The yellow benzene eluate from the chromatographic separation yielded, on removal of solvent, further XIII which, combined with that which had crystallized previously, weighed 0.51 g., m.p. 249–253° dec.

Ozonolysis of XX.—A solution of XX (0.200 g.) in ethyl acetate (50 ml.), cooled to −78°, was treated with ozonized oxygen for 2 minutes, when the solution had become blue. Excess ozone was swept out with nitrogen, water (50 ml.) was added, and, after the mixture had stood at room temperature overnight, the ethyl acetate layer was separated, dried and freed of solvent. The residue was dissolved in boiling cyclohexane (5 ml.). On cooling the solution, **1,2-naphthalenediol carbonate** (0.072 g., 65%), m.p. 135–137°, crystallized. It was identified by the identity of its infrared spectrum with that of the authentic compound, and by its failure to depress the m.p. of the latter. The cyclohexane mother liquor was placed on a column of Merck alumina (1.0 g.), which was then eluted with cyclohexane (25 ml.). Removal of solvent from the eluate gave a low-melting solid (m.p. *ca.* 40°) whose infrared spectrum was identical with that of **benzophenone**; the yield was 0.065 g. (60%). Its identity was confirmed by the preparation of a **2,4-dinitrophenylhydrazone**, m.p. 243.5–244°, undepressed by admixture with authentic benzophenone 2,4-dinitrophenylhydrazone (reported m.p. 240–241°[43]).

Acknowledgment.—We gratefully acknowledge fellowship support from the National Heart Institute of the National Institutes of Health and a grant from the Mallinckrodt Chemical Works which helped in defraying the expenses of this investigation.

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[43] J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946).

CAMBRIDGE 38, MASSACHUSETTS

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

Preparation and Reactions of α,α'-Dibromo-α,α'-dinitrocyclic Ketones[1]

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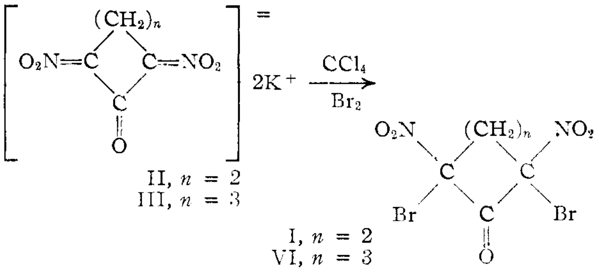
α,α'-Dinitro-α,α'-dibromocyclic ketones, such as α,α'-dinitro-α,α'-dibromocyclopentanone (I), α,α'-dinitro-α,α'-dibromocyclohexanone and β-nitro-β-bromo-α-tetralone were prepared by bromination of the corresponding potassium salts of dinitrocyclic and mononitrocyclic ketones. I was converted to 1,1,4,4-tetrabromo-1,4-dinitrobutane on treatment with aqueous base or acid. Refluxing of I with methanolic hydrogen chloride gave dimethyl 2-bromo-2-nitroglutarate and methyl 2,5-dibromo-2,5-dinitropentanoate, respectively.

The reactions of the salts of α,α'-dinitrocyclic ketones have been little investigated. Wieland[2] reported that careful acidification with mineral acid of the dipotassium salts of α,α'-dinitrocyclopentanone (II) and α,α'-dinitrocyclohexanone (III) gave first the mono-salts and then the free dinitroketones. Klager[3] has shown that the only identifiable products from the reaction of compounds II and III with bromine in either neutral or basic aqueous media are $\alpha,\alpha',\omega,\omega'$-tetrabromo-$\alpha,\omega$-dinitroparaffins (IV). It now has been found that ring opening also occurs in acidic medium, for a 10% yield of 1,1,4,4,-tetrabromo-1,4-dinitrobutane (V) was obtained when II reacted with bromine in an excess of acetic acid.

In order to obtain more insight into this reaction, the synthesis of α,α'-dinitro-α,α'-dibromocyclic ketones was undertaken, since they were considered possible intermediates in the ring opening reaction leading to IV. It was likely that ring opening during the bromination might be avoided under strictly anhydrous conditions. When compounds II and III were dried carefully at 50° and 2 mm. over concd. sulfuric acid and then brominated in carbon tetrachloride, α,α'-dibromo-α,α'-dinitrocyclopentanone (I) and α,α'-dibromo-α,α'-dinitrocyclohexanone (VI) were obtained as solids in yields of 71 and 25%, respectively.

