charcoal. There remained after distillation of the solvent 39.5 g. (57%) of red oil which was purified by fractional distillation using a glass helices packed column. The pale yellow product distilled at 141–143° at 50 mm. pressure. A second preparation was purified by sublimation at 16–18 mm. pressure, using a Dry Ice condenser and an oil-bath temperature of 80–85°. Further purification by recrystallization from petroleum ether at −20° gave white needles which melted at 23–24° to form a pale yellow oil.

*Anal.* Calcd. for $C_4H_2ClNO_2S$: S, 19.60. Found: S, 19.43.

5-Nitro-2-chlorothiophene is very soluble in benzene, methanol, ethanol and ether, slightly soluble in petroleum ether, and is insoluble in water. It penetrates the skin rapidly, producing a painful burning sensation. It could not be converted to 5-nitro-2-cyanothiophene by the method which Dann[2] used with 5-nitro-2-iodothiophene.

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(2) O. Dann, *Ber.*, **76B**, 419 (1943).

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## Some Coumarin Derivatives

Some years ago a number of coumarin derivatives were made for testing against schistosomes.[1] Samples have also been furnished for a study of fluorescence.[2] Four of these compounds do not appear to have been described previously.

**7-*n*-Propoxycoumarin-3-carboxylic acid.**—Umbelliferone-3-ethylcarboxylate was alkylated with *n*-propyl iodide and potassium hydroxide (1 mol each) in methanol. Most of the solvent was evaporated and the residue was saponified with aqueous alkali. On acidification the product separated as a light-colored powder. It was crystallized from aqueous acetone and from glacial acetic acid, forming pale yellowish prisms; m.p. 199–200°.

*Anal.* Calcd. for $C_{13}H_{12}O_5$: C, 62.9; H, 4.9. Found: C, 62.8; H, 4.8.

**7-*n*-Propoxycoumarin.**—The above acid was decarboxylated by heating at 240° with copper powder. Crystallized from ether–hexane mixtures it formed light yellow needles melting at 62.5–63°.

*Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.6; H, 5.9. Found: C, 70.8; H, 5.9.

**6,7-Dimethoxycoumarin-3-ethylcarboxylate.**—Five grams of ethyl malonate and 5.5 g. of 2-hydroxy-4,5-dimethoxybenzaldehyde[3] were dissolved in 30 cc. of absolute ethanol. A few drops of glacial acetic acid and 0.5 cc. of piperidine were added and the solution was refluxed two hours: solid began to separate after ten minutes. The product, crystallized from ethanol, formed pale yellow needles and weighed 8 g. It melted at 197–197.5°.

*Anal.* Calcd. for $C_{14}H_{14}O_6$: C, 60.4; H, 5.1. Found: C, 60.3; H, 4.9.

The condensation can also be accomplished without the use of solvent but the product is less easily handled.

**6,7-Dimethoxycoumarin-3-carboxylic Acid.**—The ethyl ester (14.5 g.) was saponified with alcoholic potassium hydroxide in an inert atmosphere. On dilution with water and acidification the acid precipitated. After recrystallization from 500 cc. of glacial acid there was obtained 10 g. of pale yellow needles melting at 252–252.5° (dec.). (If heated too slowly the compound melts lower.)

*Anal.* Calcd. for $C_{12}H_{10}O_6$: C, 57.6; H, 4.0. Found: C, 57.6; H, 4.3.

Melting points below 220° are corrected. The analyses were performed by Mr. Samuel W. Blackman.

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(1) Testing was by Dr. Maxwell Schubert of the New York University College of Medicine.

(2) R. H. Goodwin and F. Kavanagh, *Arch. Bioch.*, **27**, 152 (1950).

(3) F. S. H. Head and A. Robertson, *J. Chem. Soc.*, 2434 (1930).

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# COMMUNICATIONS TO THE EDITOR

## MECHANISM OF MOLECULAR COMPLEX FORMATION BETWEEN AROMATIC AMINES AND NITROHYDROCARBONS

*Sir:*

In a recent paper by Landauer and McConnell,[1] the formation and color of aniline–polynitrobenzene complexes is ascribed to an acid-base interaction, in the Lewis sense. Mulliken[2] has given a general quantum-mechanical treatment for the interaction between the $\pi$-electrons of a benzene ring and the acceptor orbitals of another molecule. Nakamoto[3] has suggested that aromatic molecular complexes are formed by the interaction of the $\pi$ electrons of neighboring benzene rings.

A direct observation has been made[4] of a relatively strong bond between an oxygen atom of a nitro group and a carbon atom of an adjacent benzene ring in crystalline *p*-nitroaniline, which forms a self complex. This bond, of length 2.66 Å., is normal to the plane of the benzene ring to within 1°, and hence may well be due to a $\pi$-electron interaction of the Mulliken type. By measurement of the anomalous thermal expansion in *p*-nitroaniline, McKeown, Ubbelohde and Woodward[5] have shown by extrapolation that at absolute zero this bond might contract to 2.40 Å., corresponding to ionic contact between the carbon and the oxygen atom. The absence of self-complex formation in crystalline *p*-dinitrobenzene[6] shows that the $\pi$ electrons require the activating influence of a suitable substituent in the aromatic ring before acting as donor.

These data lend support to the following mechanism for complex formation between *o*- and *p*-directing substituted aromatic hydrocarbons and nitrohydrocarbons. The attraction is of a Lewis acid–base nature, between the donated $\pi$ electrons of the activated benzene ring and the accepting orbitals of a nitro group, thus forming a carbon–

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(1) J. Landauer and H. McConnell, THIS JOURNAL, **74**, 1221 (1952).

(2) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(3) K. Nakamoto, *ibid.*, **74**, 1739 (1952).

(4) S. C. Abrahams and J. M. Robertson, *Acta Cryst.*, **1**, 252 (1948).

(5) P. J. A. McKeown, A. R. Ubbelohde and I. Woodward, *ibid.*, **4**, 391 (1951).

(6) S. C. Abrahams, *ibid.*, **3**, 194 (1950).

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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## 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
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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).

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## 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).