apparently very easily overcome. We are continuing our studies by examining the effect of other, larger ortho substituents on the resonance effect of the *p*-phenyl substituent in benzophenones.

In comparison with the result for the hindered nitrobenzenes,[13,14] these two results are startling. In the nitrobenzenes, where one begins with a system without much resonance interaction between substituent and reaction center and produces an ion where resonance stabilization is important, steric inhibition of resonance is easily achieved by flanking groups. Now juxtaposed to this system we have a case where resonance demand is lost in the product ion, yet as measured by substituent effects flanking substituents seem unable to decrease resonance interaction substantially. This latter case is of course one in which the number of free rotors increases throughout the progress of the reaction, while the nitrobenzene rearrangement involves a decreasing number of rotors as the quinonoid ion is formed in the initial stages of the reaction. In the statistical treatment,[22] the energy dependence of rates (and therefore ultimately ion intensities) is then different for the two cases. Even so, it is difficult to draw a fully consistent picture. Apparently resonance effects remain important in spite of blocking in simple cleavages like the formation of *m/e* 105 in benzophenones, fast reactions on the average, but can be blocked in at least some rearrangements, like the nitrobenzene rearrangement, which are on the average several orders of magnitude slower. Perhaps this implies that steric inhibition of resonance takes time to become effective, as if ionization on the nitrogen atom in both systems (or the first transmittal of energy to this site of lowest energy) produces at first a nonequilibrium set of states in which there is enough vibrational energy associated with the dimethylamino group to force a more nearly planar configuration of the substituent and the ring, but then over several hundred vibrational periods equilibrium among vibrational modes over the whole molecule is achieved, and the substituent then no longer can so easily achieve such a small average dihedral angle with the ring.

(22) H. M. Rosenstock, *Advan. Mass Spectrom.*, **4**, 523 (1968), and references contained therein.

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Cleavage of α,α'-Dinitrocyclanones

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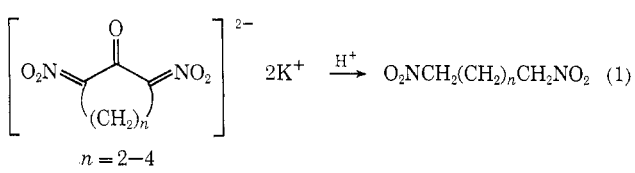
In aqueous medium at the appropriate pH, potassium salts of α,α'-dinitrocyclanones undergo ring cleavage to the corresponding α,ω-dinitroalkanes in high yield. In methanolic acetic acid, cleavage proceeds without decarboxylation to α,ω-dinitroalkyl methyl esters.

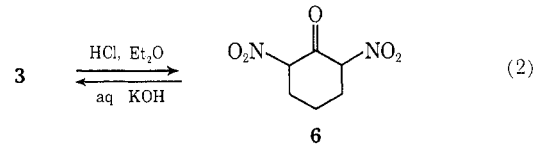
In a preliminary report,[1] we communicated a new ring-opening reaction of potassium 2-keto-3-nitrocycloalkanenitronates which provides a convenient route for the preparation of α,ω-dinitroalkanes. These salts were obtained directly from alkyl nitrate nitration mixtures[2] after acidification with glacial acetic acid and, therefore, were contaminated with potassium acetate. We are now reporting on the results of the reaction with the analytically pure salts, dipotassium 2-keto-1,3-cyclopentanedinitronate (**1**), potassium 2-keto-3-nitrocyclopentanenitronate (**2**), dipotassium 2-keto-1,3-cyclohexanedinitronate (**3**), potassium 2-keto-3-nitrocyclohexanenitronate (**4**), and dipotassium 2-keto-1,3-cycloheptanenitronate[3] (**5**) (eq 1). The purity of these



salts was conveniently determined by nonaqueous titration.[4]

The pure mononitronate salts **2** and **4** were obtained on acidifying aqueous solutions of the corresponding dinitronate salts[3] **1** and **3** at 0° with acetic acid. Compound **4** was also obtained on treating **3** with methanolic glacial acetic acid at 25°. This procedure was not applicable for the preparation of **2** because of its high solubility in methanol.

