Esters and Ethers of 2-Substituted 2,2-Dinitro-1-alkanols[1,2]

H. E. UNGNADE[3a] AND L. W. KISSINGER[3b]

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

Received September 21, 1965

The preparation and properties of esters and ethers of certain 2-substituted 2,2-dinitro-1-alkanols are described. The esters are readily prepared in good yield by reaction of the alcohol with an acid chloride in the presence of pyridine. The ethers are obtained *via* the reaction of 1,2-dichloro-1,1-dinitroethane with potassium iodide in the presence of an alcohol.

Although the 2-halo-2,2-dinitroethanols (I) and trinitroethanol (I, X = NO_2) are sensitive toward bases and are readily dissociated in polar solvents,[4] they can

$$\underset{\text{I}}{\mathrm{XC(NO_2)_2CH_2OH}}$$

be esterified with acid chlorides and pyridine in dichloromethane like other β-nitro alcohols[5] if an excess of pyridine is avoided. The corresponding esters are obtained in good yield, and even the somewhat unstable chlorosulfonate of 2-chloro-2,2-dinitroethanol (II) can be prepared in this way. When II is heated with pyridinium chloride, it is rapidly converted to 1,2-dichloro-1,1-dinitroethane (III).[6] In contrast to chlorides such as 2,2-dinitropropyl chloride,[5a] the dichloro compound III is quite reactive. It liberates iodine with potassium iodide in methanol and yields 2,2-dinitroethyl methyl ether (IV). Ethanol and 2-chloro- and 2-bromoethanol can be used in the place of methanol, but alcohols with several strong negative substituents fail to give any measurable amounts of ethers. The reaction is analogous to those of 2-bromo-2,2-dinitroethyl acetate with bases[8] and is believed to involve addition of the alcohol to the intermediate 1,1-dinitroethylene.

$$\underset{\text{II}}{\mathrm{CCl(NO_2)_2CH_2OSO_2Cl}} + \mathrm{Py{\cdot}HCl} \xrightarrow{\Delta} \underset{\text{III}}{\mathrm{CCl(NO_2)_2CH_2Cl}}$$

$$\text{III} + 2\mathrm{KI} \longrightarrow \mathrm{KC(NO_2)_2CH_2Cl} \longrightarrow \mathrm{C(NO_2)_2{=}CH_2}$$

$$\mathrm{C(NO_2)_2{=}CH_2} + \mathrm{MeOH} \longrightarrow \underset{\text{IV}}{\mathrm{HC(NO_2)_2CH_2OMe}}$$

The 2,2-dinitroethyl methyl ether formed is identical in all respects with the ether prepared from 1,1,1-trinitroethane by way of the potassium salt V, the structure of which has been established by degradation to methoxyacetic acid.[9]

2-Chloro-2,2-dinitroethyl methyl ether is readily prepared by chlorination of V, but all attempts to introduce another nitro group by nitration of the salt have failed. Tetranitromethane does not react with V, nitrogen dioxide converts it to IV, and nitryl chloride acts largely as a chlorinating agent. It has been possible to alkylate V and the 2-chloroethyl analog with methyl iodide to give the new 2,2-dinitropropyl methyl (VI) and 2,2-dinitropropyl 2-chloroethyl ethers, which are not accessible by other methods.

$$\underset{\text{V}}{\mathrm{KC(NO_2)_2CH_2OMe}} + \mathrm{MeI} \longrightarrow \underset{\text{VI}}{\mathrm{MeC(NO_2)_2CH_2OMe}}$$

The alcohols I react with aldehydes under strongly acid conditions to give acetals.[10]

The compounds described in the Experimental Section have characteristic absorption spectra. In the ultraviolet region the chlorodinitroethyl compounds have a broad band of small intensity at 276 ± 2 mμ (ε 78 ± 6 per group) compared with 276 ± 2 mμ (ε 67 ± 11 per group) for the corresponding dinitropropyl compounds (Table I). 2-Bromo-2,2-dinitroethyl acetate gives a still more intense absorption. Within a given series—*e.g.*, the 2-chloro-2,2-dinitroethyl compounds—the bands are shifted to shorter wavelengths and greater intensities as the electron-donating power of the substituent groups increases (Figure 1); *i.e.*, these bands conform to the usual criteria for $n \rightarrow \pi^*$ transitions.[11]

The infrared absorption spectra of the chlorodinitroethyl compounds (Table I) have asymmetric NO_2 stretching bands at 6.27 ± 0.02 μ, the bromo compounds at 6.29 ± 0.02 μ, the methyl compounds at 6.34 ± 0.02 μ, and the nitro compounds at 6.23 ± 0.03 μ. The corresponding symmetric stretching bands occur at 7.64 ± 0.02, 7.66 ± 0.03, 7.52 ± 0.02, and 7.68 ± 0.04 μ, respectively.

