by fractionation. Therefore, a method of preparation was sought which would produce chloroacetone with little possibility of forming polychloro compounds; a synthesis from acetyl chloride and diazomethane was found to fulfil this requirement. This type of synthesis has been applied previously to the synthesis of several higher-molecular weight chloroalkyl and chloroaryl ketones.[2] The intermediate diazoacetone was converted directly by dry hydrogen chloride to monochloroacetone in 68% over-all yield. The product boiled at 118–119° at 736 mm. and analyzed correctly for the monochloro compound.

Experimental.—A dried ether solution (approximately 500 ml.) containing 0.5 mole of diazomethane was placed in a 1000-ml. three-necked flask and Eastman Kodak practical grade acetyl chloride (0.25 mole) was added slowly from a dropping funnel with constant stirring of the solution which was maintained at a temperature not greater than 5°. The reaction mixture was allowed to stand for two hours after the addition of the acetyl chloride and was then saturated with dry hydrogen chloride over a period of two hours. The bulk of the ether was removed by distillation and the residual solution fractionated through a small column. The product boiling at 118–119° at 736 mm., d^{25}_{4} 1.1260, weighed 15.8 g. (68% based on acetyl chloride). The reported constants for monochloroacetone[1] are: b.p. 118–120° at 760 mm. and d^{25}_{4} 1.123.

Anal. Calcd. for C_3H_5OCl: Cl, 38.3. Found: Cl (Stepanov), 38.4.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission which supported the work described.

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Intramolecular Rearrangement of Isopropenyltrimethylsilane[1]

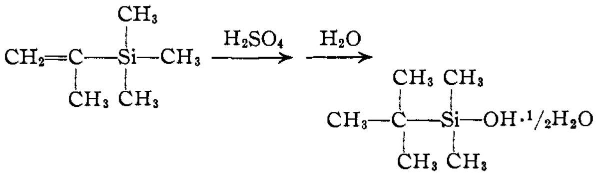
BY LEO H. SOMMER AND F. JAMES EVANS

RECEIVED JULY 29, 1953

Previous studies have demonstrated the phenomenon of intramolecular rearrangement of alkyl from silicon to carbon in chloromethyltrimethylsilane,[2] α-chloroethyltrimethylsilane, α-chloroethyltriethylsilane and dichloromethyltrimethylsilane.[3] While these rearrangements are of interest from the standpoint of demonstrating that the Wagner–Meerwein change is sufficiently general so as to include organosilicon rearrangements, a number of problems related to these new rearrangements are unsolved.

For example, in all four of the rearrangements thus far reported the reagent used was aluminum chloride and the starting material comprised an α-chloroalkylsilane.

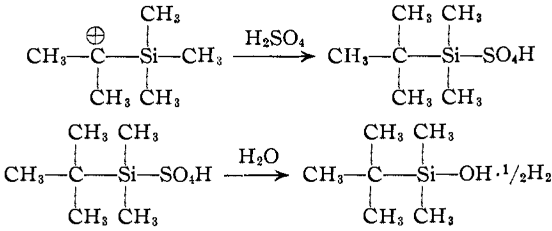
In the present work we have found that addition of isopropenyltrimethylsilane to concentrated sulfuric acid followed by treatment of the resulting solution with water gives *t*-butyldimethylsilanol hemihydrate.



$$CH_2{=}\underset{CH_3}{C}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH_3 \xrightarrow{H_2SO_4} \xrightarrow{H_2O} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OH\cdot{}^1\!/_2H_2O$$

Conversion of the hydrate to the pure silanol and comparison with an authentic sample of silanol synthesized by an unequivocal method[4] showed the substances to be identical.

The above reaction clearly involves rearrangement of methyl from silicon to carbon, and probably proceeds through an α-carbonium ion intermediate.[2,3]



$$CH_3{-}\underset{CH_3}{\overset{\oplus}{C}}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH_3 \xrightarrow{H_2SO_4} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}SO_4H$$

$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}SO_4H \xrightarrow{H_2O} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OH\cdot{}^1\!/_2H_2O$$

Experimental

Synthesis of Isopropenyltrimethylsilane.—Addition of 10 moles of isopropylmagnesium chloride in 3 liters of ether to 22 moles of silicon tetrachloride dissolved in 550 ml. of dry ether over a period of 2 hours with stirring and cooling was followed by heating of the reactants on the steam-bath at reflux temperature for 12 hours. After removal of the ether and excess silicon tetrachloride by distillation, the product was rapidly distilled under vacuum to effect removal from the magnesium salts. Fractional distillation of the crude product so obtained gave isopropyltrichlorosilane, b.p. 119° at 736 mm., 812 g., a yield of 46%.

