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

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

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.

Acknowledgment.—The authors wish to express their appreciation to Dr. K. Herrington for contributing to the discussion of the influence of electronegative groups on the stabilization of tetravalent titanium, to Dr. E. R. Scheffer and Miss D. Edelman for performing the carbon–hydrogen analyses, and to numerous other members of the Titanium Division of the National Lead Co. for their advice and technical assistance.

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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

BY DANIEL F. HERMAN AND WALTER K. NELSON

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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-

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

TABLE I

REACTION OF PHENYLMAGNESIUM BROMIDE AND BUTYL TITANATE AT VARYING MOLAR RATIOS

Reaction	a	b	c	d	e
Molar ratio, phenyl Grignard to butyl titanate	0.25:1.0	1:1	2:1	3:1	4:1
Quantity of Grignard	50 ml. 1.49 *N*	220 ml. 1.50 *N*	150 ml. 1.865 *N*	200 ml. 1.833 *N*	150 ml. 1.833 *N*
Butyl titanate, g.	100	112	47.6	41.5	24
Total ether vol., ml.	600	570	600	650	425
Time of addition, hr.	0.75	1.5	1.5	1.5	1.5
Temp., °C.	18–20	18–20	18–20	18–20	18–20
Color of product	Yellow to green	Green to dark amber	Dark sol.	Very dark and black solid	Black sol.[a] and considerable solid
Organometallic test	Very weak	Weak	Strong, rapid	Very strong, rapid	Very strong, rapid
Carbonation before storage					
Benzoic acid yield, %	None	None	None	None[b]	None[b,c]
Hydrolysis before storage					
Benzene yield, %	...	65	76	...	34
Oxidation before storage					
Phenol yield, %	23.1	23–25	21.5	...	...
Oxidation after storage for 24 days					
Phenol yield, %	23.1	1.5	4.9	3.6	1.8

[a] The black titanous material was separated by centrifugation and washed eight times with diethyl ether under nitrogen. The product gave a strong organometallic test and was contaminated with a considerable amount of magnesium and bromine containing material. [b] A small quantity of oily acidic material was obtained. [c] In the 4:1 reaction, a 5.3% yield of benzene, 0.2 g., b.p. 78–80°, 8.0 g. recovery of butanol and 14 g. of a semi-solid hydrocarbon residue were obtained.

negativity of the substituent groups and it was this study of the effects on stability of variation in R, *n* and X that made the eventual isolation of an organotitanium compound possible.

Experimental

Reagents and Equipment.—Butyl titanate and the Grignard reagents were prepared by the standard methods described previously.[1] Distillations were carried out in a Pennsylvania State type fractionating column 60 cm. × 1 cm. i.d., packed with $^1/_8$-inch stainless steel helices.

Methods.—The method of analysis for trivalent titanium, and the methods for oxidation, carbonation and hydrolysis of the titanium–carbon bond have been described in the previous publication.[1] All handling of solutions and products unless otherwise indicated was carried out under a nitrogen atmosphere.

Phenylmagnesium Bromide and Butyl Titanate at Varying Molar Ratios.—A series of reactions was carried out in which the molar equivalents of phenylmagnesium bromide added to the butyl titanate was increased stepwise to obtain molar ratios of 0.25:1, 1:1, 2:1, 3:1 and 4:1. The procedure was essentially that described previously[1] for the 1:1 molar ratio of reactants. Four replicate preparations at each molar ratio were made and the reaction products immediately processed as follows: one group was carbonated with "Dry Ice" and then analyzed for benzoic acid; the second series was hydrolyzed with 10% H_2SO_4 and analyzed for benzene; the third series was oxidized, hydrolyzed and analyzed for phenol; the fourth series was allowed to stand for 24 days under an atmosphere of nitrogen, then oxidized and analyzed for phenol. The quantities of material used for each reaction and the results of the various reactions performed with the products are listed in Table I.

In order to chart the rate of decomposition of the titanium–carbon bond, a fifth series of reactions was carried out and analyzed for trivalent titanium immediately after completion of the Grignard addition to the butyl titanate and then periodically during storage of the reaction products for 24 days.[2] During storage, a quantity of black solid containing reduced titanium was deposited in all reaction products except that prepared at molar ratio of 0.25:1, making it difficult to obtain accurate aliquots for analysis. Therefore, a replicate series of reactions was allowed to stand for 24 days, then hydrolyzed and analyzed for trivalent titanium. The data are recorded in Table II and the decomposition rates of the reaction products are shown in Fig. 1.

