Some Reactions of Nitrate Esters in Acetic Acid Containing Sulfuric Acid

SIDNEY D. ROSS, E. ROBERT COBURN, AND MANUEL FINKELSTEIN

Sprague Electric Company, Research and Development Laboratories, North Adams, Massachusetts

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In boiling acetic acid containing a catalytic quantity of sulfuric acid, alkyl nitrates, pentachlorobenzyl nitrate, and 1-pentachlorophenylethyl nitrate are converted to the corresponding acetates, but other benzyl nitrates react to give the benzaldehydes. This acid-catalyzed, aldehyde-forming reaction is best formulated as a concerted reaction of the conjugate acid of the nitrate in which the N–O bond is broken and a hydride ion is simultaneously transferred from the benzylic carbon atom to oxygen.

Nitrate esters undergo some reactions which are analogous to those observed with the alkyl halides and others which are significantly different and characteristic of the nitrates. As in the case of the halides, nucleophilic displacements on carbon can follow either the SN1 or SN2 mechanism[1,2] and the β-hydrogen elimination reaction, yielding an olefin, may proceed by either a unimolecular or bimolecular mechanism. With the nitrates nucleophilic displacements on nitrogen are also possible and have been observed in the hydrolysis of *n*-butyl nitrate, *n*-octyl nitrate, and 2-octyl nitrate.[3,4] A reaction of special interest is the α-hydrogen elimination reaction which results in a carbene in the case of the halides[5] but leads to an aldehyde with the nitrates.[1,2]

This last reaction of the nitrates, designated $E_{\mathrm{CO}}2$, is a concerted process in which removal of the α hydrogen by a base and ejection of nitrite ion occur simultaneously. Both deuterium-exchange experiments and the nitrogen isotope effect exclude the formation of a carbanion intermediate. This mechanism requires a relatively strong base, and the reaction does not occur under solvolytic conditions.[6,7]

The present report deals with the reactions of some alkyl and benzyl nitrates in boiling acetic acid containing catalytic quantities of sulfuric acid. This treatment converts alkyl nitrates to alkyl acetates, but some properly substituted benzyl nitrates react to give aldehydes in significant yields. This latter mode of reaction represents another mechanism leading to aldehyde. Since a strong acid is required, it is clearly distinguishable from the previously described Eco2 mechanism[6,7] which requires a basic reagent.

Results

The nitrate esters were all prepared in satisfactory yield by the reaction of the appropriate chloride or bromide with an acetonitrile solution of silver nitrate.[8] Since pentachlorobenzyl bromide and 1-pentachlorophenyl-1-bromoethane were both only sparingly soluble in acetonitrile, these two bromides were added to the silver nitrate solution as solutions in carbon tetrachloride. The details of these preparations are compiled in Table I.

In connection with another study[9] an attempt was made to convert benzyl nitrate to benzyl acetate by an acetolysis reaction in acetic acid containing a catalytic quantity of sulfuric acid. The product was not the expected acetate but benzaldehyde which was obtained in significant yield. When 5 ml of benzyl nitrate in 5 ml of acetic acid was added dropwise to a refluxing solution of concentrated sulfuric acid (5 drops) in 10 ml of acetic acid and the solution was refluxed an additional hour after the addition, 71% of the nitrate was converted to benzaldehyde and oxides of nitrogen were evolved.

This conversion of nitrate to aldehyde is not simply a thermal decomposition. Benzyl nitrate can be recovered unchanged after a solution in toluene is refluxed 3 hr. When a benzyl nitrate solution in acetic acid is refluxed 3 hr, one-third of the nitrate is converted to acetate, but no aldehyde is formed. The strong acid is, therefore, an essential ingredient for aldehyde formation.[10] The acetic acid solvent, on the other hand, is not essential for aldehyde formation. Benzyl nitrate can be converted to benzaldehyde in better than 30% yield by heating in either toluene or mesitylene containing a catalytic quantity of sulfuric acid.

