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SOLUBILIZED VAT DYES AND RANEY NICKEL REDUCTIONS

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A Thesis

submitted by

N. B. DESAI, B.Sc., B.Sc.(Tech.)

to the

UNIVERSITY OF BOMBAY

for the degree of

Ph.D.

(Technology)

KV
668.819(043)
DES

Department of Chemical Technology
University of Bombay

September 1957

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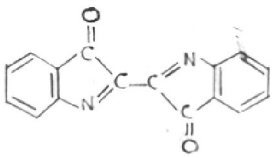
General Introduction

A. SOLUBILIZED VAT DYES

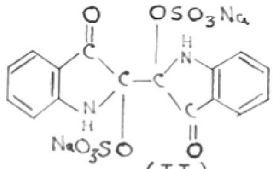
Vat dyes in their ordinary fully oxidized form are completely insoluble in water and thus in this state not suitable for dyeing. But by treatment with a reducing agent, generally, sodium hydrosulphite, $Na_2S_2O_4$, the dye is changed to the leuco form which is soluble in caustic soda, and the vat, or the solution of the leuco compound, so obtained is used for dyeing. The leuco compound attaches itself to the fibre and is oxidizdd to the original insoluble form by means of air or other oxidising agents. The dye is thus precipitated within the fibre and is consequently very resistent to washing processes.

It is evident that vat dye application by this method is somewhat more complicated than is generally desired; it is certainly unsuitable for dyeing animal fibres, which are affected by alkalis. In order to simplify the application of vat dyes and in order to make them applicable to animal fibres, a range of so-called "solubilized vat colours" was developed.[1,2] The first attempt in this direction was that of Kalb, who oxidized indigo to dehydroindigo (I), which gave a water-soluble bisulphite compound (II). The material,

wool or cotton, was treated with the aqueous solution of this compound and the colour developed by passing the

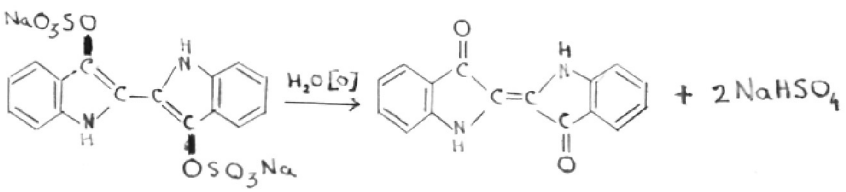


(I)



(II)

dried material through hot acid or alkali. However, only half the indigo was regenerated in this way and the method was not a commercial success.[1] Attempts were then made to make water-soluble esters of leucoindigo, and the problem was solved in 1921 by Bader and Sunder who succeeded in preparing a disulphuric ester from which indigo could be regenerated readily and quantitatively.[3] Dry leucoindigo, which is relatively a stable leuco compound, was treated with a mixture of sulphur trioxide or chlorosulphonic acid and dimethylaniline or pyridine. The mixture was eventually made alkaline, the nitrogenous base removed and the sodium salt (III) of the new dyestuff



(III)

salted out from the solution. The substance was marketed as Indigosol O (DH) and is an isomeride of Kalb's dehydroindigobisulphite compound, but unlike the

latter it regenerates indigotin quantitatively and instantaneously on treatment with suitable oxidizing agents. Although Indigosol O is decomposed by acids, in presence of wool it is unaffected even by boiling acids, and it can be applied to wool as an acid dye from a bath containing sodium sulphate, acetic acid and formic acid. To cotton, it is applied from a neutral bath like a direct dye. In either case, the colour is developed in bath containing ferric chloride and hydrochloric acid, or sodium nitrite and sulphuric acid.

The reaction $[-CO- \rightarrow -C(OH)=\rightarrow -C(O-SO_3Na)=]$ for the preparation of these sulphuric ester salts of the leuco compounds can in principle be applied to all vat dyes and Indigosols derived from several indigoid and thioindigoid dyes were prepared and marketed. However, difficulties were encountered in applying the original Bader-Sunder process to a wider range of vat dyes, particularly the anthraquinonoids, owing, it was then thought, to the instability of leuco-anthraquinone vat dyes. A notable advance in the method of preparation of such solubilized vat dyes, which could be applied with equal success to anthraquinonoid and indigoid vat dyes was then made by Morton Sundour Fabrics[4] and Scottish Dyes.[5] In this process the parent vat dye is treated with a metal (copper or iron) in a mixture of

pyridine (or other tertiary base) and sulphur trioxide. According to Coffey[6] et al., when using copper and pyridine, the reaction takes place in two stages; copper-pyridine complexes (IV) of the leuco-vat dyes are first formed, and these are then "sulphated" by the sulphur trioxide which is itself attached to the tertiary base, to form a further complex (V), which is decomposed by alkalis in the final stages of the process to give the sodium salt (VI).

Stage I

$$(C{=}O) + 2Cu + 8C_5H_5N \rightarrow [C{-}O{-}Cu(C_5H_5N)_4]_2 \qquad (IV)$$

Stage II

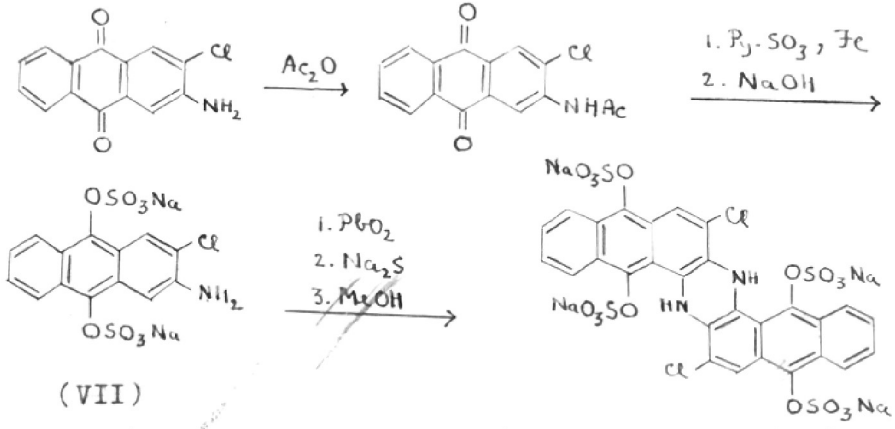
$$+ 2SO_3 \rightarrow [C{-}OSO_3Cu(C_5H_5N)_x]_2 \qquad (V)$$
$$(C_5H_5N{:}SO_3)$$

Stage III

$$+ 2NaOH \rightarrow (C{-}OSO_3Na)_2 + 2CuO + C_5H_5N + H_2O \qquad (VI)$$

This process, called the Soledon process, is widely followed by the dyestuff manufacturers and has been applied to over thirty-five vat dyes including 16:17-dimethoxydibenzanthrone, dichloroisoviolanthrone, anthanthrone and its derivative, pyranthrone and dibenzpyrenequinone. Direct application of this process to indanthrone and its derivatives gives only a diester, which

is not much useful because of poor solubility. The tetraester of indanthrone and its derivative can, however, be conveniently prepared by careful oxidation of the disulphuric ester of the leuco compound of the appropriate β-aminoanthraquinone derivative under alkaline conditions.[7] For example, Indigosol Blue IBC (the tetrasulphuric ester of leuco 3:3'-dichloroindanthrone), is prepared from 2-chloro-3-aminoanthraquinone by the indicated reactions.[8,9]



KCl ⟶ Tetrapotassium salt (Indigosol Blue IBC).

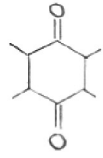
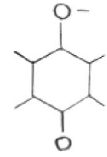
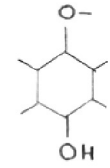
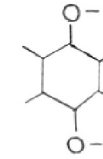
Lead peroxide may be replaced by silver oxide[10] or the oxidation of (VII) to the Indigosol may be effected electrolytically.[11] The Soledon process, however, is not without its limitations. For example, the yield and quality of leuco sulphuric ester is not satisfactory with many dyestuffs. Also the process is not applicable to certain class of dyestuffs, especially those containing

anthraquinone groupings in the molecule (e.g. acylamino-anthraquinones, anthraquinone carbazoles and anthrimide types).

To understand more about these anomalous cases and to discover methods of converting these dyestuffs into leuco sulphuric esters, research work was undertaken by Coffey[6] and coworkers at the Imperial Chemical Industries Ltd. They studied the reduction of a vat dye by metals in non-aqueous media and found that the reduction of quinones to the leuco compound proceeds through the intermediate formation of a semi-quinone, which is in equilibrium with its dimeric quinhydrone form and which may be quite stable. Thus, the reduction scheme becomes:

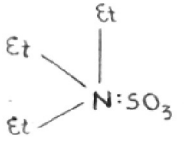
$$\text{Quinone} \overset{e}{\rightleftharpoons} \text{Semiquinone-ion} \overset{e}{\rightleftharpoons} \text{Leuco-compound}$$
$$\downarrow\uparrow$$
$$\text{Dimeric quinhydrone.}$$

Further, depending on the ionizing power of the medium and on the cations present, each of these stages may be present in an ionized state. Thus in the reduction of anthraquinone with zinc, the various stages of reductions are:

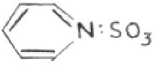
Reduction stage	Quinone	Semi-quinone ion	Leuco-compd. partially ionized	Leocu compd. fully ionized
				
		(I)	(II)	(III)
Colour in solution	Colour-less	Magenta	Brown	Scarlet

Stage I occurs quite rapidly in acetonitrile containing triethylammonium bromide at 0°. Stage II is produced by reduction in the same medium or in dimethylformamide at 50° and Stage III is reached in the same media, containing in addition, for example, an aralkylamine. It is evident that the products of stages II and III are those required to form leuco sulphuric ester. Similar, but somewhat more complicated, phenomenon occurs in the reduction of each particular vat dyestuff and by carefully adjusting the conditions, such as the ionizing power of the reaction medium and its protonotropic activity, practically all the anthraquinone dyestuffs can be reduced to the appropriate condition for conversion into a leuco sulphuric ester by treatment with sulphur trioxide loosely combined with a week organic base.

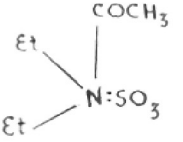
As regards sulphur trioxide-amine complexes, it is seen that sulphur thioxide by virtue of its electronic configuration can combine with any base containing an atom like nitrogen carrying a pair of unshared electrons. The stability of these sulphur thioxide-amine complexes depends on the base to which sulphur thioxide is attached and the more fimrly the latter is attached to the nitrogen the less reactive it is. Thus considering the following complexes:



(VIII)



(IX)



(X)

it is found that (VIII) is so stable that it can be crystallized from hot water without decomposition, (IX) reacts quite rapidly with cold water and very rapidly on warming and (X) is immediately decomposed. It is obvious that in the sulphation of the leuco compounds the sulphur trioxide in the sulphating agent must not be too firmly bound. In this connection, dialkylamides, particularly dimethylformamide, have proved to be useful both as reaction medium and the vehicle for introducing sulphur trioxide.

Based on these findings, Coffey and coworkers have developed a new process which may be called the

Amide process, for convering the vat dyes into leuco sulphuric esters.[12] According to this process, the dyestuff is treated in presence of a metal and an organic amide, with or without the addition of diluents, with sulphur trioxide or any suitable esterifying agent. Unlike the Soledon process, the reaction is usually carried at low temperatures (below 30°). The amides used are of the formula

$$R\text{-}CO\text{-}NR_1R_2$$

R=H or an organic radical, R_1,R_2 = hydrocarbon or substituted hydrocarbon which may be same or different and which may be connected with each other to form together with a nitrogen atom, a closed ring. Examples of suitable amides are: dimethylformamide, diethylformamide, diethylacetamide, tetramethyl urea, formyl- and acetylpiperidide, formyl morpholide, tetramethyladipamide, dimethylbenzamide, dimethylurethane and N-methylphthalimidine. The advantages of this process over the Soledon process are that it is more economical and is more widely applicable. Of the numerous compounds to which the process is applicable may be mentioned the following:

Anthraquinone, 2-chloro-3-acetamidoanthraquinone, 1:4-bisbenzamidoanthraquinone, 1:4-bis-(m-methane-

sulphonylbenzoylamino)-anthraquinone, 16:17-dimethoxy-dibenzanthrone, 1:1':4:1"-trianthrimide carbazole, tetrabromoindigo and thioindigo.

A second process, patented by I.C.I. group of workers for the manufacture of leuco sulphuric esters of vat dyestuffs and intermediates, consists in treating the dye and a metal, or the metal salt of the corresponding leuco compound, with a salt of chlorosulphonic acid in an anhydrous inert medium and substantially in absence of a free organic base.[13]

Examples of the salts of the chlorosulphonic acid used are: alkali, ammonium, alkyl- and aryl-ammonium, quaternary ammonium and ternarysulphonium.

Alkali metal salt (K, Na, NH_4) are made by reacting corresponding chloride in suitable inert liquid diluent, e.g. acetonitrile with chlorosulphonic acid or its ester. The suspension of salt of chlorosulphonic acid obtained in this way may be used directly without isolation.

Alkyl- and aryl-ammonium chlorosulphonates may be made by treating corresponding amine, e.g. methylamine or aniline with chlorosulphonic acid.

The quaternary ammonium and ternary sulphonium chlorosulphonates may be made by reacting with quaternary ammonium and ternary sulphonium salts of a different

acid with chlorosulphonic acid.

The inert liquid medium in which sulphation is carried out is preferably a non-basic, non-hydroxylic liquid in which chlorosulphonate is at least partially soluble and liquids which are good dissociating solvents, e.g. acetonitrile, are particularly valuable for the purpose.

The sulphation must be carried out in absence of organic base. The reaction products are isolated by pouring in aqueous sodium carbonate.

The process is claimed to be superior to other processes in several respects:

(1) Use of expensive tertiary bases and amides is avoided.

(2) Is more widely applicable than the earlier processes.

(3) Tetraester of chloroindanthrone is directly obtained from vat dye in quantitative yield.

While the British chemists investigated the use of sulphur trioxide compounds of weak organic bases and amides for the sulphation of leuco vat dyes in anhydrous media, the American chemists turned their attention to the use of sulphur trioxide compounds of stronger basic amines (having a dissociation constant of at least 1×10^{-7} at 25°), such as (VII), for the esterification

of leuco compounds in aqueous alkaline media.[14] These complexes are sufficiently stable to water and still sufficiently reactive to allow the desired aqueous esterification of reduced vat dyes. Thus in this process, the sulphur trioxide compound of the amine, prepared by the action of chlorosulphonic acid on the latter in an inert organic solvent, is agitated with solution of reduced vat dye in alkali at 30-40° for 4 hrs. with exclusion of air. Air is then passed through the mixture to oxidize any unchanged leuco compound. After filtration, the dyestuff is salted out as usual. The list of amines used for the process includes: triethyl amine, trimethylamine, N-ethylmorpholine and dimethyl-cyclohexylamine. The aqueous process works well with indigoids and anthrone dyes, but with anthraquinone derivatives disproportionation to anthraquinone and anthranol derivatives occurs.[15]

Besides these general methods of preparing leuco sulphuric esters of vat dyes, processes of limited applicability have been mentioned in the patent literature. For example, 1:4-bisbenzamidoanthraquinone is converted into its leuco sulphuric ester by treating a mixture of cuprous chloride, brass powder and the vat dye with a suspension of sodium pyrosulphate in pyridine.[16] A stable leuco compound (e.g. of 16:17-

dihydroxydibenzanthrone) is obtained as monosodium salt from a hydrosulphite vat by reducing the pH to 9-12 at 60-90° until precipitation is complete; it can be converted into the disulphuric ester in the normal way.[17]

Vat colours solubilized in forms other than the leuco sulphuric esters have been mentioned[18-25] but are not of much practical importance.

Processes for dyeing and printing with the leuco sulphuric esters of vat dyes have been described in a series of patents.[26,27] The solubilized vat colours were originally developed for use on wool and silks, but at present, are more important for cotton, because cheaper and comparatively fast acid mordant dyes are available for the animal fibres. The leuco sulphuric esters as a class are less substantive than the alkaline vats, the absorption is readily controlled and they are therefore specially useful in light shades. After impregnation, the solubilized vat colour has to be developed; the reaction [2-C(OSO_3Na)= $+H_2O + O \rightarrow$ 2-CO- + $2NaHSO_4$] involves hydrolysis and oxidation. The usual method in cotton dyeing is to use sodium nitrite and sulphuric acid.

The purification of leuco sulphuric esters of some of the vat dyes, their adsorptive and chromatographic

behaviourshave been studied by Ruggli and Stauble.[28] The leuco sulphuric esters can be estimated in substance by treating an aqueous solution with standard solution of ceric sulphate[29] or ferric ammonium sulphate,[28] the parent vat dye is precipitated in readily filterable form and is then collected on a sintered glass crucible, washed, dried and weighed.

REFERENCES

1. Venkataraman, The Chemistry of Synthetic Dyes, Vol. II, p. 1046, Academic Press, New York, 1952.

2. "The Chemistry of Synthetic Dyes and Pigments", p. 534, edited by Lubbs, Reinhold Publishing Corporation, New York, 1955.

3. Durand and Huguenin, BP 186,057; USP, 1,448,251.

4. Jones, Wylam, Morton and Morton Sundour Fabrics, BP 245,587; 248,802; 251,491.

5. Thomas, Harris, Wylam and Scottish Dyes, BP 258,626; Scottish Dyes, BP 334,902; IG, BP 461,430.

6. Coffey, Chem. and Ind., 1953, 1068.

7. IG, BP 416,939.

8. BIOS 960,1363; FIAT 1313, II.

9. BIOS, 1493.

10. Kuhlman, BP 577,167.

11. IG, FP 779,890.

12. Coffey, et al. and ICI, BP 610,117; 633,480-1; 633,483-7; 633-501-2; 633-504-5; 633,492-3; 633-498-9; 633-513.

13. Coffey et al. and ICI, BP 630,459.

14. Lecher, Scalera and Lester, BP 585,106; USP, 2,396,582; 2,403,226; Lecher and Hardy, J. Am. Chem. Soc., 1948, 70, 3789.

15. Scalera, et al., J.Am.Chem.Soc., 1951, 73, 3094.

16. Coffey, Driver, Fairweather and ICI, BP 605,617; USP 2,504,806.

17. USP, 2,148,042; 2,188,320.

18. Ciba, BP 291,768.

19. IG, BP 324,119; 497,327.

20. IG, BP 497,327.

21. Mieg, Wilners and General Aniline and Film Corpn., USP, 2,307,893.

22. Stallmann and DuPont, USP, 2,183,628.

23. Stallman, Prahl and DuPont, USP, 2,245,535.

24. BIOS, 987.

25. FIAT 1313, II.

26. Durand and Huguenin, BP 202,630; 202,632; 203,681; 218,649.

27. Peterhauser, J. Soc. Dyers Col., 1926, 42, 152; 1927, 43, 251.

28. Ruggli and Stauble, Helv. Chim. Acta., 1940, 23, 689-717.

29. Patni, unpublished work, quoted in Venkataraman, The Chemistry of Synthetic Dyes, Vol. II, p. 1058, Academic Press, New York, 1952.

