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SYNTHETIC STUDIES IN
ORGANOXY-TITANIUM AND ALLIED TITANIUM COMPOUNDS

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- CHAPTER I -

A. Introductory Survey and Outline of Present Work

The chemistry of organic titanium compounds has aroused considerable interest in the past twenty years. The part of literature on organic titanium(IV) compounds reviewed here has been divided into four groups of compounds: (a) compounds containing direct titanium-carbon bonds; (b) non-chelates in which organic radicals are bound to the titanium atom through an electro-negative elements such as oxygen, or groups of elements e.g., -O(PO)-, $-O(SO_2)-$ etc.; (c) chelated compounds of titanium; and (d) coordinated adducts of titanium(IV) compounds.

(a) Compounds with Ti-C bonds

In the early fifties, Hermann and Nelson[1-3] studied the reactions between alkyl titanates and organolithium or organomagnesium halides. They observed that phenyl titanium derivatives were formed, but could not be isolated pure because of their instability and high reactivity. They isolated the first compound — phenyl tri-isopropoxy titanium — from the reaction of isopropyl ortho-titanate with phenyl lithium[1,2]. It is a crystalline solid, stable at 10° in nitrogen atmosphere, but decomposes at higher temperatures. Attempts to obtain similar compounds by the same method were not equally successful, but Hermann and Nelson investigated the stability of compounds of the type $R_n TiX_{4-n}$, where R = alkyl or aryl, n = 1 – 4 and X = alkoxy or halogen. Theoretical relations concerning stability of alkyl and aryl derivatives of titanium have been discussed by Cotton[4] and Nesmeyanov[5].

Alkyl titanium halides have been isolated more recently. Some patents[6,7] describe the preparation of alkyl titanium trichlorides from titanium tetrachloride and an organo-metallic compound of zinc, cadmium, lead or aluminium in an inert atmosphere and at low temperatures:

$$TiCl_4 + Cd(CH_3)_2 \rightarrow (CH_3)TiCl_3 \qquad (1)$$

$$(CH_3)TiCl_3 + Zn(CH_3)_2 \rightarrow (CH_3)_2TiCl_2 \qquad (2)$$

$$TiCl_4 + Pb(C_2H_5)_4 \rightarrow (C_2H_5)\,TiCl_3 \qquad (3)$$

$$TiCl_4 + (CH_3)_3Al \rightarrow (CH_3)\,TiCl_3 \qquad (4)$$

$$TiCl_4 + (CH_3)_3Al \rightarrow (CH_3)_2TiCl_2 \qquad (5)$$

The reactions are carried out at low temperatures, e.g., the last reaction was carried out in hexane solution near -80°C. Methyl-titanium tribromide was prepared by the reaction between titanium tetrabromide and dimethyl zinc[7]. In another patent[8] the preparation of tetramethyl titanium has been described by reacting methyl lithium and titanium tetrachloride in butyl ether between -50° and -80°C. The product, obtained as a syrupy orange solution, was unstable at room temperature and was not isolated from the ethereal solution. By a similar reaction between titanium tetrachloride and tetraethyl lead in heptane at -80° Bawn and Gladstone[9] prepared ethyl titanium trichloride:

$$(C_2H_5)_4Pb + TiCl_4 \rightarrow (C_2H_5)\ TiCl_3 + (C_2H_5)_3\ PbCl \qquad (6)$$

Cyclopentadienyl derivatives of titanium belong to the class of ferrocenes. Wilkinson and his collaborators[10,11] reacted titanium tetrachloride and cyclopentadienyl magnesium bromide and obtained the first specimen of <u>bis</u>-cyclopentadienyl titanium dibromide. When titanium tetrachloride reacts with cyclopentadienyl-lithium, <u>bis</u>-cyclopentadienyl titanium dichloride is produced in good yield.[23,24] Another convenient method is to use cyclopentadienyl-sodium and titanium tetrachloride in tetrahydrofuran or diglyme,[11-13]

$$TiCl_4 + 2NaC_5H_5 \rightarrow (C_5H_5)_2TiCl_2 + 2NaCl. \qquad (7)$$

However, attempts to prepare these compounds from titanium tetrachloride, cyclopentadiene and organic bases gave poor yields.[14]

A reaction between <u>bis</u>-cyclopentadienyl titanium dichloride and titanium tetrachloride (in xylene) or chlorine (in carbon tetrachloride) gives cyclopentadienyl titanium trichloride:[15]

$$(C_5H_5)_2TiCl_2 + TiCl_4 \rightarrow 2(C_5H_5)TiCl_3 \qquad (8)$$

$$(C_5H_5)_2TiCl_2 + 3Cl_2 \rightarrow (C_5H_5)TiCl_3 + C_5H_5Cl_5 \qquad (9)$$

Nesmeyanov[16] prepared *bis*-cyclopentadienyl titanium chloride ethoxide, $(C_5H_5)_2TiCl(OC_2H_5)$, by the reaction between cyclopentadienyl sodium and ethoxy titanium trichloride, and also by refluxing ethanol with *bis*-cyclopentadienyl titanium dichloride. He prepared cyclopentadienyl titanium tri-isopropoxide[17] from cyclopentadienyl sodium and tri-isopropoxy titanium chloride. A reaction between cyclopentadienyl magnesium bromide and butyl titanate gave *bis*-cyclopentadienyl titanium dibutoxide.[18,19] Nesmeyanov has reported the reaction of *bis*-cyclopentadienyl titanium dichloride with potassium acetate and methacrylate giving diacylates.[20]

Indenyl and cycloheptatrienyl titanium compounds are the other π-bonded compounds of titanium known. *Bis*-indenyl titanium dichloride was reported by Marconi[21] and *bis*-cycloheptatrienyl titanium dichloride by Bruce-Smith and Perkins.[22]

Summers and his collaborators[23,24] obtained diaryl *bis*-cyclopentadienyl titaniums, $(C_5H_5)_2Ti(Ar)_2$ where Ar = phenyl, *m*-tolyl, *p*-tolyl and *p*-dimethylamino phenyl, by means of the reaction between *bis*-cyclopentadienyl titanium dichloride and appropriate aryl lithium compound. Dimethyl *bis*-cyclopentadienyl titanium[25] was obtained in poor yield from *bis*-cyclopentadienyl titanium dichloride and methyl magnesium iodide in tetrahydrofuran.

The cyclopentadienyl derivatives of titanium (except the trialkoxides) are generally crystalline, yellow to red substances with high melting points, some melting with decomposition. They are, as a class, more stable than the other organo derivatives of titanium containing direct Ti-C bonds. Their infrared spectra resemble those of ferrocene and ruthenocene[10,11] which are known to have "sandwich" structures.[26] Razuvaev et al[27] examined the thermal stability of bis(phenyl) bis-(cyclopentadienyl) titanium under various conditions. They found that the thermal decomposition of this compound gave rise to bis-cyclopentadienyl titanium and free phenyl radicals

$$(C_5H_5)_2Ti(C_6H_5)_2 \longrightarrow (C_5H_5)_2Ti + 2C_6H_5 , \qquad (10)$$

the presence of the latter being confirmed by carrying out the reaction in methanol, when formaldehyde and benzene were obtained. The thermal decomposition in either carbon tetrachloride or chloroform yielded bis-cyclopentadienyl titanium dichloride together with some chlorobenzene and diphenyl. Bis-cyclopentadienyl titanium dichloride was also obtained when bis-(phenyl) bis-(cyclopentadienyl) titanium was decomposed with hydrogen chloride or mercuric chloride. The thermal decomposition of bis-(phenyl) bis-(cyclopentadienyl)-titanium in carbon tetrachloride in the presence of metallic mercury again gave the same compound, together with phenyl mercuric chloride, and some chlorobenzene.

(b) Non-chelates with Ti-O bonds

Alkyl and aryl ortho-titanates, $Ti(OR)_4$, and their derivatives are the most extensively studied group of organic titanium compounds. Demarcay[28] in 1875 reported the preparation of ethyl titanate from titanium tetrachloride and sodium ethoxide, and 17 years later Levy[29] reported tetra-phenyl titanate and several other aryl titanates. In 1924, Bischoff and Adkins[30] prepared alkyl (C_1—C_4) titanates in 60-80% yield by ~~a~~ ~~modification of~~ Demarcay's method

$$TiCl_4 + 4NaOR \rightarrow Ti(OR)_4 + 4NaCl. \qquad (11)$$

This method was obviously restricted to only those alcohols which formed sodium alkoxides. In 1940, Nelles[31] patented a general method for the manufacture of alkyl ortho-titanates, namely, by the use of ammonia as hydrogen chloride acceptor

$$TiCl_4 + 4ROH + 4NH_3 \rightarrow Ti(OR)_4 + 4NH_4Cl. \qquad (12)$$

Nesmeyanov[34] prepared tetra-cyclohexanoxy titanium by this method. Subsequently, liquid ammonia[32], formamide or dimethyl formamide[33], and pyridine[34] were used as hydrogen chloride acceptors. In the case of more reactive alcohols such as t-butyl or allyl, $TiCl_4.8NH_3$ is first prepared in a solvent and then the alcohol is added to it.[35,36] Esters of these alcohols,[37-39] of higher alcohols[40-44] and phenols[45] could be prepared by simple exchange reaction with ethyl or propyl titanate

$$Ti(OR)_4 + 4R'OH \rightarrow Ti(OR')_4 + 4ROH \qquad (13)$$

where $R = C_2H_5$ or C_3H_7.

Trans-esterification has been used by Mehrotra[46] to prepare propyl and butyl titanates from ethyl titanate using the corresponding acetates. Several aromatic esters have also been prepared by others using this method[47,48]

$$\mathrm{Ti(OR)_4 + 4R'COOR'' \rightarrow Ti(OR'')_4 + R'COOR.} \qquad (14)$$

Menthyl and isobornyl titanates, the optically active esters of titanium, were prepared by this method by Mario Farnio and Giancarlo.[49]

Lower alkyl (C_2--C_{10}) ortho-titanates or titanium(IV) alkoxides are colourless or light yellow liquids with high boiling points (methyl titanate is a polymeric solid subliming at 300° at 18mm pressure). Determinations of their molecular weights by cryoscopic[41,50] and ebullioscopic[44,51] methods indicate that alkoxides having normal alkyl groups are associated in benzene solution, but the association diminishes with branching of the alkyl chain to form secondary or tertiary alkyl groups. The lower alkyl titanates can be distilled without decomposition at atmospheric pressure (e.g., n-amyl titanate distils at 314°[41]), but higher members decompose when distilled even under reduced pressure. Lower members, though stable, polymerize on prolonged heating.[52-55]

Hydrolysis is an important reaction of the titanic esters. When water is insufficient for complete hydrolysis, a series of condensed compounds containing -Ti-O-Ti-linkages may be formed.[56,57] Bradley has discussed these hydrolytic reactions in detail in his review of the polymeric alkoxides.[58]

Ortho-titanates undergo replacement reaction when a lower titanate ester is heated with a higher alcohol,[30,37,40,41,44,45,51,59,60] phenol, glycol or a polyhydric alcohol[61-63]

$$n\mathrm{Ti(OR)_4} + 4\mathrm{R'(OH)}_{n} \longrightarrow \mathrm{Ti}_{n}\mathrm{(OR'}_{n}\mathrm{)_4} + 4\overset{n}{\mathrm{R}}\mathrm{OH}. \qquad (15)$$

A similar reaction (trans-esterification) takes place when an organic ester reacts with alkyl titanate in which the resultant organic ester has a lower boiling point than the added ester[46,48,64] (equation 14).

Esters of ortho-titanic acid having chelated structures are formed when alkyl titantates are reacted with organic bidentate chelates e.g., acetylacetone, ethyl acetoacetate etc.[65-71] These chelated esters are less chemically reactive and more stable to moisture.

An alkyl ortho-titanate can be reduced by metallic sodium or potassium in alcohol medium to the corresponding trialkoxy titanium(III), $\mathrm{Ti(OR)_3}$, also called alkyl titanite. Ethyl-,[72] propyl-[73] and butyl[74] ortho-titanates have been reduced by this method.

Alkoxy and aryloxy titanium(IV) halides have the general formula $\mathrm{Ti(OR)_n X_{4-n}}$ where R is an alkyl or aryl group, X a halogen and n = 1,2 or 3. Demarcay[28] (1875) examined the action of titanium tetrachloride on absolute alcohol and isolated a white crystalline material which analysed to the formula $\mathrm{(C_2H_5O)_3TiCl.HCl}$. Later work in 1936 by Jennings, Wardlaw and Way[75] proved that the product was $\mathrm{(C_2H_5O)_2TiCl_2.C_2H_5OH}$, the reaction being represented as

$$\mathrm{TiCl_4} + 3\mathrm{ROH} \rightarrow \mathrm{(RO)_2TiCl_2.ROH} + 2\mathrm{HCl}. \qquad (16)$$

Further substitution of chlorine atoms attached to titanium did not take place directly. This convenient method, though sometimes it gives low yields, has been used by several workers[59,75,76] to prepare dialkoxy titanium dichlorides.

Nesmeyanov, Freidlina and Nogina[77] have shown that some alkoxy (C_2-C_6) titanium trichlorides are formed in very good yields when the corresponding alcohols react with excess of titanium tetrachloride in an inert solvent

$$TiCl_4 + ROH \rightarrow (RO)\ TiCl_3 + HCl. \qquad (17)$$

Razuvaev and collaborators[78] have prepared cyclohexanoxy titanium trichloride, isopropoxy and secondary butoxy titanium trichlorides by this method. Benzyl and allyl alcohols, however, did not react.[79]

Halogeno-alkoxides have also been prepared from alkyl ortho-titanates by direct halogenation (chlorine or bromine), by reaction with acetyl chloride, acetyl fluoride, antimony trifluoride, hydrohalides, pyridine hydrochloride or titanium tetrabromide, the nature of the products formed depending on the halogenating agent used. Nesmeyanov[80] have shown that chlorine or bromine reacts with alkyl ortho-titanates (C_2— C_4) in carbon tetrachloride to give dialkoxy titanium dichlorides by the interesting reaction

$$2(RCH_2O)_4Ti + 2X_2 \rightarrow 2(RCHO)_2TiX_2.RCH_2OH + ROOCCH_2R. \qquad (18)$$

Jennings, Wardlaw and Way[75] showed that triethoxy chloro-titanium is produced in good yield when ethyl titanate (one mole) is heated with acetyl chloride (one mole)

$$Ti(OC_2H_5)_4 + CH_3COCl \rightarrow (C_2H_5O)_3TiCl + CH_3COOC_2H_5. \quad (19)$$

Further reaction with another mole of acetyl chloride gives diethoxy dichloro-titanium

$$(C_2H_5O)_3TiCl + CH_3COCl \rightarrow (C_2H_5O)_2TiCl_2 + CH_3COOC_2H_5. \quad (20)$$

Later on, a series of mono- and dichloro-titanium alkoxides (C_3—C_5) were prepared by this method.[76,81] When three or four moles of acetyl chloride are used, a mixture of ethoxy titanium trichloride and titanium tetrachloride ethyl acetate adduct are formed:

$$Ti(OR)_4 + 3CH_3COCl \rightarrow Ti(OR)Cl_3 + 3CH_3COOC_2H_5 \quad (21)$$

$$Ti(OR)_4 + 4CH_3COCl \rightarrow TiCl_4.CH_3COOC_2H_5 + 3CH_3COOC_2H_5 \quad (22)$$

Benzoyl chloride reacts similarly, but gives poor yields.[76]

Brooker, Frenkel and Soborovskii[82] have prepared trialkoxy monofluoro-titaniums by fluorination of titanium tetra-alkoxides with acetyl fluoride or antimony trifluoride.

Nesemeyanov and his collaborators[34,60] have used pyridine hydrochloride as a chlorinating agent to prepare trialkoxy (C_2-C_4) monochloro-titaniums from tetra alkoxides:

$$Ti(OR)_4 + C_5H_5N.HCl \longrightarrow (RO)_3TiCl + C_5H_5N + ROH \qquad (23)$$

Alkyl titanates (dissolved in benzene) react with dry hydrogen chloride or hydrogen bromide giving corresponding dialkoxy titanium dihalides,[83,84]

$$Ti(OR)_4 + 2HX \longrightarrow (RO)_2TiX_2.ROH + ROH \qquad (24)$$

where R = ethyl or isopropyl.

Bradley, Hancock and Wardlaw[59] reacted alkyl titanates with titanium tetrachloride and prepared a series of alkoxy (C_2-C_4) titanium trichlorides. But they found the reaction unsuitable for the preparation of the dichlorides or monochlorides. Later, Nesmeyanov and his collaborators[85-87] found that the reaction between alkoxy (C_2-C_5) titanates and titanium tetrachloride in inert solvents proceeds further in presence of a stoichiometric quantity of piperidine, and the corresponding alkoxy chloro-titaniums separate easily in the form of their piperidine adducts.

$$nTi(OR)_4 + (4-n)TiCl_4 + 4C_5H_{10}NH \longrightarrow 4Ti(OR)_nCl_{4-n}.C_5H_{10}NH \qquad (25)$$

where n = 1,2 or 3. Titanium tetrabromide forms the corresponding bromo compounds.[87]

A process of alcohol substitution for preparing one alkoxy chloro-titanium from another was suggested by Nesmeyanov.[88] He showed that on distilling a mixture of triethoxy chloro-titanium and an alcohol having higher boiling point than ethyl alcohol, ethoxy groups are replaced practically quantitatively.

$$(C_2H_5O)_3TiCl + 3ROH \rightarrow (RO)_3TiCl + 3C_2H_5OH \qquad (26)$$

Hanic[45] prepared several higher trialkoxy chloro-titaniums by this method.

Alkoxy chloro-titaniums are colourless solids with low melting points, or viscous liquids whose viscosity decreases with increase in molecular weight.[88] The bromo compounds are yellow crystalline solids. All of them are highly hygroscopic and easily hydrolysed by excess of water, giving titanic acid, hydrochloric acid and alcohol. With small amounts of water, liquid titanoxy polymers are formed.[89] The chloro-titaniums are soluble in organic solvents, and in solution, show evidence of association[50] which diminishes with proliferation of the aliphatic chain as expected. Normal alkoxy chloro-titaniums are quite stable when stored and can be distilled in vacuum, although some disproportionate,[59,86] but secondary and tertiary alkoxy chloro-compounds are not stable towards heat. They often form 1:1 addition compounds with alcohols, esters, phenols and piperidine. The chlorine atoms in alkoxy chloro compounds can be substituted by other alkoxy groups by reaction with sodium alkoxide or with alcohol in presence of ammonia.

Several aryloxy chloro-titanium compounds have been prepared from phenols and titanium tetrachloride. Reactions of ordinary phenol with titanium tetrachloride gave compounds $(C_6H_5O)_nTiCl_{4-n}$ where n varies from 1 to 4.[29,90,91] Funk and co-workers prepared similar derivatives of chlorophenols and also (β-naphthoxy)$_2$TiCl$_2$.[92,93] Reactions of nitrophenols with titanium tetrachloride were studied by Lutschinsky;[90,94] *o*- and *p*-nitrophenols gave $TiCl_2(OC_6H_4NO_2)_2$ whereas *m*-nitrophenol gave the trichloride, $TiCl_3(OC_6H_4NO_2)$. Cresol, thymol, naphthol and resorcinol derivatives of titanium with general formula $(RO)_2TiCl_2$ were reported by Levy.[29] Pyrocatechol and titanium tetrachloride were reported to give the compound $H_2[Ti(O_2C_6H_4)_3]$.[93,95]

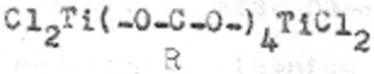
Aryloxy titanium compounds are red solids with high melting points. They are hygroscopic, but less so than the aliphatic titanium compounds. The derivatives of monohydric phenols dissolve in benzene but the pyrocatechol derivative is insoluble.

Alkoxy titanium oxides: Compounds analysing to the composition $(RO)_2TiO$ and having identical spectra[96] were prepared (a) by Nesmeyanov[97] by the careful oxidation of trialkoxy titanium compounds with dry oxygen, and (b) by Bradley[98,99] by the hydrolysis of alkyl titanates with water in 1:1 molar ratio ($R = C_2H_5$, *n*-C_3H_7). Dialkoxy titanium oxides undergo substitution reactions with isopentanol, hexanol, phenol and trimethylsilanol and also with acetyl acetone. Titanium oxide *bis*-acetylacetonate was found by Nesmeyanov to be monomeric in benzene[96] which is contrary to the dimeric structure proposed by Yamamato and Kambara (1957).[65] He carried out addition reactions at the double bond Ti=O with alkyl silicates. He found that addition took place in the case of dialkoxy titanium oxides but not with *bis*-acetylacetone titanium oxide. With the latter compound, the product formed was dialkoxy titanium *bis*-acetylacetonate.

Dialkoxy titanium oxides gave alkoxy chlorotitanium oxide in good yield when treated with titanium tetrachloride in ice-cold hexane.[100] Dipropoxy titanium oxide when reacted with dimethyl dichlorosilane at 100° gave dipropoxy dichloro-titanium. But when chlorine gas is passed through dipropoxy titanium oxide in petroleum ether and the turbid liquid treated with propanol, the addition compound $TiOCl_2.2C_3H_7OH$ separated.

Titanium acylates are generally obtainable directly by the reaction of a titanium halide with carboxylic acids. Jacini[101] prepared titanium tetraoleate and tetralinoleate by the action of titanium tetrachloride upon the corresponding acids. Prasad and Srivastava[102] prepared several tetracylates of titanium including the stearate, cinnamate, benzoate and *p*-nitrobenzoate of general formula $Ti(OOCR)_4$ we well as derivatives of dicarboxylic acids such as the succinate, adipate and camphorate of general formula $Ti[(OOC)_2R]_2$, all by the action of titanium tetrabromide upon the acid in an organic solvent. Titanium tetraphenylacetate has also been reported.[103]

Fichter and Reichert[104] prepared dichloro-titanium diacetate from titanium tetrachloride and acetic acid. Schwartz and collaborators[116] prepared the dichloro diacetate and dipropionate from titanium tetrachloride and two moles of acid. Molecular weight and infrared spectra of these compounds suggest that they exist as dimers with the acylate part acting as bridging groups between two titanium atoms:



$$Cl_2Ti(\text{-O-}\underset{R}{C}\text{-O-})_4TiCl_2$$

Benzoic acid and titanium tetrachloride react to give trichloro- and dichloro benzoates.[115] By controlling the ratio of the tetrachloride and the acid, Mehrotra[105] succeeded in isolating the trichloro-titanium acetate. An interesting method for the preparation of dichloro-titanium diacetate is to carry out the reaction in vapour phase at 136-170°.[106] Titanium tetrachloride and acetic anhydride give the diacetate[107] in the cold, but when heated the product in hexacetoxy dititanoxane, $(CH_3COO)_3$ Ti-O-Ti $(OOCCH_3)_3$.[107,108] The same products are obtained in the reaction of titanium tetra-ethoxide or tetra-isopropoxide with acetic acid or its anhydride.[109-112] Dialkoxy titanium benzoates,[113] linoleates, oleates, acrylates and propionates[114] have been prepared.

Several oxalates and complex oxalates of titanium have been reported in the literature. Freshly precipitated titanium dioxide is readily soluble in oxalic acid solution giving $(TiO)C_2O_4$, which with alcohol forms the adduct $(TiO)C_2O_4.C_2H_5OH$.[117] By dissolving hydrated titanium dioxide in potassium hydrogen oxalate solution, $K_2[TiO(C_2O_4)_2].2H_2O$ can be crystallised.[117, 118] Prasad and Tripathi[119] studied the formation of $TiCl_2C_2O_4$, $Ti(C_2O_4)_2$ etc. potentiometrically in solutions containing titanium tetrachloride, hydrochloric acid and an alkali oxalate or oxalic acid. Some dicarboxylic acids, such as succinic and adipic, do not dissolve freshly precipitated hydrated titanium dioxide. When titanium tetrachloride is refluxed with salicylic acid in benzene, titanium disalicylate, $Ti(OC_6H_4COO)_2$, separates as a red powder.[120]

Compounds with Ti-O-(SO_2)-linkage reported in the literature are few. A Japanese patent[121] describes the preparation of alkoxy titanium sulphate polymers from a reaction between tetra-alkyl titanate and sulphuric acid in a solvent. Feld[122] examined the reactions of alkyl and aryl sulphonic acids with ortho-titanates as well as titanium tetrachloride, and found that these acids resemble carboxylic acids in forming mono- or di-acylates:

$$TiX_4 + nYOH \rightarrow (YO)_nTiX_{(4-n)} + nHX \qquad (27)$$

where X = Cl, iso-OC_3H_7, n-OC_4H_9; Y-CH_3SO_2 or p-$CH_3C_6H_4SO_2$ and n = 1 or 2.

The alkoxy-titanium organo-sulphonates are soluble in organic solvents, but the chloro-titanium compounds are insoluble or very slightly soluble. They are stable to about 200°, and show normal molecular weights in solution.

In 1965, Gerrard and co-workers[123,124] reported the preparation of some more compounds containing the Ti-O-S type of linkage. By reacting titanium tetrachloride with chlorosulphonic acid they obtained products of the type $TiCl_{4-n}(OSO_2Cl)_n$ (n = 1, 2 and 3). Alkyl chlorosulphates gave similar products, but phenyl chlorosulphate did not react. By the action of sulphuryl chloride upon titanium tetra-alkoxides they isolated dialkoxy titanium sulphates, $(RO)_2TiSO_4$ ($R = CH_3$, C_2H_5, C_3H_7 and iso-C_3H_7) and, in the case of the tetramethoxide only, a compound $(CH_3O)_2Ti(OSO_2Cl)_2$. The products were all insoluble and were not studied further.

Compounds with a Ti-O-(PO)-linkage are obtained, for example, when benzene phosphinic acid reacts with either titanium tetrachloride or a tetra-alkyl titanate.[122] The products are insoluble, and dissolve in lower alcohols only with decomposition. Benzene phosphonic acid also reacts to give insoluble white solids of varying composition. Some more are described in Russian literature[125-127] and in a British patent.[128] A number of complex phosphato compounds of this class have been prepared recently in this laboratory by the action of alkyl phosphates upon titanium tetrachloride and organoxy titanium dichlorides.[129]

Compounds with Ti-O-B linkage have also been described in the literature. Tributoxy titanium benzene boronate, $(C_4H_9O)_3TiOB(OH)C_6H_5$, is obtained from equimolar quantities of butyl titanate and benzene boronic acid. Two equivalents of butyl titanate give hexabutoxy dititanium benzene boronate $[(C_4H_9O)_3\ TiO]_2\ BC_6H_5$. Both are orange yellow liquids decomposing on distillation.[122] Benzene boronic acid with titanium tetrachloride gives the corresponding dichloro-titanium bis-benzene boronate, $Cl_2Ti\,[OB(OH)C_6H_5]_2$,[122] a white solid insoluble in organic solvents, but decomposed by water and alcohols. Boric acid also reacts with titanium alkoxides yielding alkoxy titanium borates, $[(RO)_3TiO\,]_3B$ where R = butyl, amyl and 2-ethyl hexyl. They are yellow viscous liquids which decompose on distillation even under reduced pressure.

(c) Chelated compounds of titanium (IV)

Titanium forms chelated complexes with organic chelates such as β-diketones, β-keto esters, o-nitrophenol, salicylaldehyde and esters of salicylic acid. Titanium chelates are easily obtained by mixing the required amount of chelating agent with an ortho ester of titanium in a suitable solvent, the alcohol liberated in the reaction being distilled off. Yamamoto and Kambara[65] prepared acetylacetonates of general formula $(RO)_2Ti(acac)_2$ and $(RO)_3Ti(acac)$ from acetylacetone and ethyl, n-propyl and n-butyl titanates. Rust and Takimoto[130] prepared di-isopropoxy bis-dibenzoylmethane titanium and di-isopropoxy bis-8-hydroxyquinoline titanium from isopropyl titanate and dibenzoylmethane or 8-hydroxyquinoline. Similar compounds were prepared by Puri and Mehrotra[131] from alkyl titanates and acetylacetone as well as benzoylacetone. The reaction between alkyl titanates and acetoacetic esters gave similar chelated compounds.[65,67,132] The salicylaldehyde derivatives $(C_7H_5O_2)Ti(OR)_3$ and $(C_7H_5O_2)_2Ti(OR)_2$ where R = ethyl, isopropyl, t-butyl were prepared by Varma and Mehrotra[133] from the respective alkyl titanate and the required amount of salicylaldehyde. Yamamoto and Kambara[134] have prepared similar compounds using ethyl/n-propyl/n-butyl titanate and salicylaldehyde or methyl salicylate.