Additional data obtained for the replicate preparations of the 4:1 molar ratio of reactants are as follows. The product was stirred overnight to prevent the solid from caking, and it was then added dropwise with stirring to 400 ml. of 10% sulfuric acid under a nitrogen atmosphere while the evolved gas was collected. Analysis of the gas in an Orsat apparatus showed that 0.0044 mole of hydrogen was formed, indicating that 12.5% of the titanium titrating as trivalent titanium was actually in the divalent state. The yellow, opalescent, ether layer was separated from the aqueous, violet, titanous layer and dried over anhydrous sodium sulfate. Fractionation and refractionation gave the tabulated 34% yield (7.5 g.) of benzene (based on phenylmagnesium bromide), b.p. 78–80°, 11.5 g. of butyl alcohol and 14.8 g. of residue. From the latter was obtained a 37% yield (8.2 g.) of crude biphenyl, m.p. 56–60°, which when recrystallized from methyl alcohol and benzene had a m.p. of 67–69°. In addition to the 1.8% yield of phenol obtained upon hydrolysis of the oxidized reaction product there was obtained by two successive fractionations of the ether layer, a 4.0% yield of benzene (0.9 g.), b.p. 78–80°. From the residue was obtained 6.2 g. of crude biphenyl, m.p. 56–60°, and 6.2 g. of a hard resinous material.

Reaction of Various Grignard Reagents with Butyl Titanate at Molar Ratios of 1:1.—Methyl, butyl, phenyl, α-naphthyl and *p*-anisyl Grignard reagents were prepared by standard procedures. Acetylenylmagnesium bromide was prepared according to Salkind and Rosenfeld,[3] and the indenyl Grignard according to Ivanoff and Abdouloff.[4]

Ether solutions of the Grignard reagents were added to the butyl titanate in ether with continuous agitation and maintenance of a nitrogen atmosphere as described in the previous publication.[1] Where the Grignard reagents were insoluble solids, as in the case of the α-naphthyl and indenyl compounds, they were transferred from the flask in which they were prepared through a wide rubber hose into the reaction flask, the whole being protected from the atmosphere. In each case, the molar ratio of Grignard to butyl titanate was 1:1 and the temperature of the reaction mixture was held between 15 to 20°. The reaction products were analyzed for reduced titanium immediately after completion of the reaction and the products were then allowed to stand at

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(2) The extent of decomposition of the phenyl–titanium bond was followed, as in the previous work by dissolving aliquots of the stored product in 10% sulfuric acid and determining the titanous content by titration with ferric ammonium sulfate. Any divalent titanium compounds which may be formed in the decomposition cannot be determined in this way since they are immediately oxidized by water to give hydrogen and trivalent titanium. In the usual analysis no attempt was made to distinguish between these two forms. The general term "titanous" titanium was used therefore in referring to the analyzed values.

(3) Y. Salkind and A. Rosenfeld, *Ber.*, **57B**, 1690 (1924).

(4) D. Ivanoff and I. Abdouloff, *Compt. rend.*, **196**, 491 (1933).

TABLE II

DECOMPOSITION OF THE TITANIUM–CARBON BOND IN THE REACTION OF PHENYLMAGNESIUM BROMIDE AND BUTYL TITANATE AT VARYING MOLAR RATIOS

Reaction →	a	b[a]	c	d	e
Molar ratio, phenyl Grignard to butyl titanate	0.25:1.0	1:1	2:1	3:1	4:1
Storage time, days	% Titanous (Ti^{+3}) of total titanium content, (Ti^{+3}/Total Ti) × 100				
0	Trace	0.7	2.7	45.8	98.5
3 hr.	Trace	..	..	97.5	..
1	Trace	7.7	9.0	98.0	Black solid settled
2	Trace	13.6	15.2	98.0	
3	Trace	17.3	18.0	Black solid settled	
4	Trace	22.0	23.8		
7	Trace	29.7	30.0		
11		36.0	42.7		
16		40.2	44.3		
18		42.5	47.7		
21		43.5	47.7		
24		43.5[b]	Black solid settled		
		Black solid settled			
% total Ti as titanous compound following hydrolysis after maximum decomposition of the Ti–C bond	Trace	56.7	67.3	..	98.0