When incompletely dry salts were used some ring opening occurred with formation of IV.

After several recrystallizations from carbon tetrachloride, compound I melted from 122–125° depending on the rate of heating. This can be attributed to the fact that the compound may exist as a mixture of *meso*-form and *d,l*-pair. Five crystallizations with hexane yielded a solid which melted sharply at 124–125°. However, this solid as well as the mixture slowly converted at room temperature to V. Compound VI was obtained in two forms, an unstable oil which liberated bromine and a stable crystalline compound (m.p. 134–135°). Since the infrared spectrum (*vide infra*) of solid VI seems to indicate that it is the *meso*-form, the unstable oil is probably the *d,l*-pair.



II, $n = 2$
III, $n = 3$

I, $n = 2$
VI, $n = 3$

The structure of compounds I and VI was established by (1) elemental analysis, (2) infrared spectra and (3) reactions which caused ring opening. The infrared spectrum of I showed the characteristic absorption maximum for the C=O group at 5.65 μ. The maxima of the NO_2 group at 6.35 μ (asymmetric stretching) and 7.40 μ (symmetric stretching) were shifted, and this was also found in the spectrum of compound VI (6.36 and 7.42 μ). These findings agree with the observations of J. F. Brown,[4] who found that negative groups such as bromine cause a shift of the asymmetric

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[1] (a) From the Ph.D. thesis of James W. Shepherd, Purdue University, 1954; (b) presented before the Division of Organic Chemistry at the Dallas Meeting of the American Chemical Society, April, 1956.

[2] H. Wieland, P. Garbsch and J. J. Chavin, *Ann.*, **461**, 295 (1928).

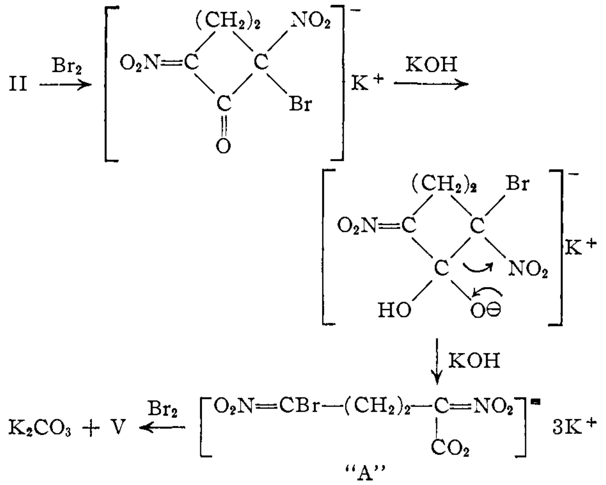
[3] K. Klager, *J. Org. Chem.*, **20**, 646 (1955).

[4] J. F. Brown, THIS JOURNAL, **77**, 6341 (1955).

stretching vibration of the NO_2 group to shorter wave length and of the symmetric to longer wave length.

With regard to the positions of nitro and bromine groups in VI, by considering the chair form, the infrared data seem to indicate that the nitro groups are in the equatorial and the bromines in the axial positions. Corey[5] has shown that an α-bromine in the equatorial position shifts the carbonyl stretching vibration to shorter wave length. Thus a shift of 23 cm.$^{-1}$ was observed in *trans*-2,6-dibromo-2-methylcyclohexanone in which one of the bromines is equatorial, while in 2,6-dibromo-2,6-dimethylcyclohexanone, in which both bromines are axial, the shift was only 8 cm.$^{-1}$. The carbonyl absorption of VI was found to be 5.80 μ (1724 cm.$^{-1}$) while that of cyclohexanone was 5.82 μ (1718 cm.$^{-1}$).

When I was added to a 20% aq. solution of potassium hydroxide a water-insoluble product was obtained which was identified as compound V (56% yield) by melting point and mixed melting point determination with an authentic sample.[3] On addition of methanol to the filtrate, a potassium salt precipitated which was identified as II (38% yield). The fact that no trace of dipotassium 1,4-dibromo-1,4-dinitrobutane could be isolated seems to indicate that the cyclic compound I is not an intermediate in the formation of V in the alkaline bromination of the salt II. Rather, it is very likely that after bromination takes place at one of the α-positions, nucleophilic attack of OH^- on the carbonyl carbon with appropriate electron shift causes ring opening to the intermediate "A" which is converted by further bromination and decarboxylation to compound V.