The high purity of **3** was demonstrated by the fact that it was converted in 93% yield to 2,6-dinitrocyclohexanone (**6**) upon treatment with hydrogen chloride in an ether suspension. Compound **6** was purified by sublimation *in vacuo* and, contrary to a previous report,[5] readily gave a 2,4-DNP derivative in 90% yield. **6** was reconverted into **3** on treatment with aqueous potassium hydroxide (eq 2).



α,ω-Dinitroalkanes.—The results of hydrolytic cleavage of compounds **1**–**6** leading to α,ω-dinitroalkanes are summarized in Table I. At about the same pH, the disalts **1** and **3** gave 1,4-dinitrobutane (**7**) and 1,5-dinitropentane (**8**), respectively, in the same yields as the monosalts **3** and **4**, except that 2 molar equiv of acid was required. However, a significant difference between **1** and **3** was observed on treatment with acetic

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(1) H. Feuer and R. S. Anderson, *J. Amer. Chem. Soc.*, **83**, 2960 (1961).

(2) H. Feuer, J. W. Shepherd, and C. Savides, *ibid.*, **78**, 4364 (1956).

(3) H. Feuer, A. M. Hall, S. Golden, and R. L. Reitz, *J. Org. Chem.*, **33**, 3622 (1968).

(4) H. Feuer and B. F. Vincent Jr., *Anal. Chem.*, **35**, 598 (1963).

(5) H. Wieland, P. Garbsch, and J. J. Chavan, *Justus Liebigs Ann. Chem.*, **461**, 295 (1928).

acid (pH 5). Compound **1** was converted to monosalt **2** in 95.5% yield while **3** was cleaved to **8** in 88% yield. On the other hand at pH ~6 disalt **5** afforded 1,7-dinitrohexane in 91% yield.[3]

The dependence of pH on ring size in the cleavage reaction was also apparent with the monosalts **2** and **4** (Table I).

TABLE I

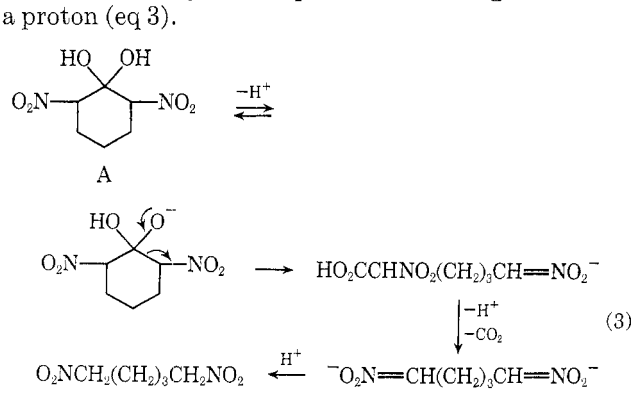
AQUEOUS ACIDIC CLEAVAGE OF POTASSIUM SALTS OF α,α'-DINITROCYCLANONES AND α,α'-DINITROCYCLOHEXANONE TO α,ω-DINITROALKANES[a]

Compd	Acid (equiv)	Initial pH	Final pH	Time, hr	α,ω-DNA,[b] yield, %
1	H_2SO_4 (1.0)	3.5	4.0	5	61.0
1	HCO_2H (2.0)	3.5	4.0	5	82.7
1[c]	CH_3CO_2H (2.0)	5.0	5.0		*d*
2	H_2SO_4 (0.5)	3.5	4.0	5	64.1
2	HCO_2H (1.0)	4.0	5.0	4	84.2
3[e]	H_2SO_4 (2.0)	1.0	1.0	1	*f*
3	H_2SO_4 (1.0)	4.0	4.0	12	70.9
3	CH_3CO_2H (2.0)	5.0	6.0	12	88.1
4	CH_3CO_2H (1.0)	5.0	6.0	12	90.2
4	CO_2 (excess)	6.0	7.0	12	90.5
5[g]	Picolinic (<2.0)	6.0	6.0	12	90.9
6	H_2SO_4 (1.0)	2.0	3.0	12	37.4[h]
6	*i*	3.0	4.0	12	89.1

