fungi. "Tetraacetylcordycepic acid"[2] was identified as D-mannitol hexaacetate and the "acetonyl derivative of cordycepic acid"[2] as 1,2:3,4:5,6-tri-*O*-isopropylidene-D-mannitol. The detailed evidence is presented in the Experimental section.

Proof that the original "cordycepic acid" is identical with the compound isolated in the present investigation was afforded by direct comparison, following the completion of this investigation, with a sample kindly furnished by Professor Chatterjee. The two materials were shown to be identical by mixture melting point and infrared spectrum.

Experimental[5]

"Cordycepic Acid."—The isolation followed the reported procedure.[2] The crude product was triturated with a little ethanol to remove a small fraction of highly colored material. The tan solid residue was dissolved in water and the solution was passed through a column of Dowex-50 (H^+) and decolorized with charcoal. Evaporation to dryness under reduced pressure yielded white crystals of "cordycepic acid." In one case 37 g. of dried fungus yielded 2.5 g. (6.8%), whereas in another 106 g. of fungus yielded 9.5 g. (9%). Recrystallization was effected by solution in water and addition of ethanol, yielding long white needles, m.p. 166–168°; $[\alpha]^{24}_{\mathrm{D}}$ +40.3° (*c* 2.29, 5% aqueous ammonium molybdate). The optical rotation in water was too small for convenient measurement.

Anal. Calcd. for $C_6H_{14}O_6$: C, 39.54; H, 7.74; O, 52.68. Found: C, 39.36; H, 7.70; direct O, 52.51.

This "cordycepic acid" exhibited no acidic properties. Its infrared spectrum (in potassium bromide) showed no absorption in the carbonyl region, but had very intense bands at 2.95–3.10 μ (O–H), 9.25 and 9.82 μ (C–O). Calculated on the basis of molecular formula $C_6H_{14}O_6$, 1 mole reacted with 5 moles of sodium periodate to yield 2 moles of formaldehyde (precipitated as the dimedon derivative). It was identified as D-mannitol by mixture melting point and comparison of infrared spectra [lit.[6] for D-mannitol gives m.p. 167°; $[\alpha]_{\mathrm{D}}$ +40.8° (*c* 3.33, 6.67% aqueous ammonium molybdate)].

Acetylation of "Cordycepic Acid."—"Cordycepic acid" (369 mg.) was suspended in a mixture of 10 ml. of acetic anhydride and 10 ml. of dry pyridine and shaken mechanically at room temperature overnight. The solid dissolved. The acetic anhydride and pyridine were removed *in vacuo*, and 50 ml. of water was added to the residue which quickly crystallized. It was collected by filtration, washed thoroughly with water, and dried, to yield 847 mg. (96%), m.p. 121–122°. Two recrystallizations from benzene raised the m.p. to 122–123°; $[\alpha]^{27}_{\mathrm{D}}$ +25.3° (*c* 7.18, chloroform).

Anal. Calcd. for $C_{18}H_{26}O_{12}$: mol. wt., 434.4; C, 49.77; H, 6.03. Found: mol. wt., 420; C, 50.06; H, 5.66.

Lit.[7] for D-mannitol hexaacetate gives m.p. 122°; $[\alpha]_{\mathrm{D}}$ +25° (*c* 1, chloroform). Identity of this compound as D-mannitol hexaacetate was further confirmed by mixture melting point with an authentic sample and comparison of infrared spectra (in chloroform and carbon tetrachloride).

Isopropylidene Derivative of "Cordycepic Acid."—"Cordycepic acid" (0.974 g.) was suspended in 300 ml. of 1% hydrogen chloride in dry acetone and stirred overnight. The solid dissolved. The solution was neutralized with silver carbonate, and the silver salts were filtered off. Evaporation of the filtrate under reduced pressure yielded an oil which crystallized readily. A cyclohexane solution of the crude product was filtered to remove insoluble material (70 mg.), and evaporated to yield 1.41 g. of crystals, m.p. 66.5–68°. Recrystallization from a minimum of hexane followed by sublimation at 0.5 torr (bath temp., *ca.* 90°) raised the m.p. to 67.5–68.5°; $[\alpha]^{24}_{\mathrm{D}}$ +12.7° (*c* 9.68, abs. EtOH) [lit.[8] for 1,2:3,4:5,6-tri-*O*-isopropylidene-D-mannitol gives m.p. 68–70°; $[\alpha]^{20}_{\mathrm{D}}$ +12.5° (*c* 9.6, abs. EtOH)].

