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.

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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

Constituent	$C_6H_5Ti(OC_3H_7)_3$ Found (average)	Calculated	Ti·Li complex[a] 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.

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RECEIVED APRIL 25, 1952

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[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°, $[\alpha]^{24}D$ $-32.4°$ (1.08, acetone). Found: C, 75.40; H, 10.22; *diacetate* (*Ia*), m.p. 156–159°, $[\alpha]^{23}D$ $-15°$ (1.0, acetone). Found: C, 72.25; H, 9.34, and II, m.p. 218.5–220.5°, $[\alpha]^{24}D$ $-63.8°$ (1.05, acetone). Found: C, 74.79; H, 10.00; *diacetate* (*IIa*), m.p. 202–206.5°, $[\alpha]^{23}D$ $-65.1°$ (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-

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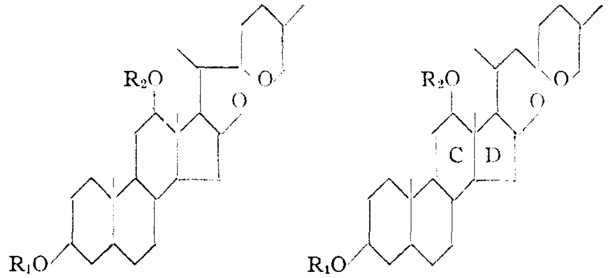
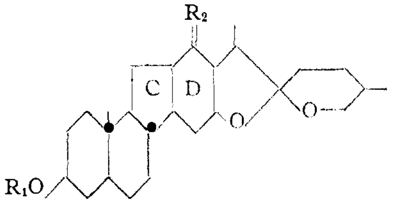
[1] (a) B. Koechlin and T. Reichstein, *Helv. Chim. Acta*, **25**, 918 (1942); (b) E. Seebeck and T. Reichstein, *ibid.*, **26**, 536 (1943); T. F. Gallagher and W. P. Long, *J. Biol. Chem.*, **162**, 521 (1946); (d) D. H. R. Barton and W. Klyne, *Chem. & Ind.*, 755 (1948).

figurations at C_{12} for I and II. Confirmation of this configurational assignment was adduced by the markedly more rapid consumption of two equivalents of alkali by IIa in contrast to Ia. This is again in accord with the observed saponification rates for the corresponding C_{12}-epimeric acetoxy cholanates,[1a] and in conformity with the greater ease of hydrolysis associated with equatorial ester groupings.[2] Rockogenin[3] isolated from natural sources was found to be identical with II and should, therefore, be assigned the 12(β)-OH configuration.



(I) $R_1 = R_2 = H$ (II)
(Ia) $R_1 = R_2 = CH_3CO^-$ (IIa)
(Ib) $R_1 = CH_3O_2C(CH_2)_2CO^-$ (IIb)
$R_2 = CH_3SO_2^-$



(III) $R_1 = CH_3CO$; $R_2 = CH_2$
(IV) $R_1 = H$; $R_2 = O$

I and II were converted by successive succinolylation and treatment with methanesulfonyl chloride in pyridine to: Ib m.p. 185–188° (dec.), $[\alpha]^{25}_D$ −13.4° (chf.). Found: C, 63.96; H, 8.50; S, 5.28, and IIb, m.p. 127–132° (dec.), $[\alpha]^{24}_D$ −48.4° (chf.). Found: C, 63.85; H, 8.45; S, 5.18, respectively. Solvolysis of IIb in refluxing methanol or *t*-butanol with or without added alkali alkoxide, produced an olefin isolated as its acetate (III) m.p. 221–225°, $[\alpha]^{23}_D$ −80.6° (chf.). Found: C, 76.21; H, 9.92, with bands in the infrared at 6.04 and 11.24 μ. Under the same conditions of solvolysis Ib was recovered essentially unchanged.