Another procedure for preparing chelated titanium compounds is to react the ligand with titanium tetrachloride in a suitable solvent medium. The reaction of titanium tetrachloride with acetyl acetone and benzoyl acetone were carried out by Dilthey[135] in 1906 who obtained the corresponding dichloro-titanium chelates. Rosenheim and co-workers[136] prepared trichloro-titanium acetylacetonate and Pande and Mehrotra[137] both trichloro- and dichloro-titanium acetylacetonates. Puri and Mehrotra[131] reported the preparation of the trichloro- and dichloro-titanium derivatives of benzoyl acetone and ethyl acetoacetate[132] and of bis-salicylaldehydo dichloro-titanium.[133]

Yamamoto and Kambara[134] prepared *bis*-salicylaldehydo and *bis*-(methylsalicylato) dichloro-titaniums. Lutschinsky[90,94] prepared *bis*-*o*-nitrophenoxy dichloro-titanium. Dibenzoylmethano chloro-titanium compounds were reported by Nyholm and co-workers.[138]

The alkoxy-titanium acetylacetonates are orange to red, viscous liquids soluble in organic solvents. They hydrolyse in water forming oxy-titanium acetylacetonates. Ethylacetoacetato, benzoylacetono and dibenzoylmethano derivatives are yellow to orange-red low-melting solids, soluble in alcohol and slightly so in benzene. The salicylaldehydo derivatives are yellow solids or viscous liquids soluble in benzene. The trichloro-titanium derivatives of acetylacetone, ethyl acetoacetate, benzoylacetone and dibenzoylmethane are chocolate to dark red solids with high melting or decomposing points. The dichloro-titanium derivatives are usually red powders, except that of salicylaldehyde which is a chocolate solid. The trichloro compounds are more hygroscopic than the corresponding dichlorides. Only acetylacetono and ethylacetoacetato chloro-titanium derivatives are soluble in benzene. All of them dissolve in alcohol, some with chemical reaction. Trichloro titanium acetylacetonate reacts with ethanol giving $(acac)(C_2H_5O)\ TiCl_2.C_2H_5OH$. Dichloro-titanium *bis*-acetylacetonate is decomposed by moisture forming oxy-titanium *bis*-acetylacetonate. Dichloro-titanium *bis*-acetylacetonate reacts with isopropanol in presence of dry ammonia gas to give di-isopropoxy titanium bis-acetylacetonate, and this product when reacted with dry hydrogen chloride gas gives back the original dichloride.[137] The dichloride forms with ethanol the adduct $(acac)_2TiCl_2.C_2H_5OH$.

(d) Coordinated adducts of titanium(IV) compounds:

Titanium halides form addition compounds often on simply mixing solutions of the halide and a donor molecule in an inert solvent. Sometimes the nucleophile itself can act as the solvent medium. A large number of addition compounds have been reported. A recent review is fortunately available in Chapter 8 of Feld's monograph[139] on "The Organic Chemistry of Titanium".

All the four titanium(IV) halides (fluoride, chloride, bromide and iodide) are known Lewis acids, but it seems that the chloride and the bromide have been studied in much greater detail. The adducts reported with titanium tetrafluoride and tetraiodide are relatively few.[140,141] The majority of adducts are oxygen or nitrogen compounds, and a few contain sulphur, phosphorus or arsenic as donors. Thus organic esters, acid halides, normal and cyclic ethers, carbonyl compounds, primary, secondary, tertiary and heterocyclic amines, cyanides, amides, imides, azo and diazo compounds all form addition compounds with titanium halides, as also thioalcohols,[142] thioethers,[143] triethyl and triphenyl phosphines,[144] and o-phenylene bis-dimethylarsine.[144,145]

Titanium tetrachloride and tetrabromide form a number of addition compounds with inorganic donor molecules also. Ammonia, nitrosyl chloride, hydrogen sulphide, nitrogen sulphides, sulphur dioxide, sulphur trioxide, sulphur tetrachloride, selenium oxychloride, phosphine, phosphorus trichloride, pentachloride and oxychloride, hydrogen cyanide, cyanogen chloride etc. form well-defined adducts with titanium tetrachloride.[147]

Addition compounds of substituted titanium(IV) chlorides with ammonia and other nitrogen bases were reported by Hans Burger as late as in 1963.[148] Trialkoxy titanium chlorides add (in liquid ammonia medium) three molecules of ammonia to form salt-like compounds $NH_4^+ [(RO)_3TiClNH_2.NH_3]^-$ which pass over into $(RO)_3TiCl.NH_3$ at 40-60°. He also reported 1:1 adducts of $(C_2H_5O)_3TiCl$ with pyridine, aniline, dimethyl sulphoxide and phenyl hydrazine.

The above rapid survey of literature, relevant to the work reported in this thesis, shows that though considerable work has been done on organic titanium compounds generally, relatively scanty work has been done in certain areas, especially those not covered by reactions with alkoxides. The following may be cited as examples:-

1. Cyclohexanoxy trichloro-titanium and tetra-cyclohexanoxy titanium, reported by Razuvaev[78] and Nesmeyanov,[34] seem to be the only two cyclohexanoxy

derivatives of titanium so far prepared. Cyclohexanol, though expected to resemble the aliphatic alcohols, has a different stereochemistry, and may give rise to less polymerized oxy-derivatives.

2. In the reactions of titanium tetrachloride with mono- and dihydroxy phenols, organic acids, chelates etc. a stepwise study in different molar proportions of the reactants appears to be lacking in many instances. Intermediate substitution products might have been missed. There is also a possibility that reaction between titanium tetrachloride and inorganic or organic esters will give reactive chloro-titanium intermediates.

3. The chlorine atoms in titanium tetrachloride are capable of being substituted stepwise by different ligands such as phenols, esters, chelates etc. forming chloro or chlorine-free derivatives. A systematic study will be useful in understanding the substitution behaviour of the successive chlorine atoms in titanium tetrachloride.

4. A proper study of the above may lead to the synthesis of more organic titanium compounds in which titanium is bonded directly with carbon.

5. Titanium tetrachloride is known to form addition compounds with nitrogen bases. The behaviour of such nitrogen donors towards organoxy titanium compounds largely remains to be studied. Substituted chloro-titanium compounds are known to be less sensitive towards moisture than the parent titanium tetrachloride. Adducts may make the compounds stabler towards moisture, besides illustrating the expandable covalency maximum for the normally hexa-coordinated tetravalent titanium atom.

B. Applications of Organic Titanium(IV) Compounds

Several reviews[149-164] on the applications of organic titanium compounds have appeared in recent years covering the rapidly growing patent literature on the subject. The bulk of the applications is in the fields of surface coatings, waterproofing compounds, polymer compositions and catalysts for polymerization.

Surface coatings- One of the earliest applications of titanium organics was the use of titanate esters as heat resistant paints. The butyl ester, diluted with an organic solvent e.g. xylene, has been extensively used for giving a heat resistant coat of aluminium powder, zinc, powdered mica etc. on metal surfaces. The smooth and elastic coating, which stands prolonged heating up to 600°C, consists of particles of the pigment bound by a film of titanium dioxide. Butyl titanate and the polymeric alkoxy-titanium acylates[165,166] are very effective dispersing agents for various pigments in paint compositions. A primary coat of diluted alkyl titanate makes paints and plastics adhere strongly to paper and metal surfaces.[163,167,168] Cellulosic materials have been claimed to develop fire-resistant property on treatment with a solution of diacetoxy-titanium dichloride.[169,170]

Waterproofing compounds- Titanium organics have been used for developing hydrophobic properties on cotton, silk, nylon, wood and glass.[150,171] Since the alkyl titanates have become available in commercial quantities, considerable interest has been shown in the use of wax-titanate mixtures for waterproofing textiles, and for re-proofing cotton garments in particular, without the attendant risk of shrinkage and colour loss. Nonyl titanate has been preferentially used in such compositions.[172] Dry-cleaning firms in U.K. use wax-titanate compositions for re-proofing of textiles subsequent to cleaning, even where the initial proofing was done by a silicone process.[173] In addition to the above, poly-organic titanium(IV) siloxanes,[174] alkoxy silyl titanates[175,176] and alkyl titanate-polysiloxane mixtures[177] have been mentioned as waterproofing agents on paper, fabric and leather.

Polymer compositions- Titanate esters have been used as cross-linking agents for cellulose derivatives,[68,179-182] polyesters,[179,180] epoxy resins[183,184] and siloxane polymers[157,178-180] for producing fast drying compositions with increased resistance to heat and solvent action. For modification of resins, the alkoxides, acylates and amides of titanium(IV) have proved useful.[186-188] Octadecenyl and cyclohexyl titanates are good plasticizing agents for urea resins.[155,157,189]

Polymerization catalysts- The decomposition of organo titanium compounds gives rise to free radicals which can catalyse other chemical reactions. Many uses have been made of this behaviour in catalyzing vulcanization and polymerization processes. The assumption that Ziegler catalysts (mixture of titanium tetrachloride and aluminium alkyls) might contain titanium organics in the aluminium-titanium complex provided the initial impetus to the search for organic titanium compounds (including those containing Ti-C bonds) of possible catalytic activity. Natta and co-workers[190] have used isopropyl ortho-titanate (on aluminium silicate carrier) with triethyl-aluminium as an effective catalyst for the polymerization of ethylenic compounds. Binary compositions of ortho titanates and aluminium chloride show good catalytic activity for low-temperature polymerization of olefines.[191,192] Diacetoxy-titanium dichloride is a catalyst for the co-polymerization of isobutylene with diolefines.[193,194] Addition of titanium tetrachloride to phenyltitanium tri-isopropoxide gave a catalyst for the intensive polymerization of propene.[195] General claims have been made for low-pressure polymerization of olefines by cyclopentadienyl titanium compounds combined with aluminium alkyls. A study of the use of bis-cyclopentadienyl titanium dichloride with aluminium alkyl has shown that the polymers of ethylene so obtained are more linear than the product from the usual

Ziegler-type catalysts.[196] The mechanism of polymerization and the reaction products of bis-cyclopentadienyl titanium dichloride and alkyl aluminiums have been reviewed.[197]

In presence of titanium tri- or di-chloride, the simple alkyl titanium(IV) halides are found effective in the polymerization of α-olefines.[198] They have even been claimed to be better than the two-component Ziegler systems for ethylene polymerization on account of a greater control over the polymerization conditions.[199] Since the lower titanium chlorides form in situ by the decomposition of alkyl titanium halides, their addition is not necessary in actual practice. Alkyl(C_1-C_{16}) and phenyl titanium(IV) chlorides have been reported as effective catalysts for obtaining white, linear and highly crystalline polystyrene.[200, 201, 203]

Miscellaneous applications- A British patent[202] claims improvement in the combustion of liquid or gaseous fuel by the addition of an organic titanium compound containing halide groups and at least one Ti-C bond. Cyclopentadienyl titanium halides have also been claimed as effective fuel additives.[204] Thin films of titanium metal is deposited on glass, metal or synthetic articles by heating them to 200-480°C in an inert atmosphere containing a thermally unstable titanium organic (e.g., a bis-cyclopentadienyl titanium compound) with complete exclusion of oxygen.[205] Titanium tetrachloride, hydrolysed partly by aqueous glycerine, is a good precipitant for acid dyes.[206,207] The hydrolysis of alkyl titanates has been used in qualitative analysis for the removal of phosphate in presence of nitric acid.[208]

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CHAPTER II

RESULTS AND DISCUSSION.

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RESULTS AND DISCUSSION

The key material for the investigation is titanium tetrachloride, colourless liquid, m.p. -23°, b.p. 136°C, fuming strongly in moist air and vigorously hydrolysed by water. Like other transitional elements, titanium shows varying valence (2,3,4) in its compounds. The electronic configuration for the titanium atom (At.No.22) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ ($3d \not\approx 4s$ in energy of the orbitals). The energy for removal of the four external electrons is high, so Ti(IV) compounds tend to be covalent. The energies of the 3d, 4s and 4p levels are all within 4ev of each other and circumstances are favourable for hybridization involving 3d, 4s and 4p orbitals. Several such hybrids are possible.[1] Tetrahedral bonds, for example, would originate from hybridization of either d^3s or sp^3 atomic orbitals, both of which are probable with titanium tetrachloride. Raman and I.R. studies on titanium tetrachloride[2,3,4] have shown that the molecule is tetrahedral (point group symmetry $T_{\underline{d}}$) with a doublet at ν_3 like carbon tetrachloride. A quantitative calculation of the force constants shows, however, that there is relatively much smaller resistance to deformation without change of the X-Y distance. The relative values of k_δ/l^2 (valence force system) and k_1 (central force system), either of which is a measure of the resistance to deformation of the tetrahedral structure, are given below for the tetrachlorides of carbon, silicon, titanium and tin for comparison:[5]

	CCl_4	$SiCl_4$	$TiCl_4$	$SnCl_4$	
k_δ/l^2	0.331	0.157	0.100	0.075	$\times 10^5$ dynes/cm
k_1	0.79	0.36	0.23	0.15	

A resemblance between Ti(IV) and Sn(IV) is again noticeable in their estimated ionic radii[8a] (Sn^{4+} = 0.71; Ti^{4+} = 0.68A°) and octahedral covalent radii (Sn(IV) = 1.45 Ti(IV) = 1.36A°).

Although an isotropic molecule of zero dipole moment, titanium tetrachloride is a strong Lewis acid. Addition compounds with ethers, esters and other oxygen donors are well known, though their structures are not often well understood. It would appear, however, that the titanium atom is somewhat easily coordinated either octahedrally, or trigonal bipyramidally with bridging oxygen.[6] Also, deviations or slight distortions from totally symmetrical structures are quite probable. Alternative modes of polymerisation, linear or cyclic, are common and, indeed, form a general structural feature in organoxy titanium compounds. Thus it appears that, although titanium belongs to the group of transitional elements, it retains certain chemical similarities, especially in the tetravalent state, with silicon and tin.

Even as a transitional element, the stereochemistry of titanium will be governed like that of the non-transitional elements by the tendency of electron pairs to occupy positions of minimum mutual interaction.

Only, in the case of transitional elements, the additional effect of the non-bonding electrons in the (n-1)d orbitals must be considered. The non-bonding d^0 configuration of Ti(IV) is symmetrical to both tetrahedral and octahedral ligand fields, so both the regular structures are expected, though the octahedral complexes will be more stable. Compounds of coordination number 5 (distorted TBP/square pyramid), 7 ($ZrF^{3-}{}_7$ type, pentagonal bipyramid) and 8 (dodecahedron) have also been reported.[8b]

However, the outstanding capacity of carbon to form homo-chain compounds, though observed to persist in a considerably and continually diminishing capacity among the Gr IV elements, Si, Ge, Sn and Pb, is totally absent in the transitional elements Ti, Zr, Hf, Th. In contrast, the possibilities of hetero-chain organic derivatives, resulting in the formation of polymeric compounds, are diverse and extensive with titanium. Since such hetero-chain skeletons can result not only from combinations of elements of different electronegativity but also from the utilization of other bond capacities in large molecules, advantage can be taken of both non-ionogenic and ionogenic bonds. Thus hetero-chain complex compounds can be synthesized containing the transitional metal atom, and other organic or organo-metalloid compounds having electron donor properties.[9]

The inherent chemical instability of homo-chains (other than of carbon) is often partly compensated in framing hetero-chain, non-ionogenic, organo-metalloidal compounds by alternating various elements in the X-Y- or

X-Y-Z-chains, selecting combinations of elements more positive and more negative than carbon in alternate positions. The compounds thus formed are more resistant to redox processes; and the nearer is the average electronegativity of the hetero-alternates to that of carbon itself, the better is the non-ionogenic character of the bonds formed. The combination of such elements makes it possible to synthesize the interesting poly-organosiloxanes, alumino-organosiloxanes and titano-organosiloxanes. The idea is continually being extended to synthesize polymers with hetero-chains -Al-O-Al-, -Ti-O-Ti-, -Sn-O-Sn-, -Al-O-P-O-Al-, -Ti-O-Si- and others.[7] However these bonds would be more susceptible to nucleophilic (and electrophilic) attack than the covalent bonds of carbon atoms.

The general principles enunciated above formed the basis of our investigation on the nature and type of organic compounds of titanium, with oxygen as the hetero-alternate between titanium and carbon (electronegativity values: Ti 1.32, O 3.5, C 2.5). In the very rapid development of the organic chemistry of titanium in the last fifteen or twenty years, mostly prompted by industrial applications of certain types of its compounds, a lack of a systematic build-up of knowledge is noticeable, even in respect of relatively simple non-ionogenic derivatives. In the following pages, we have reported the results of systematic study of a few selected types of reactions, which can be grouped under the following three categories:-

1. Primary reactions with titanium tetrachloride giving primary organoxy-titanium(IV) compounds.
2. Reactions of the primary organoxy-titanium(IV) compounds with other ligands/reagents with a view to substitution or introduction of other groups.
3. Adducts of the above organoxy derivatives with nitrogen bases.

1. Primary derivatives from titanium tetrachloride

(a) Alkyl- and aryl-oxides of titanium(IV)

The alkyl- and aryl-oxides of titanium(IV) [also regarded as esters of the hypothetical ortho-titanic acid $Ti(OH)_4$] and the partly substituted chloro-alkoxides/aryloxides form the most widely studied group of organoxy-titanium(IV) compounds. Investigation in this group of compounds was greatly stimulated by the reported use[10] of tetrabutyl titanate as a heat resistant paint material in 1948. The property results from polymerization of the ester to a viscous liquid and finally to a thermoplastic solid which may contain up to 50 or 60% of TiO_2 depending on temperature and duration of heating. It has also been shown that a mixture of air and butyl titanate vapour, on being blown to a hot surface ($\approx 600^{\circ}C$), leads to instantaneous decomposition of the ester with the formation of a transparent, adhering film of titanium dioxide. A considerable part of such data is in patent literature.

Several methods are known for the synthesis of ortho-titanates and halogeno-titanate esters. For example, it is generally known that alcoholates of dialkoxy dichloro-titanium are formed when titanium tetrachloride is made to react with excess of an alcohol (C_1-C_5).[11,12,13] The trichloro derivative is obtainable by reacting the tetrachloride with the stoichiometric amount of the alcohol.[14,15] The tetra-alkoxides are, however, obtainable with excess of the alcohol only when the hydrogen chloride formed is continuously removed by dry ammonia gas[16] or other bases.[17,18,19] Some tertiary alkoxides have been prepared[20,21] by using the 8-ammoniate of titanium tetrachloride in place of using excess of free ammonia gas. Some of the above-mentioned reactions were carried out by us in the initial preparation of the lower alkoxides and the dichloro-alkoxide alcoholates. The dichloro derivatives were of interest to our work, as we observed that inspite of the solvate alcohol present, the dichloride alcoholate dissolved in non-hydroxylic solvents and behaved normally in reactions involving the elimination of hydrogen chloride and alkyl chlorides. Experiments with dialkoxy dichlorides reported in the thesis, unless specified otherwise, were all carried out with their alcoholates as the reactant.

Cyclohexanol resembles aliphatic alcohols in its reactions with titanium tetrachloride. Nesmeyanov[22] first reported the preparation of tetra-cyclohexanoxy titanium in 1949; and the only other derivative, viz., cyclohexanoxy trichloro-titanium, was reported by Razuvaev[15] ten years later. Our interest was to study further reactions of cyclohexanol with titanium tetrachloride and also of the primary producta arising therefrom. The first new compound isolated was dicyclohexanoxy dichloro-titanium in the form of light grey crystals soluble in common organic solvents and showing normal molecular weight in benzene.

The corresponding dicyclohexanolate, however, showed about one-third the normal molecular weight in benzene, indicating almost complete dissociation of the two cyclohexanol molecules. The monochloro compound was prepared from a 3:1 mixture of the tetra-cyclohexanoxy compound and titanium tetrachloride, and also showed normal molecular weight in benzene. These compounds are listed in Table 1.

Table 1

Reaction products of $TiCl_4$ and cyclohexanol

Reactants			Product**
(A)	(B)	Molar ratio (A:B)	
$TiCl_4$	Cyclohexanol	1.5:1	$(C_6H_{11}O)TiCl_3$
"	"	1:2	$(C_6H_{11}O)_2TiCl_2$*
"	"	1:4	$(C_6H_{11}O)_2TiCl_2 \cdot 2C_6H_{11}OH$*
"	"	1:4.5	$(C_6H_{11}O)_4Ti$
"	$(C_6H_{11}O)_4Ti$	1:3	$(C_6H_{11}O)_3TiCl$*

* new compounds

** based on chemical analysis only.

Lutschinsky,[23,24] Levy[25] and Schumann[26] reported in detail the action of phenol on titanium tetrachloride. Levy reported di-resorcinol dichloro-titanium as the product of the reaction between resorcinol and titanium tetrachloride. Rosenheim and Sorge[27] reacted titanium tetrachloride with catechol in ether and reported isolation of the ammonium salt $C_6H_4O_2Ti(OC_6H_4ONH_4)_2 . H_2O$ by adding aqueous ammonia. Our studies on the action of titanium tetrachloride on catechol led to the isolation of two compounds. In one case, both the hydroxy groups of catechol reacted with titanium tetrachloride giving o-phenylenedioxy dichloro-titanium as a deep brown non-hygroscopic powder; in the other, three molecules of catechol reacted to give a chlorine-free, chocolate-red powder, which dissolved in aqueous ammonia to give a clear solution from which the ammonium salt described by Rosenheim was isolated on evaporation. The latter compound was also obtained by the action of catechol on o-phenylenedioxy dichloro-titanium, suggesting that the chlorine-free tri-catechol derivative was formed via the dichloride. Resorcinol, like catechol, readily reacted with titanium tetrachloride giving m-phenylenedioxy dichloro-titanium as a bright red stable powder insoluble in common solvents. Unlike catechol, however, the product isolated from the reaction with excess of resorcinol was (m-hydroxyphenoxy) m-phenylenedioxy chloro-titanium, which was also obtained by reacting excess of resorcinol with m-phenylenedioxy dichloro-titanium.

Both catechol and resorcinol derivatives of titanium(IV) are completely insoluble in common organic solvents and are probably polymerized compounds. They dissolve in ethanol but the solutions give decomposed products on removal of the solvent.

In the infrared spectra of the dichlorides of both catechol and resorcinol, the hydroxylic stretching frequencies of catechol (3448, 3279) and resorcinol (3175) are absent. A cyclic polymer structure for the resorcinol derivative is thus quite probable. For the catechol derivative, a simultaneous replacement of both the hydrogen of the two OH groups in the ortho position has a greater probability. A polymeric structure would result in such a case by successive coordination of the two chlorine atoms of one molecule to the next titanium atom, resulting again in a cyclic structure. These views are supported by our observations on the reactions of catechol and resorcinol with bis-acetylacetono dichloro-titanium. The latter reacts with one molecule of catechol and two molecules of resorcinol to give $(C_5H_7O_2)_2Ti(O_2C_6H_4)$ and $(C_5H_7O_2)_2Ti(OC_6H_4OH)_2$ respectively. This catechol derivative is found to be identical with the product we have obtained by reacting the dichloro catechol compound with acetylacetone in presence of ammonia. The dichloro resorcinol compound, on the other hand, forms a stable addition complex with ammonia under the same conditions, leaving the chlorine atoms unreacted with acetylacetone. The greater tendency to form ammonia adduct of the dichloro-resorcinol compound is indicated by the vacant space available for coordination around the tetra coordinated titanium atoms arising out of the proposed cyclic polymeric structure.

In addition to catechol and resorcinol, thymol (5-methyl 2-isopropyl phenol, $C_{10}H_{13}OH$) and vanillin (4-hydroxy 3-methoxy benzaldehyde, C_8H_7OH) reacted with titanium tetrachloride with elimination of hydrogen chloride. The products obtained by reacting different molar proportions of all phenolic ligands with titanium tetrachloride are listed in Table 2.

Table 2

Reaction products of $TiCl_4$ and phenolic ligands

Reactants			Product**
(A)	(B)	Molar ratio (A:B)	
$TiCl_4$	Phenol	1.5:1	$(C_6H_5O)TiCl_3$
"	"	1:2	$(C_6H_5O)_2TiCl_2$
"	"	1:3	$(C_6H_5O)_3TiCl$
"	"	1:4	$(C_6H_5O)_4Ti$
"	Catechol	1.5:1	*o*-$(C_6H_4O_2)TiCl_2$*
"	"	1:4	*o*-$(C_6H_4O_2)Ti(OC_6H_4OH)_2$
"	Resorcinol	1.5:1	*m*-$(C_6H_4O_2)TiCl_2$*
"	"	1:4	*m*-$(C_6H_4O_2)Ti(OC_6H_4OH)Cl$*
"	Thymol	2:1	$(C_{10}H_{13}O)TiCl_3$*
"	"	1:2	$(C_{10}H_{13}O)_2TiCl_2$
"	"	1:3	$(C_{10}H_{13}O)_3TiCl$*
"	"	1:5	$(C_{10}H_{13}O)_4Ti$*
"	Vanillin	2:1	$(C_8H_7O)TiCl_3$*
"	"	1:2	$(C_8H_7O)_2TiCl_2$*
"	"	1:4	$(C_8H_7O)_3TiCl$*
"	"	1:8	$(C_8H_7O)_4Ti$* +

* new compounds

** based on chemical analysis only

\+ Product contained 1-2% Cl.

The new compounds in Table 2 are coloured powders, hygroscopic and insoluble in common organic solvents, the only exception being tetra-thymoxy titanium, which dissolves in boiling benzene and shows normal molecular weight in that solvent.

(b) Acylates of titanium(IV)

Direct but partial replacement of chlorine of the $TiCl_4$ molecule by acyl groups had been observed in the preparation of tri- and dichloro-titanium acetate[28-31] and benzoate.[32] We found that phenoxyacetic acid behaved similarly, and tri- and dichloro-titanium phenoxyacetates were isolated as deep yellow to orange hygroscopic powders, dissolving only in alcohols. Attempts to prepare tri- and tetra-phenoxyacetates by direct substitution were unsuccessful as would be expected.

The possibility of controlling the reaction between some strong acids (e.g. inorganic acids) and titanium tetrachloride by the use of their esters does not seem to have been examined in the past. We have found that titanium tetrachloride reacts easily with normal alkyl (C_1-C_4) esters of sulphuric acid at ordinary temperatures to give chloro-titanium derivatives with the elimination of alkyl chlorides, the reactivity falling off from methyl to the *n*-butyl ester. Dimethyl sulphate and titanium tetrachloride react at 0° forming dichloro-titanium sulphate. Under different reacting conditions, the same reactants give chloro-titanium *tris*-methylsulphate and methylsulphato chloro-titanium sulphate as pure products.

The tris-methylsulphato titanium compound is not as stable as dichloro-titanium sulphate or methyl sulphato chloro-titanium sulphate. Diethyl, di-n-propyl and di-n-butyl sulphates give the trichloro-titanium alkylsulphate in each case. Dimethyl oxalate, on the other hand, reacts with titanium tetrachloride forming only dichloro-titanium oxalate.

A summary of the results with acids and esters is given in the Table 3.

Table 3

Reaction products of $TiCl_4$ and alkyl (C_1-C_4) sulphates and dimethyl oxalates

Reactants			Product**
(A)	(B)	Molar ratio (A:B)	
$TiCl_4$	Dimethyl sulphate	2:1	Cl_2TiSO_4*
"	"	1:2	$ClTi(CH_3SO_4)SO_4$*
"	"	1:4	$ClTi(CH_3SO_4)_3$*
"	Diethyl sulphate	2:1	$Cl_3Ti(C_2H_5SO_4)$*
"	Di-n-propyl sulphate	2:1	$Cl_3Ti(C_3H_7SO_4)$*
"	Di-n-butyl sulphate	2:1	$Cl_3Ti(C_4H_9SO_4)$*
"	Dimethyl oxalate	2:1	$Cl_2TiC_2O_4$*
"	Acetic acid	1:2.2	$Cl_2Ti(OOCCH_3)_2$
"	Benzoic acid	1:2.2	$Cl_2Ti(OOCC_6H_5)_2$
"	Phenoxyacetic acid	1.5:1	$Cl_3Ti(OOCCH_2OC_6H_5)$*
"	Phenoxyacetic acid	1:2	$Cl_2Ti(OOCCH_2OC_6H_5)_2$*

* new compounds

** based on chemical analysis only

These ester derivatives are yellow powders, very sensitive to moisture, and insoluble in common organic solvent except ethanol, in which they dissolve with decomposition. Because of their high reactivity towards hydroxylic compounds, they are powerful intermediates for the synthesis of further organoxy titanium compounds.

