tonitrile. Even when the alkylation was not carried out under pressure but merely at the boiling point of ethyl bromide where the principal reaction is dialkylation leading to diethylacetonitrile, the yield of triethylacetonitrile was sufficiently high to serve as a convenient preparative method.

In the course of our study of this procedure we also examined the behavior of acetonitrile (1 mole) with ethyl bromide (excess) and sodamide (2–2.5 moles); acetonitrile with diethyl sulfate in benzene (no alkylation); alkylation of a mixture of acetonitrile with diethylacetonitrile; and the behavior of *n*-butyronitrile with ethyl bromide (excess) in presence of sodamide (2 moles). The best conditions for the preparation of triethylacetonitrile at ordinary pressure are concisely summarized below.

Triethylacetonitrile.—To a mixture of acetonitrile (61 g., 1.5 moles), ethyl bromide (408 g., 3.75 moles) and dry ether (100 ml.) in a creased 3-liter flask with high-speed stirrer was added a slurry of sodamide (117 g., 3 moles) in dry ether. This addition was effected under slight pressure of nitrogen during a one and one-half-hour period. Although no significant reaction occurred after this period, the mixture was stirred overnight and then cautiously treated with 50 ml. of alcohol, finally with water. After washing the ether solution with dilute sulfuric acid and finally with water, it was dried over magnesium sulfate and fractionally distilled at atmospheric pressure through a one-foot packed column. The products of mono, di and trialkylation were obtained as follows:

n-Butyronitrile	24.1 g.	0.348 mole	n^{21}_D 1.3838
Diethylacetonitrile	35.2 g.	0.362 mole	n^{20}_D 1.4021
Triethylacetonitrile	28.8 g.	0.23 mole	n^{20}_D 1.4219

Fractionation of the intermediate material and residue gave more of all three products.

Triethylacetic Acid.—Triethylacetonitrile (60.3 g.) mixed with 75% sulfuric acid (106 g.) was raised to a temperature of 150° with constant stirring over a period of one-half hour. The temperature was then maintained at 145–150° for twenty-two more minutes after which the contents of the flask were cooled to 50°. Solid sodium nitrite (47 g.) was added from an attached flask during a period of about one hour at 50–60°. After cooling, diluting with water, and extracting with ether, the latter contained both the desired acid and its amide. The former was separated from the latter by extraction of the ether solution with aqueous 6% potassium hydroxide; yield of triethylacetic acid 56.6 g., 81.5%, purified with little loss by distillation under reduced pressure, b. p. 104–105° at 5 mm., f. p. 35.1°; yield of triethylacetamide 11.3 g., 17.6%.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 29, 1948

The Reaction of Certain β-Aminomercaptans with Iodine in Ethanol

BY H. R. SNYDER AND ERNEST L. ELIEL

In a recent report[1] on the synthesis of substituted mercaptans the derivatives obtained by reaction of certain β-aminomercaptans with iodine in alcohol were regarded as sulfenyl iodides. Shortly after the appearance of the report Professor Norman Kharasch[2] kindly called to our attention the fact that the properties of the derivatives were not those to be expected of simple sulfenyl iodides and suggested that the substances were the dihydriodides of the disulfides formed by oxidation of the aminomercaptans.

A quantitative study of the reaction of alcoholic iodine with the mercaptan[1] [$C_6H_{12}NCH_2C(CH_3)_2SH$] obtained from β-pipecoline and isobutylene sulfide now has been made. The iodine consumption averaged 95% of that required for conversion of the mercaptan to the disulfide salt, or only 47.5% of the amount required for conversion to the sulfenyl iodide. The reaction also was carried out on a scale large enough to permit isolation of the product, conversion to the free disulfide by the action of sodium bicarbonate, distillation of the disulfide, and reconversion of the disulfide to the salt by treatment with hydriodic acid; the original salt was regenerated. The derivative previously obtained by the action of iodine on the aminomercaptan [$(C_4H_9)_2NCH_2C(CH_3)_2SH$] from di-*n*-butylamine and isobutylene sulfide was subjected to the same cycle (except that the free disulfide was not distilled). In this instance also the regenerated substance was identical with the original sample.

