[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT OF THE ETHYL CORPORATION]

Preparation and Properties of Cyclopentadienyltitanium Trichloride[1]

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RECEIVED NOVEMBER 2, 1959

Cyclopentadienyltitanium trichloride (I) has been synthesized by two independent methods: (1) by a redistribution reaction between bis-(cyclopentadienyl)-titanium dichloride (II) and titanium tetrachloride, and (2) by cleavage of II by chlorine. Cleavage of II with bromine gives the mixed halide, cyclopentadienyltitanium bromide dichloride. Hydrolysis of I proceeds stepwise to give first $(C_5H_5TiCl_2)_2O$ (IV) and then $(C_5H_5TiClO)_n$ (V), where $n \geq 3$. Compound I reacts with methanol and with 2,2-dimethyl-1,3-propanediol to form the corresponding monoester VII and diester VIII, both of which are hydrolyzed readily to V. The esters VII and VIII and the hydrolysis products IV and V can be reconverted to I by hydrogen chloride. Sodium cyclopentadienide converts I and VII to II, and sodium methylcyclopentadienide converts I to cyclopentadienyl-(methylcyclopentadienyl)-titanium dichloride.

Relatively few organotitanium compounds having a carbon–metal bond have been reported. σ-Bonded carbon–titanium compounds that have been disclosed include phenyltitanium triisopropylate,[2] methyl-,[3] ethyl-[3,4] and isobutyltitanium trichloride,[3] and tetramethyltitanium[5] (in ether solution only). Titanium compounds having a carbon–titanium bond with delocalized bonding, commonly referred to as "sandwich" compounds, also have been reported. Typical of this class of compounds are bis-(cyclopentadienyl)-titanium dihalides,[6] bis-(cyclopentadienyl)-titanium diaryls[7] and bis-(cyclopentadienyl)-titanium dicarbonyl.[8]

This investigation is an elaboration and extension of results reported in an earlier Communication[1] on the preparation and properties of a novel type of organotitanium compound, cyclopentadienyltitanium trichloride (I). This compound has been synthesized by two methods,[9] the first of which involves a redistribution reaction between the sandwich compound, bis-(cyclopentadienyl)-titanium dichloride (II), and titanium tetrachloride. This

$$(C_5H_5)_2TiCl_2 + TiCl_4 \longrightarrow 2C_5H_5TiCl_3$$

represents the first known redistribution reaction between an organometallic compound with delocalized bonds and a corresponding metal halide.

The reaction is most conveniently carried out in about a 70% yield, by heating II with an excess of $TiCl_4$ in xylene at near reflux. The yield appears to be dependent on the temperature, time and concentration of reactants. The reaction has been achieved in the absence of a solvent, but the yield of I was considerably lower. Because of the facile hydrolysis of I in solution, the yield of I from the redistribution reaction is appreciably decreased if the solvent is not extremely dry or if the mixture is not worked up in a dry atmosphere. Both of these problems can be circumvented nicely by recrystallizing the product from solutions saturated with hydrogen chloride.

The second method for preparing I involves the preferential cleavage of one of the cyclopentadienyl radicals of II by chlorine. In refluxing CCl_4, II is cleaved by chlorine to give 79% of I identical with that obtained by the redistribution reaction, along with 31% of 1,2,3,4,5-pentachlorocyclopentane (III). To obtain optimum yields of I it is impor-

$$(C_5H_5)_2TiCl_2 + 3Cl_2 \longrightarrow C_5H_5TiCl_3 + C_5H_5Cl_5$$

tant not to expose the product to chlorine after one cyclopentadienyl radical from II has been removed since it has been demonstrated that compound I can be cleaved almost quantitatively to III and $TiCl_4$ under similar conditions. Compound III

$$C_5H_5TiCl_3 + 3Cl_2 \longrightarrow C_5H_5Cl_5 + TiCl_4$$

has been prepared previously[10] by the cleavage of ferrocene by chlorine. The reaction involving titanium is unique in that it can be controlled so that only one ring is lost.