The isopropylidene derivative was found to undergo slow hydrolysis in a moist acidic atmosphere. This may be responsible for the lower melting point reported previously.[2]

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(5) The melting points were determined on a Fisher-Johns melting point apparatus.

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gem-Dinitro Esters. IV. Pyridine-Catalyzed Esterification of β-Dinitro Alcohols[1]

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β-Dinitro alcohols have been esterified with acids in the presence of trifluoroacetic anhydride or polyphosphoric acid [2] and with acid chlorides alone, [3] in an inert solvent,[4] in the presence of aluminum chloride by the method of Hill,[5,6] or by the use of the Schotten–Bauman reaction.[7] Low yields and mixtures are obtained from base-sensitive alcohols with the last method due to a reversal of the Henry[8] reaction.

Although β-nitro alcohols are dissociated by aqueous bases, they are not affected in the same way by pyridine in certain solvents, and are readily esterified by acid chlorides in this medium. The reaction is carried out in dichloromethane solution in the presence of equal molar quantities of pyridine, acid chloride, and alcohol. It is rapid in concentrated solutions and furnishes good yields of esters (Tables I and II) under mild conditions. The method is particularly advantageous with low boiling acid chlorides, such as phosgene, and for the preparation of esters from heat-senstive alcohols and acid chlorides. A three-component complex appears to be the reactive intermediate whose fate is largely dependent on concentration.[9]

Good yields of simple esters are generally obtained from 2,2-dinitropropanol. 2-Nitro-1,3-propanediols yield diesters with acid chlorides derived from monobasic acids and mixtures of open-chain polymeric and cyclic esters with acid chlorides derived from dibasic acids, the latter predominating in the cases investigated. Thus, 2-nitrotrimethylene carbonates are the major products from 2-nitro-1,3-propanediols and phosgene, accompanied by smaller amounts of polymeric carbonates which have characteristic infrared absorption for open-chain carbonates.[10] They can be separated on the basis of the higher volatility of the cyclic carbonates.

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

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(3) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951).

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(10) Open-chain aliphatic carbonates have a broad C—O stretching band at 8.0 μ. The corresponding bands in the trimethylene carbonates are narrower and occur at 8.5 and 9.0 μ.

