

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 literature¹⁰ 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).

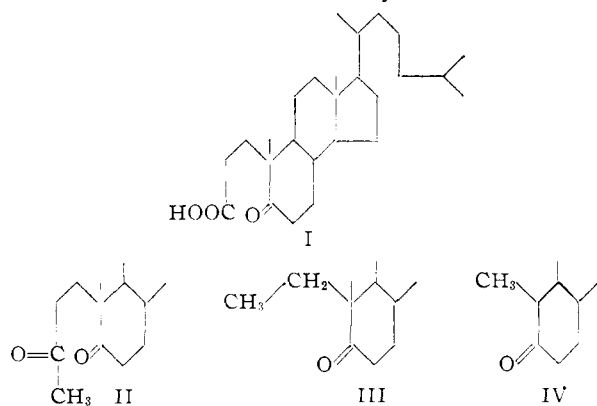
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Pyrolysis of the Windaus Acid

BY RICHARD B. TURNER

RECEIVED DECEMBER 10, 1953

Some time ago, in connection with experiments directed toward the preparation of labeled cholesterol,¹ 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-Minlon² 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. Sneed.³ 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.² Pyrolysis of the barium salt of I thereby constitutes an additional example of reversal of the Michael reaction.⁴

(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).

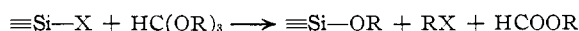
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A New Method of Preparation for Alkoxysilanes*

BY LEONARD M. SHORR

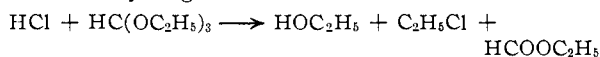
RECEIVED OCTOBER 29, 1953

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^{1,2}



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 atom³; 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).

considerable hydrolysis of the halosilane^{4,5}; it may react with silane-hydrogen accompanied by the nearly quantitative elimination of the hydrogen and the introduction of an alkoxy group in its place⁶; and it may cleave aryl and other sensitive substituents from the silicon atom. Previous efforts to minimize the effects of the hydrogen halides centered around its elimination from the system either by use of selective solvents⁶ or hydrogen halide acceptors.⁷ However, these procedures are not completely satisfactory.

Preparation of Diethoxydimethylsilane and Chloroethoxydimethylsilane.—Approximately 0.1 g. of aluminum chloride was added to a mixture of 124.0 g., 0.96 mole, of dimethyldichlorosilane and 142.0 g., 0.96 mole, of freshly distilled ethyl orthoformate. Heat was evolved and the mixture turned dark, and a gas boiling near room temperature was evolved. When the initial reaction subsided the mixture was heated at reflux for 16 hours. Further experimentation indicated that refluxing for this period of time was unnecessary.

Upon distillation there was recovered 32.8 g., 25.6%, of dimethyldichlorosilane. Chloro-(ethoxy)-dimethylsilane was obtained, b.p. 94–95° at 740.5 mm., n_D^{25} 1.3898, yield 74.4 g., 56.0%. A third fraction, diethoxydimethylsilane, also was obtained, b.p. 110° at 740.5 mm., n_D^{25} 1.3793, yield 22.5 g., 15.8%. The only other material present was ethyl formate.

(4) W. C. Schumb and D. F. Holloway, *THIS JOURNAL*, **63**, 2753 (1941).

(5) H. W. Post and H. M. Norton, *J. Org. Chem.*, **7**, 528 (1942).

(6) Martha E. Havill, I. Joffe and H. W. Post, *ibid.*, **13**, 280 (1948).

(7) S. W. Kantor, *THIS JOURNAL*, **75**, 2712 (1953).

Preparation of Diethoxymethylsilane.—To 148.0 g., 1.0 mole, of freshly distilled ethyl orthoformate was added 57.5 g., 0.5 mole, of methylchlorosilane. An exothermic reaction set in immediately with the evolution of a gas. A water-bath was used to maintain a reaction temperature below 46°. The reaction subsided within one-half hour.

