

catalyst for the hydrogenation of unsaturated hydrocarbons.

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levo-2,3-Dinitroxybutane

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In 1938, a diastereomeric mixture of 2,3-dinitroxybutanes was reported in 16% yield as one of the products arising from electrolysis of sodium methylethylacetate in aqueous solution of sodium nitrate.¹ Later sodium pentanoate was electrolyzed in the same way to yield a little of the nitrate ester, which was in the *dd*, *ll* form according to the dicarbanilide which it yielded after iron-acetic acid reduction.² Dinitroxybutane was finally reported in good yield from 2,3-butanediol, but the author does not specify the stereochemical configuration of this diol.³

In connection with studies involving plasticization of nitrocellulose, we wished to obtain 2,3-dinitroxybutane as a pure stereochemical compound. The availability of *levo*-butanediol through the courtesy of the Canadian National Research Council made this possible. The nitrate-esterification with mixed acid proceeded without incident. The crude product was sufficiently pure that its refractive index was not changed by subsequent fractional distillation. The distilled product was still clear after four years, when it gave an Abel Heat Test of two minutes at 100°. Its sensitiveness to impact between steel surfaces (glancing blow) was approximately the same as that of crystalline TNT. The compound was found to be a poor plasticizer for nitrocellulose of 13.1% nitrogen content.

Although the 2,3-butanediol from which this ester was prepared had a high *levo* rotation (-12.89°) the *levo* rotation of the resulting dinitroxybutane was less than 1° . This low rotation suggested that racemization might have occurred during nitration. This was found not to be the case. Catalytic reduction with the catalyst recommended by Kuhn⁴ regenerated 2,3-butanediol with *levo* rotation of -12.90° .

Experimental

To a mechanically stirred solution of 228 cc. (5.4 moles) of 98% nitric acid in 219 cc. (3.79 moles) of 96% sulfuric acid was added dropwise, over one hundred and sixty minutes, 185.5 g. (2.06 moles) of *levo*-2,3-butanediol, b. p. 81.0° (18 mm.), n_D^{20} 1.4315, $[\alpha]_D^{20} -12.89^\circ$. The reaction temperature was held at $0-5^\circ$ during this addition and was maintained thus for a further fifteen minutes. The cold solution was then poured into 100 g. of ice and further diluted with 500 cc. of water. The oily layer was not freed completely from acid by washing with 1 liter of 2% sodium carbonate solution. The deacidification was

therefore completed by further washing with 200 cc. of 2% aqueous ammonia and then with water until neutral to litmus.

The product was dried under 25-mm. pressure to weigh 337.5 g. or 91% of theoretical, n_D^{20} 1.4405. This refractive index was not changed by distillation at $99-100^\circ$ (15 mm.) or 91.5° (10 mm.). *levo*-Dinitroxybutane melts at 0 to 4° . Other constants are: d_4^{20} , 1.297; M_{RD} calcd. 36.94,⁵ found 36.63; $[\alpha]_D^{20} -0.88$.

Reduction of 2,3-Dinitroxybutane.—A 10% solution of 20 g. (0.11 mole) of 2,3-dinitroxybutane in absolute ethanol was reduced with 0.54 mole of hydrogen, initially at 500 lb. gage pressure, in presence of 0.5 g. of the palladium-on-charcoal catalyst recommended by Kuhn. It was necessary to heat the bomb to 48° in order to complete this reduction in seven hours. The hydrogenolysis was complete in twenty-two minutes when 2 g. of catalyst was used per 6 g. of ester. There was less evidence of ammonia formation in the quick reduction, but the reaction mixture became quite hot. The catalyst was filtered off and the filtrate distilled, finally under 14 mm. The yield of 2,3-butanediol distilling at $75-76^\circ$ was 9.6 g. or 96% of theoretical. Its rotation was $[\alpha]_D^{20} -12.90^\circ$.

(5) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley & Sons Inc., New York, N. Y., 1945.

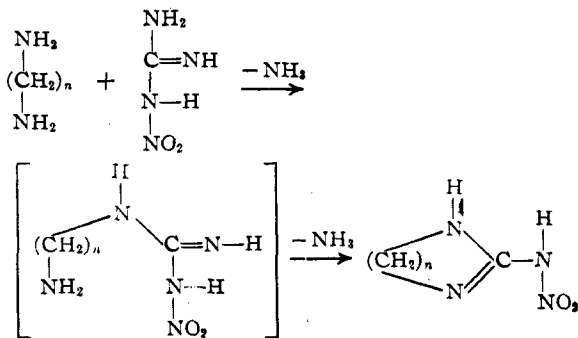
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Preparation and Properties of 2-Nitramino- Δ^2 -1,3-diazacycloalkenes

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Davis and his co-workers^{1,2} have shown that monoalkylamines react with nitroguanidine in aqueous solution to give the corresponding N-alkyl-N'-nitroguanidines. If these alkylnitroguanidines are treated with excess alkylamine then the nitramino group is replaced to give, among other products, the *sym*-dialkylguanidines.³ One might then expect that, if nitroguanidine were treated with an alkyldiamine, both reactions would occur to give a cyclic derivative from which the nitramino group had been eliminated. However, the reaction follows an alternative course. Ammonia is, indeed, liberated by the reaction of the amino group in nitroguanidine with one of the amino groups in the diamine, but the second evidently adds to the imino group in the resulting



(1) F. Fichter and P. Suter, *Helv. Chim. Acta* **21**, 1401-1407 (1938).

(2) M. Rudin, *ibid.*, **25**, 636-640 (1942).

(3) L. J. DeKreuk, *Rec. trav. chim.*, **61**, 819-830 (1942).

(4) L. Kuhn, *This Journal*, **68**, 1761-1762 (1946).

(1) T. L. Davis and A. J. J. Abrams, *Proc. Am. Acad. Sci.*, **61**, 437 (1936).

(2) T. L. Davis and S. B. Luce, *This Journal*, **49**, 2303 (1927).

(3) T. L. Davis and R. C. Elderfield, *ibid.*, **55**, 731 (1933).