Nitration Studies. XVI. Conversion of Nitrite and Nitrate Esters into Nitro Alkanes[1]

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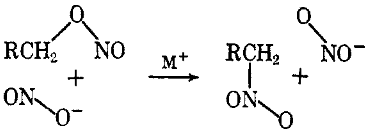
Numerous attempts to isomerize nitrite esters into nitro alkanes in the vapor phase over asbestos catalyst or in the liquid phase over metal nitrite catalysts in the dark or in sunlight were completely unsuccessful. However, nitrate esters were converted into nitro alkanes by reaction with metal nitrites in suitable solvents in optimum conversions, based on nitrate ester of about 40%, and in optimum yields, based on the starting alcohol of about 90%. The relative merits of various methods of preparation of both types of esters are discussed.

Isomerization of nitrite esters into nitro alkanes is reported[3] to be thermodynamically feasible and is reported elsewhere[4] to occur when nitrite esters are passed over heated asbestos. We have attempted repeatedly to confirm the latter results but without success. We have also tried to accomplish such a rearrangement with the aid of metal nitrites as catalysts in the hope of achieving concerted interchange of NO_2 groups, but without success. Others[5-7] have observed that nitrite esters react predominantly at the O–N bond rather than at the C–O bond.


(1)

Thermal decomposition of nitrate esters has been shown[8] to result in formation of small amounts of the corresponsing nitro alkanes, and the tendency of nitrate esters to react at the C–O bond with various anions is well documented.[9,10] It seemed desirable to attempt the conversion of alkyl nitrates into alkanes by reaction with metal nitrites.

Preparation of Alkyl Nitrates.—A wide variety of methods has been used to prepare nitrate esters,[10] but each of these methods suffers from one or more disadvantages. We wish to report the results of studies designed to obtain nitrate esters of simple aliphatic alcohols in high conversions and yields, without danger of explosions, and without rearrangement of the alkyl group.

Since nitrite esters are readily available by reaction of dinitrogen tetroxide with alcohols,[11] an attempt was first made to oxidize nitrite esters with an assortment of oxidizing agents. Only poor to fair yields were obtained except with dinitrogen pentoxide which converted octyl nitrite, for example, into octyl nitrate in over 90% yields.

$$\text{R-OH} + N_2O_4 \xrightarrow[CH_2Cl_2]{0\text{–}5°} \text{RONO} + HNO_3 \qquad (2)$$

At low temperatures alcohols react with dinitrogen tetroxide in the presence of strong base to give nitrate esters[12] (eq 3). While this synthesis is ideal in the sense that it provides both of the desired reactants for the next step in high yields (over 90%), it suffers from the disadvantage that the reaction does not proceed satisfactorily unless it is homogeneous. We were unable to find conditions for achieving this homogeneity with the higher alcohols (above C_4) and their metal salts.

$$\text{ROH} + N_2O_4 \xrightarrow[\text{NaOH}]{-75°} RONO_2 + NaNO_2 \qquad (3)$$

Eventually it was found that the reaction of alcohols with dinitrogen pentoxide provided highly satisfactory results (see eq 4). Although not new[13] this method of preparing nitrates has been largely limited to cellulose and starch, and we find no reference to its application in the preparation of simple alkyl nitrates. Generation of the nitrating agent by mixing streams of dinitrogen tetroxide and ozonized oxygen, contacting this countercurrently with the alcohol, and immediately quenching with water provided a rapid, convenient, and apparently safe method (even in large runs) for obtaining the nitrates of aliphatic alcohols and diols. A decided advantage of this method is the absence of oxidation products, especially carboxylic acids, in the product. Nitrate esters prepared with the apparatus described in the Experimental Section contained only dissolved water as a substantial impurity and could be used directly in the next step after drying.

$$\text{ROH} + N_2O_5 \longrightarrow RONO_2 + HNO_3 \qquad (4)$$

Reaction of Alkyl Nitrates with Metal Nitrites.—Nitrate esters react with nucleophilic anions in several ways: (a) displacement of NO_3^- anion from carbon, (b) displacement of RO^- anion from nitrogen, and (c) removal of H^+ cation from the α position (eq 5–8).

$$Y^- + RONO_2 \longrightarrow Y\text{-}R + NO_3^- \text{ (a)} \qquad (5)$$

$$Y^- + R\text{-}^{18}ONO_2 \longrightarrow Y\text{-}NO_2 + R\text{-}^{18}O^- \text{ (b)} \qquad (6)$$

$$Y^- + R_2CHONO_2 \longrightarrow Y\text{-}H + R_2C(ONO_2)^- \text{ (c)} \qquad (7)$$

$$R_2C(ONO_2)^- \longrightarrow R_2CO + NO_2^- \qquad (8)$$

When (a) proceeds with monomolecular kinetics, as for example, with tertiary alkyl esters,[14] olefins are often the principal products (E1 mechanism); when it proceeds with bimolecular kinetics as, for example, with primary

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[3] G. Geiseler and M. Ratzsch, *Z. Phys. Chem.* (Frankfort am Main), **26**, 131 (1960).