Hydroxylation of III with osmium tetroxide followed by saponification yielded a triol m.p., *ca.* 200°, converted quantitatively to a diacetate m.p. 212–216°. Found: C, 70.30; H, 9.37, having an OH band in the infrared at 2.8 μ. Saponification of this diacetate quantitatively regenerated the triol, and the latter on cleavage with periodic acid produced 60–65% of formaldehyde, determined by chromotropic acid titration[4] and isolation of its dimedone derivative m.p. and m.m.p. with an authentic sample 191°, together with a quantitative yield of a *nor*-ketone (IV) m.p. 180–183°; $[\alpha]^{24}_D$ −93.8° (chf.). Found: C, 75.01; H, 9.66, having a single carbonyl band in the infrared at 5.84 μ and only end absorption in the ultraviolet.

The formation of III from rockogenin by C/D ring contraction and expansion represents a rearrangement path wherein the stereoelectronic requirements are fulfilled only in the case of the natural C_{12}-β-configuration II.[5] The significance of this geometrical factor is reflected in the extraordinary ease with which this rearrangement occurs.[6] This C/D ring structural type has been advanced recently in the formulation of jervine[7] and veratramine.[8] The present work constitutes the first chemical realization of this abnormal steroid system and affords thereby not only support for the C/D ring structures assigned to these alkaloids but also suggests a highly probable mode in their biogenesis.

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[2] D. H. R. Barton, *Experientia*, **6**, 316 (1950).

[3] Kindly supplied by Dr. L. A. Sweet of Parke, Davis & Co., Detroit, Michigan.

[4] C. E. Bricker and W. A. Vail, *Ind. Eng. Chem., Anal. Ed.*, **22**, 720 (1950).

[5] Compare the rearrangement-dehydration of β- and *epi*-β-amyrin; *cf.* ref. 2. Also O. Jeger "Fortschritte der chemie organischer Naturstoffe," 1950, Vol. VII, p. 65.

[6] Compare, for example, S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, THIS JOURNAL, **74**, 1127 (1952).

[7] J. Fried, O. Wintersteiner, M. Moore, B. M. Iselin and A. Klingsberg, *ibid.*, **73**, 2970 (1951).

[8] Ch. Tamm and O. Wintersteiner, Abstr. of the Meeting-in-Miniature of the Am. Chem. Soc., Newark, N. J., Jan. 28, 1952.

MERCK & CO., INC. RALPH HIRSCHMANN
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RECEIVED MARCH 31, 1952

THE AMMONIA INDUCED DECOMPOSITION OF NITRIC OXIDE

Sir:

This is to report a serious flaw in the experimental technique of a recent investigation of the same title,[1] which invalidates its major conclusions. In that work, the extent of the decomposition of NO was determined by measuring the pressure of nitrogen in a previously evacuated bulb, partly immersed in liquid nitrogen and connected to the reaction vessel by capillary tubing. This procedure leads to entirely erroneous nitrogen pressures since nitrogen is enriched far above its correct partial pressure in the bulb when it is opened to the reaction vessel. Mass flow will bring the gas mixture instantaneously from the large reaction vessel into the bulb where all condensable gases freeze out and leave a nitrogen pressure much lower than that of the gas mixture remaining in the quartz vessel. The process therefore continues until the pressure of nitrogen in the bulb is equal to that of the gas mixture in the reaction vessel, still of its original composition, and therefore containing much nitric oxide. From then on, it is diffusion of NO into the bulb and diffusion of N_2 back into the reaction vessel which would take the system to its final state, but diffusion through capillary tubing is an exceedingly slow process.

We tested the correctness of this objection in various ways: A. By preparing known mixtures of NO and N_2, following the procedure used in the reported note and obtaining measured "N_2 pressures" which were always much too high. B. By repeating some actual NO-NH_3 experiments

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[1] C. P. Fenimore and J. R. Kelso, THIS JOURNAL, **74**, 1593 (1952).