taken; calcd. for $C_{24}H_{50}O_{14}$: mol. wt., 563. Found: mol. wt., 576 (in exaltone).

The infrared spectrum 10% in chloroform is typical of this type of peroxides and showed the following bands in cm.$^{-1}$: 3400(3), 2990(4.5), 2980 (4.5); 2800 (3); 1460 (4.5); 1430(2.5); 1365(5.5); 1335(3); 1290(3); 1260-(4); 1210–1230(2.5); 1170(6); 1130(6.5); 1115(6.5); 1055(5); 1010(5); 995(4); 920(3); 875–885(4.5); 860-(5.5).

**1,4,7,10,13-Pentamethyl-1,4,7,10,13-pentaethyl-1,4,7,10-tetraperoxy-1,13-dihydroperoxide** (III).—The fractions 12–16 from the chromatographic separation which gave a single spot on the paper chromatogram with an $R_f$ of 0.640 were combined and the peroxide (28 mg.) recovered and recrystallized at low temperatures from methanol. At room temperature this peroxide is a gum and is highly sensitive to shock and explodes with brisance.

*Anal.* Calcd. for $C_{20}H_{42}O_{12}$: (O), 20.23; mol. wt., 474.6. Found: (O), 20.4 (KI + $CH_3COOH$ method); mol. wt., 453 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 3400(4), 2990(5), 2980(5); 2800(3); 1465(5.5); 1430(3); 1365(7); 1335(4); 1290(3.5); 1250-(3); 1210–1230(3); 1170(6.5); 1130(7.5); 1115(7.5); 1055(5.5); 1010(5); 995(4); 920(4); 870–885(6); 860(6.5).

**1,4,7,10-Tetramethyl-1,4,7,10-tetraethyl-1,4,7-triperoxy-1,10-dihydroperoxide** (IV).—The fractions (22–33) from the chromatographic column which gave a single spot on the paper chromatogram with an $R_f$ of 0.475 were combined and the peroxide recovered and recrystallized at 70° from pentane. The crystals melted at room temperature to give a highly viscous and explosive liquid.

*Anal.* Calcd. for $C_{16}H_{34}O_{10}$: (O), 20.71; mol.wt., 386.4. Found: (O), 21.50 (KI + $CH_3COOH$ method); mol.wt., 372.0 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 3400(5.5), 2990(5), 2980(5), 2800(3.5); 1460(5.5); 1430(3); 1365(7.5); 1335(4); 1290(3.5); 1250(3); 1210–1230(3.5); 1170(6.5); 1130-(7.5); 1115(6.5); 1055(5); 1010(5); 995(4); 875–885(6); 860(6.5).

**1,4,7-Trimethyl-1,4,7-triethyl-1,4-diperoxy-1,7-dihydroperoxide** (V).—The fractions (38–48) from the chromatographic column which gave a single spot on the paper chromatogram with an $R_f$ of 0.278 were combined and the peroxide recovered. This was recrystallized at −70° from pentane, but at room temperature it exists as a highly viscous liquid which is sensitive to shock and explodes with brisance.

*Anal.* Calcd. for $C_{12}H_{26}O_8$: (O), 21.40; mol.wt., 298.3. Found: (O), 21.10 (KI + $CH_3COOH$ method); mol.wt., 289.0 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 3400(5.5), 2990(5), 2980(5), 2800-(3); 1460(6); 1430(3.5); 1365(7.5); 1330(4); 1290(3.5); 1250(3); 1210–1230(3); 1170(7); 1125(8); 1115(7); 1055-(5); 1010(5); 995(3.5); 915(4); 885(6.5); 875(6.5); 860(6.5).

This peroxide also formed a bis-*p*-nitrobenzoate, m.p. 77–78° from ethyl alcohol.

*Anal.* Calcd. for $C_{26}H_{32}N_2O_{14}$: C, 52.34; H, 5.41; N, 4.70. Found: C, 52.66; H, 5.59; N, 4.75.

These results complete the list of the seven different peroxides originally detected in the crude mixture.