An alternative route for synthesizing the alkoxysulphates by reacting titanium tetra-alkoxide (ethyl, n-butyl) with sulphuryl chloride gave $(RO)_3Ti-SO_3Cl$ as the only product. In a reaction with thionyl chloride under similar conditions, the tetra-alkoxides gave alkoxy-trichlorotitanium, which points to an alternative route to the synthesis of mono-substituted titanium chloride. However, the reaction did not prove to be of general applicability in the few cases tried. It often led to the isolation of the fully chlorinated titanium tetrachloride, and other unidentifiable mixtures containing both sulphur and chlorine.

(c) Chelates of titanium(IV)

Stable chelated titanium(IV) compounds, arising out of simultaneous coordination and proton replacement of potentially acidic OH groups of acetylacetone, ethyl acetoacetate, benzoylacetone, dibenzoylmethane etc. are reported in the liaterature.[23,24,33-40] Several of these compounds were prepared by us on the basis of information available in the literature, and new trichloro-titanium chelates with salicylaldehyde and methyl salicylate ligands were also synthesized. These compounds were used as intermediates for the synthesis of more complex derivatives by substitution of the chlorine, as described later. The trichloro-monochelates of salicylaldehyde and methyl salicylate, which are compounds in which titanium assumes a nominal coordination number five, are highly insoluble solids and are most probably polymerized. Both dissolve, however, in ethanol easily and the solution on evaporation yields in either case the six coordinated adduct $L(OC_2H_5)TiCl_2.C_2H_5OH$, in which LH represents a molecule of salicylaldehyde or methyl salicylate.

A list of the titanium chelates thus prepared and examined for further reactions is given in Table 4.

Table 4

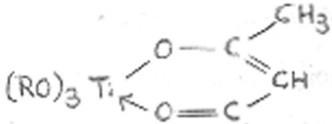
Reaction products of $TiCl_4$ and bidentate chelates

Reactants			Product**
(A)	(B)	Molar ratio (A:B)	
$TiCl_4$	Acetylacetone	1.5:1	$(C_5H_7O_2)TiCl_3$
"	"	1:3	$(C_5H_7O_2)_2TiCl_2$
"	Ethyl acetoacetate	1:3	$(C_6H_9O_3)_2TiCl_2$
"	Dibenzoylmethane	1.5:1	$(C_{15}H_{11}O_2)TiCl_3$
"	"	1:2	$(C_{15}H_{11}O_2)_2TiCl_2$
"	Benzoylacetone	1:2	$(C_{10}H_9O_2)_2TiCl_2$
"	Salicylaldehyde	1.5:2	$(C_7H_5O_2)TiCl_3$*
"	"	1:3	$(C_7H_5O_2)_2TiCl_2$
"	Methyl salicylate	1.5:1	$(C_8H_7O_3)TiCl_3$*
"	"	1:3	$(C_8H_7O_3)_2TiCl_2$
"	<u>o</u>-Nitrophenol	1:2	$(C_6H_4NO_3)_2TiCl_2$

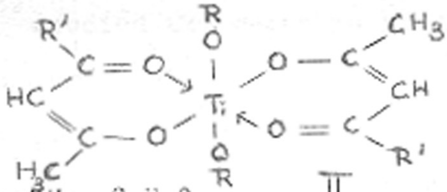
* new compounds

** based on chemical analysis only

The structures assigned to the titanium chelates are relatively simple and along the expected lines. Yamamoto and Kambara[47] prepared both penta- and hexacoordinated titanium chelates of acetylacetone and ethyl acetoacetate by reacting them with titanium tetra-alkoxides (Et, Pr, Bu) by varying the ratio of the chelating ligand to the alkoxide. These compounds were found to be monomeric in dilute benzene solutions and their structures I and II were confirmed by infrared analysis.



I



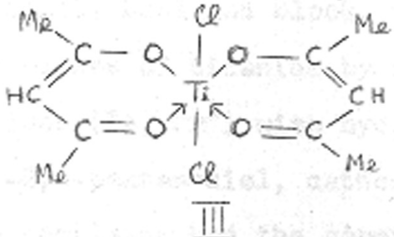
II

R = C_2H_5, C_3H_7, C_4H_9; R' = CH_3, C_2H_5O

Later, they reacted salicylaldehyde and methyl salicylate with titanium tetra-alkoxides and isolated similar products,[39] to which similar structures also were assigned on the basis of their molecular weight and infrared spectra.

Pande and Mehrotra[35] studied the properties of bis-acetylacetono dichloro-titanium and found it to be monomeric in boiling benzene. Its ethoxy derivative, which gives the parent dichloro compound when treated with dry hydrogen chloride in benzene, is also proved to be monomer. Bis-acetylacetono dichloro-titanium reacted with isopropanol in presence of dry ammonia to give bis-acetylacetono di-isopropoxy titanium.

Similar results have been obtained by taking ethylacetoacetate in place of acetylacetone. For the acetylacetone compound the authors proposed the structure III with hexa coordinated titanium atom.



III

Varma and Mehrotra[38] studied the reaction of titanium tetra-alkoxides (Et, Pr^i, Bu^t) with salicylaldehyde and obtained products similar to those reported by Yamamoto and Kambara.[39] In addition, they showed that the reaction of excess of salicylaldehyde (>4 moles) with titanium tetrachloride (in benzene) gave bis-salicylaldehydo dichloro-titanium, to which by analogy they assigned the structure proposed for the acetylacetone derivative (III). Puri and Mehrotra[37] who studied the bis-chelated dichloro-titanium of methyl- and ethyl acetoacetate and methyl salicylate found that these were monomeric in boiling benzene and proposed for them structures similar to that of the acetylacetone complex. Nyholm and co-workers[40] found that bis-benzoylacetono- and bis-dibenzoylmethano dichloro-titaniums were monomeric in nitrobenzene (cryoscopy). The formation of the cationic derivatives [Ti(benzoylacetone)$_3$][$FeCl_4$] and

[Ti(dibenzoylmethano)$_3$] [FeCl$_4$] from the dichloro compounds and ferric chloride or from ferric chelates and titanium tetrachloride was studied by conductometric titrations in nitromethane.

Recently Dahl and Block[48] prepared new chelated complexes of titanium by reacting titanium tetra-alkoxides (Et, Pr^i) with hydroxy compounds such as 2-methyl-2,4-pentanediol, catechol and salicylic acid. The complexes had the general formula Ti(BB)(OR)$_2$, where BB represents the binegative bidentate ligand and R = Et or Pr^i. Replacement of alkoxy groups with acetylacetone in the catechol derivative $Ti(O_2C_6H_4)(OR)_2$ gave the monomeric mixed chelate $Ti(O_2C_6H_4)(C_5H_7O_2)_2$. The dialkoxy catechol derivatives showed a degree of association 2-3 in benzene or chloroform solution.

2. Reactions of the primary organoxy titanium(IV) compounds

(a) Alkoxy/aryloxy/cyclohexanoxy titanium(IV) intermediates

The reactions of some titanium tetra-alkoxides with sulphuryl and thionyl chlorides were recently reported by Gerrard and co-workers.[41,42] With titanium alkoxide (C_1-C_4) (1 mole) and sulphuryl chloride (1 mol), the compound isolated was an alkoxy titanium sulphate, whereas under similar conditions thionyl chloride gave dialkoxy (Pr^n, Bu^n) titanium dichloride. With excess of sulphuryl chloride, however, Gerrard and co-workers could isolate the compound $(MeO)_2Ti(SO_2Cl)_2$ from the tetramethoxide. They also noticed that the chloro-titanates $(Bu^nO)_3TiCl$, $(Bu^nO)_2TiCl_2$ and $(Bu^nO)TiCl_3$ were successively less reactive to sulphuryl chloride in accordance with the electronegativity effect of chlorine in lowering the electron-density on oxygen. Under less drastic conditions of reaction, and in presence of a solvent medium, we have isolated a mono-substituted derivative $(RO)_3TiSO_3Cl$ [$R = Et, Pr^i, Bu^n$] in the reaction with sulphuryl chloride. The sulphuryl chloride derivative on heating leaves a white, non-melting residue free from chlorine, which appears to be dialkoxy titanium(IV) sulphate reported by Gerrard. With thionyl chloride, the substitution by chlorine could be extended to the third alkoxy group, giving $(RO)TiCl_3$ [$R = Et, Pr^i, Bu^n$] and some titanium tetrachloride.

Reactions of the tetra-alkoxides with dimethyl and diethyl sulphates gave products of indefinite composition. Dimethyl and diethyl sulphates react, however, with dialkoxy (Me, Et, Pr^i, Bu^n) titanium dichloride (alcoholate) in an excess of the former constituent to give well-defined oxy-titanium alkyl sulphates $OTi(RSO_4)_2$ as grey to violet hygroscopic solids. They are insoluble in all organic solvents except the lower alcohols. No definite product could be isolated from their alcoholic solutions.

Cyclohexanoxides of titanium, on which little work has been reported so far, made an interesting study. The tetra compound reacted with thionyl chloride, as expected, to give the highly chlorinated products cyclohexanoxy trichloro-titanium and titanium tetrachloride, but gave a product of indefinite composition with sulphuryl chloride, and did not react with dimethyl sulphate at all. With dicyclohexanoxy titanium(IV) dichloride, again, dimethyl sulphate did not give any definite product, though the two chlorine atoms could be easily replaced by alkoxy groups (MeO, EtO, Pr^nO, Bu^nO) by reaction with the alcohols in presence of dry ammonia. Phenolic reactants (phenol, catechol, resorcinol) gave both the mono-chloro and the chlorine-free derivatives easily. Even with excess of organic hydroxylic reactants, the two cyclohexanoxy groups in the dichloride remained intact.

Reactions of some titanium aryloxides were carried out with sulphuryl and thionyl chlorides. The products formed often contained both chlorine and sulphur, but were of indefinite composition. With dimethyl sulphate, the reactions were smooth with mono-, di- and tri-chlorophenoxides giving $(PhO)_3Ti(CH_3SO_4)$, $(PhO)_2Ti(CH_3SO_4)_2$ and $(PhO)Ti(CH_3SO_4)SO_4$ respectively, but the tetraphenoxide did not react. Similar results were obtained with thymoxy and vanillino derivatives of titanium in reactions with dimethyl sulphate, but the chloro-titanium derivatives of catechol and resorcinol did not give well-defined products. These methylsulphato derivatives are red powders, stable in the absence of moisture and insoluble in common organic solvents. They dissolve in alcohol with decomposition.

Table 5 sums up the results obtained in the reactions just described with alk-/aryl-/cyclohexan-oxy titanium(IV) compounds.

Table 5

Reaction Products obtained from alkoxy/aryloxy/cyclohexanoxy titanium intermediates

Reactants			Product**	
(A)	(B)	Molar ratio (A:B)		
$Ti(OR)_4$	SO_2Cl_2	1:2.5	$(RO)_3TiSO_3Cl$*	(1)
"	$SOCl_2$	1:4	$(RO)TiCl_3$	(1)
$(RO)TiCl_3$	Dimethyl sulphate	1:3	$(RO)Ti(SO_4)(CH_3SO_4)$*	(3)
$(RO)_2TiCl_2$	"	1:3	$(RO)_2Ti(CH_3SO_4)_2$*	(3)
$(RO)_3TiCl$	"	1:1.5	$(RO)_3Ti(CH_3SO_4)$*	(3)
$(RO)_2TiCl_2.ROH$	"	1:3	$OTi(CH_3SO_4)_2$*	(2)
"	Diethyl sulphate	1:3	$OTi(C_2H_5SO_4)_2$*	(2)
$(cyO)_2TiCl_2$	ROH	1:3	$(C_6H_{11}O)_2Ti(OR)_2$ *	(2)
$(cyO)_2TiCl_2.$ 2cyOH	Phenol	1.5:1	$(C_6H_{11}O)_2Ti(OC_6H_5)Cl$*	
"	"	1:3	$(C_6H_{11}O)_2Ti(OC_6H_5)_2$ *	
"	Catechol	1.5:1	$(C_6H_{11}O)_2Ti(OC_6H_4OH)Cl$*	
"	"	1:3	$(C_6H_{11}O)_2Ti(OC_6H_4OH)_2$ *	
"	Resorcinol	1.5:1	$(C_6H_{11}O)_2Ti(OC_6H_4OH)Cl$ *	
"	"	1:3	$(C_6H_{11}O)_2Ti(OC_6H_4OH)_2$*	

(1) R = Alkyl (C_2-C_4)

(2) R = Alkyl (C_1-C_4)

(3) ROH = phenol, thymol, vanillin

cyOH = cyclohexanol $C_6H_{11}OH$

* new compounds

** based on chemical analysis only.

(b) Acyloxy titanium(IV) intermediates

The synthesis of a new intermediate, dichloro-titanium sulphate, has been mentioned in the preceding section. This yellow, insoluble powder reacts vigorously with lower aliphatic alcohols (Pr^i, Bu^n) or alkyl (Me, Et) acetates (eliminating hydrogen chloride or alkyl chloride) to form white, powdery, dialkoxy-titanium sulphates. Phenol (in excess) formed diphenoxy-titanium sulphate, but dihydric phenols did not give chlorine-free products nor a definite composition for a chloro complex. Direct reaction of the dichloro-sulphate with methanol and ethanol also gave indefinite products often containing some chlorine, though the reaction through their acetate esters was quite successful. Cyclohexanol did not give any definite product even by the acetate route.

Reactions of the dichloro-titanium sulphate with chelating ligands were carried out in a solvent medium (benzene). Though the time of reaction was thus somewhat longer, the products obtained were of good purity. Chelates examined were acetyl- and benzoylacetone, aceto-acetanilide, dibenzoyl-methane, salicylaldehyde and methyl salicylate. In each case the product obtained was L_2TiSO_4 (LH = molecule of ligand), a deeply coloured product insoluble in common organic solvents.

The salicylaldehydo and methylsalicylato compounds, which were originally in solution in benzene in presence of excess of the chelate, became insoluble after precipitation with light petroleum.

In methylsulphato chloro-titanium sulphate $ClTi(MeSO_4)SO_4$, the last chlorine atom reacts easily with hydroxylic compounds. Alcohols (Pr^i, Bu^n) and phenol formed the mono-substituted products, but with cyclohexanol the product was again impure and retained 2-3 per cent of chlorine. The pure cyclohexanoxy derivative was, however, obtained by the action of cyclohexanol on the mono-ethoxy compound $(EtO)Ti(MeSO_4)SO_4$, though this may not prove that the methylsulphato bond is stronger than the ethoxy bond with titanium. The methoxy and ethoxy compounds were best prepared by the acetate route (in preference to direct substitution) as in the case of the dichloro-titanium sulphate. Chelates (LH = acetylacetone, salicylaldehyde, methyl salicylate) reacted in presence of benzene to form compounds of the type $(L)Ti(MeSO_4)SO_4$.

Other chloro-titanium acylates examined for the above-mentioned reactions were dichloro-titanium oxalate, diacetate and dibenzoate. The dichloro oxalate is not as reactive as the dichloro sulphate. Well-defined compounds were isolated only in reactions with phenol, giving $(PhO)_2TiC_2O_4$, and some chelates (LH = acetylacetone, salicylaldehyde, methyl salicylate) giving $L_2TiC_2O_4$ type compounds. With dichloro-titanium diacetate, well-defined compounds were obtained only with dimethyl and diethyl sulphates, giving $(RSO_4)_2TiO$ by simultaneous elimination of RCl and acetic anhydride at 100°. Even by changing the acetate to the corresponding dibenzoate, the acyl part could not be retained, the products being $(MeSO_4)_2TiO$ and $(EtSO_4)_2TiO$ by reactions with dimethyl and diethyl sulphate respectively.

The above two oxy-titanium bis-alkylsulphates, which were also obtained by the action of dialkyl sulphates on dialkoxy titanium dichlorides, are highly hygroscopic, insoluble powders. The compounds prepared are listed in Table 6.

Table 6

Reaction products obtained from acyloxy titanium intermediates

Reactants			Products**
(A)	(B)	Molar ratio (A:B)	
Cl_2TiSO_4	Pr^iOH, Bu^nOH	1: 4	$(Pr/BuO)_2TiSO_4$
"	CH_3COOMe	1: 4	$(MeO)_2TiSO_4$*
"	CH_3COOEt	1: 4	$(EtO)_2TiSO_4$
"	Phenol	1:5	$(C_6H_5O)_2TiSO_4$*
"	Acetylacetone	1:4	$(C_5H_7O_2)_2TiSO_4$*
"	Benzoylacetone	1:3	$(C_{10}H_9O_2)_2TiSO_4$*
"	Acetoacetanilide	1:3	$(C_{10}H_{10}O_3N)_2TiSO_4$*
"	Dibenzoylmethane	1:3	$(C_{15}H_{11}O_2)_2TiSO_4$*
"	Salicylaldehyde	1:4	$(C_7H_5O_2)_2TiSO_4$*
"	Methyl salicylate	1:4	$(C_8H_7O_3)_2TiSO_4$*
$(EtO)_2TiSO_4$	Cyclohexanol	1:2	$(C_6H_{11}O)_2TiSO_4$*

continued.....

Table 6 (continued)

Reactants			Products**
(A)	(B)	Molar ratio (A:B)	
$ClTi(CH_3SO_4)SO_4$	Pr^iOH, Bu^nOH	1: 4	$(RO)Ti(CH_3SO_4)SO_4$*
"	CH_3COOR R = Me, Et	1: 4	$(RO)Ti(CH_3SO_4)SO_4$*
"	Phenol	1:1.5	$(C_6H_5O)Ti(CH_3SO_4)SO_4$*
"	Acetylacetone	1:1.5	$(C_5H_7O_2)Ti(CH_3SO_4)SO_4$
"	Salicylaldehyde	1:1.5	$(C_7H_5O_2)Ti(CH_3SO_4)SO_4$*
"	Methyl salicylate	1:1.5	$(C_8H_7O_3)Ti(CH_3SO_4)SO_4$*
$(EtO)Ti(CH_3SO_4)SO_4$	Cyclohexanol	1:1	$(C_6H_{11}O)Ti(CH_3SO_4)SO_4$*
$Cl_2TiC_2O_4$	Phenol	1:3	$(C_6H_5O)_2TiC_2O_4$*
"	Acetylacetone	1:3	$(C_5H_7O_2)_2TiC_2O_4$*
$Cl_2Ti(OOCCH_3)_2$	Dimethyl sulphate	1:2.5	$OTi(CH_3SO_4)_2$*
"	Diethyl sulphate	1:2.5	$OTi(C_2H_5SO_4)_2$*
$Cl_2Ti(OOCC_6H_5)_2$	Dimethyl sulphate	1:2.5	$OTi(CH_3SO_4)_2$*
"	Diethyl sulphate	1:2.5	$OTi(C_2H_5SO_4)_2$*

* new compounds

** based on chemical analysis only

(c) Chelated titanium(IV) intermediates

Chelated compounds having ring structures through coordination are well known for their stability. The stability of titanium chelates was amply proved in the reactions examined and reported here.

In reactions with $LTiCl_3$, dimethyl sulphate gave coloured solids of the composition $LTi(CH_3SO_4)SO_4$ (LH = acetylacetone, dibenzoylmethane, salicylaldehyde and methyl salicylate). Ethanol gave the crystalline solvate $LTi(OC_2H_5)Cl_2.C_2H_5OH$.[43] Phenol gave the corresponding triphenoxy compound $LTi(OPh)_3$ as expected. Catechol gave $LTi(O_2C_6H_4)(OC_6H_4OH)$, but with resorcinol an ill-defined product was obtained, not corresponding to any definite compound. Acetylacetone replaced the chlorine atoms except the last, but two chlorine atoms were retained in reactions with the chelates, methyl salicylate and salicylaldehyde. Even when an excess of any reacting ligand was used, there was no sign of replacement of the chelated ligand already present.

With <u>bis</u>-chelated dichloro-titaniums, dimethyl sulphate gave the corresponding <u>bis</u>-methylsulphates, and phenol gave the diphenoxy compounds as expected. One molecule of catechol replaced both the chlorine atoms but resorcinol functioned as a monohydric phenol giving the di-derivative $L_2Ti(OC_6H_4OH)_2$, in which the presence of free OH group was indicated by its IR spectrum and by its solubility in aqueous ammonia. Chelates removed one of the two chlorine atoms giving the mono-chloro derivatives L_2TiClL' (LH = salicylaldehyde, methyl salicylate, L'H = acetylacetone).

The reactions of chelated titanium trichlorides and dichlorides with the various reactants are summed up in Table 7.

Table 7

Reaction products obtained from chelated titanium compounds*

Reactants			Products**	
(A)	(B)	Molar ratio (A:B)		
$LTiCl_3$	Ethanol	1: 4	$L(C_2H_5O)TiCl_2.C_2H_5OH$	(1)
$LTiCl_3$	Phenol	1:4	$LTi(OC_6H_5)_3$	(1)
$LTiCl_3$	Catechol	1:3	$LTi(O_2C_6H_4)(OC_6H_4OH)$	(1)
$LTiCl_3$	Dimethyl sulphate	1:3	$LTi(CH_3SO_4)SO_4$	(2)
$LTiCl_3$	L'H	1:2	$LL'TiCl_2$	(3)
$LTiCl_3$	Acetylacetone	1:2.2	$L(C_5H_7O_2)_2TiCl$	(3)
L_2TiCl_2	Phenol	1:3	$L_2Ti(OC_6H_5)_2$	(1)
L_2TiCl_2	Catechol	1:3	$L_2Ti(O_2C_6H_4)$	(1)
L_2TiCl_2	Resorcinol	1:3	$L_2Ti(OC_6H_4OH)_2$	(1)
L_2TiCl_2	Dimethyl sulphate	1:3	$L_2Ti(CH_3SO_4)_2$	(4)
L_2TiCl_2	Acetylacetone	1:2	$L_2(C_5H_7O_2)TiCl$	(3)

(1) LH = Dibenzoylmethane, salicylaldehyde, methyl salicylate

(2) LH = Acetylacetone, dibenzoylmethane, salicylaldehyde, methyl salicylate

(3) LH = L'H = Salicylaldehyde, methyl salicylate

(4) LH = Acetylacetone, benzoylacetone, dibenzoylmethane, salicylaldehyde, methyl salicylate

* All new compounds

** based on chemical analysis only

A study of the I.R. spectra of the above complexes revealed the expected features. For example, in the complexes of salicylaldehyde with titanium such as salicylaldehydo trichloro-titanium and bis-salicylaldehydo dichloro-titanium, the carbonyl band at 1667 cm^{-1} in the free ligand is replaced by an absorption near 1600 cm^{-1} indicating the coordination of the carbonyl group with the metal. The same behaviour is found in the case of the trichloro methylsalicylato complex. In the case of bis-methylsalicylato dichloro-titanium, however, there is an additional band at 1631 cm^{-1} which may indicate a mixture of two structures, as a difference in the strength of the C=O to metal binding for two molecules of the same ligand seems less plausible. The hydroxyl stretching frequency in both the parent ligands is absent in the complexes.

In the mixed complex, salicylaldehydo methylsalicylato dichloro-titanium, there is the same damping of the carbonyl frequency, the band appearing at 1600 cm^{-1} similar to the case of the individual ligand complexes. In the acetylacetone complexes, the coordination of the carbonyl to the metal is very strong and the band at 1709 cm^{-1} in the free ligand is shifted to 1527 cm^{-1} in bis-acetylacetono dichloro-titanium.

The carbonyl absorption frequencies for the three ligands acetylacetone, salicylaldehyde and methyl salicylate are given below with some of the complexes in Table 8. Complete I.R. spectral frequencies of the new compounds are given in the Experimental Section.

Table 8

Carbonyl absorption frequencies in chelated titanium complexes

Compound	CO absorption maxima in cm^{-1}
Acetylacetone	1709
Salicylaldehyde	1667
Methylsalicylate	1670
Bis-acetylacetono dichloro-titanium	1527
Salicylaldehydo trichloro-titanium	1600
Bis-salicylaldehydo dichloro-titanium	1600
Methylsalicylato trichloro-titanium	1597
Bis-methylsalicylato dichloro-titanium	1631,1592
Salicylaldehydo methylsalicylato dichloro-titanium	1606
Bis-salicylaldehydo acetylacetono chloro-titanium	1587
Salicylaldehydo *bis*-acetylacetono chloro-titanium	1562

2(d) Attempts to introduce direct Ti-C bonds

The recent successful attempts to introduce direct titanium-carbon bonds in titanium organics have been reviewed in Chapter I. One idea that had brought initial success was to load the titanium(IV) atom with sufficiently electronegative organic groups so as to lower the electron density at the opposite end, making the latter more favourable for a non-ionogenic titanium-carbon bond to form. It is also generally known that filling up of the empty 3d orbitals of the tetravalent titanium atom with electron pairs from a number of donor groups consistent with its covalency maximum would favour development of non-ionogenic character of its primary valencies.

The stability of some of the chelated organoxy titanium intermediates, particularly the chelated chloro compounds in which the chlorine is easily replaceable by non-ionogenic groups, prompted us to examine the action of lithium phenyl on some of them in the hope of isolating some phenyl-titanium compounds of good thermal stability. Only a few experiments have been carried out, but the results are positive and encouraging. The reactions go smoothly at ordinary (or slightly lower) temperature in an ether suspension of the chloro compound to which the calculated amount of lithium phenyl (dissolved in ether) is added gradually. The compounds isolated give mercuri-chloride test for the Ti-C sigma bond, and some are stable enough to show their monomeric nature in boiling benzene.

Results are given in Table 9. The reaction with lithium phenyl is, however, to be applied with some caution as there is a possibility of the ligand itself forming a derivative with the organo lithium reagent. The scope and possibilities of these reactions, including reactions with Grignard reagents, are to be investigated systematically.

Table 9

Compounds with direct Ti-C bonds*

Reactants			Product**
(A)	(B)	Molar ratio (A:B)	
Salicylaldehydo trichloro-titanium	Lithium phenyl	1:3	$(C_7H_5O_2)Ti(C_6H_5)_3$
Methylsalicylato trichloro-titanium	"	1:3	$(C_8H_7O_3)Ti(C_6H_5)_3$
Dibenzoylmethano trichloro-titanium	"	1:3	$(C_{15}H_{11}O_2)Ti(C_6H_5)_3$
Bis-salicylaldehydo dichloro-titanium	"	1:2	$(C_7H_5O_2)_2Ti(C_6H_5)_2$
Bis-methylsalicylato dichloro-titanium	"	1:2	$(C_8H_7O_3)_2Ti(C_6H_5)_2$
Bis-dibenzoylmethano dichloro-titanium	"	1:2	$(C_{15}H_{11}O_2)_2Ti(C_6H_5)_2$
Bis-benzoylacetono dichloro-titanium	"	1:2	$(C_{10}H_9O_2)_2Ti(C_6H_5)_2$
Diphenoxy dichloro-titanium	"	1:2	$(C_6H_5O)_2Ti(C_6H_5)_2$

* All are new compounds

** based on chemical analysis only

3. Adducts of titanium(IV) complexes with nitrogen bases

In the text book on Advanced Inorganic Chemistry, Cotton and Wilkinson[8c] have noted the variation of coordination number of tetravalent titanium from 4 to 8 and indicated the most probable geometry for each case. Titanium tetrachloride, a Lewis acid, is well known for forming adducts by accepting electron pairs from suitable molecules. It was of interest to see to what extent the tendency persisted in the organic titanium(IV) derivatives. We first observed that many of the complex compounds, though insoluble in ordinary solvents, were readily soluble in pyridine, from which well defined pyridine adducts could be isolated by removing the solvent carefully under reduced pressure. Ammonia adducts were then prepared by suspending the insoluble titanium compound in dry ether and passing a rapid stream of dry ammonia gas at 0°. These adducts are stable, and more resistant to moisture hydrolysis than their parent compounds. A list of the adducts prepared is given in Table 10. It will be seen that ammonia adducts form in most cases and the number of ammonia molecules accommodated is larger than that of pyridine.

