BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3462—3466 (1973)

The Nucleophilic Ring-opening Reactions of α,α'-Dinitrocycloalkanones

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(Received October 23, 1972)

The keto and enolic characters of 2,6-dinitrocyclohexanone (**1**), 2,6-dinitro-4-methylcyclohexanone (**2**), and 2,7-dinitrocycloheptanone (**3**) were spectroscopically investigated and discussed. It was found that the reactions of **1** and **2** with nucleophiles can take either of two courses, depending upon the nucleophiles used: (a) the addition to the enol carbon or carbonyl carbon of the keto form, followed by ring-opening giving 2,6-dinitro- and 2,6-dinitro-4-methyl-hexanoates respectively; (b) the abstraction of the 2- and 6-protons, followed by the formation of the corresponding di-*aci*-nitronates. Primary alkoxide ions belong to the (a) group, whereas secondary and tertiary alkoxide ions, NH^-_2, RHN^-, and AcO^-, belong to the (b) group. The IR and UV spectra of the resultant α,ω-dinitrocarboxylic acid esters were also discussed.

The basic cleavage of α-nitroketones has attracted considerable synthetic interest.[1–7] The application of this cleavage to 2,6-dinitrocyclohexanone (**1**) was supposed to realize a novel simple three-step DL-lysine synthesis starting from cyclohexanone,[8] *e.g.*, the dinitration of cyclohexanone and ring-opening to 2,6-dinitrohexanoic acid, followed by its hydrogenation. During the present investigation, the same process was independently patented.[10] However, it was found that the ring-opening reactivities of **1** and 2,6-dinitro-4-methylcyclohexanone (**2**) were largely dependent on the nucleophiles especially on the bukiness of the alkoxides, and that the corresponding di-*aci*-nitronates were formed by the attack of secondary and tertiary alkoxides instead of by cleavage. The present paper will report on the chemical behaviors of **1**, **2** and 2,7-dinitrocycloheptanone (**3**) in response to the attack of alkoxides.

Results and Discussion

The structures of α,α'-Dinitrocycloalkanones. In general, α-nitroketones can be represented by three possible tautomeric structures-nitroketone, nitroenol, and *aci*-nitroketone forms.[11] The IR spectrum of **1** in the solid state (in a KBr disk) reveals a sharp carbonyl absorption at 1740 cm^{-1}, indicating the presence of a

1) A.S. Matlack and D. S. Breslow, *J. Org. Chem.*, **32**, 1995 (1967). This paper have summarized most of the previous references.

2) P. C. Pearson, D. H. Anderson, and L. L. Alt, *J. Amer. Chem. Soc.*, **77**, 527 (1955).

3) R. E. Schaub, W. Fulmor, and M. J. Weiss, *Tetrahedron*, **20**, 373 (1964).

4) P. L. Southwick, J. A. Fitzgerald, R. Madhav, and D. A. Welsh, *J. Org. Chem.*, **34**, 3279 (1969).

5) H. Feuer, A. M. Hall, and R. S. Anderson, *ibid.*, **36**, 140 (1971).

6) Techni-Chem. Co., Neth. 6713613 (1967).

7) Gulf Research and Development Co., Japan 1969—16369.

8) Another elegant three step DL-lysine synthesis from cyclohexanone was reported by Ferris *et al.*[9] by the application of the Beckmann fission of 2,6-bis(hydroxyimino)cyclohexanone as a key step.

9) a) A. F. Ferris, F. E. Gould, G. S. Johnson, H. K. Latourette, and H. Stange, *Chem. Ind.* (London), **1959**, 996. b) A. F. Ferris, G. S. Johnson, F. E. Gould, and H. K. Latourette, *J. Org. Chem.*, **25**, 492 (1960). c) A. F. Ferris, G. S. Johnson, F. E. Gould, and H. Stange, *ibid.*, **25**, 496 (1960). d) *idem.*, *ibid.*, **25**, 1302 (1960).

10) Mitsubishi Chemical Co., Neth. 690704; 690705 (1969); Ger. Offen. 1926047; *Chem. Abstr.*, **72**, 42831p (1970).

11) T. Simmons, R. F. Love, and K. L. Krenz, *J. Org. Chem.*, **31**, 2400 (1966).