[4] P. Neogi and T. Chowduri, *J. Chem. Soc.*, 701 (1916).

[5] A. Allen, *ibid.*, 1968 (1954); M. Anbar, I. Dostrovsky, D. Samuel, and A. Yoffe, *ibid.*, 3603 (1954).

[6] P. Gray and M. Pearson, *Trans. Faraday Soc.*, **59**, 347 (1963).

[7] A. Allen and G. Schonbaum, *Can. J. Chem.*, **39**, 940 (1961).

[8] J. B. Levy, *J. Amer. Chem. Soc.*, **76**, 3254 (1954).

[9] F. Pattison and G. Brown, *Can. J. Chem.*, **34**, 879 (1956).

[10] R. Boschan, R. Merrow, and R. Van Dolah, *Chem. Rev.*, **55**, 485 (1955).

[11] A. Yoffe and P. Gray, *J. Chem. Soc.*, 1412 (1951).

[12] E. White and H. Feldman, *J. Amer. Chem. Soc.*, **79**, 5832 (1957).

[13] H. Gibson, *Proc. Roy. Soc. Edinburgh*, **28**, 705 (1908).

[14] F. Pattison and G. Brown, *Can. J. Chem.*, **34**, 879 (1956); G. Lucas and L. Hammett, *J. Amer. Chem. Soc.*, **64**, 1928 (1942).

alkyl esters, olefins are minor products. Type b reactions occur commonly with carbanions derived from active methylene compounds.[15] Type c reactions have been observed with strong bases.[16] The pathway followed in reactions of alkyl nitrates depends on the type of alkyl group, the nature of the attacking anion, and the solvent employed.[17]

Since a type a reaction with Y^- equal to NO_2^- was desired, it was concluded that best results might be obtained with primary alkyl nitrates, alkali nitrites, and a solvent which dissolves the metal salt but does not coordinate strongly with nitrite anions. Preliminary results in dimethyl sulfoxide (DMSO) with sodium nitrite and 1-propyl nitrate indicated that only about 20% yields of 1-nitropropane were obtainable and that the yields decreased with increasing time. This suggested that a secondary reaction was occurring which destroyed the product.

The reaction of nitrite anions with alkyl halides leads to alkyl nitrites as well as nitro alkanes. In a subsequent reaction the alkyl nitrite converts the nitro alkane into a nitrolic acid.[18] While this reaction is

$$RCH_2Br + NO_2^- \xrightarrow{DMSO} RCH_2ONO + RCH_2NO_2 + Br^- \quad (9)$$

$$RCH_2NO_2 + RCH_2ONO \xrightarrow[NO_2^-]{DMSO} RC(NO){=}NO_2H + RCH_2OH \quad (10)$$

troublesome with alkyl halide, it is apparently even more troublesome with alkyl nitrates as starting materials. It may, however, be suppressed by adding a nitrite ester scavenger to the reaction mixture. Phloroglucinol has been recommended for this purpose[18] but we have found that malonic esters are superior nitrite ester scavengers. With the aid of ethyl malonate yields of 1-nitropropane of 40% were obtainable.

It is evident that there are two kinetic factors to be considered in the conversion of alkyl nitrates into nitro alkanes. The first has to do with the rate of replacement of nitrate ions by nitrite anions, and this in turn is dependent on the leaving ability of the nitrate group. Exponential leaving group constants for the reaction shown in eq 11 are given[19] as follows: Br, 0.00; I,

$$CH_3O^- + CH_3X \xrightarrow[25^\circ]{CH_3OH} CH_3OCH_3 + X^- \quad (11)$$

−0.04; Cl, −1.61; ONO_2, −1.90. On this basis the nitrate group is a poorer leaving group than even chloride. For comparison we studied the relative times to completion (disappearance of RX) and yields of products in displacements of the types shown in Table I. It is clear that for these displacements the nitrate group leaves faster than chloride but slower than bromide or iodide; iodide anion is a poorer nucleophile than nitrate anion and hence does not catalyze displacements by nitrite anion (this was checked experimentally); product yields are directly related to reaction rates.