Anal. Calcd. for $C_3H_7SiCl_3$: Si, 15.99; Cl, 60.1. Found: Si, 16.05; Cl, 59.8.

Chlorination of isopropyltrichlorosilane (10.2 moles) with sulfuryl chloride (8.2 moles) in the presence of 1 g. of benzoyl peroxide by the method of Kharasch[5] gave, after fractional distillation of the product, α-chloro-*i*-propyltrichlorosilane (0.775 mole), b.p. 151°, and β-chloro-*i*-propyltrichlorosilane (2.62 moles), b.p. 164°.

The α-chloro-*i*-propyltrichlorosilane so obtained is a white, waxy solid which becomes granular on standing and sublimes readily at room temperature giving fern-like crystals. The melting point of the crystals determined in a sealed tube was found to be 109–110°.

Anal. Calcd. for $C_3H_6SiCl_4$: Si, 13.2; Cl (attached only to silicon), 50.2. Found: Si, 13.2; Cl (by alkali titration), 50.4.

The β-chloro-*i*-propyltrichlorosilane is a water-white liquid. Titration with standard sodium hydroxide of a methanol solution of this substance gave, as expected for a β-chloroalkylsilane,[6] complete reaction of the beta C–Cl bond as well as of the chlorine attached to silicon.

Anal. Calcd. for $C_3H_6SiCl_4$: Si, 13.2; Cl, 66.9. Found: Si, 13.0; Cl, 66.6.

Dehydrochlorination of β-chloro-*i*-propyltrichlorosilane with quinoline[7] gave in 76% yield isopropenyltrichlorosilane, b.p. 113° at 736 mm.

Anal. Calcd. for $C_3H_5SiCl_3$: Cl, 60.7. Found: Cl, 60.7.

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(1) Paper 39 in a series on organosilicon chemistry. For Paper 38 see THIS JOURNAL, **76**, 1030 (1954).

(2) F. C. Whitmore, L. H. Sommer and J. Gold, THIS JOURNAL, **69**, 1976 (1947).

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(4) L. H. Sommer and L. J. Tyler, *ibid.*, **76**, 1030 (1954).

(5) M. S. Kharasch and H. C. Brown, *ibid.*, **61**, 2142 (1939); L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946).

(6) L. H. Sommer, G. M. Goldberg, E. Dorfman and F. C. Whitmore, *ibid.*, **68**, 1083 (1946).

(7) D. T. Hurd, *ibid.*, **67**, 1813 (1945).

Conversion of isopropenyltrichlorosilane (2 moles) to isopropenyltrimethylsilane was achieved by treatment with methylmagnesium bromide (7.5 moles) in ether solution. After addition of the trichlorosilane to the Grignard reagent (3 hours) the reaction mixture was refluxed for 12 hours, poured into ice-water, and the organic layer separated. After removal of the ether and drying, fractionation gave isopropenyltrimethylsilane (1.46 moles) b.p. 82° at 730 mm., n^{20}_D 1.4061, d^{20} 0.7168, MR_D 39.00 (calcd. 39.07).

Anal. Calcd. for $C_6H_{14}Si$: Si, 24.6. Found: Si, 24.5.

Rearrangement of Isopropenyltrimethylsilane.—In a 3-liter, 3-necked flask was placed 475 ml. of concd. sulfuric acid. The flask was equipped with a stirrer, a reflux condenser and a dropping funnel. The reaction flask was placed in an ice–water-bath and through the dropping funnel was added 57.0 g. (0.5 mole) of isopropenyltrimethylsilane with stirring (30 minutes). The homogeneous sulfuric acid solution was then transferred to the dropping funnel and 1400 ml. of water was placed in the reaction flask. The sulfuric acid solution was added to the water with vigorous stirring in about two hours. This resulted in the formation of a white crystalline material, m.p. after drying and sublimation, 67–69° (m.p. of authentic *t*-butyldimethylsilanol hemihydrate,[4] 68–70°). The white crystals formed during the addition were filtered, washed, dissolved in 250 ml. of benzene, and then the solution was dried over calcium chloride. The above filtrate was extracted with two 100-ml. portions of benzene, which were then added to the original benzene solution. For the purpose of purifying the product, the benzene solution was treated with sodium according to a known procedure which readily converts R_3SiOH to R_3SiONa,[8] and sodium *t*-butyldimethylsilanolate was thereby isolated as a crystalline solid. An ether solution of the latter was treated with 300 ml. of water while cooling the reaction mixture in an ice-bath. The water layer was then separated and washed with two 50-ml. portions of ether. After drying over potassium carbonate, fractionation gave 28.3 g. (0.214 mole) of *t*-butyldimethylsilanol, 43% yield, b.p. 139° at 739 mm., n^{20}_D 1.4232–1.4236, d^{20} 0.8398, MR_D 40.10 (calcd. 40.08), lit.[4] b.p. 141° at 735 mm., n^{20}_D 1.4235, d^{20} 0.8397. The infrared spectra of the product obtained in the present work and of *t*-butyldimethylsilanol prepared by two unequivocal methods[4] were identical in all respects.