[a] An attempt was made to stabilize a 1:1 reaction mixture by the addition of an equivalent of pyridine. This caused the precipitation of a magnesium–pyridine complex, the ether solution containing practically all of the organotitanium product. Storage for one week gave negligible decomposition and oxidation resulted in a 17.8% yield of phenol. Thus a stabilizing effect is indicated. Ethylenediamine likewise prevented decomposition but at the same time by means of its active hydrogen reacted with the phenyltitanium bond to result in a 46% yield of benzene. [b] In reactions (b) and (c) the curves obtained on the analysis of aliquots appear to approach a maximum of 43.5 and 47.7% titanous content/total titanium, respectively, while considerably higher values are obtained on dissolving the entire amount of stored product in sulfuric acid. This discrepancy is due to the fact that the aliquots do not contain the insoluble titanous material which precipitated toward the end of the storage period thus causing an apparent premature sloping-off of the decomposition curve.

room temperature and analyzed periodically for trivalent titanium to establish the rate of decomposition of the titanium–carbon bond. The quantities of materials used for each reaction and other pertinent details are given in Table III. The data are shown graphically in Fig. 2.

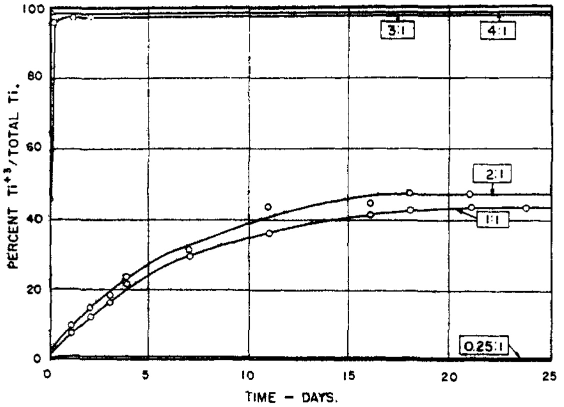

Fig. 1.—Decomposition rates of phenylmagnesium bromide and butyl titanate reaction mixtures.

Reaction of Phenylmagnesium Bromide with Titanium Tetrachloride. A. **In Benzene and Xylene.**—A half mole of phenylmagnesium bromide was prepared in ether as usual. Three-quarters of the ether was distilled under a nitrogen atmosphere. Benzene (250 ml.) was then added to the residue and the solution again distilled practically to dryness. This was repeated, and the solid Grignard reagent finally was slurried in 475 ml. of benzene. The slurry was then added to 95 g. (0.5 mole) of titanium tetrachloride in 300 ml. of benzene at 16–20° within 1.25 hours. As the reaction proceeded the mixture darkened and thickened, the product giving a faint organometallic color test. Analysis of an aliquot showed that 45.6% of the titanium was in the titanous state. The product was centrifuged, and it was found that all of the titanous product was present in the insoluble, black residue. The solids were washed three times by centrifugation in a nitrogen atmosphere, and the combined benzene solutions were distilled. Six grams of a deep-red liquid forecut containing titanium tetrachloride was obtained, followed by 23 g. (59.8% yield) of biphenyl, b.p. 114–118° (8 mm.), m.p. 68°. The red color appears to be due to a titanium tetrachloride–biphenyl complex. Biphenyl is known to form complexes with antimony halides.[5]

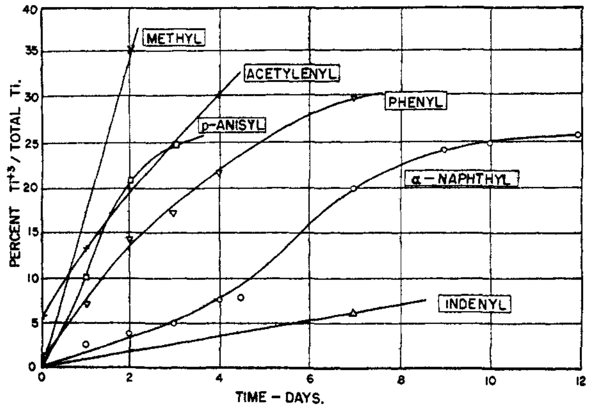

Fig. 2.—Decomposition rates of organotitanium compounds, $RTi(OBu)_3$.

