to 40–45° for 24 hours, with the *p*H of the reaction mixture maintained at 7–8, using 5 *N* hydrochloric acid. The precipitate was filtered and 5.3 g. (51%) of **5,8-dicyano-5,8-dinitro-2,11-dodecanedione**, m.p. 163–164°, was obtained. One recrystallization from methanol was sufficient for final purification.

Anal. Calcd. for $C_{14}H_{18}N_4O_6$: C, 49.70; H, 5.36; N, 16.56. Found: C, 49.65; H, 5.59; N, 16.53.

2,5-Dicyano-2,5-dinitro-1,6-hexanediol.—To a solution of 7.0 g. (0.025 mole) of dipotassium α,α'-dinitroadiponitrile in 100 ml. of water was added 12 ml. of 37% formaldehyde solution at 0°. Since no reaction occurred after 24 hours, an additional 10 ml. of formalin was added and the solution was acidified with 5% hydrochloric acid. The reaction mixture was extracted with ether and upon evaporation of the solvent *in vacuo*, a small amount (0.3 g.) of a waxy solid was obtained the infrared spectrum of which indicated the presence of 2,5-dicyano-2,5-dinitro-1,6-hexanediol (OH, st. 3.1 μ, C≡N st. 4.5 μ, NO_2 asym. st. 6.40 μ, NO_2 sym. st. 7.45 μ).

Diacetoxy-2,5-dicyano-2,5-dinitrohexane.—The 2,5-dicyano-2,5-dinitro-1,6-hexanediol prepared above was treated with 20 ml. of acetic anhydride in the presence of one drop of concd. sulfuric acid for one hour at 80°. The reaction mixture was added to 50 g. of crushed ice, and 0.4 g. of a solid was obtained melting at 177–179°. Two recrystallizations from methanol afforded pure **diacetoxy-2,5-dicyano-2,5-dinitrohexane**, m.p. 181–182°.

Anal. Calcd. for $C_{12}H_{14}N_4O_8$: C, 42.11; H, 4.12; N, 16.37. Found: C, 41.99; H, 4.25; N, 16.43.

Reaction Time Studies. (a) **Nitration of Phenylacetonitrile.**—Equimolar amounts of phenylacetonitrile, potassium *t*-butoxide and amyl nitrate were dissolved in tetrahydrofuran and aliquots of 1 ml. were removed from the reaction mixture at various time intervals. The aliquots were diluted with 95% ethanol, and the concentration of potassium nitrophenylacetonitrile was measured, spectrophotometrically, by the absorbance at 338 mμ. A standard reference curve was obtained by plotting absorbance *vs.* concentration of analytically pure potassium nitrophenylacetonitrile in 95% ethanol. A linear relationship was found at low concentrations up to 10^{-5} *M*. The results of a typical run at −78° are summarized in Table III.

(b) **Nitration of α-Tetralone.**—The reaction time studies of the nitration of α-tetralone were carried out as in (a). The concentration of the product potassium 2-nitrotetralone was measured, spectrophotometrically, by the absorbance at 373 mμ. A standard reference curve was obtained by plotting absorbance *vs.* concentration of analytically pure potassium 2-nitrotetralone[17] in 95% ethanol. The results of a run at −78° are summarized in Table III.

TABLE III

NITRATION OF PHENYLACETONITRILE AT −78°

Aliquot	Time, min.	Absorbance at 338 mμ	Concn., mole/liter	Reaction, %
1	4	0.224	1.8×10^{-2}	43
2	24	.225	1.8	43
3	242	.223	1.8	43
		NITRATION OF α-TETRALONE AT −78°		
		At 373 mμ		
1	10	0.40	13×10^{-3}	10.4
2	30	.53	17	13.5
3	65	.30	10	8.0
4	265	.22	7.5	6.0
5	1150	.14	5.0	4.0

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work and to the Ethyl Corporation for a generous gift of amyl nitrate.

[17] H. Feuer, J. W. Shepherd and C. Savides, THIS JOURNAL, **79**, 5768 (1957).

LAFAYETTE, IND.