Anal. Calcd. for $C_6H_{16}SiO$: Si, 21.2; OH, 12.85. Found: Si, 21.4; OH, 12.30 (found by treatment with sodium in boiling xylene).

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[8] *Cf.* L. H. Sommer, L. Q. Green and F. C. Whitmore, This Journal, **71**, 3253 (1949).

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New Syntheses of Thiamorpholine. The Reduction of Mono- and Diketothiazanes by Lithium Aluminum Hydride

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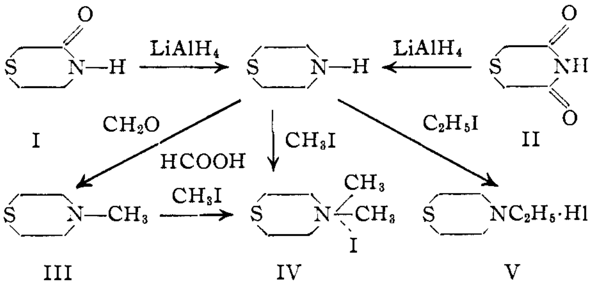
Received October 5, 1953

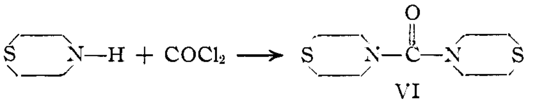
Although thiamorpholine is structurally uncomplicated, only two methods for its synthesis have been described[1,2] and only three references to its preparation were found in the literature.[1–3] These procedures require as starting materials either 2-aminoethyl mercaptan or bis-(2-chloroethyl) sulfide, neither of which is conveniently handled, and the one reported yield is 30%.[3]

We have prepared thiamorpholine in about 70% yield by the reduction of 3-keto-1,4-thiazane[4] (I) with lithium aluminum hydride. Comparison of the properties of the product and of its derivatives with those reported earlier indicates that a purer material was thus obtained. When 3,5-diketo-1,4-thiazane[5] (II) was similarly reduced, a lower yield of thiamorpholine resulted.



Although the equimolar reaction of thiamorpholine and ethyl iodide was reported by Davies[2] to yield a material which "did not melt to 260°," we obtained instead 4-ethylthiamorpholine hydroiodide (V) melting at 140–141°. By contrast, methyl iodide formed the quaternary salt, 4,4-dimethylthiamorpholinium iodide (IV), under milder conditions. This salt also was obtained from methyl iodide and 4-methylthiamorpholine (III), prepared by the Clarke–Eschweiler method.

A tetra-substituted urea, 4,4′-carbonyldithiamorpholine (VI) resulted from the reaction of thiamorpholine with phosgene. In contrast to the analogous morpholine derivative,[6] this compound did not form a hydrate.



Acknowledgment.—We are grateful to Mr. E. F. Shelberg, Mr. Robert Berg, and other members of the Microanalytical Department for the analyses reported here.

Experimental[7]

Intermediates.—Ethylenimine may be prepared in good yield from 2-aminoethyl hydrogen sulfate[8] and is available commercially.[9] Ethyl mercaptoacetate,[10] 3-keto-1,4-thiazane[4] and 3,5-diketo-1,4-thiazane[5] were prepared by methods reported in the literature.

Thiamorpholine. Method A.—A 1-l., 3-necked flask was charged with 18.1 g. (0.48 mole) of lithium aluminum hydride and 600 ml. of dry ether. A Soxhlet apparatus containing 35 g. (0.3 mole) of 3-keto-1,4-thiazane was attached, and the mixture was stirred and heated under dry nitrogen. After the ether had refluxed for six hours about 2 g. of gummy yellow solid remained undissolved. This was discarded and 45 ml. of water was cautiously added, dropwise, to the stirred mixture which was then filtered. Distillation of the filtrate through a 10-cm. Vigreux column gave 21.1 g. (68%) of thiamorpholine, b.p. 108–111° at 98 mm. Material redistilled through a 1.5 cm. × 7 cm. column packed with glass helices had these properties: b.p. 110° at 100 mm. and 174° at 746 mm.; n^{20}_D 1.5386, n^{25}_D 1.5368; d^{20}_4 1.0882; MR^{20}_D calcd. 29.87, MR^{20}_D found 29.69.

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[7] All melting points are corrected.

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[9] Obtained from Monomer-Polymer, Inc., Leominster, Mass.

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