Experimental Section[12]

2-Chloro-2,2-dinitroethanol.—The preparation of sodium dinitroethanol[13] from 2,2-dinitropropanediol (0.03 mole) and sodium methoxide in methanol gave yields of 92–96% of dry salt with λ_{max}^{KBr} 2.99 (m), 6.74 (m), 6.99 (m), 7.35 (m), 7.64 (m), 8.10 (s), 8.23 (s), 8.77 (s), 9.98 (m), 10.39 (m), 11.64 (m), 13.03 (m), 13.39 (m), and 13.67 (m) μ. This salt was suspended in dichloromethane and chlorinated with stirring at 0° with a slight excess of gaseous chlorine. The mixture was allowed to stand at 0° for 1 hr, after which it was warmed to 25° and filtered with suction. The washed and dried sodium chloride was obtained in theoretical yield. The combined filtrates, when evaporated under reduced pressure, gave solid 2-chloro-2,2-dinitroethanol in 92–94% yield. For most purposes

---

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) Correspondence should be addressed to L. C. Smith, Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, N. M. 87544.

(3) (a) Deceased Aug. 16, 1965. (b) Deceased May 10, 1965.

(4) T. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

(5) (a) L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohwer, *ibid.*, **28**, 2491 (1963); (b) H. E. Ungnade, E. D. Loughran, and L. W. Kissinger, *Tetrahedron*, **20**, Suppl. 1, 177 (1964).

(6) The preparation of this compound and its conversion to the methyl ether were first carried out by W. E. McQuistion at these laboratories. More recently an alternate procedure for the preparation of III has been described,[7] which consists of heating 2-chloro-2,2-dinitroethanol with excess thionyl chloride and catalytic amounts of pyridinium chloride.

(7) P. Noble, Jr., W. L. Reed, and F. G. Borgardt, U. S. Patent 3,180,899 (April 27, 1965).

(8) L. J. Winters and W. E. McEwen, *Tetrahedron*, **19**, Suppl. 1, 49 (1963); M. B. Frankel, *J. Org. Chem.*, **23**, 813 (1958).

(9) J. Meisenheimer and M. Schwarz, *Ber.*, **39**, 2543 (1906).

(10) M. H. Gold and H. J. Marcus, German Patent 1,150,059 (1963); *Chem. Abstr.*, **60**, 410 (1964).

(11) W. D. Closson, S. F. Brady, E. M. Kosower, and P. C. Huang, *J. Org. Chem.*, **28**, 1161 (1963).

(12) Microanalyses were performed by M. J. Naranjo. All temperatures are corrected. *Caution:* Some of the described compounds are sensitive to impact and must be handled with care.

(13) H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954).

TABLE I

ABSORPTION SPECTRA OF 2-X-2,2-DINITROETHYL COMPOUNDS

X	Compound	λ_{max},[a] mμ (ε)	λ, μ			
			as-NO_2[b]	s-NO_2	C=O	C—O
Cl	Alcohol[c]	276 (82)	6.29 (s)	7.62 (m)	...	9.28 (m)
Cl	Acetate	277 (77)	6.27 (s)	7.65 (m)	5.63 (s)	8.30 (s)
Cl	Carbonate	276 (154)	6.26 (s)	7.66 (m)	5.59 (m)	8.02 (m)
Cl	Chloride	277 (72.7)	6.27 (s)	7.67 (m)	...	...
Cl	Ethyl carbonate	275 (79)	6.26 (s)	7.65 (m)	5.64 (s)	8.00 (s)
Cl	Formal	278 (149)	6.27 (s)	7.63 (m)	...	8.87 (m)[d]
Cl	Methyl ether	275 (83.6)	6.29 (s)	7.62 (m)	...	8.99 (m)
Br	Alcohol[c]	...	6.31 (s)	7.63 (m)	...	9.25 (m)
Br	Acetate	280 (s) (124[e])	6.29 (s)	7.66 (m)	5.65 (m)	8.30 (m)
NO_2	Alcohol[c]	277 (104)	6.24 (s)	7.64 (m)	..	9.16 (m)
NO_2	Ethyl carbonate	276 (94)	6.21 (s)	7.70 (m)	5.62 (s)	8.00 (m)[f]
Me	Alcohol[c]	277 (56.2)	6.35 (s)	7.51 (m)	...	9.33 (m)
Me	Acetate	277 (56)	6.33 (s)	7.52 (m)	5.65 (s)	8.24 (s)
Me	Chloride	277.5 (56.0)	6.34 (s)	7.54 (m)	...	...
Me	Formal	277 (102)	6.33 (s)	7.53 (m)	...	8.91 (m)[g]
Me	Methyl ether	275 (s) (77.6)	6.35 (s)	7.53 (m)	...	8.90 (m)