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Reactions of α,α'-Dibromo-α,α'-dinitrodinitriles[1]

BY HENRY FEUER AND CHRISTOS SAVIDES

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α,α'-Dibromo-α,α'-dinitroadiponitrile (I) is converted to 1,1,4,4-tetrabromo-1,4-dinitrobutane (II) on treatment with aq. potassium hydroxide at 70°. Compound II is also obtained when dipotassium α,α'-dinitroadiponitrile (III) is brominated in alkaline medium at 70°. Basic hydrolysis of I at −5° or alkaline bromination of III at 0° yields 2,5-dibromo-2,5-dinitropentanamide (IV) after acidification. It has been established that IV is the intermediate in the conversion of I to II, because on treatment with base it is converted to II. Acid hydrolysis of I yields succinic acid.

The bromination products of dipotassium α,α'-dinitronitriles[2] have become available only recently, and this paper reports their properties and reactions which are summarized in Fig. 1.

The hydrolysis of α,α'-dibromo-α,α'-dinitroadiponitrile[2](I) with aq. potassium hydroxide at 70° did not yield the expected 1,4-dibromo-1,4-dinitrobutane, which would have resulted from a simple hydrolysis of I to the dicarboxylate salt and subsequent decarboxylation upon acidification. Instead, a water-insoluble solid was obtained from the alkaline solution which was identified as 1,1,4,4-tetrabromo-1,4-dinitrobutane[3,4] (II) by its melting point and a mixed melting point determination with authentic II. The same compound II was obtained directly, on treating dipotassium α,α-dinitroadiponitrile (III) in aq. potassium hydroxide with bromine at 70°.

The transformation of compounds I or III to compound II was quite unusual and in order to gain some insight into the course of these reactions, it was desirable to determine whether any possible intermediates could be isolated. When pure I was treated with aq. potassium hydroxide at −5°, complete dissolution occurred after 10 minutes. Upon acidification a new compound was obtained, which was identified as 2,5-dibromo-2,5-dinitropentanamide (IV). Compound IV was also obtained upon bromination of compound III under alkaline conditions at 0°, and subsequent acidification. The identity of compound IV was established by elemental analysis, molecular weight determination, its solubility in dilute base and its infrared spectrum. It indicated the presence of

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(1) From the Ph.D. Thesis of Christos Savides, Purdue University, 1958.

(2) H. Feuer and Ch. Savides, THIS JOURNAL, **81**, 5826 (1959).

(3) J. von Braun and W. Sobecki, *Ber.*, **44**, 2526 (1911).

(4) K. Klager, *J. Org. Chem.*, **20**, 646 (1955).

absorption bands at 2.59 and 3.20 μ, which are characteristic NH stretching vibrations of primary amides.[5] A strong band was also present at 5.92 μ, which may be attributed to the amide I band, usually observed[6] in the region of 6.06 μ. The displacement of the amide I band to lower wave lengths is probably due to the presence of bromine and nitro groups alpha to the amide group. It has been observed that this band appears as low as 5.78 μ in trichloroacetamide.[6]

The above reactions seem to indicate that the first step in the transformation of compound III to II is the formation of compound I which in the second step is converted by hydrolysis and decarboxylation to the intermediate A. Subsequent hydrolysis, decarboxylation and bromination (step 3) then gives the final product II.

$$\text{III} \xrightarrow{Br_2} \text{I} \qquad (1)$$

$$\text{I} \xrightarrow{OH^-} {}^-O_2CCBrNO_2(CH_2)_2CBrNO_2CONH_2 \longrightarrow \underset{\text{A}}{{}^-O_2N{=}CBr(CH_2)_2CBrNO_2CONH_2} \qquad (2)$$

$$\text{A} \xrightarrow[OH^-]{Br_2} \underset{\text{B}}{Br_2CNO_2(CH_2)_2CBrNO_2CO_2^-} \xrightarrow[OH^-]{Br_2} \text{II} \qquad (3)$$

The presence of the salt of the nitroamide (IV) A as an intermediate in the overall reaction was indicated by the fact that IV was obtained by the bromination of III and was converted to II upon further bromination in alkaline medium. It is interesting that no α,α'-dibromo-α,α'-dinitroadipamide was isolated during the bromination of III, nor in the alkaline hydrolysis of I at −5°. If the diamide was formed at all, its conversion to the monoamide IV must have been very rapid.