General Introduction

B. RANEY NICKEL REDUCTIONS

In 1925 and 1927 Raney patented the preparation of active nickel catalysts by a novel method in which nickel was alloyed with a catalytically inactive metal and the latter was dissolved out in aqueous sodium hydroxide, leaving nickel which was very active. Of the various alloys of nickel and alkali-soluble metals that he investigated Raney found that the aluminium alloy could be made with ease and was easily pulverized The nickel derived from nickel-aluminium alloy after dissolution of the aluminium completely or partially by aqueous caustic soda, because of its high activity, ease of preparation and other advantages, has been extensively used and is known as Raney nickel catalyst. Although Raney claimed that useful catalysts could be made from nickel aluminium alloys containing 10-85% nickel, the alloy which is generally used consists of approximately equal weights of nickel and aluminium. Raney nickel-aluminium alloy is marketed by Gilman Paint and Varnish Co., Chattanooga, Tennessee, U.S.A.

Preparation and classification of different types of catalysts:

Several methods of processing the alloy to give the catalyst have been described in the literature.[2-6] The activity of Raney nickel is influenced by the method of adding the alloy, the concentration of sodium

hydroxide, the temperature and duration of digestion and the washing treatment adopted for rendering the catalyst free from sodium aluminate and hydroxide. Adkins and his collaborators studied these factors in detail and they have described catalysts of well defined grades of activity. The catalysts were classified as W-1, W-2, W-3, W-4, W-5 and W-6, the classification being based on the hydrogenation of β-naphthol taking into account the temperature and time required for addition of two moles of hydrogen per mole of β-naphthol and the yields of ac and ar-tetrahydro-β-naphthol.[7-9] W-7 catalyst is alkaline in nature and has given good results in the hydrogenation of ketones, phenols, and nitriles for which alkali in the reaction mixture is beneficial.[10,11] Hurd and Rudner have based their classification of the catalysts on their ability to desulphurize thiophene in boiling xylene.[12]

Properties of Raney nickel catalysts:

The active catalyst is grey-black in colour and is pyrophoric in contact with air. It contains traces of impurities, such as iron, copper, cobalt, manganese and silicon present in the starting materials. The amount of aluminium present in the catalyst depends on the duration of the treatment with alkali. Catalysts containing 11-17% aluminium have been reported.[8,13]

Conflicting statements have been made in the literature concerning the deterioration of activity of Raney nickel as the preparation increases in age. Paul[13] assumed that Raney nickel catalyst can be indefinitely preserved, but according to Mozingo[6] storage for more than six months is undesirable. Raney nickel stored under water is slowly oxidized on the surface to nickel hydroxide.[14] Schroeter[15] observed that hydrogen was slowly lost on storage, rapidly in presence of air, and that the activity of the catalyst decreased with the loss of hydrogen; but the two effects were not parellel. He found that in a well sealed container the catalyst did not suffer much loss of activity. Pattison and Pegering[16] came to the conclusion that oxygen was responsible for the major part of the loss in activity, since the storage under conditions in which air or oxygen had access to the catalyst led to more rapid deterioration.

X-ray analysis of Raney nickel shows that the crystal dimensions lie between 40 and 80A, a magnitude ten times smaller than that of the reduced nickel of Sabatier and Senderens.[17] Raney nickel catalyst contains hydrogen, most of which is probably bound by van der Waals forces and can be removed by heating. Unlike ordinary nickel, Raney nickel can form an amalgam - a property which can be attributed to the

adsorbed hydrogen which acts as a third component.

The Effect of additives:

Raney nickel can be activated by the addition of small amounts of noble metals, especially platinum. Lieber and Smith have also noted the promoter action of platinic chloride.[18] Iron decreases the activity, if it is present in amount exceeding 1%. The presence of alkali accelerates the hydrogenation of phenols, ketones and nitriles, but it retards the reduction of nitro compounds. Halogens have poisoning effect on Raney nickel.[19] Sulphur is a powerful poison for the catalyst, which has strong affinity for both organic and inorganic sulphur. The activity of the catalyst decreases in the presence of the aldehydes and ketones because of their strong adsorption by the catalyst.[20]

Classification of hydrogenation procedures:

Raney nickel catalyst has been used for effecting a wide variety of reductive transformations. The quantity of the catalyst used in comparison with the amount of the substance to be hydrogenated varies considerably depending on the substance and the conditions under which hydrogenation is to be carried out. External hydrogen at pressures from atmospheric to the order of 200 atmospheres and a wide range of temperature may be employed. As sources hydrogen, hydrazine and other

compounds which liberate hydrogen in presence of the catalyst can be used.[21,22] Raney nickel functions as hydrogen transfer agent, and reductions have been carried out with aid of hydrogen donors such as cyclohexanol, which are oxidized in the process, setting up an oxidation-reduction system.[23,24] The ability of Raney nickel to reduce compounds in the absence of external hydrogen, making use of the adsorbed hydrogen was demonstrated by Mozingo.[25] This method, however, requires the use of large quantities of the catalyst to make up the necessary hydrogen and to compensate for the pressure employed in the other process. A rather unique variation in the application of Raney nickel to the reduction of organic compounds is the use of nickel aluminium alloy in the presence of aqueous alkali. The procedure, largely developed through the efforts of Papa,[26] has the advantage of ease of application. The reduction is probably due to the activation, by the freshly formed nickel catalyst, of the hydrogen liberated by the dissolution of aluminium in alkali. Obviously this treatment can be applied only to compounds which are not sensitive to alkali.

Raney nickel is the most versatile of the catalysts and there is hardly any class of unsaturated compounds whose reduction has not been tested with Raney nickel. Thus it has been used for the hydrogenation

of the double bonds, the carbonyl group and the cyanide group; for the reduction of the nitro, nitroso and azo groups, for dehalogenation, for desulphurization and for very many other reactions. Several reviews are available[27-32] on the action of Raney nickel on organic compounds. Since the present work deals mainly with the hydrogenolysis of sulphuric esters of phenols and leuco derivatives of quinones by Raney nickel, a review is made of the action of Raney nickel on various organic sulphur compounds.

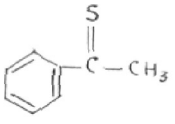
Desulphurization in constitutional work:

The remarkable discovery that Raney nickel can effectively remove sulphur from a compound, organic or inorganic, was made by Bougault, Cattelain and Chabrier in 1939.[33] The action has been described by Aubry[34] as noncatalytic in nature and can be accomplished by either the Mozingo[25] or Papa[26] method. Bonner has shown that the hydrogen retained by the catalyst brings about the hydrogenolysis by carrying out reactions in benzene which cannot act as hydrogen donor like ethanol.[35] According to Mozingo,[36] the desulphurization by Raney nickel can take place in two ways:

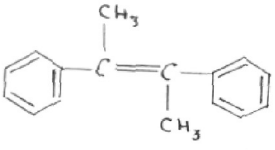
$$RSR' + Ni(H) \begin{cases} \rightarrow RR' + RR + R'R' & (A) \\ \rightarrow RH + R'H & (B) \end{cases}$$

Mozingo observed only reaction (B), obtaining toluene

from benzyl sulphide and benzene from diphenyl sulphide. Campaigne, however, was able to show that Wurtz-type reaction (A) occurred when thioacetophenone (I) was treated with W-2 Raney nickel.[37] The reaction was also

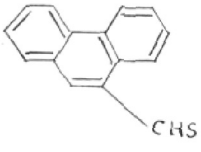


(I)

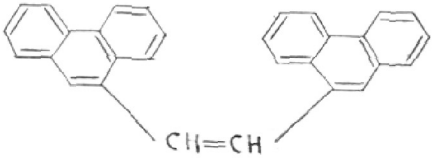


(II)

observed by Bergmann when phenanthrene-9-thioaldehyde (III) was desulphurized with Raney nickel. The sole product was that of coupling.[38] Thiohydrogenolysis with Raney



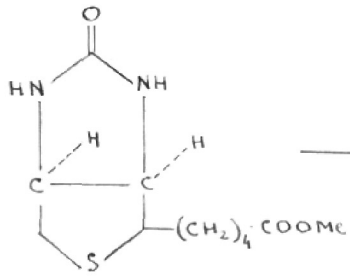
(III)



(IV)

nickel has been extensively used for the elucidation of the structures of numerous substances, both natural and synthetic, and it has found considerable application in synthetic organic chemistry. Natural methionine has been shown by Raney nickel reduction to have the same absolute configuration as the other natural l-α-amino acids.[36,39] Dextrorotatory methionine gave levorotatory α-aminobutyric acid which belongs to the 'd' series from a correlation with alamine and other amino acids. Dextrorotatory methionine must therefore belong to the 'd' series. On this basis levorotatory

methionine and dextrorotatory α-aminobutyric acid are configurationally identical and by previous correlation of the latter compound with natural amino acid series the methionine derived from proteins is l (-) methionine. The structure and stereochemistry of β-biotin (V) were elucidated by Mozingo and co-workers through the hydrogenolysis to (VI).[40]



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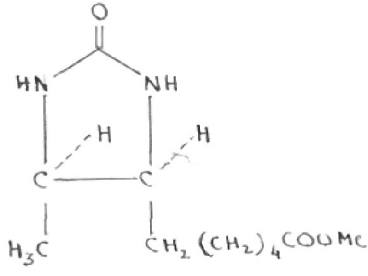
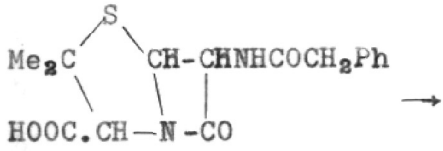
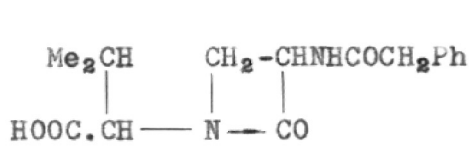


(VI)

Desulphurization played a vital part in the study of the structure and stereochemistry of benzyl penicillin.[41] Sodium benzyl penicillin(VII) gave deothiobenzyl penicillin (VIII), which provided strong evidence for



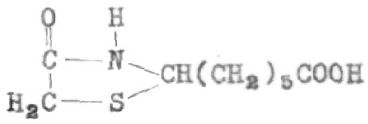
(VII)



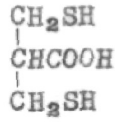
(VIII)

the β-lactam formulation of penicillin. The structures of a new thiazolidone antibiotic (IX),[42] the dimercaptoisobutyric acid (X) isolated from asparagus,[43] and the trisulphide (XI) produced from thiobenzophenone[44]

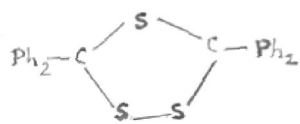
were established by Raney nickel desulphurization.



(IX)



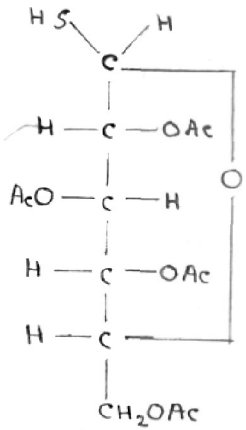
(X)



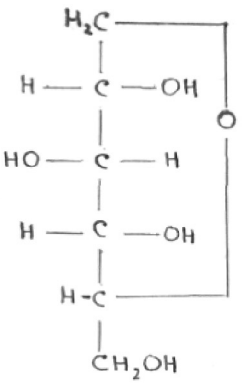
(XI)

Mercaptals

Wolfrom and Karabinos[45] have developed a novel method of converting a carbonyl to a methylene group. The carbonyl group is converted to the mercaptal or mercaptol which is hydrogenolysed over Raney nickel to give the methylene group ($\geq C=O \rightarrow \geq C(SR)_2 \rightarrow \geq CH_2$). This is a useful alternative to Wolff-Kishner and Clemmensen reductions, and since the reaction is carried out under mild conditions, no structural rearrangements are likely to occur. The method has found applications in the fields, among others, of steroids[46-48] and *streptomyces* antibiotic.[49] This type of reduction has also found application in the conversion of quinones to hydrocarbons.[50] 1:5-Anhydrides of sugar alcohols have been prepared by the removal of sulphur from the requisite intermediates as illustrated by the synthesis of 1:5-D-Sorbitan (XIII) from (XII)



(XII)



(XIII)

This route has been followed in the synthesis of some deoxyhexoses and deoxypentoses.[51] Hauptmann observed that aromatic mercaptals, mercaptols, and disulphides are transformed into simple thioethers by the action of Raney nickel that has been freed from hydrogen by heating in vacuum at 200° when benzaldehyde mercaptals are employed, stilbene and its derivatives are obtained

$$HCH(\text{-S-Ph})_2 \rightarrow \text{Ph-S-Ph}$$

$$2PhCH(\text{-S-Ph})_2 \rightarrow PhCH{=}CHPh + 2Ph\text{-S-Ph} + 2S$$

in addition.[52] Cyclic steroidal hemithioketals regenerate the ketone on Raney nickel treatment.[53]

Thiocarbonyls

Another route for the reduction of carbonyl groups is through the thiocarbynols. Dithiofluorenone has been converted to fluorene[44] and phenanthridone to phenanthridine through the phenanthridinethione.[54] Thioureas give rise to the corresponding substituted formamidines:

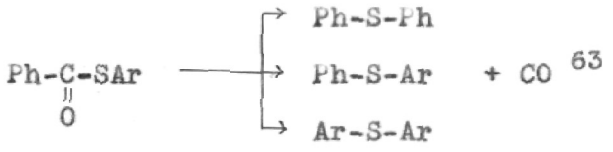
$$RNHCSNHR' \rightarrow RNHCHNR'$$ [55]

Brovet found that thioamides could be reduced to amines; but in the cold without the addition of hydrogen, thiobenzamide gave benzaldehyde in 77% yield.[56] Aldehydes could also be obtained by reduction with catalyst preheated with boiling acetone. Thioanilides produced higher yields of aldehydes but the starting materials were less accessible.[57] Reductive desulphurization of thioamides to the corresponding amines takes place smoothly by the Mozingo method. Thus phenylthioacetomorpholide gives phenylethylmorpholide. The formation of secondary rather than primary amines takes place with some thioamides which are unsubstituted on nitrogen.[58] During reduction of a cyclic thioamide to the amine in ethanol solution, N-alkylation was observed. This could be avoided by carrying out the reduction in tert.-butanol in presence of hydrogen.[59] o-Tolylisothiocynate and o-tolylthiourea are reduced to o-toluidine by cleavage of N-C bond.[12]

Thiolesters:

Thiolesters on hydrogenolysis give rise to aldehydes[60] or alcohols: $RCOSR' \rightarrow RCHO$ or RCH_2OH.[61,62] The use of fresh nickel favours the formation of alcohols, while a catalyst deactivated by acetone under standard conditions leads to aldehydes in good yields.[62] Aldehydes prepared in this manner include simple compounds,[60] steroids,[62] and sugars like aldehydo-D-ribose tetraacetate.[60]

Aliphatic, aromatic and heterocyclic acids have been smoothly converted into the corresponding alcohols in 60-90% yields through the thiolesters.[61,62] Special use of this method has been made in the sterol and triterpene fields where acid or alkaline reductions produce undesirable effects. By the action of hydrogen-free Raney nickel, aryl thiolester (XIV) yield thioethers:



[63]

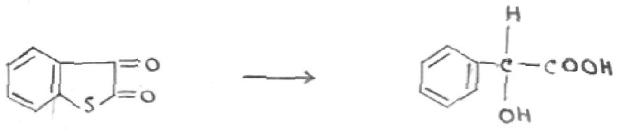
(XIV)

Thioethers:

The reduction of an alcoholic to an alkyl group through the desulphurization of a thioether intermediate, following the sequence $RCH_2OH \rightarrow RCH_2OSO_2CH_3 \rightarrow RCH_2SC_2H_5 \rightarrow RCH_3$ has been used for the synthesis of cantharidin.[64]

Thiophene derivatives:

Thiophene derivatives by treatment with Raney nickel give the corresponding alkyl derivatives.[12,65,66] β-(α-Thenoyl)-propionic acid forms Y-caprylolacetone by the Papa method. Thianaphthenequinone (XV) is converted



(XV) (XVI)

into mandelic acid (XVI) which is fairly stable to Papa reduction (except for the formation of a trace of phenylacetic acid) unlike benzyl alcohol in which alcoholic group gets reduced.[66] Baker has made the interesting observation that, when 4':5':4:5-dibenzothiopheno (2':3':3:2)thiophene (XVII) was reduced with freshly prepared Raney nickel in ethanol solution, ɛtetraphenyl cyclobutane (XVIII) was formed, while Raney nickel,

(XVII) (XVIII)

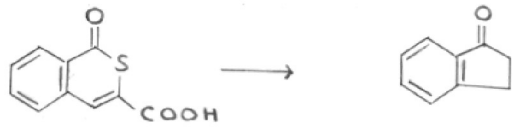
three months old, gave a mixture of (XVIII) and dibenzyl. If the reduction was carried out in methanol solution, dibenzyl was obtained.[67] The isomeric 1:2- and 3:4-benzothiafluorenes (XIX and XXI) were readily distinguished by Raney nickel in boiling alcohol, the respective products being 2-phenylnaphthalene (XX) and 1-phenylnaphthalene (XXII).[68]

(XIX) (XX)

(XXI) (XXII)

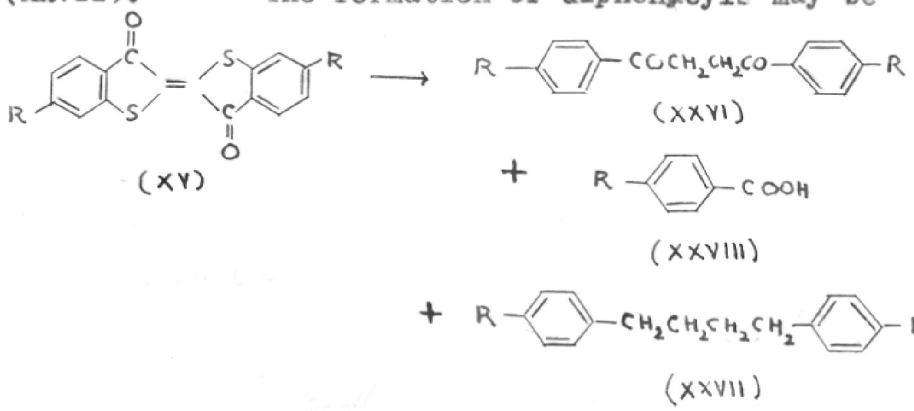
Miscellaneous cyclic systems containing sulphur:

1:2-Dihydro-1-keto-thianaphthalene-3-carboxylic acids (e.g. XXIII), on Raney nickel treatment underwent desulphurization followed by decarboxylation and cyclization to five membered ring systems (e.g. XXIV).[69]



(XXIII) (XXIV)

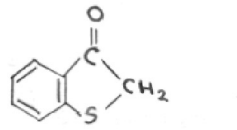
Raney nickel desulphurization of thioindigoid dyes was studied by Kao et al. By the Paper method, thioindigo and other substituted thioindigoid dyes (XXV), yielded the corresponding diphenacyls (XXVI), 1:4-diphenylbutanes (XXVII) and the small amounts of the benzoic acids (XXVIII) The Mozingo method gave mainly the diphenyl butanes (XXVII).[68,70] The formation of diphenacyls may be



attributed to the poisoning of catalyst with sulphur which prevents further reduction. In connection with isolation of benzoic acid, which may result from the

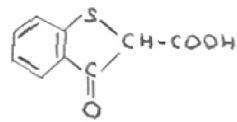
hydrolysis of diphenacyl, it was noticed that acetophenone gave benzoic acid as one of the products of Papa reduction.