TABLE I

$$Y^- + RX \xrightarrow{DMSO} RY + X^- \ (R = 1\text{-}C_3H_7)$$

Y	X	Time, hr	Temp, °C	RY, %
NO_2	NO_3	2.5	65	40
I	NO_3	4.0	75	48
NO_2	I	1.5	30	64
NO_2	Br	2.5	30	58
NO_2	Cl	4.4	65	38

The second kinetic factor is concerned with the relative rates of the reactions leading to formation of nitro alkanes and alkyl nitrites. Although much study has been devoted to reactions in which ambident anions displace other groups, it is still not possible to predict with certainty the relative rates of formation of the two possible products in new combinations of reactants. In addition to the natures of the entering and leaving groups (Table I), the solvent exerts an important influence (Table II).

TABLE II

$$NaNO_2 + RONO_2 \xrightarrow{S} RNO_2 + ROH \text{ (from RONO)}^a$$

Solvent	Time, hr	Temp, °C	RNO_2, %	ROH, %
HMPA[b]	1.0	45	42	54
DMSO[c]	2.5	65	40	57
DMF[d]	8.5	65	23	43
MF[e]	10.0	75	5	13

[a] All runs with $1\text{-}C_3H_7ONO_2$ and to completion (disappearance of $RONO_2$). [b] HMPA, hexamethylphosphoramide. [c] DMSO, dimethyl sulfoxide. [d] DMF, dimethylformamide. [e] MF, methylformamide.

Here again the yield of nitro alkane is proportional to the rate of the reaction. Hexamethylphosphoramide proved to be the best solvent found in that it gave the best yield in the shortest time and at the lowest temperature. Nitrites of the alkali metals only were found to be satisfactory in these reactions. All attempts to employ other metals in the hope of influencing favorably the product ratio RNO_2/ROH were negative. Salts of Hg(II), Co(II or III), Pd(II), or Zn(II) severely diminished the rate of the desired reaction by coordinating with nitrite ions. Reaction temperatures were ordinarily chosen to complete the reaction in a few hours, but above about 65° secondary reactions became increasingly important and the nitro alkane was destroyed. Second-order rate constants for the reaction of 1-butyl nitrate with sodium nitrite in DMSO were calculated to be $k(65^\circ) = 6.0 \times 10^{-4}$ l. mol^{-1} sec^{-1}, and $k(50^\circ) = 1.5 \times 10^{-4}$ l. mol^{-1} sec^{-1}, corresponding to an activation energy of 20 kcal mol^{-1}.

Although primary nitrates gave better than 40% conversion into nitro alkanes, a secondary nitrate ester, 2-octyl nitrate, gave only an 11% conversion into 2-nitrooctane. 2-Octanone was formed in 36% conversion probably *via* a displacement of the α-hydrogen[20] by nitrite ion (eq 8). *t*-Amyl nitrite gave only a trace of *t*-nitrobutane, and the conversion of 2-chloroethyl nitrate into 2-chloro-1-nitroethane was only 5%. Sur-

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[15] M. Anbar, I. Dostrovsky, D. Samuel, and A. Yoffe, *J. Chem. Soc.*, 3603 (1954).

[16] J. Baker and D. Easty, *ibid.*, 1193 (1952); T. Carlson, *Arkiv Kemi, Mineral. Geol.*, **3**, art. 8; *Chem. Abstr.*, **2**, 3344 (1908); T. Carlson, *Chem. Ber.*, **40**, 4191 (1907).

[17] F. Pattison and G. Brown, *Can. J. Chem.*, **34**, 879 (1956); G. Lucas and L. Hammett, *J. Amer. Chem. Soc.*, **64**, 1928 (1942); J. Baker and D. Easty, *J. Chem. Soc.*, 1193 (1952); J. Baker and D. Easty, *Nature*, **166**, 156 (1950); S. Cristol, A. Shadan, and B. Franzus, Abstracts of Papers, 125th National Meeting of the American Chemical Society, Kansas City, Mo., 1954, p 20.

[18] (a) N. Kornblum, H. Larson, R. Blackwood, D. Mooberry, E. Oliveto, and G. Graham, *J. Amer. Chem. Soc.*, **78**, 1497, 1501 (1956); (b) N. Kornblum and J. Powers, *J. Org. Chem.*, **22**, 455 (1957).

