Anal. (Parr bomb). Subs. 0.5864 g.: 39.74 cc. of 0.1010 *N* $AgNO_3$. Calcd. for $C_8H_{19}NBr_2$: Br, 55.36. Found: 54.75.

4-Bromobutyldiethylamine.—The free bromo-amine was isolated as described for the propyl compound. It boiled at 68–70° at 6 mm.; d_4^{25}, 1.0187; n_D^{25}, 1.4415. M_D, calcd., 52.38; observed, 53.92.

Anal. (Parr bomb). Subs. 0.3197: 15.43 cc. of 0.1010 *N* $AgNO_3$. Calcd. for $C_8H_{18}NBr$: Br, 38.46. Found: 38.49.

This amine gradually became opaque and after about twelve hours crystals of the quaternary ammonium compound, which was presumably diethyl pyrrolidinium bromide, began to separate. This product melted at 170–175°.

Anal. (Volhard). Subs. 0.2958 g.: 14.07 cc. of 0.1010 *N* $AgNO_3$. Calcd. for $C_8H_{18}NBr$: Br, 38.46. Found: 38.43.

Diethyl 4-Diethylaminobutyl Malonate.—This ester was prepared by the same method used for the corresponding propyl derivative. From 16 g. of sodium, 600 cc. of absolute alcohol, 128 g. of diethyl malonate and 100 g. of crude bromobutyldiethylamine hydrobromide, there was obtained 23 g. (23% of the theoretical amount) of the amino malonic ester, which boiled at 170–175° at 24 mm.; d_4^{25}, 0.9621; n_D^{25}, 1.4468. M_D, calcd., 78.90; observed, 80.46.

Anal. (Kjeldahl). Subs., 0.4047 g.: 17.93 cc. of 0.1745 *N* HCl. Calcd. for $C_{15}H_{29}O_4N$: N, 4.88. Found: 4.90.

Summary

3-Bromopropyldiethylamine and 4-bromobutyldiethylamine have been prepared by general reactions and some of their properties and reactions have been studied.

URBANA, ILLINOIS

[CONTRIBUTION NO. 16 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

ALKYL-NITROGUANIDINES

BY TENNEY L. DAVIS AND STEWART B. LUCE

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Nitroguanidine in aqueous solution at 60–70° appears to dearrange in the expected manner[1] to produce, on the one hand, ammonia and nitrocyanamide and, on the other, nitro-amide and cyanamide. If the solution is digested with ammonia, the ammonia inhibits the first of the above-mentioned dearrangements and combines with the cyanamide produced by the second to form guanidine, while the nitro-amide which is liberated at the same time decomposes to produce nitrous oxide, which escapes from the solution. By working with ammonium carbonate, guanidine carbonate is obtained in a yield amounting to 90% of the theoretical, and the by-products are a small amount of melamine from the polymerization of cyanamide, and a smaller amount of urea, from the cyanic acid which results apparently from the loss of nitrous oxide from nitrocyanamide. With aniline a small amount of phenylguanidine is produced, but

[1] Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

the principal product is phenylurea. With an aliphatic amine, such as methylamine, a small amount of the alkylguanidine is probably formed, a considerable amount of the alkylurea is produced but the principal product is the alkylnitroguanidine, evidently formed by the combination of the amine with the nitrocyanamide from the dearrangement.

$$H—NCN—NO_2 + R—NH_2 \longrightarrow R—NH—C(NH)—NH—NO_2$$

Methyl-, ethyl-, *n*-butyl- and benzylnitroguanidine have been prepared previously and described elsewhere.[1] In the present paper we wish to report a number of other alkylnitroguanidines, and include, for completeness and for comparison, a description of those which have been previously reported. The transformations of these substances are being studied in this Laboratory.

In this work, α-nitroguanidine[2] was used, for it had been found earlier that both forms of nitroguanidine yield the same methylnitroguanidine. Slightly more than one molecular proportion of nitroguanidine was added to a 10% aqueous solution of the primary amine, and the mixture was heated in the water-bath at 60–70° for 30 or 40 minutes or until almost all of the nitroguanidine had disappeared. Ammonia came off abundantly. The solution was chilled and filtered, and the filtrate was evaporated to dryness in a current of air at laboratory temperature. The combined residues were extracted with dry alcohol at 70° and yielded an insoluble portion which consisted of unchanged nitroguanidine generally associated with considerable amounts of guanidine carbonate, and a solution from which the pure alkylnitroguanidine was obtained by recrystallization, in yields varying from 30 to 50% of the theoretical.

