methyl)-cyclohexanol[3] which can be isolated as the sulfate in 77–83% yield, as the acid sulfate in the same yield or as the hydrochloride in 76% yield.

For the preparation of suberone it is not necessary to isolate the 1-(aminomethyl)-cyclohexanol. The reaction mixture obtained from the electrolytic reduction was treated directly with sodium nitrite; the yield of suberone, based on 1-(nitromethyl)-cyclohexanol, was 50–57%.

Experimental Part

1-(Nitromethyl)-cyclohexanol.—A solution prepared from 98.1 g. (1 mole) of cyclohexanone,[4] 61.0 g. (1 mole) of nitromethane[4] and 600 cc. of methanol was stirred, cooled to 5° and a solution of 50.0 g. (1.25 moles) of sodium hydroxide in 75 cc. of water was added at such a rate that the temperature of the mixture could be maintained below 10° by the use of an ice-bath. Precipitation of the colorless sodium derivative of the condensation product began after about one-third of the alkali had been added. After complete addition of the alkali (about one-half hour was required), the thick suspension was stirred and cooled for one-half hour. The sodium derivative was then filtered, suspended in 500 cc. of water, stirred and 80 cc. of acetic acid added. The mixture was extracted three times with 200-cc. portions of ether and the combined ether extracts were washed with sodium bicarbonate solution and then with water until the water became *neutral*. The ether solution was dried with magnesium sulfate and the solvent removed on a steam-bath. Upon distillation, 106 g. (67%) of product was obtained; b.p. 129–133° (19 mm.)[5]; d^{20}_4 1.1589; n^{20}_D 1.4875. In other experiments the yields varied from 64–72%.

1-(Aminomethyl)-cyclohexanol.—The apparatus employed for the reduction consisted of three cells (see drawing) connected in series. The cathode chamber of each cell consisted of a lead-plate cathode and a cylindrical porous cup which was 8 cm. in diameter and 12.5 cm. in height. The cathode chamber was placed between the two lead plates of the anode which was immersed in about 700 cc. of 10% sulfuric acid contained in a 2-liter beaker.

1-(Nitromethyl)-cyclohexanol (53.0 g., $^1/_3$ mole) was added in two equal portions to each porous cup which contained 400 cc. of 10% sulfuric acid; the first portion was added at the beginning of the operation, the second 4 hours later. The material was kept in suspension in the acid by efficient mechanical stirring. Reduction of the nitro alcohol was effected with an 8-ampere current and a current density of 0.067 ampere/cm.^{2} for a period of 9 hours. Continuous water-cooling around the beakers maintained the operating temperature of each cell at approximately 30° throughout the procedure.

The product was isolated as the sulfate (a), acid sulfate (b) or hydrochloride (c). In each instance the reaction mixtures from 3 cells were combined.

(a) The reaction mixture, if necessary adjusted to *p*H 4–5, was filtered, the filtrate evaporated to dryness and the neutral sulfate was recrystallized several times from ethanol-water; yield 137–148 g. (77–83%); m.p. 266–267°.

Anal. Calcd. for $2C_7H_{15}ON\cdot H_2SO_4$: N, 7.87; S, 9.00. Found: N, 7.86; S, 9.13.

(b) The reaction mixture was treated with sulfuric acid until the *p*H was 1–2, filtered, the filtrate evaporated to dryness and the acid sulfate was recrystallized several times from ethanol-ether; yield 175 g. (77%); m.p. 132–133°.

Anal. Calcd. for $C_7H_{15}ON\cdot H_2SO_4$: N, 6.17; S, 14.11. Found: N, 6.12; S, 14.28.

(c) The *p*H of the reaction mixture was adjusted to 4–5 and after the filtered solution had been evaporated almost to dryness, it was made alkaline by the addition of solid sodium hydroxide. The mixture was extracted with ether and the extract, after it had been dried with magnesium sulfate, was treated with hydrogen chloride. The precipitated hydrochloride was recrystallized several times from absolute ethanol; yield 126 g. (76%); m.p. 213–214°.[6]

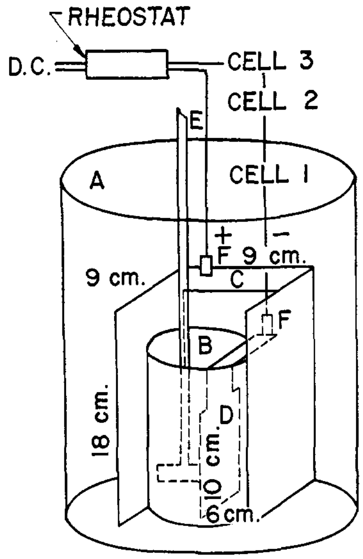

Fig. 1.—A, beaker; B, porous cup; C, lead anode; D, lead cathode; E, stirrer; F, clamp.

