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., $n^{20}\mathrm{D}$ 1.4061, d^{20} 0.7168, $MR\mathrm{D}$ 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., $n^{20}\mathrm{D}$ 1.4232–1.4236, d^{20} 0.8398, $MR\mathrm{D}$ 40.10 (calcd. 40.08), lit.[4] b.p. 141° at 735 mm., $n^{20}\mathrm{D}$ 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).

SCHOOL OF CHEMISTRY AND PHYSICS
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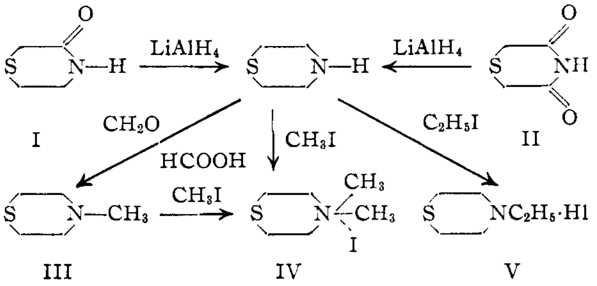
New Syntheses of Thiamorpholine. The Reduction of Mono- and Diketothiazanes by Lithium Aluminum Hydride

BY ARMIGER H. SOMMERS AND BRUCE W. HORROM

RECEIVED OCTOBER 5, 1953

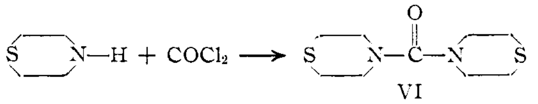
Although thiamorpholine is structurally uncomplicated, only two methods for its synthesis have been described[1,2] and only three references to its preparation were found in the literature.[1–3] These procedures require as starting materials either 2-aminoethyl mercaptan or bis-(2-chloroethyl) sulfide, 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.; $n^{20}\mathrm{D}$ 1.5386, $n^{25}\mathrm{D}$ 1.5368; d^{20}_4 1.0882; $MR^{20}\mathrm{D}$ calcd. 29.87, $MR^{20}\mathrm{D}$ found 29.69.

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[1] N. A. Langlet, *Bihang till Kgl. Svenska Vetenskapsakademiens Handlingar*, **22**, **II**, 3 (1896).

[2] W. Davies, *J. Chem. Soc.*, **117**, 297 (1920).

[3] E. J. Cragoe, Jr., and C. S. Hamilton, THIS JOURNAL, **67**, 536 (1945).

[4] H. Bestian, *Ann.*, **566**, 242 (1950).

[5] C. Barkenbus and P. S. Landis, THIS JOURNAL, **70**, 684 (1948)

[6] C. A. Weisel, H. S. Mosher and F. C. Whitmore, *ibid.*, **67**, 1055 (1945).

[7] All melting points are corrected.

[8] W. A. Reeves, G. L. Drake, Jr., and C. L. Hoffpauir, THIS JOURNAL, **73**, 3522 (1951).

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

[10] B. R. Baker, M. V. Querry, S. R. Safir and S. Bernstein, *J. Org. Chem.*, **12**, 138 (1947).

Anal. Calcd. for C_4H_9NS: C, 46.56; H, 8.79; N, 13.58; S, 31.07. Found: C, 46.82; H, 8.63; N, 13.64; S, 30.88.

Thiamorpholine hydrochloride prepared in isopropyl alcohol formed white needles which melted at 174–175°.

Anal. Calcd. for $C_4H_{10}ClNS$: C, 34.40; H, 7.22. Found: C, 34.18; H, 7.11.

Thiamorpholine picrate crystallized from ethanol as long yellow needles, m.p. 204–205°.

Anal. Calcd. for $C_{10}H_{12}N_4O_7S$: C, 36.14; H, 3.64. Found: C, 36.30; H, 3.56.

Thiamorpholine picrolonate formed dark yellow needles from ethanol, m.p. 246°.

Anal. Calcd. for $C_{14}H_{17}N_5O_5S$: C, 45.77; H, 4.67. Found: C, 46.05; H, 4.81.

Davies[2] gives the following constants for thiamorpholine and its derivatives: b.p. of base, 166–167° at 743 mm.; hydrochloride, m.p. 160–165°; picrate, m.p. 198°; picrolonate, m.p. 242°. Langlet[1] gives 165° as the boiling point of the base and 163° as the melting point of the hydrochloride. In every case these values are lower than those now reported.

Method B.—When 13.1 g. (0.1 mole) of 3,5-diketo-1,4-thiazane was reduced with 9.5 g. (0.25 mole) of lithium aluminum hydride in the same manner as described under method A, 4.4 g. (43%) of product, b.p. 173–177°, was obtained. This material, in contrast to that obtained earlier, had an unpleasant "mercaptan" odor. It was dissolved in 20 ml. of water and shaken with ether. The aqueous phase was separated and treated with 20 ml. of 25% sodium hydroxide solution. The oil which separated was extracted with ether, and the extract was dried over potassium carbonate. Distillation gave 2.2 g. (21%) of thiamorpholine, b.p. 174–175° at 758 mm.

4-Methylthiamorpholine.—A mixture of 3.8 g. of thiamorpholine, 3 cc. of 40% formalin and 1.9 g. of 98% formic acid was heated on a steam-bath for 1.5 hours after the initial vigorous reaction had subsided. About 4 ml. of concentrated hydrochloric acid was added, and the solution was evaporated to dryness. Treatment of the white solid with 10 ml. of 25% sodium hydroxide produced an oil which was distilled to give 3.1 g. (72%) of product, b.p. 164–165° at 751 mm., $n^{25}D$ 1.5068.