It thus appears certain that all the derivatives referred to as sulfenyl iodides in the previous report[1] are dihydriodides of diaminodisulfides having the general formula $[R_2NCH_2C(CH_3)_2S]_2 \cdot 2HI$. The previously recorded analyses of the substances are in good agreement with the theoretical values calculated on the basis of this structure.

Experimental[3]

Reaction of α,α-Dimethyl-β-(β-pipecolino)-ethyl Mercaptan with Iodine in Ethanol.—Samples of about 0.5 g. of the aminomercaptan[1] were dissolved in absolute ethanol and titrated with a standardized solution of iodine (0.1 *N*) in the same solvent. In four titrations the iodine consumption was 0.949, 0.950, 0.950 and 0.954 gram atoms per mole of mercaptan. The end-point was determined by the appearance of the iodine color. The preparative reaction was carried out essentially as described previously;[1] the product (85% yield) melted at 210.5–211.5 (dec.).

Anal. Calcd. for $C_{20}H_{42}N_2S_2I_2$: C, 38.22; H, 6.73. Found: C, 38.02; H, 7.00.

The free disulfide was obtained by the addition of 50 ml. of saturated aqueous sodium bicarbonate solution to a solution of 7 g. of the above salt in 200 ml. of hot water, extraction of the cooled solution with ether, drying of the ether solution with sodium sulfate, removal of the ether, and distillation. The liquid (yield 2.7 g., 64%) boiled at 155–156° (3 mm.); n^{20}_D 1.5146; mol. wt. (ebullioscopic in benzene), 328 (calcd., 372.7).

The dihydriodide was regenerated by the addition of 0.6 ml. of hydriodic acid (sp. gr. 1.5) to 0.55 g. of the disulfide in 10 ml. of absolute ethanol. The salt crystallized immediately as a solid melting at 211–212.5° (dec.); recrystallization from ethanol raised the melting point to 212–213° (dec.). A mixture of the recrystallized salt with that prepared from the aminomercaptan and iodine

---

(1) Snyder, Stewart and Ziegler, THIS JOURNAL, 69, 2672 (1947).

(2) Professor Norman Kharasch, the University of Southern California, Los Angeles; private communication, January 26, 1948.

(3) All melting points are corrected.

melted at 210.5–213° (dec.). The two specimens were identical in appearance under the microscope.

Experiment with the Dihydriodide of Di-[α,α-dimethyl-β-(di-*n*-butylamino)-ethyl] Disulfide.—The oil which separated when 0.15 g. of the product (previously obtained[1] by the action of iodine on the mercaptan) was treated with aqueous sodium bicarbonate was collected in ether. The solution was dried and the solvent was removed and replaced by absolute ethanol. Addition of concentrated hydriodic acid and ether caused the separation of 0.1 g. of the dihydriodide, m. p. 167.5–170.5 (dec.). After two recrystallizations from absolute ethanol and ether the salt melted at 174–176° (dec.) alone or mixed with the original salt of m. p. 173.5–175° (dec.). The two specimens were identical in appearance under the microscope.

NOYES LABORATORY
THE UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED MAY 12, 1948

Apparent Molar Volume of Sodium in Liquid Ammonia

By A. J. STOSICK[1] AND ELTON B. HUNT

In a series of communications Ogg[2] has reported the results of experiments with the unusual solutions of alkali metals in liquid ammonia. In one of his communications[2a] he reported that at a concentration of 3×10^{-3} molar, the molar volume of sodium was 700–1000 cc. These values are ten to fifteen times greater than the values reported by Kraus and co-workers[3] for more concentrated solutions. Since the data of Kraus, while indicating an abnormal molar volume, show no trend to larger values with increasing dilution, it seemed worth repeating measurements for dilute solutions. The error in our measurements is relatively large, since we designed our apparatus to accommodate the large effect reported by Ogg. However, our results definitely are not in accord with those of Ogg, but conform to those of Kraus. The experiments consisted in a direct measurement of the increase in volume of liquid ammonia when weighed amounts of sodium were added to form a uniform solution.

