## EXPERIMENTAL

*Preparation of Grignard reagents.* The Grignard reagents were prepared in the usual manner by the reaction of 0.5 mole of organic halides with 12.5 g. of magnesium turnings in anhydrous ether. After the addition of the halides, the solution was refluxed for 2 hr.

*Formation of sulfides.* To a vigorously stirred and cooled (below 10°) Grignard solution was added, over a period of 1 hr., 27.3 g. (0.35 mole, No. 1–5) or 31.2 g. (0.40 mole, No. 6–10) of dimethyl sulfoxide dissolved in about equal quantity of anhydrous ether. A grey-white solid deposition began almost immediately and in some cases continued stirring was impossible. The reaction mixture was then heated at the reflux point for an additional 3 hr. and allowed to stand overnight at room temperature.

When the temperature of the reaction mixture of dimethyl sulfoxide with alkyl Grignard reagent (R = ethyl, *n*-propyl, and *n*-butyl) had risen nearly to room temperature, a fairly vigorous evolvement of gas was observed. After passing the gas through a large excess of bromine, the bromine was removed and the residual oil was purified as usual. From gas chromatographic and infrared spectral data, in the case of *n*-propylmagnesium bromide, the oily product was identical with 1,2-dibromopropane. In the other two cases, the 1,2-dibromo derivative of the olefin which corresponded to the parent alkyl halide was obtained.

After adding 500–800 ml. of ice water containing about 50–80 ml. of concd. hydrochloric acid, the ether layer was separated, washed twice with water, and dried over anhydrous sodium sulfate. The solvent was removed and the residue distilled *in vacuo* to yield the strongly smelling sulfide.

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# Reaction of Methyl Bromide with Dimethylformamide

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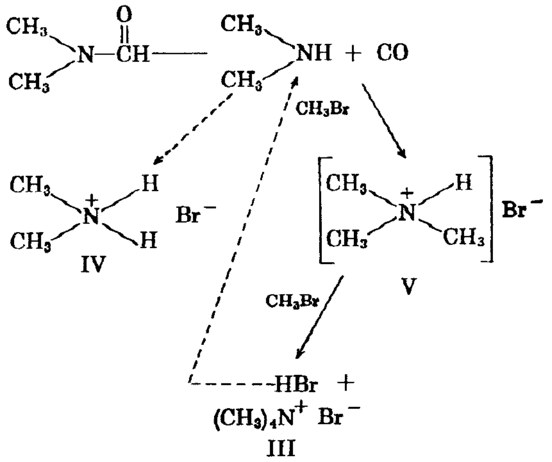
In attempts to quaternize the diamines, *N*-(5-dimethylamino-2-pentynyl)-8-methoxy-1,2,3,4-tetrahydroquinoline (I) and *N*-(4-dimethylamino-2-butynyl)-1,2,3,4-tetrahydroquinoline (II), the use of *N*,*N*-dimethylformamide (DMF) as the solvent appeared to be practicable; it was found by other investigators[1] that amines which resisted quaternization in other solvent systems often underwent facile quaternization in *N*,*N*-dimethylformamide. Treatment of I or II with an excess of methyl bromide in *N*,*N*-dimethylformamide in a sealed tube at 80° for twenty-four hours resulted in the separation of a white crystalline powder which after washing with hot isopropyl alcohol showed an elemental analysis corresponding to tetramethylammonium bromide (III). In an attempt to rationalize the formation of III, a mixture of methyl bromide and *N*,*N*-dimethylformamide was heated in a sealed tube for six days; the tube was opened and the white crystalline product was collected. This solid was found to consist of two compounds which after recrystallization were identified as tetramethylammonium bromide and dimethylammonium bromide (IV).

It is proposed that the two products were formed by decomposition of *N*,*N*-dimethylformamide into dimethylamine and carbon monoxide, and that the amines thus formed were quaternized by the methyl bromide as follows:



The evolution of carbon monoxide was confirmed by a positive reaction with phosphomolybdic acid–palladium chloride reagent solution.[2]

The identity of products III and IV was confirmed by comparison of their infrared spectra and melting points with those of known samples of the compounds. In subsequent experiments the molar ratio of *N*,*N*-dimethylformamide to methyl bromide was varied to study the effect on the yields of products. Maximum yields of 37% of IV (based on methyl bromide) were obtained when a molar ratio of eight parts of *N*,*N*-dimethylformamide to one part of methyl bromide was used. A negligible amount of IV was obtained when two parts of *N*,*N*-dimethylformamide and one part of methyl bromide were combined. It was of interest that no trimethylammonium bromide (V) could be isolated from any reaction mixture.

## EXPERIMENTAL

Dimethylformamide (Eastman White Label) purified by distillation from calcium hydride and contained in a 25-ml. Carey tube was cooled to −70° in a Dry Ice–acetone bath and the required amount of methyl bromide was added. The tube was then sealed and was placed in a heating jacket maintained at 80° for 6 days. The tube was cooled

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[1] C. K. Bradsher and H. Berger, *J. Am. Chem. Soc.*, 80, 930 (1958).

[2] F. Feigl, *Spot Tests in Organic Analysis*, Elsevier Publishing Co., New York, 1956, p. 327.

to room temperature and opened. The presence of carbon monoxide was detected by suspending a palladium chloride–phosphomolybdic acid solution[8] in a medicine dropper over the reaction mixture. In the presence of carbon monoxide the yellow solution turned blue. The crystals of quaternary salts were collected on a filter and washed with boiling anhydrous isopropyl alcohol; tetramethylammonium bromide (III) was insoluble in this solvent. It did not melt at 350°. Concentration of the isopropyl alcohol washings yielded white needles of dimethylammonium bromide (IV), m.p. 131–131.5°.

