# 285. *Aliphatic Nitro-compounds. Part VI. Reaction of α-Nitro-olefins with Hydrochloric Acid.*

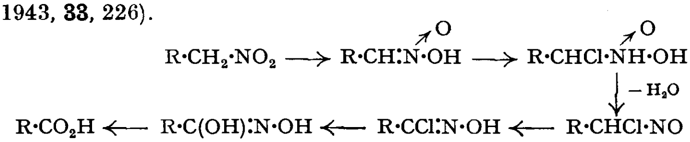
By Royden L. Heath and J. D. Rose.

α-Nitro-olefins react with anhydrous hydrogen chloride in ether giving 1 : 2-dichloronitroso-compounds which rearrange, if an α-hydrogen atom is present, into 1 : 2-dichloro-oximes. These on hydrolysis with water afford hydroxylamine hydrochloride and an α-hydroxy- or α-chloro-carboxylic acid according to the extent of the hydrolysis. Reaction of the nitro-olefins containing an α-hydrogen atom with concentrated aqueous hydrochloric acid gives similar products, but the intermediate dichloro-oximes are not isolated. It is suggested that the initial step is a 1 : 4-addition of hydrogen chloride to the nitro-olefin.

The literature on the action of hydrochloric acid on α-nitro-olefins is scanty. Haitinger (*Monatsh.*, 1881, **2**, 287; *Wien Akad. Ber.*, 1878, **77**, 428; *A*, 1879, 700) reported that 1-nitro-2-methylprop-1-ene, treated with hydrogen chloride at 20° or with boiling concentrated hydrochloric acid, gave hydroxylamine hydrochloride, carbon dioxide, and ammonia; a hydroxy-acid, m. p. 65°, was also isolated but not characterised. Our experience, below, suggests that this was probably impure α-hydroxy*iso*butyric acid (m. p. 79—80°). Priebs (*Annalen*, 1884, **225**, 319) obtained phenylchloroacetic acid by treatment of β-nitrostyrene with fuming hydrochloric acid at 100°.

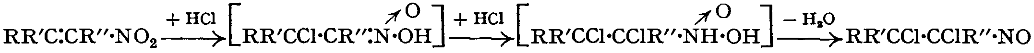
A study of the action of hydrochloric acid on α-nitro-olefins was undertaken as part of a general exploration of the chemistry of the aliphatic nitro-compounds. In the case of nitro-olefins with an α-hydrogen atom ($R_2C{:}CH{\cdot}NO_2$), treatment with ethereal hydrogen chloride gave hydroxylamine hydrochloride and an α-chloro- or α-hydroxy-acid (cf. Priebs, *loc. cit.*).

The possibility that the first stage in the reaction was 1 : 2-addition of hydrogen chloride to the double bond was excluded when it was found that 2-nitro*iso*propyl chloride, $Me{\cdot}CHCl{\cdot}CH_2{\cdot}NO_2$, was not affected by ethereal hydrogen chloride under the conditions which converted 1-nitroprop-1-ene, $Me{\cdot}CH{:}CH{\cdot}NO_2$, into α-chloropropionic acid and hydroxylamine hydrochloride. It therefore follows that the first addition is 1 : 4- to give $R_2CCl{\cdot}CH{:}\overset{\nearrow O}{N}{\cdot}OH$, which, as the *aci*-form of a primary nitro-paraffin, breaks down *via* the hydroxamic acid to hydroxylamine hydrochloride and an α-chloro- or α-hydroxy-acid (depending on the lability of the chlorine atom). The mechanism of conversion of the *aci*-primary nitro-paraffin into hydroxamic acid is still obscure but is considered to involve the following steps (cf. Yale, *Chem. Reviews*, 1943, **33**, 226).



$$\begin{tikzcd}
R{\cdot}CH_2{\cdot}NO_2 \arrow[r] & R{\cdot}CH{:}\overset{\nearrow O}{N}{\cdot}OH \arrow[r] & R{\cdot}CHCl{\cdot}\overset{\nearrow O}{N}H{\cdot}OH \arrow[d, "-H_2O"] \\
R{\cdot}CO_2H & R{\cdot}C(OH){:}N{\cdot}OH \arrow[l] & R{\cdot}CCl{:}N{\cdot}OH \arrow[l] \quad R{\cdot}CHCl{\cdot}NO \arrow[l]
\end{tikzcd}$$

