catalyst for the hydrogenation of unsaturated hydrocarbons.

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## *levo*-2,3-Dinitroxybutane

BY A. F. MCKAY, R. H. MEEN AND GEORGE F WRIGHT

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 Kuhn[4] 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.), $n^{25}_D$ 1.4315, $[\alpha]^{20}_D$ −12.89°. The reaction temperature was held at 0–5° 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, $n^{20}_D$ 1.4405. This refractive index was not changed by distillation at 99–100° (15 mm.) or 91.5° (10 mm.). *levo*-Dinitroxybutane melts at 0 to 4°. Other constants are: $d^{20}_4$ 1.297; $MR_D$ calcd. 36.94,[5] found 36.63; $[\alpha]^{20}_D$–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° was 9.6 g. or 96% of theoretical. Its rotation was $[\alpha]^{20}_D$° −12.90°.

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[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).

[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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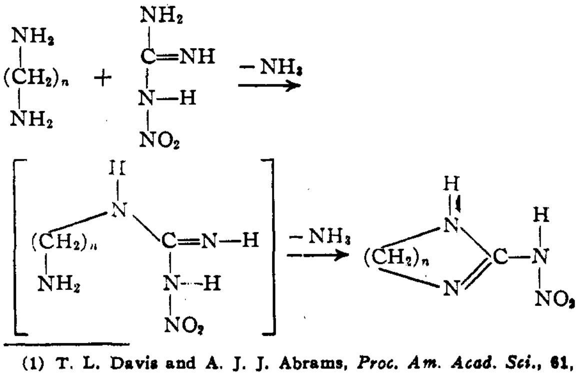
## Preparation and Properties of 2-Nitramino-$\Delta^2$-1,3-diazacycloalkenes

BY A. F. MCKAY AND GEORGE F WRIGHT

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



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[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, *ivid.*, **55**, 731(1933).

TABLE I

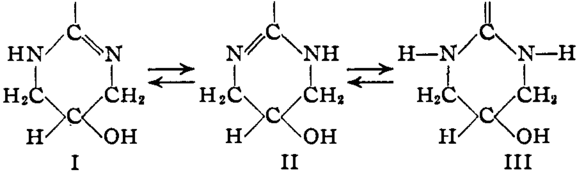
2-NITRAMINO-$\Delta^2$-1,3-DIAZACYCLOALKENES

| Compound | Yield, % | M. p., °C. | Carbon, % Calcd. | Carbon, % Found | Hydrogen Calcd. | Hydrogen Found | Nitrogen Calcd. | Nitrogen Found |
|---|---|---|---|---|---|---|---|---|
| 2-Nitramino-$\Delta^2$-1,3-diazacyclopentene | 65.4 | 220–221 dec. | 27.9 | 27.8 | 4.61 | 4.52 | 43.1 | 43.0 |
| 4(or 5)-Methyl-2-nitramino-$\Delta^2$-1,3-diazacyclopentene | 64.0 | 170.5 | 33.3 | 33.5 | 5.54 | 5.60 | 38.9 | 39.2 |
| 2-Nitramino-$\Delta^2$-1,3-diazacyclohexene | 55.0 | 251–252 dec. | 33.3 | 33.3 | 5.54 | 5.55 | 38.9 | 38.7 |
| 4(or 6)-Methyl-2-nitramino-$\Delta^2$-1,3-diazacyclohexene | 40.0 | 147–148.5 | 38.0 | 37.9 | 6.33 | 6.70 | 35.4 | 35.8 |
| 2-Nitramino-$\Delta^2$-1,3-diazacycloheptene | 64.3 | 219–220 dec. | 38.0 | 38.4 | 6.33 | 6.68 | 35.4 | 35.5 |
| 5-Hydroxy-2-nitramino-$\Delta^2$-1,3-diazacyclohexene | 59.0 | 233–233.5 dec. | 30.0 | 29.6 | 5.00 | 5.05 | 35.0 | 34.6 |

aminoalkylnitroguanidine to give a cyclic nitramine after a second molecule of ammonia is liberated. Five, six and larger membered rings can thus be synthesized.

