the higher temperature decomposition into styrene and sulfur occasionally occurred.

Pure styrene sulfide in a clean glass container can be stored for at least as long as two days at room temperature, and for ten days at 5–10° under anhydrous conditions, without its showing noticeable signs of polymerization.

Anal. Calcd. for C_8H_8S: C, 70,54; H, 5.92; S, 23.55; mol. wt., 136. Found: C, 70.15; H, 6.22; S, 23.55; mol. wt. (cryoscopic in benzene), 132.

2-Imino-3-carbethoxy-4(or 5)-phenylthiophane.—One-tenth mole (13.6 g.) of styrene sulfide was reacted with the sodium salt of ethyl cyanoacetate by the method described by Snyder and Alexander.[3] The crude product (20 g.) contained much polymeric material. The product was recrystallized from xylene–heptane solution to a constant melting point of 94–95°.

Anal. Calcd. for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.46; H, 5.88; N, 5.30.

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The Exchange of Hydrogen Gas with Lithium and Sodium Borohydrides

BY W. G. BROWN, L. KAPLAN AND K. E. WILZBACH

The alkali metal borohydrides are effective reducing agents for a variety of organic compounds;[1,2] in some cases[3,4] they are preferred to lithium aluminum hydride because of their greater selectivity. The isotopically-labeled borohydrides would, therefore, be useful reagents for the introduction of deuterium or tritium into organic compounds. Although labeled borohydrides may be prepared[5] from the corresponding hydrides,[6,7] or from labeled diborane,[8] the direct exchange of the solid borohydrides with hydrogen gas has been found to provide a more simple route to the isotopic compounds. Exchange, leading to approximately statistical isotopic distribution, occurs at a convenient rate with lithium borohydride at 200° and with sodium borohydride at 350°. Thermal decomposition is negligible in both cases.

TABLE I

EXCHANGE OF HYDROGEN WITH ALKALI METAL BOROHYDRIDES

	Metal borohydride			Hydrogen				
	Mg. atoms	Microcuries tritium		Mg. atoms	Microcuries tritium			
Run	H	Init.	Final	H	Init.	Final	T, °C.	t, hr.
			Lithium borohydride					
3	16.36	0	0[a]	1.309	28.9	28.7	95	89
4	16.36	0	26.0	1.222	27.6	1.77	200	120
1	10.46	0	8.4	1.238	28.1	19.7	200	3
2	10.46	8.4	32.5	1.252	28.2	4.14	200	16
9	16.36	23.1	21.7	1.377	0	1.35	200	66
			Sodium borohydride					
10	20.46	0	4.6	1.143	23.9	19.3	300	16
11	20.46	4.6	9.3	0.778	17.3	12.6	300	64
12	12.73	0	10.8	0.649	12.3	1.51	325	92
13	14.44	0	9.1	0.661	14.5	5.44	350	8
14	22.27	0	12.3	0.619	13.1	0.76	375	3.5

[a] Within experimental error.

The results of a number of exchange experiments, traced with tritium, are shown in Table I. The amount of tritium in the solid was calculated from the change in tritium content, measured by ion current, of the gas. The calculated values agreed well with the isotopic composition of benzyl alcohol obtained by reduction of benzaldehyde with lithium borohydride in one case and with that of hydrogen from the hydrolysis of sodium borohydride in another.

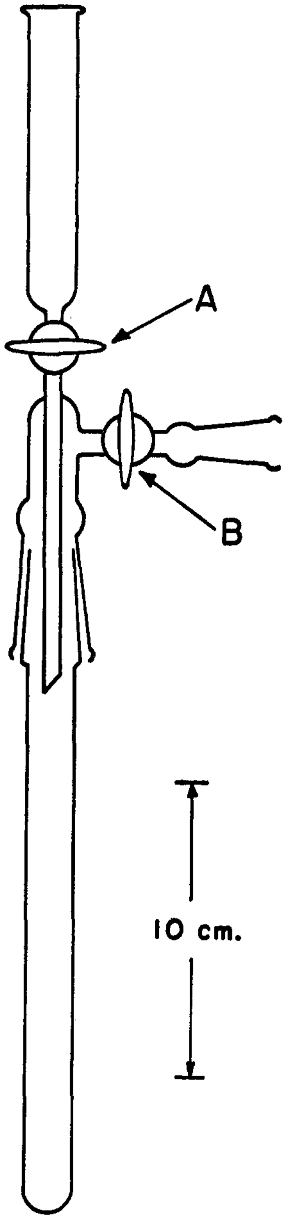

Fig. 1.—Apparatus for borohydride reactions.