[a] Ultraviolet absorption bands in MeCN. [b] Infrared absorption bands, solids in KBr, liquids as capillary films, except as noted. [c] Hydroxy bands for the alcohols: X = Cl, 2.81 (m); Br, 2.80 (m) and 2.91 (m); NO_2, 2.90 (m); Me, 2.81 (m) and 2.90 (m) μ. [d] Additional bands at 9.18 (m) and 9.64 (m) μ. [e] Approximate values because of solvolysis. [f] In CCl_4. [g] Additional band at 9.47 (m) μ.

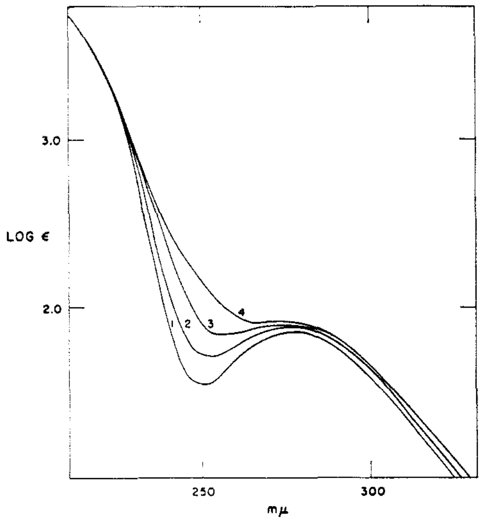

Figure 1.—The ultraviolet absorption spectra in MeCN of (1) $ClC(NO_2)_2CH_2Cl$, λ_{max} 277 mμ (ε 72.7); (2) $ClC(NO_2)_2CH_2OAc$, λ_{max} 277 mμ (ε 77.0); (3) $ClC(NO_2)_2CH_2OH$, λ_{max} 276 mμ (ε 82.0); and (4) $ClC(NO_2)_2CH_2OMe$, λ_{max} 275 mμ (ε 83.6).

this product could be used directly, the least amount of handling being advisable since it was very hygroscopic. For the determination of physical properties, the crude alcohol was sublimed at 75° (0.05 mm), yielding a colorless sublimate, mp 40–42°.[14]

Anal. Calcd for $C_2H_3ClN_2O_5$: C, 14.10; H, 1.77; Cl, 20.80; N, 16.44. Found: C, 14.09; H, 2.44; Cl, 21.20; N, 16.08.

Esterification Procedure.—The appropriate acid chloride (0.0133 mole) was added at 0° to a solution of 2-X-2,2-dinitroethanol (0.0125 mole) in dichloromethane (8 ml). To the resulting solution was added slowly with stirring at 0° a solution of pyridine (0.0125 mole) in dichloromethane (2 ml). The mixture was warmed to 25° with stirring, refluxed 1–2 hr, and allowed to stand at 25° for 1–2 hr. It was diluted with dichloromethane, washed with 3% hydrochloric acid and water, and dried over sodium sulfate. The crude esters were obtained by evaporation of the solutions under reduced pressure.

2-Chloro-2,2-dinitroethyl acetate was obtained in 84% yield as a colorless oil, bp 35° (0.03 mm) (molecular still), $n^{25}D$ 1.4491, $d^{25}{}_{25}$ 1.445.

Anal. Calcd for $C_4H_5ClN_2O_6$: C, 22.61; H, 2.37; Cl, 16.68, N, 13.19. Found: C, 22.76, 23.04; H, 2.73, 2.59; Cl, 16.60; 16.80; N, 13.32.

2-Chloro-2,2-dinitroethyl arbonnate.—The crude oily reaction product (98% yield) solidified almost immediately. Crystallization from benzene–petroleum ether (bp 30–60°) gave an 82% yield of colorless plates, mp 71–72°.