Reduction with Raney nickel and aqueous caustic soda at 0-5° gave very interesting results with thioindoxyl (XXIX); and thioindoxylic acid (XXX); the former gave acetophenone in 72% yield; the latter was completely desulphurized in five minutes with the formation of β-phenyl-β-hydroxypropionic acid as the main product, accompanied by acetophenone and β-phenylpropionic acid.[68]



$\longrightarrow$ $PhCOCH_3$

(XXIX)



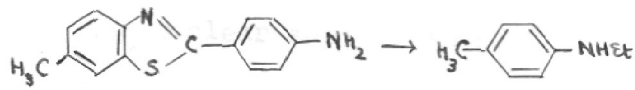
$\longrightarrow$ $PhCOCH_3$

$Ph-CHOH-COOH$

$Ph-CH_2CH_2-COOH$

(XXX)

The facile conversion of dehydrothio-p-toluidine (XXXI) to N-ethyl-p-toluidine by the action of Raney nickel in ethyl alcohol was utilized by Kao et al. for the



(XXXI)

synthesis of secondary N-alkylarylamines by the interaction of arylamines with Raney nickel and primary and secondary alcohols.[71] Similar procedures for N-alkylation of primary aromatic amines have been reported by Rice and Kohn[72] and Ainsworth.[73]

Miscellaneous sulphur-containing compounds as intermediates in synthesis:

Several 9-substituted adenines have been synthesized by Lythgoe and Todd by a general method consisting of the corresponding 2-methylthio compounds as the last stage.[74] For the synthesis of certain pyrimidine,[75] quinoline[76] and morpholine[77] derivatives, similar procedure have been followed.

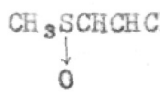
Thiazoles

Hydrogenolysis served as a valuable tool for Cook and Heilbron[78] in their studies of the structures of various azoles. Mercaptoglyoxalines are readily desulphurized. Mercaptothiazoles yield thiazoles on mild treatment with Raney nickel, as the sulphur atom in thiazole ring system is not easily affected. The ease of cleavage of thiazoles is dependent on the nature and position of the nuclear substituents.[12]

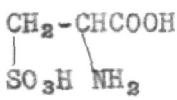
Sulphoxides, sulphones and sulphonic acids:

Sulphur in higher states of oxidation is also

displaced by Raney nickel. Diphenyl sulphoxide and diphenyl sulphone are cleaved to benzene,[36] while benzidine sulphone in alcohol solution gives N:N'-diethylbenzidine.[79] The work of Schmid and Karrer on the constitution of a naturally occurring sulphoxide, sulphoraphen (XXXII), from raddish seed includes a Raney nickel desulphurization.[80]



(XXXII)



(XXXIII)

In the course of his work on the stereochemical paths of reductive desulphurization, Bonner found that the amides of the optically active 2-phenyl-2-phenylmercaptopropionic acids gave racemic products, while the products from the corresponding sulphones were optically active. Sulphoxides also gave racemic products. The results indicate that the sulphones are not desulphurized ~~via~~ intermediate sulphides and the paths of the two reactions are distinct. The free radical theory is probably applicable only to sulphides and sulphoxides and involves the unshared electrons of sulphur.[81]

The sulphonic acid groups in p-toluenesulphonic acid ~~groups in p-toluenesulphonic~~ and in cystic acid (XXXIII) are unaffected by the Mozingo method,[82] but they are displaced by the Papa method of Raney alloy and

aqueous alkali. Benzenesulphonic is converted to benzene, J-acid to 6-amino-1-naphthol and α- and β-naphtholenesulphonic acids are desulphonated by the Papa method without any noticeable difference.[79,83] However, by the use of modified conditions 1-naphthylamine-3:8-disulphonic acid has been preferentially desulphonated to 1-naphthylamine-3-sulphonic acid by Raney alloy and aqueous sodium carbonate.[84] Aryl esters of p-toluenesulphonic acid on hydrogenolysis yield the aromatic hydrocarbons, while alkyl esters only undergo hydrolysis to the alcohol. Alkyl and aryl esters of benzylsulphonic acid are rapidly hydrolyzed under the same conditions. This method offers a convenient route for the elimination of phenolic groups.[85] Thus, hydroxy yobyrin, a degradation product of an alkaloid occurring in Rauwolfia serpentina, has been converted to yobyrin through the reduction of the p-toluenesulphonyl derivative.[86] p-Toluenesulphonamides are resistant to hydrogenation, but the benzylsulphonanilides readily give the corresponding anilines under mild conditions.[85]

REFERENCES

1. Raney, U.S.P. 1,563,787; 1,628,190.
2. Covert and Adkins, J. Am. Chem. Soc., 1932, 54, 4116.
3. Paul and Hilly, Bull. soc. chim., 1936, 3, 2330.
4. Du Pont and Piganiol, ibid., 1939, 6, 322.
5. Ruggli, Helv. Chim. Acta., 1939, 22, 478.
6. Mozingo, Org. Syn., 1941, 21, 5.
7. Palvic and Adkins, J. Am. Chem. Soc., 1946, 68, 1471.
8. Adkin and Billica, ibid., 1948, 70, 695.
9. Adkin and Krsek, ibid., 1948, 70, 412.
10. Delepine and Horeau, Compt. rend., 1935, 201, 1301.
11. Fluchaire and Chambert, Bull. soc. chim., 1944, 11, 22.
12. Hurd and Rudner, J. Am. Soc. Chem., 1951, 73, 5157.
13. Paul, Bull. soc. chim., 1940, 7, 296.
14. Aubrey, ibid., 1938, 5, 1333.
15. Schrocter, Angew. Chem., 1941, 54, 229, 252.
16. Pattison and Pegering, J. Am. Chem. Soc., 1951, 73, 486.
17. Du Pont and Piganiol, Bull. soc. chim., 1939, 6, 322.
18. Liber and Smith, J. Am. Chem. Soc., 1936, 58, 1417.
19. Pattison and Pegering, ibid., 1951, 73, 611.
20. Paul, Bull. soc. chim., 1938, 5, 1592; Compt. rend., 1939, 208, 1319.
21. Irrera, Atti XXVII riunione, Bologna, sci. ital. progresso sci., 1939, 5, 353.
22. Balcom and Furst, J. Am. Chem. Soc., 1953, 75, 4334

23. Kleider and Lornfield, J. Org. Chem., 1948, 13, 455.

24. Dubois, Compt. rend., 1947, 224, 1254.

25. Mozingo, Spencer and Folkers, J. Am. Chem. Soc., 1944, 66, 1859.

26. Papa, Schwenk and Whitman, J. Org. Chem., 1942, 7, 586.

27. Linstead, Chem. Soc. Ann. Rep., 1937, 34, 222.

28. Baxter and Spring, ibid., 1945, 42, 99.

29. McOmic, ibid., 1948, 45, 198.

30. Schroter, Newer methods of preparative organic chemistry, Interscience Publishers, Inc., New York, 1948.

31. Adkins, Reaction of hydrogen with organic compounds over copper-chromium oxide and nickel catalysts, The University of Wisconsin Press, Wisconsin.

32. Liber and Morritz, Advances in catalysis, Vol. V, Academic Press, New York, 1953.

33. Bougalt, Cattelain and Chabrier, Compt. rend., 1939, 1939, 208, 657; Bull. soc. Chim., 1940, 7, 781.

34. Aubry, Bull. soc. chim., 1938, 5, 1333.

35. Bonner, J. Am. Chem. Soc., 1952, 74, 1033.

36. Mozingo et al., ibid., 1943, 65, 1013.

37. Clime, Campaigne and Spies, ibid., 1944, 66, 1136.

38. Bergmann and Israclashevili, ibid., 1945, 67, 1951.

39. Fonken and Mozingo, ibid., 1947, 69, 1212.

40. Vigneaud et al., J. Biol. Chem., 1942, 146, 475.

41. The Chemistry of Penicillin, edited by Clarke, Thonson and Robinson, Oxford University Press, 1949; Cook, Quarterly Reviews, 1948, 2, 205, 259; Adkins, Brustschy and McWhirter, J. Am. Chem. Soc., 1948, 70, 2610.

42. McLamore, et. al., J. Am. Chem. Soc., 1953, 75, 657.

43. Jansen, J. Biol. Chem., 1948, 176, 657.

44. Campaigne and Reid, J. Org. Chem., 1947, 12, 807.

45. Wolfrom and Karabinos, J. Am. Chem. Soc., 1944, 66, 902.

46. Bernstein and Portman, ibid., 1946, 68, 1152.

47. Hauptmann, ibid., 1947, 69, 562.

48. Huffman and Lott, ibid., 1949, 71, 719.

49. Kuehl et al., ibid., 1946, 68, 2096; et sequa.

50. Bailey and Madoff, ibid., 1953, 75, 5603.

51. Mukherji and Todd., J. Chem. Soc., 1947, 969.

52. Hauptman and Weadislam, J. Am. Chem. Soc., 1950, 72, 707; Experimenta, 1948, 4, 365; Ann., 1952, 576, 45.

53. Romo, Rosenkranz and Djerassi, J. Am. Chem. Soc., 1951, 73, 4961.

54. Taylor and Martin, ibid., 1952, 74, 6295.

55. Ashworth, J. Chem. Soc., 1948, 1716; Turner, J. Am. Chem. Soc., 1948, 70, 3961; Brown, J. Appl. Chem., 1952, 2, 202.

56. Brovet, Archiv. Kem., 1948, 20, 70.

57. Cronyn and Goodrich, J. Am. Chem. Soc., 1952, 74, 3936

58. Kørnfeld, J. Org. Chem., 1951, 16, 131.

59. Cronyn, ibid., 1949, 14, 1013.

60. Wolfrom and Karabinos, J. Am. Chem. Soc., 1946, 68, 724, 1455.

61. Prelog, Norymberski and Jeger, Helv. Chim. Acta., 1946, 21, 566, et sequa.

62. Spero, McIntosh and Levin, J. Am. Chem. Soc., 1948, 70, 1907.

63. Hauptman and Wladis, ibid., 1950, 72, 710.

64. Stork et al., ibid., 1951, 73, 4501.

65. Papa, Schwenk and Ginsberg, J. Org. Chem., 1949, 14, 723.

66. Blicke and Sheets, J. Am. Chem. Soc., 1948, 70, 3768; 1949, 71, 4010; Modest and Szuszkovicz, ibid.,

67. 1950, 72, 577.

67. Baker, El-Nawawy and Ollis, J. Chem. Soc., 1952, 3165.

68. ~~Rijksmannxand~~ Kao, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1953, 38A, 244.

69. Pijksmann and Newbold, J. Chem. Soc., 1952, 13.

70. Kao, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1950, 32A, 162.

71. Kao, Tilak and Venkataraman, J. Industr. Res. Sci., 1955, 14B, 624.

72. Rice and Kohn, J. Am. Chem. Soc., 1955, 77, 4052.

73. Ainsworth, ibid., 1956, 78, 1635.

74. Howard, Lythgoe and Todd, J. Chem. Soc., 1945, 556, 1947, 355; 1948, 965.

75. Roblin et al., J. Am. Chem. Soc., 1945, 67, 290.

76. Elderfield and Claflin, ibid., 1952, 74, 2953.

77. Burger, Rector and Schmalz, ibid., 1952, 74, 3175.

78. Cook and Heilbron, J. Chem. Soc., 1947, 1598; 1948, 201, 1262, 1337, 1340.

79. Shah, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1948, 28A, 142.

80. Schmid and Karrer, Helv. Chim. Acta., 1948, 31, 1017.

81. Bonner, J. Am. Chem. Soc., 1952, 74, 1034, 5089.

82. Merck and Co. Inc., PENx46 (Report to the Therapeutic Research Corporation of Great Britain).

83. Papa et al., J. Org. Chem., 1944, 9, 1.

84. N. Ramanathan, private communication.

85. Kenner and Murray, J. Chem. Soc., 1949, 5178

86. Dorfman, et al., Helv. Chim. Acta., 1954, 37, 59.

PART I

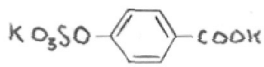
A NEW GENERAL METHOD FOR THE REDUCTION OF QUINONES TO THE CORRESPONDING HYDROCARBON DERIVATIVES

Kenner and Murray found that, when an alcoholic solution of O-tosyl (p-toluenesulphonyl) derivative of a phenol was shaken with Raney nickel and hydrogen at atmospheric pressure, the products were the aromatic hydrocarbon and nickel tosylate ($2Ar\text{-}O\text{-}SO_2C_7H_7 + Ni + H_2 \rightarrow 2ArH + Ni(OSO_2C_7H_7)_2$).[1] Thus m-acetamido phenol could be converted to acetanilide (90%), and methyl salicylate to methyl benzoate (80%), via the tosylate. The naphthalene nucleus also underwent hydrogenation under these conditions, β-naphthyl tosylate yielding tetralin. This reductive cleavage of aryl-p-toluenesulphonate with Raney nickel is useful for several synthetic purposes. It provides for instance a new and convenient route to Y-resorcilic acid by the hydrogenolysis of the mono-O-p-toluenesulphonyl derivative of phloroglucinol carboxylic acid.[2] Extending this procedure to the flavone series a general method for the preparation of 5-hydroxyflavone and its derivatives from the corresponding 5:7-dihydroxyflavones by the action of Raney nickel and hydrogen on the 7-tosyl esters was developed,[3] and was used in the synthesis of 3:5:8:3':4'-pentahydroxyflavone, which was shown to be different from the colouring matter of Ponderosa pine bark.[4]

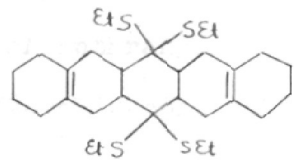
The action of Raney nickel on the sulphuric esters of phenols has now been studied to determine if sulphuric esters can be used as intermediates in place of tosyl esters for the removal of phenolic hydroxyl groups. p-Hydroxybenzoic acid was sulphated using pyridine and chlorosulphonic acid. The sulphuric ester was not isolated, but converted into the dipotassium salt (I), which was treated with Raney nickel and hydrogen. From the reaction mixture benzoic acid (65%) and a little p-hydroxybenzoic acid were isolated.

A new general method for the conversion of quinones to the corresponding hydrocarbons through the disulphuric esters of the leuco derivatives thus becomes available.[5] The usual methods of preparing hydrocarbons from quinones are (1) reduction of by zinc dust, alone or in combination with zinc chloride and sodium chloride (Clar reduction) or aqueous ammonia, and[2] reduction by phosphorus and hydriodic acid. The cleavage of sulphuric esters by Raney nickel affords an alternative route for the preparation of hydrocarbons and may have advantages over phosphorus and hydriodic acid and zinc dust distillation methods, which use high temperatures and may cause structural rearrangement. Sulphuric esters of leuco derivatives of over thirty vat dyes are available commercially and provide suitable raw materials for the preparation of

various polycyclic hydrocarbons, azahydrocarbons, etc. which are of interest in connection with cancer studies. Two further procedures were reported while the present work was in progress. A hydrogenated pentacenequinone has been converted into the dithioketal (II) and then



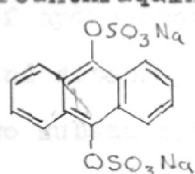
(I)



(II)

desulphurized to a hydrogenated pentacene, which was finally dehydrogenated to pentacene.[6] As an extension of the Meerwein-Ponndorf-Varley reduction, aluminium cyclohexyloxide in cyclohexanol has been used for the reduction of anthraquinone, anthrathrone and flavanthrone to the corresponding hydrocarbons.[7]

The hydrogenolysis of the disulphuric ester of anthrahydroquinone (III) was first examined. An aqueous solution of the disulphuric ester was treated with Raney nickel and hydrogen for 4 hours at room temperature and filtered. Benzene extraction of the nickel residue after deactivation gave a mixture of 1:2:3:4-tetrahydroanthraquinone and hydrogenated



(III)

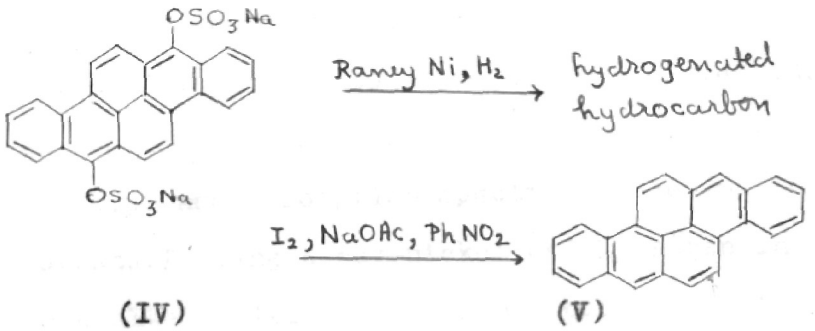
anthracene; the latter was then dehydrogenated by selenium to anthracene in an overall yield of 30%. From the aqueous filtrate, after oxidation with sodium nitrite and sulphuric acid, a further quantity of 1:2:3:4-tetrahydroanthraquinone was recovered, indicating that hydrogenation of anthrahydroquinone disulphuric ester to 1:2:3:4-tetrahydroanthrahydroquinone disulphuric ester also takes place as a side reaction. The formation of a quinonoid derivative, because of the incomplete hydrogenolysis of the ester even when a large amount of Raney nickel was used, was practically eliminated by carrying out the reaction using Raney alloy and aqueous alkali instead of Raney nickel catalyst. This modification gave an excellent yeild of hydrogenated anthracene (85%) which could be readily dehydrogenated to anthracene.

An aqueous solution of Indigosol Golden Yellow IGK the disulphuric ester (IV) of Indanthrene Golden Yellow GK (2:3:7:8-dibenzpyrene-1:6-quinone), was treated with Raney nickel and hydrogen. The nickel residue on deactivation and extraction with toluene gave a mixture of hydrogenated derivatives of the parent quinone and dibenzpyrene in equal quantities (yield 35%). Two substances, analysing for decahydrodibenzpyrene (m.p. 235°) and octahydrodibenzpyrenequinone (m.p. 268°), were isolated by chromato-

graphic separation of the mixture on alumina. Separation of the hydrocarbon and quinone components by means of alkaline hydrosulphite was unsuccessful, because the quinone was crystalline and therefore difficult to vat. Precipitation from concentrated sulphuric acid solution to obtain finely divided and readily vattable substance was not possible since sulphonation took place. On dehydrogenation by means of iodine and sodium acetate in boiling nitrobenzene solution, the hydrogenated hydrocarbon gave dibenzpyrene in an overall yield of 28%. The aqueous filtrate after removal of nickel contained unreacted Indigosol, and yielded the parent quinone by oxidation with sodium nitrite and sulphuric acid. When the reduction was carried out in a Parr hydrogenator with hydrogen at 40 lbs. pressure, the yield of the hydrogenated hydrocarbon fell to 18%; the main reaction appeared to be nuclear hydrogenation. An octahydrodibenzpyrenequinone (in a yield of 30%) was obtained from the aqueous solution after oxidation, and this quinone was different from the octahydro derivative obtained by reduction under the Kenner-Murray conditions.

