Phosphinodimethylborine.—In view of the base-weakness of phosphine and the electron-acceptor weakness of dimethylboron groups, it could be expected that the combination $H_2PB(CH_3)_2$ would be the most weakly bonded and least strongly polymerized of all of the phosphinoborines. In order to investigate it, four methods of synthesis were tried, with success only from the fourth. The first method was to heat a 2:1 mixture of PH_3 and $(CH_3)_4B_2H_2$; the main result was the disproportionation of the latter. The second method was the pyrolysis of an equimolar mixture of PH_3 and $B(CH_3)_3$, resulting chiefly in the decomposition of the phosphine. Next the reaction between $NaPH_2$ and $(CH_3)_2$-BBr was tried, without a solvent, and nothing seemed to happen until at a fairly elevated temperature there was a sudden and violent reaction with much evolution of hydrogen. Perhaps a reaction of this type could be controlled if $LiPH_2$ were used in ether; however, the success of the fourth method made it unnecessary to try this.

The method finally used to make $H_2PB(CH_3)_2$ was like that used for $[(CH_3)_2PB(CH_3)_2]_3$: a reaction between phosphine and $(CH_3)_2BBr$ in the presence of triethylamine, in benzene as a solvent. The three reactants (each 95 cc.) were put together in 10 ml. of benzene, and the resulting precipitate of triethylammonium bromide was filtered off and weighed; yield 96.5%. Now the benzene solution was evaporated and the product taken up in ether (5 ml.); in later experiments ether was used as the original solvent. On cooling of the ether solution to −78°, a thick white precipitate appeared; then after evaporation of the ether at that temperature, the wettish solid melted in the range 45–50°. When the ether solution was evaporated at ordinary temperatures, the product was a viscous oil, convertible to the solid by the ether freeze-out method.

A combustion analysis of the oil gave 33.1% C (calcd. 32.5) and 10.5% H (calcd. 10.9), as expected for the formula $H_2PB(CH_3)_2$. An attempt to distil a sample of the product under high vacuum resulted in some profound change, for the distillate melted in the range 41–125°, and gave a low analysis for both carbon and hydrogen.

Another sample of the $H_2PB(CH_3)_2$ material (19.2 mg.) was used for a determination of the molecular weight by the isopiestic method in ether, using 34.2 mg. of $[(CH_3)_2PBH_2]_3$ as the reference substance. By this method, one places the two solids in separate arms of an inverted U-tube and distils in pure ether through a connection at the top, which then is sealed shut *in vacuo*. From the comparison of heights of ether in the two arms, the molecular weights are compared on an inverse basis. Soon after the start of the experiment (75 minutes), the average molecular weight of the $H_2PB(CH_3)_2$ material was 94.2 (calcd. for monomer, 73.9); at 140 min., 98.2; at 300 min., 110; at 1410 min., 182; at 3350 min., 418; at 4665 min., 686; and at 8555 min., 2080. Thus it was clearly evident that in ether solution the material gradually forms a high polymer. The same tendency toward high polymerization probably also is shown by methylphosphinoborine, and it seems that only the dimethylphosphinoborines are more stable as trimers than as higher polymers.

Methanol Reaction to Form the New Compound $(CH_3)_2$-$BOCH_3$.—A fresh sample of $H_2PB(CH_3)_2$ material, prepared from 94.3-cc. portions of PH_3, $(CH_3)_2BBr$ and $(C_2H_5)_3N$, was treated with more methanol than required by the equation $H_2PB(CH_3)_2 + CH_3OH \rightarrow PH_3 + (CH_3)_2BOCH_3$, but yielded only 55.7 cc. of PH_3 and 52.1 cc. of $(CH_3)_2BOCH_3$. An insoluble oily residue was noticed, and it is reasonable to suppose that the polymeric forms of $H_2PB(CH_3)_2$ did not react—a conclusion supported by the initial value of the molecular weight in ether, as compared to the yield of phosphine.

Since $(CH_3)_2BOCH_3$ is a new compound, some of its properties were investigated. The molecular weight of the vapor was measured as 72.7 (calcd., 71.9) and the vapor tensions, shown in Table X, determined the equation $\log_{10} p_{\text{mm.}} = 7.935 - 1490/T$, according to which the normal boiling point is 21° and the Trouton constant 23.2 cal./deg. mole.

TABLE X

VAPOR TENSIONS OF LIQUID $(CH_3)_2BOCH_3$

t, °C.	−78.5	−63.5	−45.2	−22.9	0.0
$p_{\text{mm.}}$ (obsd.)	2.0	6.5	24.9	96.6	301
$p_{\text{mm.}}$ (calcd.)	1.9	6.8	25.1	95.9	303

Acknowledgments.—The generous support of this work by the Office of Naval Research is gratefully acknowledged. Also, the work on the molecular weight of $H_2PB(CH_3)_2$ was done with the aid of a research grant by the American Potash and Chemical Corporation.