Table 1. C=O absorptions of cyclohexanone and its nitoro derivatives

Compound	ν C=O (cm^{-1})	Shift (cm^{-1})	Ref.
Cyclohexanone	1712	—	
2-Nitrocyclohexanone	1739	27	27)
2,6-Dinitrocyclohexanone	1740 (1748)[a)]	1 (7)	5)

a) Ref. 5.

keto form.[12] As is shown in Table 1, the introduction of a nitro group to the 2-position of cyclohexanone brings a marked shift in C=O absorption, but the further introduction of a nitro group to the 6-position of 2-nitrocyclohexanone causes almost no change. This suggests that one of the nitro groups may be co-planar with C=O, while the other is not.[13] It has been pointed out[14] that, as a result of the trigonal geometry of the carbonyl carbon, an equatorial substituent in the 2-position of cyclohexanone is nearly eclipsed by the carbonyl oxygen, whereas an axial substituent in this position is staggered with respect to this oxygen atom. Therefore, the first nitro group is an equatorial substituent, and the second is axial. Thus, 2,6-dinitro-substituents exist in a *trans*-configuration in which electrostatic repulsions and Johnson's $A^{(1,2)}$ strain[15] are minimal. However, in an acetone solution, **1** was shown to exist nearly completely in the enol form by a study of the UV (λ_{max}: 310 nm) and NMR spectra (–Ċ=CH–: τ 4.20, 1H, quartet); this is in accordance with Feuer's results[16] reporting that the enol form is favored in aprotic solvents. However, even in methanol **1** showed an enol band at 310 nm (ε 4.67×10^2), suggesting that **1** has a tendency to enolize gradually even in protic solvents.[17] The crystalline solid of **2** was determined to exist in the enol form by a study of the IR spectrum (1640 (C=C) and 3450 cm^{-1} (OH); no C=O absorption). Compound **3** in the solid state was shown to exist nearly entirely in the keto form by a study of the IR spectrum (1750 cm^{-1} (C=O)). However, in an alcoholic solution of **3** the enol absorption at 339 nm (ε 3.54×10^2) appears together with keto absorption at 280 nm (ε 2.00×10^2), indicating an equilibrium between keto and enol forms.

The Ring-opening Reactions. The treatment of **1** with an aqueous solution of sodium carbonate gave 1,5-dinitropentane. This reaction is similar to that of potassium 1-nitro-2-keto-3-cyclohexanenitronate[18] and may be supposed to involve ring-opening, followed by the decarboxylation of the resultant 2,6-dinitrohexanoic acid. The ring-opening reactions of **1** and **2** in primary alcohol to 2,6-dinitrohexanoic and 2,6-dinitro-4-methylhexanoic acid esters respectively proceeded even in the presence of catalytic quantities of the corresponding alkoxide ions. The reactions proceeded similarly in alcoholic solutions of alkali hydroxides. In striking contrast, in the presence of stoichiometric amounts of secondary and tertiary alkoxide ions, **1** and **2** afforded 2-keto-1,3-cyclohexanedinitronate and 2-keto-4-methyl-1,3-cyclohexanedinitronate instead of the ring-opening products. The reactions of **1** and **2** with NH_2^-, NHR^-, or AcO^- also yielded the corresponding di-*aci*-nitro compounds, from which the starting materials were recovered by neutralization. Accordingly, it appears that the nucleophiles can be divided into two classes on the basis of their reactivity towards **1** and **2**: (a) one class which induces the ring-opening of **1** and **2** and (b) another which affords di-*aci*-nitro compounds. This discrimination was made possible by the observation of the UV spectra of **1** and **2** in alcoholic solutions in the presence of alkoxide ions. As is shown in Tables 2 and 3, the UV spectra of **1** in the presence of Class

Table 2. Time dependency of UV spectra of 2,6-dinitrocyclohexanone in basic methanol solution at 28°C

Time (hr)	1/10M-NaOH		1/10M-NaOMe	
	λ_{max} (nm)	ε (x10^3)	λ_{max} (nm)	ε (x10^3)
0	235	8.26	236	7.83
	325	3.25	325	3.30
3	235	8.25	235	8.45
	325	3.25	328	3.58
6	233	8.25	235	9.60
	325	3.25	329	3.83