It has been found[4] that the yields of alkylnitroguanidines can be improved over those previously reported, by treating nitroguanidine dissolved in aqueous alkali with the alkylamine hydrochloride. The mixture is heated to 60–70° for twenty to thirty minutes, cooled and the product recovered by filtration. This revised method is also found considerably to increase (by 15–55%) the yields of 2-nitramino-$\Delta^2$-1,3-diazacycloalkenes (1, $n = 2$ to 4) obtained from the reaction of alkyldiamines with nitroguanidine. The synthesis is found to be successful with diamines containing branched as well as straight chains. The compounds which have been prepared thus far are listed in Table I. No tautomeric forms have yet been detected. Although the products isolated from the reaction of the unsymmetrical diamines with nitroguanidine are chemical individuals, we cannot at present assign definite positions to the methyl groups.

It is interesting to note that in the substituted 2-nitramino-$\Delta^2$-1,3-diazacycloalkenes described in Table I an asymmetric carbon atom occurs. Thus the 4(or 5)-methyl-2-nitramino-$\Delta^2$-1,3-diazacyclopentene and 4(or 6)-methyl-2-nitramino-$\Delta^2$-1,3-diazacyclohexene are racemates. Especially interesting is the 5-hydroxy-2-nitramino-$\Delta^2$-1,3-diazacyclohexene. If a labile tautomerism exists between I and II, or if the acid salts of I are resonance hybrids, then resolution would be impossible. If, on the other hand, the tautomeric nitrimino form III were stable then resolution of the allene-like structure should be possible.



I II III

Work on structure and synthesis of these 2-nitramino-$\Delta^2$-1,3-diazacycloalkenes is in progress. The authors are grateful to Messrs. Scott and Farmer of London, England, from whom the original idea of cyclization wasobt ained. The National Research Council of Canada has supported this work by a grant-in-aid.

### Experimental

**Preparation of 2-Nitramino-$\Delta^2$-1,3-diazacycloalkenes.**—One mole of nitroguanidine is dissolved in 250–300 cc. of water containing two moles of potassium hydroxide and then one mole of the diamine dihydrochloride is added with stirring. A thick sludge forms which is heated at 65–70° with stirring over a period of twenty to thirty minutes. During this time the sludge becomes less viscous and it may dissolve completely. At the end of the reaction time, the reaction mixture is cooled to 1° in an ice–salt-bath and the white solid is recovered by filtration. The occluded potassium chloride may be removed by trituration with water. The final yields vary from 40–65% of theoretical, depending on the specific compound.

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[4] A. F. McKay and G. F. Wright, THIS JOURNAL, 69, 3028 (1947).

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## The Addition of Methyl Alcohol to Fluoroethylenes[1]

BY WILLIAM T. MILLER, JR.,[2] EDWARD W. FAGER[3] AND PAUL H. GRISWOLD[4]

The addition of alcohols to tetrafluoroethylene and to chlorotrifluoroethylene[5] has been reported in the patent literature. In the present work, which was carried out independently, the base catalyzed addition of methyl alcohol to these substances and to *unsym*-dichlorodifluoroethylene was shown to occur. Reaction occurred rapidly and exothermically at from zero to room temperature with a reagent prepared by dissolving two moles of sodium in 500 cc. of absolute methanol. The tetrafluoroethylene was added in portions as a gas at 20 atm. pressure to the methylate solution in a steel bomb of the rocker type with the temperature maintained below 40°. The other olefins were added at atmospheric pressure to the stirred methylate solution cooled in an ice-bath.

[1] This paper was largely based on work done for the Manhattan Project under Contract No. W-7405-Eng-50 at S. A. M. Laboratories, Columbia University and under contract No. W-7405-Eng-26, Supplement No. 4 at S. A. M. Laboratories Carbide and Carbon Chemicals Corporation, New York City. Part of the information contained in this document will appear in Volume I of Division VII of the Manhattan Project Technical Series.

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[5] Hanford and Rigby, U. S. Patent 2,409,274, Oct. 15, 1946.