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[CONTRIBUTION FROM RESEARCH LABORATORIES, TITANIUM DIVISION, NATIONAL LEAD COMPANY]

Organotitanium Compounds. I. Isolation of a Compound Containing the Titanium–Carbon Bond[1]

BY DANIEL F. HERMAN AND WALTER K. NELSON

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The reaction of phenyllithium with isopropyl titanate in equimolar proportions led to the formation of a thermally stable crystalline complex possessing the formula $C_6H_5Ti(OC_3H_7)_3 \cdot LiOC_3H_7 \cdot LiBr \cdot (C_2H_5)_2O$ as indicated by elementary analyses and chemical properties. The complex was rapidly oxidized and hydrolyzed on exposure to the atmosphere. Treatment with titanium tetrachloride converted the lithium isopropylate portion of the complex to lithium chloride and isopropyl titanate, thus freeing phenyltitanium triisopropylate from the complex. The latter was isolated as a crystalline material, m.p. 88–90°, and was stable on storage at 10° for at least a year, although it decomposed rapidly with oxygen and water. It was unaffected by carbon dioxide but reaction with benzophenone gave triphenylcarbinol. These reactions indicate phenyltitanium triisopropylate to be an organometallic compound of a somewhat lower order of activity than the common Grignard reagents. Thermal decomposition of the phenyl–titanium bond gave rise to reduced titanium compounds and free phenyl radicals, the latter being shown by the ability of the product to catalyze the polymerization of styrene. The free radicals in turn formed benzene, biphenyl and more highly condensed hydrocarbons.

Introduction

A study of the organic chemistry of titanium has been undertaken to examine the properties of compounds containing covalent titanium–carbon bonds. The preparation of such compounds has been attempted repeatedly and unsuccessfully in the past since the first study by Cahours in 1861.[2-4]

The non-existence or instability of organometallic compounds of the transition elements, including titanium, was attributed by von Grosse to the distribution of the valence electrons of the metal

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[1] A preliminary presentation of this material appeared as a "Communication to the Editor," THIS JOURNAL, **74**, 2693 (1952), and was delivered at the 123rd Meeting of the American Chemical Society in Los Angeles, California, March 15 to 19, 1953.

[2] M. A. Cahours, *Ann. chim.*, [3] **62**, 280 (1861).

[3] H. Gilman and R. G. Jones, *J. Org. Chem.*, **10**, 505 (1945).

[4] Y. M. Plets, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1298 (1938).

atoms between two principal quantum groups.[5,6] Expanding upon this, the following argument paralleling Heitler's[7] for the tetravalency of carbon is proposed to arrive at the electronic arrangement which must be obtained in order to stabilize titanium in a tetracovalent state.

Since titanium in its ground state has only its 3d electrons unpaired, interaction with four atoms or groups such as hydrogen, chlorine or methyl would lead to a repulsion. Thus, only divalent compounds such as $TiCl_2$ or $(CH_3)_2Ti$ might normally be anticipated. However, an attraction curve resulting in a tetravalent compound should be expected when the 4s electrons become unpaired resulting in a $3d^3$, $4s^1$ configuration as in the first excited state.[8] While titanium does not necessarily have to react from the first excited state to form tetravalent compounds, its existence makes it possible to form such compounds from the ground state. While the excitation of carbon (and silicon) involves an allowed transition where $\Delta l = 1$, the excitation of titanium requires the forbidden transition 4s → 3d where $\Delta l = 2$. Nevertheless such a transition is possible under the influence of a strong electrostatic field.[9] Such a field may be supplied by highly electronegative substituents such as chlorine or an alkoxy group and $TiCl_4$ or butyl titanate may be explained on this basis. On the other hand, a tetraalkyl titanium is unstable because the necessary field is not supplied. With such concepts as a point of departure, it was assumed that stable compounds of the type R_nTiX_{4-n} may exist where X is a highly electronegative group such as $-OR'$ or $-Cl$, R is a relatively electronegative aryl or alkyl group, and n is 1 or at most 2.

Experimental

Reagents.—The various titanates with the following properties were prepared in 65–80% yields according to the method described by Nelles.[10]

TABLE I

ALKYL TITANATES

Titanate	B.p., °C.	Pressure, mm.	Density
n-Propyl	167	11	[11] 0.9970^{35}_{4}
Isopropyl	82	5	0.968^{20}_{20}
n-Butyl	160–162	2	1.001^{20}_{20}
Isobutyl	134	3	(m.p. *ca.* 30–40°)

Phenyllithium was prepared in ether by the standard method using lithium shot as obtained from the Metalloy Corporation. Grignard reagents were prepared and standardized by the usual methods.

Apparatus.—Standard-taper glassware was employed for the reactions and transfers of material. A protective, dry nitrogen atmosphere was assiduously provided for the reagents and products in all cases. While taking samples for analysis a rapid stream of nitrogen was passed through the opened flask containing the phenyltitanium compound. All reactions except oxidation were carried out under a protective atmosphere.

I. Reactions with Phenylmagnesium Bromide

Reaction of Phenylmagnesium Bromide with Butyl Titanate.—Two hundred and twenty ml. of a 1.50 *N* solution of phenylmagnesium bromide in diethyl ether (0.33 mole) was added dropwise over a period of 90 minutes to 112 g. (0.33 mole) of butyl titanate in 350 ml. of diethyl ether contained in a one-liter flask fitted with a stirrer, thermometer and nitrogen inlet and outlet. The temperature was maintained at 8°. As the Grignard reagent was added the solution turned green and finally dark amber. These colors were due to titanous compounds since exposure of a sample of the product to air caused an immediate loss of color. A series of three organometallic color tests was made by adding Michler ketone to samples of the product and allowing the mixtures to stand for varying lengths of time before hydrolysis and addition of iodine in acetic acid. The intensity of the color test was observed to be weak after a five-minute reaction time, moderate after a 30 minute reaction time, and very strong after 24 hours.

