The authentic sample of 1-benzyl-1-phenylhydrazine was obtained from the reaction of benzyl chloride and phenylhydrazine.[38]

N-Ethylbenzimido Chloride.—This substance was obtained in 80% yield by the method of von Braun and Pinkernelle.[39]

Ethyl N-Ethylbenzimidate.—The product, obtained in 71% yield by the method of Landers,[40] was a colorless liquid, b.p. 101–102° (12 mm.), $n^{24}\text{D}$ 1.5020, d^{20}_4 0.960 (b.p. lit.[40] 105° (11 mm.)).

Hydroxamic Acid Test.—When the test was carried out as described by Buckles and Thelen[18] for esters (Test B in their paper), a pale yellow solution was obtained, as is customary in a negative result.

When X was heated with 20% hydrochloric acid for a few seconds, the mixture became homogeneous, then separated again into layers with an accompanying wintergreen-like odor of ethyl benzoate. Subjection of the new organic layer to Test B of Buckles and Thelen resulted in a strong wine color, a positive test for the presence of an ester. Since imido esters are readily converted to esters of carboxylic acids by the action of mineral acids,[40] these observations confirmed the structure of X.

When X was heated with hydroxylamine hydrochloride for a few seconds, the odor of ethyl benzoate was detected and a positive result was observed on application of Test B.

In a hydroxamic acid test employing the higher-boiling propylene glycol as the solvent,[41] X gave a positive result.

Reaction of Ethyl N-Ethylbenzimidate (X) with Lithium Aluminum Hydride.—The procedure was similar to that previously described.[2] Hydride: 2.3 g. (0.06 mole) in 100 ml. of dry tetrahydrofuran; X: 17.7 g. (0.1 mole) in 75 ml. of tetrahydrofuran. At the boiling point the initially colorless solution assumed a yellow-green hue, which disappeared on cooling the reaction mixture at the end of the 3-hr. reflux period. From distillation of the crude material through a short Vigreux column two products were obtained. The lower boiling material, b.p. 82–85° (11 mm.), had the properties of N-benzyl-N-ethylamine (XI) (lit.[42] b.p. 82–83° (15 mm.)). The yield was 6.6 g. (49%).

Treatment of a sample in pet. ether (b.p. 60–70°), with phenyl isothiocyanate, yielded white crystals. After one crystallization from a mixture of benzene and pet. ether (b.p. 60–70°) and three crystallizations from alcohol-water mixtures, the white needles melted at 94–95° and had the composition of N-benzyl-N-ethyl-N′-phenylthiourea.

Anal. Calcd. for $C_{16}H_{17}N_2S$: C, 71.06; H, 6.71; N, 10.37. Found: C, 71.22; H, 6.42; N, 10.36.

The higher boiling product, b.p. 97–99° (10 mm.), $n^{24}\text{D}$ 1.5020, was starting material X.

Anal. Calcd. for $C_{11}H_{15}NO$: N, 7.91. Found: N, 8.22.

It gave a negative result with the hydroxamic acid test, but on warming a sample with dilute hydrochloric acid the odor of ethyl benzoate appeared, and after being made basic, the mixture gave a positive test for the presence of an ester. Although 1.2 g. (7%) of pure material was isolated in the last fraction of the distillation, the presence of X in each of the intermediate fractions was revealed by the odor of ethyl benzoate detected when a sample of each fraction was warmed with dilute hydrochloric acid. From the refractive indexes it is estimated that at least 3% of X was present. The hold-up from the distillation also yielded the odor of wintergreen on treatment with acid and probably consisted mainly of X. Thus the total quantity of unreacted X is at least 10% of that used in the reaction.

The Behavior of Ethyl N-Ethylbenzimidate (X) in Base. (a) Aqueous Sodium Hydroxide.—A heterogeneous mixture of 40 ml. of 25% sodium hydroxide solution and 5 ml. (4.8 g.) of X was refluxed for 7 hr., cooled and extracted thrice with 25-ml. portions of ether. No precipitate formed when the aqueous solution was acidified with 20% hydrochloric acid. The combined, dried ether extracts were distilled, yielding 3.0 g. of X (63% recovery). The hold-up also contained X.

(b) Potassium Hydroxide in Aqueous Ethanol.—X (4.8 g.) was dissolved in a solution of 8 g. of potassium hydroxide in 55 ml. of 69% ethanol and boiled under reflux for 4 hr. The cooled solution was poured into 100 ml. of water and then extracted thrice with 25-ml. portions of ether. No precipitate was obtained when the aqueous solution was acidified. Distillation of the combined, dried extracts yielded 1.0 g. (21%) of X and 1.0 g. (25%) of colorless liquid, b.p. 159–161° (11 mm.). The latter crystallized on standing and melted at 68–69°. Its mixture with N-ethylbenzamide (m.p. 69–71°) melted at 69–71°.