**Acknowledgment.**—The authors are indebted to Dr. Nagy for the combustion analyses, to Dr. Nelson and associates for the infrared spectra and to Lucidol Division of Wallace and Tiernan, Inc., for financial support of this investigation.

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

# The Alkyl Nitration of Active Methylene Compounds. II.[1,2] The Nitration of Aliphatic Nitriles and Ketones

BY HENRY FEUER AND CHRISTOS SAVIDES

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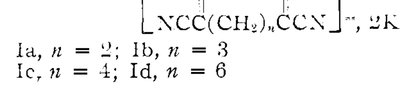
The nitration of aliphatic nitriles, dinitriles and ketones with amyl nitrate in the presence of potassium *t*-butoxide afforded in good yields the potassium salts of the corresponding α-nitronitriles, α,α'-dinitrodinitriles and α,α'-dinitroketones. Dipotassium α,α'-dinitroadiponitrile was hydrolyzed to 1,4-dinitrobutane and was found to react readily with methyl vinyl ketone to give 5,8-dicyano-5,8-dinitro-2,11-dodecanedione.

In a previous publication[2] it was shown that cyclic ketones are effectively nitrated with amyl nitrate in the presence of sublimed potassium *t*-butoxide to give the dipotassium salts of the corresponding α,α'-dinitrocyclic ketones. We have now found that the reaction is generally applicable for aliphatic mononitriles, α,ω-dinitriles, aliphatic ketones and aryl alkyl ketones.

Adiponitrile was chosen as a model compound for the study of the nitration of nitriles since the product, dipotassium α,α'-dinitroadiponitrile (Ia), was not very hygroscopic and could be readily purified. As in the case of cyclic ketones, it was found that the nitration of adiponitrile was most successful in the presence of a strong base and in the absence of hydroxylic solvents. Thus the yield of Ia was 16% when potassium ethoxide was the base and tetrahydrofuran the solvent. However, with the stronger base, sublimed potassium *t*-butoxide in tetrahydrofuran, the yield of compound Ia was increased to 93%.

By following the latter procedure (which afforded the best yield with adiponitrile), pimelonitrile, suberonitrile, sebaconitrile, butanenitrile and hexanenitrile were nitrated.[3]



$$NCCH_2(CH_2)_n CH_2CN \xrightarrow[2Me_3COK]{2AmONO_2} \left[ NC\overset{\overset{NO_2}{\|}}{C}(CH_2)_n\overset{\overset{NO_2}{\|}}{C}CN \right]^{=}, 2K$$

Ia, $n = 2$; Ib, $n = 3$
Ic, $n = 4$; Id, $n = 6$

Except for compound Ia, the potassium salts of I and α-nitronitriles II were very hygroscopic and could not be purified. Conversion of these

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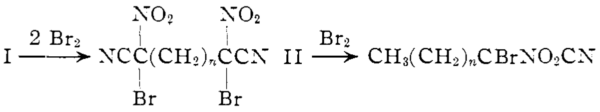
[1] From the Ph.D. thesis of Christos Savides, Purdue University, 1958.

[2] For the previous publication see H. Feuer, J. W. Shepherd and C. Savides, THIS JOURNAL, **78**, 4364 (1956).

[3] Evidence of nitration was observed with acetonitrile; however, the product could not be isolated.

salts to the corresponding nitro compounds was not satisfactory, since only unstable oils were obtained after acidification. Therefore, in order to identify the nitration products and determine the extent of nitration, the salts I and II were brominated in a mixture of anhydrous diethyl ether and carbon tetrachloride or in aqueous solution, to the α,α′-dibromo-α,α′-dinitrodinitriles III and α-bromo-α-nitronitriles IV. The results of the nitration of aliphatic nitriles and α,ω-dinitriles are summarized in Table I.



$$\text{I} \xrightarrow{2\,\text{Br}_2} \text{NC}\overset{\text{NO}_2}{\underset{\text{Br}}{\text{C}}}(\text{CH}_2)_n\overset{\text{NO}_2}{\underset{\text{Br}}{\text{C}}}\text{CN} \qquad \text{II} \xrightarrow{\text{Br}_2} \text{CH}_3(\text{CH}_2)_n\text{CBrNO}_2\text{CN}$$