In this mechanism, an important stage is the rearrangement of the 1-chloronitroso-compound to an oxime, which requires a hydrogen atom on the carbon carrying the nitroso-group. From secondary nitro-paraffins, in which this hydrogen is not available, the product expected would therefore be a 1-chloronitroso-compound or its breakdown products. In agreement with this we have found that treatment of nitro-olefins of the type $RR'C{:}CR''{\cdot}NO_2$ with ethereal hydrochloric acid gives deep blue highly lachrymatory liquids. Although it has not been possible to obtain these analytically pure on account of the closeness of their boiling points to those of the parent nitro-olefins, there seems little doubt that these are the dichloronitroso-compounds.



$$RR'C{:}CR''{\cdot}NO_2 \xrightarrow{+HCl} \left[RR'CCl{\cdot}CR''{:}\overset{\nearrow O}{N}{\cdot}OH\right] \xrightarrow{+HCl} \left[RR'CCl{\cdot}CClR''{\cdot}\overset{\nearrow O}{N}H{\cdot}OH\right] \xrightarrow{-H_2O} RR'CCl{\cdot}CClR''{\cdot}NO$$

Attempts to break down these dichloronitroso-compounds by further treatment with hydrochloric acid gave a trace of hydroxylamine hydrochloride as the only product identified.

## EXPERIMENTAL.

*Action of Anhydrous Hydrogen Chloride on Nitroethylene.*—Nitroethylene (37 g.; this series. Part I) was added dropwise to stirred saturated ethereal hydrogen chloride (300 c.c.) below 0°. Stirring was continued at 0° for 4 hours and at 20° for a further 12 hours. After removal of the ether under reduced pressure αβ-dichloroacetaldoxime remained as a colourless mobile liquid which began to decompose immediately. The crude product was stirred with water (300 c.c.) at 20° for 16 hours; the mixture, which was homogeneous, still gave a positive test for a hydroxamic acid and was refluxed for ½ hour (hydroxamic acid test negative) and evaporated to dryness under reduced pressure. The residue was extracted with ether, giving chloroacetic acid (39 g.; 82%), m. p. 62—63°, after recrystallisation from chloroform, and hydroxylamine hydrochloride (31·5 g.; 90%) as the ether-insoluble product.

*Action of Concentrated Hydrochloric Acid on* 2-*Nitroethyl Alcohol.*—2-Nitroethyl alcohol (10 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) was heated at 140° for 12 hours with concentrated hydrochloric acid (80 c.c.) in a sealed tube. The solution was evaporated and separated by ether into chloroacetic acid (6·2 g.; 60%) and hydroxylamine hydrochloride (5·3 g.; 70%).

*Action of Anhydrous Hydrogen Chloride on* 1-*Nitroprop*-1-*ene.*—This was carried out using 1-nitroprop-1-ene (51 g.; this series, Part I) and ethereal hydrogen chloride (250 c.c.) as described above for nitroethylene. The αβ-dichloropropaldoxime was distilled (80%), b. p. 78—80°/12 mm., but began to decompose immediately after distillation. A portion (37 g.) was hydrolysed by refluxing it with water (100 c.c.) for ½ hour. After evaporation the residue was separated by ether into lactic acid (8·0 g.; 33%), α-chloropropionic acid (0·7 g.; 2%), and hydroxylamine hydrochloride (10·4 g.; 60%).

*Action of Concentrated Hydrochloric Acid on* 1-*Nitroprop*-1-*ene and* 2-*Nitro*iso*propyl Alcohol.*—1-Nitroprop-1-ene (20 g.) was stirred with concentrated hydrochloric acid (100 c.c.) at 20° for 24 hours and then at 40° for 2 hours. After working up in the usual way, hydroxylamine hydrochloride (12 g.; 75%), lactic acid (6·0 g.; 30%), and α-chloropropionic acid (0·5 g.; 2%) were obtained. Similarly, 2-nitro*iso*propyl alcohol (10·5 g.) heated at 140° for 2 hours with concentrated hydrochloric acid (sealed tube) gave hydroxylamine hydrochloride (5·3 g.; 75%) and α-chloropropionic acid (5·6 g.; 54%).

