1135 (1963).
13. Versanyi, Gs., Holly, S. and Szathmary, J., Periodica Polytech., 2, 211 (1958), Chem.Abstr. 54, 20931c (1960).

14. Lieber, R. Levering, D.R. and Patterson, L.J., Anal.Chem., 23, 1594 (1951).
15. "The Chemistry of the Azido group", Ed.S. Patai, Interscience Publishers, 1971, p. 197-8 and references cited therein.
16. Munekata, S. and Kikuchi, A., Seisan-Kenkya, 20, 519 (1968), Chem. Abstr., 70, 67362h (1969).

SUMMARY OF THE THESIS

S U M M E R Y

CHAPTER - I: Introduction

This Chapter covers a brief review on the development of reactive dyes. This is followed by discussion on the relationship between the chemical constitution and fastness proportion of disperse dyes. Since the present work deals with the synthesis and application of reactive disperse dyes containing azido groups (which can be applied to synthetic fibres) chemistry of azido compounds and "nitrenes" is also discussed.

CHAPTER - II : Synthesis of Reactive Disperse dyes

containing the Azido group

Procinyl dyes are disperse dyes containing a group such as monochlorotriazyl, β -chloroethyl- sulphamoyl, epoxy, γ -chloro- β -hydroxyethyl and haioenopyrimidino groups capable of reacting with nylon under alkaline conditions. These are applied to nylon as normal disperse dyes but dye bath is made alkaline after the exhaustion to bring about the chemical reaction, Even though there is a clear evidence of the chemical reactivity of Procinyl dyes towards nylon there is no evidence of their reactivity towards other synthetic

fibres such as secondary cellulose acetate, triacetate, polyacrylonitrile and polyester fibres. In fact at present, there are no known reactive dyes for polyester, secondary cellulose acetate, cellulose-triacetate, polypropylene and polyacrylonitrile.

The search for the reactive dyes for synthetic fibres in general and polyester in particular was undertaken to overcome some of the following drawbacks of disperse dyes.

1. The relation between molecular complexity and sublimation fastness is well established. Higher the molecular weight the better is the sublimation fastness. But the primary requirement for better penetration and substantivity is the simple molecular structure of the dye. Thus, it is very difficult to get a disperse dye having high sublimation fastness in yellow to red orange. If we have a group capable of reacting with fibre substrate, one can get simple dyes with high sublimation fastness.
8. The idea of obtaining a single dye capable of reactively combining with different types of fibres in itself is very novel and attractive. A single dye can thus dye reactively a variety of fibres and their blends.

The reactive group selected was azide group which generates "nitrene" under thermalolysis and the nitrenes

so generated are known to undergo insertion reaction with aliphatic and aromatic hydrocarbons and olefins.

Dyes containing sulphonyl azido group

Dyes containing sulphonylazide groups were synthesised by two routes: (i) conversion of dyes containing sulphonic acid groups into sulphonyl chlorides with thionyl chloride in presence of dimethylformamide in suitable solvents such as chlorobenzene, benzene etc. and then treating the resultant sulphonyl chloride with sodium azide in acetone. (ii) Intermediates containing sulphocazido groups were first prepared and subsequently used for the synthesis of dyes. For example, acetanilide with or without substituents was chlorosulphonated with chlorosulphonic acid, the resultant sulphonyl chloride was treated with sodium azide in acetone to get corresponding sulphonylazide.

p-Sulphonylazido acetanilide was hydrolysed with hydrochloric acid to the corresponding amine which was diazotized without isolation and coupled with various coupling components such as β -naphthol, dimethylaniline p-cresol etc. Similarly insoluble dyes were chlorosulphonated and converted into sulphonyl azides.

Carbonylazides

The dyes containing carbonyl azide group were again prepared by two methods (i) converting the dyes containing carboxylic acid group to the corresponding carbonyl chloride by treatment with thionyl chloride in presence of dimethyl formamide and then treating the resultant carbonyl chloride with sodium azide in acetone. (ii) *p*-Aminobenzolhydrazide was prepared from *p*-aminobenzoic acid by known methods. It was diazotized with excess sodium nitrite to the *p*-carbonylazidophenyldiazonium chloride which was coupled with various coupling components such as **β**-naphthol, dimethylaniline *p*-cresol etc,

Arylazides

Arylazides were synthesised by diazotizing the dye containing a free amino group and then treating the diazo compound with sodium azide under acidic conditions.