After 3,5-dimethylbenzyl nitrate was treated with acetic acid and sulfuric acid as above it was possible to isolate by distillation a 71% yield of 3,5-dimethylbenzaldehyde. Since in this reaction, as in the others studied, no systematic effort was made to maximize the yields, this reaction may represent a convenient synthetic route to this aldehyde. The reaction sequence, mesitylene to 3,5-dimethylbenzyl bromide to the nitrate to the aldehyde, could be carried out without extensive purification of the intermediate compounds and may be more convenient than the direct oxidation of mesitylene[11,12] and as useful as the procedure involving the dimethyl sulfoxide oxidation of a benzyl tosylate.[13]

This aldehyde-forming reaction may also be of some utility in special cases where it is desired to introduce two aldehyde groups at once. *p*-Xylylene dinitrate, which can be obtained easily in almost quantitative

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(1) G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, **64**, 1928 (1942).

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(9) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **89**, 4088 (1967).

(10) At a lower temperature and with a weaker acid (5 ml of benzyl nitrate in 25 ml of methanol, 2 ml of concentrated hydrochloric acid, and 3 ml of water refluxed 2.5 hr) aldehyde is, again, not formed. In this reaction the conversion of benzyl nitrate was 28.3% to benzyl alcohol, 25.6% to benzyl chloride, and 18.7% to benzyl methyl ether.

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(12) C. S. Marvel, J. H. Saunders, and C. G. Overberger, *J. Am. Chem. Soc.*, **68**, 1085 (1946).

(13) N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

Table I
Esters of Nitric Acid

Nitrate ester	Bp or mp, °C (mm)	n_D, deg	Yield, %	Calcd, %				Found, %			
				C	H	N	Cl	C	H	N	Cl
Benzyl nitrate[b]	95 (11)	1.5192 (23)	69	54.90	4.61	9.15		54.58	4.37	8.83	
3,5-Dimethylbenzyl nitrate[c]	58–60 (0.25)	1.5172 (22)	54	59.66	6.12	7.73		60.16	6.21	7.22	
p-Chlorobenzyl nitrate[d]	109 (7)	1.5391 (23)	84	44.82	3.22	7.47	18.90	45.23	3.30	7.08	18.96
p-Methylbenzyl nitrate[e]	44–49 (0.015)	1.5157 (27)	67								
p-Nitrobenzyl nitrate[f]	66–68[a]		99								
Pentachlorobenzyl nitrate[g]	114–115[a]		92	25.84	0.62	4.31	54.48	26.01	0.60	4.16	54.52
1-Pentachlorophenylethyl nitrate[h]	131–133[a]		83	28.31	1.19	4.13	52.23	28.35	1.15	3.87	52.78
n-Octyl nitrate[i]	90–91 (8)	1.4278 (24.5)	86	54.84	9.78	7.99		54.45	8.92	8.13	
2-Octyl nitrate[j]	82–83 (8)	1.4241 (25)	66								
n-Amyl nitrate[k]	47–48 (9.5)	1.4130 (22)	60								
p-Xylylene dinitrate[l]	50–51[a]		96	42.99	3.53	12.28		42.35	3.42	12.49	

[a] Melting point. [b] Registry no.: 15285-42-4. [c] 15285-43-5. [d] 15313-94-7. [e] 13527-05-4. [f] 15539-77-2. [g] 15285-46-8. [h] 15313-95-8. [i] 629-39-0. [j] 7214-64-4. [k] 1002-16-0. [l] 15285-41-3.

yield from the dibromide, gave a 29% yield of terephthalaldehyde.

With some benzyl nitrates the reaction led to the benzoic acid as well as the benzaldehyde. From the reaction under nitrogen of *p*-nitrobenzyl nitrate it was possible to isolate a 70.9% yield of *p*-nitrobenzaldehyde and a trace amount of *p*-nitrobenzoic acid (0.2 g from 5 g of the nitrate). *p*-Methylbenzyl nitrate, also allowed to react under nitrogen, gave 50% *p*-tolualdehyde and 19.6% *p*-toluic acid. *p*-Chlorobenzyl nitrate gave a mixture of acid and aldehyde from which a more than 45% yield of the acid could be separated and in which the presence of the aldehyde could be demonstrated by conversion to the known 2,4-dinitrophenylhydrazone. In these reactions it is not known with certainty whether the acids are formed during the reaction or during the work-up.