Table 10

Ammonia and pyridine adducts of organoxy titanium compounds*

Titanium compound	No. of ammonia molecules per mole of adduct	No. of pyridine molecules per mole of adduct
Dicyclohexanoxy dichloro-titanium	4	-
Diphenoxy "	5	2
m-Phenylenedioxy "	6	2
Dithymoxy "	5	3
Diacetoxy "	5	-
Dibenzoxy "	5	-
Di-phenoxyacetoxy "	4	-
Sulphato "	6	3
Oxalato "	6	3
Bis-salicylaldehydo "	4	2
Bis-methylsalicylato "	4	3
Bis-o-nitrophenoxy "	5	3
Bis-ethylacetoacetato "	5	-
Triphenoxy chloro-titanium	4	-
m-Hydroxyphenoxy m-phenylenedioxy chloro-titanium	4	2
Tetraphenoxy titanium	4	-
Tetrathymoxy titanium	4	-
Di-o-hydroxyphenoxy o-phenylenedioxy titanium	5	3
Oxytitanium bis-methylsulphate	4	3
Oxytitanium bis-ethylsulphate	4	-
Diphenoxy titanium oxalate	5	-

* All are new compounds.

To obtain information on type of binding of ammonia in the ammonia addition compounds, the I.R. spectra of the adducts with disubstituted dichlorotitanium derivatives of salicylaldehyde, methyl salicylate, vanillin, phenol and phenoxyacetic acid were compared with parent dichloro compounds. The spectra of the adducts have all the bands of the parent compounds largely unchanged. Only the extra absorption bands observed are tabulated in Tables 11 and 12. The absorption bands obtained for gaseous ammonia, ammonium chloride and cobalt hexammine chloride[44] are also given for comparison.

Table 11

Extra bands observed in ammonia addition compounds

(Salicyl aldehydo)$_2$ $TiCl_2.4NH_3$	(Methyl-salicylato)$_2$ $TiCl_2.4NH_3$	(Vanillino)$_2$ $TiCl_2.4NH_3$	(Phenoxy)$_2$ $TiCl_2.5NH_3$	(Phenoxy acetoxy)$_2$ $TiCl_2.4NH_3$	Assignment
3155	3145	3145	3145	3125	asymmetric/ symmetric
3058	3045	3030	3067	3030	NH stretching
1634	1656	1621	1603	1678	asymmetric deformation
1304	1412	1408	1408	1408	symmetric deformation
834	800	769	760	760	rocking

Table 12

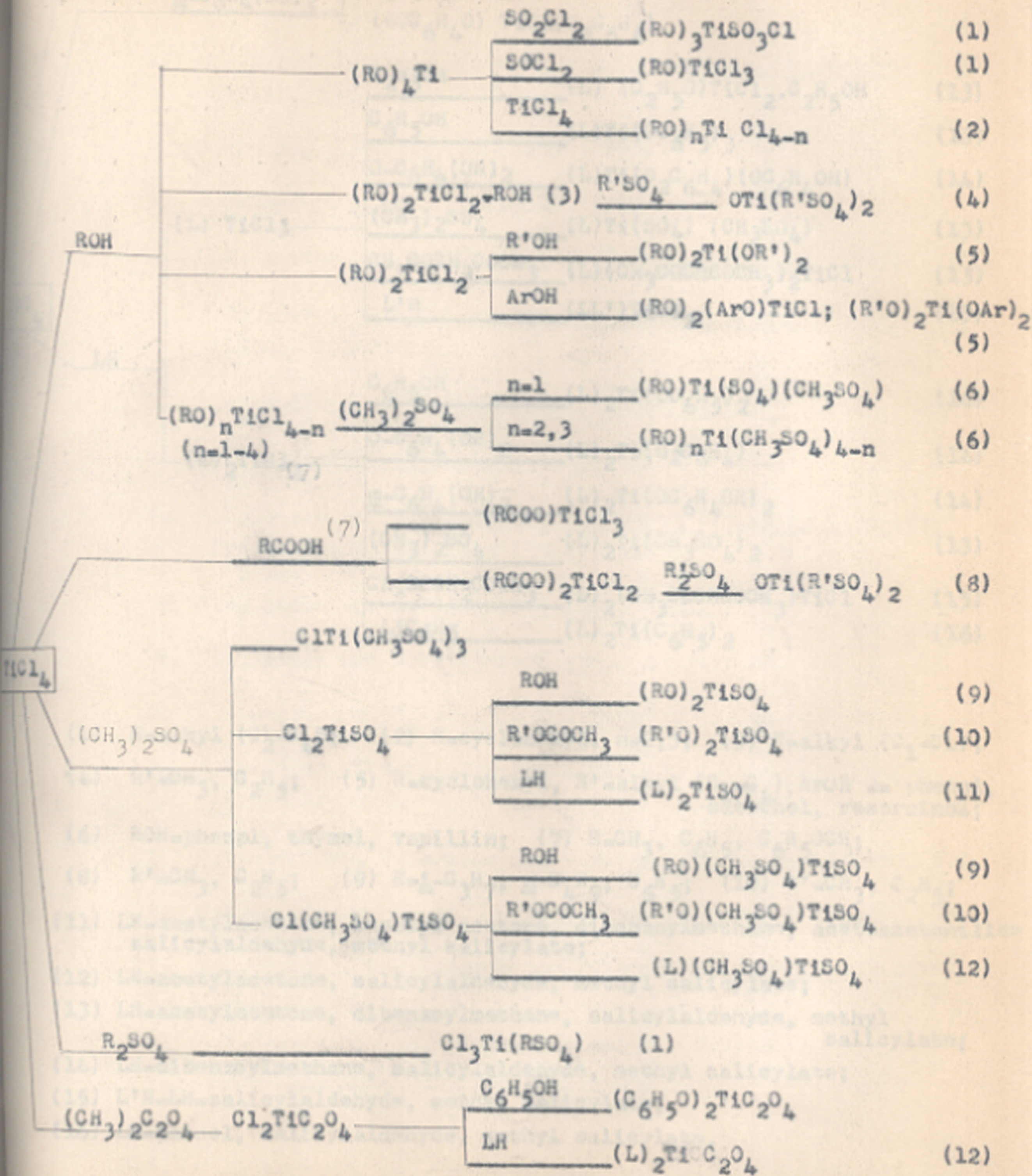
Absorption bands observed for gaseous ammonia, Cobalt hexammine chloride and ammonium chloride

NH_3	$[Co(NH_3)_6]Cl_3$	NH_4Cl
3414	3240	3138
3336	3170	3041
1628	1600	1710
	1325	1403
	820	

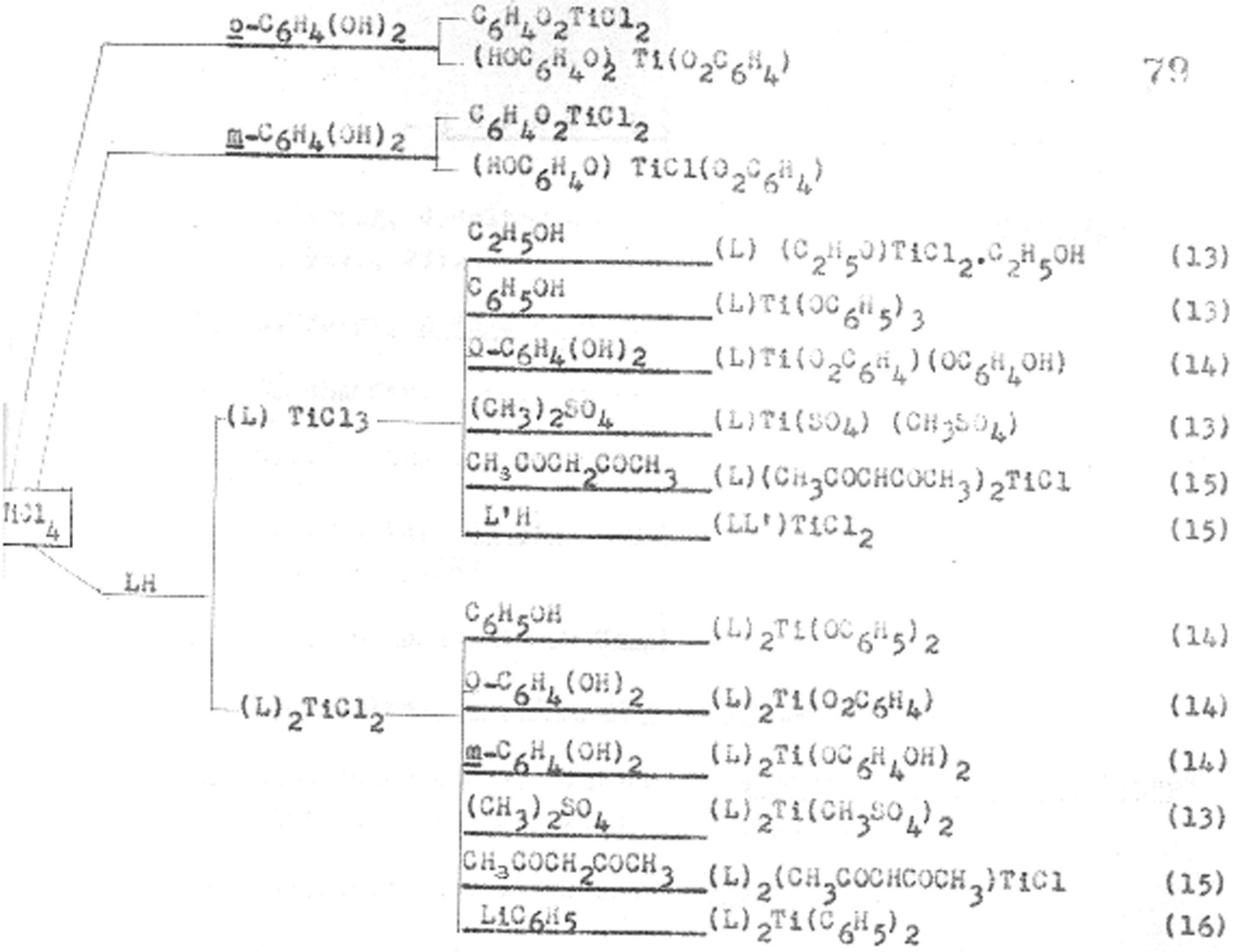
The absence of NH_4^+ ion in these adducts, though not clearly established by the spectra has been chemically proved by the absence of ammonium chloride in the liquid ammonia extract of the ammonia adducts. The absence of appreciable changes in the ligand spectra on adduct formation rules out any chemical reaction of ammonia with the ligand. The considerable similarity between the ammonia bands in the adducts and the hexammine complexes of cobalt indicate possible coordination of the metal ion to ammonia in these compounds. While the NH stretching bands in the adducts lie in the same region as observed for the hexammine, the NH deformation is appreciably shifted to higher frequencies, 1621-1678 cm^{-1}. Since the titanium atom has already coordinated with the ligand completing six coordination in the first two and four coordination in the last three, it is not immediately clear as to how four or five addition molecules of ammonia can be accommodated in the coordination sphere. However the fact that ammonia is a small molecule should be responsible for such a large number. The corresponding pyridine adducts contain only two or three molecules of pyridine. Titanium tetrachloride ammoniates containing six and eight ammonia molecules have been reported.[45] Titanium tetrachloride is also known to form adducts with a large number of organic molecules, the number of adduct molecules being sometimes as high as five.[46] The fairly stable nature of these new adducts as compared to the parent complexes, as well as the fact that infrared spectra of these show similarity to those for the cobaltammine complex, would lead us to suggest that ammonia molecules are coordinated to the central titanium in these compounds. In some cases, however, the possibility of formation of an ammonia adduct of the ligand itself is not also ruled out. Indeed, a combination of the two events may lead to an unusually high number of ammonia molecules held by the titanium complex, as observed in several cases.

A schematic representation of the typical reactions and reaction products examined and reported in the thesis is given in the next page. Certain patterns of reaction products are discernible, though more extensive data would be desirable for generalization. It must also be admitted that sufficient physical data could not be recorded to give indisputable structures, - a handicap felt also by other workers in this field on account of the insolubility of most of the products, combined with their sensitiveness to moisture. Chelation and direct metal-carbon bonding are the two promising lines pointing towards increased stability to moisture as well as better control on the degree of polymerization of the products. These are proposed to be studied more intensively in future.

Synoptic Table of synthesized titanium organics



(continued)



(1) R=alkyl (C_2-C_4); (2) R=cyclohexyl, n=2,3; (3) R=alkyl (C_1-C_4);

(4) R'=CH_3, C_2H_5; (5) R=cyclohexyl, R'=alkyl (C_1-C_4), ArOH = phenol, catechol, resorcinol;

(6) ROH=phenol, thymol, vanillin; (7) R=CH_3, C_6H_5, $C_6H_5OCH_2$;

(8) R'=CH_3, C_2H_5; (9) R=i-C_3H_7, n-C_4H_9, C_6H_5; (10) R'=CH_3, C_2H_5;

(11) LH=acetylacetone, benzoyl acetone, dibenzoylmethane, acetoacetanilide salicylaldehyde, methyl salicylate;

(12) LH=acetylacetone, salicylaldehyde, methyl salicylate;

(13) LH=acetylacetone, dibenzoylmethane, salicylaldehyde, methyl salicylate;

(14) LH=dibenzoylmethane, salicylaldehyde, methyl salicylate;

(15) L'H=LH=salicylaldehyde, methyl salicylate;

(16) LH=phenol, salicylaldehyde, methyl salicylate.

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CHAPTER III

EXPERIMENTAL DATA

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1. Purification of Starting Materials

Titanium tetrachloride, prepared by the chlorination of upgraded Indian ilmenite, was purified by refluxing over copper and distilling twice to obtain a clear, colourless liquid, B.P. 135-136°. Solid organic reagents were purified by recrystallisation, and liquid reagents by distillation, under reduced pressure where necessary. Solvents were purified and dried by procedures given by Weissburger.[1] Methyl, ethyl, *n*-propyl and *n*-butyl sulphates were purified as described by Vogel and Cowan[2] and distilled under reduced pressure. Salicylaldehyde, methyl salicylate, acetylacetone and ethyl acetoacetate were dried with anhydrous sodium sulphate and fractionally distilled under reduced pressure.

Extreme care was taken to exclude moisture at all stages. Experiments with $TiCl_4$ were usually done in a dry nitrogen atmosphere in all-glass apparatus fitted with standard ground glass joints. Reagents and chemicals were preserved under a dry atmosphere when not in use.

Unless otherwise stated, the light petroleum (pet.ether) used in the experiments had the boiling range 40-60°C.

2. Primary Reaction Products from Titanium Tetrachloride

2.1. Reactions with aliphatic and alicyclic hydroxy compounds:

2.1.1. Di-methoxy dichloro-titanium methanolate-

This was prepared by the method reported by Jennings *et al.*[3] To dry methanol (32 g; 1 mole) $TiCl_4$ (19 g; 0.1 mole) was slowly added in a dry nitrogen atmosphere at 0°. The pale yellow liquid was refluxed for two hours and then distilled under reduced pressure (40mm) at 70-80°, to remove excess of methanol. The residue in the flask, which solidified to a white mass on cooling, was dried over P_2O_5. Yield 13 g. (61% of theory; lit. yield not mentioned).

Analysis: Found Ti 22.61, Cl 33.10; calculated for $(CH_3O)_2TiCl_2.CH_3OH$, Ti 22.53, Cl 33.34 per cent.

White, hygroscopic solid, soluble in alcohol, light petroleum and benzene. Hydrolysed by water.

2.1.2. Di-ethoxy dichloro-titanium ethanolate-

This was prepared by a modification of Jennings' method.[3] A mixture of ethyl alcohol (45 g; 1 mole) and benzene (25 ml) was cooled to 0° and a solution of $TiCl_4$ (19 g; 0.1 mole) in benzene (25 ml) was added dropwise. The mixture was then refluxed for six hours, after which the solution was concentrated to half its original volume and allowed to stand overnight.

The separated crystals were filtered, recrystallised from a 1:1 mixture of benzene and alcohol, and dried at room temperature over P_2O_5. Yield 18 g. (70% of theory; lit. yield not mentioned).

Analysis: Found Ti 18.67, Cl 27.47; calculated for $(C_2H_5O)_2TiCl_2.C_2H_5OH$, Ti 18.82, Cl 27.85 per cent.

Colourless, very hygroscopic crystals, soluble in alcohol, light petroleum and benzene; easily hydrolysed on exposure to moist air.

2.1.3. Di-isopropoxy dichloro-titanium isopropanolate-

This was prepared in the above manner using isopropanol (30 g; 0.5 mole) and $TiCl_4$ (19 g; 0.1 mole). Yield 20 g. (67% of theory; lit. yield not mentioned).

Analysis: Found Ti 16.01, Cl 23.58; calculated for $(C_3H_7O)_2TiCl_2.C_3H_7OH$, Ti 16.15, Cl 23.91 per cent.

White, hygroscopic solid, soluble in alcohol, light petroleum and benzene. Hydrolysed by moist air.

2.1.4. Di-*n*-butoxy dichloro-titanium butanolate-

The compound was obtained in an analogous manner from *n*-butyl alcohol (37 g; 0.5 mole) and $TiCl_4$ (19 g; 0.1 mole). Yield 34 g. (59% of theory; lit. yield not mentioned).

Analysis: Found Ti 13.98, Cl 20.89; calculated for $(C_4H_9O)_2TiCl_2.C_4H_9OH$, Ti 14.16, Cl 20.94 per cent.

White, hygroscopic solid, easily soluble in alcohol and benzene, but less soluble in light petroleum. Easily hydrolysed in moist air.

2.1.5. Tetra-ethoxy titanium-

This was prepared by the method of Herman.[4] Ethanol (23 g; 0.5 mole) and $TiCl_4$ (19 g; 0.1 mole) each diluted with 50 ml benzene, were mixed at 0° and then refluxed for four hours, after which dry ammonia gas was passed in at a slow rate for one hour. Ammonium chloride formed was filtered off and the filtrate fractionally distilled under reduced pressure. Tetraethoxy titanium distilled at 150° at 8mm pressure (lit. 145-146° at 7mm pressure). Yield 14 g. (63% of theory; lit. yield not mentioned).

Colourless liquid, miscible with light petroleum and benzene in all proportions. Easily hydrolysed on exposure to moist air.

2.1.6. Tetra-isopropoxy titanium-

This was prepared like the previous ester from isopropanol (30 g; 0.5 mole) and $TiCl_4$ (19 g; 0.1 mole). The product distilled at 108° at 8mm (lit. 116° at 10mm). Yield 17 g.(60% of theory; lit. yield not mentioned.

Colourless liquid, miscible with light petroleum and benzene in all proportions. Hydrolysed on exposure to air.

2.1.7. Tetra-n-butoxy titanium-

This also was prepared like the two preceding esters using n-butanol (37 g; 0.5 mole) and $TiCl_4$ (19 g; 0.1 mole). The product distilled at 178° at 8mm (lit. 185° at 10mm). Yield 20 g. (58% of theory; lit. yield 72%).

Pale yellow liquid, miscible with light petroleum and benzene in all proportions. Hydrolysed in moist air.

2.1.8. Di-cyclohexanoxy dichloro-titanium-

Cyclohexanol (20 g; 0.2 mole) in benzene (50 ml) and $TiCl_4$ (19 g; 0.1 mole) in benzene (50 ml) were mixed at 0°. The pale yellow liquid was refluxed for six hours, allowed to stand overnight and then concentrated to crystallization. The crystals were washed with light petroleum and dried in vacuum at 60°. Yield 16 g (60% of theory). A purer product was obtained by recrystallization from benzene.

Analysis: Found Ti 15.11, Cl 22.31, C 44.93, H 7.21; calculated for $(C_6H_{11}O)_2TiCl_2$, Ti 15.14, Cl 22.40, C 45.42, H 6.94 per cent.

White solid, hygroscopic, soluble in all common solvents but decomposed in moist air. It melted at 105°, but could not be distilled without decomposition. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 295; calculated 317.

With aliphatic alcohols it reacted in presence of ammonia gas giving alkoxides by replacement of both the chlorine atoms.

Infrared absorption maxima (in cm^{-1}) are given below:
1626w, 1399s, 1346s, 1294s, 1258s, 1230s, 1124s, 1064s, 1028m, 961s, 893s, 840s, 784s, 676s.

2.1.9. Di-cyclohexanoxy dichloro-titanium di-cyclohexanolate-

A solution of cyclohexanol (40 g; 0.4 mole) in benzene (100 ml) was cooled in ice and $TiCl_4$ (19 g; 0.1 mole) in benzene (50 ml) was added dropwise. After one hour, the pale yellow solution was refluxed for six hours and then allowed to stand overnight. The crystals formed were filtered, washed with light petroleum and dried in vacuum at 60°. Yield 40 g (78 per cent of theory). It was purified by recrystallization from hot benzene.

Analysis: Found Ti 9.24, Cl 13.71, C 55.01, H 8.83; calculated for $(C_6H_{11}O)_2TiCl_2.2C_6H_{11}OH$, Ti 9.28, Cl 13.74, C 55.71, H 8.9 per cent.

Colourless hygroscopic crystals, m.p.115°, soluble in hot benzene, light petroleum and easily soluble in alcohol. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 181; calculated 517. When heated under reduced pressure (1mm) it gave cyclohexanol and a partly decomposed residue. In presence of ammonia it reacted with its own solvate cyclohexanol to give tetra-cyclohexanoxy titanium.

Infrared absorption maxima (in cm^{-1}) are given below:-

3280s, 1639m, 1408s, 1346s, 1294s, 1258s, 1230s, 1143s, 1053s, 1020s, 961s, 893s, 862s, 848s, 719s.

2.1.10. Tri-cyclohexanoxy chloro-titanium-

Tetra-cyclohexanoxy titanium (6.66 g; 0.015 mole) in benzene (15 ml) and $TiCl_4$ (0.95 g; 0.005 mole) in benzene (10 ml) were mixed together at 0° ; heat was evolved during mixing. The mixture was kept refluxing for one hour. Afterwards, a part of benzene was removed under reduced pressure and the solution allowed to crystallise. A white solid separated was filtered and dried under reduced pressure at 60°. Yield 5 g (65% of theory).

Analysis: Found Ti 12.72, Cl 9.41; calculated for $(C_6H_{11}O)_3TiCl$, Ti 12.61, Cl 9.32 per cent.

White hygroscopic solid, m.p.55-58°, soluble in benzene and light petroleum. On heating under reduced pressure it turned brown but did not give distillate. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 359; calculated 380.5.

2.1.11. Tetra-cyclohexanoxy titanium-

This was prepared by a modification of Nesmeyanov's procedure[5]. $TiCl_4$ (19 g; 0.1 mole) was added dropwise to cyclohexanol (45 g; 0.45 mole) in benzene (100 ml) at 0° and the mixture refluxed for four hours. On keeping overnight, crystals separated which were redissolved by warming and dry ammonia gas was passed slowly with cooling. Ammonium chloride formed was filtered off, and the liquid fractionally distilled under reduced pressure. The tetra-ester distilled at about 200° at 1mm (lit. 190-192° at 1mm) and on cooling became a white semi-solid mass. Yield 33 g (75% of theory; yield reported in literature 53%).

Analysis: Found Ti 10.79; calculated for $Ti(OC_6H_{11})_4$, Ti 10.81 per cent.

White, viscous, hygroscopic liquid, soluble in benzene and alcohol. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 444.6; calculated 444.

2.2 Reactions of $TiCl_4$ with aromatic hydroxylic compounds:

2.2.1. Phenoxy trichloro-titanium-

Lutischinsky's method[6] was used to prepare this compound. Phenol (1.88 g; 0.02 mole) in benzene (10 ml) and $TiCl_4$ (5.7 g; 0.03 mole) in benzene (10 ml) were mixed at 0°. On refluxing, HCl evolved and after three hours a part of benzene was distilled off and the solution allowed to stand. The crystals formed were washed with light petroleum and dried at room temperature at reduced pressure. Yield 3.5 g (70% of theory).

Analysis: Found Ti 19.38, Cl 43.05; calculated for $(C_6H_5O)TiCl_3$, Ti 19.40, Cl 43.01 per cent.

Chocolate coloured, hygroscopic powder, m.p.104-105°, soluble in benzene and in alcohol, but slightly so in light petroleum. Decomposed in moist air. The alcoholic solution on evaporation gives pale yellow, hygroscopic crystals of $(C_6H_5O)(OC_2H_5)\ TiCl_2.C_2H_5OH$.

2.2.2. Diphenoxy dichloro-titanium-

Levy's procedure[7] for the preparation of this compound was found to give good results. Phenol (18.8 g; 0.2 mole) in benzene (20 ml) and $TiCl_4$ (19 g; 0.1 mole) in benzene (30 ml) were mixed at 0°. On refluxing, HCl evolved and a deep red solution was obtained. A part of benzene was removed by distillation after refluxing for six hours. On keeping overnight the crude product separated, which was washed with light petroleum and dried at 60° in vacuum. Yield 21 g (69% of theory). The product was purified by recrystallization from benzene.

Analysis: Found Ti 15.83, Cl 23.34; calculated for $(C_6H_5O)_2TiCl_2$, Ti 15.73, Cl 23.28 per cent.

Deep red crystals, m.p.115°, very hygroscopic and sensitive to moisture, soluble in alcohol and benzene but slightly so in light petroleum.

2.2.3. Triphenoxy chloro-titanium-

This was also prepared by a slight modification of Levy's method[7] from phenol (28.2 g; 0.3 mole) and $TiCl_4$ (19 g; 0.1 mole) in benzene medium. The product was washed with light petroleum and dried at room temperature. Yield 30 g (80% of theory).
Analysis: Found Ti 13.15, Cl 9.69; calculated for $(C_6H_5O)_3TiCl$, Ti 13.24, Cl 9.78 per cent.

Deep red crystalline solid, m.p.132°, hygroscopic, soluble in alcohol and benzene, and slightly so in light petroleum.

2.2.4. Tetra-phenoxy titanium-

Schumann's procedure[8] was modified by using benzene as the reaction medium. Phenol (18.8 g; 0.2 mole) and $TiCl_4$ (4.5 g; 0.05 mole) were mixed and refluxed in benzene for ten hours. Then a part of benzene was distilled off and solution allowed to stand overnight. The red crystals formed were filtered, washed with light petroleum and dried at room temperature under reduced pressure. Yield 14 g (65% of theory).
Analysis: Found Ti 11.35; calculated for $(C_6H_5O)_4Ti$, Ti 11.43 per cent.

Orange-red solid, m.p.152-153°, less hygroscopic than the phenoxy chloro-titaniums, soluble in alcohol and benzene and slightly so in light petroleum.

2.2.5. o-Phenylenedioxy dichloro-titanium-

Catechol (11 g; 0.1 mole) was dissolved in light petroleum (B.P.78°, 100 ml) and $TiCl_4$ (28.5 g; 0.15 mole) in light petroleum (25 ml) was added dropwise with stirring at 0°. A vigorous reaction took place forming a red solution which gave HCl on heating. After refluxing for six hours the solution was allowed to stand overnight and the separated solid was filtered, washed with light petroleum and dried at 60° at 1mm. Yield 20 g (88% of theory).
Analysis: Found Ti 21.34, Cl 31.36, C 31.47, H 1.96; calculated for $(C_6H_4O_2)TiCl_2$, Ti 21.14, Cl 31.28, C 31.72, H 1.76 per cent.

Deep brown powder, insoluble in benzene, light petroleum and chloroform, but soluble in alcohol and pyridine. Not hygroscopic. Stable upto 250°.

Infrared absorption maxima (in cm^{-1}) are given below:-
1590w, 1255m, 1200w, 1155w, 1105m, 1070w, 1020w, 925w, 886m , 835w, 825m, 750s, 725w.