Dyes containing azidoacetamido group

Dyes containing azidoacetamido group were synthesized by treating the dyes containing a free amino group with chloroacetyl chloride. The resultant chloroacetamides were refluxed with sodium azide in tertiary butylalcohol to get corresponding dyes containing a azidoacetamido group.

CHAPTER - III - Dyeing of synthetic fibres with reactive disperse dyes containing the azido group

The dyes were applied as normal disperse dyes on cellulose acetate, polyamide polyester.

On celluloseacetate and polyamido, the dyes were applied by exhaust dyeing method at 80-90⁰.

On polyester the dyes were applied by two methods
 (i) Carrier dyeing - the dyeing of polyester was carried out at boil in presence of trichlorobenzene as carrier.
 (ii) In few cases the dyes were applied by High Temperature dyeing method (HT) at 120-130⁰.

Pad - Dry - cure method

Two dyes were applied by this method. The dispersion of the dye(10 gms/lit) was padded on to the fibres on a padding mangle. The padded samples were dried and cured at 170° for 5 minutes.

Printing

dyes dispersion was added to kerosene water thickener and printed on cellulose acetate, polyester and polyester cotton blend. The printed fabrics were dried and cured at 170° for 5 minutes.

Thermolysis

Thermolysis was carried out to generate the nitrenes and bring about the reaction between the dye

and fibre. All the dyeings were thermolysed at 170° for 5 minutes.

Light and sublimation fastness were determined for all the dyes on cellulose acetate and polyester fibres.

Evidence for the existence of reaction between dye and fibre

1. The dyed and thermolysed fibres were extracted with boiling isopropanol and chlorobenzene or with aqueous pyridine at room temperature in case of secondary cellulose acetate and polyamide.
2. The dyed fibers were dissolved in suitable solvents and precipitated which gave a colour precipitate.
3. Comparison was made with dyes containing the same chemical structure but without the azido group. In the case of dyes not containing azido group, the dyes were completely stripped from dyeings when extracted with boiling solvents. The dissolution of fibres in this case gave colourless precipitates.

In some cases the deepening of the colour was observed after thermolysis. Explanation for such a change is given with the help of UV spectra of dye containing azido group and probable compound expected after the thermolysis i.e. insertion product.

The fastness properties of dyes having the same chemical structure but different azido group were compared.

CHAPTER - IV : Spectral studies of the intermediates and dyes containing the azido group

Mass spectral study of the intermediates and dyes containing arylazido, azidoacetamido and sulphonyl azido groups was done. Few diazides of the benzene and biphenyl series were also considered. The probable fragmentation pattern is explained with the help of schemes.

Use of the IR spectroscopy to identify the presence of the azido group is illustrated with the help of the spectra of a number of dyes.

A study of UV and visible spectroscopy is made on the compounds containing same chemical structure but different azido groups.

ACKNOWLEDGEMENTS

I wish to express my deep sense of gratitude to Professor B.D. Tilak, Director, National Chemical Laboratory, Poona-8, for suggesting this problem and for his keen interest and inspiring guidance throughout the course of work.

My sincere thanks are due to Dr. N.R. Ayyangar for his help and valuable suggestions throughout the work.

I am also grateful to Professor E.H. Daruwalla, Director, U.D.C.T., Bombay-19 for allowing me to carry out the dyeing trials and his keen interest and valuable suggestions regarding the application of dyes to fibres.

I would like to thank the following firms for giving guiding me free gifts of the fibres (1) ICI, India-Polyester, (2) Century-Enka-Polyamide and (3) Sirisilk-Cellulose acetate.

Grateful acknowledgement is also made to M/s. IDI Ltd., Bombay for recording sublimation fastness and CIBA Research Centre, Bombay for recording light fastness of all the dyes.

I appreciate the efforts of (i) Dr. V.S. Pensare and his group for microanalysis recorded in this thesis, (ii) Mrs. Bhalerao and Mr. K.G. Deshpande for their help in recording UV (visible) spectra (iii) Mrs. Deshmukh for recording IR spectra and (iv) Dr. K.G. Das and his group for recording mass spectra.

I gratefully acknowledge the help given by Mr. M.S.B. Nayar in interpreting the mass spectra and Miss T.K. Homawala for helping in preparing the shade cards and proof reading.

I am grateful to Council of Scientific and Industrial Research for giving the financial support during the tenure of the work.

Finally I wish to express my sincere thanks to all TRL members for the friendliness and the co-operation they gave me.

N.V. Badami
(N.V. Badami)

TH-104