[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Nitration Studies. IX. Preparation of Haloalkyl Nitrates by Liquid Phase Reaction of Nitrogen Tetroxide and Halogens with Alkenes[1]

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Alkenes have been found to react with mixtures of halogens and dinitrogen tetroxide in liquid phase to form β-haloalkyl nitrates. The orientation of the addition suggests that the alkene first adds a positive halogen ion and then a negative nitrate ion to form a haloalkyl nitrate. The principal side reaction is the formation of the corresponding alkene dihalide. This side reaction is negligible with iodine, considerable with bromine, and entirely predominant with chlorine.

Bromoalkyl nitrates have been obtained previously by reaction of bromoalkanols with nitric acid[3] and by reaction of olefins with mixtures of (a) silver nitrate, bromine and pyridine,[4] and (b) an alkali nitrate, bromine, and water.[5] Iodoalkyl nitrates seem not to have been isolated previously except 2-iodocyclohexyl nitrate and 2-iodoethyl nitrate, which were obtained by the reaction of mercuric nitrate and iodine with cyclohexene and ethene, respectively.[6]

We have passed typical alkenes, including ethene, propene, 1-butene, 2-butene, and 2-methylpropene into liquid mixtures of bromine and dinitrogen tetroxide at about 0° and obtained the corresponding β-bromoalkyl nitrates together with the corresponding α,β-dibromoalkanes. Figure 1 shows the effect on conversions of changes in the ratio of bromine to dinitrogen tetroxide for ethene. It is evident that, as the ratio Br_2/N_2O_4 increases, conversions to bromoethyl nitrate based on N_2O_4 rise while those based on C_2H_4 fall. To avoid preponderent formation of ethylene dibromide the Br_2/N_2O_4 ratio should be kept below 1.0.

The product obtained from propene appears to be 1-bromo-2-propyl nitrate. No evidence of a second isomer, *e.g.* 2-bromo-1-propyl nitrate, was found in the distillation curve. We have confirmed the structure of the product by synthesizing it through the reaction of 1,2-dibromopropane with silver nitrate. It has been shown[7] that secondary halides react with silver nitrate much more rapidly than primary halides to form the corresponding nitrates. Hence it is reasonable to assume that 1-bromo-2-propyl nitrate would be the principal product formed in the reaction,

$$CH_3CHBrCH_2Br + AgNO_3 \longrightarrow CH_3CHONO_2CH_2Br + AgBr \quad (1)$$

In any event the product of bromonitroxylation of propene with bromine and dinitrogen tetroxide is identical in physical properties with the product of the reaction of 1,2-dibromopropane with silver nitrate.

The mechanism of halonitroxylation would appear to follow a stepwise course in which the initial attack is by the halogen on the olefin, *e.g.*

$$CH_3CH{=}CH_2 + Br_2 \longrightarrow CH_3\overset{+}{C}HCH_2Br + Br^- \quad (2)$$

$$CH_3\overset{+}{C}HCH_2Br + N_2O_4 \longrightarrow CH_3CHONO_2CH_2Br + NO^+ \quad (3)$$

$$CH_3\overset{+}{C}HCH_2Br + Br^- \longrightarrow CH_3CHBrCH_2Br \quad (4)$$

$$NO^+ + Br^- \longrightarrow NOBr \quad (5)$$

An alternative explanation to the effect that $BrNO_2$ is first formed and then added to the alkene is considered unlikely because $BrNO_2$ is not formed under the conditions of this reaction.[8] Furthermore when $ClNO_2$ is added to alkenes the principal product is a chloronitroalkane.[9] No nitro compound is formed in our process of bromonitroxylation of alkenes. A free radical mechanism for the reaction also appears unlikely since similar products are not formed in the vapor phase (see EXPERIMENTAL) and because it has been shown by Schechter[10] and by Bachman and Chupp[11] that NO_2 radicals react with olefins to produce predominantly nitro compounds rather than nitrates.