III IV

IIIa, $n = 2$; IIIb, $n = 3$ IVa, $n = 1$; IVb, $n = 3$

IIIc, $n = 4$; IIId, $n = 6$

TABLE I

| Nitrile | Bromonitronitrile | Yield,[a] % |
|---|---|---|
| $(CH_2)_2(CH_2CN)_2$ | IIIa | 78 |
| $(CH_2)_3(CH_2CN)_2$ | IIIb | 45 |
| $(CH_2)_4(CH_2CN)_2$ | IIIc | 67 |
| $(CH_2)_6(CH_2CN)_2$ | IIId | 48 |
| $CH_3(CH_2)_2CN$ | IVa | 44 |
| $CH_3(CH_2)_4CN$ | IVb | 55 |

[a] The yield is based on the starting nitrile.

The structure of the compounds of type III was indicated by elemental analysis and by the fact that two diastereoisomers were obtained by fractional crystallization of the reaction mixture. Their infrared spectra were practically identical, and it was observed that the C≡N stretching vibration[4] in the region of 4.5 μ was very weak and could not be easily detected. A similar observation was made by Kitson and Griffith[5] who found that the intensity of this band decreased considerably when oxygen-containing groups were attached to the carbon atom alpha to the nitrile group. It was further observed that this band was completely absent in the spectrum of α,α′-diacetoxy-α,α′-dimethylsuccinonitrile.

The nitration of aliphatic ketones and aryl alkyl ketones was carried out under conditions similar to those of aliphatic nitriles. Acetone, ethyl methyl ketone and 4-heptanone gave the corresponding α,α′-dinitroketones. Similarly, acetophenone afforded potassium ω-nitroacetophenone. The results are summarized in Table II.

TABLE II

| Ketone | Nitration product | Yield, % |
|---|---|---|
| $(H_3C)_2CO$ | VII | 49.0 |
| $H_3CCOCH_2CH_3$ | VI | 57.0 |
| $(H_3CCH_2CH_2)_2CO$ | V | 50.5[a] |
| $C_6H_5COCH_3$ | VIII | 40.5 |

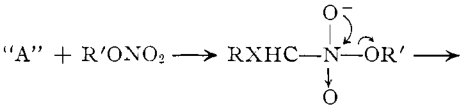
[a] Based on 3,5-dibromo-3.5-dinitro-4-heptanone.

The identity of the nitration product derived from 4-heptanone was established by its conversion to the dibromo derivative, 3,5-dibromo-3,5-dinitro-4-heptanone, since the dipotassium salt of 3,5-dinitro-4-heptanone (V) was very hygroscopic and could not be purified. Dipotassium 1,3-dinitro-2-butanone (VI) and dipotassium 1,3 dinitro-2-propanone (VII) were purified by reprecipitation with methanol from an aqueous solution and identified by elemental analysis. Acidification of the dipotassium salts of α,α′-dinitroketones to the corresponding α,α′-dinitroketones resulted in the formation of oils which were unstable at room temperature, decomposing with the evolution of oxides of nitrogen. Bromination of compounds VI and VII gave unstable products which decomposed upon distillation *in vacuo*. Potassium ω-nitroacetophenone (VIII) was identified by its conversion to the known ω-nitroacetophenone.[6]

It is seen from the above results that the nitration of active methylene compounds with alkyl nitrates, which until now was limited to aryl acetonitriles,[7] aryl acetic esters,[7] fluorene[8] and cyclic ketones,[2,9] has now been extended to include aliphatic nitriles and ketones. Our findings and observations indicate that the successful nitration of these aliphatic compounds depends on many important factors, such as base strength, reaction temperature, reaction time and solvent.