Anal. Calcd for $C_5H_4Cl_2N_4O_{11}$: C, 16.37; H, 1.10; Cl, 19.32; N, 15.27. Found: C, 16.56; H, 1.37; Cl, 19.15; N, 15.17.

2-Chloro-2,2-dinitroethyl ethyl carbonate, prepared similarly in 83% yield, boiled at 60° (0.05 mm), $n^{25}D$ 1.4473.

Anal. Calcd for $C_5H_7ClN_2O_7$: C, 24.76; H, 2.91; Cl, 14.62; N, 11.56. Found: C, 24.11, 24.63; H, 3.41, 3.01; Cl, 15.44; N, 11.21.

Bis(2-chloro-2,2-dinitroethyl)formal.—This formal was prepared from the alcohol in 86% yield according to the procedure of Gold and Marcus.[10] It could be distilled in a molecular still and boiled at 110–115° (1 × 10^{-5} mm), $n^{25}D$ 1.4793, $d^{25}{}_{25}$ 1.631.

Anal. Calcd for $C_5H_6Cl_2N_4O_{10}$: C, 17.01; H, 1.71; Cl, 20.09; N, 15.87. Found: C, 16.71, 17.36; H, 2.26, 2.23; Cl, 20.13; N, 15.85.

2-Bromo-2,2-dinitroethanol.—Bromination of sodium dinitroethanol by a procedure analogous to that used for the chlorination reaction gave a 98% yield of 2-bromo-2,2-dinitroethanol, which solidified. This material was used directly without further purification.[15]

2-Bromo-2,2-dinitroethyl acetate was prepared from crude alcohol, pyridine, and acetyl chloride in 84% yield. The acetate boiled at 45° (0.02 mm) (molecular still), $n^{25}D$ 1.4737, $d^{25}{}_{25}$ 1.717 (lit.[14] $n^{25}D$ 1.4728).

Ethyl Trinitroethyl Carbonate.—The esterification of trinitroethanol with pyridine and ethyl chlorocarbonate in dichloromethane gave an 89% yield of oil which was distilled from a molecular still and which boiled at 40° (0.05 mm), $n^{25}D$ 1.4468. The distillate solidified on cooling to a colorless solid, mp 45–46°.

Anal. Calcd for $C_5H_7N_3O_9$: C, 23.73; H, 2.79; N, 16.60. Found: C, 23.65, 23.65; H, 3.06, 3.08; N, 16.45, 16.37.

Bis(2,2-dinitropropyl)formal was obtained in 84% yield as a colorless oil which boiled at 125° (1 × 10^{-5} mm) (molecular still), $n^{25}D$ 1.4650, mp 32.5–33.5° (from aqueous methanol), λ_{max}^{EtOH} 278 mμ (ε 106).

Anal. Calcd for $C_7H_{12}N_4O_{10}$: C, 26.93; H, 3.87; N, 17.95. Found: C, 26.95, 26.83; H, 3.98, 4.17; N, 17.52, 17.67.

1,2-Dichloro-1,1-dinitroethane (III).[6]—Pyridine (2.13 g, 0.0269 mole) was added to a solution of 2-chloro-2,2-dinitroethanol (4.58 g, 0.0269 mole) in dichloromethane (15 ml) held at 0° with ice cooling and stirring. Sulfuryl chloride (3.81 g, 0.0282 mole) was added to the resulting solution, and the mixture was stirred 20 min at 0° and 30 min at 20° and was then refluxed 2 hr. The mixture was washed with three 30-ml portions of 4% hydro-

---

(14) The anhydrous alcohol could be handled only in a drybox. It picked up water from the air instantly on exposure, and the determination of the melting point was difficult. The listed value must be regarded as approximate.

(15) *Cf.* M. B. Frankel, *J. Org. Chem.*, **23**, 813 (1958).

chloric acid and dried over sodium sulfate. Evaporation under reduced pressure gave 5.24 g (72%) of crude chlorosulfonate II. A colorless product was obtained by distillation in a molecular still: bp 50° (0.04 mm); $n^{25}\mathrm{D}$ 1.4748; $\lambda^{\mathrm{liq}}_{\mathrm{NO_2}}$ 6.25, 7.69 μ; $\lambda^{\mathrm{liq}}_{\mathrm{other}}$ 7.02, 8.39 μ.