Oxidation of the Phenyl–Titanium Bond.—A stream of oxygen was passed for three hours through a freshly prepared 0.42 mole of phenylmagnesium bromide–butyl titanate reaction mixture, whereupon heat was developed and the titanous color disappeared. The product was hydrolyzed by pouring into 200 ml. of 10% sulfuric acid, and the ether layer was extracted with a 5% sodium hydroxide solution. The sodium hydroxide solution was acidified and a 10% solution of bromine in 15% aqueous potassium bromide added until complete precipitation of the phenol as 2,4,6-tribromophenol took place. The product weighed 31.8 g., a 23.0% yield based on the phenyl–titanium bond, and melted at 92–94°. After recrystallization from alcohol, it melted at 95–96° (lit. m.p. 96°). Distillation of the ether layer in a Pennsylvania State type fractionating column of approximately 10 theoretical plates gave 3.1 g. of benzene, b.p. 78–80°, 9.4% yield based on the Grignard reagent. The distillation residue crystallized on cooling. Filtration gave 5.6 g. (17.8% yield) of biphenyl, m.p. 62–65°. Recrystallization from methyl alcohol and benzene gave a m.p. of 67–69°; mixed m.p. with a known sample of biphenyl 67–69° (lit. m.p. 69°). One hundred ml. of 1.868 *N* phenylmagnesium bromide added to 300 ml. of ethyl ether was oxidized as above to give a 23.4% yield of phenol obtained as 14.5 g. of 2,4,6-tribromophenol.

Carbonation of the Phenyl–Titanium Bond.—An 0.42-mole phenylmagnesium bromide–butyl titanate reaction mixture was added dropwise in 15 minutes to an excess of powdered "Dry Ice" contained in a three-necked flask fitted with a stirrer and thermometer. The mixture was allowed to warm to 10° and carbon dioxide gas was passed over the surface for two hours. The product was hydrolyzed by pouring into 200 ml. of 10% sulfuric acid and the ether layer was extracted with 5% sodium hydroxide solution. Acidification of the extract gave no benzoic acid. Fractionation of the ether layer gave a 15.2 g. fraction of benzene boiling at 78–81°, a 45.5% yield based on equivalents of starting material. A similar carbonation of 100 ml. of 1.868 *N* phenylmagnesium bromide in 300 ml. of ether gave a 66.1% yield of benzoic acid (14.8 g., m.p. 119–121°) in agreement with the 70–71% yields reported in the literature.[15] Carbonation of a second phenylmagnesium bromide–butyl titanate reaction mixture with carbon dioxide gas passed into it for two hours at room temperature resulted in a 2.1% yield (1.5 g.) of benzoic acid.

A 0.4 mole phenylmagnesium bromide–butyl titanate reaction mixture was carbonated with "Dry Ice" as above and then oxidized by bubbling oxygen through the mixture. Again, no benzoic acid was obtained after hydrolysis, but a 24.3% yield of phenol was obtained as 32.1 g. of 2,4,6-tribromophenol.

Hydrolysis of the Phenyl–Titanium Bond.—A freshly prepared 0.467 mole phenylmagnesium bromide–butyl titanate reaction mixture was allowed to stand 15 minutes to ensure completion of the reaction and was then run into 300 ml. of 10% sulfuric acid with stirring and cooling. The ether layer was separated, dried with anhydrous sodium sulfate, and fractionated using octanol as a liquid backing; yield 24.2 g. (66.5%) of benzene, b.p. 78–81°, $n^{25}D$ 1.5005; 2.1 g. of an intermediate fraction, 81–117°; and 116 g. (84%) of recovered butyl alcohol.

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[5] A. von Grosse, *Z. anorg. allgem. Chem.*, **152**, 133 (1926).

[6] E. Krause and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen," Edwards Brothers, Ann Arbor, Michigan, 1943, p. 736.

[7] W. Heitler, "Elementary Wave Mechanics," Oxford University Press, London, 1945, p. 121.

[8] H. N. Russell, *Astrophys. J.*, **66**, 347 (1948).

[9] G. Herzberg, "Atomic Spectra and Atomic Structures," Dover Publications, New York, N. Y., 1944, p. 156.

[10] J. Nelles, U. S. Patent 2,187,821 (January 23, 1940).

[11] R. Speer, *J. Org. Chem.*, **14**, 655 (1949).

Spontaneous Decomposition of the Phenyl–Titanium Bond.—A 0.33 mole phenylmagnesium bromide–butyl titanate reaction product was stored at room temperature for 24 days and the increase in the per cent. of the total titanium reduced to the titanous state was determined periodically by analysis of aliquots of the mixture. The results are shown in Fig. 1.[12] Toward the end of the spontaneous decomposition, a black titanous material settled from solution and satisfactory sampling was not possible, which accounts for the premature levelling-off of the curve at about 45% conversion to the titanous state. The decomposed product was oxidized and only a 1.5% yield of phenol was isolated as 2,4,6-tribromophenol, showing that the phenyl–titanium bond was practically completely decomposed. Because of this instability, it was impossible to isolate the desired product by crystallization or distillation.