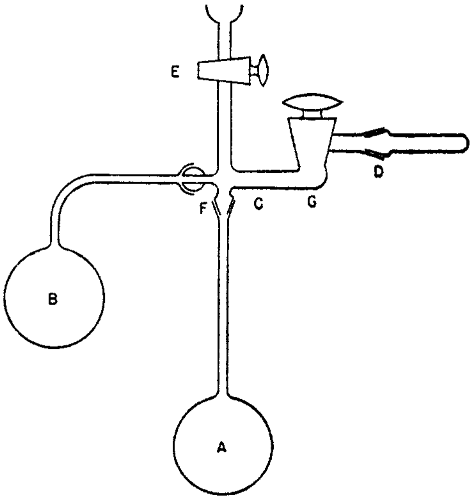

Fig. 1.

The apparatus (Fig. 1) consisted of two 100-cc. bulbs, with bulb A having a calibrated neck which served to measure the increase in volume. The whole unit was connected to a conventional vacuum line via stopcock E and a standard ball joint which permitted shaking the solution.

In the first experiment a freshly cut, massive piece of sodium (27.9 mg. in form of a cube with edge of about 3 mm.) was placed in the side-arm C and the system was quickly evacuated. Next ammonia from a concentrated sodium–ammonia solution contained in a trap on the vacuum line was distilled into bulb A. The stopcock E was then closed. The temperature of A was maintained at −44.5 ± 0.2° by means of an alcohol-bath in a large clear Dewar flask. After establishing constancy of the meniscus level, about half of the ammonia was distilled into B (previously at room temperature). This enabled the introduction of the sodium (by a magnetic pusher) to be made without splashing or "bumping" and permitted the solution to be stirred by shaking A. The ammonia in B was distilled back to A, B restored to room temperature, and A restored to −44.5°. The meniscus level was noted at intervals to be certain that constancy had been achieved. The observed rise of the meniscus, 3.0 ± 0.2 mm., the weight of the sodium, 27.9 mg., and the flask calibration lead to an apparent molar volume of 59 cc. for sodium, an excess of 36 cc. over 23 cc. for metallic sodium. The concentration of the solution was 1.1×10^{-2} molar. The precise measurements of Kraus indicate an excess volume of 41.0 to 43.5 cc. for concentrated solutions.

In the second experiment the side-arm at C was modified by the addition of an evacuable side chamber D to keep the sodium out of contact with ammonia gas until it was to be placed into solution. The side-arm had a large bore stopcock and an arrangement of magnetic pushers so that the sodium could be moved without touching stopcock grease. A second modification consisted in analyzing for the sodium remaining in A at the end of the experiment by means of a gasometric procedure. At the end of the experiment most of the ammonia was pumped from A, the temperature of A was raised to produce an ammonia pressure slightly over atmospheric. The flask A was detached at the joint F and transferred to a gasometric train where the remaining ammonia was pumped off. Dilute acid was introduced into A, the evolved hydrogen was flushed by means of carbon dioxide into a measuring vessel using concentrated potassium hydroxide as the confining fluid. Blank tests showed that this procedure introduced no gases which potassium hydroxide did not absorb.

In the second experiment the weighed amount of sodium, 5.3 mg., was placed in D and, after evacuation, was isolated by stopcock G. The subsequent steps were similar to the first experiment except for the final analysis for sodium. The temperature of A was maintained at −42.9 ± 0.1°, and no change (±0.2 mm.) was noted in the level of the meniscus. When correction is made for the ammonia gas which entered the evacuated chamber D, the meniscus rise is 0.5 ± 0.2 mm. The analysis for sodium indicated 3.0 mg., which must be taken as a minimum since no allowance was made for solubility loss of hydrogen in the gasometer. These data lead to an apparent molar volume of 52 cc. (5.3 mg. of sodium by weighing) or 92 cc. (3.0 mg. of sodium by analysis). The concentration of the solution was 2.1×10^{-3} molar or 1.2×10^{-3} molar, respectively.

It is clear that these results are not in accord with those of Ogg and conform to those of Kraus. Assuming the solutions to have the same coefficient of expansion as

---

[1] Present address: Department of Chemistry, University of Southern California, Los Angeles 7, California.

[2] Richard A. Ogg, Jr., (a) THIS JOURNAL, **68**, 155 (1946); (b) *J. Chem. Phys.*, **14**, 114, 295, 399 (1946); (c) *Phys. Rev.*, **69**, 668 (1946).

[3] Kraus, Carney, and Johnson, THIS JOURNAL, **49**, 2206 (1927).