Anal. Calcd for $C_2H_2Cl_2N_2O_7S$: C, 8.93; H, 0.75; Cl, 26.36; N, 10.42. Found: C, 9.41; H, 1.15; Cl, 28.05; N, 9.82.[16]

The distilled chlorosulfonate was found to be stable at 100° and was unchanged on standing with pyridinium chloride in dichloromethane at 20°. It was decomposed by heating the oil (1.50 g, 0.0056 mole) with pyridinium chloride (from 0.44 g, 0.0056 mole, of pyridine) on a steam bath for 15 min. The product was taken up in dichloromethane, washed with three 20-ml portions of 4% hydrochloric acid, and dried over sodium sulfate. Evaporation of the solution gave 1.16 g of 1,2-dichloro-1,1-dinitroethane (III), bp 60° (10 mm) (molecular still), $n^{25}\mathrm{D}$ 1.4672, $d^{25}{}_{25}$ 1.610 ± 0.003, MRD 32.59[17] (calcd 32.39).

Anal. Calcd for $C_2H_2Cl_2N_2O_4$: C, 12.71; H, 1.06; Cl, 37.53; N, 14.83. Found: C, 12.96; H, 1.68; Cl, 37.49, 37.55; N, 14.79.

An over-all yield of 88% was obtained when the crude reaction mixture was freed from solvent and heated on a steam bath for 20 min without isolating the intermediate sulfonate. The dichloro compound has a disagreeable odor and is irritating to the mucous membranes.

2,2-Dinitroethyl Ethyl Ether.—1,2-Dichloro-1,1-dinitroethane (0.94 g, 0.005 mole) was added to a suspension of potassium iodide (5.0 g, 0.03 mole) in 75 ml of absolute ethanol. The suspension was allowed to stand at 25° with occasional shaking for 3 hr. The volume was reduced to less than one-half by distillation under reduced pressure. The brown residue was diluted with 50 ml of water and shaken with solid sodium bisulfite. It was acidified with concentrated hydrochloric acid and extracted with five 8-ml portions of dichloromethane. The extracts were dried and evaporated to give 0.41 g (49%) of pale yellow oil which was distilled in a molecular still: bp 45° (0.3 mm); $n^{25}\mathrm{D}$ 1.4345; $\lambda^{\mathrm{liq}}_{\mathrm{NO_2}}$ 6.33, 7.49 μ; $\lambda^{\mathrm{liq}}_{\mathrm{COC}}$ 8.93 μ.

Anal. Calcd for $C_4H_8N_2O_5$: C, 29.28; H, 4.91; N, 17.08. Found: C, 28.84; H, 5.38; N, 16.91.

2,2-Dinitroethyl Methyl Ether (IV).—The analogous reaction in methanol gave a 48% yield of the methyl ether which was in all respects identical with the methyl ether prepared from trinitroethane.[9] It boiled at 35° (0.02 mm) (molecular still): $n^{25}\mathrm{D}$ 1.4368; $\lambda^{\mathrm{liq}}_{\mathrm{NO_2}}$ 6.32, 7.47 μ; $\lambda^{\mathrm{liq}}_{\mathrm{COC}}$ 8.89 μ.

Anal. Calcd for $C_3H_6N_2O_5$: C, 24.00; H, 4.03; N, 18.67. Found: C, 24.22; H, 4.50; N, 18.68.

The methyl ether was not too stable even at 0° and was stored in the form of its stable potassium salt (V), which had $\lambda^{\mathrm{KBr}}_{\mathrm{C(NO_2)_2^-}}$ 6.77, 8.09, and 8.81 μ. Authentic potassium salt was prepared by adding a solution of potassium methoxide (0.032 mole, from 1.25 g of potassium) in 40 ml of methanol to a solution of 1,1,1-trinitroethane (2.0 g, 0.012 mole) in 40 ml of methanol. The combined solutions were cooled to 0° and the yellow salt was filtered with suction, washed with methanol, and dried: yield 1.8–2.0 g (78–86%), $\lambda^{0.1\,M\ \mathrm{NaOH}}_{\mathrm{max}}$ 364 mμ (log ϵ 4.25).

Anal. Calcd for $C_3H_5KN_2O_5$: C, 19.15; H, 2.68; N, 14.89. Found: C, 19.14; H, 2.84; N, 14.95.

2-Chloro-2,2-dinitroethyl Methyl Ether.—Chlorination of the above potassium salt (2.0 g, 0.0106 mole) in 50 ml of dichloromethane at 0° gave the theoretical amount of potassium chloride. The filtrates were evaporated under reduced pressure to give 2 g of a pale yellow oil which boiled at 35° (2 mm) (molecular still), $n^{25}\mathrm{D}$ 1.4466. Carefully redistilled ether boiled at 50° (5 mm), $n^{25}\mathrm{D}$ 1.4422, $d^{25}{}_{25}$ 1.425 ± 0.001, MRD 34.28 (calcd 33.91).

