tion from 95% ethanol gave white needles, m.p. 138–139.5°.

Anal. Calcd. for $C_{10}H_{11}O_6N$: C, 49.81; H, 4.60; N, 5.81. Found: C, 50.23; H, 4.81; N, 5.89.

The isopropyl alcohol mother liquor from the preparation of the above oxalate was heated at reflux for two hours. A white precipitate, 1.66 g., gradually appeared, m.p. 150–200°. After recrystallization from water, 0.87 g. of **3-hydroxy-4-methylpyridine oxalate**, was obtained as white prisms, m.p. 243° dec. An additional 0.20 g. was obtained by working up the mother liquors.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.09. Found: C, 55.04; H, 5.61; N, 9.38.

The precipitation of the oxalates was attended by considerable gas evolution. This appears to be due to decomposition of oxalic acid induced by a combination of acetic anhydride and pyridine bases. We have found that solutions of oxalic acid vigorously evolve gas at room temperature in the presence of pyridine (or piperidine) and acetic anhydride, but the decomposition does not occur with pyridine, 2-pyridone, Ia, Ic, II or acetic anhydride alone. The nature of the reaction remains to be elucidated.

4-Pyridinemethanol acetate (Ia) was obtained by treating a solution of its oxalate with excess sodium carbonate and extracting the resulting oil with chloroform. The dried (sodium sulfate) solution was evaporated to give a pale yellow oil, $\lambda_{\mathrm{maxm}}^{\mathrm{EtOH}}$ 257 mμ, log ϵ 3.05; $\lambda_{\mathrm{max}}^{\mathrm{chf}}$ 5.72 μ. The model substance 4-methylpyridine shows λ_{max} 252 mμ, log ϵ 3.37 (in isoöctane).[16] The base was reconverted to the oxalate, m.p. 137–139°, alone or mixed with a sample isolated as above, or with an authentic sample prepared by acetylating 4-pyridinemethanol[17] and treating the product with oxalic acid.

4-Pyridinemethanol (Ic) was prepared by treating an aqueous suspension of the above acetate with an excess of 20% potassium hydroxide. The oil dissolved and the clear solution was extracted with ten portions of chloroform, the extracts dried over sodium sulfate and evaporated. The residue was a flaky, buff solid, m.p. 52–53.5°. Recrystallization from benzene gave white needles, m.p. 57.8–58.8° alone or mixed with an authentic sample[17]; reported for 4-hydroxymethylpyridine, m.p. 57–60°,[2] 57°,[18] 47–50°,[19] 58–60°.[17] **The hydrochloride** had m.p. 175–179°, reported 176–178°,[2] 176–180°,[19] 176°.[20]

The picrate, was obtained as yellow needles from ethanol, had m.p. 155° dec.

Anal. Calcd. for $C_{12}H_{10}O_8N_4$: C, 42.61; H, 2.98; N, 16.57. Found: C, 42.88; H, 3.01; N, 16.76.

When Ic was boiled in acetic anhydride for one hour, the acetic anhydride evaporated, the residue distilled and the distillate treated with oxalic acid, only the oxalate of Ia, m.p. 139.5°, was obtained.

3-Hydroxy-4-methylpyridine (II) was liberated from its oxalate with sodium carbonate, extracted with chloroform and recrystallized from benzene to give white needles, m.p. 120–121.2°; reported[7] m.p. 118–120°.

Anal. Calcd. for C_6H_7NO: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.36, 65.95; H, 6.00, 6.58; N, 12.74.

The substance gave an immediate bright red color with ferric chloride. It was reconverted to the neutral oxalate, m.p. 243° dec., alone or mixed with a sample isolated as above. Its ultraviolet behavior in neutral ethanol and in ethanol which was 1.02×10^{-3} *M* in potassium hydroxide has been reported in the theoretical section.

II was not converted to Ia under the rearrangement conditions. It was recovered as its oxalate, m.p. 243° dec., after being boiled in acetic anhydride for one hour and worked up in the same manner as the rearrangement runs.

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(16) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

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5-Aza-2,8,10-trithiaadamantan or Trithiotrimorpholine

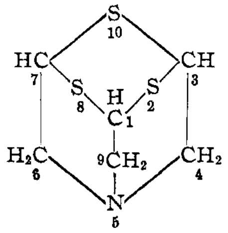
BY DAVID CRAIG, J. J. SHIPMAN, A. HAWTHORNE AND RAY FOWLER

RECEIVED OCTOBER 18, 1954

A recent review[1] of compounds having the cage structure of adamantan called our attention to an impurity (I), m.p. 147–148°, which we had isolated from crude 4-thiazoline-2-thione[2] prepared from the reaction of chloroacetaldehyde with excess ammonium dithiocarbamate. The excess of the ammonium salt was subsequently found to be essential apparently because this assured the presence of hydrogen sulfide as well as ammonia. Carbon disulfide was found to be a by-product. Analysis and molecular weight determination showed I to be $C_6H_9NS_3$. We can therefore write the equations

$$\begin{gathered} H_2NCS_2NH_4 \longrightarrow NH_4CNS + H_2S \\ N_2NCS_2NH_4 \longrightarrow NH_3 + CS_2 \\ NH_3 + 3ClCH_2CHO \longrightarrow N(CH_2CHO)_3 + 3HCl \\ 3H_2S + N(CH_2CHO)_3 \longrightarrow \underset{\mathrm{I}}{N(CH_2CHS)_3} + 3H_2O \end{gathered}$$