2.2.6. Di-*o*-hydroxyphenoxy *o*-phenylenedioxy titanium-

Catechol (8.8g; 0.08 mole) was dissolved in benzene (50 ml) and $TiCl_4$ (3.8 g; 0.02 mole) in benzene (25 ml) was added with stirring at 0° and the mixture then refluxed for 48 hours. The solid which separated was filtered, washed with light petroleum and dried at 60° at 1mm. Yield 7 g (93% of theory).
Analysis: Found Ti 12.76, C 57.67, H 4.01; calculated for $(C_6H_4O_2)Ti(OC_6H_4OH)_2$, Ti 12.83, C 57.76, H 3.74 per cent.

Chocolate-red powder, not hygroscopic, insoluble in benzene, light petroleum and chloroform, but soluble in alcohol and pyridine. Stable up to 200°. It dissolved in aqueous ammonia and the solution gave an ammonium salt on concentration.

The same compound was obtained when *o*-phenylenedioxy dichloro-titanium was refluxed with catechol in benzene for 24 hours.

Infrared absorption maxima (in cm^{-1}) are given below:-
3030w, 2732w, 2674w, 2618w, 2591w, 1577w, 1493s, 1401m, 1319m, 1285m, 1266s, 1247s, 1199m, 1182m, 1149w, 1104s, 1035w, 1022m, 959w, 922m, 908s, 873s, ~~873s~~, 801s, 740s, 673s, 663s.

2.2.7. *m*-Phenylenedioxy dichloro-titanium-

Resorcinol (11 g; 0.1 mole) in benzene (50 ml) and $TiCl_4$ (28.5 g; 0.15 mole) in benzene (25 ml) were mixed at 0°. The red solution, which gave HCl on heating, was refluxed for six hours and then kept overnight. The red powdery substance that formed was filtered, washed with hot light petroleum and dried at 60° under reduced pressure. Yield 21 g (92.5% of theory). Analysis: Found Ti 21.24, Cl 31.32, C 31.99, H 2.64; calculated for $(C_6H_4O_2)TiCl_2$, Ti 21.14, Cl 31.28, C 31.72, H 1.76 per cent.

Bright red powder, stable in air, insoluble in benzene and chloroform but soluble in alcohol and pyridine. Decomposes above 250°.

Infrared absorption maxima (in cm^{-1}) are given below:- ~~3226s~~, 1613m, 1580s, 1299w, 1266s, 1250m, 1170s, 1130s, 1081w, 986s, 862s, 833w, 787s, 671s.

2.2.8. *m*-Hydroxyphenoxy-*m*-phenylenedioxy chloro-titanium-

Resorcinol (8.8 g; 0.08 mole) in benzene (50 ml) and $TiCl_4$ (3.8 g; 0.02 mole) in benzene (25 ml) were mixed at 0° and refluxed for 48 hours. The deep red powder which separated was washed with light petroleum and dried at 60° at 1mm pressure. Yield 5.6 g (93% of theory).

Analysis: Found Ti 15.88, Cl 11.80, C 48.33, H 3.29; calculated for $(C_6H_4O_2)Ti(OC_6H_4OH)Cl$, Ti 15.97, Cl 11.80, C 47.93, H 3.00 per cent.

Deep red powder, stable in air, insoluble in benzene, light petroleum and chloroform but soluble in alcohol and pyridine. Decomposes above 250°.

The same compound was obtained when m-phenylenedioxy dichloro-titanium was refluxed with resorcinol in benzene for 24 hours.

Infrared absorption maxima (in cm^{-1}) are given below:- 2646w, 1567m, 1348w, 1272m, 1259m, 1235w, 1160m, 1129m, 1075w, 982w, 977m, 888w, 869w, 857w, 849w, 810w, 772m, 686m, 667m.

2.2.9. Vanillino trichloro-titanium-

Vanillin (1.52 g; 0.01 mole) in benzene (20 ml) and $TiCl_4$ (3.8 g; 0.02 mole) in benzene (20 ml) were mixed at 0° and refluxed for eight hours. The chocolate coloured solid was filtered, washed with light petroleum and dried at 60° at 1mm. pressure. Yield 2 g (66% of theory).
Analysis: Found Ti 15.53, Cl 34.42; calculated for $(C_8H_7O_3)\ TiCl_3$, Ti 15.71, Cl 34.92 per cent.

Shining chocolate-coloured hygroscopic solid, insoluble in benzene and light petroleum but soluble in alcohol and pyridine. Decomposes above 200°.

2.2.10. Di-vanillino dichloro-titanium-

Vanillin (3.04 g; 0.02 mole) and $TiCl_4$ (1.9 g; 0.01 mole) were reacted in benzene medium as in the above experiment. The dichloro compound was washed with light petroleum and dried at 60° at 1mm. Yield 4 g (95% of theory).

Analysis: Found Ti 11.29, Cl 16.72; calculated for $(C_8H_7O_3)_2TiCl_2$, Ti 11.40, Cl 16.87 per cent.

Chocolate-brown hygroscopic solid, soluble in alcohol and pyridine. Decomposes above 180°.

Infrared absorption maxima (in cm^{-1}) are given below:-

1656m, 1628m, 1575s, 1282s, 1230m, 1163m, 1117m, 1026w, 870m, 826m, 781m, 730m.

2.2.11. Tri-vanillino chloro-titanium-

Vanillin (6.08 g; 0.04 mole) in benzene (25 ml) and $TiCl_4$ (1.9; 0.01 mole) in benzene (15 ml) were mixed at 0° and then refluxed for 48 hours. The solid product obtained was filtered, washed with light petroleum and dried at 60° at 1mm. Yield 4 g (74% of theory).

Analysis: Found Ti 9.00, Cl 6.58; calculated for $(C_8H_7O_3)_3TiCl$, Ti 8.95, Cl 6.61 per cent.

Dark red solid, hygroscopic, soluble in alcohol and pyridine. Decomposes above 200°. This compound did not react with more vanillin to give the pure tetra derivative.

2.2.12. Thymoxy trichloro-titanium-

Thymol (1.5 g; 0.01 mole) in benzene (20 ml) and $TiCl_4$ (3.8 g; 0.02 mole) in benzene (20 ml) were mixed together at 0° and then refluxed for four hours. The crystals which separated on cooling were washed with benzene and light petroleum and dried at 60° at 1mm. Yield 2.2 g (73% of theory).

Analysis: Found Ti 15.85, Cl 35.21, C 40.02, H 4.53; calculated for $(C_{10}H_{13}O)TiCl_3$, Ti 15.81, Cl 35.10, C 39.55, H 4.28 per cent.

Chocolate crystalline solid, hygroscopic, soluble in alcohol and pyridine. Decomposes above 210°.

2.2.13. Di-thymoxy dichloro-titanium-

This was prepared by the procedure by Levy[7] by reacting thymol (3 g; 0.02 mole) with $TiCl_4$ (1.9 g; 0.01 mole) in benzene medium. After refluxing for six hours the product which separated was filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 3 g (72% of theory).

Analysis: Found Ti 11.31, Cl 16.85; calculated for $(C_{10}H_{13}O)_2TiCl_2$, Ti 11.51, Cl 17.03 per cent.

Dark red solid, hygroscopic, slightly soluble in benzene and easily in alcohol and pyridine.

Infrared absorption maxima (in cm^{-1}) are given below:-

1613w, 1290w, 1250w, 1156m, 1087w, 1058w, 1015w, 971w, 957w, 810s, 741w, 720w.

2.2.14. Tri-thymoxy chloro-titanium-

Thymol (4.5 g; 0.03 mole) and $TiCl_4$ (1.9 g; 0.01 mole) were mixed in toluene (25 ml) and refluxed for six hours. The solution was then concentrated to crystallization. The solid separated was filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 3.4 g (75% of theory).

Analysis: Found Ti 8.9, Cl 6.62; calculated for $(C_{10}H_{13}O)_3TiCl$, Ti, 9.05, Cl 6.65 per cent.

Brownish red solid, hygroscopic, slightly soluble in benzene and decomposes at about 100°.

2.2.15. Tetra-thymoxy titanium-

Thymol (7.5 g; 0.05 mole) in toluene (25 ml) and $TiCl_4$ (1.9 g; 0.01 mole) in toluene (25 ml) were slowly mixed at 0° and refluxed for 15 hours. The solution was then concentrated by distilling off a part of toluene. The orange powder formed was washed with light petroleum and dried at 60° under reduced pressure. Yield 4 g (63% of theory).

Analysis: Found Ti 7.52, C 74.69, H 8.17; calculated for $(C_{10}H_{13}O)_4Ti$, Ti 7.45, C 74.52, H 8.08 per cent.

Orange powder, slightly hygroscopic, soluble in benzene, alcohol and pyridine. Decomposes at about 180°. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 602; calculated 644.

2.3. Reactions of $TiCl_4$ with carboxylic compounds:

2.3.1. Dichloro-titanium diacetate-

This was prepared by a modification of the procedure of Schwartz *et al*[14]. $TiCl_4$ (9.5 g; 0.05 mole) and dry acetic acid (6.6 g; 0.11 mole) were mixed at 0°. The mixture was stirred for one hour and kept overnight at room temperature. The product was then extracted with an equimolar mixture of chloroform and carbon tetrachloride and crystallized. Yield 7.5 g (60% of theory). Analysis: Found Ti 20.3, Cl 30.6; calculated for $(CH_3COO)_2TiCl_2$, Ti 20.2, Cl 29.9 per cent.

Pale yellow crystalline solid, hygroscopic. Soluble in alcohol and in a mixture of chloroform and carbon tetrachloride. Insoluble in benzene and light petroleum. Decomposes at 180°.

2.3.2. Dichloro-titanium dibenzoate-

This was prepared by the method of Mehrotra and Varma.[15] $TiCl_4$ (9.5 g; 0.05 mole) in benzene (20 ml) and benzoic acid (13.4 g; 0.11 mole) in benzene (20 ml) were mixed and refluxed for four hours. On cooling, crystals separated which were washed with benzene and dried at 60° under reduced pressure. Yield 16 g (90 per cent of theory). Analysis: Found Ti 13.40, Cl 19.58; calculated for $(C_6H_5COO)_2TiCl_2$, Ti 13.29, Cl 19.67 per cent.

Pale yellow crystalline solid, hygroscopic, soluble in alcohol and insoluble in benzene, light petroleum and chloroform-carbon tetrachloride mixture. Decomposes at about 185°.

2.3.3. Trichloro-titanium phenoxyacetate-

Phenoxyacetic acid (1.52 g; 0.01 mole) in benzene (15 ml) and $TiCl_4$ (2.84 g; 0.015 mole) in benzene (15 ml) were mixed at 0° and refluxed for four hours. Hydrogen chloride evolved and the product separated, which was washed with light petroleum and dried at 60° under reduced pressure. Yield 2.5 g (80% of theory).

Analysis: Found Ti 15.69, Cl 34.71; calculated for $(C_6H_5OCH_2COO)TiCl_3$, Ti 15.71, Cl 34.85 per cent.

Deep yellow, hygroscopic, light powder. On exposure to moist air turns white. Soluble only in alcohol. Decomposes on heating above 150°.

2.3.4. Dichloro-titanium di-phenoxyacetate-

Phenoxyacetic acid (3.04 g; 0.02 mole) was dissolved in benzene (25 ml) and $TiCl_4$ (1.9 g; 0.01 mole) in benzene (10 ml) was added dropwise at 0°. A vigorous reaction took place with evolution of HCl. On refluxing for four hours the product separated. It was washed with light petroleum and dried at 60° under reduced pressure. Yield 4 g (95% of theory).

Analysis: Found Ti 11.38, Cl 17.01, C 45.31, H 4.1; calculated for $(C_6H_5OCH_2COO)_2TiCl_2$, Ti 11.40, Cl 16.87, C 45.60, H 3.33 per cent.

Orange-red light powder, slightly hygroscopic. Soluble in alcohol but insoluble in benzene and light petroleum. It turns black without melting above 150°. Infra-red absorption maxima (in cm-1) are given below:-
1567s, 1493s, 1429s, 1418s, 1351w, 1333s, 1299m, 1266m, 1240s, 1225s, 1190m, 1176m, 1100w, 1087m, 1058m, 1015w, 968m, 935w, 893w, 830s, 813m, 787w, 752s, 714w, 688m.

2.4. Reactions of $TiCl_4$ with esters:

2.4.1. Dichloro-titanium sulphate-

Dimethyl sulphate (2.52 g; 0.02 mole) was added dropwise to $TiCl_4$ (5.7 g; 0.03 mole) kept at 0°. The yellow solution slowly became viscous, evolved methyl chloride, and within 48 hours became solid. Then the volatile products and excess of $TiCl_4$ were removed at 80° at 0.1mm pressure. $TiCl_4$ (1.8 g) was collected in a cold trap. The residue in the flask was a yellow powder. Yield 4.3 g (quantitative).

Analysis: Found Ti 22.10, Cl 32.5, S 14.43; calculated for $TiCl_2SO_4$, Ti 22.32, Cl 33.03, S 14.38 per cent.

Lemon-yellow powder, extremely hygroscopic, insoluble in benzene, light petroleum, chloroform, methylene chloride, cyclohexane and tetrahydrofuran, but soluble in alcohols (with decomposition) and in pyridine (forming an adduct). It did not melt, but decomposed at about 250°. It dissolved in a small amount of water, and on dilution gave a precipitate of hydrated titanium dioxide. On exposure (one week) to moist air in a closed system, dichloro-titanium sulphate gave a clear solution (smelling strongly of HCl), which on drying under reduced pressure at 70° gave hydrated titanyl sulphate, $TiOSO_4.H_2O$.

2.4.2. Tris-(methylsulphato)chloro-titanium-

$TiCl_4$ (4.75 g; 0.025 mole) was added dropwise to dimethyl sulphate (12.6 g; 0.1 mole) at 0°. The deep yellow solution slowly became viscous, methyl chloride bubbled out, and within 48 hours became a yellow solid. Then excess of dimethyl sulphate and other volatile products were distilled off at 90° under 0.1mm pressure to give a yellow powder. Yield 10 g (nearly quantitative). Analysis: Found Ti 11.75, Cl 8.47, S 23.23; calculated for $Ti(CH_3SO_4)_3Cl$, Ti 11.53, Cl 8.51, S 23.05 per cent.

Yellow powder, very sensitive to moisture, becoming white and deliquescent on exposure. Insoluble in benzene, light petroleum and chloroform, but soluble in alcohols with decomposition. Turns black above 150°.

2.4.3. Methylsulphato chloro-titanium sulphate-

Dimethyl sulphate (12.6 g; 0.1 mole) was added dropwise to $TiCl_4$ (9.5 g; 0.05 mole) at 0°. The deep yellow viscous solution evolved methyl chloride and when kept for 48 hours under a dry atmosphere became a yellow transparent solid. This was dried at 0.1mm pressure at 90°, when a deep yellow powder was obtained. Yield 14 g (nearly quantitative). Analysis: Found Ti 16.49, Cl 12.12, S 22.13; calculated for $TiSO_4(CH_3SO_4)Cl$, Ti 16.52, Cl 12.21, S 22.04 per cent.

Deep yellow hygroscopic compound, soluble only in alcohols with chemical reaction. On heating, it decomposes at about 200°.

2.4.4. Ethylsulphato trichloro-titanium-

Diethyl sulphate (1.54 g; 0.01 mole) was added dropwise on $TiCl_4$ (3.8 g; 0.02 mole) at 0°. A vigorous reaction took place and ethyl chloride was evolved. The yellow semi-solid substance formed was kept at room temperature for 48 hours and then heated to 90° at 0.1mm pressure. The product was obtained as a yellow powder. Yield 2.7 g (nearly quantitative).

Analysis: Found Ti 17.30, Cl 37.89, S 11.53; calculated for $Ti(C_2H_5SO_4)Cl_3$, Ti 17.18, Cl 38.09, S 11.45 per cent.

Deep yellow hygroscopic powder, insoluble in benzene, light petroleum etc. solvents but soluble in alcohols with decomposition. At 120° it decomposed into dichloro-titanium sulphate and ethyl chloride.

2.4.5. n-Propylsulphato trichloro-titanium-

This was prepared similarly by reacting di-n-propyl sulphate (1.82 g; 0.01 mole) with $TiCl_4$ (3.8 g; 0.02 mole). The product was dried at 90° at 0.1mm. pressure. Yield 2.5 (85% of theory).

Analysis: Found Ti 16.91, Cl 35.98, S 10.87; calculated for $Ti(C_3H_7SO_4)Cl_3$, Ti 16.35, Cl 36.29, S 10.90 per cent.

Yellow powder, slowly turns greenish on keeping, very hygroscopic. Insoluble in common solvents and dissolves in alcohols with decomposition.

2.4.6. *n*-Butylsulphato trichloro-titanium-

Di-*n*-butyl sulphate (1.96 g; 0.01 mole) and $TiCl_4$ (3.82 g; 0.02 mole) were mixed at 0°. The solid product was kept for 48 hours and then dried at 90° at 0.1mm pressure. Yield 2 g (65% of theory).

Analysis: Found Ti 15.70, Cl 33.89, S 10.27; calculated for $Ti(C_4H_9SO_4)Cl_3$, Ti 15.01, Cl 34.66, S 10.41 per cent.

Brownish yellow hygroscopic solid, soluble only in alcohols with decomposition. Turns grey and decomposes on keeping for more than one week.

2.4.7. Dichloro-titanium oxalate-

Finely powdered dimethyl oxalate (2.36 g; 0.02 mole) was placed in a flask cooled in ice and $TiCl_4$ (5.7 g; 0.03 mole) was added dropwise. A vigorous reaction took place and a yellow solid was formed. It was kept at 0° for one hour and then kept at 120° in oil bath for four hours. Methyl chloride was given off during this period. The volatile products and excess of $TiCl_4$ were distilled off at 90° at 0.1mm pressure, the product washed with light petroleum and dried at 60° at 1mm pressure. Yield 4 g (96% of theory).

Analysis: Found Ti 22.88, Cl 34.25; calculated for $TiCl_2C_2O_4$, Ti 23.19, Cl 34.26 per cent.

Pale yellow powder, very hygroscopic, soluble in alcohols with decomposition and insoluble in all common solvents. In pyridine, it dossolves forming an adduct. On heating, it decomposes above 160°.

2.5. Reactions of $TiCl_4$ with dibentate chelates:

2.5.1. Acetylacetono trichloro-titanium-

The procedure recommended by Mehrotra[13] was used for its preparation. Acetylacetone (1 g; 0.01 mole) and $TiCl_4$ (2.85 g; 0.015 mole) both diluted with benzene (15 ml each) were mixed at 0° and refluxed for four hours. The product separated was filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 2 g (80% of theory; lit. yield 42%).

Analysis: Found Ti 19.09, Cl 41.82; calculated for $(C_5H_7O_2)TiCl_3$, Ti 18.93, Cl 42.01 per cent.

Chocolate hygroscopic powder, slightly soluble in benzene and easily in alcohol. Insoluble in light petroleum. The alcoholic solution on evaporation gives pale yellow, hygroscopic crystals of $(C_5H_7O_2)(OC_2H_5)TiCl_2.C_2H_5OH$.

2.5.2. Salicylaldehydo trichloro-titanium-

Salicylaldehyde (2.44 g; 0.02 mole) in benzene (10 ml) was added dropwise to $TiCl_4$ (5.7 g; 0.03 mole) in benzene (20 ml) at 0° and the mixture refluxed till HCl was no longer evolved (about four hours). The brown solid separated was filtered, washed with benzene and dried at 80° at 1mm pressure. Yield 4 g (73% of theory).

Analysis: Found Ti 17.42, Cl 37.99, C 30.30, H 1.84; calculated for $(C_7H_5O_2)TiCl_3$, Ti 17.43, Cl 38.64, C 30.51, H 1.816 per cent.

Chocolate powder, hygroscopic, absorbs moisture on exposure and turns yellow. Insoluble in benzene, light petroleum and chloroform but soluble in alcohol. The alcoholic solution on evaporation gives orange, hygroscopic crystals of $(C_7H_5O_2)(OC_2H_5)TiCl_2.C_2H_5OH$.

Infrared absorption maxima (in cm^{-1}) of salicylaldehydo trichloro-titanium are given below:-

1600s, 1555s, 1397m, 1333w, 1269m, 1242m, 1220m, 1156m, 1124w, 1031w, ~~837s, 749m, 712s.~~ 909s, 810m, 766s.

2.5.3. Methylsalicylato trichloro-titanium-

Methyl salicylate (3.04 g; 0.02 mole) in benzene (20 ml) and $TiCl_4$ (5.7 g; 0.03 mole) in benzene (20 ml) were mixed at 0° and refluxed for four hours. The product which separated was filtered, washed with benzene and light petroleum and dried at 80° at 1mm. Yield 5 g (82% of theory).

Analysis: Found Ti 15.88, Cl 34.58; calculated for $(C_8H_7O_3)TiCl_3$, Ti 15.71, Cl 34.85 per cent.

Chocolate powder decomposes at 160°, sensitive towards moisture and turns yellow on exposure. Insoluble in benzene, chloroform and light petroleum, but soluble in alcohol. The alcoholic solution on evaporation gives yellow hygroscopic crystals of $(C_8H_7O_3)(OC_2H_5)TiCl_2.C_2H_5OH$.

Infrared absorption maxima (in cm^{-1}) of methylsalicylato-trichloro-titanium are given below:

1597m, 1550m, 1351s, 1325m, 1307m, 1266w, 1235m, 1190w, 1163m, 1143w, 1105w, 1031w, 958w, 893s, 851m, 796w, 761m, 694w, 688m, 660w.

2.5.4. Dibenzoylmethano trichloro-titanium-

The reaction between dibenzoylmethane (2.24 g; 0.01 mole) and $TiCl_4$ (2.85 g; 0.015 mole) in benzene medium was carried out at 0° as in the previous experiments. The mixture was refluxed for four hours and allowed to stand overnight. The chocolate powder which separated was filtered, washed with light petroleum and dried at 80° at 1mm pressure.
Yield 3 g (79% of theory).

Analysis: Found Ti 12.76, Cl 27.92; calculated for $(C_{15}H_{11}O_2)TiCl_3$, Ti 12.74, Cl 28.21 per cent.

Chocolate hygroscopic powder. Soluble in alcohol but insoluble in benzene and chloroform. The alcoholic solution on evaporation gives yellow hygroscopic crystals of $(C_{15}H_{11}O_2)(OC_2H_5)TiCl_2.C_2H_5OH$.

2.5.5 Bis-acetylacetono dichloro-titanium-

This was prepared by the procedure recommended by Mehrotra and Puri[11]. Acetylacetone (15 g; 0.15 mole) in benzene (20 ml) and $TiCl_4$ (9.5 g; 0.05 mole) in benzene (20 ml) were slowly mixed at 0° and the mixture refluxed for three hours. On cooling, orange-yellow crystals separated. These were filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure.
Yield 10 g (80% of theory, lit. yield 93%).
Analysis: Found Ti 15.22, Cl 22.43; calculated for $(C_5H_7O_2)_2TiCl_2$, Ti 15.12, Cl 22.40 per cent.

Orange-yellow powder, M.P. 192-194° (with decomposition), hygroscopic. Slightly soluble in hot benzene, insoluble in light petroleum and easily soluble in alcohol.

2.5.6. *Bis*-ethylacetoacetato dichloro-titanium-

This compound was prepared according to the procedure recommended by Mehrotra and Puri[11]. Ethyl acetoacetate (19.5 g; 0.15 mole) in benzene (20 ml) was added dropwise to a well cooled solution of $TiCl_4$ (95g; 0.05 mole) in benzene (20 ml). The mixture was then refluxed for three hours and a part of benzene was distilled off. On keeping overnight crystals separated which were filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 12 g (62% of theory).

Analysis: Found Ti 12.69, Cl 18.78; calculated for $(C_6H_9O_3)_2TiCl_2$, Ti 12.74, Cl 18.84 per cent.

Orange-red crystalline hygroscopic solid, M.P.125°, soluble in benzene and ether, slightly soluble in light petroleum and dissolves easily in alcohol.

2.5.7. *Bis*-salicylaldehydo dichloro-titanium-

The procedure recommended by Mehrotra and Varma[10] was followed for its preparation. Salicyladehyde (18.3 g; 0.15 mole) in benzene (50 ml) and $TiCl_4$ (9.5 g; 0.05 mole) in benzene (50 ml) were mixed at 0° and refluxed for four hours. The dichloro compound formed was filtered, washed with benzene and light petroleum and dried at 80° at lmm. Yield 16 g (88% of theory).

Analysis: Found Ti 13.35, Cl 19.61; calculated for $(C_{14}H_{10}O_4)TiCl_2$, Ti 13.30, Cl 19.70 per cent.

Brown powder, not hygroscopic, insoluble in benzene and light petroleum but soluble in alcohol. It dissolves in pyridine forming an adduct.

2.5.8. Bis-methylsalicylato dichloro-titanium-

The procedure recommended by Mehrotra and Puri[11] was followed for the preparation of this compound. Methyl salicylate (22.8 g; 0.15 mole) and $TiCl_4$ (9.5 g; 0.05 mole) both diluted with benzene (25 ml each) were mixed at 0° and refluxed for four hours. After keeping overnight the product separated and was filtered, washed with benzene and light petroleum and dried at 80° at 1mm. pressure. Yield 19 g (90% of theory, lit. yield 96.7%).

Analysis: Found Ti 11.6, Cl 16.85; calculated for $(C_8H_7O_3)_2TiCl_2$, Ti 11.4, Cl 16.87 per cent.

Orange-red powder, M.P.205°, not very hygroscopic, almost insoluble in benzene and light petroleum but soluble in alcohol. It dissolves in pyridine forming an adduct.

2.5.9. Bis-dibenzoylmethano dichloro-titanium-

The procedure of Nyholm *et al*[12] was modified by using benzene instead of glacial acetic acid as the solvent. Dibenzoylmethane (4.48 g; 0.02 mole) in benzene (15 ml) and $TiCl_4$ (1.9 g; 0.01 mole) in benzene (15 ml) were mixed at 0°. The mixture was warmed and then refluxed till no more HCl came out (about three hours). After keeping overnight, the product was filtered, washed with light petroleum and dried at 80° at 1mm pressure. Yield 4.8 g (85% of theory, lit. yield not mentioned).

Analysis: Found Ti 8.44, Cl 12.51; calculated for $(C_{15}H_{11}O_2)_2TiCl_2$, Ti 8.49, Cl 12.57 per cent.

Red shining powder, stable up to 250°, not very hygroscopic, soluble in alcohol, but insoluble in benzene and chloroform.

2.5.10. Bis-benzoylacetono dichloro-titanium-

This compound was prepared by a slight modification of Nyholm et al[12] procedure. Benzoylacetone (3.24 g; 0.02 mole) in benzene (15 ml) was added drop by drop to $TiCl_4$ (1.9 g; 0.01 mole) in benzene (15 ml) at 0°. vigorous reaction took place and HCl evolved. The solution was refluxed for four hours and kept overnight. The crystals formed were filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 3.8 g (86% of theory, lit. yield not mentioned).

Analysis: Found Ti 10.89, Cl 16.15; calculated for $(C_{10}H_9O_2)_2TiCl_2$, Ti 10.80, Cl 16.10 per cent.

Red crystalline powder, decomposes at 205°, sensitive to moisture, insoluble in benzene and light petroleum but soluble in alcohol.

2.5.11. Bis-(o-nitrophenoxy) dichloro-titanium-

Lutischinsky's method[9] was followed to prepare this compound. o-Nitrophenol (2.78 g; 0.02 mole) and $TiCl_4$ (1.9 g; 0.01 mole) were mixed in benzene (30 ml) solutions at 0° and refluxed for four hours. Then a part of benzene was distilled off and solution allowed to stand. The dichloro compound separated was washed with light petroleum and dried at 60° under reduced pressure. Yield 2 g (50% of theory).

Analysis: Found Ti 12.25, Cl 17.82, C 36.51, H 2.12; calculated for $(C_6H_4ONO_2)_2TiCl_2$, Ti 12.15, Cl 17.95, C 36.46, H 2.025 per cent.

Scarlet red crystals, hygroscopic, soluble in benzene and alcohol but insoluble in light petroleum. It dissolves in pyridine forming an adduct.

