[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Nitration Studies. XII. Nitrohalogenation of Negatively Substituted Olefins with Mixtures of Dinitrogen Tetroxide and Halogens

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Mixtures of dinitrogen tetroxide and halogens have been shown to react with olefins to produce compounds with a halogen atom on one carbon atom and a nitrogen-containing group on the other carbon atom of the original double bond. The nitrogen-containing group is $—ONO_2$ when the olefin is ethylene itself or ethylene substituted with electron-supplying groups such as alkyl or acetoxy. It is $—NO_2$ when the olefin is ethylene substituted with electron-withdrawing groups such as halogen or cyano. These two classes of olefins are also distinguished by the orientations of the entering groups. The products seem best explained as resulting from ionic additions induced by electron-supplying groups and from free radical additions induced by electron-withdrawing groups. The mixture of dinitrogen tetroxide and halogen provides a useful tool for determining the relative tendencies of substituent groups to induce ionic *vs.* radical electron displacements in double bonds. The D_i/D_r ratios determined in this way for the olefins investigated correlate well with the known responses of these compounds to acid-catalyzed hydration and to peroxide-catalyzed polymerization.

Recently it was reported[3] that ethylene and its simple homologs react with mixtures of dinitrogen tetroxide and bromine or iodine in liquid phase at ice-bath temperatures to form β-haloalkyl nitrates to the practical exclusion of nitro compounds. The reaction was postulated to proceed by an ionic mechanism initiated by a halonium ion. We now wish to report that halogenated ethylenes under similar conditions react with mixtures of dinitrogen tetroxide and chlorine, bromine, or iodine to form β,β-dihalonitro compounds to the practical exclusion of nitrates. The mechanisms of these reactions will be discussed.

Although several of the dihalonitroalkanes obtained are new, this type of compound has been prepared before by other methods. Thus, Steinkopf and Kuhnel[4] report that nitryl chloride adds to olefins, including the halogenated ethylenes, to give the expected dihalonitro compounds:

$$CH_2{=}CHBr + NO_2Cl \longrightarrow CHBrClCH_2NO_2$$

This synthesis cannot be extended to the use of NO_2Br and NO_2I since these reagents cannot be prepared.[5] The isomers obtained in the additions of NO_2Cl to halogenated ethylenes appear to be the same as those we have obtained in the additions of nitrogen tetroxide and chlorine, but there are differences which indicate that the two syntheses may not proceed by the same mechanism. Yakubovich and Lemke[6] have prepared chloronitro compounds by the reaction of nitrosyl chloride with chloroethylenes:

$$CH_2{=}CHCl + 2NOCl \longrightarrow CHCl_2CH_2NO_2$$

This synthesis appears not to have been extended to the use of nitrosyl bromide although this reagent is known. The related nitrosyl iodide is unknown. A detailed mechanism for the nitrosyl chloride reactions is not given, but it is obvious that it must differ from those of the NO_2Cl and nitrogen tetroxide–chlorine reactions.

Another synthesis leading to dihalonitroalkanes is the reaction of halonitro alcohols with halogenating agents.[4]

$$CH_2OHCHClNO_2 + PCl_5 \longrightarrow CH_2ClCHClNO_2$$

This method appears to have been applied only to the preparation of the product indicated in the above equation. The addition of halogens to nitroalkenes leads to α,β-dihalonitroalkanes only.[7] Such additions appear not to have been attempted with halogenated nitroalkanes. Halogenated alkanes containing tertiary hydrogen atoms have been nitrated.[8a] Other types of halogenated alkanes have not been successfully nitrated, but nitroalkanes have been chlorinated by Riley and McBee.[8b] These authors did not isolate any di- or polyhalonitro alkanes.

Conditions of reactions. The liquid phase nitrohalogenations were all run at ice-bath temperatures to avoid elimination and substitution reactions both of which can become prominent at elevated temperatures. As the number of halogen atoms increased in the starting olefin molecule, the rate of the addition reaction decreased until with tetrachloroethene no products were formed a in reasonable length of time (72 hours). Possibly the use of higher temperatures and sealed tube reactors, as previously employed[4] in NO_2Cl additions to polyhalogenated alkenes, would have led to faster

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[3] G. B. Bachman and T. J. Logan, *J. Org. Chem.*, **21**, 1467 (1956).

[4] W. Steinkopf and M. Kuhnel, *Ber.*, **75**, 1323 (1942). See also Dutch Patent **58,977**, Feb. 15, 1947.

[5] N. V. Sidgwick, *Chemical Elements and Their Compounds*, Oxford University Press, London, Vol. I, 703 (1950).

[6] A. Y. Yakubovich and A. L. Lemke, *J. Gen. Chem. (USSR)*, **19**, 607 (1949).

[7] A. G. Suzie, Ph. D. Thesis, Purdue University, 1939.

[8] (a) M. I. Konovalov, *Zh. russk. khim. obshch.*, **38**, 607 (1906); *Chem. Zentr.*, **77**, II, 1552 (1906); (b) E. F. Riley and E. T. McBee, U. S. Patent **2,337,912** (Dec. 28, 1943).

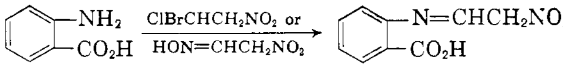
and more complete reactions between our negatively substituted alkenes and nitrogen tetroxide plus halogens, but we preferred to limit our studies to milder conditions for the reasons stated above. Chloroform and carbon tetrachloride solvents were employed exclusively in an effort to avoid the special effects observed with ether,[9] carbon disulfide, and related solvents[10] or the substitution reactions possible with hydrocarbons and other organic solvents. While light was not absolutely excluded, the reaction mixtures were only subjected to dim illumination to avoid photoexcitation of the reactants. Moisture and other polarizing substances were carefully excluded until the reaction mixtures were worked up. All organic products were isolated except for very small amounts of water soluble oxidation products.

Identification of products. The halonitroalkanes were identified by elementary analyses, physical properties, hydrolysis to substituted acetic acids, and conversion to derivatives by reaction with sodium anthranilate.

Primary nitroalkanes have long been known to react with concentrated mineral acids to produce carboxylic acids and hydroxylamine salts of the mineral acids.[11] Other functional groups may also be present without interfering with this process. Thus, Yakubovich and Lemke[6] have shown that 1,1-dichloro-2-nitroethane yields dichloroacetic acid on heating with sulfuric acid. Hawthorne and Strahm[12] have studied the mechanism of the hydrolysis of 1-chloronitroethane and 1-deutero-1-chloronitroethane and shown that these substances are converted to acetic acid, hydrogen chloride, and nitrous oxide (probably). This latter fact has interesting implications relative to previously proposed mechanisms of hydrolysis of primary nitro compounds. Neither isomerization to a hydroxamic acid as suggested by Nenitzescu and Isacescu[13a] nor dehydration to a nitrile oxide as suggested by Noland[13b] can occur when the grouping $—CCl_2NO_2$ is present (and may not occur when the grouping $—CHClNO_2$ is present). Instead the $—CCl_2NO_2$ group is probably protonated and then hydrolyzed to carboxyl, hydrochloric acid, and nitrous acid. In any event hydroxylamine salts are not formed as by-products, but oxides of nitrogen are evolved. The solution diazotizes primary aromatic amines and then couples with β-naphthol to form characteristic azo dyes.