Suberone.—The reaction mixture, obtained from the electrolytic reduction, was adjusted to a *p*H of 4, stirred, cooled to 0–5° and maintained at this temperature during the dropwise addition of 83 g. (1.2 moles) of sodium nitrite dissolved in 300 cc. of water. A pale yellow oil began to separate at the surface of the solution shortly after the addition of the nitrite was begun. During a two-hour period the mixture was stirred, allowed to warm to room temperature and the *p*H was maintained at 5–6. The mixture was heated on a steam-bath, under a reflux condenser, for one hour. The oily layer was separated, the aqueous layer extracted with ether, the oil and extract combined, and the solution was washed with aqueous sodium bicarbonate and then with water until the latter became neutral. The ether solution was dried with magnesium sulfate, the solvent removed and the residue fractionated. The suberone (56–64 g., 50–57%) boiled at 66–70° (16 mm.); d^{20}_4 0.9490; n^{20}_D 1.4608; 2,4-dinitrophenylhydrazone, m.p. 146–147°.[7]

---

[3] This compound, in the form of the acetate, was obtained by Hyp J. Dauben, Jr., *et al.*, ref. 1, from the corresponding nitromethyl derivative in 91% yield by the use of a Raney nickel catalyst. However, a small portion of the isolated acetate was *not* entirely pure.

[4] The Eastman Kodak Company product was used without further purification.

[5] Hyp J. Dauben, Jr., *et al.*, ref. 1, b.p. 132–133° (18.5 mm.).

[6] B. Tchoubar (*Bull. soc. chim. France*, 160 (1949)), m.p. 190°; M. W. Goldberg and H. Kirchensteiner (*Helv. Chim. Acta*, **26**, 293 (1943)), m.p. 210–212°; ref. 3, m.p. 215–216°.

[7] O. L. Brady (*J. Chem. Soc.*, 756 (1931)), m.p. 148°; ref. 3, m.p. 146°.

College of Pharmacy
University of Michigan
Ann Arbor, Michigan

Explosion in the Synthesis of N^{15}-Labeled Urea

By James Buzard and Charles Bishop

Received January 4, 1952

For some time now we have been using the method of Cavalieri, Blair and Brown[1] for the synthesis of uric acid containing N^{15} in the 1- and 3-positions. The first step of this method is the synthesis of urea from $N^{15}H_4NO_3$ and diphenyl carbonate, using copper powder as a catalyst. Ammonia containing N^{15} is generated, swept with nitrogen gas through a drying tower, and into a bomb tube of Pyrex glass containing the diphenyl carbonate and copper powder. The bomb tube is immersed in liquid nitrogen throughout the proce-

---

[1] L. F. Cavalieri, V. E. Blair and G. B. Brown, This Journal, **70**, 1240 (1948).

dure in order to freeze out the ammonia. After generating ammonia for several hours the bomb tube is transferred to a Dry Ice-bath, sealed off and then heated in a hot water-bath at 90–100° for four hours.

Following these directions carefully we were able to make many successful runs. Then, without explanation, the procedure began to result in explosion of the bomb tube and loss of its contents. We have had bomb tubes explode in the water-bath and in the Dry Ice-bath. After the loss of several dewar flasks we omitted the Dry Ice-bath and sealed the bomb tube in the liquid nitrogen bath. We observed that after the bomb tube had been sealed and removed from the bath, the tube first became covered with frost and that suddenly this frost began to melt. This suggested that a highly exothermic reaction had begun. If the bomb tube did not explode shortly thereafter, it usually did not explode at all.

Two possible explanations for the explosions suggested themselves. One was that due to the efficiency of the cooling system around the bomb tube and the duration of the process, there might have been some slight condensation of the sweeping nitrogen. A small amount of liquid nitrogen inside the bomb tube after it had been sealed off could give rise to many atmospheres of pressure when the tube was warmed. The other explanation was that tank nitrogen and ammonia, in the presence of copper and an organic compound might give rise to traces of an unstable compound which would detonate spontaneously as the temperature rose.