Ring opening with the formation of V (10% yield) also occurred when I was treated with acetic acid. The yield of V increased to 80% when the reaction was carried out in the presence of bromine. The reaction probably involves protonation of the carbonyl group in I, followed by hydrolytic cleavage and subsequent bromination.

The reaction of I with methanolic hydrogen chloride afforded an oil which on distillation *in vacuo* was separated into two fractions. The lower boiling material (91° (0.35 mm.)) crystallized and was identified as dimethyl 2-bromo-2-nitroglutarate (VII) by its elemental analysis and infrared spectrum. It showed the characteristic absorption peaks for the NO_2 group at 6.4 μ and the two ester C=O bands at 5.75 and 5.80 μ. One of these bands is shifted to lower wave length which is in agreement with structure VII. A similar shift in the C=O band has been observed in α-bromo acids and α-bromo ketones. For instance in α-bromostearic acid the C=O band was shifted from 5.86 μ in stearic acid to 5.83 μ.[6] By analogy, in the spectrum of VII, the peak at 5.75 μ may be assigned to the C=O group with α-bromo-α-nitro substituents.

The second fraction which distilled at 125–127° (0.35 mm.) did not solidify. The elemental analysis and infrared spectrum (C=O 5.75 μ; NO_2 6.40 μ) agreed best with that of methyl 2,5-dibromo-2,5-dinitropentanoate (VIII). The elemental analysis showed a high carbon value but this probably was due to the presence of a small amount of VII.

The structure of compound VIII was proven by the following transformations.

(1) Careful hydrolysis with methanolic potassium hydroxide and subsequent acidification resulted in decarboxylation and formation of 1,4-dibromo-1,4-dinitrobutane (IX). IX was identical with the compound previously obtained by the bromination of disodium 1,4-dinitrobutane.[7]

(2) Bromination of the methanolic alkaline hydrolysate gave the known compound V.

The formation of compound VIII very likely involves protonation of I and attack by methanol to give a hemiacetal which undergoes ring opening with loss of a proton.

The formation of compound VII is believed to involve a modified Nef[8] reaction on compound VIII.

The conversion of a bromo nitro group to a carboxyl group has not been reported previously and studies are in progress in this Laboratory to determine whether this is a general reaction.

The bromination of dry potassium β-nitro-α-tetralone (X) gave a product which analyzed correctly for β-bromo-β-nitro-α-tetralone. It differed from the compound which resulted from the bromination of X in aq. medium which was identified as 2-(3,3-dibromo-3-nitropropyl)-benzoic acid.[9]

Experimental

Preparation of the Potassium Salts of α-Nitro- and α,α'-Dinitrocyclic Ketones.[10]—**Dipotassium 2,5-dinitrocyclopentanone (II), dipotassium 2,6-dinitrocyclohexanone (III) and potassium β-nitro-α-tetralone (X)** were prepared according to a procedure described previously.[9] III could not be further purified. II and III were dried to constant weight over sulfuric acid at 50° (2 mm.). X was obtained as golden-yellow crystals, m.p. 280° dec., by dissolving it in hot 95% ethanol and cooling to −5°.

Anal. Calcd. for $C_{10}H_8NO_3K$: C, 52.38; H, 3.51; N, 6.11; K, 17.06. Found: C, 52.10; H, 3.49; N, 6.07; K, 17.00.

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[5] E. J. Corey, THIS JOURNAL, **77**, 5415 (1955).

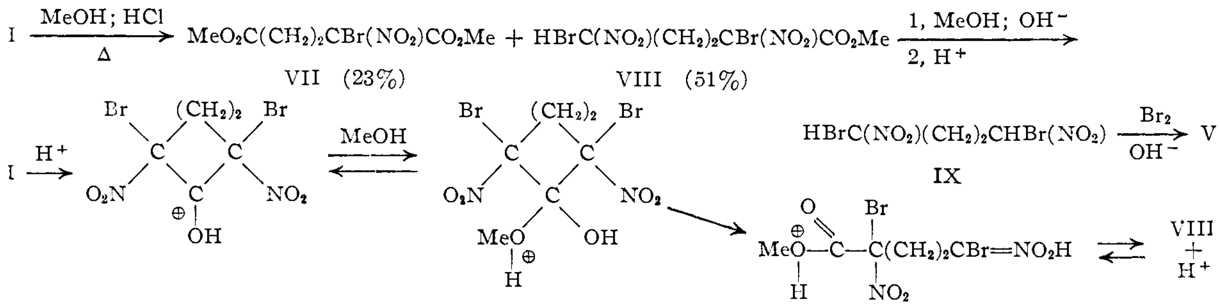
[6] R. G. Sinclair, A. F. McKay, G. S. Meyers and R. N. Jones, *ibid.*, **74**, 2578 (1952).