[19] E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, p 165.

[20] M. Anbar, I. Dostrovsky, D. Samuel, and A. Yoffe, *J. Chem. Soc.*, 3603 (1954).

TABLE III

REACTION OF BUTYL ALCOHOL AND DINITROGEN TETROXIDE AT −75°

Solution A[a]			Solution B at −75°		
Reactant	Mol	Temp of A, °C	Reactant	Mol	Yield of $BuNO_3$, %[b]
N_2O_4 (CH_2Cl_2)	0.12	0	NaOBu (BuOH)	0.25	0
N_2O_4 (CH_2Cl_2)	0.14	−75	NaOBu (BuOH)	0.20	71
N_2O_4 (CH_2Cl_2)	0.13	−75	NaOBu (BuOH)	0.15	60
N_2O_4 (CH_2Cl_2)	0.14	−75	NaOBu (BuOH)	0.30	91
N_2O_4 (CH_2Cl_2)	0.10	−75	NaOH (BuOH)	0.25	93
NaOH (BuOH)	0.25	21	N_2O_4 (CH_2Cl_2)	0.10	0
NaOH (BuOH)	0.25	21	N_2O_4 (CH_2Cl_2)	0.10	Trace
N_2O_4 (CH_2Cl_2)	0.13	21	NaOH (BuOH-Et_2O)[c]	0.12	Trace
N_2O_4 (CH_2Cl_2)	0.15	21	CaO (BuOH-CH_2Cl_2)[c]	0.12	12

[a] Solution A added to solution B in all runs. [b] Based on N_2O_4. [c] Heterogeneous systems. All other systems homogeneous.

prisingly, the dinitrate ester, 1,5-pentamethylene dinitrate, reacted somewhat more rapidly than the primary mononitrate esters and gave both 1,5-dinitropentane (16%) and 5-nitropentanol (44%) for the best total yield of nitro compounds from any nitrate ester (60%). Like the corresponding halides the nitrates of cyclohexanol and neopentanol gave no nitro alkane.

The preparation of nitro alkanes from alcohols *via* nitrate esters seems to offer but little advantage over the preparation *via* alkyl bromides. There is no possibility of a carbonium ion rearrangement in the initial step *via* the nitrate ester, but such a rearrangement may occur in preparing the alkyl halide especially from branched chain alcohols. Also any nitrate ester not converted into nitro alkane is almost completely recovered as the original alcohol, while this is apparently not true in the halide reaction.[18] Otherwise the halide approach is faster and gives better conversions. The nitrite group appears to be about as good a leaving group as chloride although this varies with the nature of the replacing group.

Experimental Section

Throughout this work many of the conversions reported were calculated from vapor phase chromatographic (vpc) analyses. An Aerograph Model A-350-B dual column temperature programmer gas chromatograph was employed. Ozonized oxygen was generated by a Welsbach T-23 ozonator. Nitrite esters were prepared from the alcohols by reaction with dinitrogen tetroxide (N_2O_4).[11]

Attempted Isomerization of Nitrite Esters into Nitro Alkanes.—Butyl nitrite was treated with various metal nitrites under a variety of conditions, both in the presence and absence of light. The metal nitrites included silver nitrite, sodium nitrite, and magnesium nitrite.[21] The solvents used were ethyl ether, dimethylformamide, methanol, and aqueous ethanol. The reaction mixtures were magnetically stirred. Analysis for 1-nitrobutane was carried out on a 10 ft × 0.25 in. 5% diisodecyl phthalate column, using Teflon 6 as the solid support. In no case was any nitrobutane detected.

A representative experiment is described as follows. In a darkened vessel were placed 5.11 g (0.033 mol) of freshly prepared magnesium nitrite dihydrate, 25 ml of anhydrous ethyl ether, and 20 ml (0.17 mol) of butyl nitrite. The vessel was sealed and kept at 0°. After 36 hr no 1-nitrobutane was detected by vpc analysis.

Attempted Isomerization of Nitrite Esters into Nitro Alkanes on Asbestos.—The apparatus consisted of a 6 ft × 0.25 in. copper column firmly packed with asbestos cord and fitted with swedge locks. A Fischer-Gulf partitioner (58416) was used as a source of uniform heat. The long preheater and exhaust columns were removed (thermal decomposition would have occurred in the preheater column) and the asbestos column was connected directly to both the injection and exhaust ports. This made it possible to inject the nitrite ester directly into the asbestos column and collect the products directly as they left it. Helium was used as the carrier gas.