TABLE I

ESTERS FROM 2,2-DINITROPROPANOL

Reactant	Ester	Yield, %	M.p., °C.	B.p., °C.	mm.	$n^{25}D$	Molecular formula	Calcd., %			Found, %			Prominent infrared bands, μ[a]							
								C	H	N	C	H	N	λ_{NO_2}		$\lambda_{C=O}$	λ_{C-O}	λ_{other}			
AcCl	Acetate[b]	92	. . .	75	1	1.4405	$C_6H_8N_2O_6$	31.26	4.19	14.58	31.53	4.52	13.80	6.33	7.52	5.65	8.24	9.42	. . .	11.80	
$PhSO_2Cl$	Benzenesulfonate	93	63–64	. . .	. . .	. . .	$C_9H_{10}N_2O_7S$	37.24	3.47	9.65	37.78	3.84	9.55	6.38	7.48	. .	.	7.36	8.40	8.48	
PhCOCl	Benzoate	86	50–51	170	0.01	1.5247	$C_{10}H_{10}N_2O_6$	47.25	3.97	11.02	47.59	4.28	10.48	6.33	7.55	5.74	7.90	9.03	. . .	. . .	
$COCl_2$	Carbonate	90	120–121	. . .	. . .	. . .	$C_7H_{10}N_4O_{11}$	25.77	3.09	17.18	26.10	3.56	16.84	6.33	7.54	5.61	7.94	9.90	. . .	. . .	
SO_2Cl_2	Chloride	62	21	73	8	1.4568	$C_3H_5ClN_2O_4$[c]	21.38	2.99	16.62	21.10	3.49	16.41	6.34	7.54	. .	. .	11.62	11.88	. . .	
Me_2SiCl_2	Dimethylsilane	54	. . .	130	0.007	1.4520	$C_8H_{16}N_4O_{10}Si$	26.96	4.53	15.72	27.12	4.75	15.34	6.33	7.51	. .	8.96[d]	7.91	12.33	($SiMe_2$)	
MeOCOCl	Methyl carbonate	71	. . .	55	0.01	1.4423	$C_5H_8N_2O_7$	28.86	3.87	13.46	28.66	4.29	12.84	6.34	7.52	5.65	7.93	8.94	11.66	11.82	
$POCl_3$	Phosphate[b]	73	149–150	. . .	. . .	. . .	$C_9H_{15}N_6O_{16}P$	21.86	3.04	17.00	22.06	3.44	16.63	6.33	7.55	. .	. .	9.41	(P-O-C)	. . .	
$SOCl_2$	Sulfite	79	. . .	130	0.005	1.4843	$C_6H_{10}N_4O_{11}S$	20.81	2.91	16.18	21.40	3.47	15.47	6.34	7.55	8.22[e]	. .	9.85	10.13	11.82	
p-$MeC_6H_4SO_2Cl$	p-Toluensulfonate	33	86–87	. . .	. . .	. . .	$C_{10}H_{12}N_2O_7S$	39.47	3.98	9.21	39.53	4.18	9.10	6.36	7.51	. .	. .	7.25	8.39	8.49	
BCl_3	Borate[f]	51	130–132	. . .	. . .	. . .	$C_9H_{15}BN_6O_{15}$[g]	23.60	3.30	18.35	23.09	3.79	17.28	6.35	7.50	. .	. .	9.35	. . .	. . .	
HNO_3	Nitrate[f]	86	−19	. . .	. . .	1.4612	$C_3H_5N_3O_7$	18.47	2.58	21.54	18.90	3.94	20.61	6.33	7.56	. .	. .	5.97	7.80	12.07	(NO_3)
SO_2Cl_2	Chlorosulfonate	82	. . .	80	0.1	1.4670	$C_3H_5ClN_2O_7S$[h]	14.49	2.03	11.27	14.98	2.52	11.42	6.31	7.58	. .	. .	7.03	8.38	9.98	12.01
p-$C_6H_4(COCl)_2$	Terephthalate	78	145–146	. . .	. . .	. . .	$C_{14}H_{14}N_4O_{12}$	39.08	3.28	13.02	39.15	3.78	13.27	6.34	7.52	5.73	7.95	8.89	9.05	13.80	

[a] Solids were run in potassium bromide and liquids as capillary films. [b] Ref. 2. [c] Calcd. for $C_3H_5ClN_2O_4$: Cl, 21.04. Found: Cl, 20.79; λ_{max}^{MeCN} 277.5 (ϵ 56); $d^{25}{}_{25}$ 1.428 ± 0.002; the chlorine was not affected by sodium iodide in acetone. [d] λ_{Si-O}. [e] $\lambda_{S=O}$. [f] See Experimental. [g] Calcd. for $C_9H_{15}BN_6O_{15}$: B, 2.36. Found: B, 2.54. [h] Calcd. for $C_3H_5ClN_2O_7S$: Cl, 14.26. Found: Cl, 13.83.