Table 3. UV spectra of 2,6-dinitrocyclohexanone in basic alcoholic solutions after heated at 48°C for 2 hr

Nucleophile class	Solvent	Base (1/10 M)	λ_{max}	ε(x10^3)
(a)	MeOH	NaOH	234	8.92
			310 (sh)	3.51
		NaOMe	236	9.03
			310 (sh)	3.79
	EtOH	NaOH	234	1.93
			321 (sh)	2.30
		NaOEt	233	1.93
			327 (sh)	2.13
(b)	*iso*-PrOH	*iso*-PrONa	234 (sh)	4.21
	tert-BuOH	*tert*-BuONa	227 (sh)	5.62

(a) nucleophiles are characterized by a maximum absorption at 233—235 nm, accompanied by a shoulder in the range between 310 and 325 nm; this shoulder remained even if the solutions were allowed to stand for a long time. However, the UV absorptions of **1** in the presence of the Class (b) nucleophiles are lacking in shoulder absorptions. The absorption bands of the nitronate anions are broad and intense ($\varepsilon\cong10000$),

12) The C=O absorption band of **1** in Nujol was also reported to be 1748 cm^{-1} (Ref. 5).

13) E. J. Corey (*J. Amer. Chem. Soc.*, **75**, 3297 (1953)) determined the stereochemistry of 2,6-dibromocyclohexanone by carbonyl bands.

14) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N.Y. (1962), p. 240.

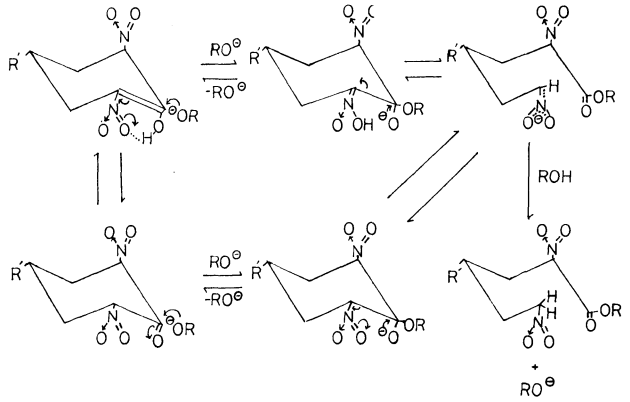
15) F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

16) H. Feuer, in Abstracts 152nd American Chemical Society Meeting, New York, N.Y., Sep. 1966 (Paper No. S-157).

17) Feuer reported that **1** exists in ethanol solely as keto form (Ref. 16).

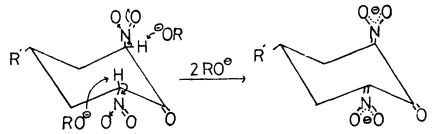
18) H. Feuer and R. S. Anderson, *J. Amer. Chem. Soc.*, **83**, 2960 (1961).

with maxima 230—240 nm[19,20] due to the π-π^* transition. The absorption in the 310—325 nm range may be due to the enol form of **1** and may be supposed to be a p-π^* transition in α-nitro-olefines.[21] The results indicate that **1** and **2** undergo the ring cleavage in nucleophilic solvents where **1** and **2** are in the enol form. The mechanism of the ring opening of **1** and **2** by the attack of the Class (a) nucleophiles may be interpreted according to Scheme I. The addition of alkoxide ions to the enol carbons or the attack of the ketonic form result in ring cleavage, thus leading to the formation of alkyl 2,6-dinitrohexanoates with nitroalkyl moieties which, in a basic solution, give the UV absorption at 233—235 nm and a shoulder absorption at 310—325 nm resulting from the small contribution of the equilibrated enol form. The ring-opening reactions proceed catalytically as the alkoxide ions are regenerated.



1:R′=H, **2**:R′=Me, **R**=primary alkyl groups
Scheme I

The Class (b) nucleophiles abstract the 2- and 6-protons to form the corresponding di-*aci*-nitro compounds, as is shown in Scheme II.



1:R′=H, **2**:R′=Me, R=secondary, tertiary alkyl groups
Scheme II

The difference in the reactivities between Class (a) and Class (b) nucleophiles may be ascribed to the steric factors and to the basicity of the alkoxide ions.