Anal. Calcd for $C_3H_5ClN_2O_5$: C, 19.53; H, 2.73; Cl, 19.22; N, 15.15. Found: C, 19.55, 19.87; H, 3.97, 3.87; Cl, 19.17; N, 15.21.

2,2-Dinitropropyl Methyl Ether (VI).—2,2-Dinitroethyl methyl ether potassium salt was crystallized from methanol. The pure salt (4.0 g, 0.0213 mole) was refluxed with 25 ml of acetone and 4 ml of methyl iodide for 120 hr. The mixture was evaporated under reduced pressure, and the residue was taken up in dichloromethane, washed with 10% aqueous bisulfite, dried over sodium sulfate, and evaporated under reduced pressure to give 2.79 g (80%) of pale yellow oil. It boiled in a molecular still at 40° (2 mm), $n^{25}\mathrm{D}$ 1.4320. Washing and redistilling gave a colorless oil with a pleasant odor: $n^{25}\mathrm{D}$ 1.4308, $d^{25}{}_{25}$ 1.256, MRD 33.78 (calcd 33.59).

Anal. Calcd for $C_4H_8N_2O_5$: C, 29.28; H, 4.91; N, 17.08. Found: C, 28.99, 29.11; H, 5.31, 5.21; N, 17.03.

2-Chloroethyl 2,2-Dinitroethyl Ether.—A suspension of potassium iodide (5.0 g, 0.03 mole) in 2-chloroethanol (50 ml) was stirred with 1,2-dichloro-1,1-dinitroethane (1.10 g, 0.0058 mole) for 20 hr at 25°. The brown mixture was evaporated at 50° (0.5 mm), and the residue was taken up in water (40 ml) and extracted with five 8-ml portions of dichloromethane. The extracts were evaporated, finally at 40° (0.5 mm), to give 1.04 g (90%) of oily ether: $\lambda^{\mathrm{liq}}_{\mathrm{NO_2}}$ 6.33, 7.50 μ; $\lambda^{\mathrm{liq}}_{\mathrm{COC}}$ 8.87 μ.

Anal. Calcd for $C_4H_7ClN_2O_5$: Cl, 17.85. Found: Cl, 17.57.

Treating the chloroethyl ether (1.41 g, 0.0071 mole) in methanol (10 ml) with potassium methoxide (0.00793 mole) in methanol (10 ml) gave 1.08 g (64%) of potassium salt: $\lambda^{\mathrm{KBr}}_{\mathrm{C(NO_2)_2^-}}$ 6.78, 8.19, and 8.92 μ.

2-Chloroethyl 2,2-Dinitropropyl Ether.—The dry potassium salt of 2,2-dinitroethyl 2-chloroethyl ether (0.00456 mole) was refluxed with 15 ml of acetone and 4 ml of methyl iodide for 168 hr. Evaporation under reduced pressure gave 0.90 g (90%) of crude ether which was washed, dried, and distilled to give a colorless oil: bp 60° (0.03 mm); $n^{25}\mathrm{D}$ 1.4620; $\lambda^{\mathrm{liq}}_{\mathrm{NO_2}}$ 6.36, 7.55 μ; $\lambda^{\mathrm{liq}}_{\mathrm{COC}}$ 8.93 μ.

Anal. Calcd for $C_5H_9ClN_2O_5$: C, 28.26; H, 4.28; N, 13.19. Found: C, 28.06; H, 4.50; N, 12.68.

Absorption Spectra.—Ultraviolet absorption spectra were determined with a Cary Model 14 spectrophotometer, infrared absorption spectra with a Perkin-Elmer Model 21.

---

[16] The chlorosulfonate probably contained traces of the dichloro compound formed in the presence of the pyridinium chloride which is obtained as a by-product. Longer refluxing caused further conversion.

[17] Molar refractions have been determined for the liquid nonterminal dinitro compounds described in this paper and for others. All of these were found to have small exaltations with an average value of 0.29 for 11 compounds. This is of the same order of magnitude as the exaltation of 0.35 which was found for terminal *gem*-dinitro compounds: L. V. Ershova, V. N. Gogitidze, V. M. Belikov, and S. S. Novikov, *Izv. Akad. Nauk SSSR*, 943 (1959).