oxygen bond. The strength of this interaction is a function of the aromatic substituent and of temperature, and ranges from a small amount of overlap of the orbitals to complete transference of the electron.

LABORATORY FOR INSULATION RESEARCH
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS S. C. ABRAHAMS

RECEIVED APRIL 14, 1952

ISOLATION OF A COMPOUND CONTAINING THE COVALENT TITANIUM-CARBON BOND

Sir:

A study of the organic compounds of titanium has been carried out resulting in isolation of a compound containing the covalent titanium–carbon bond. Since titanium is a transition element with its valence electrons divided between the third and fourth principal quantum groups, it cannot be expected to bear more than a superficial resemblance to other Group IV elements such as silicon, germanium and tin which readily form stable covalent bonds with carbon. The consequent lack of stability and difficulty of formation of the titanium–carbon bond is primarily responsible for the repeated failures reported in the literature[1] since the first attempt by Cahours in 1861.[2]

Theoretical considerations which cannot be discussed in this short space led us to the assumption that relatively stable members of the class of compounds of the type $R_nTi(CR')_{4-n}$ might be prepared if n were 1 or, at most, 2 and R were selected from the more electronegative organic groups. A series of exploratory reactions between butyl titanate and various organomagnesium and organolithium reagents in 1:1 to 4:1 molar ratios substantiated this assumption and showed that the most stable carbon to metal bonds were formed with aromatic R groups.

The reaction between phenylmagnesium bromide and butyl titanate in a 1:1 molar ratio yielded a phenyltitanium derivative which was in too unstable and reactive a state to be isolated from the reaction mixture. When phenyllithium was used in place of the magnesium reagent, significant differences were observed leading toward the eventual isolation of phenyltitanium triisopropylate in the following manner: The reaction of phenyllithium with isopropyl titanate in equimolar proportions led to the formation of a relatively insoluble crystalline, stable, lithium complex of phenyltitanium triisopropylate. Elementary analysis and chemical properties indicated the following formula: $C_6H_5Ti(OC_3H_7)_3{\cdot}LiOC_3H_7{\cdot}LiBr{\cdot}(C_2H_5)_2O$.

The lithium isopropylate portion of the molecule reacted with titanium tetrachloride, as follows, to precipitate the lithium as the chloride, thus freeing the organotitanium compound from the complex

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

The lithium salts were filtered, and crystals of phenyltitanium triisopropylate were isolated, m.p. 88–90°. No decomposition occurred on storage under a nitrogen atmosphere at 10°. However, the product decomposed rapidly when heated above its melting point. Analytical results are listed in Table I.

TABLE I

ANALYSIS OF ORGANOTITANIUM DERIVATIVES

	$C_6H_5Ti(OC_3H_7)_3$		Ti·Li complex[a]	
Constituent	Found (average)	Calculated	Found (average)	Calculated
C, %	59.1	59.62	50.1	49.95
H, %	9.2	8.63	8.9	8.13
Ti as TiO_2, %	24.6	24.46	15.1	15.12
Halogen, %	0.23 (Cl)		15.2 (Br)	15.11 (Br)
Li, %	Trace		2.5	2.62

[a] $C_6H_5Ti(OC_3H_7)_3{\cdot}LiOC_3H_7{\cdot}LiBr{\cdot}(C_2H_5)_2O$.

The reactions exhibited by phenyltitanium triisopropylate serve as a chemical proof of the presence of a titanium–carbon bond. An ether solution of the product gave a slowly developing organometallic color test with Michler ketone; it oxidized rapidly with oxygen to give a phenol derivative; it reacted with water to give benzene, titanium hydrate and butanol; it reacted slowly with diphenyl ketone to give triphenylcarbinol, and it failed to yield benzoic acid on treatment with "Dry Ice." These reactions are typical of an organometallic bond of low activity. The ether solutions of the unisolated products obtained previously from phenylmagnesium bromide and the alkyl titanates exhibited similar reactions. The titanium–carbon bond present in these compounds was found to decompose spontaneously as follows

$$C_6H_5{:}Ti\!< \longrightarrow C_6H_5{\cdot} + Ti^{+3}$$

Free radical formation was shown by the ability of the material to catalyze the polymerization of styrene.

This work will be fully described in the JOURNAL at a later date.

NATIONAL LEAD CO., TITANIUM DIV.
RESEARCH LABORATORIES DANIEL F. HERMAN
SAYREVILLE, N. J. WALTER K. NELSON

RECEIVED APRIL 25, 1952

---

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

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

CONFIGURATION AT C_{12} OF 12-HYDROXYLATED SAPOGENINS. REARRANGEMENT OF THE STEROID C/D RINGS

Sir:

Reduction of hecogenin with lithium aluminum hydride produced the C_{12}-epimeric diols: I, m.p. 216–220°, $[\alpha]^{24}\mathrm{D}$ −32.4° (1.08, acetone). Found: C, 75.40; H, 10.22; *diacetate* (*Ia*), m.p. 156–159°, $[\alpha]^{23}\mathrm{D}$ −15° (1.0, acetone). Found: C, 72.25; H, 9.34, and II, m.p. 218.5–220.5°, $[\alpha]^{24}\mathrm{D}$ −63.8° (1.05, acetone). Found: C, 74.79; H, 10.00; *diacetate* (*IIa*), m.p. 202–206.5°, $[\alpha]^{23}\mathrm{D}$ −65.1° (1.0, acetone). Found: C, 71.88; H, 8.99. Molecular rotations of I, II and their respective diacetates compared with the C_{12}-epimeric cholanates[1] are in excellent agreement with the assigned con-

---

[1] (a) B. Koechlin and T. Reichstein, *Helv. Chim. Acta*, **25**, 918 (1942); (b) E. Seebeck and T. Reichstein, *ibid.*, **26**, 536 (1943); T. F. Gallagher and W. P. Long, *J. Biol. Chem.*, **162**, 521 (1946); (d) D. H. R. Barton and W. Klyne, *Chem. & Ind.*, 755 (1948).