TABLE II

ESTERS FROM 2,2-DINITRO-1,3-PROPANEDIOL

Reactant	Ester	Yield, %	M.p., °C.	B.p., °C.	mm.	$n^{25}D$	Molecular formula	Calcd., %			Found, %			Prominent infrared bands, μ[a]							
								C	H	N	C	H	N	λ_{NO_2}		$\lambda_{C=O}$	λ_{C-O}		λ_{other}		
$COCl_2$	Carbonate (cyclic)	15	128–130	. . .	. . .	. . .	$C_4H_4N_2O_7$	25.01	2.10	14.58	24.68	2.40	14.30	6.23	7.67	5.70	sh8.41	8.49	8.95	. . .	11.78
$COCl_2$	Carbonate (poly)	8	180–200 dec.	. . .	. . .	. . .	$(C_4H_4N_2O_7)_n$	25.01	2.10	14.58	25.29	2.58	13.80	6.31	7.45	5.61	8.01	. .	9.98	. . .	11.82
$SOCl_2$	Sulfite	64	42–43	110[h]	0.03	. . .	$C_3H_4N_2O_7S$	16.98	1.90	13.21	16.88	2.13	12.53	6.27	7.58	8.29, 8.35[c]	. .	. .	9.72	10.11	11.81
AcCl	Diacetate[d]	96	. . .	75	0.02	1.4454	$C_7H_{10}N_2O_8$	33.61	4.03	11.20	34.17	4.20	11.19	6.31	7.56	5.64	8.20	. .	9.46	. . .	. . .
SO_2Cl_2	Dichloride	57	38–40	48	2	. . .	$C_3H_4Cl_2N_2O_4$[e]	17.75	1.99	13.80	17.78	2.25	13.59	6.31	7.59	. .	. .	. .	11.79	. . .	. . .
EtOCOCl	Bis(ethyl carbonate)	77	. . .	100	0.005	1.4438	$C_9H_{14}N_2O_{10}$	34.84	4.55	9.03	34.54	4.74	9.10	6.30	7.57	5.65	8.00	. .	. . .	. . .	. . .
Me_2SiCl_2	Dimethylsilane	68	>240	. . .	. . .	. . .	$(C_5H_{10}N_2O_6Si)_n$	27.02	4.54	12.61	27.21	4.69	12.31	6.33	7.51	. .	8.79	9.07[f]	7.90	12.24	($SiMe_2$)
			145–160	160[h]	0.005	. . .	$(C_5H_{10}N_2O_6Si)_n$	27.02	4.54	12.61	26.69	4.95	12.08	6.34	7.51	. .	8.81	9.07[f]	7.91	12.26	($SiMe_2$)
[i]	Mono(ethyl carbonate)	99	. . .	. . .	. . .	. . .	$C_6H_{10}N_2O_8$	30.26	4.23	11.76	30.21	4.68	11.35	6.34	7.55	5.66	7.99	. .	2.86(OH)	. . .	. . .
HNO_3	Dinitrate[b]	58	12	45	0.005	1.4777	$C_3H_4N_4O_{10}$	14.07	1.57	21.88	14.77	2.09	21.21	6.31	7.61	. .	. .	. .	5.95	7.81	12.17(NO_3)
SO_2Cl_2	Monochloride monochlorosulfonate	87	. . .	50	0.02	1.4795	$C_3H_4Cl_2N_2O_7S$[g]	12.73	1.42	9.90	13.48	1.73	9.87	6.27	7.61	. .	. .	. .	7.02 12.08	8.39	10.05

[a] Solids were run in potassium bromide, liquids as capillary films. [b] Ref. 15. [c] $\lambda_{S=O}$ doublet. [d] S. S. Novikov, G. A. Shvekhgeimer, and N. F. Pyatakov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 375, 1961; H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951). [e] Calcd. for $C_3H_4Cl_2H_2O_4$: Cl, 34.93. Found: Cl, 33.47. [f] λ_{S-O} doublet. [g] Calcd. for $C_3H_4Cl_2N_2O_7S$: Cl, 25.05. Found: Cl, 25.52. [h] Purified from a sublimation apparatus. [i] See Experimental.

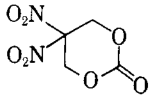
The pyridine-catalyzed esterification of 2-nitro-1,3-propanediols with thionyl chloride yields only cyclic sulfites.

Boron trichloride reacts readily with 2,2-dinitropropanol in dichloromethane in the presence of pyridine, but it is difficult to isolate the borate because of its sensitivity to water. A purer product (Table I) can be obtained when the pyridine is omitted. The analogous reaction with phosphorus trichloride and pyridine yields initially the phosphite which is oxidized to tris-(2,2-dinitropropyl) phosphate during the purification step.

The product from the reaction of dichlorodimethylsilane with 2,2-dinitro-1,3-propanediol and pyridine is a mixture, a part of which is believed to be the cyclic siloxane. It appears to be more sensitive to hydrolysis than the corresponding carbonate and sulfite.