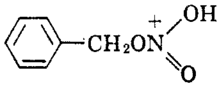
Under the reaction conditions used in the present work the three purely aliphatic nitrates, *n*-octyl nitrate, 2-octyl nitrate, and *n*-amyl nitrate, gave acetates (40–60% yield), unreacted nitrate, and a high-boiling, polymeric residue. It is possible that aldehydes or ketones might be formed under much more strongly acidic conditions, since Cristol, *et al.*,[4] have reported that 2-octanone is formed from 2-octyl nitrate in 70–90% sulfuric acid.

Pentachlorobenzyl nitrate and 1-pentachlorophenylethyl nitrate both gave acetates, in yields of 100 and 89%, respectively. These reactions, too, require both the acid catalyst and the temperature of refluxing acetic acid. Pentachlorobenzyl nitrate can be recovered unchanged after 4 hr of refluxing in acetic acid or after 20 hr of refluxing in methanol containing 1% sulfuric acid. When a solution of the nitrate (5 g) in 100 ml of dry butanol containing 1 ml of concentrated sulfuric acid was refluxed 20 hr and then poured into water, a 60% yield of pentachlorobenzyl alcohol was obtained.

Discussion

The mechanism for conversion of a nitrate to an acetate by a refluxing solution of acetic acid containing a catalytic quantity of sulfuric acid is relatively straightforward. Such acid group exchange points to a carbonium ion as an intermediate,[14] and the mechanism is of the $A_{AL}1$ type,[15] in which the rate-determining step is the unimolecular heterolysis of the conjugate acid of the nitrate ester to give nitric acid and a carbonium ion.

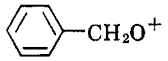
The mechanism by which the aldehydes are formed is less clear. Since the reaction does not occur in refluxing acetic acid in the absence of sulfuric acid, it is reasonably certain that the conjugate acid of the benzyl nitrate (I) is involved.



I

The conversion of I to an aldehyde requires an unsymmetrical breakage of the N–O bond and the transfer of a hydrogen atom, either as a proton or as a hydride ion.

The nature of the final product is thus, in a sense, determined by whether bond cleavage in I occurs at the C–O bond to give nitric acid and a benzyl carbonium ion or at the N–O bond to give nitrous acid and the oxygen cation, II. The relative probabilities of C–O and N–O bond cleavage are difficult to assess. The bond energy of the C–O bond is greater than that of N–O by more than 30 kcal, but these bond energies are, of course, pertinent to homolytic bond cleavage rather than the unsymmetrical bond breaking involved in these reactions. Also to be considered are the relative stabilities of the carbonium ion or oxonium ion that is formed. It is clear that the carbonium ion is the more stable species, since in the oxygen cation the positive charge is fixed on the more electronegative oxygen atom and cannot be delocalized. This factor thus operates in opposition to the relative bond strengths.



II

It should not be implied from the foregoing discussion that II is a discrete intermediate in the aldehyde-forming reaction. Cleavage of the N–O bond almost certainly occurs in concert with the process by which the hydrogen is removed from the benzylic position. If the hydrogen is removed as a proton by a base, the reaction is of the $E_{Co}2$ type even though the reaction requires a strong acid as a catalyst. In acetic acid as solvent the species most likely to serve as the base would be molecular acetic acid. However, benzyl ni-

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(14) S. G. Cohen, *J. Am. Chem. Soc.*, **66**, 1395 (1944).

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.

trate can be converted to benzaldehyde by heating with a catalytic quantity of sulfuric acid in either toluene or mesitylene. In these systems the only possible base is bisulfate ion, and it is improbable that the aldehyde is being formed by an $\mathrm{E_{CO}2}$ mechanism.