The nature of the chlorinated hydrocarbon is dependent on the reaction time and temperature. Whereas 31% of III was obtained while carrying out the reaction under reflux conditions, none was obtained when the cleavage was run at room temperature even though 65% of I was isolated; instead, there was formed an incompletely characterized chlorinated hydrocarbon shown to be unsaturated by infrared analysis. In surprising contrast, the cleavage of I by chlorine at room temperature gave III and $TiCl_4$; thus, it is difficult to rationalize the relatively high yield of I from II and chlorine under reflux conditions. This particular cleavage reaction deserves further investigation before drawing any firm conclusions. The reaction of II with chlorine is greatly accelerated when catalyzed by ultraviolet irradiation. However, the yield of I is greatly diminished while concurrently the yield of III is increased. This probably is due to the facile cleavage of both 5-membered rings by chlorine *via* a free radical process.

The cleavage reaction provides a means for the synthesis of cyclopentadienyltitanium mixed halides where two halogens are alike and the third is different. Cyclopentadienyltitanium bromide dichloride was prepared in good yield by treating II with an excess of bromine in CCl_4. The product is an orange solid which has physical and chemical

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(1) Presented at the 15th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., December 3, 1959. A preliminary presentation of this investigation appeared as a "Communication to the Editor," THIS JOURNAL, **80**, 4744 (1958).

(2) D. F. Herman and W. K. Nelson, *ibid.*, **75**, 3877 (1953).

(3) K. A. Clauss and C. Bermann, *Angew. Chem.*, **71**, 618 (1959).

(4) C. E. H. Bawn and J. Gladstone, *Proc. Chem. Soc.*, 227 (1959).

(5) K. A. Clauss and C. Bermann, *Angew. Chem.*, **71**, 627 (1959).

(6) G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 4281 (1954).

(7) L. Summers and R. H. Uloth, *ibid.*, **76**, 2278 (1954).

(8) J. G. Murray, *ibid.*, **81**, 752 (1959).

(9) Recently a third method of preparation for I, as well as for the tribromide and triiodide, has been reported by C. L. Sloan and W. A. Barber, *ibid.*, **81**, 1364 (1959). In this method magnesium cyclopentadienide was treated with an appropriate titanium tetrahalide.

(10) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina and N. A. Simukova, *Bull. Acad. Sci. U.S.S.R., Div. Sci.*, **749** (1956); *C. A.*, **51**, 1945 (1957).

properties similar to those of I. Two bromohydrocarbons were obtained and were separated with some difficulty. One was 1,2,3,4,5-pentabromocyclopentane,[10] and the other was a lower melting compound which has not been completely characterized. A significant difference in the behavior of I toward halogens is that it appears to be unaffected by bromine, whereas chlorine attacks the molecule readily to give III and $TiCl_4$.

Compound I is a yellow-orange crystalline solid melting at 208–211°[11] and is very soluble in polar solvents, but has varying solubility in non-polar solvents. As was mentioned in an earlier publication[9] and as has been confirmed in this Laboratory, molecular weight data and conductivity measurements demonstrate that I is a monomeric, non-ionic compound. Infrared analyses agree with earlier data[9] supporting a π-bonded structure.

Chemical evidence in support of the assigned structure for I is clearly afforded by the reaction of I with sodium cyclopentadienide to give a good yield of II. This type of reaction permits the preparation of unsymmetrical types of dicyclopentadienyltitanium dihalides. For example, treating I with sodium methylcyclopentadienide gives cyclopentadienyl-(methylcyclopentadienyl)-titanium dichloride (VI).

$$C_5H_5TiCl_3 + CH_3C_5H_4Na \longrightarrow C_5H_5(CH_3C_5H_4)TiCl_2 + NaCl$$

In solution, I is hydrolyzed readily *via* a process which has been shown unequivocally to involve at least a two-step reaction: In tetrahydrofuran, treatment of I with water in at least a 2:1 molar ratio, respectively, results in the displacement of one halogen, and the principal product is a binuclear organotitanium oxide, $(C_5H_5TiCl_2)_2O$ (IV).