The infrared absorption spectrum of I was essentially transparent up through seven microns except for strong bands at 3.44 and 6.99 μ. These are due to the stretching and wagging vibrations of hydrogen atoms on carbon. Thus SH, NH, C=C, C=S and C=N groups are shown to be absent and we can infer that the method of synthesis and the absorption spectrum of I show the structure to be



A Stuart type scale model of this structure was made easily. It was slightly strained due to the sulfur atoms being a little too large for close packing with the smaller nitrogen and carbon atoms. The structure is seen to have a trithiane grouping on one side and on the opposite side an exposed nitrogen atom.

Experimental

The crude "thiazolethiol" (60 g.) of Mathes and Beber was extracted serially with 200-, 100- and 50-ml. portions of boiling alcohol. The extracts were united and cooled to give 7.2 g. of crystals, m.p. 145–146°. The filtrate was used to re-extract the insoluble part and a further 2.4 g. of the 145–146° melting compound was isolated. The yield of I thus is 16% of the crude "thiazolethiol." Recrystallized from alcohol the compound came down as cream colored needles, m.p. 147–148°.

Anal. Calcd. for $C_6H_9NS_3$: C, 37.66; H, 4.74; N, 7.32; S, 50.27; mol. wt., 191. Found: C, 37.76, 37.76, 37.56; H, 4.93, 4.97, 4.76; N, 7.26, 7.31; S, 50.02, 49.82; mol. wt. in boiling benzene, 186, 186.

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[1] H. Stetter, *Z. angew. Chem.*, **66**, 217 (1954).

[2] R. A. Mathes and A. J. Beber, THIS JOURNAL, **70**, 1452 (1948). According to these authors and most usage, this compound, m.p. 79 to 80°, is called 2-thiazolethiol in spite of the fact that methods which are suitable for distinguishing the thioamide form from the thiol isomer disclose the presence of only the thioamide isomer. Compare M. G. Ettlinger, *ibid.*, **72**, 4701 (1950).

It was found to be slightly soluble in water and cold alcohol and rather strongly soluble in benzene. It dissolved readily in dilute or concentrated sulfuric acid. It was insoluble in aqueous hydrochloric acid but in benzene solution with hydrogen chloride it formed a salt, m.p. 223–225°, which was insoluble in water. A picrate could not be isolated from alcohol solution. The methiodide formed rapidly in boiling methanol and melted at 210–215° dec.

Anal. Calcd. for $C_7H_{12}NS_3I$: C, 25.22; H, 3.63. Found: C, 25.10, 25.38; H, 3.63, 3.63.

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The Reaction of Cumyl Hydroperoxide with Sodium Hydrosulfide

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RECEIVED OCTOBER 18, 1954

Cumyl hydroperoxide has been shown[1] to undergo reduction by various routes, depending upon the nature of the reducing agent employed. Boardman[1a] has shown that reduction with ferrocyanide *via* a one-electron transfer gives rise to the α,α-dimethylbenzyloxy radical[2] which decomposes to give acetophenone and methyl radical. An alternative mechanism is a two-electron transfer process, represented by the reduction of cumyl hydroperoxide to α,α-dimethylbenzyl alcohol by iodide ion.[1b] A process involving two consecutive one-electron transfers is a third alternative. This last mechanism would also give rise to α,α-dimethylbenzyl alcohol.

The reaction of cumyl hydroperoxide with alkaline sodium hydrosulfide was investigated in an effort to elucidate the mechanism of reduction by the latter reagent.[3] Under the conditions employed the organic products of this reaction were α,α-dimethylbenzyl alcohol and α-methylstyrene. The latter product is believed to have resulted from dehydration of the initially formed tertiary alcohol. Unfortunately, the formation of these products excludes only one mechanistic concept, namely, reduction by a one-electron transfer to α-cumoxy radical, followed by decomposition to acetophenone and methyl radical, but they do not exclude either a simple two-electron transfer to give cumoxide ion or a rapid reduction of cumoxide radical to cumoxide ion.