The following paragraph describes a representative experiment.

Butyl nitrite was injected into the column (heated to the desired temperature) by means of a capillary tube in approximately 0.1-ml fractions until approximately 2 ml had been added. The average residence time in the column was controlled at 35 sec by adjusting the flow rate of the helium carrier gas. Approximately 1.5 min were allowed between injections, and the total time for addition was about 30 min. Finally the column was flushed with benzene to remove any residual materials. The existing gases were collected in a U-tube immersed in a Dry Ice–acetone bath. The condensed liquids were analysed by vpc on a 10 ft × 0.25 in. 5% diisodecyl phthalate column, using Teflon 6 as the solid support. No 1-nitrobutane was found in runs made at 50, 100, 125, or 157°. Except for the run at 157° the only products of the reaction, in addition to unreacted butyl nitrite, were butyl alcohol and butyraldehyde, which were formed in essentially equal amounts. The presence of butyric acid as a reaction product in the run at 157° was indicated by vpc analysis and verified by ir analysis.

Oxidation of Nitrite Esters into Nitrate Esters.—Descriptions of representative experiments are given below.

To a 250-ml, three-necked flask fitted with a cold trap at −15°, a gas dispersion tube, and a glass plug were added 10.31 g (0.10 mol) of butyl nitrite, approximately 1 ml of liquid N_2O_4, and 40 ml of $CHCl_3$. Ozonized oxygen (100 V, 6 psi O_2, 0.02) was passed through this magnetically stirred solution at 0° for 2 hr. The conversion into butyl nitrate was 40%.

Allowing butyl nitrite to react under various conditions with $KMnO_4$ in acetone, I_2O_5 alone, or in DMSO, H_2O_2 (3%), $K_2S_2O_8$, $(NH_4)_2S_2O_8$, CrO_3, HgO, $KClO_4$, TiO_2, $Na_2S_2O_3$, or BaO_2 gave no, or at best 2–3%, conversion into butyl nitrate. However an ethereal solution of butyl nitrite gave a 12% conversion into butyl nitrate on standing for 5 days with an aqueous suspension of V_2O_5.

Irradiation of butyl nitrite with a uv lamp for 4 hr gave a 25% conversion into butyl nitrate. Oxides of nitrogen were evolved and atmospheric oxygen was absorbed.

Gaseous N_2O_5 was passed into CCl_4 at 0°, into which octyl nitrite was slowly being added from a dropping funnel. The conversion into octyl nitrate was 72% as determined by analysis of a 5 ft × 0.25 in. 5% SF-96 column, using Chromosorb G as the solid support. The conversion into octanoic acid was 28%.

Reaction of Butyl Alcohol at −75° with Dinitrogen Tetroxide at −75°.—The apparatus consisted of a three-necked flask fitted with a Teflon blade sweep stirrer, a thermometer, and a glass plug. The flask was immersed in a large dewar filled with Dry Ice and acetone.

Reactant Solutions.—The NO_2–N_2O_4 was passed directly into cold CH_2Cl_2 until the desired amount was dissolved. Into this cold solution (at −40°) was passed a slow flow of ozonized oxygen until any green color was completely removed.

The sodium butoxide solutions were prepared by adding the desired amount of sodium to excess butyl alcohol. Enough alcohol had to be used to keep the sodium butoxide in solution at −75°. The sodium hydroxide solutions were prepared by dissolving the required amounts of sodium hydroxide pellets in butyl alcohol.

Analysis for butyl nitrate was carried out on a 13 ft × 0.25 in. 20% didecyl phthalate column, using Chromosorb W as the solid support.

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(21) P. Ray, *J. Chem. Soc.*, 523 (1904).