An alternate possibility would be a concerted process in which a hydride ion migrates from the benzylic position to the cationic oxygen as the N–O bond is broken. The reaction would then be related to the Baeyer–Villiger rearrangement, where carbon rather than hydrogen migrates to the positive oxygen.[16]

The structure reactivity relationships for this mechanism are complex and involve a balancing of opposing considerations. Electron-donating substituents on the ring facilitate the hydride transfer, but they also favor cleavage at the C–O bond rather than the N–O bond, since they stabilize the carbonium ion formed by such cleavage. Electron-withdrawing substituents decrease the probability of C–O bond cleavage but, at the same time, make the hydride transfer more difficult. With the pentachloro compounds the dominating influence is the strong $-I$ effect of the five chlorine atoms which opposes the hydride ion transfer.

Experimental Section

Pentachlorobenzyl Nitrate.—A solution of pentachlorobenzyl bromide (34.3 g, 0.1 mole) in carbon tetrachloride (200 ml) was added dropwise with magnetic stirring to a solution of silver nitrate (17 g, 0.1 mole) in acetonitrile (500 ml). The reaction mixture was stirred 20 hr at room temperature; the silver bromide was separated by filtration and then washed with carbon tetrachloride. The solvents were removed with the water pump, and the product was twice crystallized from acetonitrile to yield 30 g (92%), mp 114–115°.

1-Pentachlorophenylethyl Nitrate.—The above procedure applied to 1-pentachlorophenylethyl bromide gave the nitrate in 83% yield, mp 131–133°, from acetonitrile.

***p*-Xylene Dinitrate.**—A warm solution of silver nitrate (75 g, 0.441 mole) in acetonitrile (150 ml) was added all at once to a hot, magnetically stirred solution of *p*-xylylene dibromide (53 g, 0.201 mole) in acetonitrile (700 ml). The mixture was stirred several hours, and the silver bromide was filtered. After removal of the solvent with the water pump the residue was crystallized from chloroform–hexane to yield 44 g (96%), mp 49–50°. A sample crystallized for analysis from hexane had mp 50–51°.

The remaining nitrate esters were prepared by the procedure described in the literature.[8] Physical properties and analytical values are given in Table I.

Conversion of Benzyl Nitrates to Benzaldehydes.—The following procedure for the conversion of 3,5-dimethylbenzyl nitrate to the aldehyde is typical for the reactions of the nitrates in acetic acid containing sulfuric acid. A solution of 3,5-dimethylbenzyl nitrate (10 ml, 11.2 g, 0.062 mole) in acetic acid (10 ml) was added dropwise to a refluxing solution of concentrated sulfuric acid (10 drops) in acetic acid (20 ml) over a 1.5-hr period. Refluxing was continued for 1 hr after the addition. The reaction mixture was poured into water (100 ml) and the mixture was extracted with four 100-ml portions of ether. The combined ether extracts were washed with 5% sodium hydroxide solution until the extract remained basic. The ether solution was dried over magnesium sulfate. The ether was removed with the water pump, and the residue was distilled at 0.015 mm yielding 5.9 g (71%) of 3,5-dimethylbenzaldehyde: bp 34–36°; $n^{22}\mathrm{D}$ 1.5404.

The aldehyde (1 g) converted into the semicarbazone in the usual manner gave 0.99 g of the product, mp 205–208°. A sample recrystallized from benzene had mp 207–209° and gave no depression on mixture melting point determination with an authentic sample of the semicarbazone.

In the reaction of benzyl nitrate, vpc analysis of the ether solution indicated a 71% conversion of benzyl nitrate to benzaldehyde. On distillation the yield of benzaldehyde isolated was 47%, bp 58–60° (10 mm).

The reaction with *p*-methylbenzyl nitrate was carried out in a nitrogen atmosphere, and the dilute sodium hydroxide wash was eliminated from the work-up procedure. Distillation yielded 50% *p*-tolualdehyde: bp 83° (13 mm); $n^{25}\mathrm{D}$ 1.5368. This product had the same retention time on vpc as authentic *p*-tolualdehyde and gave the same 2,4-dinitrophenylhydrozone, mp 239–241°. The residue from the distillation was crystallized from water and yielded 19.6% of *p*-toluic acid, mp 178–182°.

p-Nitrobenzyl nitrate (5 g, 0.025 mole) was treated under nitrogen in the usual manner with acetic acid containing sulfuric acid, and, after 2 hr of refluxing, the reaction mixture was poured into ice water (150 ml). The mixture was extracted with four 100-ml portions of chloroform, and the chloroform solution was dried over magnesium sulfate. Removal of the solvent and crystallization from benzene–hexane gave first 0.2 g of insoluble material, which after crystallization from water had mp 235–239° and was shown to be *p*-nitrobenzoic acid. The major product was 2.7 g (71%) of *p*-nitrobenzaldehyde, mp 103–106° after recrystallization.