This reaction is useful in determining the relative positions occupied by the halogen atoms and the nitro group in halonitroalkanes and in distinguishing these compounds from haloalkyl nitrates which do not give carboxylic acids under these conditions.[3] Usually it is sufficient to reflux the nitro compound with 86–96% sulfuric acid until the mixture becomes homogeneous and then to distill the product. However, in the one example of iodonitroalkane tried the reaction proved to be unsatisfactory. Thus, 1-chloro-1-iodo-2-nitroethane gave copious amounts of free iodine and no identifiable acetic acid. Likewise 1,2,2,2-tetrachloronitroethane gave no trichloroacetic acid. In these cases both ends of the substituted ethane molecule seem to have been hydrolyzed.

The reaction of 1-chloro-2-nitropropane with sodium anthranilate was recently shown[14] to give 2-(2′-nitro-1′-propyl)aminobenzoic acid. This reaction has now been extended to β-halonitroethanes generally and found to be admirably suitable for the derivatization of such compounds (see Table II). It proceeds fairly rapidly at room temperature in aqueous or aqueous-alcoholic solutions containing excess alkali and gives good yields of nicely crystalline solids with characteristic melting points. The reaction involves only those halogen atoms *beta* to the nitro group; α-halogens are usually not affected. If there is but one β-halogen atom the product will contain the group $—NHCH_2\overset{|}{\underset{|}{C}}NO_2$. If there are two β-halogen atoms the group will be $—N{=}CH\overset{|}{\underset{|}{C}}NO_2$, and if there are three, the group $—NHCO\overset{|}{\underset{|}{C}}NO_2$. Thus, 1-chloro-1-bromo-2-nitroethane yields the same product that is obtained from the reaction of anthranilic acid with methazonic acid.[15]



Here again 1,2,2,2-tetrachloronitroethane gave trouble, and the product seemed to be a mixture from which an analytically pure sample of the expected amide was not obtained by recrystallization. In this case satisfactory results were obtained by treating the chloronitro compound with anthranilic acid in glacial acetic acid. The product had a correct analysis for a derivative containing two anthranilic acid residues. The less reactive

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[9] T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 338 (1958).

[10] G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

[11] H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 395 (1943).

[12] M. F. Hawthorne and R. D. Strahm, *J. Am. Chem. Soc.*, **79**, 3471 (1957). See also R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 2439 (1953).

[13] (a) C. D. Nenitzescu and D. A. Isacescu, *Bull. Soc. Chim. Romania*, **14**, 53 (1932); T. Urbanski, *J. Chem. Soc.*, 3374 (1949). (b) W. E. Noland, J. H. Cooley, and P. A. McVeigh, *J. Am. Chem. Soc.*, **81**, 1213 (1959); W. E. Noland, *Chem. Revs.*, **55**, 153 (1955).

[14] G. B. Bachman and J. P. Chupp, *J. Org. Chem.*, **21**, 465 (1956). See also G. B. Bachman and D. E. Welton, *J. Org. Chem.*, **12**, 208 (1947).

[15] German Patent **347,373**, Jan. 17, 1922.

TABLE I

HALONITRATION PRODUCTS

	Reactants				Products					Analyses	
Olefin, moles	Halogen, moles	N_2O_4, moles	Solvent, ml.	Time, hr.	Formula	Conversion, %	B.P., °(mm.)	D_4^T	n_D^T	Calcd.	Found
$CH_2{=}CHCl$, excess	Cl_2, 0.25	0.50	CCl_4, 220	3.0	$CHCl_2CH_2NO_2$[e]	36.0[a]	55(8)	1.432^{25}	1.4663^{20}	C, 16.67 H, 2.10 N, 9.72 Cl, 49.30	C, 17.00 H, 2.41 N, 9.96 Cl, 48.97
	Br_2, 0.50	0.50	$CHCl_3$, 200	12.0	$CHClBrCH_2NO_2$[d]	27.7[a]	41(0.5)	1.861^{20}	1.4980^{20}	C, 12.71 H, 1.59 N, 7.43 X, 29.68	C, 12.47 H, 1.89 N, 7.70 X, 29.80
					$CHClBrCH_2Br$	24.1[a]	44(4)	2.2480^{20}	1.5540^{20}		
	I_2, 0.10	0.20	$CHCl_3$, 600	0.25	$CHClICH_2NO_2$	61.5[b]	dec.				
$CH_2{=}CHBr$, excess	Cl_2, 0.25	0.25	CCl_4, 220	3.0	$CHClBrCH_2NO_2$[d]	41.4[a]	48(1.2)		1.5070^{20}		
					$CH_2ClCHClBr$	32.2[a]	35(3)				
	Br_2, 0.25	0.25	$CHCl_3$, 200	1.0	$CHBr_2CH_2NO_2$	35.0[a]	60(1)		1.5400^{20}	C, 10.40 H, 1.29 N, 6.01 Br, 68.63	C, 10.60 H, 1.56 N, 6.05 Br, 68.33
					$CH_2BrCHBr_2$	58.0[a]	47(2.5)	2.5790^{20}	1.5802^{20}		
$CHCl{=}CHCl$, 1.00	Cl_2, 0.50	0.50	$CHCl_3$, 500	26.0	$CHCl_2CHClNO_2$[d]	7.2[c]	40(3)	1.600^{25}	1.4827^{25}	C, 13.48 H, 1.13 N, 7.85 Cl, 59.63	C, 13.54 H, 1.14 N, 8.19 Cl, 59.69
					$CHCl_2CHCl_2$	2.8[c]	29(1)	1.573^{25}	1.4959^{25}		
$CH_2{=}CCl_2$ 1.00	Cl_2, 0.50	0.50	$CHCl_3$, 500	26.0	$CCl_3CH_2NO_2$	39.7[c]	59(6)	1.608^{25}	1.4845^{25}	C, 13.43 H, 1.12 N, 7.85 Cl, 59.70	C, 13.57 H, 1.33 N, 8.01 Cl, 59.69
					CCl_3CH_2Cl	2.3[c]	123	1.578^{25}	1.4792^{25}		
	Br_2, 0.50	0.50	$CHCl_3$, 500	25.0	$CCl_2BrCH_2NO_2$	24.9[c]	89(11)	1.928^{25}	1.5168^{25}	C, 10.77 H, 0.90 N, 6.28 X, 67.50	C, 11.08 H, 1.15 N, 6.12 X, 67.51
					CCl_2BrCH_2Br[f]	8.8[c]	68(12)	2.240^{25}	1.5448^{25}		
$CHCl{=}CCl_2$, 1.00	Cl_2, 0.50	0.50	$CHCl_3$, 500	29.0	$CCl_3CHClNO_2$[d]	4.7[c]	44(5)	1.670^{25}	1.4921^{25}	C, 11.34 H, 0.48 N, 6.64 Cl, 66.54	C, 11.08 H, 0.65 N, 6.94 Cl, 66.68
					CCl_3CHCl_2[g]	2.3[c]	27(5)	1.659^{25}	1.5095^{25}		
					$CCl_2{=}CClNO_2$[h]	4.2[c]	55(4)	1.655^{25}	1.5032^{25}	C, 13.62 H, 0.00 N, 7.96 Cl, 60.35	C, 13.40 H, 0.00 N, 8.32 Cl, 60.05

TABLE I (*Continued*)