[7] Unpublished data from the Ph.D. Thesis of C. R. Colwell, Purdue University, 1950.

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

[9] H. Feuer, J. W. Shepherd and C. Savides, THIS JOURNAL, **78**, 4364 (1956).

[10] Contact of the dry salts with metal spatulas should be avoided, since it may cause decomposition.



Preparation of α,α'-Dibromo-α,α'-dinitrocyclic Ketones. (a) **2,5-Dibromo-2,5-dinitrocyclopentanone.**—A suspension of 6.25 g. (0.025 mole) of dipotassium 2,5-dinitrocyclopentanone in 70 ml. of anhydrous ether was cooled to −5° by means of a Dry Ice-bath. A solution of 8 g. (0.05 mole) of bromine in 35 ml. of dry carbon tetrachloride was added dropwise, with stirring, for one hour. The reaction mixture was filtered, and the solid residue was extracted with ether in a Soxhlet extraction apparatus for 18 hours. The ether extract and the filtrate were evaporated *in vacuo*, and the solid residue was recrystallized several times from carbon tetrachloride to give 5.27 g. (71% yield) of **2,5-dibromo-2,5-dinitrocyclopentanone**, m.p. 122–125°. Five recrystallizations from hexane raised the melting point to 124–125°.

Anal. Calcd. for $C_5H_4N_2O_5Br_2$: C, 18.05; H, 1.20; N, 8.42; Br, 48.18. Found: C, 18.22; H, 0.99; N, 8.54; Br, 47.94.

(b) **2,6-Dibromo-2,6-dinitrocyclohexanone.**—The procedure for the preparation of this compound was identical to that described in (a). The crude product was obtained as a mixture of a solid and an unstable oil. After separation of the oil and repeated crystallizations from hexane, **2,6-dibromo-2,6-dinitrocyclohexanone** m.p. 136–137°, was obtained in 25% yield.

Anal. Calcd. for $C_6H_6N_2O_5Br_2$: C, 20.83; H, 1.75; N, 8.10; Br, 46.20. Found: C, 20.87; H, 1.90; N, 8.14; Br, 46.11.

(c) **β-Bromo-β-nitro-α-tetralone.**—The compound was prepared as described in (a). The crude product was recrystallized from hexane to give 0.42 g. (35.6% yield) of **β-bromo-β-nitro-α-tetralone**, m.p. 79–79.5°.

Anal. Calcd. for $C_{10}H_8NO_3Br$: C, 44.61; H, 2.97; N, 5.20; Br, 29.37. Found: C, 44.49; H, 3.00; N, 5.21; Br, 29.52.

1,1,4,4-Tetrabromo-1,4-dinitrobutane (V). (a) **With Dipotassium 2,5-Dinitrocyclopentanone, Glacial Acetic Acid and Bromine.**—To a solution of 1 g. (4 mmoles) of dipotassium 2,5-dinitrocyclopentanone in 2 ml. of water was added dropwise 6 ml. of glacial acetic acid at 0°. Bromine was then added until the color persisted, followed by 20 ml. of water. The bromine color faded from the aqueous solution so more bromine was added until the color persisted. The solid which formed was separated by filtration and 0.5 g. (10% yield) of V was obtained.

(b) **With 2,5-Dibromo-2,5-dinitrocyclopentanone, Acetic Acid and Bromine.**—Bromine (1.60 g., 0.01 mole) was added dropwise to a solution of 1 g. (30 mmole) of 2,5-dibromo-2,5-dinitrocyclopentanone in 20 ml. of glacial acetic acid at 0°. The reaction mixture was poured into 60 ml. of water and 1.14 g. (81% yield) of V was obtained after filtration and drying.