In connection with the ring-opening reactivities, **1** seemed to be more readily ruptured than 2-nitrocyclohexanone. For example, in the aqueous solution of potassium iodide, **1** afforded 1,5-dinitropentane even at room temperature, but 2-nitrocyclohexanone remained unchanged under the same conditions.

UV and IR Spectra of α,ω-Dinitro-carboxylic Acid Esters. The ring-cleavage products of α,α'-dinitrocycloalkanones are typical compounds containing two different kinds of nitro groups in one molecule. Some spectral information about these different kinds of nitro groups was obtained.

(a) UV Spectra: It has been reported that aliphatic nitro compounds and α-nitro-carboxylic acid esters are characterized by broad π-π^* transition bands of a low intensity (ε 20—40) in the 270—284 nm[22,23] region. As is shown in Table 4, the α,ω-dinitrocarboxylic acid esters were generally found to exhibit these transitions at 255—270 nm, showing a red shift with a stronger absorption. Such trends may be interpreted in terms of the repulsions between two different nitro groups in a molecule. The introduction of methyl groups as a side chain resulted in a blue shift. The maxima absorptions were not affected by the change in carboalkoxy groups. In free nitro-forms, the difference between α- and ω-nitro groups in α,ω-dinitrocarboxylic acid esters is small. However, in *aci*-nitro forms, the

TABLE 4. UV SPECTRA OF α, ω-DINITROCARBOXYLIC ACID ESTERS

$O_2N(CH_2)_nCHCH_2CHCO_2R$ (R′, NO_2)	R	in MeOH		in 1/10M-NaOMe	
		λ_{max} (nm)	ε	λ_{max} (nm)	ε
n=2 R′=H	Me	270	77	233	1.23×10^4
	Et	261	355	306	1.27×10^4
	n-Pr	263	394	—	—
	n-Bu	264	300	—	—
	n-Amyl	265	292	—	—
n=2 R′=CH_3	Me	255	270	235	5.13×10^3
				307	3.00×10^4
	Et	255	270	—	—
n=3 R′=H	Me	265	183	183	7.71×10^3
				305	4.09×10^3
	Et	265	297	232	9.78×10^3
				300	8.35×10^3
	n-Bu	265	353	235	1.03×10^4
				305	9.42×10^4

19) F. T. Williams, Jr., P. W. K. Flanagan, W. J. Taylor, and H. Schechter, *J. Org. Chem.*, **30**, 2674 (1965).
20) A. T. Nielson, "The Chemistry of the Nitro and Nitroso Groups," Part 1, ed. by H. Feuer, Intersciences Publishers, New York, N.Y., (1969), pp. 382—383.
21) M. Montagné and P. Arnaud, *C. R. Acad. Sci. Paris*, **254**, 4001 (1962).
22) H. E. Ungnade and R. S. Smiley, *J. Org. Chem.*, **21**, 993 (1956).
23) R. N. Haszeldine, *J. Chem. Soc.*, **1953**, 2525.

Table 5. IR spectra of α, ω-dinitrocarboxylic acid esters

$O_2N(CH_2)_nCHCH_2CHCO_2R$ (R′, NO_2)	R	ν_{as} NO_2 (cm^{-1})			ν_s NO (cm^{-1})		
		α-nitro	ω-nitro	Δ	α-nitro	ω-nitro	Δ
n=2 R′=H	Me	1563	1551	12	1372	1378	−6
	Et	1562	1553	9	1374	1376	−2
	n-Pr	1562	1554	8	1378	1380	−2
	n-Bu	1562	1554	7	1376	1376	0
	n-Amyl	1563	1556	7	1380	1380	0
n=2 R′=CH_3	Me	1563	1552	11	1381	1381	0
	Et	1566	1556	10	1380	1380	0
n=3 R′=H	Me	1563	1552	11	1382	1382	−7
	Et	1563	1552	11	1374	1376	−2
	n-Bu	1563	1553	10	1378	1380	−2

conjugated α-nitronate groups $\left(O{=}C{-}C{=}N\begin{matrix}O\\O^-\end{matrix}\right)$ exhibit the π-π* transition at 305—307 nm (ε 5×10^3—1.2×10^4), while the *aci*-nitro groups isolated from carboalkoxy groups showed the absorption in a shorter-wavelength range (233—235 nm).