Experimental

Exchange Reaction.—A sample of lithium or sodium borohydride, purified[9] by recrystallization, was transferred in a dry-box to a Pyrex tube of 25 cc. capacity (Fig. 1). A nickel foil liner was used in experiments with sodium borohydride to prevent decomposition of the borohydride by glass. The sample was heated with tank hydrogen for one hour at the temperature of the subsequent exchange experiment. The reaction vessel was evacuated through stopcock B, filled with a measured volume of a stock hydrogen–tritium mixture, and heated under the conditions shown in Table I. The quantity of gas remained essentially unchanged during the exchange reaction although a small increase had been observed during the preheating. The gas was then transferred to an evacuated Borkowski-type[10] ion chamber and diluted to atmospheric pressure with tank hydrogen. The ion current collected at 500 volts was measured with a dynamic condenser electrometer. A factor of 2.1×10^{-17} coulomb per disintegration was used to convert ion currents into disintegration rates.

Reduction of Benzaldehyde with Lithium Borohydride.—A solution of the lithium borohydride from Run 2, Table I, was prepared by adding 5 ml. of tetrahydrofuran through stopcock A. The solution was maintained at 20° by cooling while 1.3 g. of benzaldehyde in 5 cc. of tetrahydrofuran was added gradually to the still partially evacuated vessel. Solvent and excess benzaldehyde were removed by evacuation and the residue was hydrolyzed with dilute sodium hydroxide. The product was extracted with

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[1] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

[2] R. F. Nystrom, S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 3245 (1949).

[3] M. L. Wolfrom and H. B. Wood, *ibid.*, **73**, 2933 (1951).

[4] N. L. Wendler, Huang-Minlon and M. Tishler, *ibid.*, **73**, 3818 (1951).

[5] H. I. Schlesinger and H. C. Brown, U. S. Patents 2,461,661 to 2,461,663, Feb. 15, 1949; *C. A.*, **43**, 4684 (1949).

[6] C. G. Shull, E. O. Wollan, G. A. Morton and W. L. Davidson, *Phys. Rev.*, **73**, 842 (1948).

[7] K. E. Wilzbach and L. Kaplan, THIS JOURNAL, **72**, 5795 (1950).

[8] F. J. Norton, *Science*, **111**, 202 (1950).

[9] W. D. Davis, L. S. Mason and G. Stegeman, THIS JOURNAL, **71**, 2777 (1949).

[10] C. J. Borkowski, Atomic Energy Commission document MDDC 1099, declassified June 12, 1947.

benzene and was isolated by fractional condensation of the mixture on a vacuum line. The benzyl alcohol weighed 1.03 g., 91% of the quantity expected from the equation

$$4C_6H_5CHO + LiBH_4 \longrightarrow LiB(OCH_2C_6H_5)_4$$

The benzyl alcohol was analyzed by combustion, and the ion current of hydrogen obtained from the water of combustion was determined.

Found: C, 77.29; H, 7.46; microcuries tritium per millimole hydrogen, 3.12. Expected: C, 77.74; H, 7.46; microcuries tritium per millimole hydrogen, 3.11.

Hydrolysis of Sodium Borohydride.—The sodium borohydride from Run 13, Table I, was freed from possible decomposition products by dissolution in isopropylamine. The clarified solution was evaporated and the residue was hydrolyzed, in an evacuated vessel, by addition of dilute hydrochloric acid. The generated hydrogen was freed from water vapor, measured manometrically, and assayed for tritium. The yield of hydrogen was 13.70 millimoles with a specific activity of 0.621 microcurie per millimole; the values expected from the equation

$$NaBH_4 + 3H_2O + HCl \longrightarrow H_3BO_3 + 4H_2 + NaCl$$

were 14.44 millimoles and 0.63 microcurie per millimole.

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Polymerization of Tris-β-nitroxyethylamine

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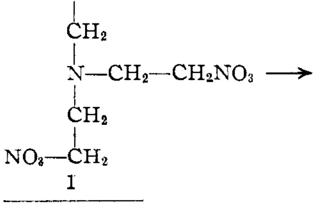
The preparation of tris-β-nitroxyethylamine has been described briefly.[1,2] We have obtained the compound by another method and confirmed the report[1] that it is unstable.

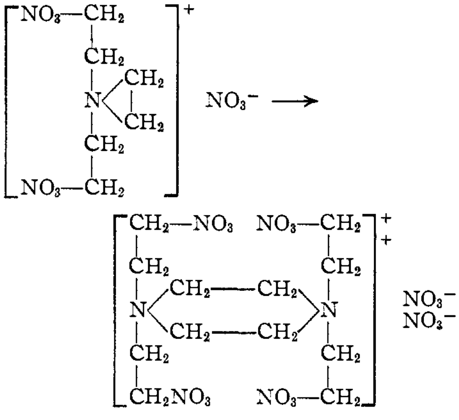
The nitrate salt of I can be prepared in 77% yield by esterification of tris-β-hydroxyethylamine in nitric acid and acetic anhydride. A new polymorph, m.p. 65° is obtained occasionally instead of the usual form,[2] m.p. 75°. This salt is reasonably stable although it would be unsuitable as an explosive since it decomposes violently after five minutes at 65° and immediately with explosion at 100°.