3. Further Reactions with the Primary Organoxy-titanium compounds

3.1. Titanium alkoxides (and cyclohexanoxides):

3.1.1. $(RO)_2TiCl_2$ + dimethyl sulphate-

($R=CH_3$, C_2H_5, i-C_3H_7, n-C_4H_9)

The dialkoxy dichloro-titanium alcoholate (0.01 mole) was mixed with dimethyl sulphate (0.03 mole) in the cold, then gradually heated to 100° and kept for four hours. Alkyl chloride escaped and the product solidified. It was powdered, washed with dry ether and dried at 60° under reduced pressure (1mm). Yield 2.8 g (nearly quantitative).

Analysis: For $R=CH_3$, found Ti 16.56, S 22.29; for $R=C_2H_5$, Ti 16.71, S 22.31; for $R=i$-C_3H_7, Ti 16.81, S 22.39; for $R=n$-C_4H_9, Ti 16.68, S 22.41 per cent; calculated for $OTi(CH_3SO_4)_2$, Ti 16.78, S 22.38 per cent.

Grey to violet-black hygroscopic solids, insoluble in benzene, light petroleum and chloroform. They dissolved in alcohol with decomposition.

3.1.2. $(RO)_2TiCl_2$ + diethyl sulphate-

($R=CH_3$, C_2H_5 i-C_3H_7, - n-C_4H_9)-

These reactions were carried out as in the preceding experiments, but using diethyl sulphate in place of dimethyl sulphate. The products, obtained in almost quantitative yields (3.1 g), were again of nearly the same composition in all the cases.

Analysis: For R=CH_3, found Ti 15.40, S 20.42; for R=C_2H_5, Ti 15.31, S 20.25; for R=i-C_3H_7, Ti 15.26, S 20.36; for R=n-C_4H_9, Ti 15.19, S 20.35 per cent; calculated for $OTi(C_2H_5SO_4)_2$, Ti 15.29, S 20.38 per cent.

Grey to black solids, more hygroscopic than the corresponding methylsulphato derivatives, insoluble in benzene, light petroleum and chloroform.

Titanium tetra-alkoxides and dimethyl/diethyl sulphate gave products of indefinite composition.

3.1.3. $Ti(OR)_4$ + sulphuryl chloride-
(R=C_2H_5, i-C_3H_7, n-C_4H_9)-

The tetra-alkoxy titanium (0.02 mole) in light petroleum (20-25 ml) was cooled in ice and sulphuryl chloride (0.05 mole) was added dropwise. An exothermic reaction took place, after which the mixture was refluxed for four hours. The excess of sulphuryl chloride and the solvent were then removed under reduced pressure, the residue washed with light petroleum and dried at 60° under reduced pressure. Yield nearly quantitative.

Analysis: For R=C_2H_5, found Ti 16.14, Cl 12.01, S 11.00; calculated for $(C_2H_5O)_3TiSO_3Cl$, Ti 16.08, Cl 11.88, S 10.72 per cent; for R=i-C_3H_7, found Ti 13.97, Cl 10.59, S 9.58; calculated for $(C_3H_7O)_3TiSO_3Cl$, Ti 14.09, Cl 10.41, S 9.40 per cent; for R=n-C_4H_9 found Ti 12.66, Cl 9.46, S 8.50; calculated for $(C_4H_9O)_3TiSO_3Cl$, Ti 12.54, Cl 9.27, S 8.36 per cent.

White to light grey, hygroscopic, non-melting solids, dissolving in alcohol with decomposition.

3.1.4. $Ti(OR)_4$ + thionyl chloride-

($R = C_2H_5$, i-C_3H_7, n-C_4H_9)-

The tetra-alkoxy titanium (0.02 mole) in light petroleum (20-25 ml) was cooled in ice and thionyl chloride (0.08 mole). was added dropwise. A vigorous reaction took place and sulphur dioxide evolved. The mixture was then refluxed for four hours, after which excess of thionyl chloride and the solvent were removed under reduced pressure till the volume of the liquid in the flask was reduced to about 10 ml. The syrupy liquid on keeping overnight at 0° gave colourless crystals which were filtered and washed with cold light petroleum and dried at room temperature under reduced pressure. Yield 2-2.2 g (45-50% of theory).

Analysis: For $R = C_2H_5$, found Ti 24.13, Cl 54.04, Cl 12.09, H 2.75; calculated for $(C_2H_5O)TiCl_3$, Ti 24.05, Cl 53.38, C 12.03, H 2.51 per cent; for $R = i$-C_3H_7, found Ti 22.53, Cl 50.07; calculated for $(C_3H_7O)TiCl_3$, Ti 22.48, Cl 49.89 per cent; for $R = n$-C_4H_9, found Ti 20.95, Cl 46.42, C 21.84, H 4.39; calculated for $(C_4H_9O)\ TiCl_3$, Ti 21.11, Cl 46.78, C 21.11, H 4.0 per cent.

Colourless, very hygroscopic crystals, soluble in benzene, light petroleum and chloroform. Melting points 76-78°, 78-79° and 68-70° respectively for $R = C_2H_5$, i-C_3H_7 and n-C_4H_9.

3.1.5. Dicyclohexanoxy dichloro-titanium + ROH
($R=CH_3$, C_2H_5, $\underline{n}-C_3H_7$, $\underline{n}-C_4H_9$)

Dicyclohexanoxy dichloro-titanium (3.17 g; 0.01 mole) was dissolved in benzene (15 ml), the alcohol (0.03 mole) added in the cold and a slow stream of dry ammonia gas was bubbled through the strongly cooled mixture for 15 minutes. The precipitate of ammonium chloride was filtered off and the filtrate evaporated under reduced pressure at 80° to obtain the dicyclohexanoxy dialkoxy derivative. Yield in all cases 80-90 per cent of theoretical.

Analysis: For $R=CH_3$, found Ti 15.67, $-OCH_3$ 19.84; calculated for $(C_6H_{11}O)_2Ti(OCH_3)_2$, Ti 15.58, $-OCH_3$ 20.13 per cent; for $R=C_2H_5$, found Ti 14.15, $-OC_2H_5$ 26.11; calculated for $(C_6H_{11}O)_2Ti(OC_2H_5)_2$, Ti 14.29, $-OC_2H_5$ 26.79 per cent; for $R=n-C_3H_7$, found Ti 13.00, $-OC_3H_7$ 30.68; calculated for $(C_6H_{11}O)_2Ti(OC_3H_7)_2$, Ti 13.18, $-OC_3H_7$ 32.42 per cent; for $R=\underline{n}-C_4H_9$, found Ti 12.11; calculated for $(C_6H_{11}O)_2Ti(OC_4H_9)_2$, Ti 12.25 per cent.

White, sticky hygroscopic substances, soluble in benzene and light petroleum. Decompose in presence of water and on distillation even under reduced pressure.

Identical compounds were also obtained from the reaction between cyclohexanol (2 mole) and corresponding titanium tetra-alkoxide (C_1-C_4; 1 mole). The alcohol formed in the reaction was removed under reduced pressure.

3.1.6. Dicyclohexanoxy dichloro-titanium + (A) phenol, (B) catechol, (C) resorcinol-

A1. Phenol (0.94 g; 0.01 mole) was added to dicyclohexanoxy dichloro-titanium dicyclohexanolate (7.75 g; 0.015 mole) in light petroleum (B.P. 76°, 20 ml). On refluxing (six hours) a yellow solid separated which was filtered, washed with small quantities of light petroleum containing ten per cent benzene (v/v), and dried at room temperature under reduced pressure. Yield 3 g (63% of theory).

Analysis: Found Ti 10.00, Cl 7.30; calculated for $(C_6H_{11}O)_2(C_6H_5O)TiCl.C_6H_{11}OH$, Ti 10.1, Cl 7.47 per cent.

Yellow hygroscopic solid, soluble in benzene but less so in light petroleum. M.P.$134-135^\circ$. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 231.5, calculated 474.5.

A2. Phenol (2.82 g; 0.03 mole) was added to dicyclohexanoxy dichloro-titanium dicyclohexanolate (5.17 g; 0.01 mole) in benzene (15 ml). After refluxing for six hours a red solid separated which was filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 2 g (46% of theory).

Analysis: Found Ti 11.23; calculated for $(C_6H_{11}O)_2\ Ti(OC_6H_5)_2$, Ti 11.13 per cent.

Orange hygroscopic powder, soluble in benzene and less so in light petroleum and chloroform. M.P.102-104°. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 402; calculated 432.

Infrared absorption maxima (in cm^{-1}) are given below:-
3175w, 2857m, 1587s, 1449m, 1399w, 1351w, 1235s, 1198s, 1163s, 1130w, 1070s, 1036m, 1020s, 1000m, 953s, 905s, 869s, 844s, 820s, 813m, 775s, 755s, 725m, 690s, 588s.

B1. Catechol (1.1 g; 0.01 mole) was added to dicyclohexanoxy dichloro-titanium dicyclohexanolate (7.75 g; 0.015 mole) in light petroleum (B.P. 76°, 20 ml) and refluxed for twelve hours. The powder separated was filtered, washed with light petroleum containing ten per cent benzene and dried at 60° under reduced pressure. Yield 3.5 g (89% of theory).

Analysis: Found Ti 12.00, Cl 8.7; calculated for $(C_6H_{11}O)_2(HOC_6H_4O)\ TiCl$, Ti 12.29, Cl 9.08 per cent.

Chocolate powder, slightly hygroscopic, insoluble in benzene, light petroleum and chloroform. M.P.134-135°.

B2. Catechol (3.3 g; 0.03 mole) was added to a benzene solution of dicyclohexanoxy dichloro-titanium dicyclohexanolate (5.17 g; 0.01 mole) and refluxed for twelve hours. The red solid separated was filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 3 g (86% of theory).

Analysis: Found Ti 10.37, C 61.12, H 5.95; calculated for $(C_6H_{11}O)_2Ti(OC_6H_4OH)_2$, Ti 10.35, C 62.07, H 6.9 per cent.

Chocolate powder, non-hygroscopic, insoluble in benzene, light petroleum and chloroform. Decomposes at 175°.

Infrared absorption maxima (in cm^{-1}) are given below:- 3509w, 1586m, 1325s, 1266s, 1250s, 1198s, 1186s, 1149m, 1105s, 1036m, 1026s, 920s, 909s, 872s, 802s, 741s.

C1. Resorcinol (1.1 g; 0.01 mole) was reacted with dicyclohexanoxy dichloro-titanium dicyclohexanolate (7.75 g; 0.015 mole) in light petroleum as in experiment B1 above. Yield 3.4 g (87% of theory).

Analysis: Found Ti 11.83, Cl 9.0; calculated for $(C_6H_{11}O)_2(OC_6H_4OH)TiCl$, Ti 12.29, Cl 9.08 per cent.

Orange-red stable powder, insoluble in benzene, light petroleum and chloroform. Decomposes at 195°.

C2. Resorcinol (3.3 g; 0.03 mole) and dicyclohexanoxy dichloro-titanium dicyclohexanolate (5.17 g; 0.01 mole) were reacted in benzene as in experiment B2. Yield 3 g (65% of theory)

Analysis: Found Ti 10.40; calculated for $(C_6H_{11}O)_2$-$Ti(OC_6H_4OH)_2$, Ti 10.35 per cent.

Red, non-hygroscopic powder insoluble in benzene, light petroleum and chloroform, m.p. 85°.

Infrared absorption maxima (in cm^{-1}) are given below:-

3175s, 1613s, 1299s, 1220m, 1316s, 1149s, 1075m, 986w, 962s, 851m, 760m, 722m, 687m.

The reaction products from dicyclohexanoxy dichloro-titanium and dimethylsulphate were of indefinite composition. Dimethyl sulphate did not react with tetra-cyclohexanoxy titanium at all.

3.2. Titanium aryloxides:

3.2.1. $(C_6H_5O)_nTiCl_{4-n}$ + dimethyl sulphate (n=1,2,3)-

(a) Phenoxy trichloro-titanium (2.47 g; 0.01 mole) was mixed with dimethyl sulphate (3.78 g; 0.03 mole) at room temperature, gradually heated up to 100° and kept for four hours in a stream of dry nitrogen. Methyl chloride evolved and the product solidified. It was washed with dry ether and dried at 60° under reduced pressure. Yield 3 g (86.2% of theory).

Analysis: Found Ti 13.89, S 18.31, C 24.32, H 3.1; calculated for $(C_6H_5O)\,Ti(SO_4)CH_3SO_4$, Ti 13.79, S 18.40, C 24.14, H 2.3 per cent.

Deep chocolate powder, hygroscopic, insoluble in common organic solvents but dissolves in alcohol with decomposition.

(b) Diphenoxy dichloro-titanium (3.05 g; 0.01 mole) was mixed with dimethyl sulphate (3.78 g; 0.03 mole) and the mixture processed as in the preceding experiment. Yield 3.5 g (76.8% of theory).

Analysis: Found Ti 10.46, S 14.11, C 37.13, H 4.02; calculated for $(C_6H_5O)_2Ti(CH_3SO_4)_2$, Ti 10.52, S 14.04, C 36.84, H 3.51 per cent.

Red hygroscopic powder insoluble in common organic solvents but dissolves in alcohol with decomposition.

(c) Triphenoxy chloro-titanium (3.63 g; 0.01 mole) was added to dimethyl sulphate (1.89 g; 0.015 mole) heated at 100° for six hours and processed as before. Yield 3.8 g (84.8% of theory).

Analysis: Found Ti 11.01, S 7.39; calculated for $(C_6H_5O)_3TiCH_3SO_4$, Ti 10.96, S 7.305 per cent.

Brown powder, hygroscopic, insoluble in common organic solvents but dissolves in alcohol with decomposition.

Tetra-phenoxy titanium did not react with dimethyl sulphate.

3.2.2. (Vanillino)$_n$TiCl$_{4-n}$ + dimethyl sulphate- (n=1,2,3)-

(a) Vanillino trichloro-titanium (3.06 g; 0.01 mole) was reacted with dimethyl sulphate (3.78 g; 0.03 mole) at 100° for four hours and product washed with dry ether and dried at 60° at reduced pressure. Yield 3.2 g (78.8% of theory).

Analysis: Found Ti 11.92, S 15.71, C 23.76, H 2.21; calculated for $(C_8H_7O_3)Ti(SO_4)CH_3SO_4$, Ti 11.82, S 15.77, C 23.64, H 1.724 per cent.

Brown powder, hygroscopic, insoluble in common organic solvents but dissolves in alcohol with decomposition.

(b) Di-vanillino dichloro-titanium (4.21 g; 0.01 mole) was reacted with dimethyl sulphate (3.78 g; 0.03 mole) at 100° for four hours and product processed by washing with ether and drying at 60° under reduced pressure. Yield 4.5 g (78% of theory).

Analysis: Found Ti 8.47, S 11.11; calculated for $(C_8H_7O_3)_2\ Ti(CH_3SO_4)_2$, Ti 8.39, S 11.19 per cent.

Chocolate hygroscopic powder, insoluble in common organic solvents but dissolves in alcohol with decomposition.

(c) Tri-vanillino chloro-titanium (5.37 g; 0.01 mole) was mixed with dimethyl sulphate (3.78 g; 0.03 mole) and mixture heated at 100° for four hours. The product was washed with ether and dried at 60° at reduced pressure. Yield 5 g (81.7% of theory).

Analysis: Found Ti 7.91, S 5.30; calculated for $(C_8H_7O_3)_3Ti\ CH_3SO_4$, Ti 7.84, S 5.23 per cent.

Chocolate hygroscopic powder, insoluble in common organic solvents but dissolves in alcohol with decomposition.

3.2.3. (Thymoxy)$_n$TiCl$_{4-n}$ + dimethyl sulphate- (n = 1,2,3)

(a) Thymoxy trichloro-titanium (3.04 g; 0.01 mole) at 100° was reacted with dimethyl sulphate (3.78 g; 0.03 mole) for four hours and product washed with ether and dried at 60° under reduced pressure. Yield 3.2 g (79% of theory).

Analysis: Found Ti 11.82, S 15.79, C 24.12, H 2.34; calculated for $(C_{10}H_{13}O)\ Ti(SO_4)\ CH_3SO_4$, Ti 11.88, S 15.84, C 23.76, H 1.733 per cent.

Brown powder, hygroscopic, insoluble in common organic solvents but dissolves in alcohol with decomposition.

(b) Di-thymoxy dichloro-titanium (4.17 g; 0.01 mole) and dimethyl sulphate (3.78 g; 0.03 mole) were reacted at 100° for four hours and product processed as before. Yield 4.5 g (79% of theory).

Analysis: Found Ti 8.39, S 11.32; calculated for $(C_{10}H_{13}O)_2Ti(CH_3SO_4)_2$, Ti 8.45, S 11.27 per cent.

Red powder, hygroscopic, insoluble in common organic solvents but dissolves in alcohol with decomposition.

(c) Tri-thymoxy chloro-titanium (2.25 g; 0.005 mole) and dimethyl sulphate (1.9 g; 0.015 mole) were reacted at 100° for four hours and product processed as before. Yield 2.5 g (80% of theory).

Analysis: Found Ti 8.0, S 5.41; calculated for $(C_{10}H_{13}O)_3Ti(CH_3SO_4)$, Ti 7.92, S 5.28 per cent.

Brown powder, hygroscopic, insoluble in common organic solvents but dissolves in alcohol with decomposition.

3.3. Titanium acylates:

3.3.1.A Dichloro-titanium sulphate + ROH-
(R=$\underline{i}$-C_3H_7, $\underline{n}$-C_4H_9, C_6H_5)

(a) Dichloro-titanium sulphate (2.1 g; 0.01 mole) was added to dry isopropanol (15 ml) and refluxed for six hours. HCl evolved and the yellow dichloro compound slowly dissolved in the alcohol. When the reaction was over, excess isopropanol was distilled off at reduced pressure, the product washed with dry ether and dried at 60° under reduced pressure. Yield 2.5 g (95% of theory).

Analysis: Found Ti 18.41, S 12.26, C 26.90, H 5.41; calculated for $(C_3H_7O)_2TiSO_4$, Ti 18.32, S 12.20, C 27.48, H 5.343 per cent.

White powder, slightly hygroscopic, insoluble in benzene, light petroleum and chloroform but dissolves in alcohol. Decomposes without melting at 145-150°.

(b) A similar reaction as the above was carried out using dry $\underline{n}$-butanol (15 ml) in place of isopropanol. Yield of product 2.8 g (96% of theory).

Analysis: Found Ti 16.51, S 11.14, C 33.22, H 6.91; calculated for $(C_4H_9O)_2TiSO_4$, Ti 16.55, S 11.04, C 33.11, H 6.207 per cent.

White powder, slightly hygroscopic, insoluble in benzene, light petroleum and chloroform but dissolves in alcohol. On heating, decomposes without melting at 135-140°.

The reaction products of dichloro-titanium sulphate with methanol and ethanol were of indefinite composition and found to contain about 2-4 per cent of chlorine which could not be removed. Cyclohexanol (and its acetate) also gave indefinite products.

(c) Diethoxy titanium sulphate (2.34 g; 0.01 mole) and cyclohexanol (2 g; 0.02 mole) were mixed and kept at 100° under reflux for one hour. Then benzene (30 ml) was added and distilled to remove all ethanol formed in the reaction azeotropically. The residue was dried, washed with light petroleum and dried at 60° under reduced pressure. Yield 3.4 g (nearly quantitative).

Analysis: Found Ti 14.12, S 9.61; calculated for $(C_6H_{11}O)_2TiSO_4$, Ti 14.04, S 9.36 per cent.

White powder, slightly hygroscopic, insoluble in benzene, but dissolves in alcohol with decomposition. Decomposes without melting at 160°.

(d) Dichloro-titanium sulphate (2.1 g; 0.01 mole) was added to phenol (5 g; 0.05 mole). The red coloured mixture on heating gave HCl. This was kept at 80-90° for eight hours for complete reaction. The solid was washed with dry ether and dried at 60° under reduced pressure. Yield 3 g (90% of theory).

Analysis: Found Ti 14.46, S 9.56, C 44.01, H 3.43; calculated for $(C_6H_5O)_2TiSO_4$, Ti 14.54, S 9.7, C 43.64, H 3.03 per cent.

(b) The above reaction was carried out using ethyl acetate (15 ml) in place of methyl acetate. Yield of product 2.3 g (98% of theory).

Analysis: Found Ti 20.37, S 13.71, $-OC_2H_5$ 38.29, calculated for $(C_2H_5O)_2TiSO_4$, Ti 20.51, S 13.68, $-OC_2H_5$ 38.46 per cent.

White powder, not very hygroscopic, soluble in alcohol but insoluble in benzene, light petroleum and chloroform. On heating, decomposes without melting at 140-145°.

Dichloro-titanium sulphate did not react with dimethyl sulphate or dimethyl oxalate.

3.3.1.C Dichloro-titanium sulphate and organic chelate LH-

(LH = acetylacetone, benzoyl acetone, aceto-acetanilide, dibenzoylmethane, salicylaldehyde, methyl salicylate)

(a) Acetylacetone (4 g; 0.04 mole) and dichloro-titanium sulphate (2.1 g; 0.01 mole) were mixed in benzene (20 ml) and refluxed in oil bath for ten hours. The mixture was then cooled, filtered and the filtrate diluted with light petroleum. The precipitate formed was filtered, washed with dry ether and dried at 60° under reduced pressure. Yield 3 g (88% of theory).

Analysis: Found Ti 13.83, S 9.40, C 34.21, H 4.5; calculated for $(C_5H_7O_2)_2TiSO_4$, Ti 14.04, S 9.34, C 35.1, H 4.1 per cent.

Brown hygroscopic powder, insoluble in common organic solvents but dissolves with decomposition in alcohol.

(b) Benzoylacetone (4.86 g; 0.03 mole) and dichloro-titanium sulphate (2.1 g; 0.01 mole) were mixed in benzene (25 ml) and refluxed for 24 hours. The solid product was washed with benzene and light petroleum and dried under reduced pressure at 60°. Yield 3.4 g (73% of theory).

Analysis: Found Ti 10.27, S 6.79, C 52.02, H 4.30; calculated for $(C_{10}H_9O_2)_2TiSO_4$, Ti 10.30, S 6.87, C 51.50, H 3.86 per cent.

Red powder, slightly hygroscopic, insoluble in common organic solvents but dissolves in alcohol with decomposition.

(c) Acetoacetanilide (5.37 g; 0.03 mole) was dissolved in benzene (20 ml) and dichloro-titanium sulphate (2.1 g; 0.01 mole) was added to it. Hydrogen chloride evolved and a red product formed. The mixture was refluxed for 24 hours, after which the product was filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 3.5 g (70% of theory).

Analysis: Found Ti 9.59, S 6.43, N 5.71; calculated for $(C_{10}H_{10}O_3N)_2TiSO_4$, Ti 9.68, S 6.45, N 5.65 per cent.

Bright red powder, slightly hygroscopic, insoluble in benzene, light petroleum and chloroform, but dissolves in alcohol with decomposition.

Infrared absorption maxima (in cm^{-1}) are given below:-
2336w, 1613w, 1592w, 1562w, 1316s, 1250s, 1180s, 1050s, 1000w, 986s, 908w, 813w, 787w, 758m, 685w.

(d) Dibenzoylmethane (6.72 g; 0.03 mole) was dissolved in benzene (30 ml) and dichloro-titanium sulphate (2.1 g; 0.01 mole) was added to it. The solution was refluxed for 24 hours, the product washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 4 g (68% of theory).

Analysis: Found Ti 8.2, S 5.45, C 61.87, H 4.1; calculated for $(C_{15}H_{11}O_2)_2TiSO_4$, Ti 8.13, S 5.42, C 61.01, H 3.73 per cent.

Bright red powder, slightly hygroscopic, insoluble in benzene and light petroleum, but dissolves with decomposition in alcohol and in pyridine.

(e) Salicylaldehyde (5 g; 0.04 mole) and dichloro-titanium sulphate (2.1 g; 0.01 mole) were refluxed in benzene (20 ml) for ten hours. The mixture was filtered and the filtrate diluted with light petroleum. The precipitate separated was filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 3.3 g (85% of theory).

Analysis: Found Ti 12.22, S 8.19, C 44.01, H 2.97; calculated for $(C_7H_5O_2)_2TiSO_4$, Ti 12.44, S 8.29, C 43.52, H 2.59 per cent.

Chocolate powder, hygroscopic, insoluble in common organic solvents but dissolves in alcohol with chemical reaction.

(f) Methylsalicylate (6 g; 0.04 mole) and dichlorotitanium sulphate (2.1 g; 0.01 mole) were mixed in benzene (20 ml) and refluxed for ten hours till the evolution of HCl was complete. The product was filtered and the filtrate diluted with light petroleum. The precipitate formed was filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 4.1 g (90% of theory).

Analysis: Found Ti 10.62, S 6.98; calculated for $(C_8H_7O_3)_2TiSO_4$, Ti 10.76, S 7.17 per cent.

Red hygroscopic powder, insoluble in common organic solvents but dissolves in alcohol with decomposition.

3.3.2.A Methylsulphato chloro-titanium sulphate + ROH-
(R=i-C_3H_7, n-C_4H_9, C_6H_5)

(a) Methylsulphato chloro-titanium sulphate (2.91 g; 0.01 mole) was refluxed for six hours with dry isopropanol (15 ml). HCl evolved and the yellow chloro compound slowly dissolved in the alcohol. Excess of the alcohol was then distilled off at reduced pressure, the product washed with dry ether and dried at 60° under reduced pressure. Yield 2.6 g (83% of theory).

Analysis: Found Ti 16.08, S 21.73; calculated for $(CH_3SO_4)(C_3H_7O)TiSO_4$, Ti 16.11, S 21.48 per cent.

White, hygroscopic powder, insoluble in benzene but dissolves in alcohol.

(b) A similar reaction was carried out as the above, but using n-butanol (15 ml) in place of isopropanol. Yield of product 2.6 g (83% of theory).

Analysis: Found Ti 15.13, S 20.22; calculated for $(CH_3SO_4)(C_4H_9O)\ TiSO_4$, Ti 15.38, S 20.51 per cent.

White hygroscopic powder, insoluble in benzene but dissolves in alcohol.

The reaction products of methylsulphato chloro-titanium sulphate with methanol and ethanol were of indefinite composition containing 2-3 per cent of chlorine which could not be removed.

(c) Cyclohexanol (and its acetate) also gave an indefinite product by reaction with methylsulphato chloro-titanium sulphate, but a pure cyclohexanoxy derivative could be prepared by starting with methylsulphato ethoxy-titanium sulphate 3.3.2.B(b) and reacting as follows:-

Methylsulphato ethoxy titanium sulphate (2.84 g; 0.01 mole) and cyclohexanol (4 g; 0.04 mole) were mixed and kept at 100° under reflux for one hour. Then benzene (30 ml) was added and azeotropically distilled off all ethanol formed in the reaction. The residue was dried, washed with light petroleum and dried again at 60° under reduced pressure. Yield 3.5 g (95% of theory).

Analysis: Found Ti 12.87, S 17.24; calculated for $(CH_3SO_4)(C_6H_{11}O)TiSO_4$, Ti 13.01, S 17.35 per cent.

White hygroscopic powder, insoluble in benzene but dissolves in alcohol with decomposition.

(d) Phenol (1.41 g; 0.015 mole) was dissolved in benzene (20 ml) and methylsulphato chloro-titanium sulphate (2.91 g; 0.01 mole) was added. On heating HCl evolved and a red product separated. The mixture was refluxed for ten hours and the solid product filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure.
Yield 2.78 g (77.6% of theory).

Analysis: Found Ti 13.82, S 18.43, C 24.82, H 2.91; calculated for $(CH_3SO_4)(C_6H_5O)TiSO_4$, Ti 13.79, S 18.40, C 24.14, H 2.3 per cent.

Chocolate powder, slightly hygroscopic, insoluble in common solvents but dissolves in alcohol with decomposition.

3.3.2.B Methylsulphato chloro-titanium sulphate + CH_3COOR
($R=CH_3$, C_2H_5)

(a) Methylsulphato chloro-titanium sulphate (2.91 g; 0.01 mole) was mixed with dry methyl acetate (15 ml) and refluxed, when a white solid gradually separated with the evolution of pungent smelling acetyl chloride. After four hours, excess of the acetate ester was distilled off under reduced pressure and the product dried at 60° under reduced pressure. Yield 2.5 g (93% of theory).

