181. *The Action of Hydrogen Chloride on Isoprene.*

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Addition of hydrogen chloride to isoprene occurs in the 1 : 4-position. The purification and properties of the product are described.

BOUCHARDAT (*Compt. rend.*, 1879, **89**, 1117), Tilden (*J.*, 1884, **45**, 410), Gadziatsky (*Bull. Soc. chim.*, 1887, **47**, 168), Aschan (*Ber.*, 1918, **51**, 1303), and Claisen, Kremers, Roth, and Tietze (*J. pr. Chem.*, 1922, **105**, 76) examined the reaction between hydrogen chloride and isoprene, but did not establish the constitution of the monohydrochloro-compound formed. In a sentence occurring in a paper describing their investigation of the structure of isoprene hydrobromide, Staudinger, Kreis, and Schilt (*Helv. Chim. Acta*, 1922, **5**, 745) stated that they had shown the compound to be dimethylallyl chloride, but they described neither the compound nor its preparation. Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1983) proposed to estimate isoprene quantitatively by treatment with fuming aqueous hydrochloric acid, thereby forming 1 : 3-dichloro-3-methylbutane, but Bassett and Williams (*J.*, 1932, 2324) showed that, owing to unavoidable, but serious, losses during fractionation and separation of the product, this method was not quantitative.

The chief difficulty of the earlier investigators arose from their direct use of the fractionated product of pyrolysis of rubber, which, in addition to isoprene, b. p. 34°, contains 3-methylbut-1-ene, b. p. 24°, 2-methylbut-1-ene, b. p. 32°, and 2-methylbut-2-ene, b. p. 37°. In the present work, highly purified, freshly redistilled isoprene only has been used, and it has been found to combine readily with hydrogen chloride at ordinary temperature to give 1-*chloro*-3-*methylbut*-2-*ene*, as is indicated by the results of oxidation of the product both with permanganate and with ozone. The fact that the products it gives with neutral permanganate solution are acetic acid, chloroacetic acid, and carbon dioxide indicates that its double bond is medial and its chlorine atom terminal, while the formation of acetone and chloroacetaldehyde, identified as their respective oxidation products, acetic and chloroacetic acids, from its ozonide shows that its structural formula is $\mathrm{CMe_2{:}CH{\cdot}CH_2Cl}$, and not $\mathrm{CHMe{:}CMe{\cdot}CH_2Cl}$, which on similar treatment would yield acetaldehyde and monochloroacetone, the sole organic oxidation product of both of which would be acetic acid (Jones and Williams, *J.*, 1934, 834). The reaction between isoprene and hydrogen chloride is, therefore, similar to that between isoprene and hydrogen bromide, which gives 1-bromo-3-methylbut-2-ene (Claisen *et al.*, *loc. cit.*; Staudinger *et al.*, *loc. cit.*).

The boiling point, $t°$ c., of 1-chloro-3-methylbut-2-ene under a pressure, p mm. of mercury, is given, between 100 mm. and 780 mm., by the saturated-vapour pressure equation

$$\log_{10} p = 59{\cdot}1415 - \frac{4546{\cdot}103}{273{\cdot}1 + t} - 17{\cdot}1805 \log_{10} (273{\cdot}1 + t)$$

This equation, which is of the Kirchhoff type (*Ann. Physik*, 1858, **104**, 617), gives the value $4546{\cdot}103\boldsymbol{R} \log_e 10 - 17{\cdot}1805\, \boldsymbol{R}T = 7755$ cals. to the g.-molecular latent heat at the boiling point, $T = 273{\cdot}1° + 109°$, under atmospheric pressure, so that the value of the Despretz–Trouton function is 20·3, compared with 21·1, that indicated by the equation of Wartenberg (*Z. Elektrochem.*, 1914, **20**, 444) for a non-associated liquid of this b. p.

The gram-molecular volume of 1-chloro-3-methylbut-2-ene at 15°, corresponding to $d_{4°}^{15°}$ 0·9380, is 111·5 c.c., agreeing fairly well with 114·8 c.c., the value given by Traube's rule (*Ber.*, 1895, **28**, 2724, 2924) for a liquid of its constitution, while its Lorenz–Lorentz refractivity for D light given by $d_{4°}^{20°}$ 0·9331 and $n_{\mathrm{D}}^{20°}$ 1·4450 is 29·83, which is close to 29·69, the value calculated by means of Eisenlohr's values (*Z. physikal. Chem.*, 1911, **75**, 605) of atomic and bond refractivities for a liquid of its structure. In the present work, readings of mass, temperature, pressure, and refractive index have been corrected for all known errors.

EXPERIMENTAL.

Preparation and Purification of Product.—The isoprene used had been prepared and purified through its sulphone by the method of Bassett and Williams (*loc. cit.*; Jones and Williams, *loc. cit.*), and had b. p. 33·9°/760 mm. Dry hydrogen chloride was bubbled for about 6 hours through 272 g. (4 mols.) of the freshly redistilled isoprene, continuously mechanically stirred, and contained in a tared glass bottle which had been provided with a reflux condenser fitted with a calcium chloride guard-tube and was kept in ice–salt. The reaction proceeded practically in an atmosphere of hydrogen chloride. When the bottle had gained about 146 g. in weight (4 mols. of hydrogen chloride, loss of isoprene by evaporation not being allowed for), the product was fractionally distilled essentially as described by Jones and Williams (*J.*, 1934, 833). After two redistillations the fraction of b. p. 51·5—52·5°/100 mm. amounted to about 76 g., while in addition there were collected about 110 g. of less pure monohydrochloride. The material used in the following experiments was the fraction of b. p. 51·5—52·5°/100 mm., freshly redistilled for the purpose in hand.