Dimethylamine is the only secondary amine with which we have succeeded in carrying out the reaction. It required more vigorous treatment than the primary amines, a 20% aqueous solution needing about 2 hours' digestion at 70–80° to cause the nitroguanidine to go into solution.

TABLE I

PROPERTIES OF ALKYL-NITROGUANIDINES

Derivative of nitroguanidine	M. p., °C.	Crystal habit	Total nitrogen, % Calcd.	Total nitrogen, % Combustion	Nitro group nitrogen, % Calcd.	Nitro group nitrogen, % Nitrometer
Methyl-	160.5–1.0	Short prisms	...	.....	...	.....
Dimethyl-	193.6–4.5	Fine needles	42.42	42.18, 42.40	10.60	10.57, 10.63
Ethyl-	147.0–8.0	Cubes	...	.....	...	.....
n-Propyl-	98.0–8.5	Stout needles	38.35	38.45	9.59	9.54
*iso*Propyl-	154.8–5.6	Cubes	38.35	38.61, 38.45	9.59	9.53
n-Butyl-	84.0–5.0	Stout needles	...	.....	...	.....
*iso*Butyl-	121.0–1.5	Waxy plates	35.00	34.97, 35.16	8.75	8.71, 8.74
n-Amyl-	98.8–9.3	Shiny leaflets	32.18	32.23, 32.22	8.05	8.03, 8.04
*iso*Amyl-	145.5–6.2	Fine needles	32.18	32 02, 32.17	8.05	8.02, 8.02
tert.-Amyl-	154.8–5.6	Plates	32.18	32.03	...	.....
Benzyl-	183.5	Needles	...	.....	...	.....

[2] Davis, Ashdown and Couch, THIS JOURNAL, **47**, 1063 (1925).

The alkylnitroguanidines are colorless, crystalline solids, moderately soluble in alcohol, insoluble or slightly soluble in cold water, more soluble in hot, and insoluble or slightly soluble in ether. Benzylnitroguanidine is the least soluble, requiring about 1050 parts of cold water and about 200 parts of boiling water for solution, and is sparingly soluble even in hot alcohol. It chars with concd. sulfuric acid. The others dissolve readily in concd. sulfuric acid, give a blue color with a solution of diphenylamine in that substance, and give up their nitro group nitrogen quantitatively in the nitrometer. They decompose slowly when boiled in aqueous solution.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE CATALYTIC REDUCTION OF *d*-GLUCONIC ACID TO *d*-GLUCOSE

BY J. W. E. GLATTFELD AND EDNA H. SHAVER[1]

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The work reported below is an outgrowth of the efforts that are being made in this Laboratory to prepare and study the C_4-saccharinic acids.[2] This preparation work has now progressed to such an extent that the possibility of extending it to the C_5-saccharinic acids is being considered. This extension would involve as one step the reduction of the C_4-acids to the corresponding aldehydes. The realization of the extension depends, in large measure, on the possibility of discovering a practical procedure for this reduction. Of possible reduction methods the catalytic hydrogenation of the acids in the presence of oxides of platinum seemed to hold promise and the work reported below was done to test it. In order to conserve material, the easily obtained *d*-gluconic acid was used instead of the C_4-saccharinic acids for this preliminary study.

W. E. Cake[3] has recently stated that glucose in neutral solution is not reduced by hydrogen in the presence of platinum black. It occurred to us, therefore, that if the reduction of the aldonic acids could be effected by hydrogen in the presence of platinum oxides in neutral or slightly acid solution (that is, with no added acid or very little), the yield of aldoses

[1] The dissertation of which this paper is a condensation was presented by Edna H. Shaver in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in the University of Chicago. Some of the material reported in this paper was presented at the meeting of the Midwest Sections of the American Chemical Society in Chicago, May 27–28, 1927.

[2] (a) Glattfeld and Miller, THIS JOURNAL, **42**, 2314 (1920). (b) Glattfeld and Sander, *ibid.*, **43**, 2675 (1921). (c) Glattfeld and Sherman, *ibid.*, **47**, 1742 (1925). (d) Glattfeld and Woodruff, *ibid.*, **49**, 2309 (1927).

[3] Cake, THIS JOURNAL, **44**, 861 (1922).