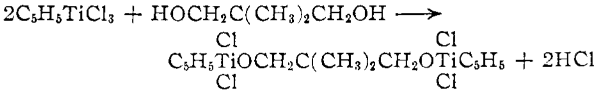
$$2C_5H_5TiCl_3 + H_2O \longrightarrow (C_5H_5TiCl_2)_2O + 2HCl$$

This appears to be the first monomeric organotitanium compound to contain *only one* Ti–O–Ti linkage; it is an orange crystalline solid which possesses physical properties very similar to those of I. Further hydrolysis with an excess of water results in displacement of a second halogen to give a product having the formula $[C_5H_5TiClO]_n$ (V). Due to its

$$n(C_5H_5TiCl_2)_2O + nH_2O \longrightarrow 2[C_5H_5TiClO]_n + 2n\,HCl \quad (n \geq 3)$$

limited solubility in organic solvents, cryoscopic and ebullioscopic molecular weight determinations have been unsuccessful and consequently it has not been possible to differentiate between a trimeric product ($n = 3$) and a higher homolog. Further hydrolysis of V by aqueous sodium hydroxide results in loss of the cyclopentadienyl grouping as well as the halogens; V is most conveniently prepared by treating I with water in refluxing acetone.

One unique and unprecedented property of I is its ability to form monoesters of the type $C_5H_5TiCl_2OR$. The esters, which are formed under relatively mild conditions, represent the first instance wherein a monoester of titanium has been formed easily by a direct reaction between the alcohol and a titanium halide. Esters of tetravalent titanium, containing one alkoxy grouping, are generally formed by redistribution reactions. Compound I dissolves in an excess of hot methanol to give cyclopentadienyl-(methoxy)-titanium dichloride (VII) in good yield. Likewise a diester of 2,2-dimethyl-1,3-propanediol, $C_5H_5TiCl_2OCH_2C(CH_3)_2CH_2OCl_2TiC_5H_5$ (VIII), is readily obtained when I is treated with the diol in a 2:1 molar ratio.



$$2C_5H_5TiCl_3 + HOCH_2C(CH_3)_2CH_2OH \longrightarrow C_5H_5\overset{Cl}{\underset{Cl}{Ti}}OCH_2C(CH_3)_2CH_2O\overset{Cl}{\underset{Cl}{Ti}}C_5H_5 + 2HCl$$

There is no evidence for the formation of a cyclic ester consisting of a six-membered ring. This is not unexpected since attempts to introduce more than one alkoxy grouping into I have failed. For example, refluxing I in methanol resulted in the formation of some cyclopentadiene and an unidentified organic-insoluble titanium compound. The use of diethylamine in the reaction did not alter the nature of the products.

The esters are lower melting than I but readily are hydrolyzed by an excess of water to give the hydrolysis product V. No attempt was made to obtain the intermediate hydrolysis product IV.

$$nC_5H_5TiCl_2OCH_3 + nH_2O \longrightarrow [C_5H_5TiClO]_n + nHCl + nCH_3OH$$

Like other organotitanium esters, the monocyclopentadienyl types reacted smoothly with anhydrous hydrogen chloride to give I and the corresponding alcohol. This acid cleavage reaction is also

$$C_5H_5TiCl_2OCH_3 + HCl \longrightarrow C_5H_5TiCl_3 + CH_3OH$$

applicable to the hydrolysis products IV and V, both of which react smoothly with hydrogen chloride in benzene to give I and water which is removed by azeotropic distillation.

$$\left.\begin{array}{l}(C_5H_5TiCl_2)_2O\\ {[C_5H_5TiClO]_n}\end{array}\right] \xrightarrow{HCl} C_5H_5TiCl_3 + H_2O$$

Earlier attempts to prepare esters of the type $(C_5H_5)_2TiClOR$ by reaction of II with an alcohol in the presence of pyridine failed.[6] It was rationalized that such an ester might be accessible *via* reaction of VII with sodium cyclopentadienide. However, II was the only pure product which could be isolated from the reaction mixture.