Sulfuryl chloride reacts with β-nitro alcohols and pyridine to form the corresponding β-chloro compounds in good yield (Tables I and II). By altering the reaction conditions to include a short reaction time, low temperatures, dilute solutions, and late addition of pyridine, the intermediate chlorosulfonates may be isolated in good yield as, *e.g.*, in the case of 2,2-dinitropropanol. With 2,2-dinitro-1,3-propanediol, however, the bis(chlorosulfonate) cannot be isolated since it reacts further, even under these conditions, to give 3-chloro-2,2-dinitropropyl chlorosulfonate.

The simple β-nitro esters are quite stable and relatively unreactive. Open-chain carbonates are resistant to boiling 100% nitric acid and can be purified in this fashion. The cyclic carbonates are among the most reactive of the esters investigated and the dinitro compound I is more reactive than the alkylnitrotrimethylene carbonates II. Acid catalysts, such as aluminum chloride, boron trifluoride, or sulfuryl chloride, which convert II to polycarbonates III, decompose I to red water-soluble products. Heating with water or acetic acid converts I to 2,2-dinitro-1,3-propanediol and carbon dioxide. Boiling ethanol causes ring opening to give the monoethyl carbonate IV in theoretical yield,



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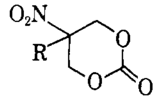

II

$(CH_2C(NO_2)RCH_2OCOO)_n$ III $HOCH_2C(NO_2)_2CH_2OCOOEt$ IV

a reaction which presumably involves nucleophilic attack of the alcohol on the carbonate carbon. The carbonate I is unchanged by acylating agents, such as acetic anhydride, acetyl chloride, and ethyl chlorocarbonate at temperatures below 100°, but reacts with boiling acetic anhydride or acetyl chloride in the presence of pyridine to give 2,2-dinitro-1,3-propanediol diacetate. Boiling pyridine decomposes I, but under mild conditions pyridine slowly precipitates a pyridine-free, salt-like solid $(C_3H_5N_2O_4)_n$, which is devoid of carbonyl. On prolonged standing, the cyclic carbonates decompose to diols and carbon dioxide, plus small amounts of polymeric carbonates. Unlike the polymeric carbonates, the cyclic esters undergo nitrolysis with 100% nitric acid to give 2-nitro-1,3-propanediol dinitrates.

The 2-nitrotrimethylene sulfites are surprisingly stable. They are unchanged by boiling with water and one representative, the 2-methyl compound, can be distilled unchanged at atmospheric pressure. They fail to react with sodium iodide in acetone, but undergo nitrolysis on heating with 100% nitric acid to give 2-nitro-1,3-propanediol dinitrates.

A similar lack of reactivity is observed with 2,2-dinitropropyl benzenesulfonate and the 2,2-dinitropropyl chlorides, which are unchanged by boiling with alcoholic lithium chloride or potassium acetate.

The 2-nitroalkyl chlorosulfonates, on the other hand, are rapidly converted to the corresponding chlorides by heating with pyridine hydrochloride.

Experimental[11]

β-Nitro Alcohols.—2,2-Dinitropropanol[12] and 2,2-dinitro-1,3-propanediol[7,13] were prepared by literature methods.

Esterification Procedure.—Pyridine (0.1 mole) was added with stirring and cooling to a solution of alcohol (0.1 mole monohydric or 0.05 mole dihydric alcohol) in 50 ml. of dichloromethane. A 5% excess of acid chloride was added during 0.5 hr. with cooling and stirring and the mixture was refluxed 1–2 hr. The reaction mixture was washed with several portions of 3–5% hydrochloric acid, dried over magnesium sulfate, and evaporated under reduced pressure to give the crude ester. Liquids were distilled through a modified Hickman still[14] and solids were recrystallized to constant melting point, usually from benzene–petroleum ether. The properties of the esters from 2,2-dinitropropanol and 2,2-dinitro-1,3-propanediol are given in Tables I and II.

2,2-Dinitropropyl Nitrate.—2,2-Dinitropropanol (2.0 g., 0.013 mole) was added with stirring to 10 ml. of 100% nitric acid at 20°. The mixture was stirred for 1 hr. at 20°, poured onto ice, and extracted with dichloromethane. The extracts were washed with water, dried over sodium sulfate, and evaporated *in vacuo* to give 86% of crude nitrate. Distillation at 50°, 0.02 mm., gave a water-white oil, $d^{25}{}_{25}$ 1.491, with the properties given in Table I.