Decomposition and Pyrolysis of the Phenyl–Titanium Bond.—The ether was stripped from a 0.75-mole phenylmagnesium bromide–butyl titanate reaction mixture and the black titanous residue was heated with the following results: In the range of 80–130°, an exothermic decomposition took place during which a major portion of the titanous material was formed. Some distillate was obtained along with a small amount of gas evolution. At 180–240° a second exothermic reaction took place during which additional distillate was obtained and considerable gas was evolved and collected. Total gas volume was 3400 cc. In the last stage the titanous material was autoöxidized to the titanate state to yield a fluid yellow polymeric residue which solidified on cooling. Redistillation of the combined distillates gave 20.2 g. of benzene, b.p. 78–82°, yield 33.7% based on the phenyl group, and 19 g. of a complex hydrocarbon mixture boiling up to 224°. The pyrolyzed titanate residue was dissolved in 10% sulfuric acid, ether extracted, and the extract distilled. No additional benzene was obtained, indicating the complete decomposition of the carbon–titanium bond during pyrolysis. A 20.0 g. fraction, b.p. 114–126° (3 mm.), solidified on cooling. Recrystallization from methyl alcohol and benzene gave biphenyl, m.p. 66–68° (yield of crude, 33.3%). From a 8.2-g. fraction, b.p. 165–172° (2 mm.), was obtained a small amount of crystals of an unidentified aromatic hydrocarbon. Recrystallization from methyl alcohol several times gave: m.p. 100.5–101.5°; C = 89.0%; H = 9.5%. Molecular weight by the cryoscopic method in benzene gave 226–234. Analysis of the gas fraction in a Fischer Unitized Gas Analyzer showed 12% inert (nitrogen) and 88% combustible gas, with the empirical formula of $C_{3.8}H_{10.0}$. Absorption in bromine water showed 43% unsaturated gas leaving a saturated hydrocarbon analyzing as $C_{3.5}H_{9.8}$. The gas was passed through a solution of bromine water giving 5.5 g. of a crude oil, $d^{25}{}_4$ 1.745. Literature values of various dibromobutanes range from 1.759 to 1.820.

In a second pyrolysis of a 0.33-mole phenylmagnesium bromide–butyl titanate reaction mixture, the product was heated to 70–90° for 30 minutes and then dissolved in 500 ml. of 10% sulfuric acid. Analysis of the aqueous layer showed 40.5% of the total titanium to be in the titanous state. Fractionation of the dried, light colored organic layer gave an 8.5% yield (2.8 g.) of benzene, b.p. 78–80°, an 81% yield (102 g.) of butyl alcohol, b.p. 116–118°, and 20.8 g. of a complex hydrocarbon oil, boiling range 107–195° (5 mm.). The yield of this latter cut, assuming it be formed solely from the free phenyl radical, was 79.5%. The butyl groups of the titanate may also have contributed to this fraction.

Polymerization of Styrene by Means of a Phenyltitanium Compound.—A series of solutions containing 20 ml. (19 g.) of styrene plus benzene sufficient to make up 40 ml. of solution was heated for 5 hours at 80° in the presence of the catalysts indicated in Table II. The products were poured into excess methyl alcohol, and the precipitated polymer was filtered, washed with methyl alcohol and water, and dried at 100°. The results are given in Table II.

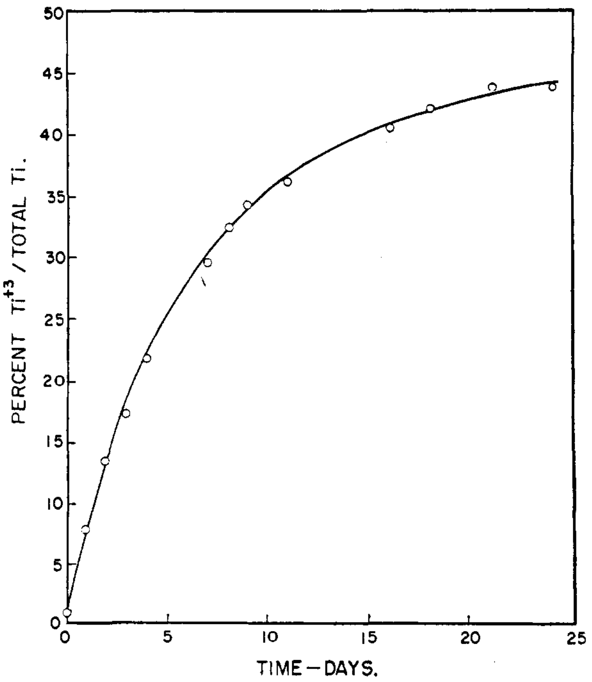

Fig. 1.—Rate of titanous compound formation in reaction mixture of phenylmagnesium bromide and butyl titanate, molar ratio 1:1.

TABLE II

POLYMERIZATION OF STYRENE

Catalyst	% Yield of polymer I	II
0.1 g. benzoyl peroxide	53	48
0.0018 equivalent of phenyl Grignard–titanate mixture[a]	49	46
No catalyst	0.0	0.6
0.5 g. butyl titanate	0.0	
0.5 g. reduced titanate[b]	0.6	
2 ml. 1.5 *N* C_6H_5MgBr (0.003 equivalent)	1.7	1.7

[a] The usual phenylmagnesium bromide–butyl titanate mixture stored for 24 hours before use. [b] Prepared by reducing 50 g. of butyl titanate in 250 ml. of butanol with 8 g. of sodium. The black insoluble titanous product was separated by centrifugation under a nitrogen atmosphere.