It seemed of some interest to attempt to determine the fate of the sulfur in the reaction under consideration, particularly in view of a transitory yellow coloration of the reaction mixture which appeared momentarily after the addition of each drop of sodium hydrosulfide solution to an ethanolic solution of cumyl hydroperoxide. Subsequent investigation showed that polysulfide solutions undergo immediate decoloration when treated with cumyl hydroperoxide and that the acidified aqueous extracts of such solutions showed qualitative tests for sulfate ion.

Analysis of the inorganic products of the reaction of cumyl hydroperoxide with sodium hydrosulfide disclosed that 37% of the theoretical amount of sulfate ion (determined as barium sulfate) based on the equation

$$4\ \mathrm{ROOH} + \mathrm{HS}^- + \mathrm{OH}^- \longrightarrow 4\ \mathrm{ROH} + \mathrm{SO_4}^{=} + \mathrm{H_2O}$$

was formed. Acidification of the aqueous extracts of the reaction mixture led to deposition of sulfur and to the evolution of large amounts of sulfur dioxide. Formation of the latter compound indicates that a portion of the hydrosulfide was oxidized to sulfite and/or thiosulfate. No attempt was made to determine these latter ions in a quantitative manner. In view of the excess hydrosulfide present in the reaction mixture and the isolation of sulfate as a product,[5] it is conceivable that the aqueous extracts from the reaction mixture may have contained sulfur in other valence states.

The reduction of cumyl hydroperoxide to the alcohol by sodium hydrosulfide is, therefore, analogous to the results reported in the reduction by sodium sulfide of methyl 9-hydroperoxydehydroabietate and methyl 9-oxo-14-hydroperoxydehydroabietate.[6]

Acknowledgment.—The authors wish to acknowledge support of this work by the U. S. Naval Ordnance Test Station Inyokern, U. S. Navy Bureau of Ordnance, under contract N123s-82337, Task Order No. 2, and by the Office of Ordnance Research, U. S. Army. They further wish to acknowledge a gift of a sample of cumyl hydroperoxide from the Hercules Powder Company.

Experimental

Materials.—Sodium hydrosulfide reagent was prepared by saturating an approximately 6 *N* sodium hydroxide solution with hydrogen sulfide gas. Dilutions were made as required, and the resulting solutions were standardized by potentiometric titration against standard silver nitrate solutions. Cumyl hydroperoxide was a Hercules Powder Company product containing 70% hydroperoxide.

Procedure.—To cumyl hydroperoxide dissolved in a large volume of 95% ethanol (usually 10 g. of 70% cumyl hydroperoxide in *ca.* 400 ml. of 95% ethanol) was added dropwise with stirring an equimolar quantity of 0.5 *M* sodium hydrosulfide solution. The reaction was conducted in an atmosphere of nitrogen and proceeded vigorously at room temperature. Following the addition of sodium hydrosulfide the mixture was stirred for an hour and allowed to stand overnight. After removal of ethanol by distillation at a pressure of 20 mm., the mixture was extracted with ether; the ether extracts were washed with water and dried over anhydrous sodium sulfate. Removal of ether left a colorless liquid which distilled at 63–102° (18 mm.). Fraction 1, b.p. 63–64° (18 mm.), was shown to be α-methylstyrene by its reaction with an equivalent amount of bromine and the identity of its infrared spectrum with that of an authentic sample.[7] Fraction 3, b.p. 101–102° (18 mm.), which was shown to be α,α-dimethylbenzyl alcohol by the identity of its infrared spectrum with that of the authentic alcohol (b.p., *101–102° (18 mm.),* $n^{20}\mathrm{D}$ *1.5216), comprised the* major portion of the distillate. A small intermediate fraction

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(1) (a) H. Boardman, THIS JOURNAL, **75**, 4268 (1953); (b) H. Boardman and G. E. Hulse, *ibid.*, **75**, 4272 (1953).

(2) M. S. Kharasch, W. Nudenberg and F. S. Arimoto, *Science*, **113**, 392 (1951).

(3) It has been shown[4] that alkaline hydrosulfides reduce alkyl nitrates to the corresponding alcohols. We were interested in the possibility of finding a single one-electron transfer reaction in this medium, in view of the polysulfide catalysis of the nitrate ester reduction.[4]

(4) R. T. Merrow, S. J. Cristol and R. W. Van Dolah, THIS JOURNAL, **75**, 4259 (1953).

(5) H. Hock and S. Lang, *Ber.*, **77B**, 257 (1944), showed that cumyl hydroperoxide may be reduced to α,α-dimethylbenzyl alcohol by sodium sulfite.

(6) P. F. Ritchie, T. F. Sanderson and L. F. McBurney, THIS JOURNAL, **75**, 2610 (1953); **76**, 723 (1954).

(7) α-Methylstyrene was prepared by dehydration of α,α-dimethylbenzyl alcohol by the method of K. Matsubara and W. H. Perkin, Jr., *J. Chem. Soc.*, **87**, 672 (1905).