The replacement of bromine by iodine in the halonitroxylation reaction leads to iodoalkyl nitrates, probably by a mechanism similar to that for bromine. However, whereas bromine and dinitrogen tetroxide liquids mix in all proportions, iodine has a rather limited solubility in liquid dinitrogen tetroxide. In such cases the undissolved iodine does not enter into the reaction, and only a

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TABLE I

HALOALKYL NITRATES

Formula of product	Conversion, % on N_2O_4	Mole Ratio Br_2/N_2O_4	B.P., °C.	MM.	d^{20}_{20}	n^{20}_D	Calc'd C	Calc'd H	Calc'd N	Calc'd Br	Found C	Found H	Found N	Found Br
$CH_2ONO_2CH_2Br$	23.9	0.744	90	48[a]	1.807	1.4786	14.10	2.35	8.22	47.10	14.10	2.48	8.52	46.94
$CH_3CHONO_2CH_2Br$	24.2	0.744	108	97	1.637	1.4695	19.55	3.26	7.60	43.50	19.55	3.43	7.60	43.55
$CH_3CH_2CHONO_2CH_2Br$	24.6	0.744	83.5	18	1.539	1.4697	24.20	4.04	7.07	40.40	24.30	3.97	7.27	40.21
$CH_3CHONO_2CHBrCH_3$	25.8	0.744	93.5	34	1.531	1.4692	24.20	4.04	7.07	40.40	24.43	4.15	7.13	40.22
$(CH_3)_2CONO_2CH_2Br$	15.2	0.744	79.5	18	1.547	1.4690	24.20	4.04	7.07	40.40	24.46	4.10	7.13	39.85
		I_2/N_2O_4												
$CH_2ONO_2CH_2I$[b]	93.6[c]	0.980	33	0.5	2.113	1.5375	11.06	1.84	6.45	58.50[d]	11.42	2.06	6.55	58.22[d]
$CH_3CHONO_2CH_2I$	90.0	0.500	37	0.5	1.926	1.5180	15.58	2.59	6.06	54.90[d]	15.68	2.74	6.24	54.92[d]

[a] B.p. 164–165° at 760 mm., reference 4. [b] B.p. 80° at 22 mm., reference 6. [c] Conversion on I_2 in solution. [d] Analysis for iodine.

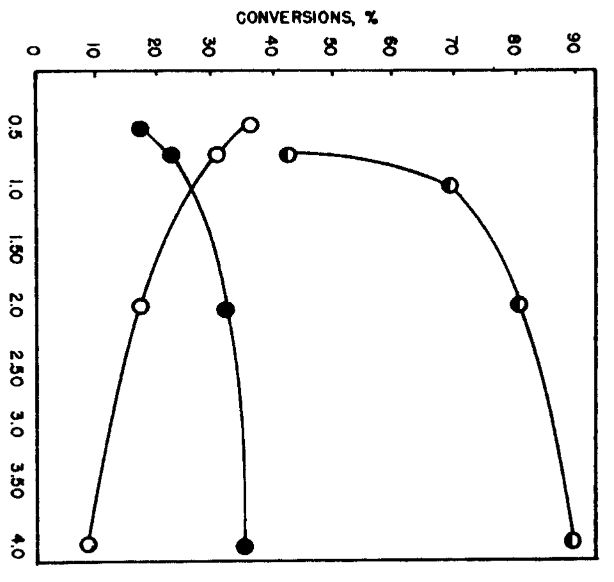

FIG. 1. EFFECT ON CONVERSIONS OF CHANGES IN THE Br_2/N_2O_4 MOLE RATIO. ○ Conversions to $C_2H_4NO_3Br$ based on C_2H_4. ● Conversions to $C_2H_4NO_3Br$ based on N_2O_4. ◐ Conversions to $C_2H_4Br_2$ based on Br_2.

relatively small amount of alkene can be iodonitroxylated in the usual size run. However, the reaction yields only iodoalkyl nitrates and essentially no diiodoalkanes. Therefore, conversions based on dinitrogen tetroxide are high.

Replacement of bromine by chlorine does not lead to any detectable amounts of chloroalkyl nitrates but instead yields only alkene dichlorides. It may therefore be assumed that the ratio of the rates of reactions (4) to (3) is much greater for chlorine (and much less for iodine) than it is for bromine. This precludes chloronitroxylation by this procedure unless a catalyst can be found which alters these relative rates.

It is interesting to note that several attempts to bromonitroxylate acetylene were unsuccessful. No organic products were isolated from a bromine-dinitrogen tetroxide mixture through which acetylene gas had been bubbled for 45 minutes.

The lower iodoalkyl nitrates are reasonably stable liquids in the sense that they can be distilled at very low pressures. They cannot be steam-distilled, since on heating to about 100° they split out iodine in copious amounts. This instability is more apparent in impure samples containing free iodine which tend to decompose even on standing. The bromoalkyl nitrates are considerably more stable and can be steam distilled, purified, and isolated with little difficulty.

