Kinetic Runs.—Weighed amounts of the glycols were dissolved in 99.5% acetic acid.[37] Lead tetraacetate solutions were prepared weekly by dissolving the requisite amount of the solid in 99.5% glacial acetic acid[12] and were titrated immediately before use. The solutions were thermostated at 25° (fluctuation less than 0.1°) for one hour, then mixed. Aliquots were withdrawn at periodic intervals and quenched by running them into 100 ml. of a solution 0.15% in sodium iodide and 0.5% in sodium acetate. The iodine liberated was then back-titrated with 0.001 N thiosulfate solution.

Several runs were made for compounds III and IV, both with equal and unequal initial concentrations of glycol and lead tetraacetate. As observed by Criegee,[18] the kinetics is cleanly second order (order one in glycol and in tetraacetate). Table III summarizes typical variations of k within two individual runs. Table IV compares average constants from different runs. The average of the values for each compound in Table III is listed in Table I. Some of the faster reactions (*cis* isomers) were followed up to 70% completion, the slower runs (*trans* isomers) up to 40% completion.

Infrared Spectra.—The infrared spectra reported in Table II were recorded on a Perkin-Elmer double beam instrument equipped with a calcium fluoride prism.[38] Solutions of compounds III and IV in carbon tetrachloride were saturated. Solutions of the cyclopentanediols and cyclohexanediols in carbon tetrachloride were diluted until a convenient intensity of absorption was observed. All solutions were seen through a 1-cm. quartz cell.

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[37] Since slight variations of the concentration of water in the acetic acid affect the rates considerably—R. Criegee and E. Büchner. *Ber.*, **73**, 563 (1940)—the same stock solution of acetic acid was used throughout this work.

[38] We are indebted to Mr. George Svatos for these determinations.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH DAKOTA]

Diaryl Bis-(cyclopentadienyl)-titanium Compounds[1]

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Reaction of bis-(cyclopentadienyl)-titanium dichloride with the appropriate aryllithium compound produced diaryl bis-(cyclopentadienyl)-titanium derivatives, $Ar_2[(C_5H_5)_2Ti]$ (where Ar = aryl). The diphenyl-, di-*m*-tolyl-, di-*p*-tolyl- and di-*p*-dimethylaminophenyl compounds were obtained as crystalline substances with varying thermal stabilities. Attempts to isolate the di-*o*-tolyl or di-α-naphthyl derivatives were unsuccessful.

Bis-(cyclopentadienyl)-iron[2] represents a new type of non-benzenoid aromatic system,[3] and several investigations of the organic chemistry of this complex have been reported.[3,4] From another point of view, these "penetration" or "sandwich" complexes of transition metals may be regarded as being themselves of the nature of metals, and their properties in this respect may be investigated.[5] In connection with our program of research on organometallic chemistry, we have considered such complexes from this latter point of view, and have investigated the possibility that they would form "organometallic" derivatives in which the complex itself would act like a central metal. The preparation and properties of diaryl derivatives of bis-(cyclopentadienyl)-titanium(IV) were mentioned in a preliminary communication.[6] The present paper presents the experimental data pertaining to these preparations.

The diaryl bis-(cyclopentadienyl)-titanium compounds were prepared by reaction of bis-(cyclopentadienyl)-titanium dichloride with aryllithium solutions in diethyl ether.

$$[(C_5H_5)_2Ti]Cl_2 + 2ArLi \longrightarrow Ar_2[(C_5H_5)_2Ti] + 2LiCl$$

In general the use of chlorides rather than bromides in such preparations is advantageous, because the lithium chloride formed then precipitates out immediately. Lithium bromide may tend to remain in solution in the diethyl ether, and to complicate the preparation. The bis-(cyclopentadienyl)-titanium dichloride was prepared from titanium tetrachloride and cyclopentadienyllithium. The latter was obtained by reaction of cyclopentadiene with *n*-butyllithium, which in turn was made from *n*-butyl chloride and lithium in an alkane solvent. Since the *n*-butyllithium solution was to be refluxed with cyclopentadiene, the presence of diethyl ether was avoided in this step, because warm diethyl ether reacts with alkyllithium compounds.

The technique described avoids the presence of more than one kind of halogen in the reaction mixtures. If more than one halogen is present, uncertainty arises as to the composition of the bis-(cyclopentadienyl)-metal halide. (In one case, for example, cyclopentadienyllithium was prepared from cyclopentadiene and phenyllithium which had been prepared as usual from bromobenzene and lithium in diethyl ether. When this cyclopentadienyllithium was treated with zirconium tetrachloride, the product was bis-(cyclopentadienyl)-zirconium dibromide, and not the dichloride.[7]) In such cases, saturation of the reaction mixture with the appropriate hydrogen halide has been used as a means of assuring conversion to the desired product.[8] The use, in such preparations, of cyclopentadienylsodium prepared from cyclopentadiene and sodium[5] would avoid some of these complications.

