

*Anal.* Calcd. for  $C_{16}H_{34}$ : C, 84.86; H, 15.14. Found: C, 84.33; H, 14.56.

When 155 g. (0.62 mole) of 5-ethyl-5-bromodecane was caused to react with *n*-dodecylmagnesium bromide, prepared from 200 g. (0.8 mole) of *n*-dodecyl bromide and 19.2 g. (0.8 gram atom) of magnesium, the following fractions were obtained on distillation: 200 ml., b.p. 95–125° (15 mm.); 10 ml., b.p. 125–235° (15 mm.); and 30 ml., b.p. 235–241° (15 mm.). The latter solidified on cooling and after crystallization from acetone melted at 49–50°. The literature<sup>10</sup> reports the melting point of tetracosane to be 51°.

Similar results were obtained in an attempt to condense *n*-dodecylmagnesium bromide with crude 7-butyl-6-bromotetradecane. The major product isolated distilled at 132–133° (1 mm.),  $n_D^{20}$  1.4460, and presumably consisted of octadecenes. In addition, the residue from the distillation solidified and yielded a compound which melted at 49–50° after crystallization from acetone.

Treatment of a solution of *n*-propyllithium, prepared from 0.7 g. (0.1 gram atom) of lithium, 6.2 g. (0.05 mole) of *n*-propyl bromide and 30 ml. of anhydrous ether, with 13 g. (0.05 mole) of 5-ethyl-5-bromodecane gave only a mixture of low-boiling compounds.

(10) J. H. Hildebrand and A. Wachter, *THIS JOURNAL*, **51**, 2487 (1929).

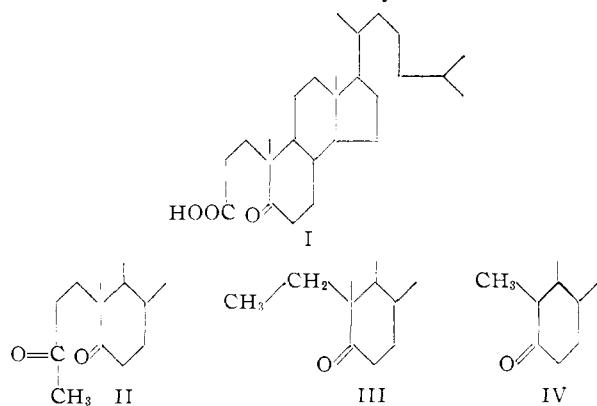
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### Pyrolysis of the Windaus Acid

BY RICHARD B. TURNER

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Some time ago, in connection with experiments directed toward the preparation of labeled cholesterol,<sup>1</sup> the barium salt of the Windaus acid (I) was subjected to pyrolysis in the presence of barium acetate in the hope that the diketone II might be obtained. There was formed instead, in 45% yield, a neutral monoketone, m.p. 55–55.5°,  $[\alpha]_D +9.5^\circ$  (chloroform), for which structure III was proposed. The same product resulted from pyrolysis of the barium salt of I in the absence of added barium acetate. Analytical values for



carbon and hydrogen (found: C, 83.40; H, 12.17) were satisfactory for the formula  $C_{25}H_{44}O$  (Calcd.: C, 83.26; H, 12.30), and the substance furnished an oxime, m.p. 142.5–143° (*Anal.* Calcd. for  $C_{25}H_{45}ON$ : C, 79.94; H, 12.07; N, 3.73. Found: C, 79.66; H, 11.82; N, 4.07.) Apart from routine examination of the infrared spectrum, the substance was not further investigated.

(1) R. B. Turner, *THIS JOURNAL*, **72**, 579 (1950).

More recent consideration of this product and of its mode of formation suggested that it might alternatively be formulated as IV, previously obtained as an oil by Inhoffen and Huang-Minlon<sup>2</sup> from the oxidation of 1,4-cholestadien-3-one. The carbon and hydrogen content of IV (C, 83.07; H, 12.12) and of the corresponding oxime (C, 79.48; H, 11.89; N, 4.03) is such that a clear choice between structures III and IV cannot be made on the basis of the available analytical data.

In 1951, a crystalline, though somewhat impure, preparation (m.p. 42°) of the Inhoffen ketone was obtained in the Oxford laboratories by Dr. R. P. A. Sneeden.<sup>3</sup> Through the courtesy of Sir Robert Robinson a more highly purified specimen, m.p. 52°, has recently been made available for direct comparison with the ketone derived from I. The two samples give no mixed melting point depression and show identical absorption in the infrared. The identity of the two substances was further confirmed by comparison of the corresponding semicarbazones, m.p. 224–225° dec.<sup>2</sup> Pyrolysis of the barium salt of I thereby constitutes an additional example of reversal of the Michael reaction.<sup>4</sup>

(2) H. H. Inhoffen and Huang-Minlon, *Ber.*, **72**, 1686 (1939).

(3) Cf. A. R. Pinder and R. Robinson, *Nature*, **167**, 484 (1951).

(4) NOTE ADDED IN PROOF.—A discussion of the cleavage of 1,5-dicarbonyl compounds and a conversion somewhat analogous to the one described above have now been reported by S. A. Julia, A. Eschenmoser, H. Heusser and N. Tarköy, *Helv. Chim. Acta*, **36**, 1885 (1953).

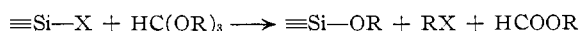
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### A New Method of Preparation for Alkoxysilanes\*

BY LEONARD M. SHORR

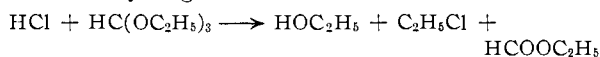
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This paper concerns itself with a new procedure for the alkoxylation of halosilanes which is rapid, efficient and does not yield hydrogen halide by-products. Ethyl orthoformate has been found to react with halosilanes in the manner



Presumably, other orthoesters would behave similarly. Chlorosilanes may be ethoxylated more easily than fluorosilanes.

This reaction is similar to that of ethyl orthoformate with hydrogen chloride<sup>1,2</sup>



In the usual preparation of alkoxysilanes employing the reaction of alcohols with variously substituted halosilanes, difficulties are often incurred because the hydrogen halides formed may react deleteriously in several side reactions. In the presence of an alcohol it may cause disproportionation with a different alkoxy group already attached to the silicon atom<sup>3</sup>; it may react with alcohol to produce an alkyl halide and sufficient water to cause

\* Contribution from the Multiple Fellowship at Mellon Institute sustained by the Corning Glass Works and Dow Corning Corporation.

(1) M. Arnold, *Ann.*, **240**, 195 (1887).

(2) W. Lippert, *ibid.*, **276**, 177 (1893).

(3) D. F. Peppard, W. G. Brown and W. C. Johnson, *THIS JOURNAL*, **68**, 70 (1946).