It was felt that sweeping with tank helium ("Medical Helium Gas," Liquid Carbonic Corp.) rather than tank nitrogen might eliminate both of these possibilities since helium liquifies well below the boiling point of nitrogen and is not known to form compounds. Since this modification was adopted, thirty successful runs have been made. Insofar as we can determine, no other conditions have been altered.

Drs. Cavalieri and Brown have indicated in a personal communication a third possible explanation which should be offered for these explosions. They point out that "oxygen is readily condensed from the air in tubes cooled with liquid nitrogen, and a small amount of oxygen condensed with organic matter can lead to violent explosions. Condensation of oxygen could thus occur; if the vessel is cooled before the flow of inert gas is begun, if the tank nitrogen contains appreciable oxygen, or if the period of time and length of tubing is such that there is appreciable diffusion of air oxygen through the tubing leading from the tank. Commercial nitrogen invariably contains small amounts of oxygen and this may vary from tank to tank, but helium seems less likely to contain it."

Whether these explanations are valid remains to be seen. We offer this communication so that others may be aware of the potential danger which may be involved in this synthesis and in the hope of obtaining a more rigorous explanation.

CHRONIC DISEASE RESEARCH INSTITUTE
UNIVERSITY OF BUFFALO MEDICAL SCHOOL
BUFFALO 14, NEW YORK

Physical Properties of Thioacetic Acid and Diacetyl Sulfide

BY W. W. CROUCH

RECEIVED DECEMBER 8, 1951

In the course of experimental work on sulfur compounds, products were isolated which were believed to be thioacetic acid and diacetyl sulfide (thioacetic anhydride); however, considerable disagreement is found in the literature regarding even the boiling points of these commonplace materials and little information is available as to other physical properties. In the purification of the thioacetic acid by fractionation at atmospheric pressure, nearly all of the product was recovered at an overhead temperature of 86°, uncorrected, and further refractionation of the purest cuts led to no change in the boiling point. The boiling point for this product listed in Beilstein, Heilbron and the other conventional chemical handbooks is 93°, apparently based on the data of Kekulé,[1] although Clark and Hartman[2] reported a boiling range of 88 to 91.5° for their product. It was suspected that an azeotrope-forming agent might be present in our acid; however, no such impurity could be separated, and after purifying the product further by dissolving in caustic, extracting with ether to remove any inert material and recovering the acid, no change in boiling point was observed. Furthermore, fractionation of samples of Eastman thioacetic acid and thioacetic acid prepared in the conventional way by the reaction of hydrogen sulfide with acetic anhydride[2] also gave products boiling at an overhead temperature of 86°, uncorrected. Since their behavior during distillation, sulfur contents, neutral equivalents and infrared analyses all indicated the products to be uncontaminated by appreciable quantities of other materials, it was concluded that the boiling point of 93° reported in the literature is in error. The properties of the purified thioacetic acid are as follows: b.p. (corrected) 87.5° (760 mm.); d^{20}_4 1.0696; and $n^{20}\text{D}$ 1.4636. It freezes sharply to a white, crystalline solid at a temperature of approximately −75°.

Anal. Calcd. for C_2H_4OS: S, 42.12; neut. equiv., 76.11. Found: S, 42.03; neut. equiv., 75.62.

The infrared examination[3] of thioacetic acid was of particular interest. A strong absorption band was found at 3.9 microns characteristic of the sulfhydryl group, but no bands were obtained at 2.9 and 10.4 μ indicating the absence of the —OH and $-\underset{|}{C}{=}S$ groups, respectively. It was concluded that the acid is substantially completely in the thiol rather than the thion form, confirming the observations of Bloch.[4]

The boiling point of diacetyl sulfide at atmospheric pressure has been reported as 121°,[1] 119–120°[5] and 156–158°.[6] The last figure was found to be approximately correct; how-

---

[1] F. A. Kekulé, *Ann.*, **90**, 311.

[2] H. T. Clarke and W. W. Hartman, THIS JOURNAL, **46**, 1731 (1924).

[3] Infrared studies were performed and interpreted by Vernon Thornton of the Physics Branch of this Laboratory.

[4] F. Bloch, *Compt. rend.*, **206**, 679 (1938).

[5] H. Tarugi, *Gazz. chim. ital.*, **27**, II, 157 (1897).

[6] S. H. Davies, *Ber.*, **24**, 3548 (1891).