Analysis: Found Ti 18.01, S 24.0; calculated for $(CH_3SO_4)(CH_3O)TiSO_4$, Ti 17.77, S 23.70 per cent.

White powder, hygroscopic, soluble in alcohol but insoluble in benzene.

(b) The above reaction was carried out using ethyl acetate (15 ml) in place of methyl acetate. Yield of product 2.5 g (88% of theory).

Analysis: Found Ti 17.11, S 22.81; calculated for $(CH_3SO_4)(C_2H_5O)TiSO_4$, Ti 16.90, S 22.54 per cent.

White powder, hygroscopic, soluble in alcohol but insoluble in benzene.

Methylsulphato chloro-titanium sulphate did not react with dimethyl sulphate or dimethyl oxalate.

3.3.2.C Methylsulphato chloro-titanium sulphate + organic chelate LH-

(LH = acetylacetone, salicylaldehyde, methyl salicylate)

(a) Acetylacetone (1.5 g; 0.015 mole) and methylsulphato chloro-titanium sulphate (2.91 g; 0.01 mole) were mixed in benzene (20 ml) and the mixture refluxed for ten hours. The solid residue was filtered off and the filtrate diluted with light petroleum. The precipitate formed was filtered off, washed with light petroleum and dried at 60° under reduced pressure. Yield 2.7 g (77% of theory).

Analysis: Found Ti 13.63, S 17.97; calculated for $(CH_3SO_4)(C_5H_7O_2)TiSO_4$, Ti 13.55, S 18.08 per cent.

Chocolate powder, hygroscopic, dissolves in alcohol with decomposition but insoluble in other common organic solvents.

(b) Salicylaldehyde (1.88 g; 0.015 mole) and methylsulphato chloro-titanium sulphate (2.91 g; 0.01 mole) were mixed in benzene (20 ml), reacted for ten hours and product processed as in the above experiment. Yield 3 g (80% of theory).

Analysis: Found Ti 12.81, S 16.89, C 25.69, H 2.45; calculated for $(CH_3SO_4)(C_7H_5O_2)TiSO_4$, Ti 12.76, S 17,02, C 25.54, H 2.13 per cent.

Chocolate powder, slightly hygroscopic, insoluble in common solvents but dissolves with reaction in alcohol.

(c) Methyl salicylate (2.28 g; 0.015 mole) and methylsulphato chloro-titanium sulphate (2.91 g; 0.01 mole) were reacted in boiling benzene (20 ml) and product processed as in the above experiments. Yield 3.6 g (88% of theory).

Analysis: Found Ti 11.88, S 15.81; calculated for $(CH_3SO_4)(C_8H_7O_3)TiSO_4$, Ti 11.82, S 15.77 per cent.

Orange red powder, slightly hygroscopic, insoluble in common solvents but dissolves in alcohol with decomposition.

3.3.3.A Dichloro-titanium oxalate + ROH-

($R=C_6H_5$)

Dichloro-titanium oxalate (2.07 g; 0.01 mole) was slowly added to phenol (2.82 g; 0.03 mole). The reaction was exothermic and HCl evolved. The mixture was heated upto 100° and kept for twelve hours in an oil bath. The HCl-free product was then dissolved in benzene and precipitated with light petroleum. The precipitate was filtered, washed with light petroleum and dried at 60° at 1mm pressure. Yield 2.2 g (68% of theory).

Analysis: Found Ti 14.80, C 52.13, H 4.06; calculated for $(C_6H_5O)_2TiC_2O_4$, Ti 14.90, C 52.17, H 3.11, per cent.

Red powder, slightly hygroscopic, insoluble in benzene and soluble in alcohol with decomposition.

The reaction products of dichloro-titanium oxalate with lower aliphatic alcohols or their acetates (C_1-C_4) were of indefinite composition.

3.3.3.B Dichloro-titanium oxalate + organic chelate LH-

(LH=acetylacetone, salicylaldehyde, methyl salicylate)

(a) Dichloro titanium oxalate (2.07 g; 0.01 mole) was added to acetylacetone (3 g; 0.03 mole) in xylene (20 ml) and refluxed for six hours. The HCl-free brown-coloured solution was treated with excess of light petroleum and the product thus separated was filtered, washed with light petroleum and dried at 60° at 1 mm pressure. Yield 2.3 g (69% of theory).

Analysis: Found Ti 14.41, C 43.28, H 5.01; calculated for $(C_5H_7O_2)_2TiC_2O_4$, Ti 14.37, C 43.12, H 4.39 per cent.

Brown light powder, slightly hygroscopic, insoluble in benzene but dissolves with decomposition in alcohol.

(b) Dichloro-titanium oxalate (2.07 g; 0.01 mole) was added to salicylaldehyde (3.66 g; 0.03 mole) in xylene (20 ml) and refluxed for six hours when a dark red HCl-free solution was obtained. This was diluted with light petroleum and the solid product thus separated was washed with light petroleum and dried at 60° in vacuum. Yield 2.4 g (63% of theory).

Analysis: Found Ti 12.66, C 51.14, H 3.89; calculated for $(C_7H_5O_2)_2TiC_2O_4$, Ti 12.70, C 50.79, H 2.65 per cent.

Yellowish brown powder, stable in air, insoluble in benzene but dissolves in alcohol with decomposition.

(c) Dichloro-titanium oxalate (2.07 g; 0.01 mole) was added to methyl salicylate (4.56 g; 0.03 mole) in xylene (20 ml) and refluxed for eight hours. A red HCl-free solution was obtained to which light petroleum was added in excess, and the solid product thus separated was washed with light petroleum and dried at 60° under reduced pressure. Yield 2.8 g (64% of theory).

Analysis: Found Ti 11.03, C 49.48, H 4.02; calculated for $(C_8H_7O_3)_2TiC_2O_4$, Ti 10.96, C 49.32, H 3.196 per cent.

Orange-yellow, light powder, stable in air, insoluble in benzene but dissolves in alcohol with decomposition.

3.3.4. Dichloro-titanium diacetate + R_2SO_4 ($R=CH_3$, C_2H_5)

The dialkyl sulphate (0.025 mole) was added to dichloro-titanium diacetate (0.01 mole) and mixed well. The mixture was then heated to 100° and kept there for six hours under a slow stream of dry nitrogen. Alkyl chloride and acetic anhydride evolved during the reaction. The white mass formed was washed with dry ether and dried at 60° under reduced pressure. Yield nearly quantitative.

Analysis: For $R=CH_3$, found Ti 16.81, S 22.36; calculated for $(CH_3SO_4)_2TiO$, Ti 16.78, S 22.38 per cent; for $R=C_2H_5$, found Ti 15.26, S 20.45; calculated for $(C_2H_5SO_4)_2TiO$, Ti 15.29, S 20.38 per cent.

White very hygroscopic powders, insoluble in benzene and light petroleum, but dissolve in alcohol with decomposition. They start decomposing at 110° and turn black above 250°.

The reaction products of dichloro-titanium diacetate with lower aliphatic alcohols (C_1-C_4) or their acetates, cyclohexanol, phenol and chelating agents of the type LH were of indefinite compositions.

3.3.5. Dichloro-titanium dibenzoate + R_2SO_4

($R=CH_3$, C_2H_5)

The dialkyl sulphate (0.025 mole) was mixed with dichloro-titanium dibenzoate (0.01 mole) and the mixture heated upto 100° for eight hours under a slow stream of dry nitrogen. Alkyl chloride was evolved during the reaction. The white mass formed was washed with dry ether and dried at 60° under reduced pressure. Yields nearly quantitative.

Analysis: For $R=CH_3$, found Ti 16.82, S 22.45; calculated for $(CH_3SO_4)_2TiO$, Ti 16.78, S 22.38 per cent;
for $R=C_2H_5$, found Ti 15.20, S 20.27; calculated for $(C_2H_5SO_4)_2TiO$, Ti 15.29, S 20.38 per cent.

White powders, very hygroscopic, insoluble in benzene but dissolve with decomposition in alcohol.

The reaction products of dichloro-titanium dibenzoate with lower aliphatic alcohols (C_1-C_4) or acetates, cyclohexanol, phenol, dimethyl oxalate and chelating agents were of indefinite composition.

3.4. Titanium chelates:

3.4.1.A L $TiCl_3$ + dimethyl sulphate-

[LH = (a) acetylacetone (b) dibenzoylmethane
(c) salicylaldehyde (d) methyl salicylate]

(a) Acetylacetono trichloro-titanium (2.54 g; 0.01 mole) was reacted with dimethyl sulphate (3.78 g; 0.03 mole) at 100° for five hours. The product was washed with dry ether and dried at 60° under reduced pressure. Yield 3 g (85% of theory).

Analysis: Found Ti 13.36, S 17.97; calculated for $(C_5H_7O_2)Ti(SO_4)CH_3SO_4$, Ti 13.55, S 18.08 per cent.

Chocolate powder, hygroscopic, dissolves in alcohol with decomposition.

(b) Dibenzoylmethano trichloro-titanium (3.78 g; 0.01 mole) was treated with dimethyl sulphate (3.78 g; 0.03 mole) similar to above experiment (a). Yield 3.5 g (73% of theory).

Analysis: Found Ti 9.98, S 13.45, C 39.84, H 3.33; calculated for $(C_{15}H_{11}O_2)Ti(SO_4)CH_3SO_4$, Ti 10.04, S 13.39, C 40.17, H 2.93 per cent.

Brown hygroscopic powder, dissolves in alcohol with decomposition.

(c) Salicylaldehydo trichloro-titanium (2.75 g; 0.01 mole) was treated with dimethyl sulphate (3.78 g; 0.03 mole) similar to experiment (a). Yield 3 g (80% of theory).

Analysis: Found Ti 12.79, S 17.11, C 25.63, H 2.90; calculated for $(C_7H_5O_2)Ti(SO_4)CH_3SO_4$, Ti 12.76, S 17.02, C 25.54, H 2.127 per cent.

Chocolate powder, slightly hygroscopic, dissolves in alcohol with decomposition.

(d) Methyl-salicylato trichloro-titanium (3.06 g; 0.01 mole) was treated with dimethyl sulphate (3.78 g; 0.03 mole) similar to experiment (a). Yield 3.2 g (81% of theory).

Analysis: Found Ti 12.21, S 16.20; calculated for $(C_8H_7O_3)\ Ti(SO_4)CH_3SO_4$, Ti 12.12, S 16.16 per cent.

Orange red powder, slightly hygroscopic, soluble in alcohol with decomposition.

3.4.1.B $L\ TiCl_3$ + phenol-

[LH = (a) dibenzoymethane (b) salicylaldehyde
(c) methyl salicylate]

(a) Dibenzoylmethane trichloro-titanium (3.78 g; 0.01 mole) and phenol (3.72 g; 0.04 mole) were reacted in boiling light petroleum (B.R.60-80°, 15 ml) for six hours. The product which separated was filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 4.5 g (82% of theory).

Analysis: Found Ti 8.80; calculated for $(C_{15}H_{11}O_2)\ Ti(OC_6H_5)_3$, Ti 8.73 per cent.

Red stable powder, m.p.205°, soluble in alcohol with decomposition.

(b) Salicylaldehydo trichloro-titanium (2.75 g; 0.01 mole) and phenol (3.72 g; 0.04 mole) were reacted similar to above experiment (a). Yield 3.5 g (78% of theory).

Analysis: Found Ti 10.72; calculated for $(C_7H_5O_2)Ti(OC_6H_5)_3$, Ti 10.71 per cent.

Yellow non-hygroscopic solid, insoluble in benzene, dissolves with decomposition in alcohol. Melts with decomposition at 190°.

(c) Methyl-salicylato trichloro-titanium (3.06 g; 0.01 mole) and phenol (3.72 g; 0.04 mole) were reacted and processed as in experiment (a). Yield 3.5 (73% of theory).

Analysis: Found Ti 10.3; calculated for $(C_8H_7O_3)Ti(OC_6H_5)_3$, Ti 10.1 per cent.

Deep yellow non-hygroscopic powder, insoluble in benzene. Melts with decomposition at 145°.

3.4.1.C L $TiCl_3$ + catechol-

[LH = (a) dibenzoylmethane (b) salicylaldehyde
(c) methyl salicylate]

(a) Dibenzoylmethano trichloro-titanium (3.78 g; 0.01 mole) and catechol (3.3 g; 0.03 mole) were reacted in boiling light petroleum (B.R. 60-80°, 15 ml) for twelve hours. The product separated during the reaction was filtered, washed with light petroleum and dried at 60° under reduced pressure. Yield 4.5 g (92% of theory).

Analysis: Found Ti 9.76; calculated for $(C_{15}H_{11}O_2)Ti(O_2C_6H_4)(OC_6H_4OH)$, Ti 9.84 per cent.

Chocolate violet powder, stable, insoluble in benzene but dissolves with decomposition in alcohol. Does not undergo any visible change up to 200°.

(b) Salicylaldehydo trichloro-titanium (2.75 g; 0.01 mole) and catechol (3.3 g; 0.03 mole) were reacted similar to above experiment (a). Yield 3.3 g (85% of theory).

Analysis: Found Ti 12.45; calculated for $(C_7H_5O_2)Ti\ (O_2C_6H_4)(OC_6H_4OH)$, Ti 12.44 per cent.

Chocolate powder, stable, insoluble in benzene. Does not undergo any visible change up to 200°.

Infrared absorption maxima (in cm^{-1}) are given below:- 3226w, 2326w, 1613m, 1587w, 1538w, 1449s, 1316w, 1266s, 1242s, 1176m, 1079m, 1020m, 971w, 917w, 905m, 870m, 800m, 741s.

(c) Methyl-salicylato trichloro-titanium (3.06 g; 0.01 mole) and catechol (3.3 g; 0.03 mole) were reacted and processed as in experiment (a). Yield of product 3.1 g (75% of theory).

Analysis: Found Ti 11.60; calculated for $(C_8H_7O_3)Ti\ (O_2C_6H_4)(OC_6H_4OH)$, Ti 11.53 per cent.

Red, non-hygroscopic powder, insoluble in benzene. Does not undergo any visible change up to 200°.

3.4.1.D L $TiCl_3$ + acetylacetone

[LH = (a) salicylaldehyde (b) methyl salicylate]

(a) Salicylaldehydo trichloro-titanium (2.75 g; 0.01 mole) was added to acetylacetone (2.2 g; 0.022 mole) in benzene (15 ml). The deep red solution formed gave HCl on warming. It was refluxed for six hours and a part of solvent was distilled off. On cooling in ice a red solid which separated was washed with light petroleum and dried at room temperature under reduced pressure. Yield 2 g (50% of theory).

Analysis: Found Ti 11.79, Cl 8.86; calculated for $(C_7H_5O_2)(C_5H_7O_2)_2$ TiCl, Ti 11.92, Cl 8.81 per cent.

Red-brown solid, not hygroscopic, soluble in benzene. Decomposes at 125°. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 407; calculated 402.5.

Infrared absorption maxima (in cm^{-1}) are given below:- 1562m, 1515m, 1274w, 1026s, 930s, 816s, 740s.

(b) Methyl-salicylato trichloro-titanium (3.06 g; 0.01 mole) and acetylacetone (2.2 g; 0.022 mole) were reacted in benzene and processed as in the preceding experiment (a). Yield 2.2 g (54% of theory).

Analysis: Found Ti 11.40, Cl 8.35; calculated for $(C_8H_7O_3)(C_5H_7O_2)_2$TiCl, Ti 11.36, Cl 8.39 per cent.

Red, non-hygroscopic solid, soluble in benzene. Decomposes at 105°. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2% w/w) found 412; calculated 422.5.

3.4.1.E $LTiCl_3$ + methyl salicylate-

(LH = salicylaldehyde)

Salicylaldehydo trichloro-titanium (2.75 g; 0.01 mole) and methyl salicylate (3.04 g; 0.02 mole) were mixed in benzene (20 ml) and refluxed for four hours. The red solid which separated was washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 3.5 g (90% of theory).

Analysis: Found Ti 12.36, Cl 18.04; calculated for $(C_7H_5O_2)(C_8H_7O_3)TiCl_2$, Ti 12.27, Cl 18.16 per cent.

Red powder, stable in dry air, insoluble in benzene and chloroform, but soluble in ethanol without decomposition. M.P.195°.

Infrared absorption maxima (in cm^{-1}) are given below:- 1606s, 1550s, 1412s, 1330w, 1316m, 1282s, 1266s, 1242s, 1220w, 1205w, 1163w, 1149m, 1124w, 1105m, 1036w, 957w, 913s, 893s, 851s, 803s, 778m, 772s, 766s, 697w, 678s.

An identical product was obtained when methyl-salicylato trichloro-titanium (0.01 mole) and salicylaldehyde (0.02 mole) were reacted in benzene medium.

3.4.2.A L_2TiCl_2 + dimethyl sulphate-

[LH = (a) acetylacetone (b) benzoylacetone
(c) dibenzoylmethane (d) salicylaldehyde
(e) methyl salicylate]

(a) Bis-acetylacetono dichloro-titanium (3.17 g; 0.01 mole) was mixed with dimethyl sulphate (3.78 g; 0.03 mole) and kept at 100° for four hours. The product was washed with ether and dried at 60° under reduced pressure. Yield 4 g (85.5% of theory).
Analysis: Found Ti 10.42, S 13.80; calculated for $(C_5H_7O_2)_2Ti(CH_3SO_4)_2$, Ti 10.26, S 13.68 per cent.

Hygroscopic brown powder, dissolves in alcohol with decomposition.

(b) Bis-benzoylacetono dichloro-titanium (4.41 g; 0.01 mole) was reacted with dimethyl sulphate (3.78 g; 0.03 mole) similar to above experiment (a). Yield of product 5.5 g (95% of theory).
Analysis: Found Ti 8.10, S 10.73; calculated for $(C_{10}H_9O_2)_2Ti(CH_3SO_4)_2$, Ti 8.11, S 10.81 per cent.

Deep red powder, hygroscopic, dissolves in alcohol with decomposition.

(c) Bis-dibenzoymethano dichloro-titanium (5.65 g; 0.01 mole) was reacted with dimethyl sulphate (3.78 g; 0.03 mole) similar to experiment (a). Yield of product 6.5 g (90% of theory).
Analysis: Found Ti 6.8, S 9.09; calculated for $(C_{15}H_{11}O_2)_2Ti(CH_3SO_4)_2$, Ti 6.704, S 8.94 per cent.

Orange yellow hygroscopic powder, dissolves in alcohol with decomposition.

(d) Bis-salicylaldehydo dichloro-titanium (3.61 g; 0.01 mole) was reacted with dimethyl sulphate (3.78 g; 0.03 mole) similar to experiment (a). Yield of product 4.1 g (82% of theory).

Analysis: Found Ti 9.41, S 12.39, C 37.84; H 3.87; calculated for $(C_7H_5O_2)_2Ti(CH_3SO_4)_2$, Ti 9.37, S 12.50, C 37.50, H, 3.125 per cent.

Chocolate hygroscopic solid, dissolves in alcohol with decomposition.

(e) Bis-(methyl-salicylato) dichloro-titanium (4.21 g; 0.01 mole) was reacted with dimethyl sulphate (3.78 g; 0.03 mole) similar to experiment (a). Yield of product 4.4 g (77% of theory).

Analysis: Found Ti 8.43, S 11.08, C 38.02, H 4.16; calculated for $(C_8H_7O_3)_2Ti(CH_3SO_4)_2$, Ti 8.40, S 11.19, C 37.77, H 3.496 per cent.

Dark red hygroscopic solid, dissolves in alcohol with decomposition.

3.4.2.B L_2TiCl_2 + phenol-

[LH = (a) dibenzoylmethane (b) salicylaldehyde
(c) methyl salicylate]

(a) Bis-dibenzoylmethano~~l~~ dichloro-titanium (5.65 g; 0.01 mole) and phenol (2.82 g; 0.03 mole) were mixed in benzene (30 ml) and refluxed for ten hours. Then the solvent was distilled off and residue washed with light petroleum and dried at 60° under reduced pressure. Yield 5.5 g (80.8% of theory).

Analysis: Found Ti 6.93, C 74.26, H 4.94; calculated for $(C_{15}H_{11}O_2)_2Ti(OC_6H_5)_2$, Ti 7.06, C 74.11, H 4.71 per cent.

Yellow powder, non-hygroscopic, insoluble in benzene but dissolves in alcohol with decomposition.

(b) *Bis*-salicylaldehydo dichloro-titanium (3.61 g; 0.01 mole) and phenol (2.82 g; 0.03 mole) were reacted similar to above experiment (a). Yield of product 3.5 g (73.5% of theory).

Analysis: Found Ti 9.93, C 66.12, H 4.51; calculated for $(C_7H_5O_2)_2Ti(OC_6H_5)_2$, Ti 10.08, C 65.55, H 4.20 per cent.

Orange powder, insoluble in benzene but dissolves in alcohol with decomposition.

(c) *Bis*-(methyl-salicylato) dichloro-titanium (4.21 g; 0.01 mole) and phenol (2.82 g; 0.03 mole) were reacted similar to experiment (a). Yield of product 3.5 g (80% of theory).

Analysis: Found Ti 11.00, C 76.92, H 5.72; calculated for $(C_8H_7O_3)_2Ti(OC_6H_5)_2$, Ti 11.11, C 77.05, H 5.50 per cent.

Yellow stable powder, insoluble in benzene but dissolves in alcohol with decomposition.

3.4.2.C L_2TiCl_2 + catechol-

[LH = (a) dibenzoylmethane (b) salicylaldehyde
(c) methyl salicylate]

(a) *Bis*-dibenzoylmethano dichloro-titanium (5.65 g; 0.01 mole) and catechol (3.3 g; 0.03 mole) were refluxed in benzene (30 ml) for ten hours. The product which separated was filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 5 g (83% of theory).

Analysis: Found Ti 7.88, C 72.04, H 4.53; calculated for $(C_{15}H_{11}O_2)_2Ti(O_2C_6H_4)$, Ti 7.97, C 71.76, H 4.32 per cent.

Chocolate stable powder, insoluble in benzene but dissolves in alcohol with decomposition.

(b) *Bis*-salicylaldehydo dichloro-titanium (3.61 g; 0.01 mole) and catechol (3.3 g; 0.03 mole) were reacted in benzene medium similar to experiment (a). Yield of product 2.9 g (73% of theory).

Analysis: Found Ti 11.89, C 61.93, H 3.94; calculated for $(C_7H_5O_2)_2Ti(O_2C_6H_4)$, Ti 12.06, C 61.70, H 3.52 per cent.

Chocolate stable powder, insoluble in benzene but dissolves with decomposition in alcohol.

Infrared absorption maxima (in cm^{-1}) are given below:- 1639m, 1613m, 1587m, 1550m, 1504s, 1429w, 1408w, 1325m, 1290m, 1250s, 1183s, 1156m, 1111s, 1042w, 1031m, 926s, 909s, 877s, 807s, 769w, 741s.

(c) *Bis*-(methyl-salicylato) dichloro-titanium (4.21 g; 0.01 mole) and catechol (3.3 g; 0.03 mole) were reacted in boiling benzene similar to experiment (a). Yield of product 3.7 g (81% of theory).

Analysis: Found Ti 10.31, C 57.59, H 4.24; calculated for $(C_8H_7O_3)_2Ti(O_2C_6H_4)$, Ti 10.47, C 57.63, H 3.93 per cent.

Chocolate stable powder, insoluble in benzene but dissolves with decomposition in alcohol.

3.4.2.D L_2TiCl_2 + resorcinol-

[LH = (a) dibenzoylmethane (b) salicylaldehyde
(c) methyl salicylate]

(a) Bis-dibenzoylmethano dichloro-titanium (5.65 g; 0.01 mole) and resorcinol (3.3 g; 0.03 mole) were refluxed in benzene (30 ml) for ten hours. The product separated was filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 6 g (84% of theory).

Analysis: Found Ti 6.59, C 71.11, H 4.77; calculated for $(C_{15}H_{11}O_2)_2Ti(OC_6H_4OH)_2$, Ti 6.74, C 70.78, H 4.49 per cent.

Orange stable powder, insoluble in benzene but dissolves in alcohol with decomposition.

(b) Bis-salicylaldehydo dichloro-titanium (3.61 g; 0.01 mole) and resorcinol (3.3 g; 0.03 mole) were reacted in boiling benzene similar to above experiment (a). Yield of product 3.9 g (77% of theory).

Analysis: Found Ti 9.51, C 62.05, H 4.10; calculated for $(C_7H_5O_2)_2Ti(OC_6H_4OH)_2$, Ti 9.45, C 61.42, H 3.94 per cent.

Red stable powder, insoluble in benzene but dissolves in alcohol with decomposition.

Infrared absorption maxima (in cm^{-1}) are given below:-
3774w, 1613s, 1550m, 1294s, 1258w, 1220m, 1156s, 1099m, 990s, 913s, 800m, 661s.

(c) Bis-(methyl-salicylato) dichloro-titanium (4.21 g; 0.01 mole) and resorcinol (3.3 g; 0.03 mole) were reacted in boiling benzene similar to experiment (a). Yield of product 4.9 g (88% of theory).

Analysis: Found Ti 8.30, C 60.01, H 4.52; calculated for $(C_8H_7O_3)_2Ti(OC_6H_4OH)_2$, Ti 8.45, C 59.16, H 4.23 per cent.

Yellow stable powder, insoluble in benzene but dissolves in alcohol with decomposition.

3.4.2.E L_2TiCl_2 + acetylacetone-

[LH = (a) salicylaldehyde (b) methyl salicylate]

(a) Bis-salicylaldehydo dichloro-titanium (3.61 g; 0.01 mole) and acetylacetone (2.0 g; 0.02 mole) were slowly mixed in benzene (15 ml) and refluxed for six hours. The product which separated was filtered, washed with benzene and light petroleum and dried at 60° under reduced pressure. Yield 4 g (94% of theory).

Analysis: Found Ti 11.14, Cl 8.43; calculated for $(C_7H_5O_2)_2(C_5H_7O_2)TiCl$, Ti 11.31, Cl 8.36 per cent.

Chocolate-red powder, not hygroscopic, slightly soluble in benzene and dissolves readily in alcohol without decomposition.

Infrared absorption maxima (in cm^{-1}) are given below:-
1587m, 1527s, 1337m, 1290w, 1282w, 1031w, 933w, 909w, 820m, 775s.

(b) Bis-(methyl-salicylato) dichloro-titanium (4.21 g; 0.01 mole) and acetylacetone (2.0 g; 0.02 mole) were reacted in boiling benzene similar to above experiment (a). Yield of product 4 g (83% of theory).

Analysis: Found Ti 10.02, Cl 7.50; calculated for $(C_8H_7O_3)_2(C_5H_7O_2)TiCl$, Ti 9.91, Cl 7.32 per cent.

Red powder, not hygroscopic, slightly soluble in benzene and dissolves readily in alcohol without decomposition.