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(38) G. Minunni, *ibid.*, **22** [II], 217 (1892).

(39) J. v. Braun and W. Pinkernelle, *Ber.*, **67B**, 1218 (1934).

(40) G. D. Landers, *J. Chem. Soc.*, **83**, 320 (1903).

(41) S. Soloway and A. Lipschitz, *Anal. Chem.*, **25**, 898 (1952).

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, RADIATION LABORATORY, LIVERMORE SITE]

Some Methylhydrazonium Salts; An Improved Synthesis of Tetramethylhydrazine[1]

BY ROBERT T. BELTRAMI AND EUGENE R. BISSELL

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1,1-Dimethyl-2-formylhydrazine, 1-formyl-1,2,2-trimethylhydrazine, pentamethylhydrazonium iodide and bromide, 1-formyl-2,2,2-trimethylhydrazonium iodide and 1-formyl-1,2,2,2-tetramethylhydrazonium iodide have been synthesized. A new synthesis of trimethylhydrazine and tetramethylhydrazine is reported.

Although tri-[2] and tetra-[3] methylhydrazonium salts have been known for some time, the preparation of the pentamethyl salts has not been reported due, no doubt, to the inability of earlier workers to prepare the necessary precursor, tetramethylhydrazine, the synthesis of which has only recently been reported.[4] Various attempts to prepare pentamethylhydrazonium salts from other precursors have been unsuccessful. Direct alkylation of hydrazine with methyl halides, methyl *p*-toluenesulfonate, trimethyl phosphate or trimethyl phosphite produced only trimethylhydrazonium salts.[2,5] Likewise alkylation of *sym*-dimethylhydrazine produced tetramethylhydrazonium salts.[3] Attempted alkylation of trimethylhydrazonium iodide with methyl iodide resulted in cleavage of the N–N bond to produce tetramethylammonium iodide.[2]

The work of Class, Aston and Oakwood[4] has now made available the necessary tetramethylhydrazine, but their method is erratic and affords

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(1) This work was performed under the auspices of the Atomic Energy Commission, Contract W-7405-eng-48.

(2) C. Harries and T. Haga, *Ber.*, **31**, 56 (1898).

(3) H. Wieland and E. Schlamberg, *ibid.*, **53B**, 1329 (1920).

(4) J. B. Class, J. G. Aston and T. S. Oakwood, THIS JOURNAL, **75**, 2937 (1953).

(5) F. Klages, G. Nober, K. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

very low yields (0–6% over-all). This paper reports a somewhat improved synthesis of tetramethylhydrazine together with its reaction with methyl iodide to form pentamethylhydrazonium iodide. The conversion of this salt to the corresponding bromide as well as the preparation of two formylmethylhydrazonium iodides is also reported.

Both *unsym*-dimethylhydrazine and trimethylhydrazine react with methyl formate to yield, respectively, the previously unknown 1,1-dimethyl-2-formylhydrazine and 1-formyl-1,2,2-trimethylhydrazine. These formyl derivatives are readily reduced by lithium aluminum hydride, the former to trimethylhydrazine and the latter to tetramethylhydrazine. The facile reduction of 1,1-dimethyl-2-formylhydrazine is in marked contrast to the results of Hinman[6] in the lithium aluminum hydride reduction of other 1,1-dialkyl-2-acylhydrazines.

Tetramethylhydrazine reacts nearly quantitatively with methyl iodide with the liberation of considerable amounts of heat to yield pentamethylhydrazonium iodide. The iodide is readily converted by the action of an aqueous suspension of silver oxide to the corresponding hydroxide which on neutralization with hydrobromic acid yields the bromide. X-Ray analysis shows that both the iodide and the bromide have a face-centered-cubic structure with a_0 = 10.06 and 9.666 Å., respectively. They are nearly identical in crystal structure with the corresponding tetraalkylammonium analogs, isopropyltrimethylammonium iodide and bromide which are face-centered-cubic with a_0 = 10.09 and 9.720 Å.

Both of the formylhydrazine derivatives mentioned above also react with methyl iodide to give crystalline quaternary derivatives. The structure of that from 1,1-dimethyl-2-formylhydrazine was confirmed by its acid hydrolysis to the known trimethylhydrazonium iodide.

Experimental[7]

1,1-Dimethyl-2-formylhydrazine.—Equal weights of *unsym*-dimethylhydrazine[8] and methyl formate were stored together at room temperature for several days. Cooling overnight at −18° resulted in crystallization of the product which was removed by filtration and washed with petroleum ether (30–60°), yield 63.5%, m.p. 50–52°. The analytical sample was recrystallized several times from ether and sublimed under vacuum, m.p. 57.8°. *Anal.* Calcd.: C, 40.89; H, 9.15; N, 31.80. Found: C, 41.00; H, 8.99; N, 31.98.