We confirmed the previous report[2] that the free base was unstable. Several days after the amine had been freed from a water solution of its salt by addition of alkali, it set to a gum from which a crystalline solid melting at 216° could be separated.

This solid is a nitrate salt since its aqueous solution will precipitate nitron nitrate. It is probably tetra-β-nitroxyethylpiperazinium dinitrate (II) analogous with the piperazinium di-salt reported by Crane and Rydon[3] from a corresponding decomposition of tris-β-chloroethylamine.

Although the dinitrate, II, was more stable than I or its nitrate salt the melting (decomposition) point of this quaternary salt decreased about 20° after storage for eight years.


I


II

Experimental[4]

Tris-β-nitroxyethylammonium Nitrate.—A stirred flask containing 580 g. (5.68 moles) of acetic anhydride was maintained at −5 to −10° while 156 g. (1.00 mole) of 95% tris-β-hydroxyethylamine and 284 g. (4.51 moles) of 99% nitric acid were added proportionately from burets. After a five-hour addition period the mixture was stirred for 90 minutes longer and then poured into sufficient ice and water to give a final volume of 3 liters. The heavy oil that separated soon crystallized. It was filtered off and vacuum-dried to weigh 266 g. (77%), m.p. 72–73°.

The salt may be crystallized from methanol or it may be precipitated from an acetic acid solution by addition of water. It melts at 74.5–75°. X-Ray diffraction with CuKα gave powder spacings (Å.) with intensities $[I/I_0]$: [10] 4.06; [9] 5.69; [8] 4.63; [7] 7.79; [5] 3.00; [4] 3.90, 2.46; [3] 4.90, 3.68, 3.44, 3.29, 2.91, 2.34; [2] 4.28, 4.18, 3.19, 2.83, 2.58; [1] 5.35, 4.44, 2.74, 2.28.

Anal. Calcd. for $C_6H_{13}N_5O_{12}$: C, 20.7; H, 3.77; N, 20.2. Found: C, 21.1; H, 3.73; N, 19.7.

When this salt is decomposed in concentrated sulfuric acid no acetic acid is released. The salt is slightly soluble in water and its aqueous solution gives positive brucine and nitron tests for nitrate ion.

Occasionally the salt was obtained in another polymorphic form, m.p. 64–65°. X-Ray diffraction with CuKα gave principal powder spacings (Å) with intensities $[I/I_0]$: [10] 3.70; [8] 3.28; [6] 5.12; [4] 4.62; [2] 3.02; [1] 3.15. The higher melting polymorph was obtained on seeding methanol solutions of the lower melting form.

Tris-β-nitroxyethylamine (I).—To a solution of 0.17 g. (0.0043 mole) of sodium hydroxide in water at 0° was added 1.5 g. (0.0043 mole) of the nitrate salt. The oil which formed after agitation was separated, washed twice with water, twice with cold methanol and again with water and was dried quickly over anhydrous sodium sulfate. The 0.5 g. thus obtained was analyzed immediately since it would not withstand distillation. Analysis indicated that it was not pure.

Anal. Calcd. for $C_6H_{12}N_4O_9$: C, 25.4; H, 4.26; N, 19.7. Found: C, 25.8; H, 4.07; N, 19.0.

Tetra-β-nitroxyethylpiperazinium Dinitrate (II).—When 7 g. of the dry amine was allowed to stand at 25° for 2 days, it set to a gummy mass. When this gum, after a total time of 16 days, was shaken with 20 cc. of acetone a suspension was produced. The brown solid was filtered off, washed with water and dried under vacuum to weigh 1.27 g. (18%), m.p. 199°. After periods of 3, 5 and 10 days the crude yields were 0.8, 1.6 and 9%, respectively. The same compound was also precipitated in about the same yields when the polymerization was carried out in 2 volumes of methanol. Treatment of the crude product with Nuchar followed by three crystallizations from boiling water (60 cc. per g.) gave a 60% recovery of crystals, m.p. 216° (dec.). The compound was soluble in hot water, slightly soluble in dimethylformamide and insoluble in anhydrous acetone, methanol, ethanol, ether, benzene, nitromethane and acetic acid. It was stable in hot water, and it dissolved in lime-

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[1] Dynamit-A.-G. vorm Nobel & Co. Brit. 350,293 (Nov. 22, 1929).

[2] J. Barbiere, *Bull. soc. chim.*, [5] **11**, 470 (1944).

[3] C. W. Crane and H. N. Rydon, *J. Chem. Soc.*, **527** (1947).

[4] All melting points were corrected against reliable standards.