As in the case of anthrahydroquinone disulphuric ester, reduction of the sulphuric ester (IV) by means of Raney alloy and aqueous alkali afforded an excellent

yield (80%) of a mixture hydrogenated hydrocarbons, which were separated by chromatography into hexahydrodibenzpyrene (m.p. 240-41°) and decahydrodibenzpyrene (m.p. 235-36°); the latter was identical with the decahydrodibenzpyrene obtained by the Kenner-Murray procedure. The mixture of hydrogenated hydrocarbons was dehydrogenated to dibenzpyrene by treatment with iodine and sodium acetate in boiling nitrobenzene.



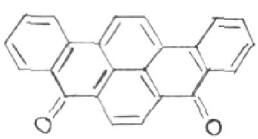
(IV) (V)

2:3:7:8-Dibenzpyrene (V) has been prepared earlier from 2:3:7:8-dibenzpyrene-1:6-quinone by zinc dust distillation,[8] Clar reduction,[9] and reduction with phosphorus and hydriodic acid.[10]

The cleavage of leuco sulphuric esters with Raney nickel provides a good degradative method in constitutional work. It was utilized in determining the constitution of the newly introduced red vat dye, Mayvat Brilliant Red AF double paste. The latter, claimed to be "entirely new homogeneous anthraquinone vat colour" is a bright red vat dye, introduced by Otto B. May, Inc., Newark, N.J., U.S.A. (manufactured

at present in pilot plant quantities). A preliminary examination of this dyestuff showed that it was halogenated quinonoid compound, containing chlorine and bromine, but no nitrogen or sulphur. The product was chromatographically homogeneous and crystallized in red needles from o-dichlorobenzene. The reduction of its leuco sulphuric ester (prepared by the usual Soledon process) with Raney alloy and caustic soda gave a mixture of hydrogenated hydrocarbons, the dehydrogenation of which led to an aromatic hydrocarbon, which was identified as 2:3:6:7-dibenzpyrene (VI) by its m.p. and absorption spectrum. Dehalogenation of the dyestuff using Raney nickel and hydrogen in aqueous alkali yielded the parent quinone, which was identified as 2:3:6:7-dibenzpyrene-1:8-quinone (VII).[11] The dye was, therefore, formulated as halogenated 2:3:6:7-dibenzpyrene-1:8-quinone.

(VI)



(VII)

The mixture of hydrogenated hydrocarbons was separated by chromatography into a tetrahydro derivative as the major fraction and an octahydro derivative of (VI)

EXPERIMENTAL

Sulphation of p-hydroxybenzoic acid:

p-Hydroxybenzoic acid (5 g.) was dissolved in dry technical pyridine (b.p. 135-45°, 25 ml.). The solution was cooled in a freezing mixture and chlorosulphonic acid (3 ml., 1.2 mols.) was added drop by drop under stirring. After the addition, the paste was stirred for one hour, and then neutralized with 50% caustic potash solution. Pyridine separated as a layer and was decanted off. The mass was transferred to a buchner funnel and sucked dry. The last traces of pyridine were removed by washing the product with benzene.

Reduction of p-carboxyphenyl sulphate (I):

The sulphuric ester obtained from the above experiment was divided into two parts. One part was dissolved in water (100 ml.), Raney nickel (40 g.) added, and the mixture agitated for 6 hours in a stream of hydrogen. The mixture was filtered, the filtrate acidified, saturated with salt and extracted with ether. The nickel residue was deactivated under acid and extracted with ether. The two extracts were combined and ether distilled off. The residue (1.8 g.) crystallized from water in colourless leaflets (1.5 g.), m.p. 122°, undepressed when mixed with benzoic acid. The yield of benzoic acid was 65%. From the mother liquor, p-hydroxybenzoic acid (0.2 g.) was recovered.

Reduction of anthrahydroquinone disulphuric ester (III):

Method (a): The ester (3 g., 75% pure) was dissolved in water (200 ml.), Raney nickel (30 g.) added, and the mixture stirred for 4 hours while a stream of hydrogen was led in. The violet fluorescence of the solution disappeared in the course of one hour. The mixture was then filtered. The filtrate on treatment with sodium nitrite and sulphuric acid gave pale yellow needles (0.55 g.), m.p. 158°, undepressed when mixed with 1:2:3:4-tetrahydroanthraquinone.

The nickel residue was deactivated under hydrochloric acid, separated, and extracted successively with alkaline hydrosulphite solution and benzene. Air oxidation of the alkaline vat gave 1:2:3:4-tetrahydroanthraquinone (0.1 g.). The benzene extract yielded a substance (0.35 g.), which was mixed with selenium (1 g.) and heated to 300° gradually. The product was extracted with alcohol and the extract gave colourless plates (0.3 g., 30% yield), m.p. 217°, undepressed on admixture with anthracene.

Method (b): The ester (1.2 g., corresponding to 0.55 g. of anthraquinone) was dissolved in 10% aqueous sodium hydroxide (60 ml.) Raney alloy (6 g.) was gradually added to the solution at 70-80° with vigorous stirring in the course of 1 hour. The temperature was then raised to 90° and stirring

continued for 3 hours. The reaction mixture was filtered, and the filtrate on oxidation with nitrous acid gave no precipitate. The nickel residue was deactivated under hydrochloric acid, filtered, dried and extracted with alcohol. The alcohol extract on evaporation gave colourless plates (0.4 g.), which gave no colour with alkaline hydrosulphite. After crystallization from acetic acid, m.p. was 86.5-87° (Found: C, 92.1; H, 8.2. $C_{14}H_{14}$ requires C, 92.3; H, 7.7%). This hydrogenated anthracene on dehydrogenation with selenium gave anthracene.

Reduction of Indigosol Golden Yellow IGK:

Method (a): The commercial Indigosol crystallized from water in golden yellow needles (Found: S, 11.3. Calc. for $C_{24}H_{12}O_8S_2Na_2$: S, 11.6%). The Indigosol (11 g.), water (1000 ml.) and Raney nickel catalyst (100 g.) were stirred for 3 hours in presence of hydrogen. The mixture was filtered and the nickel residue washed with water. The aqueous portion on oxidation with sodium nitrite and sulphuric acid gave the parent dye (1.05 g.). The nickel residue was kept under hydrochloric acid, filtered, washed, dried, and extracted in a Soxhlet with toluene for 2 days. The toluene extract on concentration to 120 ml. gave a substance (A) (0.94 g.). The mother liquor on further concentration to 20 ml. gave a second substance (B)

(1.58 g.). The residual mother liquor on removal of the solvent gave a third substance (C) (1.7 g.). A solution of 0.5 g. of (C) in benzene was chromatographed on alumina. The first pale yellow percolate, which showed a greenish fluorescence, gave yellow plates (0.25 g.), which did not show a sharp m.p. even after several crystallizations from benzene. The benzene mother liquor from the first crystallization was evaporated to dryness; the residue crystallized from benzene-hexane mixture in colourless plates, m.p. 235° (Found: C, 92.3; H, 7.2. $C_{24}H_{22}$ requires C, 92.9; H, 7.1. $C_{24}H_{24}$ requires C, 92.3; H, 7.7%). The alumina column on further elution with alcohol gave a brown fraction. The solid obtained after the removal of the solvent gave a brown substance (0.2 g.) which vatted completely with alkaline hydrosulphite. Crystallization of the product did not give a substance with a sharp m.p.

Substance (C) (0.5 g.), iodine (1.5 g.) and fused sodium acetate (1.0 g.) were refluxed with nitrobenzene (25 ml.) for 6 hours. Then the solvent was steam distilled. The black residue was washed with water, dried, extracted with benzene (125 ml.) and the benzene extract chromatographed on alumina. The yellow percolate, which had a green fluorescence gave a yellow compound (0.20 g.) crystallizing from benzene in rhombic plates, m.p. 320° (Found: C, 95.7; H, 4.6. Calc. for

$C_{24}H_{14}$: C, 95.4; H, 4.6%). The properties agreed with the properties of 2:3:7:8-dibenzpyrene,[7] m.p. 320°. The benzene-insoluble residue contained a vattable substance. A solution of (A) (0.5 g.) in benzene was chromatographed on alumina. The first yellow percolate, which had a green fluorescence, gave a non-vattable yellow compound (0.2 g.), whose m.p. did not become constant on crystallization. On further elution with alcohol, a brown substance (0.2 g.), was recovered, which dissolved completely in alkaline hydrosulphite solution giving a red vat and dyeing cotton an orange-yellow shade. Crystallization from benzene gave brown needles, m.p. 268° (Found: C, 84.4; H, 5.9. $C_{24}H_{20}O_2$ requires C, 84.7; H, 5.9. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.4%).

Substance (B) could also be resolved into a hydrocarbon and a hydrogenated quinone in the same proportion by chromatography, but no compound with a constant m.p. could be isolated.

Method (b): The Indigosol (8 g., corresponding to 3.9 g. of parent vat dye) was dissolved in water (300 ml.) and the solution shaken with Raney nickel (80 g.) for 7 hours in a Parr hydrogenator with hydrogen at 40 lbs. pressure. The pressure dropped to 38 lbs. after about an hour and remained constant for the rest of the period. The mixture was filtered and

the nickel residue washed with water. The colourless filtrate had a bluish-green fluorescence. On oxidation with sodium nitrite and sulphuric acid it gave an orange-yellow precipitate (1.35 g.), which crystallized from toluene in orange-red needles, m.p. 305-06° (Found: C, 85.1; H, 6.2. $C_{24}H_{20}O_2$ requires C, 84.7; H, 5.9%). The substance dissolves in alkaline hydrosulphite solution to form a brown vat and dyes cotton a yellow shade. The nickel residue, after deactivation under acid, was extracted with benzene. The benzene extract on evaporation gave a yellow brown product (2.6 g.). A part (0.5 g.) was dissolved in benzene and separated into a hydrocarbon (0.125 g.) and a quinone (0.35 g.) by chromatography on alumina, but no compound with a sharp m.p. could be isolated. Attempts to separate the hydrocarbon and the quinone components by vatting with alkaline hydrosulphite were unsuccessful. The above mixture (0.5 g.) on dehydrogenation with iodine and sodium acetate in nitrobenzene, followed by chromatography of a benzene solution on alumina, gave dibenzpyrene (0.1 g.).

(Method (c): The Indigosol (3 g., corresponding to 1.45 g. of parent vat dye) was suspended in 10% aqueous sodium hydroxide (300 ml.), Raney alloy (30 g.) was gradually added to the mixture with vigorous stirring in the course of 2 hours at 70-80°.

The temperature was then raised to 90° and stirring continued for 4 hours. The mixture was filtered and the almost colourless filtrate on oxidation gave the parent vat dye (0.07 g.). The nickel residue, after deactivation under acid, was extracted with benzene. Evaporation of the benzene extract, which was yellow in colour with a bluish green fluorescence, gave yellow plates (1.2 g.). This product on dehydrogenation with iodine and sodium acetate in nitrobenzene gave dibenzpyrene (V) (0.88 g.).

The reduction was repeated using 1.5 g. of the Indigosol. The product (0.6 g.) obtained by extraction of the nickel residue with benzene was redissolved in dry hexane (400 ml.) and chromatographed on freshly activated alumina in ultraviolet light. The chromatogram was developed and eluted with hexane-benzene mixture. The first fraction, colourless with a blue fluorescence, gave colourless plates (0.27 g.), m.p. 235-36°, undepressed when mixed with the decahydrodibenzpyrene obtained in method (a) (Found: C, 92.2; H, 7.5. $C_{24}H_{24}$ requires C, 92.3; H, 7.7%). The second fraction colourless with a blue fluorescence gave pale yellow plates (0.21 g.) m.p. 240-41° (Found: C, 93.7; H, 6.5. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%). The third fraction gave yellow plates (0.052 g.), m.p. 255-56°, while the fourth fraction gave orange-yellow plates (0.018 g.), m.p. 300-02°

On further eluting the column with benzene-alcohol mixture, the nonfluorescent orange-brown percolate yielded a brown substance (0.02 g.), which completely dissolved in alkaline hydrosulphite giving a red vat.

Leuco sulphuric ester of Mayvat Brilliant Red AF:

Chlorosulphonic acid (5 ml.) was slowly run into pyridine (50 ml.) below 20°. The temperature was then raised to 50° and finely divided dye (5 g.) added to it, followed by copper bronze (5 g.). After stirring the mixture at 60-65° for 3 hours, it was poured into 200 ml. of water containing 20 g. caustic soda, and filtered. The solution obtained after the removal of pyridine by steam distillation from the filtrate, contained ester corresponding to 4.5 g. of the dye. The estimation was carried out by oxidizing an aliquot part with ceric sulphate and weighing the precipitated dye.

Reduction of the leuco sulphuric ester of Mayvat Brilliant Red AF:

The solution containing ester (sodium salt) corresponding to 3.0 g. of the dye was made up to 500 ml. and caustic soda (50 g.) added. The alkaline solution was heated on boiling water-bath and Raney alloy (50 g.) added in course of 2 hours. After stirring for 2 hours more, the reaction mixture was

filtered. The nickel was deactivated and extracted with benzene. The benzene extract, after running through a short column of alumina, gave on concentration and cooling, pale yellow plates (1.4 g.). The product (~~0.5~~ 1 g.) was dissolved in hexane and chromatographed on alumina. The chromatogram was developed and eluted with hexane-benzene mixture. The first fraction, colourless with a faint blue fluorescence, gave colourless needles (~~0.08~~ 16 g.), m.p. 175° (Found: C, 93.5; H, 7.1. $C_{24}H_{22}$ requires C, 92.9; H, 7.1%). The second fraction, colourless with blue fluorescence, gave colourless, shining plates (~~0.38~~ 76 g.), m.p. 223° (Found: 93.8; H, 5.7. $C_{24}H_{18}$ requires C, 94.1; H, 5.9%). The product (~~0.2~~ 1 g.) was mixed with selenium (~~0.4~~ 1.2 g.) and heated at 290-300° for 3 hours. The mass was cooled and extracted with benzene. The benzene extract, after running through a short column of alumina, ~~on concentration and cooling gave~~ led to shining yellow plates (~~0.15~~ 4 g.), m.p. 281° (Found: C, 94.9; H, 4.7. $C_{24}H_{14}$ requires C, 95.4; C, 4.6%). Identity with ~~2:3:6:7~~ 3:4:9:10-dibenzpyrene (~~VI~~) was proved by its absorption spectrum, ~~which was identical with that recorded by Clar.~~[13] & mixed m.p. with the hdcb obtained by the redn of 3:4:9:10-dibenzopyrene-5:8-quinone with Al tri-cyclohexoxide.[17]

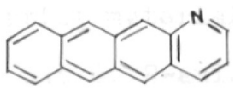
REFERENCES

1. Kenner and Murray, J. Chem. Soc., 1949, S178.
2. Ramanathan and Venkataraman, Curr. Sci., 1952, 21, 283.
3. Ramanathan and Venkataraman, Proc. Indian Acad. Sci., 1953, 38A, 40.
4. Ramanathan and Venkataraman, ibid., 1954, 39A, 90.
5. Desai, Ramanathan and Venkataraman, J. Sci. Industr. Res., 1955, 14B, 330.
6. Bailey and Madoff, J. Am. Chem. Soc., 1953, 75, 5603.
7. Coffey and Boyd, J. Chem. Soc., 1954, 2468.
8. Vollmann et al., Ann., 1937, 531, 1.
9. Clar, Ber., 1939, 72B, 1645.
10. Zilbermann, J. Gen. Chem. (U.S.S.R.), 1937, 7, 234.
11. Unni, private communication.
12. Patni, unpublished work quoted in Venkataraman, The Chemistry of Synthetic Dyes, Vol. II, Academic Press, New York, 1952, p. 1058.
13. Clar, Ber., 1936, 69, 1677.

PART II

THE SYNTHESIS OF 1-AZANAPHTHACENE

Many aromatic polycyclic azahydrocarbons have been synthesized and studied because of the interest in their chemical reactivity, electronic structure, absorption spectra, carcinogenic and other physiological properties, and photochemical behaviour in relation to the corresponding aromatic hydrocarbons. As an application of the Raney nickel method for the reduction of quinones to the corresponding hydrocarbon derivatives, the synthesis of the hitherto unknown 1-azanaphthacene (I) was undertaken.[1] Among the three possible azanaphthacenes (I, II and III) only 5-azanaphthacene (III) is known. As Allen has stated,[2] all the 1-azanaphthacenes found in the literature are 6:11- or 5:12-diketo derivatives; naphthacene can be readily obtained by zinc dust distillation of unsubstituted and hydroxynaphthacenediones, but there is no record of the reduction of a 1-azanaphthacenedione to 1-azanaphthacene.