3.5. Adducts with nitrogen bases:

3.5.1. Ammonia adducts-

A general method was worked out for the preparation of ammonia adducts. It was to suspend (or dissolve) the substance (organoxy titanium compound) in dry ether and pass dry ammonia gas at 0°C under constant stirring with a magnetic stirrer. Ammonia gas from a cylinder was dried by passing through caustic soda towers and bubbled at a slow rate when the gas was absorbed and the adduct separated. Usually, a reaction with 1-2 g of the titanium compound was complete within 30 minutes. The product was filtered, washed with dry ether and dried at room temperature at reduced pressure. The yields were nearly quantitative. Adducts isolated are given in Table.1

AMMONIA ADDUCTS

	Titanium Compound	No. of NH_3 molecules per mole of adduct.	Colour	Analysis							
				Found				Calculated			
				Ti	Cl	S	NH_3	Ti	Cl	S	NH_3
1.	Dicyclohexanoxy dichloro-titanium	4	white	12.48	18.51		17.03	12.47	18.44		17.66
2.	Diphenoxy dichloro-titanium	5	orange -red	12.45	18.37		20.82	12.30	18.21		21.79
3.	*m*-Phenylenedioxy dichloro-titanium	6	"	14.62	21.47		30.56	14.59	21.58		31.00
4.	Dithymoxy dichloro-titanium	5	"	9.57	14.01		16.20	9.56	14.15		16.93
5.	Diacetoxy dichloro-titanium	5	white	14.84	21.90		25.97	14.90	22.05		26.39
6.	Dibenzoxy dichloro-titanium	5	yellow	10.71	15.88		18.71	10.76	15.92		19.05
7.	Diphenoxyacetoxy dichloro-titanium	4	white	9.90	14.67		14.02	9.82	14.52		13.91
8.	*Bis*-salicylaldehydo dichloro-titanium	4	yellow	11.09	16.44		15.53	11.19	16.55		15.85
9.	*Bis*-methylsalicylato dichloro-titanium	4	buff	10.00	14.30		13.49	9.82	14.52		13.91
10.	*Bis*-*o*-nitrophenoxy dichloro-titanium	5	orange -red	9.90	15.01		17.35	10.00	14.79		17.71
11.	*Bis*-ethylacetoacetato dichloro-titanium	5	orange -red	10.36	15.26		18.17	10.36	15.33		18.40
12.	Dichloro-titanium sulphate	6	yellow	15.11	22.29	10.23	33.00	15.14	22.40	10.09	32.18
13.	Dichloro-titanium oxalate	6	white	15.64	23.20		33.61	15.53	23.00		33.01
14.	Triphenoxy chloro-titanium	4	orange	11.15	8.30		15.55	11.15	8.24		15.80
15.	*m*-Hydroxyphenoxy *m*-phenylenedioxy chloro-titanium	4	orange red	13.00	9.69		18.15	13.02	9.62		18.45
16.	Tetra-phenoxy titanium	4	yellow	10.00			13.80	9.84			13.93
17.	Tetra-thymoxy titanium	4	yellow	6.59			9.09	6.74			9.55
18.	Di-*o*-hydroxyphenoxy *o*-phenylenedioxy titanium	5	yellow	10.47			19.02	10.46			18.52
19.	Oxytitanium *bis*-methylsulphate	4	white	13.71		17.92	18.66	13.54		18.08	19.21
20.	Oxytitanium *bis*-ethylsulphate	4	white	12.65		17.00	17.61	12.56		16.75	17.80
21.	Diphenoxy oxalato-titanium	5	orange	11.71			20.42	11.80			20.88

Properties - They are in general white or light coloured powders, more stable to moisture than the parent organoxy titanium compound. They are insoluble in all common organic solvents and in thionyl chloride, pyridine, tetramethyl urea and liquid ammonia, but dissolve in dimethyl sulphoxide and dimethyl formamide (except the ammonia adducts of diacetoxy and dibenzoxy dichloro-titaniums). They are decomposed by water and ethanol. They do not melt, but decompose on heating at about 120°.

3.5.2. Pyridine adducts-

A general method in this case was to dissolve the organoxy titanium compound in excess of dry pyridine (by warming if necessary) and keep the solution overnight at 0°. Crystals of the adduct separated which were filtered, washed with light petroleum and dried at 60° under reduced pressure. In cases where the adduct did not separate, the excess of pyridine was distilled off at reduced pressure and the product washed with light petroleum and dried at 60° under reduced pressure (yield 60 to 90% of theory). The adducts isolated are given in Table.2

<u>Table 2</u>

<u>PYRIDINE ADDUCTS</u>

Titanium Compound	No.of Py molecules per mole of adduct	Colour	Analysis							
			Found				Calculated			
			Ti	Cl	S	N	Ti	Cl	S	N
1. Diphenoxy dichloro-titanium	2	red	10.45	15.24		5.8	10.36	15.35		6.05
2. *m*-Phenylenedioxy dichloro-titanium	2	"	12.50	18.40		7.19	12.47	18.44		7.27
3. Dithymoxy " "	3	"	8.27	12.13		4.67	8.35	12.35		4.87
4. *Bis*-salicylaldehydo " "	2	choco-late	9.23	13.61		5.55	9.25	13.68		5.40
5. *Bis*-methylsalicylato " "	3	red	7.22	10.81		6.40	7.30	10.79		6.38
6. *Bis*-*o*-nitrophenoxy " "	3	red-brown	7.71	11.36		11.21	7.60	11.24		11.08
7. *Bis*-dibenzoylmethano " "	3	yellow	5.98	8.79		5.36	5.98	8.85		5.24
8. Dichloro-titanium sulphate	3	white	10.71	15.79	7.15	9.16	10.62	15.71	7.08	9.29
9. Dichloro-titanium oxalate	3	"	11.01	16.15		9.28	10.81	15.99		9.46
10. *m*-Hydroxyphenoxy *m*-phenylenedioxy chloro-titanium	2	red	10.61	7.80		5.98	10.47	7.73		6.11
11. Di-*o*-hydroxyphenoxy *o*-phenylenedioxy titanium	3	Choco-late	8.99			5.15	9.02			5.26
12. Oxy titanium *bis* methylsulphate	2	white	10.78		14.38	6.61	10.81		14.42	6.31

Pyridine adducts are white or coloured solids, more hygroscopic and less stable than the corresponding ammonia adducts. They dissolve in pyridine, dimethyl sulphoxide and dimethylformamide. They are decomposed by water and ethanol. On heating they decompose without melting at about 120°.

3.6. The lithium phenyl reaction on some organoxy chloro-titanium compounds - Attempts to introduce Ti-C bonds

3.6.1. Preparation of lithium phenyl-

It was prepared according to the method given by George Wittig.[16] Lithium dust (280 mg; 0.04 mole) and bromobenzene (3.12 g; 0.02 mole) were mixed in absolute ether (15 ml) in nitrogen atmosphere. The reaction which started immediately was completed by refluxing for two hours. Lithium phenyl so formed was used as such without isolating it from the ether solution.

3.6.2. *Bis*-salicylaldehydo dichloro-titanium (3.61 g; 0.01 mole) in ether suspension was reacted with lithium phenyl (0.02 mole) in ether at 0°. A vigorous reaction took place which was completed by refluxing for one hour. Then ether was distilled off after adding benzene (15 ml). The benzene solution was filtered to remove insolubles and the filtrate evaporated under reduced pressure. The residue was washed with ether and dried at 60° under 1mm pressure. Yield 3.3 g (75% of theory). Analysis: Found Ti 10.78, C 69.14, H 4.60; calculated for $(C_7H_5O_2)_2\,Ti(C_6H_5)_2$, Ti 10.81, C 70.28, H 4.504 per cent.

Orange red, stable powder, m.p. 160°, soluble in benzene. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2 per cent w/w) found 465; calculated 444.

3.6.3. *Bis*-(methylsalicylato) dichloro-titanium (4.21 g; 0.01 mole) (ether suspension) was added to an ethereal solution of lithium phenyl (0.02 mole) at 0° and the product isolated from benzene as in the preceding experiment.

Yield 3.5 g (70% of theory).

Analysis: Found Ti 9.57, C 68.51, H 4.98; calculated for $(C_8H_7O_3)_2Ti(C_6H_5)_2$, Ti 9.52, C 66.67, H 4.762 per cent.

Yellow, stable powder, m.p. 110°, soluble in benzene. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2 per cent w/w) found 521; calculated 504.

3.6.4. An ethereal suspension of bis-dibenzoylmethano dichloro-titanium (5.65 g; 0.01 mole) was added to lithium phenyl (0.02 mole) in ether at 0° and the product processed and isolated as in the previous experiments. Yield 5 g (80% of theory).

Analysis: Found Ti 7.40; calculated for $(C_{15}H_{11}O_2)_2Ti(C_6H_5)_2$, Ti 7.41 per cent.

Yellow, stable powder, m.p. 120°, soluble in benzene. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2 per cent w/w) found 643; calculated 648.

3.6.5. Bis-benzoylacetono dichloro-titanium (4.4 g; 0.01 mole) was added in ether suspension to an etheral solution of lithium phenyl (0.02 mole) at 0° and the mixture refluxed for one hour. Then benzene (15 ml) was added and ether distilled off. The benzene solution was filtered to remove insolubles and the filtrate evaporated under reduced pressure at 60°. Yield 3.1 g (60% of theory).

Analysis: Found Ti 9.0; calculated for $(C_{10}H_9O_2)_2\ Ti(C_6H_5)_2$, Ti 9.16 per cent.

Red, sticky solid, soluble in benzene, ether and light petroleum. Decomposed in boiling benzene

3.6.6. An ethereal solution of diphenoxy dichloro-titanium (3.05 g; 0.01 mole) was added to lithium phenyl (0.02 mole) in ether at 0° and the product processed and isolated as in previous experiment. Yield 2.6 g (65% of theory).

Analysis: Found Ti 12.34; calculated for $(C_6H_5O)_2\ Ti(C_6H_5)_2$, Ti 12.37 per cent.

Red, sticky solid, soluble in benzene but decomposed on boiling the solution.

3.6.7. Salicylaldehydo trichloro-titanium (2.75 g; 0.01 mole) in ether suspension was added to lithium phenyl (0.03 mole) in ether at 0°. A vigorous reaction took place, which was completed by refluxing for one hour. Then benzene (15 ml) was added and ether distilled off. The benzene solution was filtered to remove insolubles and the filtrate evaporated under reduced pressure. The residue was washed with dry ether and dried at 60° under 1mm pressure. Yield 3 g (75% of theory).

Analysis: Found Ti 11.93, C 74.7, H 5.3; calculated for $(C_7H_5O_2)\ Ti(C_6H_5)_3$, Ti 12.0, C 75.0, H 5.0 per cent.

Yellow stable powder, m.p. 75°, soluble in benzene. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2 per cent w/w) found 408; calculated 400.

3.6.8. Methylsalicylato trichloro-titanium (3.06 g; 0.01 mole) (ether suspension) was added to lithium phenyl (0.03 mole) solution in dry ether at 0° and the product isolated from benzene as in the preceding experiment.

Yield 3.3 g (75% of theory).

Analysis: Found Ti 10.9; calculated for $(C_8H_7O_3)\ Ti(C_6H_5)_3$, Ti 11.16 per cent.

Orange colored stable powder, m.p.105° soluble in benzene and slightly so in light petroleum. Molecular weight (ebullioscopy in benzene in the concentration range 0.2-1.2 per cent w/w) found 385; calculated 430.

3.6.9. An ethereal suspension of dibenzoylmethano trichloro-titanium (3.8 g; 0.01 mole) was added to lithium phenyl (0.03 mole) in ether at 0° and the product processed and isolated as in previous experiments.

Yield 4 g (80% of theory).

Analysis: Found Ti 9.69; calculated for $(C_{15}H_{11}O_2)\ Ti(C_6H_5)_3$, Ti 9.56 per cent.

Yellow stable powder, m.p. 90°, soluble in benzene and light petroleum. Molecular weight (ebullioscopy in benzene in the concentration range 0.4-1.2 per cent w/w) found 475; calculated 502.

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CHAPTER IV

ANALYTICAL METHODS

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1. **Titanium-**

A known amount of the compound dried in vacuum was treated with two-three drops of nitric acid (A.R., 5N) in a Sillax crucible, dried on a steam bath, ignited to pure white titanium dioxide and weighed.

2. **Sulphur-**

A known amount of the sulphur-containing compound was digested with nitric acid (A.R., concentrated) in a Kjeldahl's flask for one hour, after which the excess of nitric acid was removed by evaporation with hydrochloric acid (A.R., concentrated). The hydrochloric acid solution was now diluted to about 2N, filtered (where necessary) heated to the boiling point and treated with warm dilute barium chloride solution (5%). After digesting for one hour, the precipitate of barium sulphate was filtered, washed and ignited in a Sillax crucible at 800°. After cooling, a drop of strong sulphuric acid was added, heated again to the same temperature, cooled and finally weighed as $BaSO_4$.

3. **Chlorine-**

This element was estimated gravimetrically as silver chloride, and in some cases by titration. A known amount of the chlorine-containing compound was boiled with a strong solution of sodium carbonate (A.R.) for 30 minutes.

The solution was filtered, the filtrate acidified with dilute nitric acid, warmed and an excess of silver nitrate solution (0.1N) added. The solution was now heated to the boiling point, allowed to stay hot for one hour, then cooled completely and filtered through a sintered glass crucible (porosity 4). The washed precipitate of silver chloride was dried at 135-140^{0} and weighed. This method was usually followed when the solution was deeply coloured, e.g. with phenolic or some acetylacetone derivatives. In colourless solutions, chlorine was estimated by titration. To the dilute nitric acid solution a known volume (excess) of a standard silver nitrate solution was added, and the excess of silver nitrate estimated by titration against a standard ammonium thiocyanate solution using ferric alum indicator (40%, 1 ml; in presence of 5 ml. nitrobenzene).

4. Ammonia-

In the addition compounds, ammonia was estimated by the following method: A known amount of the sample was boiled with strong caustic soda solution (a small amount of zinc dust also added) in a Kjeldahl flask and the ammonia evolved was distilled and absored in standard sulphuric acid. After distillation, the excess of acid in the receiver was estimated by titration against standard alkali using (methyl orange) - (indigo carmine) indicator.

5. Carbon, hydrogen and nitrogen were estimated by micro-combustion analysis.

6. Methoxy and ethoxy group estimations were done with a micro-Zeisel set-up.

7. Molecular weights were determined in Cottrels pump type ebulliometer using a Beckmann thermometer of 1/100° sensitivity. Naphthalene and p-dichlorobenzene were used for standardization.

8. Infrared spectra were taken on a Perkin-Elmer 221 IR spectrophotometer or on an Infracord machine equipped with sodium chloride optics. Wherever possible, a spectrum of the pure ligand was also recorded for comparison. The spectra of liquids were taken as liquid films; solids were taken in nujol mull. The absorption bands for nujol are at 2900, 1460 and 1380 cm^{-1} which are omitted in the absorption maxima of the compounds given in this thesis.

SUMMARY

- SUMMARY -

The key material for this investigation is titanium tetrachloride. It has been made to undergo various condensation reactions with hydroxy compounds and alkyl esters eliminating hydrogen chloride and alkyl chlorides respectively. Among the hydroxylic reactants examined are aliphatic and alicyclic alcohols, phenols, carboxylic acids and potentially hydroxylic bidentate ligands; among the esters some normal esters of sulphuric and oxalic acids. In some cases synthesis has been effected by the alternative route through acid chlorides reacting with ortho-titanic esters.

Many of the products of the 'primary' reactions with titanium tetrachloride are found in their turn to be good starting materials for further reactions with organic hydroxy compounds etc. yielding interesting and new organoxy titanium compounds. In several cases, the latter form further adducts with nitrogen bases (e.g. ammonia, pyridine) which are stable and easily characterised.
A synopsis of the syntheses with important properties of the compounds are outlined in the following pages.

Primary reactions with titanium tetrachloride:

Aliphatic and alicyclic alcohols - It was generally known that alcoholates of dialkoxy dichloro-titanium are formed when titanium tetrachloride (1 mole) reacts with excess of an alcohol (C_1-C_4); also, that the corresponding tetra-alkoxides are obtained from titanium tetrachloride and excess of the alcohol in presence of dry ammonia gas. Cyclohexanol resembles aliphatic alcohols in its reaction with titanium tetrachloride. Tetra-cyclohexanoxy titanium and cyclohexanoxy trichloro-titanium were the only two cyclohexanoxy compounds of titanium reported in the literature. We have prepared di-cyclohexanoxy dichloro-titanium and its dicyclohexanolate (melting points 105°, 115°), and tri-cyclohexanoxy chloro-titanium (m.p. 55-58°) by direct reactions with titanium tetrachloride. In boiling benzene, di-cyclohexanoxy chloro-titanium was found to be monomeric and its dicyclohexanolate showed almost complete dissociation into di-cyclohexanoxy dichloro-titanium and the solvate molecules. All the three new cyclohexanoxy compounds are white crystalline products soluble in benzene and light petroleum but are hygroscopic and unstable in moist air. They show a general resemblance with the aliphatic chloro-titanium compounds in their properties.

Mono- and dihydric phenols - Detailed reports are available on the action of phenol upon titanium tetrachloride. Levy reported di-resorcinol dichloro-titanium as the product of the reaction between resorcinol and titanium tetrachloride. Rosenheim and Sorge reacted titanium tetrachloride with catechol in ether and reported isolation of the ammonium salt $C_6H_4O_2Ti\ (OC_6H_4ONH_4)_2.H_2O$ by adding aqueous ammonia. Our studies on the action of titanium tetrachloride on catechol and resorcinol led to the isolation of four new compounds. In one case, both the hydroxy groups of catechol reacted with titanium tetrachloride giving o-phenylenedioxy dichloro-titanium as a deep brown non-hygroscopic powder; in another, a chlorine-free chocolate-red powder analysing to the composition di-(o-hydroxy-phenoxy) o-phenylenedioxy titanium was isolated. The latter dissolved in aqueous ammonia to give a clear solution which on evaporation yielded the ammonium salt described by Rosenheim and Sorge. The same chlorine-free compound was obtained from the action of catechol on o-phenylenedioxy dichloro-titanium, proving that the chlorine-free tri-catechol derivative was formed via the dichloride. The stability of the two catechol compounds and their complete insolubility in common organic solvents suggest a polymeric structure. Resorcinol, like catechol, readily reacted with titanium tetrachloride giving m-phenylenedioxy dichloro-titanium as a bright red, stable powder insoluble in common solvents; unlike catechol, however, the product isolated from the reaction with excess of resorcinol was (m-hydroxyphenoxy) m-phenylenedioxy chloro-titanium. The same product was also obtained by reacting excess of resorcinol with m-phenylenedioxy dichloro-titanium. These products also are probably polymers similar to the catechol derivatives. On account of the insolubility of both catechol and resorcinol derivatives in benzene, chloroform and other non-hydroxylic solvents, their molecular weights could not be determined. They dissolve in alcohol, but give decomposed products on evaporation of the solvent.

In addition we have also prepared some new aromatic oxytitanium compounds (three each from vanillin and thymol). Vanillin reacted with titanium tetrachloride in different molar proportions to give $(\text{vanillino})_n\text{TiCl}_{4-n}$ in which n = 1, 2 and 3. Attempts to prepare tetra-vanillino titanium by direct reaction with excess of vanillin gave a product containing 1-2% chlorine. But thymol and titanium tetrachloride reacted in different molar ratios to give all the four compounds $(\text{thymoxy})_n\text{TiCl}_{4-n}$ where n = 1,2,3 and 4. Vanillino derivatives are red to chocolate and thymoxy derivatives red to orange powders. They are all hygroscopic, insoluble in common organic solvents except the tetra-thymoxy titanium, which is soluble in boiling benzene giving a molecular elevation corresponding to the monomer.

Acids - Dichloro-titanium diacetate and dibenzoate, and trichloro titanium acetate and benzoate are known compounds. We have prepared trichloro-titanium phenoxyacetate and dichloro-titanium di-phenoxyacetate from phenoxyacetic acid and titanium tetrachloride. The deep yellow trichloro compound melts at 83° and the orange-red dichloro compound decomposes at 175°. Both are insoluble in benzene and chloroform but dissolve in alcohol with decomposition. Attempts to prepare titanium tri- and tetra-phenoxyacetates led to decomposition of the product, as in the case of other acids like acetic and benzoic.

Esters - Titanium tetrachloride reacts with normal alkyl (C_1-C_4) esters of sulphuric acid at ordinary temperatures to give chloro-titanium derivatives, with elimination of alkyl chlorides. The reactivity decreases from methyl to the *n*-butyl ester. Dimethyl sulphate and titanium tetrachloride react at 0° forming dichloro-titanium sulphate. Under different reacting conditions, the same reactants give chloro-titanium *tris*-methylsulphate and methylsulphato chloro-titanium sulphate as pure products. The *tris*-methylsulphate compound is not as stable as dichloro-titanium sulphate or methylsulphato chloro-titanium sulphate. From reactions with diethyl, di-*n*-propyl and di-*n*-butyl sulphates, we could only isolate unstable trichloro-titanium alkylsulphates. Dimethyl oxalate reacts with titanium tetrachloride forming only dichloro-titanium oxalate.

All these reaction products from esters are yellow powders, sensitive to moisture, and insoluble in common organic solvents. They dissolve in alcohol with decomposition. Because of their general reactivity towards hydroxylic compounds, they are potential intermediates for the synthesis of more complex organoxy-titanium compounds.

Hydroxylic bidentate chelates - The formation of chloro-titanium compounds containing chelating groups had attracted the attention of many chemists. Bis-chelated dichloro-titaniums of acetylacetone, ethyl acetoacetate, benzoylacetone, dibenzoylmethane, o-nitrophenol, salicylaldehyde and methyl salicylate have been prepared by us following methods reported in the literature, to make a further study of their reactivity. New compounds synthesized in the class of chelated trichloro-titaniums are those of salicylaldehyde and methyl salicylate.

Further reactions of primary organoxy-titanium compounds

Titanium alkoxides and cyclohexanoxides- Dialkoxy (C_1-C_4) dichloro-titaniums are observed to react easily with dimethyl or diethyl sulphate forming the dealkoxylated products $OTi(CH_3SO_4)_2$ or $OTi(C_2H_5SO_4)_2$ as grey to violet-black, insoluble solids sensitive to moisture. Tetra-alkoxy (C_2-C_4) titaniums react with sulphuryl chloride giving another (Ti-O-S) series of active intermediates of the type $(RO)_3TiSO_3Cl$. Tetra-alkoxy titaniums react also with thionyl chloride, but the main product here is the alkoxy trichloro-titanium. The two chlorine atoms in di-cyclohexanoxy dichloro-titanium are replaced by alkoxy groups with the aliphatic alcohols (C_1-C_4) in presence of dry ammonia gas to give sticky solids soluble in benzene and light petroleum. Phenol, catechol and resorcinol also react to give mono-chloro as well as chlorine-free coloured derivatives. The phenoxy derivatives are soluble in benzene but the others are insoluble.

<u>Titanium aryloxides</u> - Dimethyl sulphate is found to react with chloro-titanium derivatives of phenol, thymol and vanillin giving chlorine-free alkylsulphates. Unlike the reactions with alkoxides, the phenolic part is retained after the reaction. Trichloro-titanium compounds gave derivatives of the type $(RO)Ti(SO_4)CH_3SO_4$, dichloro-titanium compounds gave $(RO)_2Ti(CH_3SO_4)_2$ and monochloro-titanium compounds gave $(RO)_3Ti\ CH_3SO_4$ where ROH = phenol, thymol or vanillin. These compounds are also deeply coloured products insoluble in benzene, chloroform and light petroleum.

<u>Titanium acylates</u> - Dichloro-titanium sulphate reacts with two molecules of isopropoanol, *n*-butanol or with the acetate esters of methanol and ethanol to give the corresponding dialkoxy titanium sulphates. Diethoxy titanium sulphate, in its turn, reacts with cyclohexanol giving di-cyclohexanoxy titanium sulphate, which appeared to be the best method for preparing the dicyclohexanoxy

compound. Phenol and dichloro-titanium sulphate react to form diphenoxy titanium sulphate. Hydroxylic chelating agents LH = acetylacetone, benzoylacetone, dibenzoylmethane, acetoacetanilide, salicylaldehyde, methyl salicylate give products of the type L_2TiSO_4. The alkoxy and cyclohexanoxy titanium sulphates are white moisture-sensitive powders, whereas those of phenol and chelating agents are red and more stable to moisture. They are, however, all insoluble in benzene, chloroform and other common organic solvents.

Methylsulphato chloro-titanium sulphate reacts with methyl and ethyl acetates, isopropanol, n-butanol and phenol forming chlorine-free derivatives of the type $CH_3SO_4(RO)TiSO_4$. The cyclohexanoxy derivative is, however, best obtained from a reaction between the ethoxy derivative and cyclohexanol. With chelating agents (LH) like acetylacetone, salicylaldehyde and methyl salicylate, compounds of the type $(CH_3SO_4)(L)TiSO_4$ are obtained. The alkoxy and cyclohexanoxy derivatives are white, moisture-sensitive powders whereas those of phenol and chelating agents are red coloured and fairly stable. They are all insoluble in benzene, chloroform and common organic solvents.

Dichloro-titanium oxalate, when reacted with the lower alcohols or acetates, does not give well-defined compounds. However, substitution of the chlorine atoms is readily effected with phenol, acetylacetone, salicylaldehyde and methyl salicylate. These are coloured, stable compounds insoluble in benzene, chloroform and common organic solvents.

Dichloro-titanium di-acetate and di-benzoate readily react with dimethyl and diethyl sulphates to give chlorine-free, de-acylated bis-alkylsulphates, $OTi(CH_3SO_4)_2$ and $OTi(C_2H_5SO_4)_2$ respectively as white, insoluble, moisture-sensitive powders. Titanium phenoxy-acetates do not give any definite product when reacted with the alkyl sulphates.

Titanium chelates - Chelated trichloro-titaniums react with dimethyl sulphate to give compounds of the type $LTi(SO_4)CH_3SO_4$ where LH = acetylacetone, dibenzoylmethane, salicylaldehyde and methyl salicylate. They also react with phenol giving the corresponding triphenoxy derivatives, $LTi(OC_6H_5)_3$. With catechol, the products have the general formula $LTi(O_2C_6H_4)(OC_6H_4OH)$ where LH = dibenzoylmethane, salicylaldehyde and methyl salicylate. Acetylacetone reacts with the trichloro-titaniums giving monochlorides $L(acac)_2TiCl$ where LH = salicylaldehyde, methyl salicylate.

Salicylaldehydo- or methylsalicylato trichloro-titanium reacts with methyl salicylate or salicylaldehyde respectively, giving the same product methylsalicylato salicylaldehydo dichloro-titanium. All these are coloured, stable compounds, but insoluble in benzene, chloroform and common organic solvents.

Bis-chelated dichloro-titaniums react with dimethyl sulphate forming bis-methylsulphates, $L_2Ti(CH_3SO_4)_2$ where LH = acetylacetone, dibenzoylmethane, salicylaldehyde, methyl salicylate. They react also with phenol giving diphenoxy derivatives, $L_2Ti(OC_6H_5)_2$ and with catechol and resorcinol $L_2Ti(O_2C_6H_4)$ and $L_2Ti(OC_6H_4OH)_2$ respectively where LH = dibenzoylmethane, salicylaldehyde, or methyl salicylate. Acetylacetone gives monochloro compounds of the type L_2(acac)TiCl where LH = salicylaldehyde or methyl salicylate.

Adducts with nitrogen bases

There are very few reports of nucleophilic addition products of organo-substituted titanium halides, though such products are well known with the halides themselves. In our studies, anhydrous pyridine and ammonia have been found to form addition compounds with a large number of organoxy titanium compounds including those not containing the halogen. The number of ammonia molecules in the adduct is found to be not less than four, while in the pyridine adducts the number is less in all the adducts prepared and examined. The ammonia adducts are somewhat stabler to moisture than the corresponding pyridine compounds and more so than the parent organoxy titanium compounds. They are insoluble in most solvents like benzene, ether and chloroform, and are decomposed by alcohol and water, and also on heating.

Attempts to prepare compounds with direct Ti-C bonds

It is only recently that sigma-bonded organo-titanium compounds have been isolated. Like metal-carbon covalent compounds of other transitional metals, they are unstable, exist only at low temperatures, are sensitive to oxygen and atmospheric moisture. Lately, titanium has been found capable of forming relatively stable Ti-C sigma bonded compounds provided the metal atom is loaded with two or three negative substituents. Stabilizing ligands containing carbonyl, phosphine, cyanide or cyclopentadienyl groups which may contribute a number of electron pairs to fill up the empty d orbitals of transitional metal atoms, are known to form complexes with stabler metal-carbon sigma-bonds.

The excellent stability of some chelated organoxy titanium compounds, combined with the easy replaceability of the residual chlorine atoms, led us to attempt the introduction of direct Ti-C bonds in these complexes. With salicylaldehydo-, methylsalicylato- and dibenzoylmethano trichloro-titaniums, and with bis-salicylaldehydo-, bis-methylsalicylato, bis-dibenzoylmethano-, bis-benzoylacetono- (and diphenoxy) dichloro-titaniums, the chlorine atoms are readily replaced by phenyl groups when reacted with phenyl lithium. The new compounds are yellow to red, stable powders with definite melting points (except the last two which are red, sticky solids). They are all soluble in benzene, and a majority of them show normal molecular weight in the boiling solvent, the others decomposing at the elevated temperature.

The above results, though not sufficiently exhaustive to warrant a generalization, do seem to indicate that chelation may prove to be yet another powerful method for synthesizing thermallystable sigma-bonded organo-titanium compounds, having properties comparable with organo-metallic complexes of non-transitional elements.