Olefin, moles	Reactants: Halogen, moles	N_2O_4, moles	Solvent, ml.	Time, hr.	Products: Formula	Conversion, %	B.P., °(mm.)	D_4^T	n_D^T	Analyses: Calcd.	Analyses: Found
$CCl_2{=}CCl_2$, 2.0	Cl_2, 1.0	1.0	$CHCl_3$, 500	30.0	None						
$CH_2{=}CHCN$	Cl_2, 0.5	0.5	$CHCl_3$, 500	6.0	$CHNO_2{=}CHCN$[i]	24.5[c]	58(2)	1.294^{28}	1.4877^{25}		
					NH_4Cl	2.8					
$CH_3CH{=}CH_2Cl$	Cl_2, 1.0	1.0	$CHCl_3$, 1000	10.0	$CH_3CH(NO_2)CHCl_2$	23.8[c]	54(3.5)	1.353^{25}	1.4629^{25}	C, 22.98 H, 2.55 N, 8.93 Cl, 45.21	C, 23.15 H, 2.69 N, 9.01 Cl, 44.90
$CH_3C(OCOCH_3){=}CHCH_3$, 0.2											
	Cl_2, 0.1	0.1	CCl_4, 100	2.0	$CH_3COCHClCH_3$	58.0	40(45)				
	Br_2, 0.1	0.1	CCl_4,	2.0	$CH_3COCHBrCH_3$[j]	50.0	52(30)				
	I_2, 0.1	0.1	$CHCl_3$,	2.0	$CH_3COCH_2CH_3$	34.0	76–8				
					$CH_3COCOCH_3$	23.0	86–8				

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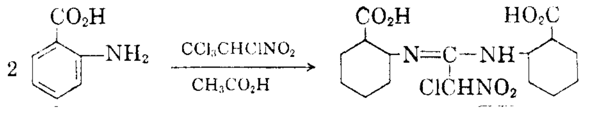
[a] Based on moles of product/mole of halogen. [b] Calculated from the yield of anthranilic acid derivative. [c] Based on olefin. [d] See Ref. 4. [e] See Ref. 6. [f] H. Van de Walle, *Bull. acad. roy. Belg.*, **1924**, 94; b.p. 65° (13), b.p. 175° dec., D_{15} 2.2695, n_D^{25} 1.5593. [g] J. Timmermen and F. Martin, *J. chim. phys.*, **23**, 733 (1926); b.p. 162.00°, D_{15} 1.68813, D_{30} 1.66530, n_D^{15} 1.50542. [h] The infrared spectra showed absorption peaks for a conjugated nitro group at 6.50 and 7.40 mμ. [i] H. Shechter, F. Conrad, A. Daulton, and B. Kaplan, *J. Am. Chem. Soc.*, **74**, 3052 (1952); b.p. 53° (3.4), n_D^{20} 1.4929, D_4^{20} 1.268. [j] D. H. Hey, E. Jones, J. Catch, and D. Elliott, *J. Chem. Soc.*, **1948**, 272; b.p. 44° (2), n_D^{25} 1.4571.



β-haloalkyl nitrates do not give these reactions with anthranilic acid and may be distinguished from the halonitroethanes by this fact.

The above two reactions are supplementary in determining the structures of the halonitroethanes, since the first of them affects one end of the molecule, *i.e.*, the end containing the nitro group, while the second affects the other end. Consideration of the results shown in Tables I and II together with the analyses and physical constants of the products makes it possible to establish unequivocally the orientations of the entering groups in the additions studied except possibly in the case of the product from trichloroethylene.

By-products. An anticipated by-product in each of these reactions was the halogenated ethane formed by the addition of halogen alone to the double bond. The extent to which this occurred using a 1:1 mole ratio of nitrogen tetroxide:halogen was greatest for bromine and least for iodine. However, this reaction was greatly suppressed by increasing the mole ratio of nitrogen tetroxide:halogen to 2:1. From Fig. 1 it may be seen that the conversion of vinyl chloride to 1,1-dichloro-2-nitroethane based on dinitrogen tetroxide is nearly independent of the nitrogen tetroxide:chlorine ratio, while the conversion based on chlorine increases as this ratio increases. These facts suggest that the rate controlling step in the reaction involves the olefin and the nitrogen tetroxide but not the halogen.

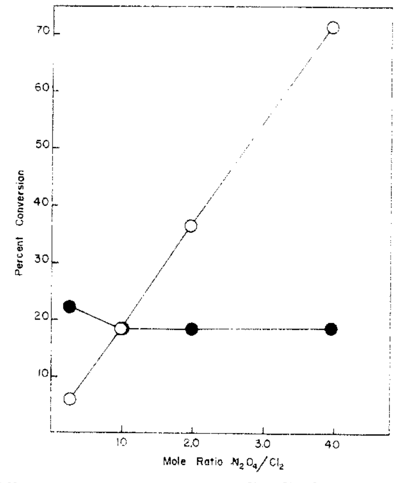


Fig. 1. Effects on conversions to $CHCl_2CH_2NO_2$ of changes in reactant ratios
●—Conversions based on N_2O_4
○—Conversions based on Cl_2

As the nitrogen tetroxide:halogen ratio was increased above 1, the amounts of high boiling residues increased. These heavy oils contained higher percentages of nitrogen and oxygen and were un-

TABLE II

IDENTIFICATION OF NITROHALOGENATION PRODUCTS

Compound for Identification	Reagent,[a] Reaction Time	Identifying Product	Solvent for Recrystallization	M.P.°	Conversion, %	Analyses Calcd.	Analyses Found
$CHCl_2CH_2NO_2$	AH_2	A = $CHCH_2NO_2$[b]	C_6H_6	198–199			
	H_2SO_4, 88%, 8 hr.	$CHCl_2CONHC_6H_5$[c]	CH_3CH_2OH	117–118	50		
$CHClBrCH_2NO_2$	AH_2	A = $CHCH_2NO_2$	C_6H_6	198–199			
	H_2SO_4, 88%, 8 hr.	$CHClBrCOOH$[d]		27.5	38.1		
		$CHClBrCONHC_6H_5$	CH_3CH_2OH	119–120		C, 38.66	C, 38.43
						H, 2.84	H, 2.88
						N, 5.64	N, 5.53
$CHClICH_2NO_2$	AH_2	A = $CHCH_2NO_2$	C_6H_6	198–200			
$CHBr_2CH_2NO_2$	AH_2	A = $CHCH_2NO_2$	C_6H_6	198–199			
	H_2SO_4, 88%, 8 hr.	$CHBr_2COOH$		liq.	25.5		
$CHCl_2CHClNO_2$	AH_2	A = $CHCHClNO_2$	CH_3CH_2OH–$CHCl_3$	200 (dec.)		C, 44.60	C, 44.32
						H, 3.03	H, 3.30
						N, 11.50	N, 11.19
	H_2SO_4, 88%, 1 hr.	$CHCl_2CONHC_6H_5$[c]	CH_3CH_2OH	117	18.0	Cl, 14.60	Cl, 14.88
$CCl_3CH_2NO_2$	AH_2	A = $CClCH_2NO_2$	C_6H_6–CH_3OH_2OH	204–205 (dec.)	45.4	C, 44.60	C, 44.87
						H, 2.91	H, 2.89
						N, 11.30	N, 11.05
						Cl, 14.64	Cl, 14.34
$CCl_3CH_2NO_2$	AH_2	$AHCOCH_2NO_2$	CH_3COOH	239 dec.		C, 48.49	C, 48.64
						H, 3.19	H, 3.48
						N, 12.55	N, 12.30
	H_2SO_4, 88%, 1 hr.	CCl_3COOH[e]		58	78.5		
$CCl_2BrCH_2NO_2$	AH_2	$AHCOCH_2NO_2$	CH_3CH_2OH	239 dec.			
	H_2SO_4, 88%, 1 hr.	$CCl_2BrCOOH$[f]		60–61	27.4	C, 11.57	C, 11.92
						H, 0.48	H, 0.67
						X, 72.50	X, 72.32
$CCl_3CHClNO_2$	AH_2	A = $C(AH)CHClNO_2$	C_6H_6–CH_3CH_2OH	264 dec.		C, 50.90	C, 51.12
						H, 3.21	H, 3.35
						N, 11.12	N, 11.40
						Cl, 9.31	Cl, 9.20
	H_2SO_4, 88%	dec.					
$CHNO_2{=}CHCN$	AH_2	$AHCH(CN)CH_2NO_2$	CH_3CH_2OH	164 dec.	29.8	C, 51.20	C, 50.92
						H, 3.86	H, 3.80
						N, 17.89	N, 18.00
	H_2SO_4, 85%, 5 hr.	$CHNO_2{=}CHCONH_2$[g]	C_6H_6	165			
$CH_3CH(NO_2)CHCl_2$	AH_2	A = $CHCH(NO_2)CH_3$	C_6H_6–CH_3CH_2OH	196–197	84.3	C, 54.10	C, 53.88
						H, 4.86	H, 4.78
						N, 12.59	N, 12.56
$CH_3COCHClCH_3$	$NH_2NHCONH_2$	Semicarbazone[h]	$CH_3CO_2C_2H_5$	138			
$CH_3COCHBrCH_3$	2,4-$(NO_2)C_6H_3NHNH_2$	Hydrazone	C_6H_5–Pet. ether	112			
$CH_3COCH_2CH_3$	2,4-$(NO_2)C_6H_3NHNH_2$	Hydrazone[i]	C_6H_6–Pet. ether	310			