Steps 2 and 3 in the above reaction path involve essentially the decarboxylation and bromination of an α-bromo-α-nitrocarboxylate salt. A similar type reaction has been recently reported from this Laboratory[7]; methyl 2,5-dibromo-2,5-dinitropentanoate was converted to compound II upon saponification and subsequent addition of bromine to the hydrolysate. It has been demonstrated in the decarboxylation of α-nitroacids that the α-nitrocarboxylate ion is actually the intermediate.[8]

Perhaps the most unusual transformation in the above series of reactions is the conversion of compound I to II by aq. potassium hydroxide. The intermediate in this reaction also appears to be the salt A, since treatment of I with base at low temperatures afforded on acidification compound IV, which on further reaction with base was converted to compound II.

The conversion of I to II is not very well understood. It probably involves the removal of bromine by potassium hydroxide to form potassium hypobromite, which then acts as a brominating agent for the further bromination of IV and its hydrolysis product B, as illustrated above in step 3. A similar transformation was observed recently when 2,5-dibromo-2,5-dinitrocyclopentanone was converted to compound II by treatment with base. Basic debromination has been previously demonstrated with compounds in which the bromine group is activated by the presence of two or three nitro groups.[9,10] For example, trinitrobromomethane and phenyldinitrobromomethane were converted to potassium trinitromethane and phenyldinitromethane, respectively, after treatment with base.

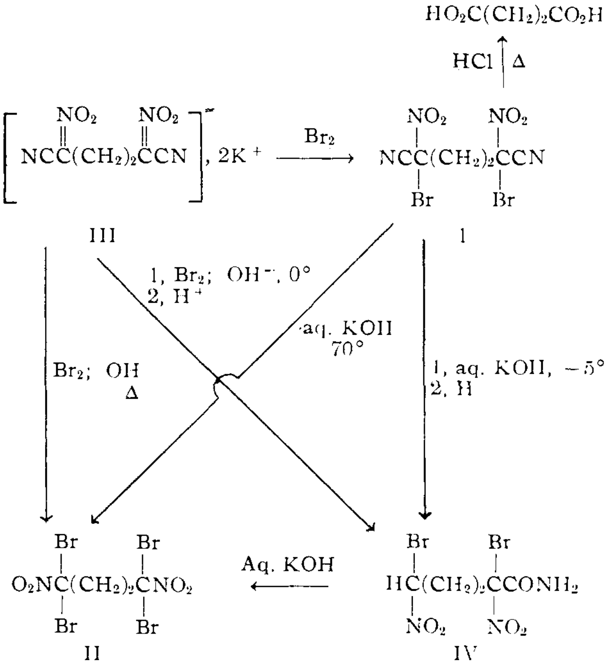

Fig. 1.—Reactions of α,α'-dibromo-α,α'-dinitroadiponitrile.

It is interesting to note that compound I hydrolyzed rather easily in the presence of base, in contrast to compound III, for which drastic conditions were required.[2] The hydrolysis of the former probably is facilitated by the presence of two electron withdrawing groups alpha to the nitrile group. In the latter compound, the presence of a nitronate group (NO_2^-), an electron-donating group, results in a relative increase of the electron density of the nitrile carbon atom; consequently, the relative ease of nucleophilic attack by base would be decreased.

The hydrolysis of compound I with 12% aq. hydrochloric acid afforded succinic acid. It is likely that the expected 1,4-dibromo-1,4-dinitrobutane was formed, but was then converted to succinic acid in a modified Nef[11] reaction. The conversion of bromo nitro compounds to carbonyl compounds has been previously demonstrated in this Laboratory.[7] Thus α,α'-dibromo-α,α'-dinitrocyclopentanone was converted in methanolic hydrogen chloride, to methyl 2,5-dibromo-2,5-dinitropentanoate and dimethyl 2-bromo-2-nitroglutarate, respectively.