In considering the most probable reaction path for the nitration of aliphatic nitriles and ketones, as illustrated below, it would be expected that the presence of a strong base would be extremely important, for it favors the formation of the carbanion of the active methylene compound (step 1). This was indeed shown by the fact that under identical conditions, potassium *t*-butoxide afforded much better yields than the weaker base potassium ethoxide (*vide supra*). However, with sodium or potassium amide, which are stronger bases than potassium *t*-butoxide, the yields were decreased.[2] This unexpected result is probably due to the decomposition of the alkyl nitrate by base; it has been well demonstrated that alkyl nitrates undergo several reactions with alkaline reagents.[10] This becomes especially important in dinitration reactions. If it is assumed that the nitration of compounds possessing two active methylene groups occurs stepwise, the presence of excess base required for the formation of the carbanion of the second methylene group would enhance the de-

$$\text{RCH}_2\text{X} + \text{RO}^- \rightleftarrows \underset{\text{“A”}}{[\text{RCHX}]^-} + \text{ROH} \quad (1)$$



$$\text{“A”} + \text{R}'\text{ONO}_2 \longrightarrow \text{RXHC}{-}\overset{\text{O}^-}{\underset{\text{O}}{\text{N}}}{-}\text{OR}' \longrightarrow$$

$$\underset{\text{“B”}}{\text{RCHXNO}_2} + \text{R}'\text{O}^- \quad (2)$$

$$\text{“B”} + \text{R}'\text{O}^- \longrightarrow [\text{RCX}{=}\text{NO}_2]^- + \text{R}'\text{OH} \quad (3)$$

$X = COCH_3$ or CN

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[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 223.

[5] R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952.)

[6] ω-Nitroacetophenone has been previously prepared by the reaction of phenacyl bromide and silver nitrite [L. Lucas, *Ber.*, **32**, 600 (1899)], and by the oxidation of 1-phenyl-2-nitroethanol [M. M. Holleman, *Rec. trav. chim.*, **23**, 298 (1904)].

[7] W. Wislicenus and A. Endres, *Ber.*, **35**, 1755 (1902).

[8] W. Wislicenus and M. Waldmueller, *ibid.*, **41**, 3336 (1908).

[9] H. Wieland, P. Garbsch and J. J. Chavin, *Ann.*, **461**, 295 (1938).

[10] G. R. Lucas and L. P. Hammett, THIS JOURNAL, **64**, 1928 (1942); J. W. Baker and D. M. Eastey, *J. Chem. Soc.*, 1193, 1208 (1952).

composition of the alkyl nitrate. On the other hand, potassium *t*-butoxide apparently does not react with the alkyl nitrate as rapidly as alkali metal amides under comparable reaction conditions and therefore is very effective in the nitration of nitriles and ketones.

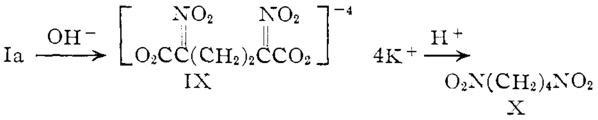
Upon consideration of step 1, it is clear that the presence of hydroxylic solvents would not favor the formation of the carbanion of active methylene compounds. It was found that the presence of *t*-butyl alcohol in the nitration of cyclopentanone resulted in a drastic decrease in the yield of dipotassium $\alpha,\alpha'$-dinitrocyclopentanone. The same effect has now been observed in the nitration of adiponitrile in which the yield of Ia decreased from 93 to 11%, when *t*-butyl alcohol was added to a slurry of potassium *t*-butoxide in ether. An added advantage in using sublimed potassium *t*-butoxide may be the fact that it forms a "complex" with *t*-butyl alcohol,[11] favoring the formation of the carbanion.

The temperature is also an important factor for the success of the reaction. Thus, it was found that best yields were obtained when the reaction was carried out below $-30°$. This indicated that at low temperatures the decomposition of the alkyl nitrate and the self-condensation of the starting ketones were greatly minimized, and that the nitration reaction was faster than both of these side reactions. It was indeed found that the nitration of phenylacetonitrile was complete within 4 minutes at $-78°$. The temperature effect may be further illustrated by the fact that the yield of potassium $\omega$-nitroacetophenone, in the nitration of acetophenone, increased from 6.7 to 40.5% by decreasing the reaction temperature from $-10$ to $-40°$.