Experimental[12]

Materials.—Tetrahydrofuran was distilled from $LiAlH_4$ just prior to its use. The aromatic hydrocarbons as well as petroleum ethers were dried over sodium. Chloroform, carbon tetrachloride and methylene chloride were used without additional purification.

Cyclopentadienyltitanium Trichloride (I). A. From Bis-(cyclopentadienyl)-titanium Dichloride and Titanium Tetra-

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[11] This melting point is in contrast with the 145.5–147° reported by others[9] and even in sharper disagreement with the boiling point of 29–34° (1 mm.) claimed in British Patent 793,354 (April 16, 1958). Since our initial communication in which a melting point of 185° was reported, it has been observed that the melting point of I is greatly depressed if slight hydrolysis has occurred prior to taking the melting point. ADDED IN PROOF.—I wish to thank Dr. W. A. Barber for informing me of some unpublished results about compound I, which include agreement on the melting point of 208–211°. He has observed that I, crystallized from xylene, is orange or orange-brown and that V is yellow. Both he and L. Porri, who has independently synthesized V [reported as a footnote by P. Corradini and G. Allegra, THIS JOURNAL, **81**, 5511 (1959)], have determined the correct infrared spectra of I and V. The new spectrum of I is different from that given in ref. 9.

[12] All melting points are uncorrected and were determined in capillaries heated by an oil-bath. Molecular weights were determined cryoscopically in sodium-dried benzene.

chloride.—A mixture of 12.0 g. (0.048 mole) of $(C_5H_5)_2TiCl_2$,[6] 25.9 g. (0.136 mole) of $TiCl_4$, and 90 ml. of *p*-xylene was heated at 140° for 2.5 hr. under a nitrogen atmosphere while stirring. Subsequently, the mixture was allowed to cool to room temperature and the resulting crystals were filtered off rapidly and washed once with *n*-hexane while exposed to the atmosphere. The solid was dissolved in refluxing benzene and decolorized with activated charcoal while hydrogen chloride was continuously passed through the mixture. After 15-min. reflux, the mixture was filtered while hot and the filtrate was concentrated while gassing with HCl until yellow-orange crystals began to deposit. The mixture was allowed to cool to room temperature and then was further chilled by an ice-bath. The crystals were filtered rapidly and dried *in vacuo* to give 12.6 g. of cyclopentadienyltitanium trichloride (I), m.p. 208–211° with very slight softening at 150°. Concentration of the filtrate gave an additional 1.7 g. of product, m.p. 195–200°. The total yield was 14.3 g. (68%). The product can be recrystallized readily from a mixture of CCl_4 and CH_2Cl_2 saturated with HCl or from a mixture of ethyl acetate and *n*-pentane. Inasmuch as it is difficult to separate I from $TiCl_4$ in the mother liquor after crystallization of the first crop of crystals, a higher yield of product can be obtained by using a smaller volume of xylene.

Anal. Calcd. for $C_5H_5TiCl_3$: C, 27.37; H, 2.30; Cl, 48.49; Ti, 21.84; mol. wt., 219. Found: C, 27.6; H, 2.38; Cl, 48.0; Ti, 22.1; mol. wt., 231.[13]

Other xylenes like *m*-xylene and commercial xylene are equally effective solvents for the redistribution reaction. However, unless the solvent is dry and unless the reaction mixture is worked up in a dry atmosphere it is important that gaseous HCl be used during the crystallization process to avoid the formation of the hydrolysis product $(C_5H_5TiCl_2)_2O$ in varying amounts. This compound can be separated from I (with some difficulty) by fractional crystallization from CCl_4, for it is considerably more soluble than I. The reaction can be carried out in the absence of a solvent by using an excess of $TiCl_4$ and heating the mixture between 120 and 125° for 22 hr., but the yield is considerably lower than that obtained by using a solvent, mainly because of the difficulty in working up the reaction mixture.