[a] In all experiments the reaction temperature was 25° unless noted otherwise. [b] DNA, dinitroalkane. [c] The reaction was carried out at 3° for 1 hr and then at 25° for 3 hr. [d] A 95.5% yield of compound **2** was obtained. [e] The reaction temperature was 3°. [f] Compounds **6** (50.6%) and **3** (23.4%) were obtained, the latter after basifying the aqueous layer with potassium hydroxide. [g] See ref 3. [h] There were also obtained **6** (19.4%) and **3** (11.2%). [i] The reaction was carried out in water and the initial pH was taken after a homogeneous solution was obtained (1 hr).

When disalt **3** was treated with sulfuric acid at pH 1 at 3°, the cleavage reaction was exceedingly slow and 74% of **3** was accounted for as uncleaved. Extraction of the aqueous reaction mixture with ether gave 50.6% of **6**. Neutralization of the aqueous layer with potassium hydroxide led to a 23.4% recovery of **3**. Similarly, cleavage of **6** was retarded with sulfuric acid at pH 2–3 because only 37.4% **8** was obtained. On the other hand, compound **6** was cleaved to **8** in 89% yield in water alone.[6]

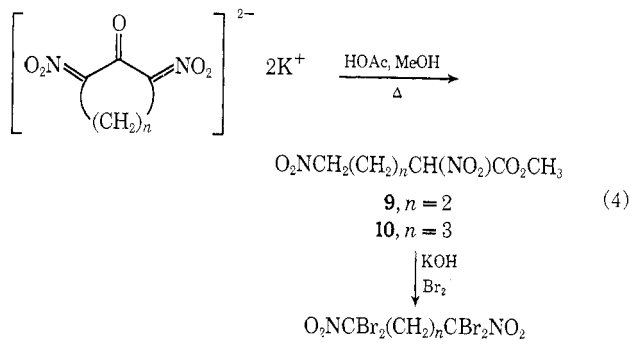
The retardation of the cleavage reaction of α,α'-dinitro ketones at low pH can be readily understood if one postulates[7,8] that the cleavage proceeds *via* an anion formed from a hydrated species "A" through the loss of a proton (eq 3).



(3)

(6) The monosalts **2** and **4** also underwent cleavage in water, in an apparent disproportionation reaction, to give approximately equal amounts of the corresponding α,ω-dinitroalkanes **7** and **8** and disalts **1** and **3**.

α,ω-Dinitroalkyl Esters.—Compounds **1**, **3**, and **6** were cleaved in refluxing methanolic acetic acid without decarboxylation to give, respectively, methyl 2,5-dinitropentanoate (**9**) and methyl 2,6-dinitrohexanoate (**10**) in yields of about 65% (eq 4).[9] The cleavage reaction was also successful with compound **5** as ascertained from infrared and nmr spectra of the crude reaction product. However, attempts to purify the crude ester by glpc or vacuum distillation led to decomposition. The structure of **9** and **10** was confirmed by spectral data and by conversion to the corresponding $\alpha,\alpha,\omega,\omega$-tetrabromo-$\alpha,\omega$-dinitroalkanes on treatment with bromine in alkaline medium (eq 4).



(4)

Compounds **9** and **10** were found to be relatively strong pseudo acids. This property was rather well illustrated by the fact that treating disalt **3** with an equivalent amount of **10** at 25° in anhydrous methanol gave a 96% yield of monosalt **4** and a 90% yield of the monopotassium salt of **10**.