The first distillation of the product of treatment of isoprene with hydrogen chloride permitted of a rough estimate of the relative proportions of its constituents by the method of Young and Fortey (*J.*, 1902, **81**, 752), but carried out under 100 mm. instead of normal pressure; after allowing for losses, it was so found that the product consisted of about 360 g. of the monohydrochloride, 20 g. of 1 : 3-dichloro-3-methylbutane, and 38 g. of unconverted isoprene.

The preparation was several times repeated, with variation of the conditions, but the product obtained was always the same. In some experiments, ether containing its peroxide was added originally with the isoprene, but the presence of the oxidant made no difference to the mode of addition, which, therefore, cannot be hypersensitively influenced by oxidising agents (Kharasch, McNab, and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2531; Kharasch and Hinckley, *ibid.*, 1934, **56**, 1243).

Properties of Product.—1-*Chloro*-3-*methylbut*-2-*ene* (Found: C, 57·2; H, 8·7; Cl, 34·0. C_5H_9Cl requires C, 57·4; H, 8·7; Cl, 33·9%) is a colourless liquid which darkens slowly, particularly in the presence of air and in sunlight. On being kept for any considerable time at its boiling point under atmospheric pressure, it decomposes slightly, but it can be safely distilled under diminished pressure; its b. p. is 52°/100 mm., 79°/300 mm., and 109°/760 mm.; it has $d_{4^\circ}^{15^\circ}$ 0·9380, $d_{4^\circ}^{20^\circ}$ 0·9331, and $n_D^{20^\circ}$ 1·4450.

Its *nitrosate* (Found: N, 14·2; Cl, 18·4. $C_5H_9O_4N_2Cl$ requires N, 14·3; Cl, 18·0%), colourless needles, m. p. 105°, from carbon disulphide, separates after ½ hour when fuming nitric acid (3·7 c.c.) is dropped on to a shaken mixture of the chloro-olefin (2·5 c.c.), glacial acetic acid (6 c.c.), and *iso*amyl nitrite (4·5 c.c.), cooled with ice–salt (Wallach, *Annalen*, 1888, **245**, 243). The *nitrosochloride* (Found: N, 8·3; Cl, 42·0. $C_5H_9ONCl_2$ requires N, 8·2; Cl, 41·7%), colourless, microscopic, square plates, m. p. 117°, from carbon disulphide, forms immediately at the surface of separation when a mixture of concentrated hydrochloric acid (3 c.c.) and glacial acetic acid (2 c.c.) is added dropwise with shaking to a solution of isoprene monohydrochloride (2·5 c.c.), glacial acetic acid (5 c.c.), and *iso*amyl nitrite (2 c.c.), cooled with ice–salt (Wallach, *Annalen*, 1902, **324**, 97). Both the nitrosate and the nitrosochloride melt to bluish-green liquids, and are probably dimeric in their colourless crystalline forms (Schmidt, *Ber.*, 1903, **35**, 2336).

Oxidation by Neutral Permanganate.—To a mixture of isoprene monohydrochloride (6·9 g.) and water (80 c.c.), a small amount of hot permanganate solution was added to start the reaction, and thereafter solid potassium permanganate (50 g.) was dropped in small portions with shaking, the temperature being kept low by cooling. Some carbon dioxide was evolved, and manganese dioxide was precipitated. The oxide was reduced by passing in sulphur dioxide, and in 24 hours was completely dissolved. The pink liquid was extracted with ether, and the ethereal extract dried (Na_2SO_4). After filtration of the solution, the ether was evaporated; the residue on distillation gave 1·2 g. of b. p. 118°/760 mm., and 1·7 g. of b. p. 101—105°/20 mm.

The first fraction was proved to be acetic acid by its smell, its b. p., and by refluxing it with aniline for 3 hours, precipitating excess of aniline as sulphate, and extracting with ether; after drying, the ethereal extract on concentration gave crystals, m. p. 111°, which after recrystallisation had m. p. 113° and mixed m. p. 113·5° with pure acetanilide of m. p. 114°.

The second fraction solidified in a vacuum desiccator to a solid, m. p. 59°, which recrystallisation from ether raised to 60°, mixed m. p. 61° with pure chloroacetic acid of m. p. 62°.

Ozonolysis.—Chloroform was washed with water, left over concentrated sulphuric acid, separated, and distilled from phosphorus pentoxide, the fraction of b. p. 61° being collected. In 60 c.c. of this chloroform, 15·7 g. of isoprene monohydrochloride were dissolved, and in the course of 25 hours $1·5 \times 10^6$ c.c. of ozonised oxygen, containing 10 g. of ozone, were passed through the solution at 0°. The chloroform was then removed under reduced pressure, and the viscous, oily, ozonide treated with water and warmed to 50°. The reaction was mild, and there was no evolution of gas. The aqueous solution so obtained was oxidised with neutral permanganate in the manner described in the last section. After evaporation of the ether there was left a residue which on distillation gave 7·5 g. of b. p. 118°/760 mm. and 7·5 g. of b. p. 101—105°/20 mm.

The first fraction was identified as acetic acid by its smell, its b. p., and its formation of an anilide of m. p. 112·5°, mixed m. p. 113° with pure acetanilide. The second fraction solidified to colourless crystals, identified as chloroacetic acid by their m. p. 62°, mixed m. p. 62° with pure chloroacetic acid, and b. p. 104—105°/20 mm. The total amount of acids collected (15·0 g.) represents a 65% yield. The acetic acid is derived from the acetone, and the chloroacetic acid from the chloroacetaldehyde (Jones and Williams, *loc. cit.*, p. 831), formed in the hydrolysis of the ozonide. Formaldehyde was tested for in the aqueous decomposition product of the ozonide, but its presence could not be detected.

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[*Received, February* 26*th*, 1946.]