The effect of reaction time, especially in the nitration of ketones, is of interest. It was previously[2] found that the nitration of cyclic ketones afforded best yields when the reaction mixture was worked up as soon as room temperature was attained. From reaction time studies of the nitration of $\alpha$-tetralone, we have now found that the concentration of the product, potassium $\beta$-nitro-$\alpha$-tetralone, in the reaction mixture decreased with time. A likely explanation for this is that a side reaction between the product and, possibly, $\alpha$-tetralone might have occurred. Indeed, it was observed that the amount of potassium $\beta$-nitro-$\alpha$-tetralone in a mixture of the latter and $\alpha$-tetralone decreased steadily and was virtually zero after 6 hours at room temperature.

**Reactions of Dipotassium $\alpha,\alpha'$-Dinitrodinitriles.**—Although the *free* $\alpha,\alpha'$-dinitrodinitriles were not stable at room temperature, their salts could be utilized in further reactions.

**Hydrolysis.**—It was anticipated that hydrolysis in alkaline medium of dipotassium $\alpha,\alpha'$-dinitroadiponitrile (Ia) and subsequent acidification would afford 1,4-dinitrobutane (X). When the reaction was carried out in 25% boiling potassium hydroxide, the evolution of ammonia was very fast, but acidification did not result in decarboxylation and no water-insoluble material was obtained upon extraction with ether. When the temperature was kept at 70°, 6 days was required for complete evolution of ammonia. This extended heat treatment again caused decomposition of either compounds Ia or IX, for no water-insoluble products could be isolated upon acidification with either dil. hydrochloric acid or glacial acetic acid. However, hydrolysis in aq. potassium hydroxide for 18 hours with steam passing through the vigorously stirred solution led to a 32% yield of compound X after acidification of the hydrolysate at 0° with glacial acetic acid.



$$\text{Ia} \xrightarrow{OH^-} \left[ O_2C\overset{NO_2}{\overset{\|}{C}}(CH_2)_2\overset{NO_2}{\overset{\|}{C}}CO_2 \right]^{-4} 4K^+ \xrightarrow{H^+} O_2N(CH_2)_4NO_2$$

IX X

**Michael Type Addition to Methyl Vinyl Ketone.**—In order to determine the reactivity of compound Ia toward reagents which are known to react with aliphatic primary and secondary nitro compounds, a Michael type addition reaction was carried out with methyl vinyl ketone. It was desirable to determine whether the reaction would be successful by utilizing the salt of an $\alpha$-nitronitrile directly, instead of the free nitro compound and catalytic amounts of base. The latter procedure is usually employed for Michael type additions with secondary nitro compounds.[12,13] It was found that no reaction occurred between Ia and methyl vinyl ketone in aq. methanol. Since the liberated base might have caused a reversal[14] of the Michael addition, the reaction was carried out at a *p*H of 7–8. This procedure was very effective and the product 5,8-dicyano-5,8-dinitro-2,11-dodecanedione was isolated in 51% yield.

The addition of formaldehyde to Ia did not proceed readily, and only trace amounts of the product 2,5-dicyano-2,5-dinitro-1,6-hexanediol were isolated. It was identified by its infrared spectrum and by its conversion to diacetoxy-2,5-dicyano-2,5-dinitrohexane which analyzed correctly.

### Experimental

**Dipotassium $\alpha,\alpha'$-Dinitroadiponitrile (Ia).**—Adiponitrile (5.4 g., 0.05 mole) was added to a solution of 18.5 g. (0.165 mole) of sublimed potassium *t*-butoxide in 90 ml. of purified tetrahydrofuran[15] at $-50°$, followed by the dropwise addition of 14.6 g. (0.11 mole) of amyl nitrate at $-45$ to $-50°$. The Dry Ice-bath was removed and the stirred reaction mixture was allowed to reach room temperature. The solid formed was filtered through a pressure filtration apparatus under nitrogen. The residue was washed, successively, with 30-ml. portions of tetrahdyrofuran, absolute ethanol, a mixture of 15 ml. of absolute ethanol and 15 ml. of methanol, and 30 ml. of anhydrous diethyl ether. Drying *in vacuo* over sulfuric acid gave 13.0 g. (93% yield) of **dipotassium $\alpha,\alpha'$-dinitroadiponitrile.**

*Anal.* Calcd. for $C_6H_4N_4O_4K_2$: C, 26.27; H, 1.47; N, 20.43; K, 28.46. Found: C, 25.92; H, 1.52; N, 20.50; K, 28.78.