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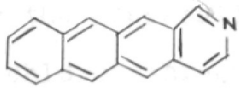

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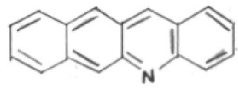
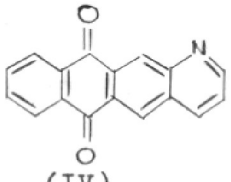


(III)

The first 1-azanaphthacene derivative was the 6:11-dione (IV), obtained as a by-product in the reaction of 2-aminoanthraquinone with glycerol and sulphuric acid,[3] but it was only characterized as an isomer of Graebe's "β-anthraquinonequinoline", which Graebe had shown to be angular compound (V).[4] The main product in this reaction is Bally's "Benzanthronequinoline", the constitution of which is (VI) was recently demonstrated.[5] Isomeric benzanthronequinolines are also formed. Reduction to anthranols and cyclization to benzanthrones can be avoided by the addition of an adequate amount of arsenic pentoxide, but the product is then a not readily separable mixture of (IV) and (V) in which the latter predominates.[6]



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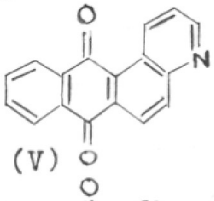

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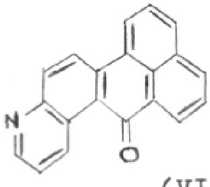

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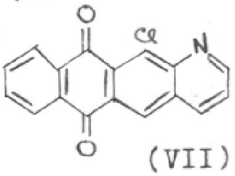


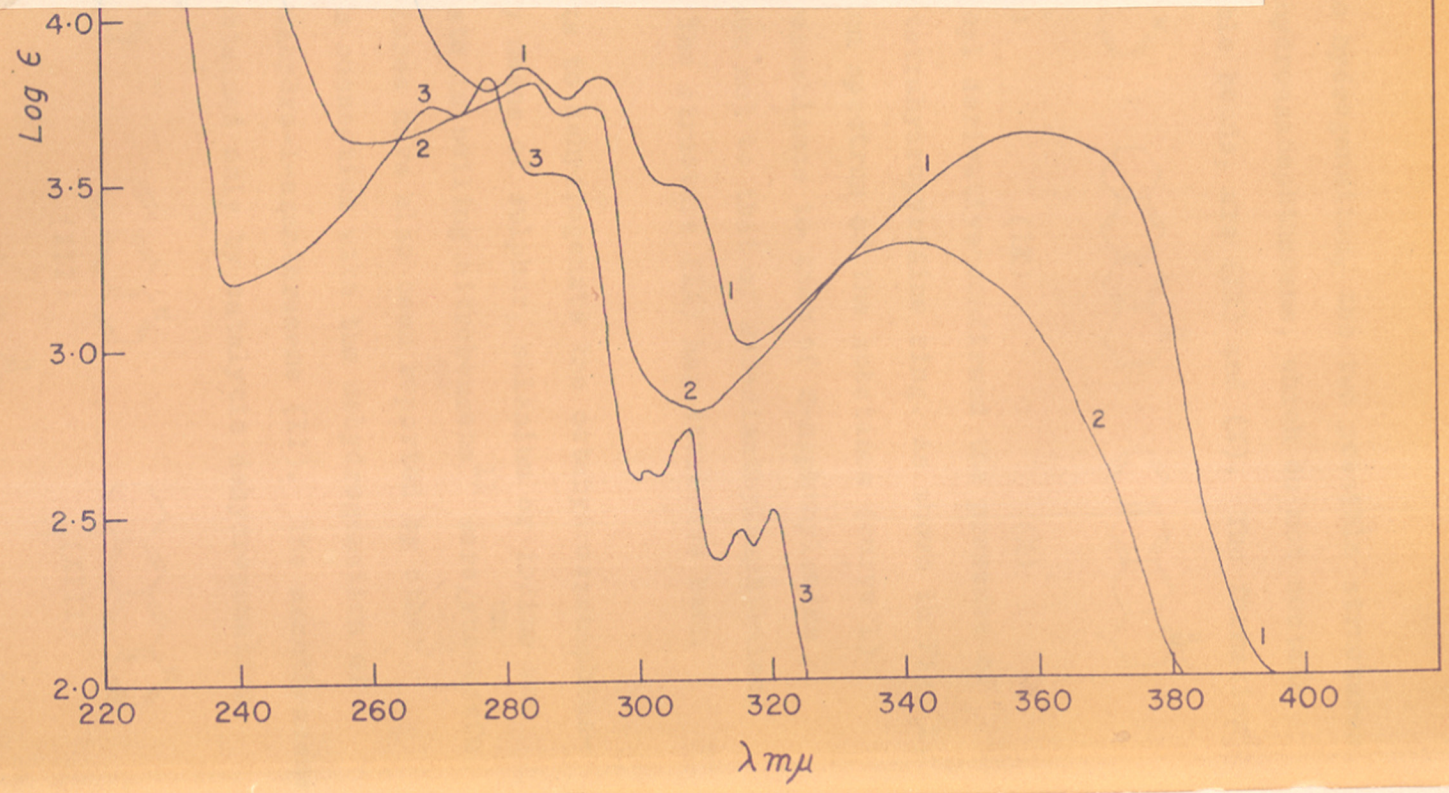
(VII)

2-Aminoanthraquinone is therefore unsuitable as the starting material for the preparation of the dione (IV). The use of 2-amino-1-chloroanthraquinone for the Skraup synthesis eliminates the formation of the angular isomer (V), and the addition of arsenic pentoxide to suppress the benzanthrone reaction gives a good yield of 12-chloro-1-azanaphthacene-6:11-dione (VII). This compound was

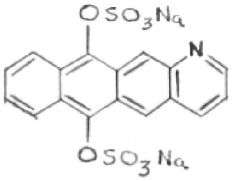
described in a patent[7] as a grey powder obtainable in a crystalline form from high boiling solvents, but it readily crystallizes from o-dichlorobenzene in yellow needles, m.p. 318°. For the preparation of 2-amino-1-chloroanthraquinone, direct chlorination of 2-amino-anthraquinone with sulphuryl chloride and subsequent treatment with aqueous caustic soda has been found to be the most convenient method.[8] The dechlorination of 12-chloro-1-azanaphthacene-6:11-dione was effected by reduction with caustic soda and sodium hydrosulphite, and air oxidation of the vat yielded the desired azanaphthacenedione (IV).

The quinone (IV) was converted into the disulphuric ester of the leuco compound by the process developed by Coffey et al., using dimethylformamide as a reaction medium.[9] This procedure afforded the maximum yield of the sodium salt (VIII) of the disulphuric ester. The substance (VIII) was not isolated, but the aqueous solution was estimated for its content of (VIII) by ceric sulphate oxidation,[10] and then treated with caustic soda and Raney alloy. The hydrogenolysis gave in 30% yield an octahydroazanaphthacene, which crystallized in shining greenish-yellow plates, m.p. 209°. Since the pyridine ring in quinoline is known to be more

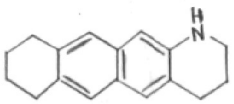
Fig. 1: Absorption spectra of (1) 1:2:3:4:7:8:9:10-octahydroazanaphthacene in n-heptane; (2) 2-naphthylamine in ethanol (Hirshberg and Jones, Canad. J. Res., 1949, 27B, 437); (3) 2:3-dimethylnaphthalene in iso-octane (Friedel and Orchin, Ultraviolet Spectra of Aromatic Compounds (Wiley, New York, 1951.



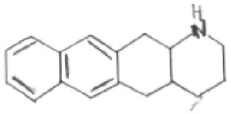
vulnerable to hydrogenation, the two possible structures for the octahydroazanaphthacene, which do not contain isolated double bonds, are (IX) and (X). The formation



(VIII)



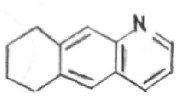
(IX)



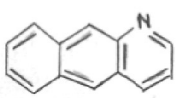
(X)

of an N-benzoyl derivative confirmed the presence of the 1:2:3:4-tetrahydropyridine ring. As shown in Fig. 1, the absorption spectrum of the substance (curve 1) revealed a resemblance to that of 2-naphthylamine (curve 2), but not to that of 2:3-dimethylnaphthalene (curve 3). The structure (IX) has therefore been assigned.

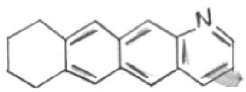
Attempts to dehydrogenate the octahydroazanaphthacene (IX) by means of sulphur, selenium or iodine and sodium acetate in boiling nitrobenzene[11] were unsuccessful. Similar failures have also been reported by other workers[12] in connection with the dehydrogenation of 6:7:8:9-tetrahydro-1-azanthracene (XI). The azanthracene (XII) was obtained only by catalytic dehydrogenation



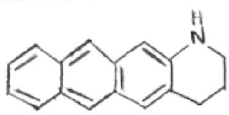
(XI)



(XII)



(XIII)



(XIV)

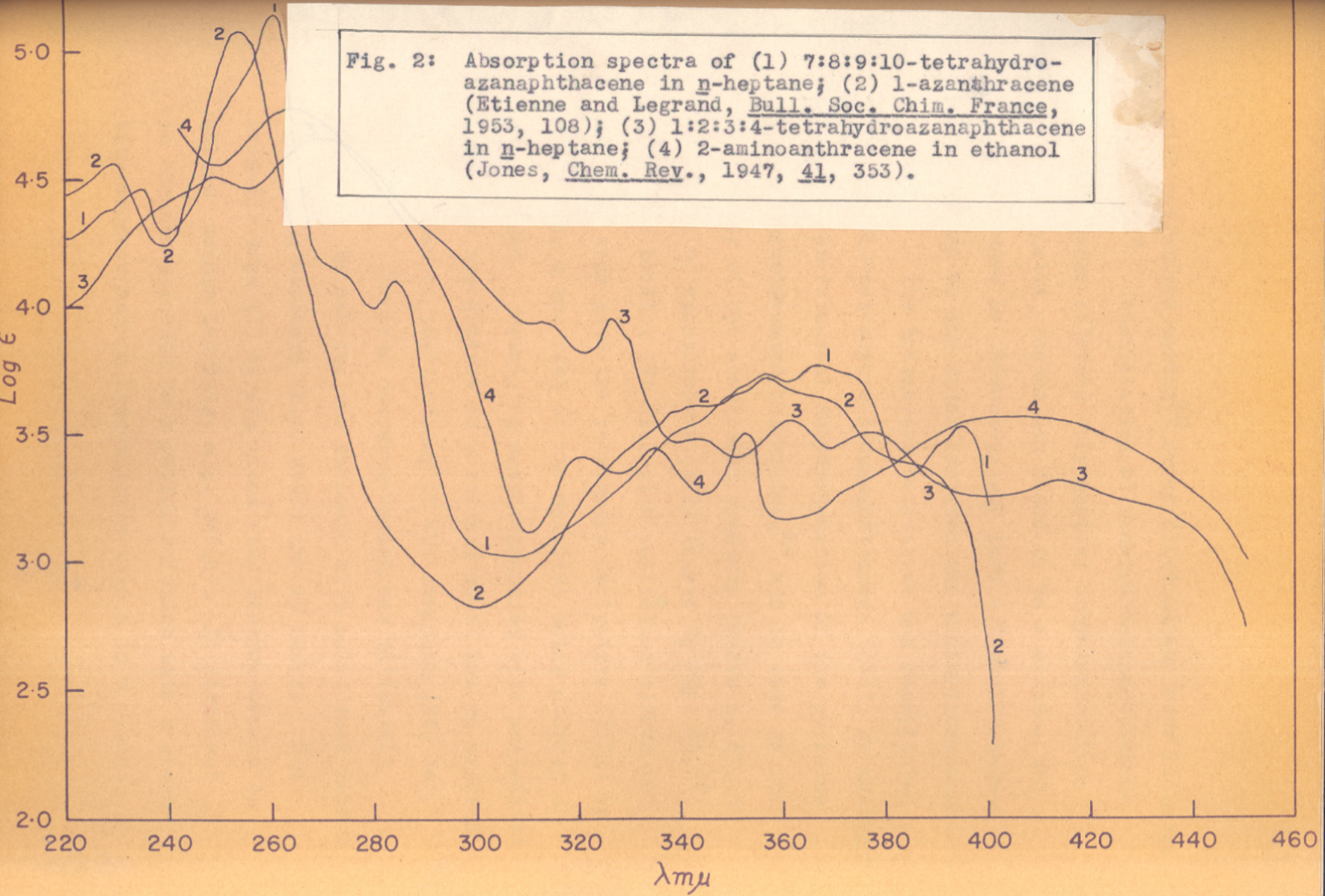


Fig. 2: Absorption spectra of (1) 7:8:9:10-tetrahydro-azanaphthacene in n-heptane; (2) 1-azanthracene (Etienne and Legrand, Bull. Soc. Chim. France, 1953, 108); (3) 1:2:3:4-tetrahydroazanaphthacene in n-heptane; (4) 2-aminoanthracene in ethanol (Jones, Chem. Rev., 1947, 41, 353).

with palladized carbon[12] or by distillation over litharge at 700°.[13] Distillation of octahydroazanaphthacene over litharge effected only partial dehydrogenation. Dehydrogenated product was found to be a mixture and was separated by chromatography into a tetrahydroazanaphthacene as the major fraction and a dihydroazanaphthacene. The tetrahydro derivative was constituted as 7:8:9:10-tetrahydro-1-azanaphthacene (XIII) by analogy with the preferential dehydrogenation of the pyridine ring in hydrogenated quinolines,[14] and in view of the similarity of the absorption spectrum (curve 1, Fig.2) with that of azanthracene (XII) (curve 2, Fig. 2).[15] Prolonged boiling (72 hr.) with palladized carbon in p-cymene also gave the tetrahydro derivative (XIII) in 20% yield, the rest of the material being charred in the process. Catalytic dehydrogenation with palladized carbon in the absence of a solvent could not be carried out because of the tendency of the compound (IX) to sublime. Complete dehydrogenation was ultimately achieved by heating the compound with palladized carbon in boiling Dowtherm (b.p. 260°) for 10 hours. The aromatic base (I) crystallized from benzene-hexane in golden orange leaflets, m.p. 245.5°. It dissolved in organic solvents to a yellow solution with a green fluorescence and in hydrochloric acid to a violet

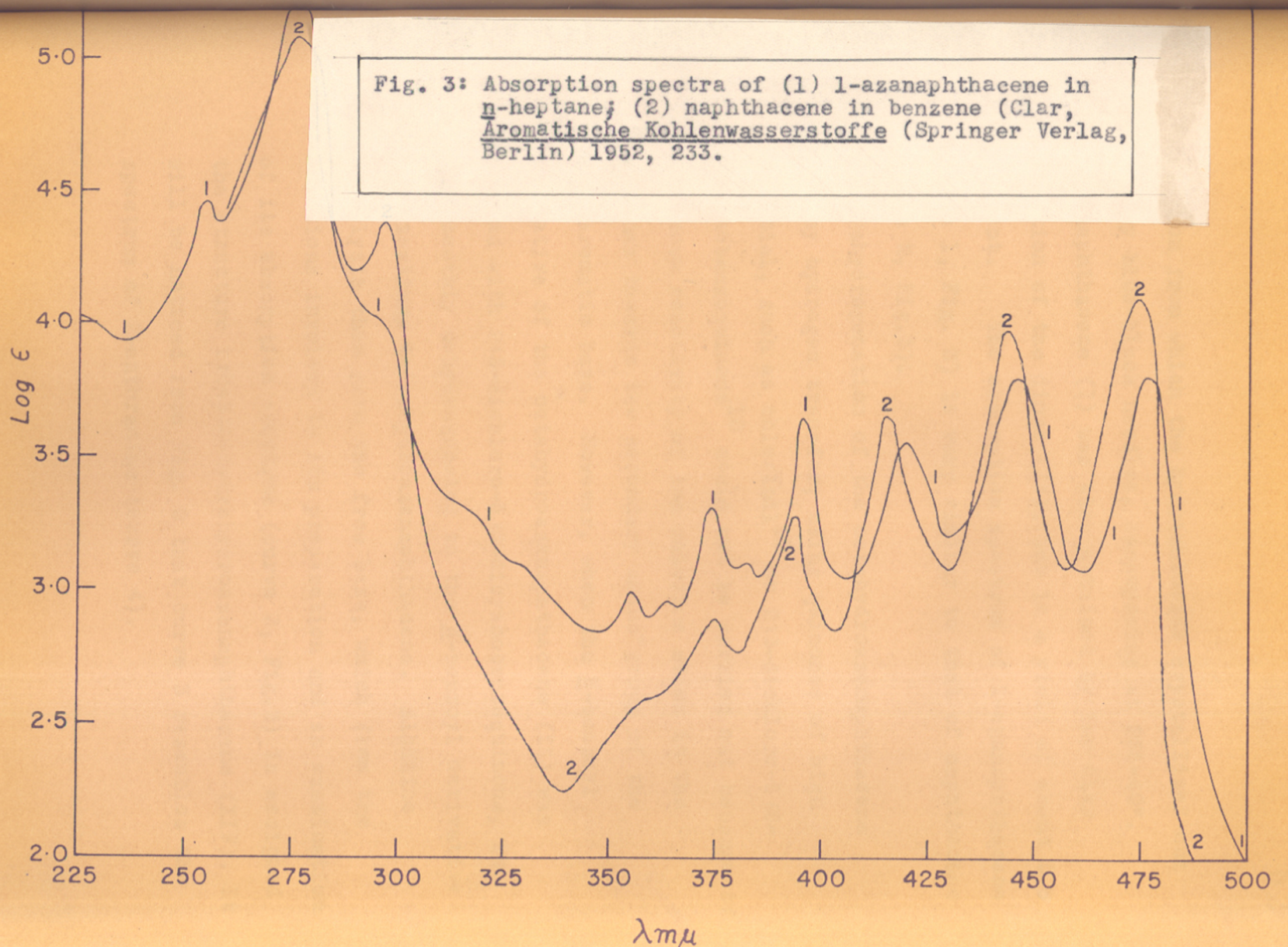


Fig. 3: Absorption spectra of (1) 1-azanaphthacene in n-heptane; (2) naphthacene in benzene (Clar, Aromatische Kohlenwasserstoffe (Springer Verlag, Berlin) 1952, 233.

solution from which the hydrochloride crystallized out in tiny blue-black needles, decomposing at 235-40°. 1-Azanaphthacene (I) was also obtained by the Clar reduction of the dione (IV), but in a yield of about 0.5 per cent. The absorption spectrum of 1-azanaphthacene (curve 1, Fig. 3) is very similar to that of naphthacene (curve 2, Fig.3).

Dehydrogenation of the octahydroazanaphthacene (IX) by hydrogen transfer, using quinones of high potential, such as chloranil[17] or 2:3-dichloro-5:6-dicyanobenzoquinone[18] could not be carried out because of the known reactivity of the chlorine atoms in the quinones towards the secondary amino group of the hydroaromatic base. However, when the N-benzoyl derivative of the octahydroazanaphthacene (IX) was treated with 2:3-dichloro-5:6-dicyanobenzoquinone, it was smoothly dehydrogenated to the N-benzoyl derivative of a tetrahydroazanaphthacene. Alkaline hydrolysis then gave the free base, which from the reactions involved in its preparation and an examination of its absorption spectrum (curve 3, Fig.2) is assigned the structure 1:2:3:4-tetrahydroazanaphthacene (XIV). It will be noticed from Fig. 2 that curve 3 resembles the spectrum of 2-anthramine (curve 4).

EXPERIMENTAL

12-Chloro-1-azanaphthacene-6:11-dione (VII):

1-Chloro-2-aminoanthraquinone (50 g.) was dissolved in conc. sulphuric acid (400 ml.), finely powdered arsenic pentoxide (50 g.) added and stirred. A mixture of glycerine (50 g.) and water (75 ml.) was added at 100° in the course of 1 hr. The temperature was cautiously raised to 135° and this temperature maintained for 1 hour. After cooling, the reaction mixture was drowned in water and filtered. The residue was washed free from acid, dried, and extracted with boiling o-dichlorobenzene. On cooling, 12-chloro-1-azanaphthacene-6:11-dione crystallized in greenish yellow needles (32 g.), m.p. 318° (Found: N, 4.3; Cl, 12.4. $C_{17}H_8ClNO_2$ requires N, 4.7; Cl, 12.1%).

1-Azanaphthacene-6:11-dione (IV):

12-Chloro-1-azanaphthacene-6:11-dione (30 g.) was precipitated from sulphuric acid, filtered, washed, and the wet cake suspended in water (2 l.) containing caustic soda (75 g.). On warming to 60° sodium hydrosulphite (90 g.) was added slowly with mechanical agitation. The green solution of the vat gradually became deep red. The temperature was maintained at 60° for 3 hours with stirring. The precipitate obtained by

air oxidation crystallized from o-dichlorobenzene in yellow-brown needles (22 g.), m.p. 322°.

Disodium salt of the disulphuric ester of 6:11-dihydroxy-1-azanaphthacene (VIII):

Methyl chlorosulphonate (70 g.), prepared from methanol and sulphuryl chloride and fractionally distilled to remove dimethyl sulphate, was added to a mixture of dimethyl formamide (120 ml.) and acetone (80 ml.) kept at 5°. Finely divided 1-azanaphthacene-6:11-dione (IV; 20 g.) was then added, followed by an equal weight of copper bronze. After stirring for 5 hours at 10°, the mixture was poured into water (1 l.) containing caustic soda (60 g.) and filtered. The deep orange-brown filtrate was extracted with benzene to remove dimethyl formamide. The aqueous solution contained 21.6 g. of the disodium salt (VIII), corresponding to 12 g. of the quinone (IV). The estimation was carried out by the ceric sulphate method.