Tris(2,2-dinitropropyl) Borate.—Boron trichloride (1.16 g., 0.01 mole) in 15 ml. of dichloromethane was added dropwise with stirring at 0° to a solution of 2,2-dinitropropanol (4.8 g., 0.03 mole) in 85 ml. of dichloromethane. The reaction mixture was stirred at 0° for 1 hr., at 25° for 1 hr., and refluxed to complete the reaction. Evaporation of the solvent gave a colorless solid residue which, after crystallization from benzene–hexane, gave the borate with the properties listed in Table I.

2,2-Dinitrotrimethylene Carbonate (I).—Infrared analyses indicate that in the standard procedure the cyclic carbonate was formed in 80–85% yield and the polycarbonate in around 10% yield. Upon removal of the pyridine hydrochloride by water washing, however, much of the cyclic carbonate was converted to the original diol and only the indicated yield was isolated. The mixture of cyclic and polymeric carbonates was separated by sublimation at 100° (0.04 mm.). The colorless sublimate melted, resolidified, and remelted at 128–130°. It was soluble in dichloromethane and acetone and dissolved slowly in cold water. When the 2,2-dinitro-1,3-propanediol·2 pyridine complex in dichloromethane was added to phosgene in dichloromethane in such a way that phosgene was always in excess, the reaction mixture contained only I and pyridinium chloride. This mixture could be separated by crystallization from little dichloromethane and gave 43% of pure I.

On prolonged standing at 25°, I gradually decomposed to a mixture of 2,2-dinitro-1,3-propanediol and little polymeric carbonate.

Hydrolysis.—A solution of I (0.050 g.) in 5 ml. of water was warmed on a steam bath. Carbon dioxide was evolved at 40–50°. The reaction was completed by heating to 80°, and the aqueous solution was cooled, washed with a little dichloromethane, and evaporated to dryness at 25° (0.1 mm.). The residue of 2,2-dinitro-1,3-propanediol weighed 0.0287 g. (66%). Heating I (0.050 g.) on a steam bath with 1 ml. of acetic acid and distilling to dryness at 0.01 mm. gave 0.035 g. (81%) of diol.

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[11] Microanalyses by M. J. Naranjo. Melting points are corrected.

[12] E. E. Hamel, J. S. Dehn, J. A. Love, J. J. Scigliano, and A. H. Swift, *Ind. Eng. Chem. Prod. Res. Develop.*, **1**, 108 (1962).

[13] H. Plaut, U. S. Patent 2,522,959; *Chem. Abstr.*, **45**, 3413 (1951).

[14] H. E. Ungnade, *Anal. Chem.*, **31**, 1126 (1959).

Alcoholysis.—When refluxed with 5 ml. of absolute ethanol, I (0.215 g.) gave 0.270 g. (100%) of pale yellow oil after distilling the alcohol under reduced pressure. The oil was decolorized with charcoal in dichloromethane, evaporated, and degassed to give 2,2-dinitro-3-hydroxypropyl ethyl carbonate (IV).

Reaction with Pyridine.—I was destroyed when it was refluxed for 15 min. with dry pyridine. When purified I (0.192 g., 0.001 mole) in 10 ml. of dichloromethane was stirred for 18 hr. with pyridine (0.079 g., 0.001 mole) at 25°, a pale yellow precipitate was formed. It was filtered with suction, washed with dichloromethane, and dried; m.p. (with darkening) 180°, incomplete melting at 250°; yield, 0.10 g. (75%).

Anal. Calcd. for $(C_3H_5N_2O_4)_n$: C, 27.07; H, 3.79; N, 21.05. Found: C, 27.27; H, 3.72; N, 20.20.

Evaporation of the filtrates and washings gave 0.08 g. of yellow oil containing pyridine plus traces of the same solid. The new compound was insoluble in most organic solvents, but dissolved in concentrated hydrochloric acid. The salt-like character of the compound was further confirmed by its infrared absorption spectrum in potassium bromide with λ_{NO_2} 6.37 and 7.45, and $\lambda_{\bar{C}(NO_2)_2}$ 6.76, 8.09, and 8.71 μ.