(b) IR Spectra: On the effect of an electron-attracting α-substituent on the IR spectra of aliphatic nitro compounds, Haszeldine[23] and Brown[24] reported that asymmetrical stretching bands shifted to higher frequencies, whereas the symmetrical stretching bands moved to lower frequencies and there was no significant change in the C–N stretching vibrations. As is shown in Table 5, the present results on α,ω-dinitro-carboxylic acid esters are in exact accordance with the previously reported data. It was shown that both the asymmetrical and symmetrical stretching bands were doublets, whereas the C–N stretching vibrations were singlets. The shifts upon the introduction of carboalkoxy groups were greater in the asymmetrical stretching of nitro groups than in the symmetrical stretching. The shifts seemed to be increased in the order of the electron-attractive properties of carboalkoxy groups.

Experimental

The UV spectra were determined by means of a Hitachi double-beam spectrophotometer, Model 124. The IR spectra were recorded on a Hitachi infrared spectrophotometer, EPI-G_2. The NMR spectra were kindly determined by Drs. Kenkichi Nukada and Hajime Saito of the Basic Research Laboratories, Toray Industries, Inc., using a Varian HA-100 apparatus with TMS as the internal standard. The mp's were measured on a Yanagimoto micro-melting points apparatus with a heat block and are uncorrected.

Disodium 2-Keto-1,3-cyclohexanedinitronate (4). The dinitration procedure was similar to that described for the dipotassium salt,[26] except that sodium amide was used instead of potassium amide. The salt was purified by the use of aqueous methanol. Yield, 92.0%. Mp 240—245 °C (dec). IR (KBr): 1620 (C–O), 1410 and 1230 cm^{-1}(C–NO_2^-). UV (MeOH): 205 (ε 9.65×10^2), 280 (sh, 4.21×10^2), and 308 nm (9.65×10^2). NMR (D_2O): τ 7.80 (2H, t, J=6 Hz, 5-CH_2), and 6.83 (4H, t, J=6 Hz, 4- and 6-CH_2). Found: C, 30.94; H, 2.87; Na, 18.85%. Calcd for $C_6H_6N_2O_5Na_2$: C, 31.05; H, 2.61; Na, 19.81%.

2,6-Dinitrocyclohexanone (1). The compound was obtained from 4[25]. Colorless needles. Mp 110 °C (lit,[25] 110.5 °C). IR (KBr): 3600 (OH, w), 1740 (C=O, vs), 1560 (ν_{as} NO_2), and 1380 cm^{-1} (ν_s NO_2). UV (MeOH): 310 nm (ε 4.67×10^2). NMR (acetone-d_6): τ 4.20 (1H, q, J_{aa}=12 Hz, J_{ae}=6 Hz, 2- and 6-CH), and 7.1—8.2 (7H, m.).

Disodium 2-Keto-5-methyl-1,3-cyclohexanedinitronate. The salt was prepared by the dinitration of 4-methylcyclohexanone.[26] Scaly yellow crystals (from water-acetone). Yield, 75%; mp 222—223 °C. IR (KBr): 1648 (C=N), 1600 (C=O), 1430, 1380 (CH_3), 1280 (ν_{as} NO_2^-), and 1170 cm^{-1} (ν_s NO_2^-). Found: C, 34.39; H, 3.38; N, 11.03%. Calcd for $C_7H_8N_2O_5Na_2$: C, 34.16; H, 3.28; N, 11.38%.

2,6-Dinitro-4-methylcyclohexanone (2). The compound was prepared by the neutralization of the above disodium salt. Yield, 100%. Colorless granular crystals from methanol; mp 76—77.5 °C. IR (KBr): 3450 (OH), 1740 (C=O, vw), 1640 (C=C), 1555 (ν_{as} NO_2), 1460, 1380 (CH_3), and 1360 cm^{-1} (ν_s NO_2). The compound exists in the enol form. However, after having been allowed to stand overnight, the solid was transformed into an oily state in the keto form. IR (neat) 3450 (OH, vw), 1740 cm^{-1} (C=O, vs).