Experimental Section

Potassium 2-Keto-3-nitrocyclopentanenitronate (2).—A solution of dipotassium 2-keto-1,3-cyclopentanedinitronate[3] (**1**) (3.69 g, 14.7 mmol) in 10 ml of water was cooled to 0° and 3 ml of glacial acetic acid was added all at once. Filtering the mixture after 10 min and drying *in vacuo* gave 2.41 g (77.5%) of tan **2**:[10] explosion point 152° (lit.[5] explosion point 154–158°); neutralization[4] equivalent found, 211 (calcd, 212); ir (Nujol) 1645 (C=O), 1658 (C=N), 1550 and 1357 (NO_2), and 1232 and 1160 cm^{-1} (NO_2^-); nmr (DMSO-d_6) δ 5.25 (t with spacing of 7 Hz, 1, $CHNO_2$) and 2.60 (m, 4, CH_2); uv max (95% C_2H_5OH) 212 mμ (log ϵ 3.70), 248 (3.53), 357 (4.14), and 405 (3.58); uv max (H_2O) 224 mμ (log ϵ 3.62), 250 (3.57), and 402 (4.37).

Potassium 2-Keto-3-nitrocyclohexanenitronate (4). A. From Compound 3 and Acetic Acid.—The procedure was similar to that described for **2** except that compound **3**[3] (3.36 g, 15 mmol) was used.

Drying the red solid *in vacuo* gave 1.655 g (92.8%) of **4**:[10] explosion point 214° (lit.[5] explosion point 221°); neutralization equivalent found, 227 (calcd, 226); ir (Nujol) 1651 (C=O), 1658 (C=N), 1534 and 1370 (NO_2), and 1227 and 1152 cm^{-1} (C=NO_2^-); nmr (DMSO-d_6)[11] δ 2.60 (m, 4, $CH_2C{=}NO_2^-$ and CH_2-$CHNO_2$) and 1.70 (m, 2, $CH_2CH_2CH_2$); uv max (95% C_2H_5OH) 214 mμ (log ϵ 3.52), 269 (3.58), and 422 (4.29); uv max (H_2O) 233 mμ (log ϵ 3.37) and 386 (4.35).

B. From Compound 3 and Methyl 2,6-Dinitrohexanoate (10).—To a suspension of **3** (0.676 g, 2.56 mmol) in 60 ml of anhydrous methyl alcohol was added **10** (0.564 g, 2.56 mmol).

Stirring for 1 hr at room temperature and filtering gave 0.556 g (96.0%) of **4**, explosion point 213°.

(7) R. G. Pearson, D. H. Anderson, and L. L. Alt, *J. Amer. Chem. Soc.*, **77**, 527 (1955).

(8) H. Feuer and P. M. Pivawer, *J. Org. Chem.*, **34**, 2917 (1969).

(9) Cleavage of **1** and **3** in anhydrous methanolic hydrogen chloride and of **6** in anhydrous methyl alcohol was found to be slow and gave considerable amounts of starting material. No convenient method was found to separate these from the cleavage products.

(10) No suitable solvent for recrystallization could be found.

(11) The α hydrogen exchanged with the solvent.

Evaporating the filtrate *in vacuo* and slurrying the remaining paste with ether gave after filtering and drying 0.595 g (89.9%) of **potassium 1-carbomethoxy-5-nitropentanenitronate**: mp 132–135° dec; neutralization equivalent found, 253 (calcd, 258); ir (Nujol) 1688 (C=O), 1664 (C=N), 1555 and 1381 (NO_2), and 1255 and 1110 cm^{-1} ($C{=}NO_2^-$); nmr (D_2O) δ 4.59 (m, CH_2NO_2), 3.73 (s, 3, OCH_3), 2.60 (m, 2, $CH_2C{=}NO_2^-$), and 1.75 (m, 4, CH_2); uv max (H_2O) 294 mμ (log ϵ 3.94).