For the preparation of the diaryl bis-(cyclopentadienyl)-titanium, an aryllithium solution—which could be prepared in diethyl ether, since aryllithium

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[1] This work was carried out under contract Nonr-582(00) with the Office of Naval Research.

[2] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[3] R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

[4] See for instance P. L. Pauson, *ibid.*, **76**, 2187 (1954); R. A. Benkeser, D. Goggin and G. Schroll, *ibid.*, **76**, 4025 (1954).

[5] For leading references on bis-(cyclopentadienyl) complexes of various transition metals, see especially recent publications of G. Wilkinson and others in THIS JOURNAL and of E. O. Fischer and others in *Z. Naturforsch.*

[6] L. Summers and R. H. Uloth, THIS JOURNAL, **76**, 2278 (1954).

[7] L. Summers and R. H. Uloth, unpublished data.

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

compounds do not react with ether—was added slowly to a suspension of bis-(cyclopentadienyl)-titanium dichloride. Rapid addition led to lower yields. The reaction proceeded without external heating. The product precipitated in part, along with the lithium chloride, but much product remained in solution. It precipitated on treatment with water, or simply on exposure to atmospheric moisture.

The thermal stability of the $Ar_2[(C_5H_5)_2Ti]$ compounds varied with the nature of the Ar group. The diphenyl, di-*m*-tolyl and di-*p*-tolyl compounds could be kept for some days at room temperature, but there was slow decomposition, and they were best stored at lower temperatures. The di-*p*-dimethylaminophenyl derivative decomposed completely in a few hours at 25–30°, but could be preserved in crystalline form in a cold chest. We have not been able to isolate di-*o*-tolyl-bis-(cyclopentadienyl)-titanium, in spite of repeated attempts, nor have we succeeded in isolation of the di-α-naphthyl derivative. In both the latter cases, the aryllithium compound reacted with bis-(cyclopentadienyl)-titanium dichloride, but the product was apparently not stable enough for isolation in pure form. If information were available as to the spatial configuration of these diaryl compounds, it might be possible to decide whether steric factors are responsible for this apparent instability of the *ortho*-substituted examples.

Experimental[9]

General.—All operations with organolithium solutions were carried out under dry nitrogen. *n*-Butyllithium was prepared from *n*-butyl chloride, in petroleum ether (purified by sulfuric acid treatment), b.p. 30–60°. Cyclopentadienyllithium was prepared by refluxing this *n*-butyllithium solution with cyclopentadiene in xylene. The cyclopentadienyllithium is insoluble in hydrocarbons, and a considerable volume of solvent had to be added to keep the slurry stirrable. The yield of cyclopentadienyllithium was assumed to be equivalent to the *n*-butyllithium used.

Titanium tetrachloride was a pure commercial sample,[10] used as received. Cyclopentadiene was prepared by heating technical dicyclopentadiene, with iron filings as catalyst.

Bis-(cyclopentadienyl)-titanium Dichloride.[6,8]—A slurry (prepared from 1.16 moles of *n*-butyllithium, final volume about 4000 ml.) of cyclopentadienyllithium was stirred while 138 g. (0.73 mole) of titanium tetrachloride in 250 ml. of xylene was added, over a period of one hour. The mixture was refluxed for five hours more, then sufficient petroleum ether (about 1400 ml.) was distilled off to bring the internal temperature to 100°. The mixture was cooled to 60°, stirred 14 hours at that temperature, then cooled to room temperature and filtered (in air—nitrogen was not employed after this point). A reddish residue and a dark red filtrate were obtained. Both of these contained product. The residue was extracted with chloroform for four or five days. The product was isolated in part from this extract, and in part from the previous filtrate, by evaporating the solution to small volume and filtering out the crystals which formed; yield 130 g. (71%, based on $TiCl_4$).

This preparation was repeated several times. Yields varied from 71 to 74%. In smaller runs, for the preparation of 10–15 g. of bis-(cyclopentadienyl)-titanium dichloride, it was found that the product settled out of the solution quite well, while the lithium chloride (which is the main by-product in the solid residue) remained suspended in the solvent. This suspension could simply be decanted off, leaving the product pure enough for immediate recrystallization, and thus avoiding the lengthy extraction procedure. In larger runs, this separation by decantation was not practicable.

The dark-red crystalline product could be purified by crystallization from chloroform or xylene, or from methylene chloride–petroleum ether mixtures. It could be sublimed at 190° at 2 mm. pressure, to give beautiful red-orange crystals, m.p. 289–291°.