Disodium 2-Keto-1,3-cycloheptanedinitronate. This compound was prepared by the dinitration of cycloheptanone in the presence of sodium amide. Yellowish-red crystals (from water-methanol). Yield 71%; mp 215—216.5 °C(dec). IR (KBr): 1600 (C=O), 1240 (ν_{as} NO_2), and 1140 cm^{-1} (ν_s NO_2).

2,7-Dinitrocycloheptanone (3). The compound was obtained by the neutralization of the above disodium salt. Yield, 79%. Colorless needles (from methanol), mp 84.5—86.0 °C. IR (KBr): 3450 (OH, vw); 1720 (C=O), 1540 (ν_{as} NO_2), and 1340 cm^{-1} (ν_s NO_2). UV (EtOH): 339 (ε 3.52×10^2), and 280 nm (sh. 2.00×10^2). Found: C, 41.86; H, 5.43; N, 13.60%. Calcd for $C_7H_{10}N_2O_5$; C, 41.58; H, 4.99; N, 13.86%.

The Ring-opening Reactions of 2,6-Dinitrocyclohexanone (1)

(a) In an Aqueous Sodium Carbonate Solution: *1,5-Dinitropentane*: To an aqueous sodium carbonate solution (62 mg; 0.7 mmol in 10 ml), we added **1** (1.0 g, 5.3 mmol). The mixture was then stirred at room temperature for 1 hr, followed by acidification with concd HCl. Then, the acidic solution was extracted with ether and the ethereal extract was dried over anhydrous sodium sulfate. After the removal of the solvent, the residue was distilled *in vacuo*. Yield, 0.81 g (94%);

24) J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **77**, 6341 (1955).
25) H. Wieland, P. Garbsch, and J. J. Chavan, *Ann.*, **461**, 295 (1928).
26) H. Feuer, A. M. Hall, S. Golden, and R. I. Ritz, *J. Org. Chem.*, **33**, 3622 (1968).
27) H. Feuer snd P. M. Pivawer, *ibid.*, **31**, 3152 (1966).

bp 135 °C/1.5 mmHg. IR (neat): 1550 (ν_{as} NO_2), which is superimposable upon that of an authentic sample[18].

(b) By Sodium Methoxide: *Methyl 2,6-dinitrohexanoate*: *(i) Stoichiometric reaction*: To **1** (3.0 g, 15.9 mmol) in methanol (50 ml), we added, drop by drop, sodium methoxide (18.3 mmol) in methanol (25 ml) at 47—50 °C. After stirring for 2 hr, the solution was acidified with HCl gas. After the removal of the solvent, dry ether was added to the residue, followed by filtration. The filtrate was dried over anhydrous sodium sulfate. After the removal of the ether, the residue was distilled *in vacuo*. Bp 141—144 °C/0.5 mmHg. Yield, 2.9 g (83%). The IR, NMR, and UV spectra were identical with those reported by Feuer *et al.*[5]

(ii) Catalytic Reaction: To **1** (11.3 g, 0.06 mol) in methanol (200 ml), we added, drop by drop, sodium methoxide (0.55 g, 0.01 mol) in methanol (50 ml) at 50 °C. The whole solution was then worked up by the procedure described above. Yield, 11.4 g (86%).

(c) By Sodium Ethoxide. Ethyl 2,6-Dinitrohexanoate: The procedure was similar to that described for (b), but using sodium ethoxide in ethanol. Bp 132 °C/0.5 mmHg. Yield, 75%. n_D^{25} 1.4612. IR (neat): 1750 (C=O), 1562, 1553 (ν_{as} NO_2), 1376, 1374 (ν_s NO_2), 1200 (C–O), and 860 cm^{-1} (C–N). UV (MeOH): 261 nm (ε 3.55×10^2). NMR (acetone-d_6), τ 4.56 (1H, t, J=7.0 Hz, 2-CH), 5.44 (2H, t, J=7.0 Hz, 6-CH_2), 5.77 (2H, q, J=7.0 Hz, –COOC$H_2$$CH_3$) 7.6 8.6 (4H, m, 4-, 5-$CH_2$), and 8.42 (2H, q, J=8.0 Hz, 3-CH_2). Found: C, 41.39; H, 5.91; N, 12.30%, mol wt (in acetone), 228. Calcd for $C_8H_{14}N_2O_6$: C, 41.02; H, 6.03; N, 11.96%; mole wt, 234.2.