A similar reaction was carried out in xylene at −50°, and an aliquot at the end showed 13.6% of the titanium in the titanous state.

B. **In Ether.**—Eighty-one grams of titanium tetrachloride (0.426 mole) was added to 400 ml. of ether with cooling to form a slurry of the insoluble ether complex. The product was cooled to −50° and 0.426 mole of phenylmagnesium bromide in 300 ml. of ether was added to the slurry in 1.25 hours. The solid turned orange and finally blood-red. A positive organometallic color test was observed, and 2.8% of the titanium was in the titanous state. The mixture was stored overnight at −10° and the quantity of titanous product was found to have increased to 4.2%. On being warmed to room temperature, the red solid melted to a reddish-black dense liquid phase which was insoluble in benzene and petroleum ether and dissolved in butanol with evolution of heat to give a clear green solution.

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(5) B. N. Menschutkin, *J. Russ. Phys. Chem. Soc.*, **43**, 1806 (1911), *C. A.*, **6**, 1281 (1912).

TABLE III

REACTIONS OF VARIOUS GRIGNARD REAGENTS WITH BUTYL TITANATE IN 1:1 MOLAR RATIO

	Methyl[a]	Butyl[b]	Acetylenyl[c]	α-Naphthyl[d]	Indenyl[d]	*p*-Anisyl[e]
Quantity of Grignard, mole	0.39	0.33	0.426	0.33	0.40[f]	0.25
Butyl titanate, g.	136	114	144	114	140	85
Total diethyl ether vol., ml.	500	450	750	450	300	500
Time of addition, hr.	1.5	1.5	1.5	1	1	1.5
Temp., °C.	15	15	18	15	18	15
Color of reaction product	Green→ Black	Yellow→ Green→ Black	Green→ Black	Amber	Amber	Green→ Black
% Ti^{+3} of total Ti at end of reaction	0.3	59.5	5.5	Trace	None	
Organometallic test	Strong in 4 hr.		Very strong and rapid	Positive within 6 hr.	Positive within 4 days	Very strong and rapid

[a] This reaction is completely described in the previous publication.[1] [b] A gas, presumably a C_4 hydrocarbon, was evolved during the reaction. Within 30 minutes of the completion of the addition the reaction product set to a dark green paste. [c] No gas was evolved but a sample of the product hydrolyzed at the end of the addition generated a large quantity of acetylene. No gas was evolved during storage. After four days, considerable black solid had settled making further analysis difficult. The product still gave an organometallic color test, but hydrolysis of an aliquot gave very little gas. [d] The crystalline Grignard reagents dissolved immediately on addition to the butyl titanate solutions indicating rapid reactions. [e] *p*-Anisylmagnesium bromide when prepared in ether settled as a lower insoluble layer which was found to disappear immediately on being added to the butyl titanate–ether solution. [f] In 300 ml. of xylene.

Reaction of Titanium Tetrafluoride and Phenyllithium.—Two-tenths mole (24.8 g.) of titanium tetrafluoride was added to 100 ml. of ether. Heat was evolved during the addition and the tetrafluoride remained insoluble. To this mixture was added 200 ml. of 1.05 *N* phenyllithium in ether. The solid gradually became dark and pasty, and analysis of an aliquot of the product showed 75% of the titanium to be in the titanous state. The entire product was hydrolyzed with 300 ml. of 10% sulfuric acid. By ether extraction a 78% yield (11.1 g.) of biphenyl, m.p. 67–68° was obtained.

Reaction of Methyl Titanate with Phenyllithium.—A solution of 0.55 mole of phenyllithium in 550 ml. of ether was added in 1.5 hours to a slurry of 94 g. (0.55 mole) of methyl titanate, m.p. 185–189°, in 400 ml. of ether. The solid titanate changed character, darkening and diminishing in quantity during the reaction. Storage overnight at room temperature resulted in 14.0% of the titanium being reduced to the titanous state. A large amount of insoluble titanous material precipitated on further storage making satisfactory sampling impossible. Hydrolysis of the entire product and stripping of the ether layer yielded a residue which on recrystallization twice from methyl alcohol and benzene gave an as yet unidentified hydrocarbon, m.p. 196–197°. That it was not *p*-diphenylbenzene was shown by the mixed m.p. 170–190°.