Anal. Calcd. for $C_{10}H_{10}TiCl_2$: C, 48.23; H, 4.05; Ti, 19.24; Cl, 28.48. Found: C, 48.24; H, 4.10; Ti, 19.10; Cl, 28.68.

Repeated sublimation of sublimed material left always a cream-colored residue, which contained a trace of chlorine and did not dissolve in water.

This product was apparently completely stable at room temperature.

Phenyllithium and Other Aryllithium Solutions.—These solutions were prepared in the usual fashion,[11] in diethyl ether, from the aryl bromide and lithium.

Diphenyl-bis-(cyclopentadienyl)-titanium.—The volume of clear phenyllithium solution necessary to contain 0.12 mole of phenyllithium was added slowly, over a period of 3 hours, to 15 g. (0.06 mole) of bis-(cyclopentadienyl)-titanium dichloride, stirred in 250 ml. of dry diethyl ether at room temperature. The mixture was stirred one hour longer, then filtered (in air—the use of nitrogen was discontinued at this point). The residue was washed with methylene chloride until only white lithium chloride remained, and the washings were added to the filtrate. This solution was then concentrated to small volume under the vacuum of a water aspirator, with the internal temperature kept always below room temperature. From time to time during this operation the product which precipitated was filtered out; yield 11.4 g. (55%).

For purification the product was dissolved in methylene chloride and any insoluble material was filtered out (the amount of such material is an index of the purity of the sample, since the substance decomposes to produce a product insoluble in methylene chloride). Petroleum ether, b.p. 30–60°, was added until crystals formed. These were filtered out, and the filtrate was concentrated to small volume at a water aspirator, with the internal temperature below room temperature, to obtain other crops of crystals, which were combined with the first.

Anal.[12] Calcd. for $C_{22}H_{20}Ti$: C, 79.52; H, 6.07; Ti, 14.42. Found: C, 79.35; H, 6.15; Ti, 14.36, 14.28.

In three other preparations by this method, the yields of recrystallized product were 81, 71 and 50%. In other cases, the technique was varied by treating the reaction mixture with water, essentially as in the isolation of the *p*-tolyl derivative (below). This technique also gave good yields of unrecrystallized products, but the procedure above is preferred, because the water treatment caused some decomposition and led to rather impure crude products.

Diphenyl-bis-(cyclopentadienyl)-titanium formed orange-yellow crystals, m.p. 146–148° with decomposition, with a characteristic odor which was not that of benzene or of cyclopentadiene. Molecular weight, found (cryoscopic, in benzene), was 300, 317, calculated value is 332. The compound could be stored, apparently without decomposition, in a cold chest; but at room temperature it decomposed gradually over a period of days, more rapidly if in solution. This decomposition left a light-yellow residue, insoluble in organic solvents.

Pyrolysis above 105°, under nitrogen, of 6.93 g. of recrystallized diphenyl-bis-(cyclopentadienyl)-titanium gave 1.77 g. (53%) of benzene (identified by b.p. and by conversion to *m*-dinitrobenzene), and left 3.72 g. of shining black residue containing 23.5% Ti (88% recovery). This residue contained also about 64% C and 1.9% H, and was possibly essentially a mixture of titanium nitride and carbide.

Di-*p*-tolyl-bis-(cyclopentadienyl)-titanium.—The volume of *p*-tolyllithium solution necessary to contain 0.08 mole of *p*-tolyllithium was added dropwise, over a period of three hours, to 10 g. (0.04 mole) of bis-(cyclopentadienyl)-titanium dichloride stirred in 150 ml. of diethyl ether, at room temperature. The mixture was stirred one hour longer, then filtered (in air). The residue was washed with methyl-

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(9) Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois.

(10) Anderson Laboratories, Weston, Michigan.

(11) See H. Gilman, L. Summers and R. W. Leeper, *J. Org. Chem.*, **17**, 630 (1952).

(12) The analytical laboratory reported that this and similar compounds tended to explode when heated with oxygen.

ene chloride until it was nearly white in color (lithium chloride) and the washings were added to the filtrate. This solution was poured into an equal volume of water, and the whole was filtered (to remove gummy material which formed on hydrolysis). The organic layer was separated and petroleum ether, b.p. 30–60°, was added to it until crystals formed. These were removed, and the filtrate was concentrated at a water aspirator, with the internal temperature below room temperature, to obtain other crops which were combined with the first; yield 8.8 g. (61%). Another preparation gave 77%.

Recrystallization was carried out as for the diphenyl compound, to give well-defined orange-yellow crystals. Recovery of recrystallized material was low, and there was much more residue insoluble in methylene chloride—that is, decomposition of the crude *p*-tolyl compound was apparently more extensive than for the phenyl compound.

