the absorption of two moles of nitric oxide; however, the products obtained are unstable.

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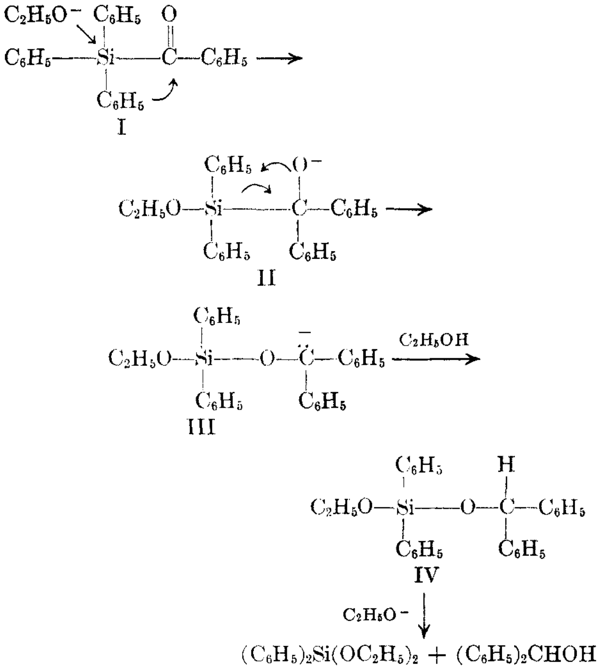
Alkoxide-Catalyzed Rearrangements of Benzoyltriphenylsilane

Sir:

It has been reported that benzoyltriphenylsilane (I) decomposes in dilute aqueous sodium hydroxide solution at room temperature to triphenylsilanol and benzaldehyde.[1] An even more interesting reaction occurs when the ketone is treated with sodium ethoxide. The major product isolated is benzhydryloxyethoxydiphenylsilane (IV), obtained in 61% yield along with small quantities of benzhydrol and diphenyldiethoxysilane, shown to be formed by subsequent reaction of ethoxide ion with IV.

Evidently nucleophilic attack by ethoxide ion on silicon results in the displacement of a phenyl group from silicon to the carbonyl-carbon atom, the formation of a bond between silicon and the carbonyl-oxygen, and the cleavage of the silicon carbonyl—carbon bond. The result of these 1,2-rearrangements, probably proceeding *via* anion II, is the carbanion III, leading to the final product by reaction with the solvent. A similar result was obtained using sodium methoxide.



The reaction may be presumed to occur in two steps, both of which have been observed before. The migration of an aryl group from silicon to an *alpha* carbon has been reported by Eaborn and Jeffrey[2] under similar conditions, and bond formation between silicon and an oxygen atom once removed is observed in the rearrangement of α-silylcarbinols to their isomeric ethers.[3] The distinctive feature of the present reaction is the occurrence of two successive rearrangements. Further work is in progress.

Treatment of 5.0 g. (0.0137 mole) of benzoyltriphenylsilane in 50 ml. of benzene with the sodium ethoxide from approximately 0.1 g. of sodium in 25 ml. of ethanol for 6 hr. at room temperature, during which time the yellow color faded, followed by hydrolysis in dilute acid led to the isolation of a total of 3.24 g. (61%) of benzyhydroxyethoxydiphenylsilane (IV), m.p. 77–78.5° from ethanol (*Anal.* Calcd. for $C_{27}H_{26}O_2Si$: C, 79.0: H, 6.38. Found: C, 78.8: H, 6.38). The mother liquors on distillation at 126°/1 mm. gave partially crystalline material from which was isolated 0.20 g. (8%) of benzhydrol, m.p. 67–68°, and 0.3 g. (8%) of di. phenyldiethoxysilane, b.p. 130°/2 mm., n_D^{20} 1.5303- The infrared spectra of all compounds were consistent with the proposed structures: the latter two compounds were compared with authentic samples.

Treatment of IV in ethanol with hot dilute aqueous sodium hydroxide for 1 hr. gave 73% diphenylsilanediol, m.p. 163–166°, and 68% benzhydrol, m.p. 66–68°, both identified by infrared spectra and mixed melting point. Treatment of IV with one equivalent of sodium ethoxide over 22 hr. at room temperature gave 90% benzhydrol, m.p. 66–68°, a trace of diphenylsilanediol, and 30% of diphenyldiethoxysilane, b.p. 131°/2 mm., n_D^{20} 1.5281.

Similar treatment of I with sodium methoxide gave 20% of benzhydryloxymethoxydiphenylsilane, m.p. 45–47.5° from methanol. *Anal.* Calcd. for $C_{26}H_{24}O_2Si$: C, 78.8: H, 6.06. Found: C, 78.8: H, 6.03. In addition benzhydrol (31%) and diphenyldimethoxysilane (15%), b.p. 108°/0.5 mm., n_D^{20} 1.550 were obtained, and were identified by comparison with authentic samples. All compounds had infrared spectra consistent with the proposed structures.

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(1) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).

(2) C. Eaborn and J. C. Jeffrey, *J. Chem. Soc.*, 137 (1957).

(3) A. G. Brook, *J. Am. Chem. Soc.*, **80**, 1886 (1958); A. G. Brook, C. M. Warner and M. McGriskin, *J. Am Chem. Soc.*, **81**, 981 (1959).