[a] A is 2-$(COOH)C_6H_4N{=}$. [b] Mixture melting point with product of reaction of methazonic acid and anthranilic acid gave no depression. *cf.* German Patent **347,375** (Jan. 17, 1922). [c] H. Doughty, *J. Am. Chem. Soc.*, **47,** 1097 (1925); m.p. 118°. [d] P. L. Vanderstickele, *J. Chem. Soc.*, **123,** 1227 (1923); m.p. 23.8°. [e] L. Wooten and L. Hammett, *J. Am. Chem. Soc.*, **57,** 2289 (1935); m.p. 58°. [f] R. Neumeister, *Ber.*, **15,** 602 (1882); m.p. 64°. [g] H. Shechter, F. Conrad, A. Daulton, and R. Kaplan, *J. Am. Chem. Soc.*, **74,** 3055 (1952); m.p. 165°. [h] F. H. Curd and A. Robertson, *J. Chem. Soc.*, **1933,** 717. [i] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262; m.p. 314–315°.

stable. On attempted distillation under vacuum they evolved gases and more often than not fumed off. Even on standing at room temperatures they decomposed with evolution of gases and deposition of solids in small amounts. Thus the oils from the reactions with 1,1- and 1,2-dichloroethene gave crystals of oxalic acid dihydrate (m.p. 100°). The oil from the reaction of chlorine and nitrogen tetroxide with vinyl chloride deposited dichloroglyoxime[16] (m.p. 199°), a substance capable of causing violent sneezing and swelling of the mucous membranes if small amounts of the powder become dispersed in the air. No other products from these oils were identified, but nitroso compounds were probably present as indicated by the blue or green colors of the small amounts of distillates obtained before decomposition become extensive. Hydrolyses of these oils with 90% sulfuric acid yielded no identifiable products other than oxides of nitrogen and carbon and hydrogen halides.

Mechanisms of the reactions. The reacting state of a molecule may be considered to arise from the resting state through displacements of electrons. In an olefin such displacements may occur ionically (D_i) through displacement of a pair of electrons in one direction, or radically (D_r) through displacement of a single electron in one direction and

$$D_i \quad CH_2{=}CHG \rightleftharpoons \overset{-}{\underset{\cdot\cdot}{C}}H_2{-}\overset{+}{C}HG$$

$$D_r \quad CH_2{=}CHG \rightleftharpoons \underset{\cdot}{C}H_2{-}\underset{\cdot}{C}HG$$

another electron in the other direction. The relative extents to which D_i and D_r occur will depend on the nature of the substituent group G, on the substance with which the olefin is reacting, and on various conditions of the reaction. The influence of G may be seen by comparing the properties of propene (G = methyl) with those of vinyl chloride (G = chlorine). Propene, in which D_i predominates, is more readily attacked by protonium and other cations than it is by free radicals. The reverse is true of vinyl chloride, in which D_r predominates. Thus, propene will dissolve rapidly with hydration in 85% sulfuric acid; vinyl chloride will not. Vinyl chloride will polymerize rapidly in the presence of traces of peroxide; propene will not. Unfortunately, existing data do not permit quantitative comparisons of the relative effects of various other groups.

Similar statements apply to the reacting states of molecules which add to olefins. Thus both nitrogen tetroxide and halogen molecules are able to split ionically or free radically according to their intrinsic natures, the natures of the molecules with which they are reacting, and the conditions.

$$Br\cdot + Br\cdot \leftrightharpoons Br_2 \rightleftharpoons Br^+ + :Br^-$$

$$\begin{tikzcd}
NO_2\cdot + NO_2\cdot \arrow[r, leftrightharpoons] & N_2O_4 \arrow[r, rightleftharpoons] \arrow[d, shift right] & NO^+ + :ONO_2^- \\
 & NO_2^+ + :NO_2^- \arrow[u, shift right] &
\end{tikzcd}$$

Bromine is generally conceded to add to olefins at ordinary temperatures or below by a stepwise process initiated by a bromonium ion. In keeping with this belief is the fact that electron-pair-supplying groups such as alkyl groups facilitate the addition reactions of olefins with bromine. Unfortunately the products of addition would appear to be the same whether the process occurs ionically or free radically and hence give no clue as to the mechanism followed. The situation with nitrogen tetroxide is somewhat more complicated since dissociation can occur in three different ways instead of two. However, as has been pointed out previously,[17] the dissociation of nitrogen tetroxide into NO_2^+ and NO_2^- ions occurs only under the influence of powerful acids and hence may be disregarded for reactions of the types here considered. Of the remaining two types of dissociation one would be expected to lead to dinitro compounds and the other to nitroso nitrates. Unfortunately this simple assumption is complicated by several facts: (1) nitroso groups are easily oxidized to nitro groups by nitrogen tetroxide so that the presence of a single nitro group in the product is no guarantee that addition of a nitro group occurred by a free radical process, and (2) $\cdot NO_2$ must be considered an ambident radical and therefore capable of attaching itself to carbon either at the nitrogen atom to form the $C{-}NO_2$ group or at an oxygen atom to form the C—ONO group which may then be oxidized to a $C{-}ONO_2$ group. Hence the presence of a nitrite or a nitrate group in the product is no guarantee that the addition occurred by an ionic process. Finally, (3) the addition may proceed by both the free radical and the ionic processes simultaneously leading thereby to a variety of products. Cases in which a single substance constitutes the bulk of the product in nitrogen tetroxide additions have been the exception rather than the rule.[18]

Some of the complexities mentioned above are suppressed or eliminated in reactions of olefins with equimolar mixtures of nitrogen tetroxide and halogens. Thus there are only two principal products, one formed by the addition of two halogen atoms, the other by the addition of a halogen atom and a nitrogen-containing group. When the substituent group on the olefin is alkyl the nitrogen-containing group is $—ONO_2$ and is located on the carbon holding the alkyl group.[3] When the substituent group is chlorine the nitrogen-containing group is $—NO_2$ and is located on the carbon once removed from the carbon holding the chlorine.

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[16] W. Steinkopf and B. Jurgens, *J. prakt. Chem.*, **83**, 467 (1911).

[17] G. B. Bachman and C. M. Vogt, *J. Am. Chem. Soc.*, **80**, 2987 (1958).

[18] J. L. Riebsomer, *Chem. Revs.*, **36**, 157 (1945).