Hydrogenolysis of the disodium salt of the disulphuric ester (VIII):

The solution obtained above, containing 20 g. of (VIII), was made up to two litres, and caustic soda (200 g.) added. The alkaline solution was heated on a boiling water-bath and Raney alloy (200 g.) gradually added in the course of 3 hours. After stirring for 3

hours more, the reaction mixture was filtered. The nickel residue was not deactivated by treatment with acid, but washed with water and extracted with alcohol. The alcohol extract, which was reddish brown in colour with a blue fluorescence, on concentration and cooling gave almost colourless, shining plates of octahydro-1-azanaphthacene (IX; 3.1 g.). Vacuum sublimation (200°/0.5 mm.) and crystallization of the sublimate from petroleum ether (b.p. 70-80°) gave pale greenish yellow plates, m.p. 209° (Found: C, 86.4; H, 8.1; N, 6.3. $C_{17}H_{19}N$ requires C, 86.0; H, 8.1; N, 5.9%). The substance dissolved in dilute hydrochloric acid giving a colourless solution from which the hydrochloride ~~acid-giving-a-colourless-solution-~~ crystallized in colourless plates, decomposing at 195-200° (Found: C, 74.9; H, 7.8. $C_{17}H_{20}ClN$ requires C, 74.8; H, 7.3%). The trinitrobenzene derivative of the substance crystallized from alcohol in long black needles, m.p. 196° (Found: C, 61.8; H, 4.8; N, 13.0. $C_{23}H_{22}N_4O_6$ requires C, 61.3; H, 4.9; N, 12.5%). The N-benzoyl derivative, prepared by shaking the substance with benzoyl chloride and aqueous caustic soda, crystallized from alcohol in long colourless needles, m.p. 188° (Found: C, 84.5; H, 6.5; N, 4.5. $C_{24}H_{23}NO$ requires C, 84.4; H, 6.7; N, 4.1%).

Dehydrogenation of octahydro-1-azanaphthacene (IX):

(a) By distillation over litharge: A mixture of (IX)(0.5 g.) and litharge (10 g.) was heated on an open flame in a current of carbon dioxide, and the vapours passed over a heated bed of litharge. An orange sublimate (0.2 g.) collected on the cooler part of the tube. The substance was dissolved in hexane containing a little benzene and the solution chromatographed on alumina in ultraviolet light. The chromatogram was developed and eluted with hexane-benzene mixture. The first fraction, colourless with a blue fluorescence, gave pale yellow plates (0.025 g.) m.p. 209°, undepressed when mixed with octahydro-azanaphthacene (IX). The second fraction, pale yellow with a bluish green fluorescence, gave shining greenish yellow plates (0.1 g.), m.p. 212° (Found: C, 87.1; H, 6.7. $C_{17}H_{15}N$ requires C, 87.5; H, 6.5%). The picrate of the substance crystallized from alcohol in long reddish brown needles, m.p. 271° (decomp.) (Found: N, 12.4. $C_{23}H_{18}N_4O_7$ requires N, 12.1%). The third fraction, yellow with a green fluorescence, gave yellow plates (0.015 g.), m.p. 214° (Found: C, 87.7; H, 5.8. $C_{17}H_{13}N$ requires C, 88.3; H, 5.7%). A brown zone at the top could not be eluted with benzene.

(b) With palladium-charcoal in p-cymene: A mixture of (IX)(200 mg.) and 10% palladium-charcoal (100 mg.) was refluxed with p-cymene (10 ml.) for 72 hours. The catalyst was filtered and washed with benzene. The filtrate and washings were steam-distilled. The brown sticky residue was dissolved in benzene and the solution run through a short column of alumina. Removal of the solvent from the clear yellow percolate, which had a green fluorescence, gave yellow plates, which were recrystallized from hexane-benzene. The substance (20 mg.) had m.p. 212°, undepressed when mixed with the tetrahydroazanaphthacene obtained by litharge dehydrogenation (Found: C, 87.5; H, 6.5; N, 6.1. $C_{17}H_{15}N$ requires C, 87.5; H, 6.5; N, 6.0%).

(c) With palladium-charcoal in Dowtherm: A mixture of (IX) (200 mg.) and 10% palladium-charcoal was refluxed with Dowtherm (5 ml.) in a small dehydrogenation apparatus, which was heated in a metal bath at 280°. Dry carbon dioxide was led in, and the hydrogen evolved was collected in a nitrometer. Ten hours refluxing was required for the evolution of the theoretical amount of hydrogen. After removing the catalyst, the solvent was steam-distilled. The residue was dissolved in benzene, and the solution run through a short column of alumina. The orange-yellow percolate,

which had a green fluorescence, yielded golden orange plates (20 mg.). After recrystallization from hexane-benzene the substance melted at 245.5° with partial sublimation (Found: C, 88.7; H, 4.9; N, 5.9. $C_{17}H_{11}N$ requires C, 89.0; H, 4.8; N, 6.1%). The aromatic base dissolved in hydrochloric acid giving a violet solution, from which the hydrochloride crystallized in tiny black needles, decomposing at 235-40° (Found: Cl, 12.7. $C_{17}H_{12}ClN$ requires Cl, 13.3%).

Dehydrogenation of the N-benzoyl derivative of octahydroazanaphthacene with 2:3-dichloro-5:6-dicyanobenzoquinone:

N-Benzoyl-octahydroazanaphthacene (0.4 g.) was dissolved in benzene (5 ml.), 2:3-dichloro-5:6-dicyanobenzoquinone (0.55 g.) partially dissolved in benzene (10 ml.) was gradually added, and the mixture refluxed for 2 hours, during which the initial red solution became colourless and a white precipitate appeared. After dilution with petroleum ether, the mixture was filtered. The residue was crystallized from aqueous alcohol giving 2:3-dichloro-5:6-dicyanoquinol, m.p. 265° (decomp.). The filtrate on evaporation of the solvent gave a yellow powder, which was washed with dilute caustic soda solution and

filtered. Crystallization from alcohol gave long yellow needles (300 mg.), m.p. 216° (Found: C, 85.1; H, 5.6; N, 4.2. $C_{24}H_{19}NO$ requires C, 85.4; H, 5.6; N, 4.2%).

1:2:3:4-Tetrahydroazanaphthacene (XIV):

The N-benzoyl derivative (0.15 g.) obtained above was refluxed with 15% methanolic caustic potash (5 ml.) for 5 hrs. when the free base separated as an orange powder. The mixture was diluted with water and filtered. The substance crystallized from hexane-benzene in orange plates, m.p. 251° (decomp.) (Found: C, 87.6; H, 6.4. $C_{17}H_{15}N$ requires C, 87.5; H, 6.5%). The substance was found to be unstable in solution when exposed to light, and crystallization had to be carried out in flasks protected from light.

~~Clear~~

Clar reduction of 1-azanaphthacene-6:11-dione (IV):

A mixture of (IV)(1 g.), sodium chloride (1 g.), zinc dust (1 g.) and freshly fused zinc chloride (5 g.) was heated at 290-300° for 10 minutes. The product was then taken up in 3% hydrochloric acid (100 ml.) and filtered. The filtrate was pale yellow and did not give any precipitate on adding excess of caustic soda. The residue was extracted with alkaline hydrosulphite

and then with benzene. The hydrosulphite extract on air oxidation, gave a small amount (50 mg.) of the original quinone. The benzene extract, after passing through a short column of alumina, yielded orange plates (4 mg.), which after recrystallization hexane-benzene had m.p. 245°, undepressed when mixed with 1-azanaphthacene obtained by palladium-charcoal dehydrogenation.

References

1. Desai, Ramanathan and Venkataraman, J. Sci. Ind. Res. 1956, 15B, 279.

2. Allen, Six-membered heterocyclic nitrogen compounds with four condensed rings, p.3, Interscience, 1951.

3. D.R.P. 171,939; Frdl. 8 (1905-7), 369.

4. Graebe, Ber., 1884, 17, 170; Ann., 1880, 201, 333.

5. Pandit, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1950, 32A, 39.

6. Pandit, Ph.D. Thesis, Bombay University, 1952.

7. D.R.P. 565,968; Frdl., 1934, 27, 2456.

8. BIOS Final Report 987, p.27.

9. Coffey, Driver, Fairweather, Irving and ICI, BP. 610,117.

10. Patni, unpublished work, quoted in Venkataraman, The Chemistry of Synthetic Dyes, vol. II, p. 1058, Academic Press, New York, 1952.

11. Ramanathan, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1953, 38A, 161.

12. Albert, Brown and Duewell, J. Chem. Soc., 1948, 1284.

13. von Braun and Gruber, Ber., 1922, 55, 1710.

14. Ehrenstein and Bunge, ibid., 1934, 67B, 1715.

15. Etienne and Legrand, Bull. soc. chim. France, 1953, 108.

16. Clar, Ber., 1939, 72B, 1645.

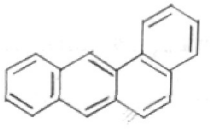
17. Arnold and Collins, J. Am. Chem. Soc., 1939, 61, 1407.

18. Braude, Brook and Linstead, J. Chem. Soc., 1954, 3569.

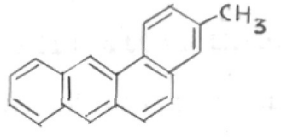
Part III

THE SYNTHESIS OF 1:2-BENZANTHRACENE AND METHYLBENZANTHRACENES

1:2-Benzanthracene (I) and all the twelve theoretically possible monomethyl derivatives of it have been synthesized and evaluated as to their physiological action. Several of these methyl benzanthracenes show marked carcinogenic activity,[1] and are often required in appreciable amount by the research workers in that field. In this Part are described alternative methods for preparing 1:2-benzanthracene (I), 3'- and 4-methylbenzanthracenes (II and III). The synthesis is based on our new



(I)



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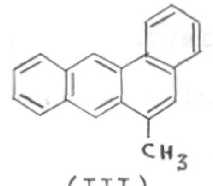


(III)

general method described earlier (see Part I) for reducing quinones to the corresponding hydrocarbon derivatives and may have advantages over the syntheses previously reported for these hydrocarbons.

In the synthesis of (I), 1:2-benzanthraquinone was converted into its leuco sulphuric ester by the process employed for the preparation of disulphuric ester of anthrahydroquinone.[2] The hydrogenolysis of the ester gave an octahydrobenzanthracene, the

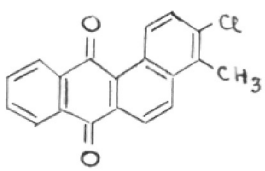
dehydrogenation of which led to benzanthracene (I) in an overall yield of 70%. Benzanthracene (I) was also obtained in high yield (70%) by the reduction of benzanthraquinone with aluminium cyclohexyloxide in cyclohexanol (the Coffey reduction).[3]

Elbs obtained (I) in impure state by the reduction of benzanthraquinone with zinc and aqueous ammonia.[4] Badger and Cook prepared it by refluxing the quinone with stannous chloride and conc. hydrochloric acid in glacial acetic acid and then reducing the intermediate resinous anthol to the hydrocarbon with sodium hydroxide and zinc dust. However, the product obtained was crude and required purification through the crystallization from acetic acid and boiling in benzene solution with maleic anhydride.[5] The same procedure was followed for the synthesis of (I) by Newman and Gaertner.[6]

For the synthesis of 3'-methylbenzanthracene (II), use was made of 1-chloro-2-methylnaphthalene as a component in a phthalic anhydride synthesis. It was observed by Scholl that phthalic anhydride condensed with 1:2-disubstituted naphthalene derivatives in the 6-position of the unsubstituted ring. For example, 2-chloro-1-methylnaphthalene condensed with phthalic

anhydride to give 2-(5'-methyl-6'-chloronaphthoyl-2')-benzoic acid, which, on cyclization, gave 3'-chloro-4'-methylbenzanthraquinone (IV).[7] It was thought, therefore, that the condensation of 1-chloro-2-methylnaphthalene with phthalic anhydride should lead to the formation of 3'-methyl-4'-chlorobenzanthraquinone (V). As expected the hydrogenolysis of the leuco sulphuric ester of the methylchlorobenzanthraquinone so obtained and the subsequent dehydrogenation of the intermediate hydrogenated product, gave 3'-methylbenzanthracene (II).

3'-Methylbenzanthracene was obtained by Cook in poor yield (5-10%), by the pyrolysis of 1-benzoyl-2:6-dimethylnaphthalene.[8] It was synthesized by Newman by a laborious process which involved several steps.[6] The sulphuric ester method has considerable advantages over both these methods as it is short and gives pure product in an overall yield of 40%.



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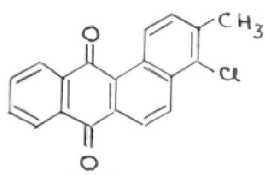

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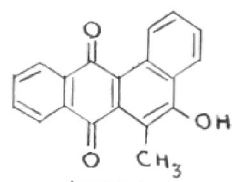

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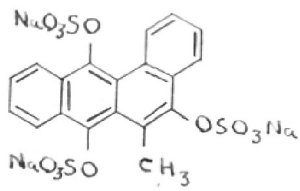


(VII)

(A) Common end to this ff. Fieser reduces to benzanthracene, demethylates & oxidizes

The synthesis of 4-methyl-1:2-benzanthracene (III) was achieved through the trisulphuric ester of leuco 3-hydroxy-4-methylbenzanthraquinone (VII). The desired benzanthraquinone derivative, viz. 3-hydroxy-4-methyl-benzanthraquinone (VI) was obtained by condensing 3-hydroxybenzanthraquinone with aqueous caustic soda, sodium hydrosulphite and formaldehyde (the Marschalk reaction).[9] The intermediate 3-hydroxybenzanthraquinone was prepared by a slight modification of Fieser's method[10] as follows. α-Methoxynaphthalene was condensed with phthalic anhydride, the resulting keto acid, 2-(4'-methoxynaphthoyl-1')-benzoic acid was reduced to (4-methoxynaphthyl-1)-phenylmethane-2'-carboxylic acid, the latter was cyclized to 3-methoxy-1:2-benz-10-anthrone, (A) which was oxidized to 3-methoxybenzanthraquinone with sodium dichromate in aqueous acetic acid.[11] The latter was demethylated to 3-hydroxybenzanthraquinone with aluminium chloride-sodium chloride melt at 130-40° in high yield. As a pilot experiment the trisulphuric ester of leuco 2-hydroxyanthraquinone was reduced by Raney alloy and aqueous caustic soda to a hydrogenated anthracene, which was then dehydrogenated to anthracene. (*) The reduction of the trisulphuric ester of leuco-3-hydroxy-4-methylbenzanthraquinone (VII), similarly,

(*) showing that nuclear hydroxyl groups in the ag series can be reduced via the sulphonic ester.

gave a hydrocarbon, analyzing for a hexahydro-4-methyl benzanthracene which was dehydrogenated to 4-methyl-benzanthracene (III) by boiling in benzene with dichloro-diacyano benzoquinone.[12]

The formation of 4-methyl-1:2-benzanthracene by pyrolysis of 1-benzoyl-2:3-dimethylnaphthalene was first described by Fieser and Peters.[13] It was later on synthesized by Fieser and Jones, using 6-methyltetralin as a compound in the Friedel-Crafts condensation with phthalic anhydride.[14] The method was modified by Newman, the main improvement lay in the use of pure methyl tetralin obtained by the reduction of 7-methyl-1-tetralone instead of the mixture of methyltetralins obtained from the hydrogenation of 2-methylnaphthalene.[6] Bachman and coworkers prepared (III) in five steps, starting from 9-methyl-1:2:3:4-tetrahydrophenanthrene and succinic anhydride.[15] More recently Mukherji and coworkers have worked out a new route to this hydrocarbon in four steps, starting from 2-alkylcyclohexanone and tetralin, based on the method develpped by them for the synthesis of polycyclic aromatic hydrocarbons.[16] Our method provides an alternative route to this hydrogarbon and has the advantage of using easily available intermediates. Also, since the Marschalk reaction is a general reaction for introducing an alkyl

group in anthraquinone nucleus, this route provides a general method for making 4-alkyl-1:2-benzanthracenes.

E X P E R I M E N T A L

Disodium salt of the disulphuric ester of benzanthrahydroquinone:

Chlorosulphonic acid (5 ml.) was slowly run into pyridine (50 ml.) below 20°. The mixture was heated to 60°, benzanthraquinone (5 g.) was added, followed by an equal weight of copper bronze. After stirring at 60-65° for 3 hrs., the mixture was poured into 150 ml. of 10% caustic soda solution and filtered from copper residue. From the filtrate pyridine was removed by steam distillation, the residue was cooled, just acidified with hydrochloric acid, and filtered from the impurities. The filtrate, which exhibited violet fluorescene on dilution, contained the ester (disodium salt) in quantitative yield.

Hydrogenolysis of the disodium salt of the disulphuric ester of benzanthrahydroquinone:

The solution obtained above, containing 6.2 g. of the ester (disodium salt), corresponding to 3.5 g. of the quinone, was made up to 620 ml., and caustic soda (62 g.) added. The alkaline solution was heated on boiling water bath and Raney alloy (62 g.) added in course of 2 hrs. After stirring for 2 hrs. more, the mixture was cooled, filtered, the nickel residue deactivated with hydrochloric acid and extracted with

W. The Chem. of S. D. (Vol. II), p. 1058. Academic Press, New York, 1952.

alcohol. The alcohol extract on removal of the solvent gave 2.7 g. of a pale yellow viscous oil, b.p. 175-8°/0.7 mm. (Found: C, 91.3; H, 8.3. $C_{18}H_{20}$ requires C, 91.5; H, 8.5%).

1:2-Benzanthracene (I):

Hydrogenated hydrocarbon (0.2 g.) was dissolved in benzene (5 ml.), 2:3-dichloro-5:6-dicyanobenzoquinone (1 g.) in 10 ml. benzene was added, and the mixture refluxed for 2 hrs. After dilution with petroleum ether, the precipitated quinol was filtered and the filtrate run through a short column of alumina. The colourless percolate, which had a blue fluorescence, on removal of the solvent, gave the aromatic hydrocarbon, which crystallized from alcohol in shining leaflets (0.20 g.), m.p. 159° (Found: C, 94.6; H, 5.3; $C_{18}H_{12}$ requires C, 94.7; H, 5.3%). lit. (ref.5) m.p. 158-59°).

Reduction of 1:2-benzanthraquinone with aluminium cyclohexyloxide:

1:2-Benzanthraquinone (1 g.) was refluxed with a solution of aluminium (1 g.) in cyclohexanol (20 ml.) for 40 hrs. The solvent was distilled off, and the residue poured into 3% caustic soda solution. The colourless solution was filtered and the residue extracted with alcohol. The alcohol extract, on

concentration and cooling, gave pale yellow plates (0.7 g.), m.p. 151-52°. Recrystallization from alcohol gave almost colourless, shining plates, m.p. 159°, undepressed when mixed with 1:2-benzanthracene obtained in the previous experiment.

1-Chloro-2-methylnaphthalene:

Chlorine gas generated from potassium permanganate (10 g.) and conc. hydrochloric acid was bubbled through 2-methylnaphthalene (14.2 g.), containing traces of iodine at room temperature (30°) until the increase in weight was 3.5 g. After removing the hydrogen chloride, the product was distilled under reduced pressure and the fraction, b.p. 108-110°/2 mm. was collected (yield 14 g.).