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[5] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 176.

[6] R. N. Jones and C. Sandorfy, "Weissberger's Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 458.

[7] H. Feuer, J. W. Shepherd and Ch. Savides, THIS JOURNAL, **79**, 5768 (1957).

[8] K. J. Pedersen, *J. Phys. Chem.*, **38**, 559 (1934).

[9] A. K. Macbeth and D. D. Pratt, *J. Chem. Soc.*, **119**, 354, 1356 (1921).

[10] E. L. Hirst and A. K. Macbeth, *ibid.*, **121**, 2169 (1922).

[11] W. E. Noland, *Chem. Revs.*, **55**, 137 (1955).

Experimental

Preparation of 2,5-Dibromo-2,5-dinitropentanamide (IV). (a) **From Dipotassium α,α'-Dinitroadiponitrile**[2] (III).—To a solution of potassium hypobromite, prepared by the addition of 8.0 g. (0.05 mole) bromine to a solution of 7.0 g. (0.105 mole) of potassium hydroxide (85% assay) in 100 ml. of water, was added rapidly at 0° 6.0 g. (0.0218 mole) of dipotassium α,α'-dinitroadiponitrile dissolved in 30 ml. of water. The resulting solution was acidified with 5% hydrochloric acid at 0°, the precipitate filtered and washed with water to give 5.5 g. (72.5% yield) of **2,5-dibromo-2,5-dinitropentanamide** (IV), m.p. 198–203°. Recrystallization from 80% ethanol and 50% ethanol gave pure IV melting at 201–203° dec.

Anal. Calcd. for $C_5H_7N_3O_5Br$: C, 17.20; H, 2.02; N, 12.03; Br, 45.85; mol. wt., 349. Found: C, 17.32; H, 2.04; N, 12.23; Br, 46.37; mol. wt.,[12] 338.

Concentration of the filtrates of the above recrystallizations afforded a second compound, m.p. 192–193°, the infrared spectrum of which was practically identical to the spectrum of the high melting material, indicating that they were diastereisomers; Infrared: bands at 2.99, 3.20 μ (N–H st.); 5.92 μ (amide I); 6.42 μ (NO_2 asym. st.); 7.34 μ (NO_2 sym. st.).

(b) **From α,α'-Dibromo-α,α'-dinitroadiponitrile**[2] (I).—Compound I (1.5 g., 4.2 mmoles) was treated with 50 ml. of 17% potassium hydroxide solution for 30 min. at −5°. The resulting clear solution was acidified with 5% hydrochloric acid at 0° and 0.5 g. (34% yield) of 2,5-dibromo-2,5-dinitropentanamide (IV) was obtained, m.p. 190–194°. A mixed melting point determination with authentic IV was not depressed (m.p. 195–197°). The infrared spectrum of the obtained solid and authentic IV were superimposable.

Preparation of 1,1,4,4-**Tetrabromo**-1,4-**dinitrobutane** (II). (a) **From Compound** III.—To a solution of 9.6 g. (0.035 mole) of compound III in 100 ml. of water was added 21.2 g. (85% assay) of potassium hydroxide. Bromine 28.4 g. (0.18 mole) was added and the solution was heated at 70–80° until ammonia evolution ceased. The crystalline solid of 1,1,4,4-tetrabromo-1,4-dinitrobutane, m.p. 98–100° (lit. value[3] 99–100°), was obtained in 5.9 g. or 36% yield. A mixed melting point determination with authentic II was not depressed (m.p. 99–100°). The infrared spectra of the obtained solid and authentic II were superimposable.

(b) **From Compound** I.—To an aqueous solution of 20% potassium hydroxide (85% assay) was added 0.3 g. (8.4 mmoles) of α,α'-dibromo-α,α'-dinitroadiponitrile, and the suspension was heated to 70°. Complete dissolution occurred after 10 minutes and the precipitate formed was identified as 1,1,4,4-tetrabromo-1,4-dinitrobutane (II), m.p. 98–100° (lit. value[3] 99–100°). A mixed melting point determination with authentic II showed no depression (m. p. 99–100°).