1-Formyl-1,2,2-trimethylhydrazine.—Trimethylhydrazine (40.0 g., 0.53 mole) and methyl formate (100 ml., 97.5 g., 1.51 moles) were stored together at room temperature for several days. Fractionation at 20 mm. through a 15″ vacuum jacketed Vigreux column of the liquid remaining after stripping off the volatile components at atmospheric pressure yielded 36.7 g. (66.6%) of colorless liquid, b.p. 70–73° (20 mm.). The analytical sample was twice redistilled, once at 20 mm. and once at atmospheric pressure, b.p. 171, $n^{20}\text{D}$ 1.43885, d_{23} 0.952. *Anal.* Calcd.: C, 47.03; H, 9.87; N, 27.43; *MR*, 28.07. Found: C, 47.29; H, 9.87; N, 27.53; *MR*, 28.21.

Trimethylhydrazine.—A solution of 20.7 g. (0.24 mole) of 1,1-dimethyl-2-formylhydrazine in 150 ml. of sodium-dried ether was added dropwise and with stirring to a suspension of 10 g. of lithium aluminum hydride in 200 ml. of sodium-dried ether under an argon atmosphere. After stirring for an additional 2 hours at room temperature the reaction mixture was decomposed by addition of 20 ml. of ethyl acetate followed by 250 ml. of 6 *N* hydrochloric acid. The ether layer was separated and discarded, and the aqueous layer was concentrated under reduced pressure to about 125 ml. The concentrate was added dropwise to a hot mixture of 280 g. of sodium hydroxide and 75 ml. of water, the liberated trimethylhydrazine being distilled off as fast as formed. The distillate was saturated with solid sodium hydroxide keeping the temperature below 30° by external cooling. The organic phase was separated, dried over fresh sodium hydroxide and fractionated through a 15″ vacuum jacketed Vigreux column to yield 9.06 g. (63.8%) of trimethylhydrazine, b.p. 59–61°, $n^{25.2}\text{D}$ 1.39983, d_{25} 0.765.

Tetramethylhydrazine.—This compound was obtained in 55% yield by lithium aluminum hydride reduction of 1-formyl-1,2,2-trimethylhydrazine in substantially the same manner as for trimethylhydrazine, b.p. 71–72°, $n^{25.2}\text{D}$ 1.40138, d_{24} 0.768.

Pentamethylhydrazonium Iodide.—Pentamethylhydrazonium iodide was obtained in nearly quantitative yield by careful addition of one equivalent of methyl iodide to a cooled methanolic solution of tetramethylhydrazine. The precipitated salt, m.p. 186–188° dec., was recrystallized several times from ethanol, m.p. 222–223° dec., X-ray density 1.500. *Anal.* Calcd.: C, 26.10; H, 6.57; N, 12.18; I, 55.16. Found: C, 25.86; H, 6.47; N, 12.07; I, 54.96.

Pentamethylhydrazonium Bromide.—Pentamethylhydrazonium iodide was converted to its hydroxide by shaking an aqueous solution with an excess of solid silver oxide. Filtration, neutralization with concd. hydrobromic acid and concentration to dryness yielded the crude bromide, m.p. 220–221° dec., which was purified by recrystallization from ethanol, m.p. 223–224° dec., X-ray density 1.3456. *Anal.* Calcd.: C, 32.79; H, 8.26; N, 15.30. Found: C, 32.92; H, 8.36; N, 15.65.

1-Formyl-2,2,2-trimethylhydrazonium Iodide.—Methyl iodide (14.1 g., 0.1 mole) was added slowly to a solution of 8.8 g. (0.1 mole) of 1,1-dimethyl-2-formylhydrazine in 5 ml. of methanol. On cooling the reaction mixture, the hydrazonium iodide crystallized out in nearly quantitative yield. It crystallized from ethanol as colorless needles, m.p. 166–167°. *Anal.* Calcd.: C, 20.88; H, 4.82; N, 12.18. Found: C, 21.03; H, 4.90; N, 12.08.

1-Formyl-1,2,2,2-tetramethylhydrazonium Iodide.—Equivalent amounts of 1-formyl-1,2,2-trimethylhydrazine and methyl iodide were stored together at room temperature for several days. The crystal mass thus formed was washed with ether and recrystallized several times from absolute ethanol, m.p. 180–181° dec. *Anal.* Calcd.: C, 24.60; H, 5.37; N, 11.48. Found: C, 24.82; H, 5.38; N, 11.56.

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(6) R. L. Hinman, Abstracts, 128th Annual Meeting of the A.C.S., Minneapolis, Minn., Sept., 1955, p. 69-O.

(7) Melting points are corrected; boiling points are uncorrected.

(8) Metalectro Corporation, Laurel, Maryland.