These differences indicate a difference in the mechanisms of the two reactions. Since the reaction with the alkyl substituted ethylene is difficult to conceive of as other than an ionic reaction initiated by a halonium ion,[3] the reaction with the chlorine substituted ethylene is most probably a radical reaction initiated by an NO_2 radical.

$$ClCH{=}CH_2 + \cdot NO_2 \longrightarrow Cl\underset{\cdot}{C}HCH_2NO_2$$

$$Cl\underset{\cdot}{C}HCH_2NO_2 + Cl_2 \longrightarrow Cl_2CHCH_2NO_2 + Cl\cdot$$

This is in accord with a D_i/D_r ratio of less than 1, as might be expected from other reactions of vinyl chloride. It is also in accord with the orientation of the entering groups, since the reverse orientation would be expected if the reaction were initiated by a halogen atom. Finally it may be noted that nitrogen tetroxide is reported to be 0.15% dissociated[19] to NO_2 radicals at 0° while chlorine and bromine are dissociated to atoms to only a vanishingly small extent at this temperature.[20] Even assuming considerably greater reactivities of halogen atoms relative to NO_2 radicals, the tremendous preponderance of the latter in the mixture would favor their preferential reaction with a D_r-activated olefin.

The absence of substantial amounts of dinitro products indicates a preference of the $Cl\underset{\cdot}{C}HCH_2NO_2$ radicals for combination with chlorine rather than with NO_2 a fact which may be attributed to the greater electrophyllicity of the chlorine. This point provides further reason for assuming a free radical mechanism for the addition. If the first step in the reaction had been the creation of $Cl\overset{+}{C}HCH_2NO$ or $Cl\overset{+}{C}HCH_2NO_2$ cations, the second step should have led to considerable amounts of $ClCH(ONO_2)$-CH_2NO or $ClCH(ONO_2)CH_2NO_2$, since the ONO_2^- anion is about as nucleophilic as the Cl^- anion, as evidenced by the similar degrees of ionization of nitric and hydrochloric acids. In other words the fact that $Cl\cdot$ is considerably more electrophilic than $\cdot NO_2$ while Cl^- is about equally nucleophilic with ONO_2^- is in agreement with a radical mechanism better than with an ionic mechanism for the addition reaction.

The D_i/D_r ratios of other groups. The above arguments apply equally well to the additions of mixtures of nitrogen tetroxide and halogens to olefins substituted by other groups. If we assume validity for the arguments then it is apparent that these mixtures constitute valuable tools for distinguishing radical from ionic mechanisms in addition reactions of olefins and in evaluating D_i/D_r ratios for various substituent groups as being greater or less than 1.

As a working hypothesis for the prediction of D_i/D_r ratios for various groups we have adopted the viewpoint that electron-supplying groups (+I or +E effects as defined by Ingold[21]) promote ionic displacements while electron-withdrawing groups promote radical displacements. In further corroboration of this hypothesis we have treated a vinyl ester with mixtures of nitrogen tetroxide and halogens, then hydrolyzed and obtained halocarbonyl compounds but no nitro compounds.

$$CH_3CH{=}C(CH_3)OCOCH_3 \xrightarrow[0°]{N_2O_4 + X_2} \xrightarrow{H_2O}$$
$$50\text{–}58\%\ CH_3CHXCOCH_3 + HOCOCH_3$$

In this case the electron-supplying properties of the ester oxygen atom seem to have promoted an ionic reaction initiated by halonium ions at the β-position of the double bond. Contrariwise acrylonitrile reacted under similar conditions to give 3-nitroacrylonitrile, which on hydrolysis gave 3-nitroacrylamide.[22] Here the electron-withdrawing cyano group seems to have promoted a reaction initiated by the NO_2 radical at the β-position of the double bond.

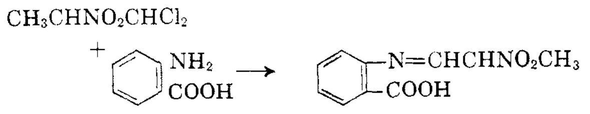
$$CH_2{=}CHCN \xrightarrow[O°]{N_2O_4 + Cl_2} (CH_2NO_2CHClCN) \longrightarrow$$
$$CHNO_2{=}CHCN + HCl$$

$$CHNO_2{=}CHCN + H_2O \longrightarrow CHNO_2{=}CHCONH_2$$

The saturated chloronitronitrile is postulated as an intermediate because copious amounts of hydrogen chloride were evolved during the first distillation of the product.

While the above studies served to indicate the absolute values of D_i/D_r ratios as being greater or less than 1 for various groups, it remained of interest to determine the relative potencies of two different groups with opposite tendencies in electron displacements. To study this effect we chose 1-chloropropene, which may be considered to be ethene substituted on one end by a group (methyl) promoting ionic reaction and on the other end by a group (chlorine) promoting free radical reaction. Treatment of this compound with a mixture of nitrogen tetroxide and chlorine gave a product whose reactions with anthranilic acid and whose analysis showed it to be 1,1-dichloro-2-nitropropane.

$$CH_3\ CH{=}CHCl \xrightarrow[0°]{N_2O_4 + Cl_2} CH_3CHNO_2CHCl_2$$



This result is surprising only because we are accustomed to thinking in terms of ionic displace-

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[19] F. Verhoek and F. Daniels, *J. Am. Chem. Soc.*, **53**, 1250 (1931); C. C. Addison and J. Lewis, *J. Chem. Soc.*, 2837 (1951).

[20] F. Ephraim, *Inorganic Chemistry*, 5th ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 115.

[21] C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

[22] H. Shechter, F. Conrad, A. Daulton, and R. Kaplan, *J. Am. Chem. Soc.*, **74**, 3052 (1952). These authors obtained 2-chloro-3-nitropropionitrile by treating vinyl cyanide with nitryl chloride, and postulated a mechanism involving free radical dissociation of the nitryl chloride.

TABLE III

VAPOR PHASE NITROHALOGENATION OF VINYL HALIDES[a,b]

	$VBr + Br_2$	$VBr + Cl_2$	$VCl + Br_2$	$VCl + Cl_2$
Reactor temperature	250	250	325	325
Contact time, seconds	7	7	4	3.6
Mole ratio: $VX:X_2:NO_2$	3.2:0.3:1.0	9.8:2.3:1.0	11.1:0.3:1.0	7.3:0.5:1.0
Moles VX reacted	4.6	6.9	23.4	5.4
Products, moles				
Nitrohalogenated	0.56[c]	0.098[e]	0.126[g]	0.154[i]
Halogenated	0.31[d]	0.28[f]	0.02[h]	0.08[j]
Conversion to nitro compound, percent				
Based on NO_2	3.9	13.9	5.95	22.2
Based on X_2	6.5	3.06	6.73	20.6
Yield of nitro compound, percent				
Based on VX	12.8	20.3	29.2	44.5

[a] The data listed here represent optimum conditions found from many experiments for the temperature, contact time, mole ratios, etc. [b] In this table V is $CH_2{=}CH—$ and X is Cl or Br. [c] 1,1-Dibromo-2-nitroethane. [d] 1,1,2-Tribromoethane. [e] 1-Bromo-1-chloro-2-nitroethane. [f] 1,2-Dichlorobromoethane. [g] 1-Chloro-2-bromonitroethane. [h] 1,2-Dibromochloroethane. [i] 1,2-Dichloronitroethane. [j] Trichloroethane.

ments, where methyl is ordinarily more powerful than chlorine. In comparing D_i/D_r ratios, chlorine is evidently more powerful in promoting free radical displacements than is methyl in promoting ionic displacements of the π electrons of the double bonds. The above reaction was remarkable in another respect also; it gave little or no trichloropropane, although chlorine addition is the principal reaction when propene is treated with a mixture of nitrogen tetroxide and chlorine.[3] Apparently the presence of the chlorine atom in 1-chloropropene strongly influences any ionic reaction which may occur and prevents formation of the anticipated dichloride.