The effects of solvents on halonitroxylation have not been studied in detail but it has been found that cyclohexane and 2-nitropropane cause an increased conversion to bromoalkyl nitrates, while ethyl ether has the opposite effect. Temperature control is imperative in all halonitroxylation reactions since conversions begin to decrease rapidly if the temperature is allowed to rise much above 0° during the reaction.

The physical properties and analyses of the haloalkyl nitrates prepared are given in Table I.

EXPERIMENTAL

General procedure. The desired quantities of halogen and liquid dinitrogen tetroxide were introduced into a glass vessel fitted with a thermometer, a gas inlet tube reaching to the bottom of the vessel, and an internal cold water cooling coil. The vessel was immersed in an ice-water bath.

The mixture was cooled to 0° and the alkene introduced slowly enough to prevent the temperature from rising appreciably. The reactor was shaken occasionally during the introduction of alkene. When no more alkene was absorbed the mixture was allowed to warm to room temperature, extracted with water (to remove minor amounts of unstable by-products), dried, and distilled. Specific details for the preparation of 1-bromo-2-propyl nitrate and 2-iodoethyl nitrate are given below.

1-Bromo-2-propyl nitrate. Propene was bubbled slowly into a mixture of bromine (160 g., 1.0 mole) and dinitrogen tetroxide (46.0 g., 0.5 mole) at about 0°. After 45 minutes no more propene was being absorbed. The mixture was allowed to warm to room temperature, extracted with four 25-ml. portions of water, and dried over Drierite. Distillation yielded 1,2-dibromopropane, 157.0 g., b.p. 77° (96 mm.), n_D^{20} 1.5182, and 1-bromo-2-propyl nitrate, 27.4 g., b.p. 108° (97 mm.), n_D^{20} 1.4695.

2-Iodoethyl nitrate. Iodine (50.8 g., 0.2 mole) was dissolved in 200 ml. of chloroform and to this solution was added 18.4 g. (0.2 mole) of liquid N_2O_4. Ethene was passed in and when no more was absorbed the supernatant liquid was poured off of what proved to be 23.9 g. of solid unreacted iodine. The liquid was washed with 2 *N* $Na_2S_2O_3$ solution until the iodine color disappeared. The $Na_2S_2O_3$ washing removed an additional 2.1 g. of unreacted iodine. Removal of the chloroform left 31.7 g. of a clear liquid that gave a positive nitrate ester test.[12] Fractional distillation gave 19.5 g. of a colorless liquid, b.p. 33° (0.5 mm.), n_D^{20} 1.5375.

Preparation of 1-bromo-2-propyl nitrate from silver nitrate and 1,2-dibromopropane. A mixture of 1,2-dibromopropane (50.4 g., 0.25 mole) and silver nitrate (42.5 g., 0.25 mole) was stirred for 12 hours at 25°, filtered, and the liquid fraction was distilled. There were obtained 7.4 g. of recovered 1,2-dibromopropane and 34.3 g. (75% yield) of 1-bromo-2-propyl nitrate, b.p. 108° (97 mm.), n_D^{20} 1.4685. No other nitrogen-containing organic compound was found. The ester gave a positive nitrate ester test[12] and an infrared spectrum practically identical with that for the same compound prepared from propene, dinitrogen tetroxide, and bromine.

Effects of solvents. Similar bromonitroxylation reactions to those described above were also run in the presence of 200 ml. of various solvents. The effects observed are listed in Table II. The use of solvents considerably decreases the time needed for each run because the heat of the reaction can be more rapidly dissipated, with the result that the alkene may be added at a greater rate.

TABLE II

EFFECTS OF DIFFERENT SOLVENTS ON BROMONITROXYLATION OF ETHYLENE[a]

Solvent	Time, min.	Conversion, % on N_2O_4
None	71	32
Ether	50	17
Cyclohexane	45	44.6
2-Nitropropane	33	48.2

[a] A Br_2/N_2O_4 ratio of 2.0 was used in each run.

Vapor phase reaction of propene with bromine and nitrogen dioxide. The reactants were metered into a glass tube reactor heated to 257° at $NO_2/Br_2/C_3H_6$ ratios of 1/.333/7.42, 1/.472/7.4, and 1/.265/7.47 using contact times of approximately 3 seconds in three separate runs. The product from each run was condensed in a Dry Ice condenser and then steam-distilled. Neither bromo nitro nor bromo nitrate compounds could be detected in the distillation curves.

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