Compound I is a yellow-orange crystalline material which melts at 208–211°. The melting point can be greatly depressed if, during crystallization, some hydrolysis of the product to $(C_5H_5TiCl_2)_2O$ occurs; I is more resistant toward hydrolysis in the crystalline form. The product is very soluble in tetrahydrofuran, acetone, methylene chloride, chloroform; moderately soluble in benzene; and slightly soluble in carbon tetrachloride and petroleum ether. A 0.021 molar solution of I in benzene showed a conductivity of less than 10^{-8} ohm^{-1} cm.$^{-1}$, indicating the compound to be essentially non-ionic.

B. From Bis-(cyclopentadienyl)-titanium Dichloride and Chlorine.—Chlorine was bubbled through a mixture of 8 g. (0.032 mole) of $(C_5H_5)_2TiCl_2$ and 200 ml. of CCl_4 at a moderate rate. The reaction temperature was kept within 5° of reflux for 2.56 hr. and between 55 and 60° until all of the $(C_5H_5)_2TiCl_2$ was consumed (2 hr.) as evidenced by the disappearance of the scarlet crystals. Nitrogen was passed through the mixture for 3 hr. while the temperature was maintained between 55 and 65°. The mixture was chilled by an ice-bath and then the yellow crystalline material was filtered off to give 5.0 g. (71%) of I which was shown to be identical with that described in A by comparison of infrared spectra and elemental analysis.

The solvent was distilled under reduced pressure and the residue was dissolved in *n*-pentane and filtered. The filtrate was chilled by Dry Ice and the white crystalline solid was filtered off and dried at room temperature *in vacuo* to give 2.39 g. (31%) of 1,2,3,4,5-pentachlorocyclopentane (III), m.p. 39–41°. A sublimed sample melted at 41–42°.

Anal. Calcd. for $C_5H_5Cl_5$: C, 24.87; H, 2.08. Found: C, 25.1; H, 2.16.

In a second run using the same quantity of reactants, the reaction mixture was gassed with chlorine at room temperature for 10 hr. Work-up as described above yielded 4.6 g. (65%) of I. The filtrate after removal of solvent left an oil which distilled between 50 and 80° (0.01 mm.). This material is a chlorinated hydrocarbon which has not been characterized completely. The infrared spectrum shows the presence of a C═C linkage.

In a third run using the same quantity of reactants, the reaction was catalyzed by ultraviolet irradiation (G.E. sunlamp). Chlorine was passed through the mixture (60°) for 20 min. after which time all of the $(C_5H_5)_2TiCl_2$ had been consumed. The solid was filtered off and suspended in CH_2Cl_2. The white insoluble material was filtered off to give 1.3 g. of a solid which did not melt below 320°. Concentration and chilling of the filtrate gave 3.0 g. (43%) of I. Work-up of the original CCl_4 solution afforded 7.44 g. (84% assuming the cleavage of one C_5H_5 grouping) of III. Compound I was recovered unchanged when irradiated alone in CCl_4 at 60°

Cyclopentadienyltitanium Bromide Dichloride.—To a suspension of 10 g. (0.04 mole) of $(C_5H_5)_2TiCl_2$ in 150 ml. of CCl_4 was added 34.2 g. (0.214 mole) of bromine. The reaction mixture was stirred at room temperature overnight and then was refluxed until the excess bromine distilled off. The yellow-orange solution was concentrated until crystals began to deposit. The mixture was cooled by an ice-bath and then the orange crystals were filtered off to yield, after drying *in vacuo* at room temperature, 7.0 g. (66%) of cyclopentadienyltitanium bromide dichloride which melted between 165 and 170° with decomposition after recrystallization from a mixture of $CHCl_3$ and CCl_4.

Anal. Calcd. for $C_5H_5BrCl_2Ti$: C, 22.76; H, 1.91; mg. equiv./g. (BrCl), 11.36. Found: C, 22.4; H, 1.87; mg. equiv./g. (BrCl), 10.94.

The infrared spectrum was compatible with the above structure.