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## Ionization Constant of Hexanethiol from Solubility Measurements

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The ionization constant of hexanethiol has been determined from measurements of its solubility in aqueous solutions of varying *p*H. This method of determining the ionization constant is not in common use, even though it follows straightforwardly from well known principles. Potentiometric titration is the means most often used for determining ionization constants, but this method can be applied to most organic compounds only in mixed-solvent systems because of solubility limitations. The solubility method, on the contrary, can best be applied to sparingly soluble compounds and gives the value of the ionization constant in water.

When this investigation was begun, the only values for the ionization constants of alkanethiols in water had been reported by Yabroff.[1] This investigator examined the mercaptans from ethyl to butyl by potentiometric titration (*pK* 10.64 and 10.78, respectively) and the mercaptans from ethyl to heptyl (excepting hexyl) by partitioning between isooctane and 0.5*M* sodium hydroxide (*pK* 10.60 to 10.75; hexyl was not measured, but interpolation of the other data gives 10.7). Recently, Danehy[2] has reported the value 10.50 for ethanethiol. In 23% *tert*-butyl alcohol Fletcher[3] found 11.51 for butanethiol and 11.72 for octanethiol. In aqueous ethanol, Maurin and Paris[4] reported 12.0 for ethanethiol and 13.5 for hexanethiol. The last results are of uncertain significance, because they were estimated from the extent of reaction with indicators in aqueous ethanol, using the indicator constants determined in *water.* It seems unlikely that the difference between ethanethiol and hexanethiol would be as large as was reported by those investigators.

In addition to determining the ionization constant for hexanethiol in water by solubility measurements, the constant was determined by titration in 44.4% aqueous ethanol, and similar measurements were carried out for ethanethiol. Their significance will be discussed after the description of the experimental procedure.

### EXPERIMENTAL

*Materials.* Hexanethiol (I) used in the solubility measurements was an American Petroleum Institute standard sample obtained from the Chemical and Petroleum Research Laboratories, Carnegie Institute of Technology, Pittsburg, Pa., and certified to contain less than 0.1 mole % impurities. It was transferred to a number of smaller bulbs in the following way: the bulbs, of about 0.5-ml. capacity with long capillary necks, were placed in a vacuum desiccator, which was first evacuated and then filled with nitrogen; the bulbs were then placed neck down in the opened ampule of hexanethiol, the whole was put in the vacuum desiccator, and the procedure repeated. The pressure of nitrogen forced the hexanethiol into the bulbs, the capillary ends of which were then sealed.

Hexanethiol (II) used in the titrations was an Eastman Kodak White Label product which was redistilled under nitrogen; the middle one-third, boiling at 133–135° and 740 mm., was stored in small bulbs as described above. Iodimetric titration[5] indicated a purity of 88%.

Ethanethiol was an Eastman Kodak technical-grade product; it was redistilled and the fraction collected that boiled at 30–31° and 741 mm. The purity was 94%. It was stored like hexanethiol (II).

Nitrogen was a commercial product, passed through three successive gas washing bottles containing vanadous ion to remove oxygen[6] and one bottle containing ascarite to remove any acid vapors that could be carried over from the washing bottles.

The water used in the preparation of all solutions was doubly distilled, deaerated by boiling, and cooled with a stream of nitrogen bubbling through it. It was stored under nitrogen and dispensed with the aid of nitrogen under slight pressure.

Ethanol, 95% was diluted with an equal volume of water; such a mixture contains 44.4% ethanol by weight. It was deoxygenated by bubbling nitrogen through it, which had been passed through a solution of vanadous ion, ascarite, and a washing bottle containing 44.4% ethanol.

*Absorbancy coefficients.* Approximately 0.1 g. of hexanethiol (I) was weighed accurately and dissolved in 250 ml. of 0.1*M* sodium hydroxide; this was diluted fifty times, giving about a $5 \times 10^{-5}$ *M* concentration of mercaptan.

The absorbance was determined at 240 mμ with a Beckman Model DU spectrophotometer in a 1-cm. silica cell; the blank cell was filled with 0.1*M* sodium hydroxide. Six determinations gave an average value of 5290 ± 50.

The absorbance of hexanethiol in water at 240 mμ is negligible.

*Solubility of hexanethiol.* An excess of hexanethiol (I) was added to the buffer solution in a glass-stoppered flask and the air was displaced by nitrogen. The mixture was shaken by hand for 5 min. and put in a thermostat at 25 ± .05° for 0.5 hr. This procedure was repeated once. After shaking a third time, the mixture was allowed to stand in the thermo-

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[1] D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940).

[2] J. P. Danehy and C. J. Noel, *J. Am. Chem. Soc.*, **82**, 2511 (1960).

[3] W. H. Fletcher, *J. Am. Chem. Soc.*, **68**, 2726 (1946).

[4] J. Maurin and R. A. Paris, *Compt. rend.*, **232**, 2428 (1951).

[5] J. W. Kimball, R. L. Kramer, and E. E. Reid, *J. Am. Chem. Soc.*, **43**, 1199 (1921).

[6] L. Meites, *Polarographic Techniques*, Interscience, New York, page 34, (1955).