[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Nitration Studies. VII. The Vapor Phase Nitration of Olefins: Chloronitration[1]

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Investigation of the vapor phase nitration of olefins in the presence of chlorine has led to the observation that chloronitration occurs. Propene, nitrogen dioxide, and chlorine in a ratio of 7:7:1, react at 260–275° and a contact time of a few seconds to produce 1-chloro-2-nitropropane in 12% conversions. 1-Butene similarly yields 1-chloro-2-nitrobutane. No other isomers are formed in appreciable amounts. The same reaction does not occur in the liquid phase.

INTRODUCTION

Vapor phase nitration of olefins is potentially capable of providing many useful products. Substitutive nitration would give nitroölefins, while additive nitration would provide nitroalcohols, nitronitrates, and dinitro compounds. Furthermore, it would be of considerable theoretical interest to ascertain whether nitration of olefins would proceed by mechanisms similar to those found applicable to the nitration of saturated hydrocarbons,[3] and whether addition reactions would predominate over substitution reactions with olefins in the vapor phase as they do in the liquid phase. The present work was started to study the action of nitric acid and nitrogen dioxide on simple olefins.

Propene reacts rapidly with nitric acid at temperatures above 250°. The readily condensable products are mixtures which are largely water-soluble. In spite of numerous variations in conditions, reactant ratios, and possible catalysts the reaction does not yield any identifiable nitroölefin in our hands. Isolation of aliphatic acids and ketones indicates that the principal mechanism occurring is oxidation rather than nitration.

Since nitrogen dioxide is a less powerful oxidizing agent than nitric acid, it was hoped that it could be used in place of nitric acid to obtain nitroolefins. Levy and Scaife[4] found that ethylene and isobutylene in the vapor phase at 150° give only heavy viscous oils, probably arising from complex addition reactions with nitrogen oxides, 1,2-dinitroethane being found in only small amounts. The reaction was studied in this laboratory with propylene at higher temperatures (275–300°) in the hope that more stable nitrogen-containing compounds would be found. The viscous, unstable oils obtained served only to confirm the findings of Levy and Scaife.

The principal difficulty in reactions of this sort lies in the multiplicity of ways in which nitrogen dioxide may react. Thus, in each step of the addition, a bond may presumably be formed between carbon and either nitrogen or oxygen.

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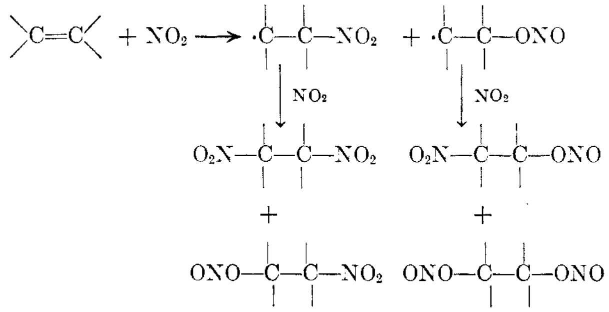

Although this complexity is somewhat simplified by the more rapid relative rates of certain of the possible reactions, it is compounded by the further reaction of nitrogen dioxide with nitrites to produce nitrates and by rapid hydrolysis of ester groupings to alcohols by the water formed in the reaction or subsequently added in working up the product. Furthermore, the fact that most of these compounds are sensitive to heat, especially in the presence of nitric and nitrous acids, makes the whole process appear impractical for preparative purposes.

It occurred to us to add chlorine to the reaction mixture in more than catalytic amounts in order to provide a different species to react with the olefin in the first or second stage of the addition process and hence to simplify the reaction. A chlorine atom can add in only one way to a carbon atom, and the

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(3) G. B. Bachman, H. B. Hass, and J. V. Hewett, *J. Org. Chem.*, **17**, 928 (1952).

(4) N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093 (1946).

TABLE I

EFFECT OF REACTANT RATIOS ON CONVERSIONS IN VAPOR PHASE CHLORONITRATION

Experiment No.	G-68	G-77	G-79	G-82	G-81	G-73
Conditions						
Temp., °C. of reactor	275	260	265	275	250	275
Cont. time, sec.	4	4	3.8	2	4	4
Reactants, relative moles						
Olefin	7.5[a]	7.2[a]	24.4[a]	11[a]	4[a,c]	7.5[b]
NO_2	1	1	1	1	1	1
Cl_2	0.45	1	1	1	1	1
Conversion, %						
NO_2 to 1-chloro-2-nitroalkane	5.5	12.0	8.0	8.0	0.0	9.0
Cl_2 to 1-chloro-2-nitroalkane	11.0	12.0	8.3	8.0	0.0	9.05
Cl_2 to 1,2-dichloroalkane	47.5	38.0	44.5	29.4	13.0	56.0
Yield, % (on olefin)						
1-chloro-2-nitroalkane	—	14.1	8.1	10.0	0.0	—
1,2-dichloroalkane	—	45.0	43.0	36.8	8.3	—

[a] Propene. [b] Butene. [c] Near the explosive limits; reaction unstable.

bond formed is not readily susceptible to either oxidation or hydrolysis. Hence the number of possible products in the reaction is decreased and their stability and isolatability increased.

The reaction of olefins with approximately equimolar amounts of chlorine and nitrogen dioxide did indeed lead to chloronitration and the formation of readily isolated and purified *beta*-chloronitroalkanes.

EXPERIMENTAL

Apparatus. The reactor system was similar to that described previously.[5]

Procedure. The reactants were introduced into the reactor in the same manner as for vapor phase nitration. The product consisted of two portions: that collected in the water-condenser trap, and that collected in the Dry Ice trap. After evaporation of unreacted propylene from the latter, the two products were combined and steam-distilled. They then were dried and fractionated.