$\alpha,\alpha'$-Dibromo-$\alpha,\alpha'$-dinitroadiponitrile (IIIa).—A stirred suspension of 8.90 g. (0.033 mole) of Ia in 150 ml. of anhydrous diethyl ether was cooled to 0°, and a solution of 10.4 g. (0.066 mole) of bromine in 40 ml. of carbon tetrachloride was added, dropwise, over a period of one hour. The reac-

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[11] S. M. McElvain and L. R. Morris, THIS JOURNAL, **73**, 206 (1951).

[12] E. P. Kohler, *ibid.*, **38**, 889 (1916).

[13] H. Shechter, D. E. Ley and L. Zeldin, *ibid.*, **74**, 3664 (1952).

[14] C. K. Ingold and E. A. Perren, *J. Chem. Soc.*, **121**, 1414 (1922).

[15] Tetrahydrofuran was purified by refluxing over sodium hydroxide, followed by distillation over potassium metal, under nitrogen.

tion mixture was filtered and the residue was extracted with ether in a Soxhlet extraction apparatus for 12 hr. The combined ether extracts and the filtrate were evaporated *in vacuo* and 9.90 g. (85.5% yield) of **α,α'-dibromo-α,α'-dinitroadiponitrile**, m.p. 120–124°, was obtained (over-all yield, based on adiponitrile 78.5%).

Separation of the two diastereoisomeric forms was accomplished by partial fractional crystallization. The solid, obtained above, was treated with 10 ml. of 95% ethanol and filtered. The precipitate was recrystallized, successively, from 95% ethanol, 80% ethanol and 70% ethanol until a constant m.p. 130–131° was obtained.

*Anal.* Calcd. for $C_6H_4N_4O_4Br_2$: C, 20.22; H, 1.13; N, 15.73; Br, 44.94. Found: C, 20.20; H, 1.39; N, 15.69; Br, 44.90.

The filtrates from the above recrystallizations were evaporated *in vacuo* and the residue was recrystallized from 95% ethanol. Concentration of the filtrate and subsequent recrystallizations from 80% ethanol afforded the second diastereomer, m.p. 119–120°. Its infrared spectrum was practically identical to the spectrum of the above higher melting isomer.

**α,α'-Dibromo-α,α'-dinitropimelonitrile (IIIb).**—Pimelonitrile (6.10 g., 0.05 mole) was nitrated with amyl nitrate as described for Ia. The product dipotassium α,α'-dinitropimelonitrile (Ib) was partially purified by successive washings with absolute ethanol and anhydrous ether. The dry, crude Ib was brominated with 16 g. (0.1 mole) of bromine as described for the preparation of IIIa. An oil was obtained which crystallized upon standing at −15° for 30 days to give 8.45 g. (45.5% yield, based on pimelonitrile) of **α,α'-dibromo-α,α'-dinitropimelonitrile**, m.p. 56–59°. Repeated recrystallizations from 95% ethanol afforded a crystalline material, m.p. 60–62°. Concentration of the filtrates afforded a second compound, m.p. 70–71.5°. The two diastereoisomeric forms isolated above showed practically identical infrared spectra.

*Anal.* Calcd. for $C_7H_6N_4O_4Br_2$: C, 22.70; H, 1.62; N, 15.13; Br, 43.25. Found: High melting isomer, C, 22.64; H, 1.59; N, 15.30; Br, 42.98; low melting isomer, C, 22.71; H, 1.71; N, 14.95; Br, 43.11.