TABLE IV

PREPARATION OF NITRATE ESTERS USING DINITROGEN PENTOXIDE

Starting material	Registry no.	Conversion into $RONO_2$ based on ROH, %	Conversion into $RONO_2$ based on N_2O_4, %	Bp, °C (mm)	$n^{20}D$	Ref
$CH_3(CH_2)_7OH$	629-39-0	$95^{a,b}$	83	45–46 (0.2)	1.4279	*d*
		$93^{a,c}$	80			
$(CH_2)_5OH$	21823-29-0	91^{e}	77	37–38 (1.5) 70–72 (12)	1.4542	*f–h*
$CH_3(CH_2)_9OH$	2050-78-4	$92^{a,c}$	81	58–59 (0.3)	1.4349	*i*
		$95^{b,e}$	83			
$CH_3(CH_2)_2OH$	627-13-4	$91^{c,e}$	79	110 (770) 25 (10)	1.3980	*f, j*
$CH_3(CH_2)_5CH(CH_3)OH$	7214-64-4	$90^{c,k}$	76	44–45 (0.3)	1.4251	*g, h*
$(CH_3)_3CCH_2OH$	926-42-1	$90^{c,e}$	77	27–28 (7) 47–48 (31)	1.4077	*f, l*
$Cl(CH_2)_2OH$	21823-34-7	$90^{c,e}$ (94^{n})	80 (84^{m})	43–44 (10)	1.4442	*f*
$HO(CH_2)_5OH$	21823-35-8	$83^{c,n,o}$ (92^{n})	68 (75^{m})	85 $(0.3)^{p}$	1.4488	*q, r*
$CH_3CH_2C(CH_3)_2OH$	21823-36-9	$76^{c,e,s}$	65	38–39 (16)	1.4083	*t*
$CH_3(CH_2)_7ONO$		$93^{b,k}$	81	45–46 (0.2)	1.4279	*d*

[a] No solvent. [b] Conversion calculated by vpc methods. [c] Conversion based on distilled product. [d] A. Ferris, K. McLean, I. Marks, and W. Emmons, *J. Amer. Chem. Soc.*, **75**, 4078 (1953). [e] In CH_3NO_2 solution. [f] T. Urbanski and M. Witanowski, *Trans. Faraday Soc.*, 59, 1039 (1963). [g] N. Kornblum, N. Lichtin, J. Patton, and D. Iffland, *J. Amer. Chem. Soc.*, **69**, 313 (1947). [h] G. Hammond, M. Hawthorne, J. Waters, and B. Graybill, *ibid.*, **82**, 704 (1960). [i] F. Pattinson and G. Brown, *Can. J. Chem.*, **34**, 879 (1956). [j] P. Gray and M. Pratt, *J. Chem. Soc.*, 2163 (1957). [k] In $CH_3CH_2NO_2$ solution. [l] S. Tsay, A. Paul, and M. Giaimo, *J. Org. Chem.*, **29**, 3387 (1964). [m] Conversion based on undistilled product. [n] In CH_3NO_2 solution containing some DMSO. [o] Dinitrate ester. [p] Mp −16 to −17°. [q] A. Lawrence and A. Matusko, *J. Phys. Chem.*, **65**, 1903 (1961). [r] M. Kemp, S. Goldhagen, and Z. Zihlman, *ibid.*, 61, 240 (1957). [s] Product collected in hexane–sodium fluoride. [t] A. Michael and G. Carlson, *J. Amer. Chem. Soc.*, **57**, 1268 (1935).

Procedure.—Solution A at some specified temperature was added to solution B at −75°. The quantities used and the results for a few runs are shown in Table III.

Reaction of Octyl Alcohol with Dinitrogen Pentoxide.—The NO_2 and ozonized oxygen flows were balanced, and the resultant N_2O_5 was passed through 1.0 mol of octyl alcohol at 5° for 22 hr. Analysis on a 5 ft × 0.25 in. 5% SF-96 column, using Chromosorb G as the support, showed that the conversion into octyl nitrate was 60%. The octanoic acid (36%) was determined by titration with 1.0 *M* sodium hydroxide in 50% aqueous ethanol.

Countercurrent Flow Nitrations. A peristaltic pump was used to transfer the alcohol from the reservoir to the top of the reaction column. To achieve a steady drop-rate the level of alcohol in the calibrated reservoir was kept nearly constant by the continuous addition of fresh alcohol from a buret. A 33 × 2.5 cm tube fitted with a standard Y adapter was the main part of the N_2O_5 generator used. The NO_2 was introduced at the bottom of the reactor tube *via* a gas dispersion tube, while the ozonized oxygen was introduced about 10 cm from the top of the tube in the form of a fine jet to ensure fast mixing with the NO_2. The individual flows were balanced so that the gases leaving through the side arm were colorless. The Welsbach T-23 ozonator was set at standard conditions (110 V, 8 psi O_2, 0.04). A glass spiraled distillation column (58 cm in height × 1.5 cm o.d.) was used as the reactor column. An adapter seal was used to minimize contact between the N_2O_5 and the water in the receiver and to keep the crude nitrate ester formed moving smoothly against the surface tension of the water. A side arm admitted the incoming N_2O_5. The receiving system consisted of a 500-ml flask through which water was passed slowly and continuously to wash away the nitric acid formed. The contents of the receiver syphoned into a 40 × 5 cm settling flask, from which the nitrate ester layer was continuously withdrawn. For further details of construction and operation of the apparatus see ref 1.