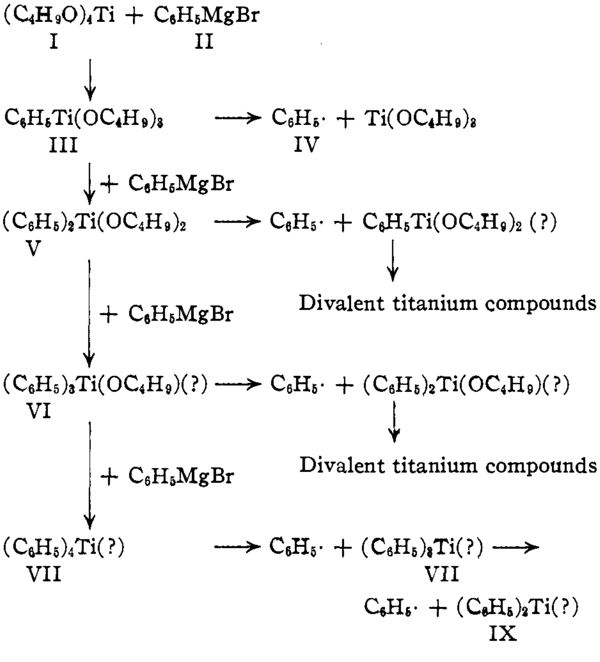
Discussion

Effect of the Value of *n* on the Stability of R_nTiX_{4-n}.—In the previous publication, it was shown that the reaction of phenylmagnesium bromide with butyl titanate in a 1:1 molar ratio results in phenyltitanium products of very much less stability than the corresponding reaction products of phenyllithium with butyl titanate. The stability of the latter products is attributed to the initial formation of a stable lithium–monophenyltitanium complex which apparently has no magnesium counterpart.

The instability of the products derived from the Grignard reaction may be attributed to consecutive competitive reactions where unstable or more highly phenylated titanium derivatives are formed. The complete reaction scheme involving all postulated products is shown in Table IV.

TABLE IV

POSTULATED PRODUCTS OF THE REACTION OF BUTYL TITANATE AND PHENYLMAGNESIUM BROMIDE



Since it has been impossible thus far to separate the constituents of the Grignard–titanate reaction mixtures, it is difficult to demonstrate clearly that the postulated di- and polyphenyltitanium species exist or to assign stabilities to them. Some conclusions can be drawn, however, from the data in Fig. 1 and Table II for the decomposition of the products formed when phenylmagnesium bromide and butyl titanate are reacting in various molar ratios ranging from 0.25:1.0 to 4:1.

In reaction (a) using one quarter the theoretical amount of Grignard reagent required to replace one of the butoxy groups, the Grignard reagent reacts rapidly and completely (as shown by the lack of formation of benzoic acid upon carbonation) to form a phenyl–titanium bond which is stable at room temperature. Oxidation yields 23.1% phenol, based on the phenylmagnesium bromide used. Such a value has been shown previously[1] to indicate a good yield of a phenyl–titanium bond. It is reasonable to assume that the principal product is the relatively stable monophenyltitanium butylate, III.

In reaction (b) using a 1:1 molar ratio of reactants, the 65% yield of benzene obtained on hydrolysis before decomposition is indicative of at least a 65% yield of phenyl–titanium bonds based on Grignard reagent used. On storage roughly 90% of the phenyl–titanium bonds decompose as evidenced by the maximum final value of 56.2% Ti^{+3}/total Ti shown in Table II. Considering the calculations of Fuoss[6] for the general case for consecutive competitive reactions, the above results may be explained in terms of the substitution reaction going beyond the monophenyl stage, III, to form unstable di- or polyphenyltitanium compounds, V, VI, etc. The extensive decomposition observed on storage does not necessarily indicate a high yield of these compounds since in the course of their decomposition they could induce the decomposition of the hitherto stable monophenyl titanium compound, III.

