397. *The Chemistry of Nitryl Chloride. Part IV.* Addition to Styrene, Ethylene, and Propene.*

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Nitryl chloride with styrene forms 1 : 2-dichloro-1-phenylethane, with ethylene forms 1-chloro-2-nitroethane and 2-chloroethyl nitrite, and with propene forms 2-chloro-1-nitropropane and a small quantity of 2-chloro-1-methylethyl nitrite.

Nitryl chloride with olefins normally forms a chloro-nitro-adduct in which the nitro group is attached to the terminal position of the double bond irrespective of the electronic demands of substituents. Thus the direction of addition is the same in propene as in methyl acrylate. Shechter *et al.*[1] suggest that the mechanism involves homolysis of the nitryl chloride molecule. However, for the reactions of nitryl chloride with styrene in benzene Steinkopf and Kuhnel[2] reported the formation of 2-chloro-1-nitro-1-phenylethane in which the orientation is opposite to the usual one. In ether they obtained a *pseudo*-nitrosite. This work has been repeated and it has been found that nitryl chloride reacts with styrene both in benzene and in ether, to give 1 : 2-dichloro-1-phenylethane in 70—80% yield (based on the nitryl chloride). Another product, 1-chloro-2-nitro-1-phenylethane, was thought to be present, but could not be isolated: on distillation it decomposed, evolving hydrogen chloride, and ω-nitrostyrene was obtained though it was not present in the original reaction mixture.

Steinkopf and Kuhnel[2] report that nitryl chloride with ethylene gives only 1 : 2-dichloroethane. On the other hand, Petri[3] reports that 1-chloro-2-nitroethane (45% yield) and 2-chloroethyl nitrite (35% yield) are formed, and Ville and Dupont[4] confirmed the formation of 1-chloro-2-nitroethane (in 50% yield). The possible formation of a 2-chloroethyl nitrite was interesting in that it could be regarded as an indication of a mechanism involving heterolysis of nitryl chloride $^{+}\mathrm{Cl}\,\vdots\,{-}\mathrm{NO}_2^{-}$, the direction expected in view of the chlorinating properties of nitryl chloride. The present author found that nitryl chloride with ethylene in methylene chloride or benzene gave a product which decomposed, evolving oxides of nitrogen, on distillation. The presence of nitrite was suspected but unlike Petri (who gives no experimental details) the author was unable to isolate 2-chloroethyl nitrite. To avoid decomposition another sample of the product was mixed with

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* Part III, preceding paper.

[1] Shechter, Conrad, Daulton, and Kaplan, *J. Amer. Chem. Soc.*, 1952, **74**, 3052.

[2] Steinkopf and Kuhnel, *Ber.*, 1942, **75**, 1323.

[3] Petri, *Z. anorg. Chem.*, 1948, **257**, 180.

[4] Ville and Dupont, *Bull. Soc. chim. France*, 1956, 804.

methyl alcohol, to convert the nitrite into an alcohol, and on subsequent distillation 1-chloro-2-nitroethane (36% yield) and ethylene chlorohydrin (15% yield) were obtained.

After reaction of nitryl chloride with propene in ether, Price and Sears[5] isolated 2-chloro-1-nitropropane in 50% yield and a smaller quantity of *pseudo*nitrosite. Ville and Dupont,[4] using carbon tetrachloride and chloroform as solvents, obtained only 2-chloro-1-nitropropane in 40% yield. The author has re-investigated the reaction in order to see if a chloro-nitrito-product, similar to that obtained with ethylene, is formed, since an ionic addition mechanism would be expected to be more important in the case of a more reactive olefin. Methylene chloride and benzene were used as solvents (polar solvents dried by accepted methods could not be used owing to the hydrolysis of the nitryl chloride by the moisture that they contain[6]) and the reaction mixtures were treated immediately with an excess of methyl alcohol to convert any nitrite into an alcohol. On distillation 2-chloro-1-nitropropane was separated in 20—30% yield and, in low yield, impure 2-chloro-1-methylethyl alcohol. The total yield of products (based on the chlorine content) was low. Since very little residue was left after the distillation of the two compounds mentioned, the remaining product must have been evolved as a gas or have distilled with the solvent (see p. 1957). No dichloro-adduct could be detected.

The high proportion of dichloro-compound formed in the addition to styrene is difficult to explain, although it is interesting that a similar high proportion has been obtained with stilbene[2] and a smaller proportion with other olefins such as *cyclo*hexene.[5] The orientation of the chloro-nitro-compounds formed with styrene and propene is consistent with a mechanism involving homolysis of nitryl chloride, although heterolysis $NO_2^+ \cdots Cl^-$ cannot be excluded. The orientation of the chloro-nitrito-compound formed with propene supports the theory that such compounds are formed by a heterolysis $Cl^+ \cdots NO_2^-$.

EXPERIMENTAL

Styrene was distilled under reduced pressure. Ethylene, supplied by British Oxygen Co., was 98·2% pure, the main impurity being nitrogen. Propene was prepared by passing *iso*propyl alcohol vapour over alumina pellets at 300—400°: the liquefied product was fractionally distilled (b. p. constant ±0·2°).