4-Methylthiamorpholine hydrochloride crystallized from isopropyl alcohol as stout colorless needles, m.p. 248–249°.

Anal. Calcd. for $C_5H_{12}ClNS$: C, 39.08; H, 7.87. Found: C, 39.32; H, 7.64.

Clarke prepared 4-methylthiamorpholine by the action of mustard gas on methylamine.[11] He reported that the base boiled at 163–164° at 757 mm., and the hydrochloride melted at 239°.

4,4-Dimethylthiamorpholinium Iodide.—When a solution of 2 g. of 4-methylthiamorpholine in 10 ml. of absolute ethanol was treated with 4 ml. of methyl iodide, a white crystalline precipitate formed which weighed 4.4 g. and melted at 297°, unchanged by recrystallization from ethanol.

Anal. Calcd. for $C_6H_{14}INS$: C, 27.81; H, 5.45. Found: C, 28.10; H, 5.18.

The same quaternary salt was obtained when an alcoholic solution of thiamorpholine and methyl iodide was allowed to stand 12 hours.

4-Ethylthiamorpholine Hydroiodide.—When a solution of 0.5 g. of thiamorpholine and 5 ml. of ethyl iodide in 10 ml. of ethanol stood for several days at room temperature no solid formed. The solution was concentrated on steam to a volume of 5 ml., and when cooled gave white needles, m.p. 140–141°.

Anal. Calcd. for $C_6H_{14}INS$: C, 27.81; H, 5.45. Found: C, 27.99; H, 5.45.

The identity of this compound was established by conversion to the *picrate*, m.p. 189–190°, reported[11] to melt at 185–186°.

Anal. Calcd. for $C_{12}H_{16}N_4O_7S$: N, 15.57. Found: N, 16.00.

4,4′-Carbonyldithiamorpholine.—A solution of 10.3 g. (0.1 mole) of thiamorpholine in 20 ml. of dry toluene was added with stirring to a solution of 5 g. (0.05 mole) of phosgene and 20 g. (0.25 mole) of pyridine in 250 ml. of anhydrous ether. The mixture was then stirred for 30 minutes and shaken three times with water. Evaporation of the ether solution and crystallization of the residue from isopropyl alcohol gave 5.5 g. (47%) of product. Upon recrystallization from aqueous methanol it formed white crystals, m.p. 143–144°.

Anal. Calcd. for $C_9H_{16}N_2OS_2$: C, 46.52; H, 6.94; N, 12.06. Found: C, 46.71; H, 6.89; N, 11.89.

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5-Ethyl-5-(β-phenylpropyl)-barbituric Acid from β-Chlorocumene

BY GLENN S. SKINNER AND DONALD L. KNAUSS

RECEIVED OCTOBER 17, 1953

We have prepared 5-ethyl-5-(β-phenylpropyl)-barbituric acid from β-chlorocumene through the intermediate diethyl ethyl-β-phenylpropylmalonate. The β-chlorocumene required was prepared by the action of dry chlorine on hot cumene in sunlight. It was shown to have the assigned structure by oxidation to benzoic acid and conversion through the Grignard reaction to β-phenylbutyramide.

β-Chlorocumene is relatively inert[1] in its reaction toward alkali or silver acetate. Under ordinary conditions of refluxing in benzene we found it to be inert also toward sodioethylmalonic ester, but reaction occurred after distilling enough benzene to permit a temperature of 140°.

Orally administered to rats this barbiturate produced no hypnosis, but convulsions and death at 400 mg./kg. Since it is ineffective, no resolution of the compound was attempted.

Experimental

β-Chlorocumene.—Cumene in lots of 350 cc. at gentle reflux in sunlight was subjected to the action of a rapid stream of dry chlorine until the temperature of the boiling liquid reached 190–195°. Fractional distillation of the combined product from several runs gave 656 g. of unchanged cumene, b.p. 45–50° (14 mm.); 80 g. of a mixture, b.p. 50–90° (14 mm.); 1259 g. of β-chlorocumene, b.p. 90–95° (14 mm.); 694 g. of products of undetermined constitution, b.p. 95–160° (14–3 mm.) and 62 g. of viscous residue. There was no evidence of decomposition during the distillation. β-Chlorocumene is reported[2] to boil at 95–100° (21 mm.) while α-chlorocumene is decomposed with the loss of hydrogen chloride when boiled under diminished pressure.

Characterization of β-Chlorocumene.—Oxidation with hot alkaline permanganate under reflux gave benzoic acid, showing that in our preparation the chlorine is located in the side chain. The Grignard reagent prepared from the chloro compound was treated with solid carbon dioxide and the resulting acid was converted through the acid chloride to β-phenylbutyramide, m.p. 104–105°, showing that the chlorine is in the beta position. Kohler and Reimer[3] give m.p. 105° for this amide which they prepared by an independent method.

Diethyl Ethyl-(β-phenylpropyl)-malonate.—Diethyl ethylmalonate (376 g., 2 moles) was added to a stirred and cooled suspension of 23 g. of powdered sodium in 600 cc. of dry benzene. When the reaction was complete 154.5 g. (1 mole) of the above β-chlorocumene was added at once with stirring. No precipitation of sodium chloride occurred, and very little at 90–95° in 15 hours. Benzene was then distilled through a column until the temperature of the

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[11] H. T. Clarke, *J. Chem. Soc.*, **101**, 1586 (1912).

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[2] M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

[3] E. P. Kohler and Marie Reimer, *Am. Chem. J.*, **33**, 353 (1905).