Decomposition of the Methyl–Titanium Bond.—A solution of 0.39 mole methylmagnesium bromide in 100 ml. of ether was added in the usual manner to 0.40 mole (136 g.) of butyl titanate dissolved in 400 ml. of ether. An aliquot gave at first a weak organometallic test but gave a strong test on standing with Michler ketone for four hours before hydrolysis. Reaction of an aliquot with water gave immediate hydrolysis of the methyl–titanium bond and the evolution of a gas, presumably methane. The bulk of the reaction product was stored at room temperature, and the rate of increase of titanous material *vs.* gas evolution was determined with the results shown in Table III.

TABLE III

DECOMPOSITION OF METHYL–TITANIUM BOND

Storage time, hr.	Decomposition, % $\frac{Ti^{+3}}{\text{Total Ti}} \times 100$	Ti^{+3}, moles	Gas, moles
0	0.3	0.0014	0.0
24	13.5	.057	.045
48	34.7	.147	.150

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[12] Analysis consisted of addition of aliquots to 10% sulfuric acid and titration with ferric ammonium sulfate in the presence of ammonium thiocyanate. The more general term "titanous" rather than "trivalent" is used to describe the reduced state of titanium formed in the decomposition of the titanium–carbon bond, although the analysis actually determines trivalent titanium. It is shown in the second publication of this series that some divalent titanium compounds may be formed in addition to trivalent compounds, but that during the analysis they are immediately oxidized by water to the trivalent state and determined as such.

After 48 hours a black insoluble material deposited, making it impossible to obtain further aliquots accurately. Analysis of the gas gave the empirical formula $C_{1.0}H_{5.7}$.

II. Reactions with Phenyllithium

Isolation of a Phenyltitanium Isopropylate–Lithium Isopropylate Complex.—A solution of 0.302 mole of phenyllithium in 225 ml. of diethyl ether was added within two hours to 0.302 mole (86 g.) of isopropyl titanate in 300 ml. of ether maintained at 8–15°. An orange coloration appeared initially and immediately disappeared on stirring. Toward the end of the phenyllithium addition, a large batch of white crystals precipitated. The product gave a negative organometallic color test and no reduction of the titanium was observed. The mixture was cooled in an ice-bath and the supernatant liquid was forced under nitrogen pressure through a sintered-glass filtering stick into a nitrogen-filled receiver, leaving the crystals behind. The crystals were then washed with four successive portions of cooled petroleum ether, which were likewise removed through the filter stick. The combined filtrate and washings contained 21.4% of the total titanium. The crystalline solid remaining in the flask was pumped at 2–3 mm. for eight hours to remove the remaining solvent, yielding 123.3 g. (76% of theory). Analysis of the complex is given in Table IV.

TABLE IV

PHENYLTITANIUM ISOPROPYLATE–LITHIUM ISOPROPYLATE COMPLEX

Analysis,[a] %	I	II	III	IV	Average	Calcd. for $C_6H_5Ti(OC_3H_7)_3 \cdot LiOC_3H_7 \cdot LiBr \cdot (C_2H_5)_2O$ m.w. = 528.92
C	51.2	49.7	50.3	49.3	50.1	49.95
H	8.89	8.9	9.3	8.58	8.9	8.13
Ti as TiO_2	15.15	15.10			15.1	15.12
Br	15.08	14.92			15.0	15.11
Li	2.5				2.5	2.62
Ether	8.7				8.7	14.00

[a] Titanium was determined by digestion of the sample in a sulfuric acid, nitric acid, ammonium sulfate mixture, followed by dilution with water, reduction with a mercury–zinc amalgam, and titration with ferric ammonium sulfate solution using ammonium thiocyanate as an indicator. Bromine was determined gravimetrically, and lithium was determined by the Perkin–Elmer flame photometer standardized against known lithium–titanium solutions. The ether content of the complex was obtained by dissolving 100 g. of the complex in 100 ml. of toluene and adding the mixture dropwise with stirring to 250 ml. of 2% sulfuric acid. The product was dried and distilled and the distillate fractionated in a Pennsylvania State type column to give 8.7 g. of ether, b.p. 35–37°. The volatility of the ether caused considerable losses resulting in a 67% yield based on theory.

Oxidation of a 15.3-g. sample in the usual manner gave a 35.3% yield of phenol based on the assigned formula, isolated as 3.38 g. of the tribromo derivative. The complex failed to react with powdered "Dry Ice." A similar carbonation of phenyllithium gave a 41% yield of benzoic acid in agreement with values found in the literature.[13]

Ten grams of aluminum chloride in 50 ml. of diethyl ether was added to a solution of 0.296 mole of the organotitanium–lithium complex, resulting in the precipitation of 94.7% of the lithium content as the halides. Oxidation of the decanted ether solution gave a 5.2% yield of phenol as the tribromo derivative based on titanium content. This method of freeing the organotitanium compound from the complex is inferior to that described below.