A series of alcohols and octyl nitrite also were nitrated by this process (Table IV). The receiving system had to be modified in the nitration of *t*-amyl alcohol, because of the rapid rate of hydrolysis of tertiary nitrate esters.[22,23] In this case the receiver was partially filled with hexane containing suspended sodium fluoride to remove nitric acid.[24] The mixture was cooled to 0° and stirred. The product was filtered, neutralized, and distilled to purify.

Conversion of Nitrate Esters into Nitro Alkanes.—The desired amounts of materials were dissolved in the appropriate solvents and the resultant solutions was magnetically stirred at the selected temperature. Certain reactions had to be worked up before analysis. They were poured into excess ice–water layered with either petroleum ether or ethyl ether. Petroleum ether was the solvent of choice when nitrosophloroglucinol was a reaction product. The aqueous layers were extracted with the appropriate solvent and the product conversion was measured directly by passage of the solvent solution through a vpc column. See Table V.

TABLE V

CONVERSION OF NITRATE ESTERS INTO NITRO ALKANES

Nitrate ester[a]	Conversion into ROH, %	Conversion into RNO_2, %	Yield[b] of RNO_2, %
Propyl	56	40	83
Butyl	57	41	
Octyl	59	41	95
Decyl	58	39	88
2-Octyl	38^{c}	11	16
1,5-Pentamethylene[d,e]	34	$16^{f,g}$	22
2-Chloroethyl	47^{h}	5	9
t-Amyl	65–70	Trace	

[a] In DMSO at 65° with ethyl malonate present. [b] Based on ROH used to prepare $RONO_2$. See Table IV. [c] Plus 36% 2-octanone. [d] A dinitrate ester. [e] In DMSO at 60° with ethyl malonate present. [f] A dinitro alkane. [g] Plus 44% 5-nitro-1-pentanol. [h] Plus 23% ethylene glycol.

Descriptions of representative experiments are given below.

1-Nitropropane.—To 60 ml of DMSO were added 5.26 g (0.05 mol) of propyl nitrate, 5.52 g (0.08 mol) of sodium nitrite, and 6.41 g (0.04 mol) of ethyl malonate. The resultant solution was magnetically stirred at 65° for 2 hr. Analysis by vpc showed that the conversions into 1-nitropropane and propyl alcohol were 40 and 57%, respectively.

1-Nitrooctane.—To 60 ml of hexamethylphosphoramide were added 8.76 g (0.05 mol) of octyl nitrate, 5.52 g (0.08 mol) of sodium nitrite, and 6.41 g (0.04 mol) of ethyl malonate. The resultant solution was stirred at 45° for 1 hr. Analysis by vpc showed that the conversions into 1-nitrooctane and octyl alcohol were 41 and 60%, respectively.

2-Nitrooctane.—A mixture of 20.70 g (0.30 mol) of sodium nitrite, 35.05 g (0.20 mol) of 2-octyl nitrate, and 32.03 g (0.20

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mol) of ethyl malonate was allowed to react at 65° for 8.5 hr in 200 ml of DMSO. The conversions into 2-nitrooctane (11%), 2-octanol (38%), and 2-octanone (36%) were determined by vpc analysis on a 6 ft × 0.25 in. 5% Carbowax on 20M Chromosorb G column.

1,5-Dinitropentane and 5-Nitro-1-pentanol.—A mixture of 48.51 g (0.25 mol) of 1,5-pentamethylene dinitrate, 48.3 g (0.70 mol) of sodium nitrite, and 64.01 g (0.04 mol) of ethyl malonate in 400 ml of DMSO was allowed to react at 60° for 2 hr. The conversion into 1,5-pentamethylene glycol (34%) was determined by vpc analysis on the 5% SF-96 column. The conversions into 1,5-dinitropentane (11%) and 5-nitro-1-pentanol (44%) were determined by analysis on the 5% Carbowax 20M column. 5-Nitropentanol (44%) is a new compound and has the following physical constants: bp 262–266°; $n^{20}D$ 1.4546.

Anal. Calcd for $C_5H_{11}NO_3$: C, 45.11; H, 8.27; N, 10.52. Found: C, 44.58; H, 8.26; N, 10.50.