The reaction with *p*-chlorobenzyl nitrate (6.6 g, 0.035 mole) was run in an air atmosphere and yielded 6.5 g of crude product, mp 180–210°. Crystallization from ethanol gave 2.5 g (45%) of *p*-chlorobenzoic acid, mp 239–242°. The mother liquors treated with 1 g of 2,4-dinitrophenylhydrazine gave 1.6 g of the known 2,4-dinitrophenylhydrazone of *p*-chlorobenzaldehyde, mp 271–272° from acetic acid–methyl acetate.

In the reaction of *p*-xylylene dinitrate a solution of the diester (10 g, 0.044 mole) in acetic acid (35 ml), warmed slightly to effect solution, was added dropwise over a 45-min period to a refluxing solution of concentrated sulfuric acid (1 ml) in acetic acid (35 ml), and the refluxing was continued for an additional hour. The reaction mixture was poured into water (1 l.). Filtration yielded 3.5 g of white solid and an additional 2.6 g was obtained by extraction of the filtrate with benzene. The combined solids were sublimed with an oil pump and yielded 1.7 g (29%) of terephthalaldehyde, mp 113–115° from water. The dialdehyde gave the known dioxime, mp 214–216°.[17]

Conversion of Nitrates to Acetates.—The reaction with *n*-octyl nitrate is typical. The nitrate (14.3 g, 0.081 mole) in acetic acid (35 ml) containing sulfuric acid (10 drops) was refluxed for 4 hr. The reaction mixture was partitioned between water and ether, and the ether solution was dried and concentrated to a volume of 100 ml. By vpc analysis it contained 7.13 g (50.9%) of *n*-octyl acetate.

n-Amyl nitrate was treated the same way, but the product was isolated by distillation. The yield of *n*-amyl acetate was 59%: bp 145–147°; $n^{22}\mathrm{D}$ 1.4033.

With 2-octyl nitrate vpc analysis indicated that the reaction mixture contained 37.4% 2-octyl acetate and unreacted nitrate after 4 hr of refluxing. After 17 hr of refluxing 49.6% 2-octyl acetate was formed.

Pentachlorobenzyl nitrate (5 g, 0.0154 mole) in acetic acid (50 ml) was added dropwise to a refluxing solution of sulfuric acid (10 drops) in acetic acid (50 ml), and the solution was refluxed for 3 hr. The reaction, when poured into water (600 ml), gave a quantitative yield of pentachlorobenzyl acetate, mp 87–90° (mp 89–92° after recrystallization from ethanol). There was no depression in melting point upon admixture with authentic pentachlorobenzyl acetate.[18]

The above procedure applied to 1-pentachlorophenyl ethyl nitrate gave 1-pentachlorophenylethyl acetate in 89% yield which had mp 96–98° after recrystallization from methanol; there was no depression in melting point upon admixture with an authentic sample.[19]

Registry No.—Acetic acid, 64-19-7; sulfuric acid, 7664-93-9.

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[16] S. L. Friess, *J. Am. Chem. Soc.*, **71**, 2571 (1949). For other reactions involving electron-deficient oxygen intermediates, see J. E. Leffler, *Chem. Rev.*, **45**, 385 (1949); P. D. Bartlett, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **11**, 47 (1950); P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, Chapter 8; E. Hedaya and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1661 (1967).

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[18] S. D. Ross and M. Markarian, *ibid.*, **71**, 2756 (1949).

[19] S. D. Ross, M. Markarian, and M. Nazzewski, *ibid.*, **69**, 2468 (1947).