Isolation of Phenyltitanium Triisopropylate.—One mole of 1.00 *N* phenyllithium was added as before to one mole (284 g.) of isopropyl titanate in 600 ml. of ether to give a slurry of the complex. A 10% excess of titanium tetrachloride, 0.276 mole (52.6 g.) in one liter of ether was then added in 1.5 hours with stirring and cooling. The large volume of ether was required because of the low solubility of the yellow crystalline titanium tetrachloride–ether complex which formed. As the reaction proceeded, the organotitanium–lithium complex disappeared and a mixture of lithium chloride and bromide precipitated. The clear supernatant liquid was decanted into a nitrogen-filled distillation apparatus and the ether was stripped under reduced pressure at −40 to −20°, leaving a dark gray crystalline residue of crude phenyltitanium triisopropylate. Because of their slight solubility in diethyl ether, a small amount of lithium chloride and bromide still contaminated the product. The crude crystals were freed of the last traces of lithium salts by dissolving in 750 ml. of petroleum ether, b.p. 30–60° and filtering through a filter stick. Half of the petroleum ether was stripped from the clear filtrate at 100–200 mm. nitrogen pressure and white crystals deposited. They were filtered, washed with three 100-ml. portions of cold petroleum ether and dried by evacuation. Yield of purified phenyltitanium triisopropylate was 75 g. Additional crude yellow crystals were recovered from the filtrate and washings giving a total yield of 160 g., equal to 53% of theory. The analysis is given in Table V.

TABLE V

ANALYSES OF PHENYLTITANIUM TRIISOPROPYLATE

Theoretical, $C_{15}H_{26}TiO_3$; Calcd. from anal., $C_{14.8}H_{27.6}TiO_3$

	I	II	III	Average	Theoretical for $C_6H_5Ti(OC_3H_7)_3$
C	59.2	59.0		59.1	59.62
H	9.0	9.4		9.2	8.63
Ti as TiO_2	26.5	26.8	26.4	26,6	26.46
Cl	0.23			0.23	None
Li	Trace			Trace	None

A sample of the purified phenyltitanium triisopropylate in a sealed nitrogen-filled capillary tube melted at 88–90°. Oxidation of a 10-g. sample gave a 23.2% yield of phenol isolated as 2.59 g. of 2,4,6-tribromophenol. Hydrolysis of a 50-g. sample under nitrogen resulted in 20.4 g. of a mixture of isopropyl alcohol and benzene, b.p. 65–85°. The alcohol was washed out with 70 ml. of water, and the benzene layer was dried and distilled to give 11.0 g. (85.5% yield), b.p. 78–80°, $n^{20}D$ 1.5002. No reaction was observed upon carbonation with "Dry Ice." Phenyltitanium triisopropylate gave a slowly developing but strong color test with Michler ketone. It decomposed on heating at 100–120° to give a violet titanous product but it has been stored for over a year in the dark at 10° without darkening. Extensive decomposition was observed in an attempted distillation at 60–100° and a pressure of one micron.

Reaction of Phenyltitanium Triisopropylate with Benzophenone.—A solution of 0.21 mole (39 g.) of benzophenone in 300 ml. of ether was added with stirring to 0.21 mole of phenyltitanium triisopropylate in 850 ml. of ether after which the mixture was stored overnight and then refluxed seven hours. The product was added to 400 ml. of 5% sulfuric acid and the ether layer was separated, stripped and steam distilled. The distillate was ether extracted and the extract distilled to remove by-products and starting materials, leaving a residue of crude triphenylcarbinol which crystallized on cooling. Recrystallization from carbon tetrachloride gave a yield of 9.9 g. (19.1%); m.p. 162–163° (lit. m.p. 162.5°).

Reaction of Phenyllithium and Isobutyl Titanate (1:1 Molar Ratio).—One-half mole of phenyllithium in 500 ml. of diethyl ether was added in 1.5 hours in the usual manner to 0.5 mole (170 g.) of isobutyl titanate in 400 ml. of diethyl ether. The reaction mixture darkened as the reagent was added, but no insoluble complex separated. A 15% excess of titanium tetrachloride (27.9 g.) in 550 ml. of ether was added resulting in the precipitation of 97.4% of the lithium present as the insoluble halides. The organotitanium product was recovered in the form of a dark yellow-green, viscous residue containing a trace of titanous product. It gave a positive organometallic color test. It was very soluble in petroleum ether, benzene, toluene and carbon tetrachloride, but could not be crystallized from these solvents even on cooling to −80°. Found: TiO_2, 23.1%. Calculated for $C_6H_5Ti(OC_4H_9)_3$: TiO_2, 23.15%; for $(C_4H_9O)_4Ti$: TiO_2, 23.53%. Oxidation of a 10-g. sample gave a 24% yield of phenol, based on equivalents of titanium. No benzoic acid was formed on carbonation. The product de-

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[13] H. Gilman and P. VanEss, THIS JOURNAL, 55, 1258 (1933).

composed slowly on storage, resulting in reduction of 35% of the titanium within six weeks. A reaction of phenyllithium with *n*-propyl titanate was carried out as above with similar results.

Reaction of Phenyllithium and Butyl Titanate (2:1 Molar Ratio).—A half mole of phenyllithium as a 1.07 *N* solution in diethyl ether was added to 0.25 mole of butyl titanate in 250 ml. of ether within two hours. No crystalline complex precipitated because of the high solubility in diethyl ether, but crystallization could be effected by replacing a portion of the diethyl ether with petroleum ether. Storage overnight gave only a trace of titanium in the titanous state. A 15% excess of titanium tetrachloride, 27.4 g. in 500 ml. of ether, was added, and lithium chloride precipitated. Rapid decomposition took place resulting in the reduction of 54.3% of the titanium within six days.