2-(5'-Chloro-6'-methylnaphthoyl-2')benzoic acid:

To a clear solution of phthalic anhydride (8.5 g.) and 1-chloro-2-methylnaphthalene (9.8 g.) in acetylene tetrachloride (50 ml.) was added anhydrous aluminium chloride (15 g.) in four lots in one hour at room temperature. The mixture was stirred ~~at room temperature~~ for ~~eight hours~~ 8 hrs and left overnight, ~~It was~~ poured into ice-cold hydrochloric acid, and the solvent removed by steam distillation. The resinous residue was washed with water, dissolved in sodium carbonate solution

and reprecipitated with acid, when the keto acid was obtained as granular mass (16 g.), (A)

3'-Chloro-4'-methylbenzanthraquinone (V):

Ten grams of 2-(5'-chloro-6'-methyl-2'-naphthoyl-1')-benzoic acid was stirred with conc. sulphuric acid (100 ml.) and boric acid (10 g.) at 60-70° for 4 hrs. The mixture was poured into water, the greenish yellow precipitate was filtered, washed with dilute caustic soda solution and dried (yield 6.5 g.). It crystallized from benzene in thin long yellow needles, m.p. 227° (Found: C, 74.4; H, 3.5; $C_{19}H_{11}ClO_2$ requires C, 74.3; H, 3.6%).

Disodium salt of the disulphuric ester of 3'-methyl-4'-chlorobenzanthrahydroquinone:

The esterification was carried out exactly as in case of benzanthraquinone; thus, 6.5 g. of the quinone (V) gave a solution containing 8.7 g. of the ester (disodium salt) corresponding to 5.25 g. of the quinone.

Hydrogenolysis of the disodium salt of the disulphuric ester of 3'-methyl-4'-chlorobenzanthrahydroquinone:

A solution containing 8 g. of the ester (disodium salt) was made up to 800 ml., and 80 g. caustic soda added. The alkaline solution was heated on boiling water-

(A) m.p. 90–100° after softening at 60°. The ~~B~~ was substance was non-crystallizable, but cyclization yielded a readily xallizable ag. deriv. When the air was pumped by running the dark brown soln in benzene ~~was~~ thro a short column of Florex, recovering the pale yellow product from the percolate, ~~by~~ diluting the alcoholic soln with water, & letting stand in a refrigerator for a few days, it was obtd as a buff coloured powder, melting indefinitely at about 120° (Anal.: C, 70·1; H, 4·6; Cl, 9·4. ~~C~~ $C_{19}H_{13}O_3Cl$ requires C, 70·4; H, 4·6; Cl, 11·0%). Fieser & Peters[13] encountered similar difficulty in xalg the condensation prods of phth. anh. & methylnaphthalenes.

bath and Raney alloy (80 g.) added in 2 hrs. After stirring for 3 hrs. more, the mixture was cooled, filtered, and the nickel residue, after deactivation with acid, extracted with alcohol. The alcohol extract ~~on removal of the solvent~~ yielded 3.6 g. of a viscous oil, b.p. 205-10°/2 mm. (Found: C, 91.8; H, 8.3. $C_{19}H_{14}$ requires C, 91.6; H, 8.4%).

3'-Methylbenzanthracene (II):

A mixture of the hydrogenated hydrocarbon (~~0.4~~ 2 g.) and 2:3-dichloro-5:6-dicyanobenzoquinone (1.5 g.) was refluxed with benzene (~~20~~ 100 ml.) for 2 hrs. The precipitated quinol was filtered off and the filtrate run through a short column of alumina. The pale yellow percolate on removal of solvent gave yellow plates, which crystallized from alcohol in shining pale yellow plates (~~0.35~~ 1.75 g.), m.p. 160° (Found: C, 93.4; H, 6.0. $C_{19}H_{14}$ requires C, 94.2; H, 5.8%. ~~lit. (ref.8) m.p. 160°~~). The picrate crystallized from alcohol in red needles, m.p. 144° ~~(lit.(ref.8) m.p. 144-5°)~~. Cook[9] quotes m.p. 160° for the hydrocarbon & 144-45° for the picrate.

3-Methoxy-1:2-benzanthraquinone: from p. 85

3-Methoxy-1:2-benz-10-anthrone was prepared according to Fieser and Dietz, starting from α-methoxynaphthalene and phthalic anhydride.[10] The anthrone (40 g.) was suspended in ~~200 ml. of~~ (200 ml) glacial acetic acid and

treated with sodium dichromate (40 g.) dissolved in ~~20 ml. of~~ water (20 ml). The mixture was stirred on ~~boiling~~ a water-bath for 15 minutes, during which the reaction mixture boiled vigorously. Dilution into cold water gave a bright orange-brown precipitate (33 g.) of the quinone. Crystallization from benzene gave brown needles, m.p. 188° (~~lit. (ref. 10)~~ Fieser & Dietz, m.p. 188.5°).

3-Hydroxy-1:2-benzanthraquinone:

An intimate mixture of aluminium chloride (50 g.) and sodium chloride (10 g.) was melted on a free flame. 3-Methoxybenzanthraquinone (10 g.) was quickly added to the melt and the mixture stirred with a thermometer at 140-45° for 2 mins. The melt was poured into ice-cold 5% hydrochloric acid, when the hydroxy compound separated as an orange-brown precipitate (9.5 g.). The product dissolved in alkali with a deep purple colour, which changed to orange-red on adding sodium hydrosulphite. ~~Its~~ The acetyl derivative, prepared by refluxing ~~it~~ with acetic anhydride and a drop of sulphuric acid, crystallized from benzene in stout, yellow needles, m.p. 232° (~~lit. (ref. 10)~~ Fieser & Dietz, m.p. ~~229-30°~~ 231°). The acetyl derivative ~~could be easily~~ was hydrolysed by dissolving in cold conc. sulphuric acid and pouring into water. The hydroxy compound ~~obtained as bright orange precipitate~~ crystallized

from dioxane in orange-red plates, decomposing at about 250° (Found: C, 78.6; H, 3.8. $C_{18}H_{10}O_3$ requires C, 78.8; H, 3.7%). Diesser & Dietz have not recorded the m.p. or analysis of this compound.

3-Hydroxy-4-methyl-1:2-benzanthraquinone (VI):

3-Hydroxybenzanthraquinone (6 g.) was dissolved in 600 ml. of 3% caustic soda solution (600 ml. 2.N.) and vatted with 15 g. of sodium hydrosulphite at 40-45° for 10 mins. under a nitrogen atmosphere. The soln. was then treated with 4.2 ml. of 37.5% formaldehyde solution (4.2 ml.) and stirred on a boiling water-bath for 1 hr. The mixture was cooled and air-oxidized; on acidification it gave 3-hydroxy-4-methyl-1:2-benzanthraquinone (VI) as an orange-brown precipitate (4.8 g.). The acetyl derivative crystallized from benzene-hexane mixture in thin yellow needles, m.p. 203° (Found: C, 76.7; H, 4.1. $C_{21}H_{14}O_4$ requires C, 76.4; H, 4.2%). The methyl ether (prepared by the action of dimethyl sulphate and sodium hydroxide soln.) crystallized from alcohol in thin yellow needles, m.p. 146°. The acetyl derivative was hydrolyzed by cold conc. sulphuric acid; the hydroxy compound (VI) obtained as orange brown precipitate crystallized from dioxane in orange-brown platelets, m.p. 228° (Found: C, 79.1; H, 4.4. $C_{19}H_{12}O_3$ requires C, 79.2; H, 4.2%).

(Found: C, 79.3; H, 4.5. $C_{21}H_{14}O_3$ requires C, 79.5; H, 4.6%).

Trisodium salt of the trisulphuric ester of leuco 2-hydroxyanthraquinone:

(B) Chlorosulphonic acid (6.5 ml.) was slowly run into a mixture of 2-hydroxyanthraquinone (5 g.) and pyridine (60 ml.) below 20°. After stirring the paste at 20° for 30 mins., the temperature was raised to 60° and copper-bronze (5 g.) added to it. The stirring was continued at this temperature for 3 hrs. more, the reaction mixture was then poured into 250 ml. of 10% caustic soda solution (250 ml) and filtered. From the filtrate, pyridine was removed by steam distillation and the solution filtered again to remove the precipitated impurities. The filtrate was assumed to contain the ester (trisodium salt) in quantitative yield. The solution of the ester exhibited green fluorescence, which changed to blue on adding acid.

→ To p. 82

Hydrogenolysis of the trisodium salt of the trisulphuric ester of 2-hydroxyanthrahydroquinone:

(B) The solution obtained above containing 5 g. of the ester (trisodium salt)(corresponding to 2.25 g. of the quinone) was made up to 500 ml. and made alkaline with 50 g. caustic soda. The solution was heated on a boiling water-bath and Raney alloy (50 g.) added to it in course of 2 hrs. After stirring for 2 hrs. more,

mixture was filtered, the nickel residue deactivated with acid and extracted with alcohol. The alcohol extract on removal of solvent gave a colourless product (~~1.5~~ 3.3 g.), which crystallized from aqueous acetic acid in colourless plates, m.p. 93° (Found: C, 91.1; H, 8.0. $C_{14}H_{14}$ requires C, 92.3; H, 7.7%). The ~~product~~ tetrahydroanthracene (~~0.5~~ 3 g.) was mixed with selenium (1 g.) and heated to 300° gradually. The product was extracted with alcohol, ~~and the extract gave~~ leading to (2.7 g.) (63%) colourless plates, m.p. 217°, undepressed when admixed with anthracene.

~~(crude yield 63%)~~

Trisodium salt of the trisulphuric ester of leuco 3-hydroxy-4-methylbenzanthraquinone (VII):

(A) Chlorosulphonic acid (6 ml.) was slowly run into a mixture of 3-hydroxy-4-methylbenzanthraquinone (VI) (5 g.) and pyridine (50 ml.) below 20°. The paste was stirred at 20° for ~~half an hour~~ 30 min, the temperature then raised to 60° and copper bronze (5 g.) added. After stirring the mixture at this temperature for 3 hrs., it was poured into 200 ml. of 10% ~~caustic soda~~ o-h. solution and filtered. The filtrate, after removal of pyridine, was cooled, just acidified and filtered from brown impurities. The filtrate, which was almost colourless with a blue fluorescence, was used for ~~the~~ hydrogenolysis

Hydrogenolysis of the trisodium salt of the trisulphuric ester (VII): of 3-hydroxy-4-methylbenzanthrahydroquinone

(A) The solution ~~obtained above, containing 10.4 g. of the ester (VII), was~~ made up to 1040 ml., and heated ~~caustic soda (104 g.) added. The alkaline solution was heated to~~ 70° and Raney alloy (104 g.) gradually added ~~to it in course of~~ during 3 hrs. The mixture was then stirred on a boiling water-bath for 3 hrs. ~~more~~, cooled and filtered. The nickel residue was deactivated with dilute hydrochloric acid and extracted with alcohol. The brown viscous oil, obtained after the removal of alcohol, was dissolved in hexane and run through a short column of alumina. The colourless percolate on removal of solvent gave an almost colourless oil (3.2 g.), b.p. 205-8°/2 mm. (Found: C, 91.9; H, 8.1. $C_{19}H_{14}$ requires C, 91.6; H, 8.4%).

4-Methylbenzanthracene (~~III~~):

The ~~H~~ydrogenated hydrocarbon (0.44 g.), 2:3-dichloro-5:6-dicyanobenzoquinone (0.6 g.) and benzene (40 ml.) were refluxed for ~~½ hour~~ 30 min. More quinone (0.6 g.) was added, the mixture refluxed for 2 hrs. ~~more~~, filtered, and the brown filtrate run through a short column of alumina. The clear yellow percolate on removal of solvent gave a brown oil, which was dissolved in alcohol. The alcoholic solution was concentrated and

treated with picric acid. On cooling red-brown needles of the picrate crystallized. After two crystallizations from the same solvent it melted at 148° (Found: C, 64.2; H, 3.6; N, 9.2. $C_{25}H_{17}N_3O_7$ requires C, 63.7; H, 3.6; N, 8.9%). The picrate was decomposed with dilute ammonia and the ~~separated~~ hydrocarbon crystallized from alcohol containing a little benzene; the colourless needles, m.p. 124° (Found: C, 94.0; H, 6.2%. $C_{19}H_{14}$ requires C, 94.2; H, 5.8%). ~~lit. (ref. 14) m.p. 124-124.6°).~~ Diese cf Jones[14] cite m.p. 124-124.6°.

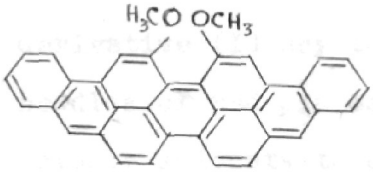
REFERENCES

1. Shear and Lieter, J. Nat. Cancer.Inst., 1941, 2, 214.
2. GP 473,471; Iwamato, Bull. Chem. Soc. Japan, 1936 11, 201.
3. Coffey and Boyd, J. Chem. Soc., 1954, 2468.
4. Elbs, Ber., 1886, 19, 2209.
5. Badger and Cook, J. Chem. Soc., 1939, 802.
6. Newman and Gaertner, J. Am. Chem. Soc., 1950, 72, 264.
7. Schobl, et al., Monatsh., 1921, 41, 583.
8. Cook, J. Chem. Soc., 1932, 456.
9. Marschalk, Bull. Soc. Chim., 1936, 3(5), 1545.
10. Fieser and Dietz, J. Am. Chem. Soc., 1929, 51, 3141.
11. Blicke, ibid., 1932, 54, 146.
12. Braude, Brook and Linstead, J. Chem. Soc., 1954, 3569.
13. Fieser and Peters, J. Am. Chem. Soc., 1932, 54, 3742.
14. Fieser and Jones, ibid., 1938, 60, 1940.
15. Bachman et al., J. Org. Chem., 1947, 12, 596.
16. Vig. Kessar and Mukherji, Nature, 1954, 174, 834.

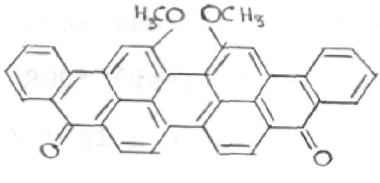
PART IV

THE SYNTHESIS OF 16:17-DIMETHOXYVIOLANTHRENE AND STUDY OF ITS ABSORPTION SPECTRUM

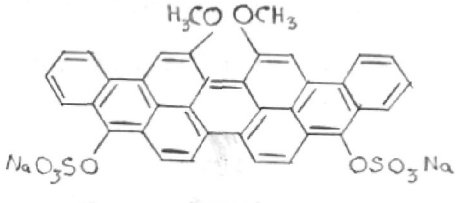
16:17-Dimethoxyviolanthrene (I), the hydrocarbon derivative of the well-known dye, 16:17-dimethoxyviolanthrone (Caledon Jade Green; C.I. 1101; II) has not been described so far in the literature. Its synthesis ~~of~~ is of interest from the point of view of colour and chemical constitution and its stereochemistry. Commercially available Indigosol Green IB, the disulphuric ester (III)



(I)



(II)

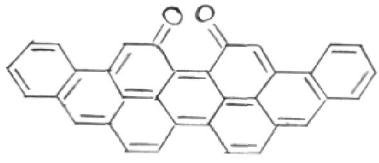


(III)

of leuco 16:17-dimethoxyviolanthrone, provides a suitable raw material for the synthesis of (I) by the method developed earlier (see Part I) for reducing quinones to the corresponding hydrocarbon derivatives. The hydrogenolysis of this ester carried out under usual conditions, using Raney alloy ten times the weight of the ester, gave directly in 20% yield the aromatic hydro-

carbon derivative (I) without nuclear hydrogenation. The yield of (I) was improved to 50% by carrying out the reduction in presence of toluene and using twice the normal amount of Raney alloy. Whether the absence of nuclear hydrogenation is due to the presence of methoxyl groups or is the characteristic property of violanthrene ring system is yet to be investigated. 16:17-Dimethoxy-violanthrene (I) could also be prepared conveniently by the reduction of (II) with aluminium cyclohexyloxide in cyclohexanol (the Coffey reduction).[1] The hydrocarbon derivative (I) crystallized from benzene in orange-red needles or red plates, m.p. 290° (dec.). It dissolved in organic solvents to orange solution with intense green fluorescence; it was sparingly soluble in sulphuric acid giving blue solution.

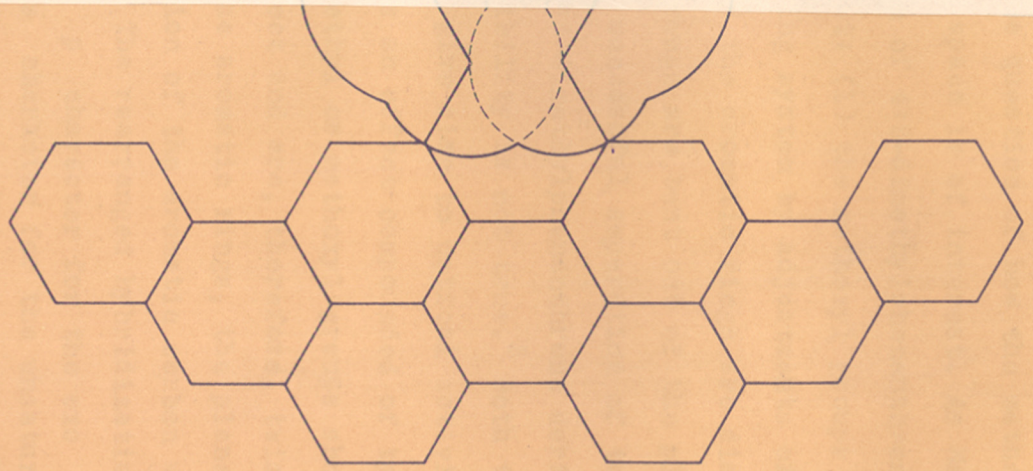
Demethylation of 16:17-dimethoxyviolanthrene (I) with hydrobromic acid in acetic acid gave a quinone,



(IV)

which was formulated as violanthrene-16:17-dione (IV), an isomer of violanthrone. The quinone dissolves in conc. sulphuric acid with blue green colour and dyes cotton an olive-green shade from a blue vat.

Fig. 1: Scale drawing of the 16:17-dimethoxyviolanthrene molecule.