**α,α'-Dibromo-α,α'-dinitrosuberonitrile (IIIc).**—Dipotassium α,α'-dinitrosebaconitrile (Ic) was prepared from 0.05 mole of suberonitrile as described for Ia, and brominated by the procedure given above for IIIa. A mixture of a crystalline solid and an oil was obtained. Dilution with 20 ml. of 95% ethanol, filtration of the solid, and recrystallization from 95% ethanol to a constant m.p. 98–99°, gave **α,α'-dibromo-α,α'-dinitrosuberonitrile (IIIc)**.

*Anal.* Calcd. for $C_8H_8N_4O_4Br_2$: C, 25.00; H, 2.08; N, 14.58; Br, 41.68. Found: C, 25.24; H, 2.30; N, 14.57; Br, 41.62.

The solution containing the oil was evaporated *in vacuo* and was crystallized by trituration with 10 ml. of methanol at −15°, m.p. 91–92°. Its infrared spectrum was practically identical to that of the high melting solid. The combined weight of the two diastereoisomeric forms of α,α'-dibromo-α,α'-dinitrosuberonitrile was 12.90 g. (67% yield, based on suberonitrile).

**α,α'-Dibromo-α,α'-dinitrosebaconitrile (IIId).**—Dipotassium α,α'-dinitrosebaconitrile (Id) was prepared from 0.05 mole of sebaconitrile, as described for Ia and brominated according to the procedure given for IIIa. A crystalline solid was obtained which upon recrystallization from 95% ethanol afforded one diastereoisomeric form of **α,α'-dibromo-α,α'-dinitrosebaconitrile (IIId)**, m.p. 77–77.5°.

*Anal.* Calcd. for $C_{10}H_{12}N_4O_4Br_2$: C, 29.12; H, 2.94; N, 13.59; Br, 38.83. Found: C, 29.08; H, 3.06; N, 13.38; Br, 38.89.

Concentration of the filtrates and cooling gave the second diastereoisomer (IIId) which was recrystallized from 50% ethanol, m.p. 69–70.5°. The infrared spectra of the two forms were practically identical. The combined yield of IIId was 8.31 g. (48.5% yield, based on the starting sebaconitrile).

**α-Bromo-α-nitrobutyronitrile (IVa).**—Butyronitrile (8.30 g., 0.12 mole) was nitrated according to the procedure for Ia. The product potassium α-nitrobutyronitrile (IIa) was brominated as described for IIIa and **α-bromo-α-nitrobutyronitrile (IVa)** was isolated as a liquid, and purified by fractional vacuum distillation; b.p. 60–60.5° (7 mm.), $n^{22}D$ 1.4710, yield 44%, based on butyronitrile.

*Anal.* Calcd. for $C_4H_5N_2O_2Br$: C, 24.87; H, 2.59; N, 14.50; Br, 41.45. Found: C, 24.89; H, 2.82; N, 14.33; Br, 41.72.

**α-Bromo-α-nitrohexanenitrile (IVb).**—Hexanenitrile (9.71 g., 0.10 mole) was nitrated as described for the preparation of Ia. Since the product potassium α-nitrohexanenitrile (IIb) was somewhat soluble in tetrahydrofuran, the reaction mixture was evaporated *in vacuo*, and the residue was brominated without further purification. **α-Bromo-α-nitrohexanenitrile (IVb)** was obtained as a pale yellow liquid, b.p. 79–80° (4 mm.), $n^{22}D$ 1.4668, in 55% yield, based on hexanenitrile.

*Anal.* Calcd. for $C_6H_9N_2O_2Br$: C, 32.57; H, 4.07; N, 12.66; Br, 36.18. Found: C, 32.79; H, 4.33; N, 12.70; Br, 36.46.

**3,5-Dibromo-3,5-dinitro-4-heptanone.**—4-Heptanone (5.7 g., 0.05 mole) was nitrated as described for the preparation of Ia. The crude dipotassium 3,5-dinitro-4-heptanone was washed only with anhydrous ether and brominated as previously. **3,5-Dibromo-3,5-dinitro-4-heptanone** was obtained as a yellow liquid, b.p. 110–116° (1 mm.), 8.66 g. (50.5% yield based on 4-heptanone). A pure sample was obtained by fractional vacuum distillation, b.p. 100–101° (0.5 mm.), $n^{20}D$ 1.5151.