(d) By Sodium n-Propoxide. n-Propyl 2,6-Dinitrohexanoate: The procedure was similar to that described for (b). Bp 152—162 °C/0.5 mmHg. Yield, 81%; n_D^{25}: 1.4627. IR (neat): 1750 (C=O), 1562, 1554 (ν_{as} NO_2), 1380, 1378 (ν_s NO_2), and 1200 cm^{-1} (C–O). UV (MeOH): 263 nm (ε 3.94×10^2). NMR (acetone-d_6): τ 4.52 (1H, t, J=7.0 Hz, 2-CH), 5.46 (2H, t, J=8.0 Hz, 6-CH_2), 5.83 (2H, t, J=7.0 Hz, –COOCH_2 CH_2CH_3), 7.35—8.05 (4H, m, 4-, 5-CH_2), 8.40 (2H, sex, J=7.0 Hz, –OCH_2C$H_2$$CH_3$) and 8.42 (2 H, q, J=7.0 Hz, 3-CH_2). Found: C, 40.36; H, 6.55; N, 11.06%; mol wt (in acetone), 221. Calcd for $C_6H_{16}N_2O_6$: C, 40.67; H, 6.83; N, 11.86%; mol wt 236.2.

(e) Di-aci-nitration by Sodium Isopropoxide. To **1** (3 0 g, 15.9 mmol) in isopropoxide, we added, drop by drop, sodium isopropoxide (16.0 mmol) in 2-propanol at 65—70 °C. After continuing stirring for 5.5 hr at 70 °C, the solution was cooled to room temperature and then acidified with HCl gas. After the subsequent evaporation of the solvent *in vacuo*, acetone was added to the residue. The whole solution was then filtered, and the solvent was distilled off. The residue was found to be the recovered starting material (2.5 g). In secondary and tertiary alcoholic solutions containing the corresponding sodium alkoxide, such as isopropoxide and *iso-*, *sec-*, and *tert-*butoxides, **1** and **2** gave the di-*aci*-nitro derivatives from which the corresponding starting materials were recovered by acidification.

(f) By Sodium n-Butoxide: *n-Butyl 2,6-Dinitrohexanoate*: In a manner similar to that described for (b), **1** (3.0 g, 15.9 mmol) was transformed into *n*-butyl 2,6-dinitrohexanoate. Yield, 3.1 g (74.5%). Bp 142 °C/0.5 mmHg. n_D^{25}, 1.4603. IR (neat): 1740 (C=O), 1562, 1555 (ν_{as} NO_2), and 1376 cm^{-1} (ν_s NO_2). UV (MeOH): 264 nm (ε 300). NMR (acetone-d_6); τ 4.54 (1H, t, J=7.0 Hz, 2-CH), 5.47 (2H, t, J=8.0 Hz, 6-CH_2), and 5.78 (2H, t, J=7.0 Hz, –COOCH_2–CH_2–). Found: C, 46.14; H, 7.03; N, 11.05%; mol wt (in acetone), 224. Calcd for $C_{10}H_{18}N_2O_6$: C, 45.79; H, 6.92; N, 10.68; mol wt 262.3.

(g) By Potassium Hydroxide in n-Amyl Alcohol: *n-Amyl 2,6-Dinitrohexanoate*: To **1** (3.0 g, 15.9 mmol) in *n*-amyl alcohol (100 ml) at 60 °C, we added, drop by drop, *n*-amyl alcohol (50 ml) containing potassium hydroxide (0.1 g). After stirring for 4.5 hr at 60 °C, the whole solution was worked up in the usual manner. Bp 137 °C/0.5 mmHg. Yield, 2.98 g (68%). IR (neat): 1750 (C=O), 1570, 1556 (ν_{as} NO_2), and 1380 cm^{-1} (ν_s NO_2). UV (MeOH): 265 nm (ε 292). NMR (acetone-d_6): τ 4.55 (1H, t, J=7.0 Hz, 2-CH), 5.45 (2H, t, J=7.0 Hz, 6-CH_2), and 5.80 (2H, t, J=7.0 Hz, –$COOCH_2$), Found: C, 48.69; H, 7.50; N, 10.27%; mol wt (in acetone) 250. Calcd for $C_{11}H_{20}N_2O_6$: C, 47.82; H, 7.30; N, 10.14%; mol wt 276.3.