Comparison of NO_2Cl with nitrogen tetroxide and chlorine. Although these two reagents appear to give the same products in additions to halogenated ethenes and vinyl cyanide they give different products with other types of olefins. Thus, with simple olefins[23] nitryl chloride gives principally chloronitroalkanes while nitrogen tetroxide and chlorine gives principally dichloroalkanes with small amounts of chloronitroalkanes being obtained only in vapor phase reactions.[24] Nitryl chloride adds to vinyl esters to give products which hydrolyze to nitroketones or nitroaldehydes, while nitrogen tetroxide and chlorine give products which hydrolyze to chloroketones or chloroaldehydes.[25] The products and orientation of entering groups are such as to suggest that NO_2Cl adds as free radicals, the $\cdot NO_2$ and $\cdot Cl$, to double bonds with electron-withdrawing substituents but adds ionically, as NO_2^+ and Cl^-, to double bonds with electron-supplying groups. The reagent nitrogen tetroxide–chlorine is similar in that it adds free radically as $\cdot NO_2$ and $\cdot Cl$ to double bonds with electron-withdrawing substituents, but different in that it adds ionically as Cl^+ and NO_2^- or NO_3^- to double bonds with electron-supplying substituents.

Vapor phase halonitration. In view of the interesting variability in the mechanisms of addition of mixtures of dinitrogen tetroxide and halogens to olefins in the liquid phase, it seemed desirable to investigate these same reactions in the vapor phase. It has already been shown by one of us[24] that simple olefins may be nitrochlorinated in this way. Thus, propene yields 1-chloro-2-nitropropane and 1,2-dichloropropane at 260–275° by an assumed free radical process initiated by chlorine atoms.

Since substituent halogen atoms seem to increase the tendencies of olefins to react by free radical rather than by ionic processes, it seemed likely that vinyl halides would nitrohalogenate somewhat more readily than would propene. Initial experiments were performed with vinyl bromide, nitrogen dioxide, and chlorine. It was found that reaction temperatures could not exceed 255° without liberating bromine by oxidation of the vinyl bromide. However at temperatures below this point the reaction proceeded smoothly and gave 1-bromo-1-chloro-2-nitroethane, the same product obtained in the liquid phase experiments and probably formed by a similar mechanism. Similarly vinyl bromide, nitrogen dioxide, and bromine gave 1,1-dibromo-2-nitroethane. Since reactions in the vapor phase commonly proceed by free radical processes, the isolation of these products in improved yields (over propene[24]) lends support to the previously proposed free radical nature of the liquid phase nitrohalogenation of halogenated olefins. Results of these experiments are summarized in Table III.

It next occurred to us that at still higher temperatures halogen atoms might be formed through thermal dissociation of halogen molecules in sufficient amounts to initiate the addition process and give reversed orientation of the entering groups and hence isomers of the nitrohalogenated compounds obtained at the lower temperatures.

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(23) C. M. Himel, U. S. Patent **2,511,915** (June 20, 1950).

(24) G. B. Bachman and J. P. Chupp, *J. Org. Chem.*, **21**, 465 (1956).

(25) G. B. Bachman and T. Hokama, *J. Org. Chem.*, **25**, 178 (1960).

$$CH_2{=}CHX + NO_2 \xrightarrow[\text{temp.}]{\text{low}} CH_2NO_2CHX\cdot \qquad (1)$$

$$CH_2NO_2CHX\cdot + X_2 \longrightarrow CH_2NO_2CHX_2 \qquad (2)$$

$$CH_2{=}CHX + \cdot X \xrightarrow[\text{temp.}]{\text{high}} CH_2XCHX\cdot \qquad (3)$$

$$CH_2XCHX\cdot + NO_2 \longrightarrow CH_2XCHXNO_2 \qquad (4)$$

$$X = \text{Cl or Br}$$

Accordingly vinyl chloride was treated at 325° with mixtures of nitrogen dioxide and chlorine or bromine. As expected, the nitrogen-containing products were now 1,2-dichloronitroethane and 1-chloro-2-bromo-1-nitroethane respectively. The The products were identified by analyses, physical properties, acid-catalyzed hydrolysis to halogenated acetic acids, and conversion to derivatives by reaction with anthranilic acid.

The 1,2-dichloronitroethane reacted normally with anthranilic acid to give 2-(2′-chloro-2′-nitroethyl) aminobenzoic acid. It hydrolyzed readily in acid solution to chloroacetic acid. With bases, even aqueous sodium bicarbonate, it dehydrohalogenated and formed in 90% conversion a polymer having a correct analysis for $(\text{—}CH_2CClNO_2\text{—})_x$. The pure monomer[26] could not be obtained, since it polymerized immediately under basic conditions. Uncatalyzed hydrolysis with steam proceeded rapidly and gave 2-chloro-2-nitroethanol in over 90% conversions.[27] Steam distillation of β-chloronitroalkanes is not generally recommended as a means of purification because of the ease with which such hydrolyses occur.

An attempt to extend the vapor phase study of nitrochlorination to trichloroethene at 325° resulted in the formation of pentachloroethane (26% yield) and dichloroacetic acid (69% yield). Trichloroethene is known to oxidize readily to dichloroacetyl chloride which is easily hydrolyzed to dichloroacetic acid.[28] Such an oxidation evidently supersedes addition of NO_2 under these conditions. It should be noted that although trichloroethene is not inflammable in air it produces flames with NO_2 when ratios of less than about 2.7/1 of C_2HCl_3/NO_2 are heated. Similarly 1,2-dichloroethene gives dangerous mixtures with NO_2. We experienced a violent explosion on one occasion and flames on several occasions while attempting to nitrochlorinate this olefin in the vapor phase. No nitro compound was found from any of these reactions, but we did note that much of the *trans*-1,2-dichloroethene used was isomerized to *cis*-1,2-dichloroethene.

$$CHCl{=}CCl_2 + [O] \longrightarrow CHCl_2COCl \xrightarrow{H_2O} CHCl_2CO_2H + HCl$$

Conclusions. The reactions of mixtures of nitrogen tetroxide and halogens with olefins lead to addition products of remarkable variability in composition and orientation. Substituent groups on the olefin as well as reaction conditions such as temperature and phase determine the types of products formed. These factors influence the relative tendencies of olefins to react by ionic (D_i) *vs.* radical (D_r) mechanisms, and the variability observed can be correlated with the type of mechanism which predominates in any given case. The D_i/D_r ratio for substituent groups in apparently greater than 1 for those groups which supply electrons and less than 1 for those groups which withdraw electrons as judged by the cases we have studied. Further studies of the relative magnitudes of these ratios for various substituents would be valuable in explaining polymerization behavior and other addition reactions of olefins.

EXPERIMENTAL

Addition reactions in liquid phase. The general procedure involved placing weighed quantities of liquid dinitrogen tetroxide, halogen, and solvent in a suitable glass vessel immersed in a salt-ice-water cooling bath and adding the requisite amount of the substituted olefin with stirring as rapidly as possible without causing the temperature to rise above 5°. When the halogen was chlorine a sufficient quantity of solvent was used to hold the gas in solution. Chlorine dissolves in carbon tetrachloride at 0° to the extent of about 8.0 g. per 100 ml. When the halogenated olefin was gaseous (vinyl chloride and vinyl bromide) it was bubbled into the liquid reactants through a gas delivery tube; the liquid olefins were added through a dropping funnel. The reaction rate was fastest and hence the rate of addition of the olefin was slowest for the least highly substituted olefins.