Registry No.—Dinitrogen pentoxide, 10102-03-1; 5-nitropentanol, 21823-27-8; dinitrogen tetroxide, 10544-72-6.

The Reaction of Nitriles with Phosgene. III.[1]
A New Synthesis of 2-Chloro-4,6-diaryl-s-triazines

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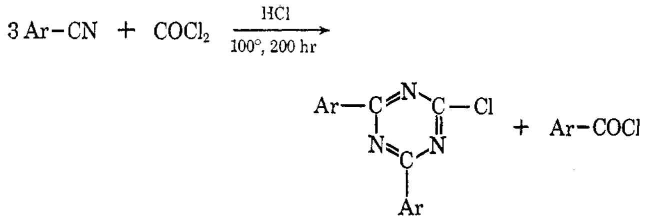
The reaction of benzonitrile with phosgene in the presence of hydrogen chloride at 100° in a sealed glass tube gives approximately equal yields of 2-chloro-4,6-diphenyl-*s*-triazine and benzoyl chloride. This has also been demonstrated with *p*-tolunitrile and *p*-methoxybenzonitrile. In the case of *p*-chloro- and *p*-nitrobenzonitrile, however, the reactions are unsuccessful. The mechanism of this reaction is discussed.

It is well known that nitriles having no α-hydrogens easily trimerize into *s*-triazines in the presence of strong acids, such as hydrogen chloride[2] and chlorosulfonic acid,[3] or under the influence of high pressure.[4] In the preceding papers of this series,[1,5] we reported that upon treatment of aliphatic nitriles with phosgene in the presence of hydrogen chloride at 60–70°, 6-chloro-2,5-dialkyl-4(3H)-pyrimidones were obtained in good yields, in addition to small amounts of 4,6-dichloro-2,5-dialkylpyrimidines.

It has now been found that when benzonitrile reacts with phosgene in the presence of hydrogen chloride at 100° for 200 hr and the well-cooled reaction mixture is filtered, 2-chloro-4,6-diphenyl-*s*-triazine is obtained in high yield. It was identified by direct comparison of its physical properties with those of an authentic sample prepared by the reaction of cyanuric chloride with phenylmagnesium bromide.[6] Glpc analysis of the filtrate showed the presence of benzoyl chloride, which was confirmed by converting it into benzamide. Both products were found in almost equal yields (Scheme I).

SCHEME I



This cyclization did not occur in the absence of hydrogen chloride. Employment of other chlorinating agents, such as phosphorus pentachloride, phosphorus trichloride, phosphorus oxychloride, sulfuryl chloride, and thionyl chloride instead of phosgene, gave only 2,4,6-triphenyl-*s*-triazine.[7]

We examined the yields of the reaction with varying molar ratios of the reactants. It was demonstrated (Table I) that excess hydrogen chloride favored this reaction, but that a large excess of phosgene lowered the yield.

TABLE I
EFFECT OF MOLAR RATIO OF REACTANTS

	Product yields, %[a]	
Molar ratio $C_6H_5CN:COCl_2:HCl$	2-Chloro-4,6-diphenyl-*s*-triazine	Benzoyl chloride[b]
3:0.5:1	10	15
3:1:1	16	19
3:1.5:1	25	26
3:2:1	6	10
3:1:1.5	62	
3:1:2	83	
2:0:1	20[c]	0

[a] Reaction time 200 hr, based on phosgene used. [b] Determined by glpc. [c] 2,4,6-Triphenyl-*s*-triazine.

On close examination of the reaction mixture obtained when excess phosgene was employed, a small amount of a high-boiling product was detected. It was isolated by distillation under reduced pressure and identified as N-(1-chlorobenzylidene)carbamoyl chloride (II, Ar = phenyl) on the basis of ir and mass spectra and elemental analysis.

The reaction of benzonitrile with phosgene and hydrogen chloride has been extended to *p*-tolunitrile, *p*-methoxybenzonitrile, *p*-chlorobenzonitrile, and *p*-nitrobenzonitrile. In the case of *p*-tolunitrile, the products were 2-chloro-4,6-bis(*p*-tolyl)-*s*-triazine and *p*-toluoyl chloride. Glpc analysis of the filtrate also showed the formation of a small amount of the corresponding carbamoyl chloride. The reaction of *p*-

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(7) In our laboratory, it has been found that phosphorus pentachloride was able to catalyze the trimerization to 2,4,6-triphenyl-*s*-triazine. This reaction is now under investigation.