The Ring-Opening Reactions of 4-Methyl 2,6-Dinitrocyclohexanone (2): *(a) By Potassium Hydroxide in Methanol. Methyl 2,6-Dinitro-4-methylhexanoate*: To **2** (4.0 g, 19.8 mmol) in methanol (100 ml), we added, drop by drop, methanol (50 ml) containing potassium hydroxide (0.3 g) at 50—55 °C. After stirring for 1 hr at this temperature, the solution was worked up in the usual manner. Yield, 4.0 g (86.3%); bp 132—138 °C/2.0 mmHg. IR (neat): 1740 (C=O), 1563, 1552 (ν_{as} NO_2), and 1381 cm^{-1} (ν_s NO_2). UV (MeOH): 225 nm (ε 270). NMR (CCl_4): τ 4.8 (1H, t, J=8.0 Hz, 2-CH), 5.6 (2H, t, J=8.0 Hz, 6-CH_2), and 6.2 (3H, s, –$COOCH_3$). Found: C, 41.65; H, 6.33; N, 11.57%. Calcd for $C_8H_{14}N_2O_6$: C, 41.02; H, 6.03; N, 11.98%.

(b) By Potassium Hydroxide in Ethanol: *Ethyl 2,6-Dinitro-4-methylhexanoate*: The procedure was similar to that described above. Yield, 85%; bp 120—126 °C/1.5 mmHg. IR (neat): 1740 (C=O), 1566, 1552 (ν_{as} NO_2), and 1380 cm^{-1} (ν_s NO_2). UV (MeOH): 255 cm (ε 266). Found: C, 44.06; H, 6.88; N, 11.73%. Calcd for $C_6H_{16}N_2O_6$: C, 43.58; H, 6.50; N, 11.29%.

The Ring-opening Reactions of 2,7-Dinitrocycloheptanone (3).

(a) By Potassium Hydroxide in Methanol: *Methyl 2,7-Dinitroheptanoate*: To **3** (3.0 g) in methanol, we added, drop by drop, methanol (50 ml) containing potassium hydroxide (0.5 g) at 65 °C. After stirring for 1.5 hr, the whole solution was worked up in the usual manner. Yield, 72%. Bp 164 °C/0.01 mmHg. IR (neat): 1750 (C=O), 1563, 1552 (ν_{as} NO_2), 1376, and 1374 cm^{-1} (ν_s NO_2). UV (MeOH): 265 nm (ε 183). Found: C, 41.77; H, 6.45; N, 11.64%. Calcd for $C_8H_{14}N_2O_6$: C, 41.02; H, 6.03; N, 11.96%.

(b) By Potassium Hydroxide in Ethanol. Ethyl 2,7-Dinitroheptanoate. By the usual method, ethyl 2,7-dinitroheptanoate was obtained in an 81% yield. Bp 105 °C/2×10^{-3} mmHg. IR (neat): 1750 (C=O), 1563, 1552 (ν_{as} NO_2), 1376, and 1374 cm^{-1} (ν_s NO_2). UV (MeOH): 265 nm (ε 297). Found: C, 44.19; H, 7.08; N, 11.01%. Calcd for $C_9H_{16}N_2O_6$: C, 43.54; H, 6.50; N, 11.29%.

(c) By Potassium Hydroxide in n-Butanol. n-Butyl 2,7-Dinitroheptanoate. The method was similar to those described in (a). Yield, 80%. Bp 146 °C/5×10^{-3} mmHg. IR (neat): 1750 (C=O), 1563, 1553 (ν_{as} NO_2), 1380, and 1378 cm^{-1} (ν_s NO_2). UV (MeOH): 255 nm (ε 357). Found: C, 48.35; H, 7.87; N, 9.49%. Calcd for $C_{11}H_{20}N_2O_4$: C, 47.82; H, 7.30; N, 10.14%.