2,6-Dinitrocyclohexanone (6).—Hydrogen chloride was introduced for 1 hr at room temperature into a suspension of disalt **3** (1.437 g, 5.44 mmol) in 200 ml of anhydrous ether. After stirring for an additional 2.5 hr at room temperature, the mixture was filtered and the filtrate was evaporated *in vacuo*. Washing the residue with ether and drying *in vacuo* gave 0.94 g (93.5%) of **2,6-dinitrocyclohexanone** (6): mp 100–101° (lit.[5] mp 110.5°); ir (Nujol) 1748 (C=O) and 1570 and 1379 (NO_2); nmr (DMSO-d_6) δ 6.10 (m, 2, $CHNO_2$) and 2.3 (m, 6, CH_2); nmr (CH_2Cl_2)[12] δ 5.25 (m, $CHNO_2$), 12.72 (s, OH), and 2.22 (m, CH_2); uv max (CH_3OH) 228 mμ (log ϵ 3.70), 259 (3.63), 321 (3.53), and 422 (4.21).

Anal. Calcd for $C_6H_8N_2O_6$: C, 38.30; H, 4.26; N, 14.90. Found: C, 38.56; H, 4.54; N, 14.94.

2,4-DNP derivative of 6 showed mp 162° dec, ethanol–ethyl acetate; ir (Nujol) 1620 (C=N) and 1560 and 1553 cm^{-1} (NO_2).

Anal. Calcd for $C_{12}H_{12}N_6O_8$: C, 39.13; H, 3.26; N, 22.83. Found: C, 39.26; H, 3.20; N, 22.02.

1,4-Dinitrobutane (7). **A. From Compound 1.**—To a solution of **1** (2.53 g, 10.1 mmol) in 60 ml of water (pH 7.9) was added 85% formic acid (1.105 g, 20.4 mmol) all at once (pH 3.5). After this had stirred for 5 hr at room temperature the pH was 4.3.

Extracting the solution with ether, evaporating the combined extracts *in vacuo*, and recrystallizing the residue from 95% ethanol gave 1.231 g (82.7%) of compound **7**, mp 30–31° (lit.[13] mp 31–32°).

B. From Compound 2.—By following a similar procedure as described in part A, 1.374 g (6.48 mmol) of **2** and 0.352 g (6.5 mmol) of 85% formic acid afforded 84.2% **7**.

1,5-Dinitropentane (8). **A. From Compound 3.**—From 2.64 g (9.98 mmol) of **3** and 1.205 g (20.1 mmol) of glacial acetic acid there was obtained 1.423 g (88.1%) of compound **8**: bp 92–93° (0.01 mm); $n^{20}D$ 1.4600 (lit.[13] $n^{20}D$ 1.4601).

B. From Compound 4.—Introducing carbon dioxide for 12 hr into 2.208 g (9.8 mmol) of **4** dissolved in water gave 1.442 g (90.5%) of **8**.

C. From Compound 6.—From 0.605 g (3.3 mmol) of **6** dissolved in 60 ml of water there was obtained 0.475 g (89.1%) of **8**.

Methyl 2,5-Dinitropentanoate (9).—To a suspension of compound **1** (3.20 g, 12.8 mmol) in 80 ml of methanol was added glacial acetic acid (3.84 g, 64 mmol). After the mixture refluxed for 12 hr at 65° the resulting solution was concentrated *in vacuo*, the residue was taken up in ether, and the precipitated potassium acetate was filtered off. Concentrating the filtrate *in vacuo* gave 1.76 g (66.7%) of **methyl 2,5-dinitropentanoate**: bp 130–132° (0.28 mm); $n^{20}D$ 1.4634; ir (Nujol) 1748 (C=O) and 1575, 1567, and 1374 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 5.28 (t with spacing of 6 Hz, 1, $CHNO_2$), 4.52 (m, 2, CH_2NO_2), 3.88 (s, 3, CH_3), and 2.28 (m, 4, CH_2); uv max (CH_3OH) 284 mμ (log ϵ 2.18).