The reaction mixture was worked up by stirring repeatedly with fresh quantities of ice and water until no more material appeared to dissolve, drying and distilling. The water soluble materials were not investigated. The color of the product after washing but before distilling varied from pale yellow to light green; it was usually highly lachrymatory. The 1-chloro-1-iodo-2-nitroethane decomposed on attempted distillation and hence was analyzed and converted to a derivative in its crude form after removal from it of materials volatile at room temperature under 5 mm. pressure.

The above procedure with acrylonitrile, 106 g. (2 moles), dinitrogen tetroxide, 92 g. (1 mole), chlorine, 71 g. (1 mole), and chloroform, 1000 ml., allowed to react for 3 hr. yielded on distillation a product of substitution as well as addition, $C_3H_2Cl_2N_2O_2$, which may have been 2,3-dichloro-3-nitropropionitrile or 2,2-dichloro-3-nitropropionitrile; b.p. 66° (1 mm.) n_D^{25} 1.5049, d_4^{25} 1.441, conversion 7.1%. This product, 4.12 g. (0.03 mole), was dissolved in anhydrous ether, 10 ml., and treated at 0° with sodium acetate, 2.97 g. (0.033 mole), for 1 hr. The mixture was filtered, the solvent removed and the product distilled; b.p. 74° (3 mm.), n_D^{25} 1.5170, d_4^{25} 1.433, conversion 98%. This dehydrohalogenated product may have been 3-chloro-3-nitro-acrylonitrile, or 2-chloro-3-nitroacrylonitrile.

Anal. Calcd. for $C_3HN_2ClO_2$: C, 27.20; H, 0.76; N, 21.08; Cl, 26.80. Found: C, 26.90; H, 0.72; N, 20.66; Cl, 27.16.

The NMR spectrum showed a single peak for hydrogen.

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(26) R. Wilkendorf and M. Trenel, Ber., **57,** 306 (1924) prepared the monomer by pyrolysis of 2-chloro-2-nitroethyl nitrate. They also prepared the polymer.

(27) M. Simonette and G. Favini, *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat.*, **14,** 119 (1953); *Chem. Abstr.*, **48,** 2568^d (1954), have studied the kinetics of hydrolysis of the closely related 2-chloronitroethane.

(28) E. H. Huntress, *Organic Chlorine Compounds*, John Wiley and Sons, Inc., 1948, p. 611.

In order to avoid the substitutive halogenation which occurred in the above experiment another run was made in which the nitrogen tetroxide and chlorine were added to the acrylonitrile and chloroform instead of the reverse. Distillation was accompanied by evolution of hydrogen chloride and eventually yielded 3-nitroacrylonitrile as the sole product; b.p. 57° (2 mm.), n_D^{25} 1.4877, d_4^{25} 1.294, conversion 24.5%. Hydrolysis of this product by heating 3.0 g. (0.03 mole) with 25 ml. of 88% sulfuric acid for 5 hr. at 55°, pouring onto ice, filtering the solid, and recrystallizing from benzene gave 3-nitroacrylamide, m.p. 165°.

Preparation of anthranilic acid derivatives. The reagent was prepared by dissolving anthranilic acid (54.0 g., 0.393 mole) in methanol (166 ml.) and adding this mixture to a solution of sodium bicarbonate (34.0 g., 0.404 mole) in water (100 ml.), warming until all gaseous carbon dioxide was evolved, clarifying with a little decolorizing charcoal, and filtering. The resulting solution was yellow-brown in color and stable enough for use over periods of several months.

The halogenated nitroethane (2.0 g.) was added to the above reagent (10 ml.) and stirred until the solid reaction product appeared. The time required varied from a few seconds to about an hour being somewhat longer with the more highly halogenated compounds. The anthranilic acid derivative was collected, washed with water and recrystallized from a suitable solvent (see Table II).

Better results were obtained with the β,β,β-trichloronitroalkanes by preparing the anthranilic acid derivative in glacial acetic acid. For this purpose 0.01*N* quantities of the chloronitronitro compound and anthranilic acid were dissolved in 30 cc. of glacial acetic acid and allowed to stand at room temperature for 6 hr. The product was filtered and recrystallized from a benzene-ethanol mixture; conversions about 50%.

Hydrolysis of halonitroethanes to halogenated acetic acids. A 0.05-mole sample of the nitro compound and 10 ml. of 88% sulfuric acid were heated together under reflux until homogeneous and then directly distilled at about 1 mm. pressure to recover the substituted acetic acid. The distilled halogenated acetic acids were also converted to their chlorides by warming with thionyl chloride and then to their anilides by reaction with aniline. The melting points of these solid derivatives served to confirm the identity of the acid obtained.

The reaction failed to give the expected product from 1-chloro-1-iodo-2-nitroethane, and free iodine was liberated in copious quantities. It also failed with the tetrachloronitroethane obtained from trichloroethene and gave only gaseous products.

Addition reactions in vapor phase. The techniques employed were similar to those previously described in publications from this laboratory.[29] The reactor system differed however in that it was not immersed in a molten salt bath. Instead the temperature was controlled electrically and automatically with nichrome heating ribbons, thermocouples, and a sensitive relay. Gases were metered through flowmeters of the floating ball type and liquids through a pump of the peristaltic action type. All parts were carefully calibrated and frequently rechecked to ensure accuracy. The greatest difficulty was encountered in metering those reactants which boil a little above or a little below room temperature. Tanks of dinitrogen tetroxide and vinyl bromide had to be immersed in heated water or oil baths to maintain adequate pressures. The di- and trichloroethenes tended to soften the elastic polyethylene tubing used in the peristaltic pump and alter the tubing's effective diameter, thus necessitating frequent replacement. The bromine was vaporized by a stream of nitrogen. Careful control of the temperature and the nitrogen flow rate gave reproducible rates of bromine flow.

In operation the halogen and nitrogen dioxide streams were mixed and then merged with the vinyl halide stream which had been preheated to 250°. This final mixing occurred just before the reactor. Since the vinyl halide made up the bulk of the reactant mixture it quickly raised the temperature of the other reactants to near the reaction temperature.

The products of reaction were condensed in a series of water and Dry Ice condensers and the off gases were passed through a wet test meter. All of the products were analyzed, but since nothing of recognized significance was found beyond that reported in the tables, these data are not included here.

1,2-Dichloronitroethane identification and reactions. The product from the vapor phase reaction of vinyl chloride with nitrogen dioxide and chlorine showed the following constants: b.p. 47.5° (6.5 mm.), d_{20}^{24} 1.483, n_D^{20} 1.4680. Steinkopf and Kuhnel[4] report b.p. 124° (10 mm.).

Anal. Calcd. for $C_2H_3NO_2Cl_2$: C, 16.67; H, 2.10; N, 9.72; Cl, 49.30; MR_D 26.78. Found: C, 16.60; H, 2.22; N, 9.61; Cl, 49.18; MR_D 26.93.

The anthranilic acid derivative was *o*-(2-chloro-2-nitroethylamino)benzoic acid, m.p. 139.0–139.5°.

Anal. Calcd. for $C_9H_9N_2O_4Cl$: C, 44.18; H, 3.71; N, 11.45; Cl, 14.49. Found: C, 44.40; H, 3.73; N, 11.31; Cl, 14.42.

Hydrolysis of the dichloronitroethane in 88% sulfuric acid for 8 hr. gave a 74% yield of chloroacetic acid, m.p. 52–54°.