Addition to Styrene.—A 4·7M-solution (50 c.c.) of nitryl chloride in ether at −80° was added during *ca.* 1·5 hr. to 0·5 mole of styrene in ether at −80° (in Part I[6] it was shown that nitryl chloride and ether interact only above 0°). Reaction of the nitryl chloride was shown to be complete by hydrolysing a sample and titrating the total acid and the chloride (Mohr method). Ether was then removed at a water-pump and the excess of styrene at 2 mm. The residue was fractionally distilled through a 1-foot helix-packed column at 1 mm., giving: (*a*) 1 : 2-dichloro-1-phenylethane (15 c.c.), b. p. 67—69°/1 mm. (Found: Cl, 36·4%), giving on refractionation at 8 mm. 2 c.c., b. p. 99°/8, 232°/760 mm. (lit.,[7] b. p. 115°/15, and 233—234°/760 mm.) (Found: C, 55·0; H, 4·7; Cl, 40·2. Calc. for $C_8H_8Cl_2$: C, 54·9; H, 4·6; Cl, 40·5%); (*b*) ω-nitrostyrene (7 c.c.), b. p. 100—115°/1 mm., crystallising from aqueous alcohol as pale yellow needles, m. p. 57° (lit., 58°) (Found: C, 64·7; H, 4·9; N, 9·9. Calc. for $C_8H_7O_2N$: C, 64·6; H, 4·7; N, 9·4%), $\lambda_{max.}$ 310 mμ (in EtOH) (lit.,[8] 318 mμ in dilute HCl). Since the spectrum of the original reaction mixture (after removal of solvent) did not possess a maximum in this region and since hydrogen chloride was evolved continuously during the fractionation, it was concluded that the ω-nitrostyrene was formed by the decomposition of 1-chloro-2-nitro-1-phenylethane. In a similar experiment, instead of fractionally distilling the product it was chromatographed on alumina. 1 : 2-Dichloro-1-phenylethane was separated pure but the remainder was a brown oil of variable composition, owing presumably to decomposition by the alumina. Other chromatographic materials, *e.g.*, acid-washed alumina and silica, were tried without success.

In other experiments, benzene and methylene chloride were used as solvents. The products

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[5] Price and Sears, *J. Amer. Chem. Soc.*, 1953, **75**, 3275.
[6] Collis, Gintz, Goddard, Hebdon, and Minkoff, *J.*, 1958, 438.
[7] Biltz, *Annalen*, 1897, **296**, 263.
[8] Kortum, *Z. phys. Chem.*, 1939, **43**, 271.

were separated chromatographically. Only 1 : 2-dichloro-1-phenylethane was obtained pure (yields: 74% in benzene; 67% in methylene chloride).

Addition to Ethylene.—Ethylene was slowly bubbled into a 1·75M-solution (100 c.c.) of nitryl chloride in methylene chloride at −5° to 0° and after 4 hr. reaction of the nitryl chloride was found to be complete. Methyl alcohol (50 c.c.) was added to convert any nitrite into alcohol, experience having shown that decomposition takes place if the mixture is distilled directly. After evaporation at atmospheric pressure, the residue was fractionally distilled at 32 mm.; the main fractions were: ethylene chlorohydrin (1·6 g.), b. p. 52—53°/32 mm., 125°/760 mm. (Found: C, 30·4; H, 7·0; Cl, 43·2. Calc. for C_2H_5OCl: C, 29·8; H, 6·3; Cl, 44·0%) (3 : 5-dinitrobenzoate, m. p. 94°; α-naphthylurethane, m. p. 100°), and 1-chloro-2-nitroethane (6·4 g.), b. p. 87—88°/32 mm., 173°/760 mm. (Found: C, 23·2; H, 3·85; N, 13·6; Cl, 31·5. Calc. for $C_2H_4O_2NCl$: C, 21·9; H, 3·7; N, 12·8; Cl, 32·4%) [gives *N*-2-nitroethylaniline hydrochloride, m. p. 104—106° (lit.,[4] m. p. 110°) (Found: Cl, 16·7. Calc. for $C_8H_{11}O_2N_2Cl$: Cl, 17·5%)]. Estimated yields (based on NO_2Cl) were ethylene chlorohydrin 16% and 1-chloro-2-nitroethane 35%. The same yields were obtained when benzene was used as solvent.

Addition to Propene.—A 5M-solution (85 c.c.) of nitryl chloride in benzene, at −5°, was added dropwise to benzene cooled to its f. p., through which propene (in a stream of nitrogen) was bubbled. When the reaction of the nitryl chloride was complete, 80 c.c. of absolute methyl alcohol were added. The methyl alcohol–benzene azeotrope was distilled off under reduced pressure and the residue fractionated, main fractions being impure 1-chloropropan-2-ol (4·2 g.), b. p. 46—50°/30 mm. (giving with dichromate a ketone whose 2 : 4-dinitrophenylhydrazone, m. p. 125°, did not depress the m. p. of chloroacetone 2 : 4-dinitrophenylhydrazone), and 2-chloro-1-nitropropane (9·3 g.), b. p. 64—65°/10 mm., 170—172°/760 mm. (lit.,[9] b. p. 172°) (Found: C, 29·5; H, 4·8; N, 11·1; Cl, 28·4. Calc. for $C_3H_6O_2NCl$: C, 29·2; H, 4·9; N, 11·3; Cl, 28·7) [giving *N*-(1-methyl-2-nitroethylaniline hydrochloride, m. p. 141° (Price and Sears [5] give m. p. 139—140°)]. Estimated yields (based on NO_2Cl) were 1-chloropropan-2-ol 5% and 2-chloro-1-nitropropane 30%. A number of minor fractions were obtained, some smelling of acetaldehyde, probably the result of oxidation of propene by the nitryl chloride. The benzene–methyl alcohol distillate (175 c.c.) contained 2·2% of organically combined chlorine because part of the product had formed a constant-boiling mixture with the solvent.

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Henry, *Bull. Acad. roy. Belg.*, 1897, **34**, 547.