Discussion

Preparation of Organotitanium Compounds.—While it was not possible to isolate an organotitanium compound from mixtures of phenylmagnesium bromide and the alkyl orthotitanates reacting according to equation (1)

$$C_6H_5MgBr + (RO)_4Ti \longrightarrow C_6H_5Ti(OR)_3 + ROMgBr \quad (1)$$

the existence of the titanium–carbon bond in these mixtures was demonstrated by the following reactions.

(1) The organotitanium compounds give a slowly developing, but eventually strong, organometallic color test with Michler ketone,[14] indicating that phenylmagnesium bromide has disappeared from the reaction mixture to form a phenyltitanium derivative which exhibits a lower order of organometallic activity.

(2) Carbonation of the unisolated product with excess "Dry Ice" gives a very small amount of benzoic acid as compared to a 70% yield obtainable in the carbonation of phenylmagnesium bromide.[15] This demonstrates the essentially complete reaction of the Grignard reagent while still allowing for the presence of a less reactive non-carbonatable organotitanium compound.

(3) Oxidation followed by hydrolysis gives phenol, biphenyl and benzene indicating that the product is easily oxidized, undergoing the reactions shown

$$C_6H_5Ti(OC_4H_9)_3 + {}^1/_2O_2 \longrightarrow C_6H_5OTi(OC_4H_9)_3 \quad (2)$$

$$C_6H_5OTi(OC_4H_9)_3 + H_2O \longrightarrow C_6H_5OH + TiO_2 \text{ hydrate} + 3C_4H_9OH \quad (3)$$

The 20–25% yield of phenol and accompanying biphenyl are not surprising in view of similar yields and by-products obtained in the oxidation of phenylmagnesium bromide[16] and phenyllithium.[17]

(4) Benzene is formed upon hydrolysis and is a further indication of a phenyltitanium link reacting as

$$C_6H_5Ti(OC_4H_9)_3 + H_2O \longrightarrow C_6H_6 + TiO_2 \text{ hydrate} + 3C_4H_9OH \quad (4)$$

(5) The phenyltitanium product reacts with benzophenone in a manner analogous to a Grignard reagent to give a 19% yield of triphenylcarbinol according to equations (5a) and (5b)

$$C_6H_5Ti(OC_3H_7)_3 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3COTi(OC_3H_7)_3 \text{ (not isolated)} \quad (5a)$$

$$(C_6H_5)_3COTi(OC_3H_7)_3 + H_2O \longrightarrow (C_6H_5)_3COH + TiO_2 \text{ hydrate} + 3C_3H_7OH \quad (5b)$$

This relatively low yield may be attributed to the lesser activity of the carbon–titanium bond, as is shown also in the Michler ketone test and the carbonation reaction.

(6) The thermal decomposition of the reaction products to give free phenyl radicals and titanous products is further evidence for an organotitanium bond.

Fortunately, the reaction products of phenyllithium with alkyl orthotitanates, exhibit a marked increase in stability over the corresponding phenyl Grignard compositions. From a 1:1 molar ratio of phenyllithium and isopropyl titanate a 76% yield of a crystalline organotitanium complex is isolated. Analysis and chemical properties indicates it to possess the formula[18]

$$C_6H_5Ti(OC_3H_7)_3{\cdot}LiOC_3H_7{\cdot}LiBr{\cdot}(C_2H_5)_2O$$

It shows no decomposition on storage for prolonged periods of time and except for its failure to give a color test with Michler ketone, it exhibits all the chemical properties which have been previously associated with the organotitanium compounds.[19]

Phenyltitanium triisopropylate is isolated from the complex by treatment with anhydrous titanium tetrachloride or aluminum chloride in ether. The lithium isopropylate portion of the complex is converted to insoluble lithium chloride and isopropyl titanate as shown in equation (6).

$$C_6H_5Ti(OC_3H_7)_3{\cdot}LiOC_3H_7{\cdot}LiBr{\cdot}(C_2H_5)_2O + {}^1/_4TiCl_4 \longrightarrow C_6H_5Ti(OC_3H_7)_3 + {}^1/_4(C_3H_7O)_4Ti + LiCl + LiBr + (C_2H_5)_2O \quad (6)$$

Of the two reagents, titanium tetrachloride is preferred over aluminum chloride since it introduces no new metallic impurity and the by-product isopropyl titanate is easily removed from the product. If more than a 10–15% excess is used the stability of the organotitanium compound is impaired, presumably, due to replacement of a portion of the isopropoxy groups by chlorine atoms. A total yield of 53% of phenyltitanium triisopropylate was crystallized from the reaction product, representing the first isolation of a compound containing a covalent titanium–carbon bond. Isolation of this compound tends to confirm the theoretical considerations regarding the stabilizing effect of substituents on the titanium–carbon bond.

In attempting to synthesize diphenyltitanium dibutylate by the above procedure, a stable intermediate lithium complex also is obtained but

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[14] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[15] *Org. Syntheses*, **5**, 77 (1925).

[16] E. Muller and T. Topel, *Ber.*, **72B**, 273 (1939).

[17] H. A. Pacevitz and H. Gilman, THIS JOURNAL, **61**, 1603 (1939).

[18] Lithium bromide is available for complex formation since it is formed in the original preparation of phenyllithium from bromobenzene and remains dissolved in the ether solution used in the preparation of the phenyltitanium compound. Lithium isopropylate is, of course, a by-product of the reaction.