*Action of Anhydrous Hydrogen Chloride on* 2-*Nitroprop*-1-*ene.*—2-Nitroprop-1-ene (26·1 g.; this series, Part I) was added dropwise with stirring to dry ether saturated at 0° with anhydrous hydrogen chloride (200 c.c.); a deep blue colour rapidly developed. Stirring was continued at 0° and precipitated hydroxylamine hydrochloride (1·8 g.) removed. Separated water was absorbed by the addition of anhydrous magnesium sulphate, and the solution distilled giving 1 : 2-dichloro-2-nitrosopropane, b. p. 48—50°/60 mm., as a deep blue, mobile, powerfully lachrymatory liquid (20 g.; 45%). It was not possible to obtain this material analytically pure owing to difficulties of separating small amounts of unchanged 2-nitroprop-1-ene (b. p. 45—48°/60 mm.).

*Action of Anhydrous Hydrogen Chloride on* 2-*Nitrobut*-2-*ene.*—2-Nitrobut-2-ene (20·2 g.; this series, Part III) was treated as described above for 2-nitroprop-1-ene. 2 : 3-Dichloro-2-nitrosobutane, b. p. 61—63°/40 mm., was obtained as a deep blue lachrymatory liquid (11 g.; 35%). After hydrolysis with water at 20° for 16 hours only hydroxylamine hydrochloride (0·1 g.) could be identified.

*Action of Concentrated Hydrochloric Acid on* 2-*Nitrobut*-2-*ene.*—2-Nitrobut-2-ene (20 g.) was stirred at 20° for 40 hours with concentrated hydrochloric acid (100 c.c.). The deep blue colour which developed initially disappeared in ½ hour. Evaporation to dryness under reduced pressure gave only hydroxylamine hydrochloride (7 g.; 52%).

*Action of Anhydrous Hydrogen Chloride on* 1-*Nitro*-2-*methylprop*-1-*ene.*—1-Nitro-2-methylprop-1-ene (60 g.; Levy and Scaife, in the press) was treated with saturated ethereal hydrogen chloride (400 c.c.) as described above for nitroethylene. αβ-Dichloro*iso*butaldoxime, b. p. 79°/10 mm., was obtained as a colourless liquid which began to decompose immediately after distillation (75 g.; 80%). Hydrolysis of this dichloro-oxime (24 g.) with boiling water (250 c.c.) for 16 hours gave hydroxylamine hydrochloride (9·5 g.; 90%) and α-hydroxy*iso*butyric acid, m. p. 80° (4·8 g.; 30%). Hydrolysis of the dichloro-oxime with concentrated hydrochloric acid for 1½ hours gave a 50% yield of α-hydroxy*iso*butyric acid.

*Action of Concentrated Hydrochloric Acid on* 1-*Nitro*-2-*methylprop*-1-*ene.*—1-Nitro-2-methylprop-1-ene (20·2 g.) was added dropwise with vigorous stirring to concentrated hydrochloric acid (100 c.c.) at 15—20°. Stirring was continued for 16 hours, and the mixture then boiled for 15 minutes and worked up in the usual way, giving hydroxylamine hydrochloride (12 g.; 86%) and α-hydroxy*iso*butyric acid (11·3 g.; 54%).

*Action of Anhydrous Hydrogen Chloride on* 1-*Nitro*-2-*chloropropane.*—1-Nitro-2-chloropropane (Henry, *Bull. Soc. chim.*, 1895, **13**, 1000) was treated with anhydrous ethereal hydrogen chloride under the conditions described for 1-nitroprop-1-ene (see above). On distillation unchanged 1-nitro-2-chloropropane, b. p. 60—65°/14 mm., was recovered quantitatively.

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