In reaction (c) using a 2:1 ratio of reactants, the low value of titanium in the titanous state (2.7%) at zero storage time, the lack of formation of benzoic acid on carbonation, and the relatively good yield of phenol based on the Grignard reagent used again indicates that the Grignard reagent reacts completely to form phenyl–titanium bonds. Comparing (b) and (c), the substantially equivalent yields of phenol based on Grignard reagent implies that actually twice as many phenyl–titanium bonds per titanium are formed in (c) as in (b). In (c), the 76% yield of benzene on hydrolysis before decomposition indicates the yield of phenyl–titanium bonds based on Grignard reagent to be roughly in that order. The number of phenyl groups bonded to titanium in (c) is, therefore, about 1.5 per titanium, while it is roughly 0.65 per titanium in (b). The inevitable conclusion is, therefore, that diphenyltitanium butylate, V, and possibly more highly substituted derivatives are formed in (c).

In (d) and (e) in which the molar ratio of the reactants is increased to 3:1 and 4:1, complete reaction of the Grignard reagent is also observed as indicated by the lack of formation of benzoic acid on carbonation. Ordinarily, one might expect to form triphenyltitanium butylate, VI, and tetraphenyltitanium, VII, in (d) and (e), respectively. However, the very rapid formation of compounds of titanium in its lower valence states indicates that these tetravalent compounds exist only as intermediates, if at all. While the decomposition or reduction appears to approach a maximum where all of the titanium is reduced to the trivalent state, this is not necessarily so since any divalent titanium formed may be spontaneously oxidized by water during hydrolysis and be titrated as trivalent titanium.

$$2Ti^{+2} + 2H_2O \longrightarrow 2Ti^{+3} + 2OH^- + H_2 \quad (1)$$

Divalent titanium compounds are formed, in fact, as shown by the evolution of hydrogen upon hydrolysis of the products of reaction (e). The quantity of hydrogen evolved indicates that 12.5% of the titanium is reduced to the divalent state. Hydrogen had been observed previously in a similar reaction by Gilman and Jones.[7] Since no more than one or two moles of Grignard reagent can conceivably be consumed in reducing the titanium, and all four moles react originally, the existence of compounds such as triphenyltitanium, VII, diphenyltitanium, IX, are postulated. Diphenyltitanium, in fact, may be expected to be a thermally stable compound, according to the argument presented in the preceding publication.[1] Further evidence for VIII or IX is the 34% yield of benzene, based on phenylmagnesium bromide, produced by hydrolysis of the black reaction mass. This may arise as

$$2(C_6H_5)_2Ti + 6H_2O \longrightarrow 4C_6H_6 + 2Ti^{+3} + 6OH^- + H_2 \quad (2)$$

$$(C_6H_5)_3Ti + 3H_2O \longrightarrow 3C_6H_6 + Ti^{+3} + 3OH^- \quad (3)$$

A portion of the benzene may form, however, from the attack of free phenyl radicals upon a hydrogen donor. A 37% yield of biphenyl is formed by the coupling of the phenyl radicals produced during the decomposition.

Effect of Variations in the R Group on the Stability of R_nTiX_{4-n}.—The reduction of titanium to the titanous state is considered to parallel the decomposition of the R–Ti bond. On this basis, the data presented in Fig. 2 indicate that the R–Ti compounds formed from 1:1 molar ratios of Grignard reagent to butyl titanate[8] increase in stability in the following order: butyl < methyl < acetylenyl < *p*-anisyl < phenyl < *α*-naphthyl < indenyl. The butyl derivative is not shown in the graph since 60% of the titanium was reduced to the titanous state at zero time. In the case of the butyl-, methyl-, phenyl- and *α*-naphthyltitanium compounds, the increasing stability parallels the increasing electronegativity of the R groups as given by Kharasch.[9] The order of increasing stability is in general agreement with the published results on organogold[10] and organosilver[11] compounds.

The acetylenyl group is not listed in Kharasch's table but it may be expected to be more electronegative than most alkyl groups, considering the activity of the carbon–hydrogen bond. It is in agreement with the theory, therefore, that the acetylenyltitanium compound is more stable than the methyl or butyl derivatives. The indenyl group which forms the most stable organotitanium compound is likewise not listed in the table of electronegativities. However, it too may be considered to be highly electronegative in view of the activity of the number one carbon–hydrogen bond in indene. The *p*-anisyl compound is appar-

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(6) R. M. Fuoss, This Journal, **65**, 2406 (1943).