A scale drawing of 16:17-dimethoxyviolanthrene molecule is given in Fig. 1, and the overlap of the van der Waals radii of the vicinal methoxyl group is clear. The compound is of the 4:5-dimethylphenanthrene-type and the question of how the methoxyl groups are located in space is of interest. As Newman[2] has pointed out in case of 4:5-dimethylphenanthrene, three possibilities exist: (1) the methoxyl groups become coplanar with the ring system by adjustments of bond lengths and angles; (2) the aromatic rings are distorted; (3) the methoxyl groups are bent out of the plane of the aromatic rings. The successful separation of the optically active forms of 4:5-dimethylphenanthrene derivative shows that the first possibility is not true.[3] Both the latter possibilities can give rise to optical activity. Theoretically one expects an effect compounded of types (2) and (3). When the methyl or methoxyl groups show a pronounced steric effect and are, therefore, twisted out of the plane of the aromatic rings, the planar triagonal sp^2 hybridization of the aromatic carbon valencies is disturbed. The rearranged hybridization involves pronounced p character for the exo C-C bond and enhanced s character for the unsaturation electron on the aromatic carbon. This leads to slight non-planarity of the substituted aromatic ring. The characteristics of the spectra of such bent benzene rings are: (1) a lack of fine structure and (2) a slight

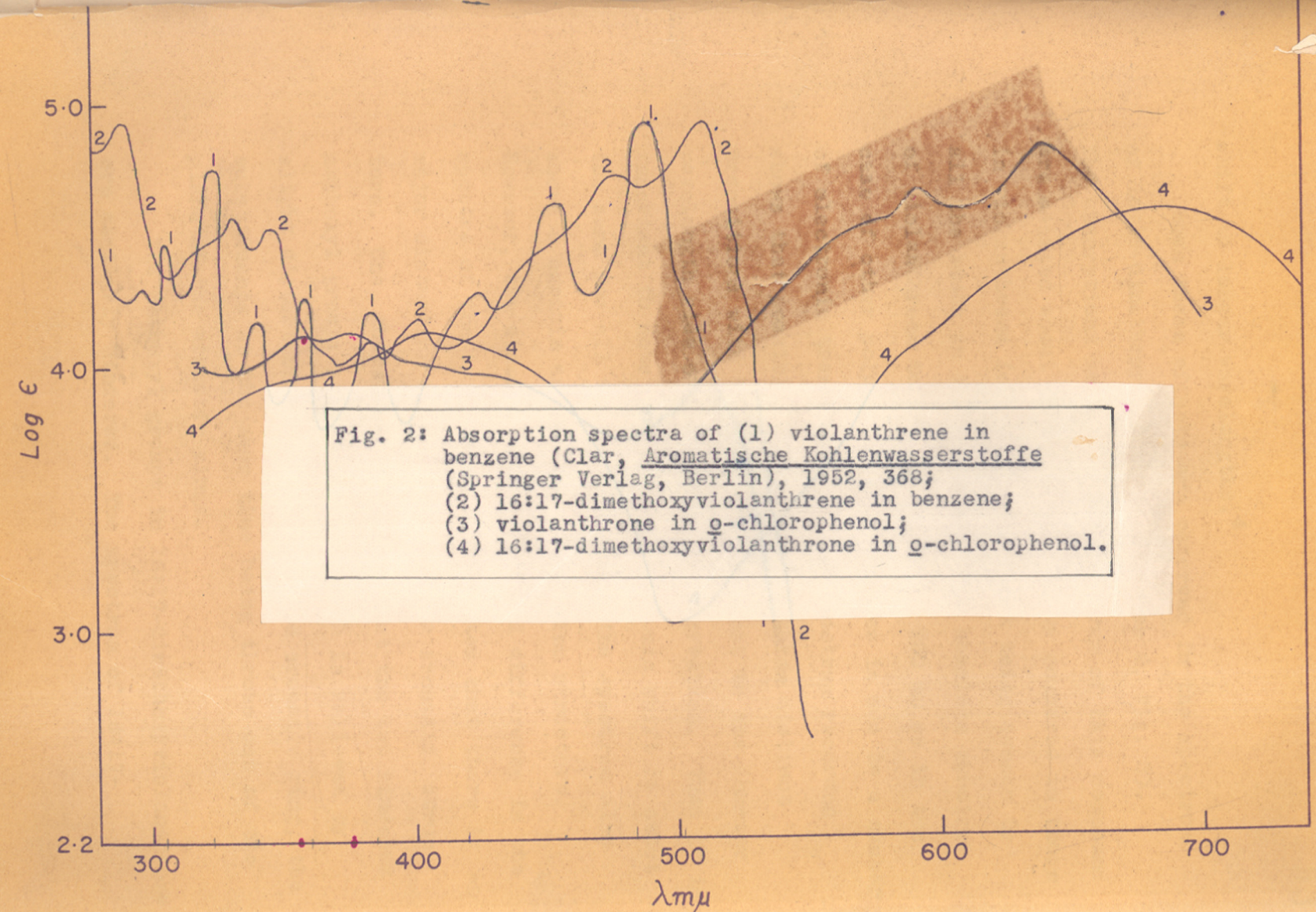


Fig. 2: Absorption spectra of (1) violanthrene in benzene (Clar, Aromatische Kohlenwasserstoffe (Springer Verlag, Berlin), 1952, 368;
(2) 16:17-dimethoxyviolanthrene in benzene;
(3) violanthrone in o-chlorophenol;
(4) 16:17-dimethoxyviolanthrone in o-chlorophenol.

shift to longer wavelengths.[4]

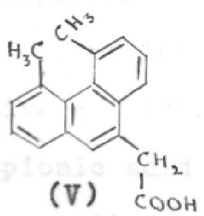
Both these effects are observed in the spectrum of 16:17-dimethoxyviolanthrene (curve 2, Fig. 2). The absorption maxima in the spectrum of this compound are shifted about 20 mμ to the red as compared to those in violanthrene (curve 1), the shift being common to all the bands in the spectrum. The complete spectrum of violanthrene to the red of about 200 mμ as in the case of other polycyclic hydrocarbons is due to a number of electronic transitions.[5] The spectrum recorded shows that possibly it consists of three distinct transitions with the fourth lying just to the shorter wavelength side of the limit of observation. Thus it is important to note that the bathochromic shift is about the same for all the transitions. The spectrum also shows a certain amount of loss of fine structure. However, the absence of a pronounced difference in the spectra of the two compounds indicates that there is no major distortion in the rigid planar aromatic structure. One, therefore, concludes that the two hindered methoxyl groups produce strain which is relieved by slight distortion of the substituted aromatic ring, the substituents at the same time being thrown out of the plane of the aromatic rings.

The methoxyl groups in 16:17-dimethoxyviolanthrone are similarly hindered. The spectrum of 16:17-

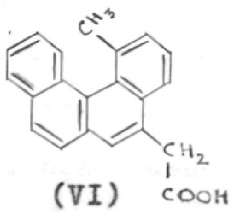
dimethoxyviolanthrone (curve 4, Fig. 2) in relation to that of parent violanthrone (curve 3) was studied by Rao *et al*.[6] The bathochromic shift in the spectrum of 16:17-dimethoxy compound clearly shows that the methoxyl groups do exercise their normal auxochromic effect; but they can do so only if they enter into electronic interaction with the violanthrone ring system, which in turn is contingent on the coplanarity of the methoxyl groups and the violanthrone ring system. It was therefore concluded that, on account of the high energy of resonance stabilization, the polynuclear ring system of the violanthrone undergoes a slight adjustment of bond angles and tends to remain coplanar with the two methoxyl groups. To force the methoxyl groups into the same plane as the ring system in this manner needs extra energy, so that the potential energy of the dimethoxyviolanthrone molecule increases, leading to a bathochromic shift of the absorption spectrum. The present investigation on the spectrum of 16:17-dimethoxyviolanthrene corroborates the conclusions. In case of 16:17-dimethoxyviolanthrone, however, the bathochromic effect on the bonds arising out of different transitions is not constant, the long wavelength band being displaced to greater extent than the short wavelength band, as compared to those of violanthrone. This can be explained if it is remembered that the long wavelength band in

violanthrone arises out of an n-π transition of the carbonyl groups and hence the distortion envisaged probably affects the non-bonding as well as excited π one electron orbitals. In case of polycyclic hydrocarbons the transitions are all π-π transitions and therefore the effect on the bonding and anti-bonding one electron orbitals is common in all the energy levels, but here again the fact that the shift is of the same order in all the transitions could probably be taken to indicate the ground state which is common to all the transitions is affected.

"Optical activity which arises from out-of-plane distortions of aromatic polycyclic compounds represents a newer development in the field of molecular assymetry"[4]. The stereoisomerism of this type has been termed optical activity due to intramolecular overcrowding by Bell and Waring[7] and is now well established in a number of compounds in which a normal planar molecule becomes slightly nonplanar due to steric hindrance. The possibility that the compounds of this type may be resolved into its optically active forms was first pointed by Newman[2] in 1940 and has been successfully demonstrated by the partial resolution of V,[3] VI,[8]



(V)



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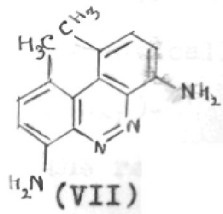
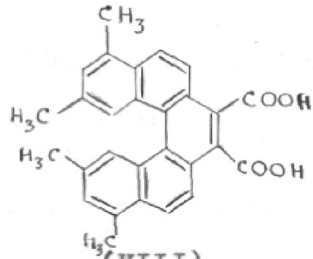
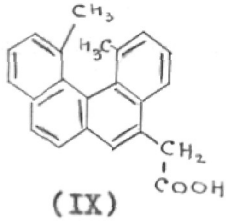


(VII)

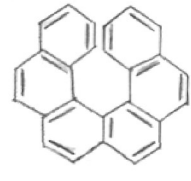


(VIII)

VII,[9] and VIII.[7] The optical stability in each case, however, was low; the compounds racemized readily, either at room temperature or, in case of 1:8-diamino-4:5-dimethyldiazaphenanthrene (VII) when kept in methanolic solution for one hour at 60°. Hall and Turner[10] have prepared 9:10-dihydro-3:4:5:6-dibenzophenanthrene in optical active form, α_D 1496°. The hydrocarbon is stable in benzene at 60° but racemizes in boiling toluene or, more quickly in boiling ethylbenzene. The most stable (from the point of view of optical activity) compounds of this type are 1,12-dimethylbenzo [c] phenanthrene-5-acetic acid[11] (IX) and phenanthro-[3:4;c]-phenanthrene[12] (X; hexahelicene), the former being stable upto 200°.



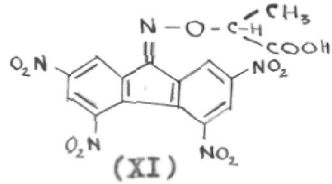
(IX)



(X)

An important development in the resolution of stereoisomers of this type is the synthesis of the optically active α-(2:4:5:7-tetranitrofluorenidylaminooxy)-propionic acid (XI), a reagent useful for the resolution of aromatic compounds of this type which do not have

the functional groups usually needed to effect the resolution by convential reagents.[13]



(XI)

The compound (XI) forms crystalline complexes with a number of aromatic hydrocarbons and has been used in the resolution of 1-naphthyl sec-butyl ether[13] and hexahelicene[12] (X).

The spectral study of 16:17-dimethoxyviolanthrene (I) reveals that it is an overcrowded molecule and it should be possible to separate it into its optically active forms by complex formation with the enantiomorphic forms of (XI). Equimolecular quantities of (I) and (XI) in boiling benzene gave the crystalline addition compound, brown needles with green reflex, decomposing at 255°. Further work on the regeneration of the hydrocarbon derivative from the complex and the determination of its optical activity is in progress.

EXPERIMENTAL

Reduction of Indigosol Green IB:

Method (a): The commercial Indigosol (2.5 g., corresponding to 1 g. of parent vat dye) was dissolved in 140 ml. of 10% sodium hydroxide solution and Raney alloy (14 g.) was gradually added to the mixture with vigorous stirring in the course of 3 hrs. at 90°. After stirring for 4 hours more at this temperature, the mixture was filtered. The deep red filtrate contained the unhydrogenolyzed ester (III), corresponding to 0.6 g. of parent vat dye. The nickel residue, after deactivation under acid, was extracted with toluene. The toluene extract was concentrated and run through a short column of alumina. The bright orange percolate, which had a green fluorescence, was again concentrated to 100 ml. and treated with picric acid (500 mg.). On cooling, the picrate crystallized in brown needles (300 mg., m.p. 212 (dec.). The picrate was decomposed with ammonia, when the hydrocarbon derivative (I) separated as bright red powder (190 mg.). It crystallized from benzene in orange-red needles, m.p. 290° (dec.) (Found: C, 89.3; H, 4.6; OMe, 12.1. $C_{36}H_{22}O_2$ requires C, 88.9; H, 4.6; OMe, 12.7%).

Method (b): The Indigosol (2.5 g., corresponding 1 g. of parent vat dye) was dissolved in 140 ml. of 20% sodium hydroxide solution. The alkaline solution was covered with a layer of toluene (150 ml.) and heated on boiling water-bath and Raney alloy (28 g.) gradually added to the mixture in the course of 3 hrs. After stirring for ¾4 hrs. more, the mixture was filtered. The aqueous layer was colourless indicating complete hydrogenolysis. The toluene layer was orange-brown with intense green fluorescence. The nickel residue was deactivated and extracted with toluene. The toluene extracts were combined, run through alumina, concentrated and treated with picric acid (500 mg.). The picrate (730 mg.) on treatment with ammonia gave 480 mg. of the hydrocarbon derivative (I).

Reduction of 16:17-dimethoxyviolanthrone (II) with aluminium cyclohexylooxide:

16:17-Dimethoxyviolanthrone (1 g.) was refluxed with a solution of aluminium (1 g.) in cyclohexanol (50 ml.) for 20 hrs. The excess of cyclohexanol was distilled off, and the residue taken up in dilute sodium hydroxide solution. The almost colourless solution was filtered and the residue extracted with toluene. The toluene extract on treatment with picric acid (1 g.) gave the picrate, which on decomposition

with ammonia gave the hydrocarbon derivative (I) (0.6 g.) identified by comparison with the specimen obtained in the previous experiments.

Demethylation of 16:17-dimethoxyviolanthrene:

16:17-Dimethoxyviolanthrene (100 mg.) was refluxed with acetic acid (10 ml.) and 48% hydrobromic acid solution (1 ml.) for 3 hrs., when reddish black precipitate (90 mg.) separated. The product was insoluble in caustic soda but dissolved in alkaline hydrosulphite to a blue solution. The quinone dissolved in high boiling solvents like o-dichlorobenzene, nitrobenzene, cresol and quinoline, but could not be obtained in crystalline form suitable for analysis.

Addition compound of 16:17-dimethoxyviolanthrene (I) with α-(2:4:5:7-tetranitrofluorenidylaminoxy)-propionic acid (XI):

(I) (0.130 g.) and (XI, $[\alpha]_D$ + 86.7°) (0.10 g.) were dissolved in boiling benzene (30 ml.) and the solution allowed to cool. The complex separated as dull brown needles (0.07 g.). It was recrystallized from toluene in shining brown needles with green reflex, decomposing at 255° (Found: C, 66.4; H, 3.3; N, 7.6. $C_{52}H_{31}N_5O_{13}$ requires C, 66.8; H, 3.3; N, 7.5%).

REFERENCES

1. Coffey and Boyd, J. Chem. Soc., 1954, 2468.
2. Newman, J. Am. Chem. Soc., 1940, 62, 2295.
3. Newman and Hussey, ibid., 1947, 69, 3023.
4. Steric Effects in Organic Chemistry, edited by Newman, J. Wiley and Sons, Inc., New York, 1956.
5. Klevens and Platt, J. Chem. Phys., 1948, 16, 831.
6. Padhye, Rao and Venkataraman, Proc. Indian Acad. Sci., 1953, 38A, 307.
7. Bell and Waring, J. Chem. Soc., 1949, 2689.
8. Newman and Wheatley, J. Am. Chem. Soc., 1948, 70, 1913.
9. Theilacker and Baxmann, Ann., 1953, 581, 117.
10. Hall and Turner, J. Chem. Soc., 1955, 1242.
11. Newman and Wise, J. Am. Chem. Soc., 1956, 78, 450.
12. Newman and Lutz, ibid., 1956, 78, 4765.
13. Newman, Lutz and Lednicer, ibid., 1955, 77, 3420.

SUMMARY

Part I

The method of Kenner and Murray for the reductive cleavage of aryl p-toluenesulphonates with Raney nickel has been extended to the sulphuric esters of phenols for the removal of the phenolic hydroxyl groups. p-Hydroxybenzoic acid was thus converted into benzoic acid in 65% yield. A general method for the preparation of hydrocarbons from the corresponding quinones by Raney nickel reduction of the disulphuric esters of the leuco derivatives, followed by dehydrogenation of the resultant hydrogenated hydrocarbon is described. The best condition for the hydrogenolysis is found to be the action of Raney alloy on the alkaline solution of the ester. Thus anthrahydroquinone disulphuric ester (III) was reduced to anthracene, the disulphuric ester of leuco 2:3:7:8-dibenzpyrene-1:6-quinone (Indigosol Golden Yellow IGK) (IV) to 2:3:7:8-dibenzpyrene (V) and the leuco sulphuric ester of Mayvat Brilliant Red AF to 2:3:6:7-dibenzpyrene (VI) in good yields.

Part II

The synthesis of 1-azanaphthacene (I) is described. Hydrogenolysis of the sodium salt of the disulphuric ester of 1-azanaphthacene-6:11-dione (VIII) with Raney alloy and aqueous caustic soda, gave 1:2:3:4:7:8:9:10-octahydroazanaphthacene (IX), which was dehydrogenated to 1-azanaphthacene (I) with palladium charcoal in boiling Dowtherm. Two tetrahydroazanaphthacenes (1:2:3:4 and 7:8:9:10) were obtained by other dehydrogenation procedures.

Part III

Alternative synthesis of 1:2-benzanthracene (I), 3' and 4-methylbenzanthracenes (II and III) is described. (I) was prepared by the hydrogenolysis of the disulphuric ester of 1:2-benzanthrahydroquinone with Raney alloy and aqueous caustic soda and also by the reduction of 1:2-benzanthraquinone with aluminium cyclohexyloxide in cyclohexanol. 3'-Methylbenzanthracene (II) was obtained by the reduction of leuco sulphuric ester of 3'-methyl-4'-chloro-1:2-benzanthraquinone. The synthesis of 4-methylbenzanthracene (III) was achieved through the trisulphuric ester of 3-hydroxy-4-methylbenzanthrahydroquinone.

Part IV

The synthesis of hitherto unknown 16:17-dimethoxyviolanthrene (I) is described. The reduction of Indigosol Green IB, the disulphuric ester (III) of leuco 16:17-dimethoxyviolanthrone with Raney alloy and aqueous alkali gave directly the aromatic hydrocarbon derivative (I), without nuclear hydrogenation. (I) could also be obtained by the reduction of 16:17-dimethoxyviolanthrone (II) with aluminium cyclohexyloxide in cyclohexanol.

Demethylation of (I) led to the formation of violanthrene-16:17-dione (IV).

The absorption spectrum of 16:17-dimethoxyviolanthrene in relation to that of parent violanthrene has been discussed. The work on the resolution of the optically active forms of (I) by complex formation with α-(2:4:5:7-tetranitrofluorenidylaminooxy)-propionic acid (XI) is in progress.

ACKNOWLEDGMENT

I am very grateful to Professor K. Venkataraman for suggesting this problem and for his guidance during its progress.

I thank Professor B. D. Tilak for his keen interest in the work.

My thanks are also due to Dr. M. R. Padhye for his help in the determination and interpretation of absorption spectra recorded in the thesis.

I am grateful to Dr. T. S. Gore for carrying out the microanalyses.

I am also grateful to Professor M. S. Newman of Ohio State University, U.S.A., for a gift of α-(2:4:5:7-tetranitrofluorenidylaminooxy)-propionic acid.

I am greatly indebted to the Ministry of Education, Government of India, and to the Council of Scientific and Industrial Research for the awards of fellowships which made the present investigation possible.

N. B. Desai
Candidate.