Distillation revealed the presence of the following ethoxysilanes in addition to ethyl formate: methyldiethoxysilane, b.p. 94° at 731.3 mm., n_D^{25} 1.3724, d_4^{25} 0.829; sp. ref. 0.2747, calcd. sp. ref. 0.2732; yield 54.8 g., 82%. *Anal.* Calcd. for $\text{CH}_3\text{SiH}(\text{OC}_2\text{H}_5)_2$: active H, 0.74; Si, 20.92. Found: active H, 0.78, 0.82; Si, 20.57, 20.59.

There was also obtained methyltriethoxysilane, b.p. 135–138° at 731.3 mm., n_D^{25} 1.3838–67, d_4^{25} 0.877; sp. ref. 0.2677, calcd. sp. ref. 0.2605; yield 14.2 g., 16%.

Ethoxylation of Phenyltrifluorosilane.—Phenyltrifluorosilane, 52.5 g., 0.324 mole, was heated with 218.0 g., 1.47 moles, of freshly distilled ethyl orthoformate in the presence of a catalytic quantity of anhydrous aluminum chloride for approximately 30 hours. The distillate contained the following ethoxysilanes in addition to ethyl formate and unreacted ethyl orthoformate: phenylfluorodiethoxysilane, b.p. 110° at 25 mm., n_D^{25} 1.4487, d_4^{25} 1.029; sp. ref. 0.2605, calcd. sp. ref. 0.2558; neut. equiv. 214, 217, calcd. neut. equiv. 214; yield 27.5 g., 39.6%.

There was also obtained phenyltriethoxysilane, b.p. 133° at 25 mm., n_D^{25} 1.4580, d_4^{25} 0.988; sp. ref. 0.2761, calcd. sp. ref. 0.2757; yield 44.5 g., 57.5%.

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Anabasine

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A value for the second acid dissociation constant of α -(β -pyridyl)-piperidine has been determined spectrophotometrically. This compound is reduced polarographically when present as BH^+ *via* a 2-electron step. The Ilkovic equation is obeyed.

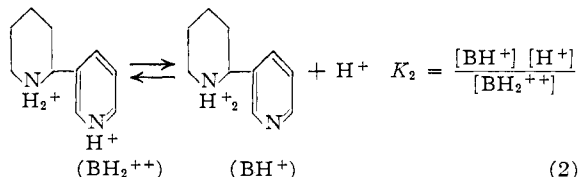
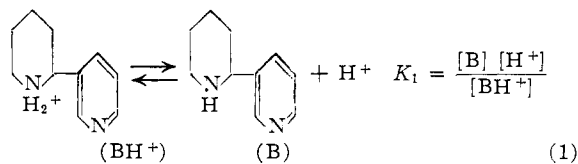
As part of a research program on nitrogen heterocyclic molecules it was necessary to study the polarographic reduction and ultraviolet solution spectra (to obtain the dissociation constant) of α -(β -pyridyl)-piperidine. As these results are of some general interest they are reported here.

Experimental

All ultraviolet spectra were determined on a Beckman Model DU instrument; pH measurements were made with a Cambridge Instrument Co. portable pH meter. The polarograms were recorded photographically on a Sargent-Heyrovsky Model XII polarograph using a Heyrovsky Erlenmeyer type cell with Hg anode. The capillary characteristics were $m = 1.62$ mg./sec., $t = 3.80$ sec./drop (determined with 66.5 cm. open circuit, in distilled water). The anabasine was provided by Dr. Roark, U. S. Dept. of Agriculture and was used without further purification; it had the following physical constants: n_D^{25} 1.5387, m.p. $12.0 \pm 0.1^\circ$ (determined with Cu-constantan thermocouple from time-temperature warming curves of frozen anabasine—cooling curves could not be used due to supercooling). All chemical reagents were analytical grade. The methylcyclohexane was purified with fuming H_2SO_4 .

Results and Discussion

The ultraviolet solution spectra are shown in Fig. 1. The following equilibria are assumed to exist in aqueous anabasine solutions



The value of K_1 should be similar to that of piperidine since a substituent in the 3-position cannot