Anal. Calcd. for $C_{24}H_{24}Ti$: C, 79.99; H, 6.71; Ti, 13.29. Found: C, 79.97; H, 6.73; Ti, 13.20, 13.19.

Di-*m*-tolyl-bis-(cyclopentadienyl)-titanium.—This compound was prepared like the phenyl derivative. From 7.5 g. (0.03 mole) of bis-(cyclopentadienyl)-titanium dichloride and 0.06 mole of *m*-tolyllithium, the yield was 9.4 g. (87%). Another experiment, worked up like the *p*-tolyl compound above, gave 58% yield.

The product was purified like the diphenyl compound, and gave orange-yellow crystals of the same appearance, which melted with decomposition in the neighborhood of 135 or 140°.

Anal. Calcd. for $C_{24}H_{24}Ti$: C, 79.99; H, 6.71; Ti, 13.29. Found: C, 79.48, 79.26; H, 6.67, 6.65; Ti, 13.10, 13.09.

Attempted Preparation of Di-*o*-tolyl-bis-(cyclopentadienyl)-titanium.—Four attempts were made to prepare this substance, by the method used for the *p*-tolyl derivative (above), or by modifications of that method. None of the *o*-tolyl compound was obtained. *o*-Tolyllithium apparently reacted readily enough with bis-(cyclopentadienyl)-titanium dichloride, but the course of the reaction was somewhat different. In the preparations above, as reaction progressed, the products had appeared as orange solids admixed with whitish lithium chloride, while the solution became dark orange-brown; reaction of these solutions with water precipitated additional amounts of the orange-yellow products. In the experiments with *o*-tolyllithium the appearance was not the same. The precipitate formed was light yellow in a dark green solution. Hydrolysis produced greenish or blue products of unknown nature, which changed to yellow on standing in air. The solution was slightly acidic after hydrolysis, rather than slightly basic as in the other cases. From some of the experiments, small amounts of the light yellow material were isolated. Its Ti content was 20 or 25%, and it was quite different in odor and crystalline form from the diaryl bis-(cyclopentadienyl)-titanium compounds.

Attempted Preparation of Di-α-naphthyl-bis-(cyclopentadienyl)-titanium.—Two attempts produced none of this compound. The behavior of the reaction was somewhat as in the case of the *o*-tolyl compound. α-Naphthyllithium and bis-(cyclopentadienyl)-titanium dichloride gave a dark green mixture, which was acidic after hydrolysis. In this case, again, hydrolysis produced a green product which turned yellow on standing in air. In one experiment, isolation of the material as in the preparation of the diphenyl compound above—that is, without the use of water—was attempted. The reaction mixture was filtered (in air), but the residue burst into flame as it began to dry. A small amount of tan material containing about 15% Ti was isolated.

Di-*p*-dimethylaminophenyl-bis-(cyclopentadienyl)-titanium.—Clear *p*-dimethylaminophenyllithium solution sufficient to contain 0.08 mole of the lithium compound was added, over a period of 2.5 hours, to 10.0 g. (0.04 mole) of bis-(cyclopentadienyl)-titanium dichloride, stirred in 150 ml. of ether, at room temperature. The mixture changed to a maroon color as reaction proceeded. The reaction mixture was filtered and the filtrate was discarded. The solid was washed with methylene chloride, which left a tan residue (presumably mostly lithium chloride). Petroleum ether, b.p. 30–60°, was added to the methylene chloride solution until crystals just began to form. The solution was then concentrated to small volume at a water aspirator, while the internal temperature was kept below room temperature, and the product was filtered out; yield 5.8 g. (35%) of beautiful maroon crystals.

Anal. Calcd. for $C_{26}H_{30}N_2Ti$: Ti, 11.45. Found: Ti, 11.31, 11.25.

Sodium fusion showed nitrogen present. These crystals decomposed completely in 12 hours at room temperature, to a black gummy material. In a cold chest at about −20°, a sample of the product remained crystalline, although oil droplets had begun to appear.

Two other preparations of this substance were carried out, with essentially the same results. The product was always well-defined crystalline material, but was not stable.

Pyrolysis, under nitrogen, of 5.8 g. of di-*p*-dimethylaminophenyl-bis-(cyclopentadienyl)-titanium gave 2.5 g. (75%) of N,N-dimethylaniline and a trace of cyclopentadiene. The black residue, 2.85 g., contained 19% Ti (82% recovery). Final temperature of the pyrolysis was that of a Meker burner flame. Pyrolysis of a moist sample, 7.1 g. plus 6.9 g. of water, gave 2.3 g. (57%) of N,N-dimethylaniline (identified by conversion to the picrate) and 1.1 g. (48%) of cyclopentadiene (identified through the maleic anhydride adduct). Recovery of titanium in the residue was 88%.

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