Anal. Calcd for $C_6H_{10}N_2O_6$: C, 34.95; H, 4.85; N, 13.60. Found: C, 34.97; H, 4.61; N, 13.69.

Treating **9** (0.485 g, 2.35 mmol) with aqueous potassium hypobromite gave 0.834 g (76.5%) of 1,1,4,4-tetrabromo-1,4-dinitrobutane, mp 99–100° (hexane) (lit.[2] mp 99–100°).

Methyl 2,6-Dinitrohexanoate (10).—The procedure similar to that described for **9**, except that 2.12 g (8 mmol) of **3** was used, afforded 1.15 g (65.2%) of **methyl 2,6-dinitrohexanoate**: bp 138–140° (0.3 mm); $n^{20}D$ 1.4630; ir (Nujol) 1770 (C=O), and 1575, 1558, and 1380 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 5.19 (t with spacing of 7 Hz, 1, $CHNO_2$), 4.43 (m, 2, CH_2NO_2), 3.86 (s, 3, CH_3), and 2.10 (m, 6, CH_2); uv max (CH_3OH) 268 mμ (log ϵ 1.96).

Anal. Calcd for $C_7H_{12}N_2O_6$: C, 38.18; H, 5.45; N, 12.73. Found: C, 38.46; H, 5.55; N, 12.86.

Registry No.—**1**, 12286-73-6; **2**, 26717-79-3; **3**, 12286-74-7; **4**, 26785-71-7; **6**, 26785-72-8; **6**, 2,4-DNP derivative, 26736-24-3; **7**, 4286-49-1; **8**, 6848-84-6; **9**, 26736-27-6; **10**, 26074-70-4; 1-carbomethoxy-5-nitropentanenitronate, 26736-29-8.

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

(12) By integration of signal areas it was estimated that in this solvent, **6** was enolized to the extent of 75%.

(13) H. Feuer and G. Leston, *Org. Syn.*, **34**, 37 (1954).

The Stereochemistry of Halogenation of Cyclohex-4-ene-1,2-dicarboxylic Acids

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trans-Cyclohex-4-ene-1,2-dicarboxylic acid gives on bromination the product of trans-diaxial addition. A product of similar stereochemistry is obtained on reacting the same acid with bromine chloride. The cis diacid yields with bromine chloride a trans-addition product with the bromine cis to the carboxyl group. It is inferred that the cis acid forms a bromomium ion cis to the carboxyl group. A series of halolactones can be prepared from the halogenated compounds. *cis,cis*-3-Phenylcyclohex-4-ene-1,2-dicarboxylic acid, its salt, and mono- and dimethyl ester give direct lactonization on treatment with bromine.

Remote polar substituents exert an influence on the rates[1] and the steric course of electrophilic addition to cyclohexenes.[2] The electrophile enters generally trans to an electron-withdrawing substituent,[2] but a cis epoxidation of the anhydride of I was observed.[3] This was ascribed to the boat conformation of this anhydride[3] or to a complex formation with the peracid,[2] in view of the different steric course of the epoxidation of the ester I.[2]

Halolactonization of cyclohexene-1- and -2-acetic acids gave *cis*-γ-lactones with the halogen trans to the lactone ring.[4] The reason for this stereospecificity could have been a result of a stereospecific halonium ion formation trans to the carboxylate group or simply a consequence of the unreactivity of the cis halonium ion with the carboxylate group in the side chain, due to the strain that would be created by formation of a trans lactone. The *cis*-halonium ion would in this case revert to the olefin, which could then yield a reactive *trans*-halonium ion. Bromination of cyclohex-3-enecarboxylic

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(1) H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961).

(2) H. B. Henbest, *Proc. Chem. Soc.*, 159 (1963).

(3) A. P. Gray, D. E. Heitmeier, and H. Krauss, *J. Amer. Chem. Soc.*, **84**, 89 (1962).

(4) J. Klein, *ibid.*, **81**, 3611 (1959).