Nitrolysis.—Heating I (0.19 g., 0.001 mole) with 1 ml. of 100% nitric acid at 93° for 0.5 hr. gave 0.11 g. (43%) of 2,2-dinitro-1,3-propanediol dinitrate, $n^{25}{}_D$ 1.4780.

Acylation.—The carbonate I was unchanged by boiling acetyl chloride, ethyl chlorocarbonate, or heating with acetic anhydride at 90°. Refluxing with acetic anhydride for 0.5 hr. gave 2,2-dinitro-1,3-propanediol diacetate as the only product. The same diacetate was formed in 76% yield when I (0.050 g., 0.00026 mole) was refluxed in dichloromethane with 2 molar equivalents of acetyl chloride and pyridine for 2 hr.

2,2-Dinitro-1,3-propanediol Polycarbonate.—The polymeric carbonate was insoluble in dichloromethane and water. When heated with 100% nitric acid at 93° for 0.5 hr. it was recovered unchanged in 91% yield. [Under the same conditions, bis(2,2-dinitropropyl) carbonate was recovered in 95% yield.]

2,2-Dinitrotrimethylene Sulfite.—This compound was insoluble in cold water and remained undissolved in boiling water. After heating for 1 hr., it was recovered unchanged. Stirring with 8 ml. of 100% nitric acid at 80° for 0.5 hr. converted the sulfite (0.40 g.) to 2,2-dinitro-1,3-propanediol dinitrate in 20% yield.

2,2-Dinitro-1,3-propanediol Dinitrate.—Direct nitration of 2,2-dinitro-1,3-propanediol with 100% nitric acid was carried out by stirring at constant temperature for 35 min. and pouring on ice.[15] The nitrate was extracted with dichloromethane, the extracts washed with water, dried over sodium sulfate, and evaporated under reduced pressure. The yield at 10° (58%) was greater than those at higher temperatures. The crude nitrate melted at 12° and had d^{25}_{25} 1.640 and λ_{max}^{MeCN} 265 mμ (ϵ 85.5). It could be distilled[14] and boiled at 45° (0.005 mm.), but the distillate contained small amounts of impurities which depressed the melting point to 8°. On prolonged standing, it decomposed to the parent diol.

2-Methyl-2-nitrotrimethylene Carbonate.—The condensation reaction of 2-methyl-2-nitro-1,3-propanediol with phosgene and pyridine gave a 78% yield of carbonate, m.p. 138–145°. Sublimation at 90–115° (0.05 mm.) yielded 40% of pure cyclic carbonate, m.p. 112–114°; $\lambda_{C=O}$ 5.68, λ_{NO_2} 6.42, 7.39, λ_{C-O} 8.45, 9.00 μ in potassium bromide.

Anal. Calcd. for $C_5H_7NO_5$: C, 37.27; H, 4.38; N, 8.69. Found: C, 37.16; H, 4.97; N, 8.73.

When the phosgene was added very slowly to the diol–pyridine solution, the methanol-insoluble polymeric carbonate was formed as main product (56% yield). It was purified by adding methanol to the dichloromethane solution, melted at 218°, and had $\lambda_{C=O}$ 5.66, λ_{NO_2} 6.43, 7.40, and λ_{C-O} 7.95 μ in potassium bromide.

Anal. Calcd. for $(C_5H_7NO_5)_n$: C, 37.27; H, 4.38; N, 8.69. Found: C, 37.28; H, 4.79; N, 9.13.

2-Ethyl-2-nitrotrimethylene Carbonate.—The crude reaction product from 2-ethyl-2-nitro-1,3-propanediol and phosgene (89% yield) was crystallized from dichloromethane–petroleum ether. It melted at 72–74° and had $\lambda_{C=O}$ 5.68, λ_{NO_2} 6.45, 7.36, and λ_{C-O} 8.47, 9.02 μ in potassium bromide.

Anal. Calcd. for $C_6H_9NO_5$: C, 41.16; H, 5.18; N, 8.00. Found: C, 41.08; H, 5.57; N, 7.83.

The cyclic carbonate was unchanged by refluxing with excess acetyl chloride. When heated with 3% aluminum chloride at 120° it was converted to polycarbonate. The product was taken up in acetone and precipitated with water. The colorless solid had the following absorption bands in potassium bromide: $\lambda_{C=O}$ 5.65, λ_{NO_2} 6.43, 7.40, λ_{C-O} 8.02 μ.