A typical run (83) involving 8.15 moles of propylene, 1.11 moles of nitrogen dioxide, and 1.11 moles of chlorine was completed in 30 minutes (3.2 seconds contact time) at 270°. The steam-distillate charge amounted to 88 g. from the first trap and 50 g. from the second trap. The steam-distillate consisted of 78 g. of nonaqueous heavy oil with a pale yellow color. Ordinary distillation of 72 g. yielded the following fractions: (a) 45 g., b.p. 40–45° (110 mm.), n_D^{20} 1.4385, d_4^{28} 1.585, 1,2-dichloropropane; (b) 14 g., b.p. 60–80° (75–40 mm.) unidentified, contains 2.5% N; (c) 13 g., b.p. 89–91° (40 mm.), n_D^{21} 1.4432, d_4^{22} 1.245, 1-chloro-2-nitropropane. McBee and Riley[6] prepared this compound by the chlorination of 2-nitropropane.

For further identification, fraction (c) was caused to react with anthranilic acid to give 2-(2′-nitro-1′-propylamino)benzoic acid according to the directions of Bachman and Welton.[7] The product melted at 156°, identical with an authentic sample. Similarly 1-chloro-2-nitrobutane, prepared from 1-butene, was converted to 2-(2′-nitro-1′-butylamino)benzoic acid, m.p. 140–141°. This same compound with the same melting point was prepared previously from the reaction of anthranilic acid with the acetate ester of 2-nitro-1-butanol.[6] 1-Chloro-2-nitrobutane shows the following physical constants: b.p. 92–94° (40 mm.), n_D^{20} 1.4324, d^{30} 1.244. This compound is reported by Pauwels[8] to be formed by the reaction of 2-nitro-1-butanol with phosphorus pentachloride: b.p. 190° (760 mm.), d^{21} 1.165.

DISCUSSION

In the reaction of nitrogen dioxide and chlorine in the vapor phase with olefins, it would be expected that several important side reactions would occur beside formation of the chloronitro compound. Thus, nitrogen dioxide alone could react, forming the complex unstable, nitrogenous materials previously mentioned along with oxidation products. Secondly, chlorine alone could react to form 1,2-dichloropropane and allyl chloride. Because of these side reactions, the conversions to the chloronitroalkanes are low. Table I illustrates experiments made in attempts to increase conversions of the chloronitro compound by changes in the reactant ratios. The best conversion (12%) obtained was in run 77. Nitration of 1-butene gave a 9 per cent conversion to 1-chloro-2-nitrobutane. The principal reaction in both cases however is the addition of two atoms of chlorine, 1,2-dichloropropane being formed in 37–45 percent yields.

Table II shows the effect of temperature in chloronitration. Decreasing the temperature from 370° to 275° increases the conversion to chloronitroalkane, but also slows the reaction considerably. In run 70 at 225° a 10 second contact time is required for the reaction to occur. Even at this longer contact time, not all the nitrogen dioxide color fades in traversing the reactor.

During the course of this work, several experiments were attempted in the liquid phase, in an effort to synthesize chloronitroalkanes. It was found however that when chlorine and propylene were introduced separately into liquid nitrogen dioxide at 0–5°, the chlorine reacted preferentially with the olefin, producing 1,2-dichloropropane, but no chlo-

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(5) G. B. Bachman, H. B. Hass, and L. M. Addison, *J. Org. Chem.*, **17**, 914 (1952).

(6) E. T. McBee and E. Riley, U. S. Patent 2,337,912 (Dec. 28, 1943).

(7) G. B. Bachman and D. E. Welton, *J. Org. Chem.*, **12**, 208 (1947).

(8) Pauwels, *Bull. acad. roy. Belg.*, (3) **34**, 645 (1898).

TABLE II

EFFECT OF TEMPERATURE ON CONVERSIONS IN VAPOR PHASE CHLORONITRATION

Experiment No.	G-67	G-66	G-68	G-70
Conditions				
Temp., °C. of reactor	370	315	275	225
Cont. time, sec.	4	4	4	10
Reactants, relative moles				
C_3H_6	7.52	7.52	7.52	7.5
NO_2	1	1	1	1
Cl_2	0.45	0.45	0.45	0.45
Conversion %				
NO_2 to 1-chloro-2-nitropropane	3.06	4.5	5.5	4.0
Cl_2 to 1,2-dichloropropane	31.5	44.5	47.5	40.5

ronitroalkane. This indicates that in order for chloronitration to occur, either the vapor phase or a higher temperature is required.

It is interesting to note that only one isomer is produced in the chloronitration of propene and 1-butene. This implies that the reaction proceeds by a single, specific mechanism. If it is assumed that it is a free radical process, the following sequence of reactions may be postulated:

2. $Cl\cdot + RCH=CH_2 \rightarrow R\underset{\cdot}{C}HCH_2Cl$
3. $R\underset{\cdot}{C}HCH_2Cl + NO_2 \rightarrow RCHNO_2CH_2Cl$
4. $R\underset{\cdot}{C}HCH_2Cl + Cl_2 \rightarrow RCHClCH_2Cl + Cl\cdot$

The relative rates of reactions 3 and 4 control the relative amounts of dichloride and chloronitroalkane produced. In an attempt to alter these rates relative to each other, a chlorination catalyst, charcoal impregnated with mercuric chloride, was placed in the reaction tube for one run with propene. In this case no chloronitration occurred and 1,2-dichloropropane was the only identifiable product found.

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