[19] In the second publication of this series, it is indicated that the reaction of phenylmagnesium bromide and butyl titanate in a 1:1 molar ratio leads to a mixture of mono- and diphenyltitanium derivatives, and that the more highly substituted derivative is the cause of the instability. In the present case using phenyllithium, the formation of the insoluble complex which has no magnesium counterpart apparently prevents the reaction from going past the monophenyl stage. This is undoubtedly a contributing factor to the stability of the product.

reaction with titanium tetrachloride to release the organotitanium compound results in a rapid and extensive decomposition. These results substantiate the contention that the stability of R_nTiX_{4-n} compounds decreases when n is greater than 1.

Decomposition of the Titanium–Carbon Bond.—While purified phenyltitanium triisopropylate is relatively stable, the 1:1 molar reaction product of Grignard reagents and butyl titanate offers an excellent opportunity to examine the decomposition of the titanium–carbon bond (Fig. 1). Since a freshly prepared reaction mixture contains less than 1% of its titanium content in the titanous state, and since the Grignard reagent which might act as a reducing agent is no longer present, any subsequent formation of titanous products on storage may be attributed to the decomposition reaction

$$C_6H_5Ti\!< \longrightarrow C_6H_5\cdot + Ti^{+3} \qquad (7)$$

Formation of the free phenyl radicals predicted in eq. 7 is demonstrated by the fact that a catalytic amount of the crude phenyltitanium product is capable of inducing the polymerization of styrene. The rate is comparable to that of a benzoyl peroxide-catalyzed polymerization. Ziegler, *et al.*,[20] found that free radicals from tetraalkyldiphenylethanes reacted similarly.

In the pyrolysis of a phenylmagnesium bromide–butyl titanate reaction mixture, the phenyl radicals couple to yield biphenyl and unidentified higher-boiling condensed hydrocarbons. Benzene is also obtained probably resulting from an attack of the phenyl radicals on hydrogen donors. Heating in the range of 180–270° results in the rapid evolution of approximately a 50–50 mixture of saturated and unsaturated C_4 hydrocarbons. This is accompanied by the complete autoöxidation of the black solid titanous material to a tetravalent polymeric titanium product. The following reactions are postulated, the butyl radicals disproportionating as shown

$$(C_4H_9O)_3Ti \longrightarrow C_4H_9\cdot + [(C_4H_9O)_2TiO]_n \qquad (8)$$

$$2C_4H_9\cdot \longrightarrow C_4H_{10} + C_4H_8 \qquad (9)$$

When the phenylmagnesium bromide–butyl titanate mixture is stored at room temperature the increase in both titanous compounds and coupling products of phenyl radicals is paralleled by a marked reduction in the titanium–carbon bond content. This is as expected and is shown by the low yield of phenol upon oxidation of the stored product.

The methyltitanium compound formed in the reaction of methylmagnesium bromide and butyl titanate apparently undergoes a similar decomposition to that observed for the phenyltitanium product.

$$CH_3Ti(OC_4H_9)_3 \longrightarrow CH_3\cdot + Ti(OC_4H_9)_3 \qquad (10)$$

Methane, which is evolved from the solution probably forms by reaction of the methyl radical with the solvent.[21] As predicted by eq. 10, roughly a 1:1 correspondence is observed in the rate of formation of methane (methyl radical) and titanous compounds as is shown in Table III.

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[20] K. Ziegler, W. Deparade and H. Kuhlhorn, *Ann.*, **567**, 151 (1950).

[21] W. V. Evans, *et al.*, THIS JOURNAL, **58**, 720, 2284 (1936); **61**, 898 (1936); **62**, 534 (1940).

[CONTRIBUTION FROM RESEARCH LABORATORIES, TITANIUM DIVISION, NATIONAL LEAD COMPANY]

Organotitanium Compounds. II. Stability of the Titanium–Carbon Bond

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The stability of the titanium–carbon bond was studied in compounds of the type R_nTiX_{4-n}. Variations in R, n and X were made and the following effects were observed. 1. In general, as R increased in electronegativity the stability of the compounds increased. The order found was: butyl < methyl < acetylenyl < p-anisyl < phenyl < α-naphthyl < indenyl. 2. The stability decreased rapidly as n increased from one to four. Phenyltitanium compounds with titanium in the di- or trivalent state may be possible, however. When phenylmagnesium bromide and butyl titanate reacted in a 1:1 molar ratio, indications were obtained that both mono- and diphenyltitanium compounds were formed. The decomposition of the reaction mixtures appeared to be due to the diphenyltitanium compound since the pure monophenyl compound is relatively stable. 3. The stability increased in the following order when X was: butoxy > methoxy, chloride > fluoride. The use of diethyl ether as solvent favorably affected stability as compared to the use of benzene or petroleum ether. Addition of amines such as ethylenediamine and pyridine increased the stability of the titanium–carbon bond, but undesirable side reactions occurred.

Introduction

The previous paper[1] in this series demonstrated the existence of the covalent titanium–carbon bond in compounds formed from the phenyl Grignard reagent and orthoesters of titanic acid and described the preparation and isolation of phenyltitanium triisopropylate from phenyllithium and isopropyl titanate. Parallel to this work, a more general study has been made of the stability of the titanium–carbon bond in the class of compounds represented by the general formula R_nTiX_{4-n}. In accordance with the principles outlined previously, the stability of the titanium–carbon bond was considered to be a function of the electro-

[1] D. F. Herman and W. K. Nelson, THIS JOURNAL, **75**, 3877 (1953).