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

(8) Since both mono- and polyalkylated compounds may be formed in undetermined proportions in such reactions, the decomposition rates obtained are due to this mixture of products and cannot be ascribed to the simple R–Ti bonds alone. In a strict sense, therefore, a comparison of the curves of Fig. 2 gives only the relative stability of the mixture of alkyl- or aryltitanium compounds formed from equimolar quantities of the reactants.

(9) M. Kharasch, This Journal, **54**, 674 (1932); *J. Chem. Ed.*, **11**, 82 (1934).

(10) M. Kharasch and H. S. Isbell, This Journal, **52**, 2919 (1930).

(11) H. Gilman and J. M. Straley, *Rec. trav. chim.*, **55**, 821 (1936).

ently out of line, being less stable than the phenyltitanium derivative although the *p*-anisyl group is above both the phenyl and naphthyl groups in Kharasch's electronegativity series.

Effect of Variations in the X Group on the Stability of R_nTiX_{4-n}.—Having determined the effect on stability of variations in R and *n*, the effect of variations in X was next examined with R being limited to the phenyl group. For simplicity the molar ratio of phenylmagnesium bromide to the titanium compound was maintained at 1:1. The products formed from isopropyl, *n*-propyl and isobutyl titanates show no significant differences in stability when compared with that obtained from butyl titanate, and they have already been described.[1]

The product prepared from phenyllithium and methyl titanate on storage for 24 hours at room temperature is found to give 14% decomposition to titanous compounds as compared to zero decomposition for the product from butyl titanate and phenyllithium.[1]

The reaction of phenylmagnesium bromide with titanium tetrachloride in ether is complicated by the formation of insoluble ether complexes, thus making it difficult to compare the influence of the chloride with the influence of the other X groups on the stability of the phenyl–titanium bond. Storage of the reaction product at −10° for 24 hours results in 4.2% decomposition. Using benzene as the solvent to avoid the difficulties encountered with ether, a 45.6% decomposition to the titanous state is observed at room temperature at the end of the reaction. A similar reaction in xylene results in a 14% decomposition at the end of the reaction even at −50°. The solvent is thus seen to have a considerable effect on the stability of the phenyl–titanium bond.

In an attempt to prepare phenyltitanium trifluoride by the reaction of phenyllithium and titanium tetrafluoride, very extensive decomposition occurs during the reaction itself as evidenced by a 75% conversion of titanium to the titanous state and a 78% yield of biphenyl. From the above information the following order of stabilizing effects of the X group on R_nTiX_{4-n} is suggested: butoxy > methoxy, chloride > fluoride. In a general way the stability is decreased with increasing electronegativity of the X group. However, additional information is required to fully substantiate this observation.

The following conclusions may now be drawn regarding the effects of the three factors R, *n* and X on the stability of the organotitanium compounds: 1. A sufficiently high electronegative field is required surrounding the titanium to stabilize it in the tetravalent state. The R groups in themselves are not sufficiently electronegative to supply this field and accordingly, a compound such as R_4Ti is unstable.

2. The stability of the compounds of the class R_nTiX_{4-n} is greatest when $n = 1$ and decreases markedly with $n = 2$ or more.

3. Increasing electronegativity of the R group is paralleled by the increasing stability of the organometallic bond. Thus aryl compounds are more stable than alkyl compounds.

4. A delicate balance of the electronegativities of the R and X group appears to be necessary in order to stabilize $RTiX_3$. It is suggested that although the electronegativity of an OR group such as $-OC_4H_9$ is necessary for the stabilization of the R–Ti bond, a second mechanism comes into play tending to weaken the bond when groups of greater electronegativity such as methoxy, chloride and fluoride are used. The strong electron attraction of three fluorine atoms, for example, should cause a decrease of the screening effect of the three binding electron pairs. As a result, the electron pair forming the R–Ti bond should move closer to the titanium, the net effect being to weaken the organotitanium bond.

5. While more than one R group causes marked instability in a tetravalent titanium compound, there are indications that compounds of the type R_2Ti or R_3Ti are relatively stable.

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