The solvent was distilled from the filtrate under reduced pressure and the residue was hydrolyzed with water. Extraction and work-up as described earlier left 10.5 g. of a white solid which was fractionally crystallized from petroleum ether to give two compounds. The first, 1.63 g. (9%), crystallized at room temperature and was identified as 1,2,3,4,5-pentabromocyclopentane, m.p. 101–103°, by infrared analysis, elemental analysis and comparison with an earlier reported melting point.[10]

Anal. Calcd. for $C_5H_5Br_5$: C, 12.92; H, 1.08. Found: C, 12.8; H, 1.08.

The second compound, 2.42 g. (15%), crystallized after chilling with an ice-bath and melted at 51–53°. The compound has not been fully characterized, but elemental analysis and molecular weight data indicate it to have the empirical formula $C_6H_6Br_4$.

Reaction of Cyclopentadienyltitanium Trichloride with Sodium Cyclopentadienide.—A tetrahydrofuran (THF) solution (65 ml.) containing 0.025 mole of sodium cyclopentadienide was added during 15 min. under nitrogen to a stirred solution of 5 g. (0.023 mole) of I in about 40 ml. of THF. The reaction was exothermic and the color changed from yellow to red, with red crystals eventually forming. The mixture was stirred at room temperature for 1 hour and then most of the solvent was distilled under reduced pressure. The residue was extracted continuously with $CHCl_3$ for 2 days. Concentration of the extract resulted in the deposition of 4.8 g. (85% based on I) of bis-(cyclopentadienyl)-titanium dichloride identified by a mixture melting point with an authentic sample.

Cyclopentadienyl-(methylcyclopentadienyl)-titanium Dichloride (VI).—A THF solution (50 ml.) of sodium methylcyclopentadienide (0.027 mole) was added during 30 minutes to a stirred solution of 5 g. (0.023 mole) of I in about 15 ml. of THF. The red solution was stirred at room temperature for 2 hr. and refluxed for an additional 2 hr. The solvent was distilled under reduced pressure (water aspirator). The residue was extracted with CH_2Cl_2. The extract was concentrated and chilled by Dry Ice, and 0.75 g. (13%) of red crystals, m.p. 200° dec., was filtered off and dried. Sublimation at 170–180° (0.05 mm.) gave pure scarlet needles of cyclopentadienyl-(methylcyclopentadienyl)-titanium dichloride, m.p. 205–206°. The yield of a dark unidentified residue was 1.4 g. The infrared spectrum of the product was compatible with the assigned structure. Bands characteristic of both cyclopentadienyl and methylcyclopentadienyl groupings were present. No

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[13] Contrary to an earlier assertion[9] that cryoscopic measurements of molecular weight in benzene yield values much higher than theoretical, we have obtained satisfactory values by this method. Abnormally high results are obtained if the solvent is not dry because of the facile formation of $(C_5H_5TiCl_2)_2O$.

further attempt was made to find conditions or work-up procedures leading to higher yields.

Anal. Calcd. for $C_{11}H_{12}Cl_2Ti$: C, 50.22; H, 4.60. Found: C, 50.0; H, 4.77.

Cyclopentadienyl-(methoxy)-titanium Dichloride (VII).—A mixture of 1.5 g. (0.0068 mole) of I and about 15 ml. of methanol was heated to reflux until dissolution was complete. The yellow solution was allowed to cool to room temperature and the yellow crystals were filtered off and dried (25°, 0.2 mm.) to give 1.11 g. (77%) off $C_5H_5TiCl_2(OCH_3)$ (VII), m.p. 90–96°. Recrystallization of the product from methanol raised the melting point to 93–96°.

Anal. Calcd. for $C_6H_8Cl_2OTi$: C, 33.53; H, 3.76; Cl, 33.00. Found: C, 33.7; H, 4.2; Cl, 32.9.