Calcd. for $(C_6H_9NO_5)_n$: C, 41.16; H, 5.18; N, 8.00. Found: C, 41.09; H, 5.67; N, 7.62.

Partial isomerization occurred also when the cyclic carbonate was heated with excess sulfuryl chloride 0.5 hr. at 75°.

2-Methyl-2-nitrotrimethylene Sulfite.—The known sulfite[16] was obtained in 83% yield. It melted, resolidified, and remelted at 110°, boiled without change at 234° (cor.), (575 mm.), and had λ_{NO_2} 6.41, 7.41, $\lambda_{S=O}$ 8.48, λ_{other} 9.76, 10.15, 10.85, and 11.83 μ (in potassium bromide). The crystalline sulfite (0.09 g.) could be dissolved in 4 ml. of boiling water (92°, 570 mm.) and crystallized unchanged on cooling.

Anal. Calcd. for $C_4H_7NO_5S$: C, 26.52; H, 3.89; N, 7.73. Found: C, 26.85; H, 4.29; N, 7.07.

It was similarly unaffected by refluxing with sodium iodide in acetone and was stable toward potassium permanganate in acetone.

2-Methyl-2-nitrotrimethylene sulfite (0.10 g.) was dissolved in 100% nitric acid (2 ml.), heated at 93° for 0.5 hr., poured on ice, and extracted with dichloromethane. The dried extracts furnished 0.11 g. (87%) of 2-methyl-2-nitro-1,3-propanediol dinitrate,[17] $n^{25}{}_D$ 1.4710; λ_{NO_2} 6.40, 7.42, λ_{NO_3} 6.02, 7.81, 11.95 μ in a liquid film. Authentic dinitrate, prepared by direct nitration of the diol, had $n^{25}{}_D$ 1.4711, d^{25}_{25} 1.485, and an identical infrared spectrum.

1,3-Dichloro-2-methyl-2-nitropropane.—The reaction of 2-methyl-2-nitro-1,3-propanediol with sulfuryl chloride and pyridine gave 68% of crude product which on fractionation yielded about 30% of colorless liquid, b.p. 50–52° (1.5 mm.), with $n^{25}{}_D$ 1.4730 and λ_{NO_2} 6.41, 7.41 μ in a liquid film.

Anal. Calcd. for $C_4H_7Cl_2NO_2$: C, 27.93; H, 4.10; Cl, 41.23. Found: C, 27.78; H, 4.11; Cl, 40.90.

This compound is presumably identical with the one described in the literature.[18]

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[15] H. Plaut, U. S. Patent 2,978,484; *Chem. Abstr.*, **55**, 15934 (1961).

[16] S. P. Lingo, U. S. Patent 2,471,274; *Chem. Abstr.*, **43**, 6222 (1949).

[17] J. A. Wyler, U. S. Patent 2,195,551; *Chem. Abstr.*, **34**, 5283 (1940); W. de C. Crater, U. S. Patent 2,112,749; *Chem. Abstr.*, **32**, 3964 (1938).

[18] R. Preussmann, *Arzneimittel-Forsch.*, **8**, 638 (1958).

sym-Difluorotetrachloroacetone as a Source of Chlorofluorocarbene

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Hine, Ketley, and Tanabe[1] suggested that chlorofluorocarbene was an intermediate in the reaction of dichlorofluoromethane with strong nucleophiles. Attempts by Parham and Twelves[2] at preparing 1-chloro-1-fluoro bicyclo[4.1.0]heptane using dichlorofluoromethane as the carbene precursor and cyclohexene as the acceptor were only moderately successful in that very low yields of an impure product were isolated. Consequently, an efficient chlorofluorocarbene precursor and therefore, a direct route to 1-chloro-1-fluorocyclopropanes is not available.

We wish to report a convenient method for the preparation of chlorofluorcarbene in good yields by the reaction of *sym*-difluorotetrachloroacetone[3] with potas-

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[1] J. Hine, A. D. Ketley, and K. Tanabe, *J. Am. Chem. Soc.*, **82**, 1398 (1960).

[2] W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **23**, 730 (1958).

[3] Allied Chemical Corporation, General Chemical Division, Morris Township, N. J.