*Anal.* Calcd. for $C_7H_{10}N_2O_5Br_2$: C, 23.20; H, 2.76; N, 7.73; Br, 44.19. Found: C, 23.47; H, 2.99; N, 8.00; Br, 43.71.

**Dipotassium 1,3-Dinitro-2-butanone (VI).**—Ethyl methyl ketone (3.60 g., 0.05 mole) was nitrated as described for Ia. The product was washed, successively, with 20-ml. portions of methanol and anhydrous ether (11.9 g.). Further purification was accomplished by dissolution of the salt in 10 ml. of water and reprecipitation with 150 ml. of ethanol to give 6.8 g. (57% yield) of pure **dipotassium 1,3-dinitro-2-butanone.**

*Anal.* Calcd. for $C_4H_4N_2O_5K_2$: C, 20.16; H, 1.68; N, 11.78; K, 32.77. Found: C, 19.84; H, 1.99; N, 11.67; K, 33.18.

**Dipotassium 1,3-Dinitro-2-propanone (VII).**—Acetone (2.90 g., 0.05 mole) was nitrated and purified as described above for compound VI to give 10.8 g. of VII. Further purification by reprecipitation with methanol from an aqueous solution afforded 5.45 g. (49% yield) of pure **dipotassium 1,3-dinitro-2-propanone.**

*Anal.* Calcd. for $C_3H_2N_2O_5K_2$: C, 16.07; H, 0.90; N, 12.50; K, 34.82. Found: C, 15.72; H, 1.02; N, 13.03; K, 34.59.

**Potassium ω-Nitroacetophenone (VIII).**—Acetophenone was nitrated as described for the preparation of VI and **potassium ω-nitroacetophenone** was obtained in 40.5% yield. Acidification with dil. sulfuric acid afforded ω-nitroacetophenone, m.p. 107–108° (lit.[6] m.p. 108°).

**Potassium 2-Nitrophenylacetonitrile.**—Phenylacetonitrile was nitrated as described for Ia and **potassium 2-nitrophenylacetonitrile** was obtained in 95% yield. An analytical sample was obtained after one recrystallization from hot absolute ethanol.

*Anal.* Calcd. for $C_8H_5N_2O_2K$: C, 48.00; H, 2.50; N, 14.00; K, 19.50. Found: C, 48.01; H, 2.77; N, 14.10; K, 19.79.

**1,4-Dinitrobutane (X).**—To a 7.5% aqueous potassium hydroxide solution was added 7.00 g. (0.0254 mole) of dipotassium α,α'-dinitroadiponitrile (Ia). The stirred solution was heated to 90° and steam was passed through until ammonia evolution was complete (18 hr.). The reaction mixture was cooled to 0° and glacial acetic acid was added dropwise until carbon dioxide evolution stopped. The mixture was extracted with ether in a liquid–liquid extraction apparatus and the extract was evaporated *in vacuo*. The residual oil was dissolved in 10 ml. of 95% ethanol and cooled to Dry Ice temperatures to give 1.20 g. (32% yield) of **1,4-dinitrobutane (X)**, m.p. 32–34° (lit.[16] 33–34°), mixed m.p. with authentic X, 33–34°.

**5,8-Dicyano-5,8-dinitro-2,11-dodecanedione.**—To a solution of 8.5 g. (0.031 mole) of dipotassium α,α'-dinitroadiponitrile in 100 ml. of 70% aqueous methanol was added 10 g. of methyl vinyl ketone. The reaction mixture was heated

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[16] J. von Braun and W. Sobecki, *Ber.*, **44**, 2526 (1911).

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 $\alpha,\alpha'$-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 | $1.8 \times 10^{-2}$ | 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 | $13 \times 10^{-3}$ | 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 |

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

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

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

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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).