When 5 g. of I was dissolved in 50 ml. of methanol together with 5.1 g. of diethylamine and the mixture refluxed for 3 hr., the solvent containing cyclopentadiene was distilled off. The residue was suspended in CH_2Cl_2 and filtered to give 2.8 g. of a white solid which did not melt below 300°, and which had an infrared spectrum that indicated the absence of a η-bonded cyclopentadienyl grouping. The filtrate on chilling afforded 5 g. of diethylamine hydrochloride.

Refluxing only I in methanol for 24 hr. did not yield any VII. Instead, some brown insoluble material formed which could not be purified. In the green filtrate only cyclopentadiene (monomer and dimer) could be detected.

Diester of I with 2,2-Dimethyl-1,3-propanediol (VIII).—Three grams (0.0137 mole) of I was dissolved in sodium-dried benzene. To this refluxing solution was added 0.72 g. (0.0069 mole) of purified 2,2-dimethyl-1,3-propanediol. Petroleum ether (b.p. 30–60°) was added slowly until crystallization began. The mixture was allowed to cool to room temperature and was further cooled by an ice-bath. The yellow crystals were filtered off and dried *in vacuo* to give 3.0 g. (93%) of $C_5H_5TiCl_2OCH_2C(CH_3)_2$-$CH_2OCl_2TiC_5H_5$, m.p. 157–159°.

Anal. Calcd. for $C_{15}H_{20}Cl_4O_2Ti_2$: C, 38.3; H, 4.29; Cl, 30.2. Found: C, 38.6; H, 4.31; Cl, 29.7.

A small amount of the ester was dissolved in refluxing alcohol and treated with water to give $[C_5H_5TiClO]_n$, m.p. 258° dec.; VIII is very soluble in polar solvents such as acetone and THF, as well as in CH_2Cl_2 and benzene. It is slightly soluble in alkanes.

Bis-(cyclopentadienyltitanium Dichloride) Oxide (IV).—To a stirred solution of 5 g. (0.023 mole) of I in 200 ml. of THF freshly distilled from $LiAlH_4$ was added 0.41 g. (0.023 mole) of water in 40 ml. of THF during 2 hr. while maintaining a nitrogen atmosphere. The yellow solution turned orange. Subsequently, most of the THF was distilled off and *n*-hexane was added. An orange granular material settled out and was filtered and dried *in vacuo* to give 4 g. (91%) of $(C_5H_5TiCl_2)_2O$, m.p. 145–150°. The product was recrystallized from CCl_4 to give 3.13 g. (72%) of compound, m.p. 149–151°.

Anal. Calcd. for $C_{10}H_{10}Cl_4OTi_2$: C, 31.29; H, 2.63; Ti, 24.96; mol. wt., 383. Found: C, 31.3; H, 2.73; Ti, 24.6; mol. wt., 352.

Preparation of V. A. From Cyclopentadienyltitanium Trichloride.—A solution of 1.7 g. of I was prepared in about 100 ml. of acetone. Water was added dropwise to the refluxing yellow solution until crystals began to deposit. Subsequently, the mixture was allowed to cool and stand at room temperature overnight. The yellow needles were filtered off to give 0.9 g. (78%) of product melting at 258–260° with decomposition and believed to be the trimeric compound V.

Anal. Calcd. for C_5H_5TiClO: C, 36.52; H, 3.07; Cl, 21.57; Ti, 29.13. Found: C, 36.6; H, 3.14; Cl, 21.0; Ti, 29.1.

B. From Cyclopentadienyl-(methoxy)-titanium Dichloride.—Cyclopentadienyl-(methoxy)-titanium dichloride (obtained from 2 g. of I) was dissolved in refluxing acetone. Water was added dropwise until crystals began to form. Work-up as described above gave 1.25 g. (92%) of V, m.p. 259° dec. A mixture melting point with the sample described in A was undepressed.

C. From Bis-(cyclopentadienyltitanium Dichloride) Oxide.—An acetone solution (about 15 ml.) containing 0.6 g. (0.0016 mole) of $(C_5H_5TiCl_2)_2O$ was heated to reflux. An aqueous acetone solution was then added dropwise to the yellow solution until crystals began to deposit. The mixture was allowed to stand at room temperature overnight and the crystalline material was filtered off and dried to give 0.4 g. (86%) of V, m.p. 260° dec.