(c) **From 2,5-Dibromo-2,5-dinitropentanamide** (IV).—A solution of 0.3 g. (8.6 mmoles) of 2,5-dibromo-2,5-dinitropentanamide in 20 ml. of 10% potassium hydroxide solution was stirred for two hours at 25°. The precipitate which formed in the reaction mixture was filtered, recrystallized from hexane, and identified as 1,1,4,4-tetrabromo-1,4-dinitrobutane (II), m.p. 99–100° (lit. value[3] 99–100°).

Compound II was also obtained by the addition of bromine to a solution of 2,5-dibromo-2,5-dinitropentanamide in 10% sodium hydroxide at 70°. It was identified by its melting point 98–100°, and a mixed melting point determination with authentic II, m.p. 99–100°.

Reaction of α,α'-Dibromo-α,α'-dinitroadiponitrile (I) and Aqueous Hydrochloric Acid.—A suspension of 5.30 g. (0.015 mole) of α,α'-dibromo-α,α'-dinitroadiponitrile (I) in 30 ml. of 12% hydrochloric acid was heated at 80° for four hours. The resulting solution was evaporated to dryness *in vacuo* and the residue was extracted with ether in a Soxhlet extraction apparatus. The extracts were evaporated *in vacuo* and 1.30 g. (73.5% yield) of succinic acid, m.p. 186–188°, was obtained. A mixed melting point determination with authentic succinic acid was not depressed (m.p. 187–189°). The infrared spectra of the obtained solid and authentic succinic acid were superimposable.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work.

LAFAYETTE, IND.

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[12] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 123.

COMMUNICATIONS TO THE EDITOR

THE HYDROBORATION OF DIENES

Sir:

The hydroboration of olefins, followed by hydrogen peroxide oxidation, provides a convenient technique for the stereospecific (*cis*, anti-Markownikoff) hydration of double bonds.[1] Likewise, hydroboration of acetylenes provides a convenient route for the synthesis of *cis* olefins and for the conversion of terminal acetylenes into aldehydes.[2] The extension of this reaction to dienes provides a new, useful means of converting such dienes into the diols or related unsaturated alcohols.

Treatment of 3 moles of 1,3-butadiene with 1 mole of diborane at −10° yields an organoborane[3] which is converted by alkaline hydrogen peroxide into butanediol (82%), predominantly the 1,4-isomer, but with small quantities of 1,3-indicated by vapor phase chromatrographical examination. Similarly, 1,5-hexadiene is readily converted into 1,6-hexanediol.

Diborane, 0.33 mole, generated from sodium borohydride and boron trifluoride etherate in diglyme,[1b] was passed into 0.1 mole of 1,5-hexadiene contained in 50 cc. of tetrahydrofuran during 1 hour. After oxidation at 0° with alkaline hydrogen peroxide,[1c] the product was distilled: b.p. 105–108° at 0.6 mm., 9.3 g., 79%, m.p. 40–43°.

Treatment of excess 1,3-butadiene with diborane results in the predominant formation of the diol accompanied by minor amounts (2–10%) of allylcarbinol (v.p.c. analysis). Competitive hydroboration of 1,3-butadiene and 1-hexene results in preferential reaction of the olefin, indicating that conjugation decreases the reactivity of the double bonds. Apparently, the first addition to 1,3-butadiene occurs predominantly 1:2, followed by a relatively fast second addition to the unconjugated double bond in the 3:4 position.

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[1] (a) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956); (b) *J. Org. Chem.*, **22**, 1136 (1957); (c) H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247 (1959); (d) R. Dulou and Y. Chrétien-Bessiere, *Compt. rend.*, **248**, 416 (1959); (e) W. J. Wechter, *Chemistry and Industry*, 294 (1959); (f) S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

[2] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 1512 (1959).

[3] R. Köster, Abstracts of XVIIth International Congress of Pure and Applied Chemistry, Munich, 1959, p. 8.