Dehydrohalogenation of the dichloronitroethane was accomplished with a variety of bases. The following procedure gives a good yield of light colored polymer. The product, 14.0 g., was added to a solution of 8.4 g. of sodium bicarbonate in 100 ml. of water at room temperature. After 3 hr. carbon dioxide evolution ceased. The solid polymer (9.2 g., 88% yield) was filtered, washed, reprecipitated from solution in glacial acetic acid with water, and dried. It began to melt at 118°, was a clear liquid at 187°, and became black at 218°.

Anal. Calcd. for $C_2H_2NO_2Cl$: C, 22.34; H, 1.87; N, 13.03; Cl, 32.98. Found: C, 22.60; H, 2.16; N, 12.67; Cl, 32.70.

Uncatalyzed hydrolysis of the dichloronitroethane was accomplished by passing steam through it until the liquid became homogeneous (about 15 min. for a 35-g. sample). Ether extraction and distillation yielded 2-chloro-2-nitroethanol in 92% yield; b.p. 55° (0.4 mm.), n_D^{22} 1.4692, MR_D calcd. 23.53, found 23.44.

Anal. Calcd. for $C_2H_4NO_3Cl$: C, 19.14; H, 3.21; N, 11.16; Cl, 28.17. Found: C, 19.06; H, 2.97; N, 11.20; Cl, 28.40.

This alcohol is a colorless, odorless, acidic liquid which turns yellow on standing in the air. It is completely miscible with water, ether, and benzene. We were unsuccessful in our attempts to characterize it by reaction with *p*-nitro- and 3,5-dinitrobenzoyl chlorides, phenyl- and α-naphthylisocyanates, and benzoyl bromide. The procedure of Brewster and Ciotti[30] also failed to yield a derivative.

The distillation residue from the vapor phase nitrochlorination of vinyl chloride gave no anthranilic acid derivative and showed the following properties: $d_{20}^{24.5}$ 1.470, $n_D^{24.5}$ 1.4981. It may have been 1,3,4-trichloro-1-nitrobutane, although our data is inadequate to confirm this.

Anal. Calcd. for $C_4H_6NO_2Cl_3$: C, 23.27; H, 2.93; N, 6.78; Cl, 51.52; MR_D 40.88. Found: C, 25.32; H, 3.36; N, 7.40; Cl, 52.00; MR_D 39.83.

Similar residues were found in the other vapor phase nitrohalogenation experiments and increased in amount with increasing mole ratios of vinyl halides in the reactants.

Identification of chloronitro olefins. Gas chromatographic analysis proved to be a most useful tool in determining the purity of products obtained and in detecting the small amounts of chloronitro olefins formed in certain cases. Thus, the chloronitration products from 1,2-dichloroethylene and trichloroethylene gave peaks for the expected saturated chloronitroethanes and other peaks suspected of arising

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[29] *J. Org. Chem.*, **17**, 906, 914, 928, 935 (1952); **19**, 312 (1954); **21**, 465, 655 (1956); *Ind. Eng. Chem.*, **46**, 713 (1954).

[30] J. H. Brewster and C. J. Ciotti, *J. Am. Chem. Soc.*, **77**, 6214 (1955).

from the corresponding nitroethenes. To check this conclusion the saturated compounds were dehydrohalogenated by treatment with sodium acetate[22] in anhydrous ether, the olefins isolated in pure form, and their chromatographic peaks determined. In both cases the peaks obtained corresponded in elution time to the peaks observed in the original product mixtures. The following example illustrates the procedure employed:

Sodium acetate, 3.6 g (0.035 mole), was slowly added with stirring to a solution of 1,1,1,2-tetrachloro-2-nitroethane, 6.4 g. (0.03 mole), in anhydrous ether, 15 ml., at 0°. After 1 hr., the solution was filtered to remove excess sodium acetate and sodium chloride, and the ether and acetic acid removed under reduced pressure. Distillation gave 1,2,2-trichloronitroethylene, 4.1 g. (77.5% yield), b.p. 55° (4 mm.).

A Perkin-Elmer Vapor Fractometer with a 2-meter stainless steel column containing Celite packing coated with dodecyl phthalate, a temperature of 140°, and a flow rate of 20 cc. of helium per min. were used to determine the gas chromatographic peaks. Applications of gas chromatography to analysis of nitroparaffin mixtures have been discussed more fully by Bethea and Wheelock.[31]

1-Chloro-2-bromonitroethane identification and reactions. The product from the vapor phase reaction of vinyl chloride with nitrogen dioxide and bromine showed the following constants: b.p. 68° (6.7 mm.), n^{20}_{D} 1.4970. The anthranilic acid derivative melted at 139–140° and showed a mixture m.p. of 139–140° with the same derivative from 1,2-dichloronitroethane. Hydrolysis with 88% sulfuric acid for 5 hr. gave a 40% yield of bromoacetic acid, b.p. 66–67° (1.0 mm.), m.p. 50°

Nitrohalogenation of the enol acetate of methyl ethyl ketone. (We are indebted to Dr. Takeo Hokama for conducting these experiments.) 2-Buten-2-yl acetate, 23 g. (0.2 mole), was added dropwise in about 2 hr. to a solution of the nitrohalogenating agent (0.2 mole) in 100 ml. of carbon tetrachloride at ice bath temperatures. After stirring for an additional hour the mixture was washed with 10% urea solution, and water, and then dried and distilled. The products were as follows:

Nitrohalogenating Agents	Products (% yld.)	Properties
$N_2O_4 + Cl_2$	3-Chlorobutanone (58)	B.p. 40° (45 mm.)
$N_2O_4 + Br_2$	3-Bromobutanone (50)	B.p. 52° (30 mm.)
NO_2Cl	3-Nitrobutanone (36)	B.p. 56° (2 mm.)

They were further characterized by preparation of derivatives whose properties coincided with those reported in the literature.[32]

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N-Acylation of Unsubstituted Glycosylamines

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N-Monoacylation of unsubstituted glycosylamines has been conveniently achieved by the reaction with acid anhydride in *N*,*N*-dimethylformamide or in methanol. *N*-Acetyl-α-D-arabinopyranosylamine, -β-D-xylopyranosylamine, and -β-D-glucopyranosylamine, *N*-benzoyl-β-D-xylopyranosylamine, and a series of *N*-acyl-β-D-glucopyranosylamines with even-numbered fatty acids as the acyl group have been prepared by these methods in good yields.

N-Monoacetylglycosylamines have been prepared by partial hydrolysis of fully *O*-acetylated derivatives of *N*-acetylglycosylamines,[1–4] or by the reaction of unsubstituted glycosylamines and ketene.[5,6] They have also been formed by the action of ammonia on acetylated sugars,[7,8] acetylated aldehydo-sugars,[7,9] or acetylated glycononitriles.[9,10] *N*-Benzoyl-D-mannosylamine, apparently the only reported *N*-monobenzoyl derivative of glycosylamine, has been formed in a small yield by the reaction of D-mannose cyanohydrin hexabenzoate with silver nitrate and methanolic ammonia,[11] the major product of the reaction being *N*,*N*-dibenzoyl-D-mannosylamine. In their studies on the syntheses of purine biosynthesis intermediates, Baddiley, Buchanan, Handschumacher, and Prescott[12] prepared *N*-chloroacetyl-β-D-glucopyranosylamine by the reaction of chloroacetyl chloride and 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine and subsequent *O*-deacetylation; the reactions of *N*-benzyloxycarbonylglycyl chloride or *N*-benzyloxycarbonylglycylethyl carbonate with 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine and with 2,3,5-tri *O*-benzoyl-D-ribofuranosylamine followed

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