Reaction of HCl with Bis-(cyclopentadienyltitanium Dichloride) Oxide.—Two grams (0.005 mole) of $(C_5H_5TiCl_2)_2O$ was dissolved in 100 ml. of $CHCl_3$; HCl was bubbled through the mixture while concentrating the solution by boiling. About 30 ml. of CCl_4 was added and the solution was concentrated to about 25 ml. The solution was chilled by an ice-bath and the yellow crystals were filtered off to give 0.92 g. of I, m.p. 203°. Work-up of the filtrate afforded an additional 0.86 g. of product, m.p. 190–195°; total yield, 1.78 g. (78%).

Reaction of HCl and V.—Hydrogen chloride was bubbled through a refluxing suspension of 1.0 g. of V in about 75 ml. of benzene until all of the water had been removed by azeotropic distillation. Subsequently, the mixture was concentrated until crystals began to settle out. After cooling to room temperature the mixture was further cooled by an ice-bath. The orange crystals were filtered off and dried *in vacuo* to give 1.05 g. (88%) of I melting over the range 196–202° (identified by mixture melting point and infrared spectrum). The product was recrystallized from a saturated HCl mixture of CCl_4 and CH_2Cl_2 to give a product melting at 204–205°.

Chlorination of Cyclopentadienyltitanium Trichloride.—A solution of 4.0 g. (0.018 mole) of I in 85 ml. of CCl_4 was gassed with chlorine at room temperature for 4 hr. The yellow milky mixture was filtered to leave a small amount of insoluble material. The CCl_4 was distilled off at 40° under reduced pressure and the residue, which fumed vigorously, was hydrolyzed with a saturated NH_4Cl solution. The aqueous solution was extracted with ether and the extract was dried over anhydrous Na_2SO_4. The ether was distilled off and the residue was crystallized from *n*-pentane to give 3.58 g. (81%) of pentachlorocyclopentane.

Bromination of Cyclopentadienyltitanium Trichloride.—A mixture of 2.0 g. (0.009 mole) of I, 10 g. (0.063 mole) of bromine and 50 ml. of CCl_4 was refluxed under a nitrogen atmosphere for 4 hr. The solution was chilled and the yellow crystals were filtered off to give 1.15 g. of product, m.p. 170°, with an infrared spectrum identical to that of I. Work-up of the mother liquor afforded 0.88 g. of less pure material.

Reaction of Cyclopentadienyl-(methoxy)-titanium Dichloride with Sodium Cyclopentadienide.—To a THF solution containing 5.77 g. (0.027 mole) of VII was added 8.5 ml. of a THF solution containing 0.027 mole of sodium cyclopentadienide during 15 min. while maintaining a nitrogen atmosphere. The solution was concentrated to one-half volume under reduced pressure and *n*-pentane was added. The mixture was filtered and the insolubles were extracted with CH_2Cl_2. The extract was concentrated and CCl_4 was added. On standing overnight there was deposited 0.8 g. (12%) of $(C_5H_5)_2TiCl_2$, m.p. 290°, identified by infrared analysis. Further concentration of the filtrate yielded 4.2 g. of orange product which began to decompose at 174° and which contained some $(C_5H_5)_2TiCl_2$ and possibly $(C_5H_5)_2TiCl(OCH_3)$. Further purification of this mixture could not be achieved.

Infrared Spectra.—The infrared absorption spectra of the titanium compounds in KBr disks and $CHCl_3$ were determined on a Perkin–Elmer model 21 recording double beam spectrometer with a sodium chloride prism. Both of the esters show bands characteristic of the monocyclopentadienyltitanium compounds as well as a band at 9.1 μ characteristic of a Ti–OR linkage.

Acknowledgment.—The author is most grateful to Dr. R. P. Curry for assistance in interpreting infrared absorption data. He is also thankful to Messrs. W. J. Easley, R. A. Ashby and J. W. Figgins for obtaining elementary analyses.

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