(c) **With 2,5-Dibromo-2,5-dinitrocyclopentanone and Potassium Hydroxide.**—One gram (3 mmoles) of 2,5-dibromo-2,5-dinitrocyclopentanone was added in small portions to 3 ml. of 20% potassium hydroxide maintained at 0°. The water-insoluble product was identified as compound V (0.39 g., 56%) by melting point, 99–100°[8] and a mixed melting point determination which gave no depression.

Upon addition of 12 ml. of methanol to the filtrate, a solid was obtained which was identified as dipotassium 2,5-dinitrocyclopentanone (0.14 g., 37%) by its explosion point, 259°.[9]

The Reaction of 2,5-Dibromo-2,5-dinitrocyclopentanone with Methanolic Hydrogen Chloride.—A solution of 8.3 g. (0.025 mole) of 2,5-dibromo-2,5-dinitrocyclopentanone in 40 ml. of methanol saturated with hydrogen chloride was refluxed for five minutes. After evaporation of the solvent *in vacuo*, the remaining oil was fractionated.

The first fraction distilled at 91° at 0.35 mm. and solidified after standing for several days in the freezer compartment. Several crystallizations from hexane gave **dimethyl 2-bromo-2-nitroglutarate**, m.p. 67.5–68.0°, in 23% yield.

Anal. Calcd. for $C_7H_{10}NO_6Br$: C, 29.60; H, 3.55; N, 4.95; Br, 28.14. Found: C, 29.91; H, 3.76; N, 5.18; Br, 28.40.

The second fraction was collected at 125–127° and 0.35 mm., $n^{20}D$ 1.5120. It was identified as **methyl 2,5-dibromo-2,5-dinitropentanoate** (50.6% yield).

Anal. Calcd. for $C_6H_8N_2O_6Br_2$: C, 19.77; H, 2.91; N, 7.69. Found: C, 20.56; H, 2.45; N, 7.76.

Structure Determination of Methyl 2,5-Dibromo-2,5-dinitropentanoate (VIII). (a) **Formation of 1,4-Dibromo-1,4-dinitrobutane.**—Compound VIII was refluxed with methanolic potassium hydroxide for 20 minutes. Upon acidification with 5 *N* hydrochloric acid, extraction with ether, and evaporation of the solvent *in vacuo*, an oil remained. This was heated on a steam-bath for five minutes with 5 ml. of concd. hydrochloric acid and extracted with ether. Upon evaporation of the solvent a crystalline product was obtained, m.p. 58–59°, which was identified as **1,4-dibromo-1,4-dinitrobutane**. A mixed melting point determination with an authentic sample was 58°.

(b) **Formation of 1,1,4,4-Tetrabromo-1,4-dinitrobutane.** Compound VIII was hydrolyzed with methanolic potassium hydroxide. The solution was cooled to 0° and bromine was added dropwise to give a crystalline compound, m.p. 99–100°, which was identified as 1,1,4,4-tetrabromo-1,4-dinitrobutane. A mixed melting point with an authentic sample was not depressed.

Preparation of 1,4-Dibromo-1,4-dinitrobutane.[7]—Disodium 1,4-dinitrobutane (14.3 g., 0.075 mole) was suspended in 250 ml. of anhydrous ether by rapid stirring and the suspension cooled to 5°. A solution of 23.85 g. (0.150 mole) of bromine in 32 ml. of chloroform was added dropwise, and after 30 minutes the ether solution was decanted and evaporated to yield 18.6 g. (80% yield) of a yellow liquid. On chilling, 6.21 g. of a white solid was obtained which was recrystallized from methanol. This solid, m.p. 58°, analyzed correctly for **1,4-dibromo-1,4-dinitrobutane.**

Anal. Calcd. for $C_4H_6N_2O_4Br_2$: C, 15.69; H, 1.96; N, 9.15. Found: C, 15.95; H, 2.13; N, 9.10.

The remaining liquid was twice distilled to 8.8 g. of a straw-colored liquid, b.p. 149° at 3 mm.; $n^{20}D$ 1.5340.

Anal. Calcd. for $C_4H_6N_2O_4Br_2$: C, 15.69; H, 1.96; N, 9.15. Found: C, 16.05; H, 1.99; N, 9.09.

The two forms of 1,4-dibromo-1,4-dinitrobutane isolated represent the meso and *dl* pair.

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

LAFAYETTE, IND.