

354. Addition of Hydrogen Chloride and Iodide to Olefins. Undecenoic Acid.

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BROUWER and WIBAUT (*Rec. trav. chim.*, 1934, **53**, 1001) investigated the reaction between hydrogen chloride and propylene from 15° to 140° in presence and in absence of oxygen: the product was 2-chloropropane and the 1-chloro-compound was not detected. In the gas phase there was no combination unless catalysts were added. Kharasch and Hannum (*J. Amer. Chem. Soc.*, 1934, **56**, 712) found that in the absence of such catalysts as ferric chloride no appreciable reaction occurred between hydrogen chloride and vinyl chloride; in the presence of ferric chloride ethylidene dichloride was the sole product. These results are in accordance with the Markownikoff rules (*Annalen*, 1879, **153**, 1870). It seemed desirable to make a further attempt to bring about a "peroxide catalysed" reaction (Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468) with hydrogen chloride.

When hydrogen chloride was allowed to act for several weeks on undecenoic acid in benzene solution, sufficient change occurred to enable an analysis of the products to be made. The reactions were carried out with and without catalysts, in the presence and the absence of oxygen; in every case 10-chloroundecenoic acid was the main product. Much smaller amounts of the oxidants used in these experiments (or even air with the benzene solutions) would have brought about the "peroxide catalysed" reaction between hydrogen bromide and undecenoic acid. Ferric chloride greatly speeded the reaction, allowing good yields of 10-chloroundecenoic acid to be obtained.

Kharasch and Hannum (*ibid.*, 1934, **56**, 1782) found that, in additions of hydrogen iodide to terminal double bonds, only the "normal" orientation occurred; no terminal addition of the iodine was detected. Although peroxides were reduced even at -40° by hydrogen iodide, these authors found that peroxides caused a great acceleration of the rate of addition of hydrogen iodide to allyl bromide.

It was of interest to try the reaction between hydrogen iodide and undecenoic acid in the presence of 10:11-epoxyundecenoic acid. This substance, which had proved a very powerful catalyst for the abnormal ("peroxide catalysed") reaction between hydrogen bromide and undecenoic acid, should not be reduced by hydrogen iodide. In all the experiments, however, 10-iodoundecenoic acid was the only product isolated and the easily detectable 11-iodo-acid must have been present in small quantity, if at all.

Hydrogen bromide thus differs from hydrogen chloride and iodide in that its reactions with olefins containing a terminal double bond may be accelerated and the orientation reversed in the presence of catalysts (usually "oxidants").

EXPERIMENTAL.

11-Chloroundecenoic Acid.—11-Hydroxyundecenoic acid (m. p. 68°, 7 g.) was added in small portions to phosphorus pentachloride (16 g., 2.2 mols.), the mixture being well shaken and finally warmed at 40° for 10 minutes. After addition of ice-water the *chloro-acid* was isolated by ether extraction and distillation (b. p. 148°/0.3 mm., m. p. 37—38°). By crystallisation from light petroleum it was obtained as plates, m. p. 40.5° (Found: C, 59.8; H, 9.3. $C_{11}H_{21}O_2Cl$ requires C, 59.9; H, 9.5%).

10-Chloroundecenoic Acid.—10-Hydroxyundecenoic acid and phosphorus pentachloride as

described above yielded the *chloro-acid*, b. p. $147^{\circ}/0.2$ mm., m. p. 29° . After several crystallisations from light petroleum the acid (plates) melted at $32-33^{\circ}$ (Found: C, 59.9; H, 9.6. $C_{11}H_{21}O_2Cl$ requires C, 59.9; H, 9.5%).

Mixtures of 10- and 11-Chloroundecoic Acids.—Sufficient points were determined on the system to show that it was of the eutectic type. The m. p.'s were taken in narrow tubes with slow heating.

10-Chloro-acid, mols. %	100	97	92	85	78	71	50	39.7	0.0
M. p.	31.9°	31.3°	30.0°	28.6°	26.7°	25.0°	23.4°	28.2°	40.0°

Separation by Crystallisation.—A mixture of the chloro-acids (71% of 10-chloro), m. p. 25° , twice crystallised from light petroleum, had m. p. 31° , and again crystallised had m. p. 32° . A mixture (m. p. 28°) containing 60% of the 11-chloro-acid was twice crystallised from light petroleum and then melted at $35-37^{\circ}$. These experiments showed that the *main* constituent of each mixture was easily isolated.

Addition of Hydrogen Chloride.—(i) *In presence of ferric chloride.* Undecenoic acid (m. p. 23° , 10 g.) and anhydrous ferric chloride (0.3 g.) were added to pure benzene (60 c.c.), and dry hydrogen chloride passed slowly for 3 hours on each of 8 days. As the mixture still reduced potassium permanganate solution, the flask was sealed for 1 month; the product was then found to be almost saturated. Hydrogen chloride was passed, and the flask again left for 1 month. The mixture was then filtered, shaken with water, dried, and evaporated. The residue (b. p. $130-160^{\circ}/0.3$ mm., m. p. $14-18^{\circ}$) was allowed to stand, and the viscous liquid drained away (B). Fractional distillation of the solid portion (A) gave 0.5 c.c., b. p. $115-140^{\circ}/0.2$ mm. (unsaturated), and 5 c.c., b. p. $138-143^{\circ}$ (slightly unsaturated), m. p. 26° . The second fraction (m. p. 26°), twice crystallised from light petroleum at -15° , gave plates, m. p. $32-32.5^{\circ}$ alone or when mixed with synthetic 10-chloroundecoic acid, m. p. $32-33^{\circ}$ (Found: *M*, 220. Calc., 220.5). The viscous liquid (B) yielded 2 c.c. of chloro-acid (which crystallised from ligroin in plates, m. p. 30° , raised by admixture with the 10-chloro-acid), and a high-boiling residue. When 11-chloroundecoic acid was added to the crude or the purified products above there was a large depression of m. p.

(ii) *In presence of diphenylamine* ("anti-oxidant"). Undecenoic acid (40 g., m. p. 24.0°) and diphenylamine (2 g.) were dissolved in benzene (300 c.c.), the air displaced by hydrogen, hydrogen chloride passed, and the bottle sealed; this procedure was repeated three times in 4 months. The product on fractional distillation gave (a) undecenoic acid, b. p. $117-120^{\circ}/0.1$ mm., (b) 6.5 g., b. p. $120-130^{\circ}$, m. p. 19° , (c) 5.5 g., b. p. $130-140^{\circ}$, m. p. 18.5° . Redistillation of (b) and (c) gave 3 g., b. p. $130-136^{\circ}/0.1$ mm., m. p. 26° (slightly unsaturated), from which the 10-chloro-acid, m. p. 32° , was obtained.

(iii) *In presence of "oxidants."* Undecenoic acid (30 g., m. p. 21.5° , containing peroxidic impurity) was dissolved in benzene (300 c.c.), and hydrogen chloride and oxygen added at intervals during $2\frac{1}{2}$ months. The product was 1 g. of the 10-chloro-acid, m. p. 26° , which yielded crystals, m. p. 32° , on recrystallisation.

(iv) Similar to (iii) but with addition of benzoyl peroxide (1.5 g.). The yield was about 1 g., m. p. $25-27^{\circ}$, and 30° after recrystallisation. Admixture with the 11-chloro-acid depressed the m. p. to 19° .

(v) Similar to (iii) but with addition of perbenzoic acid (1 g.). The yield was 1.5 g. of crude 10-chloro-acid, m. p. $25-26^{\circ}$.

Experiments were also made at 80° in presence of anhydrous calcium chloride, but addition of hydrogen chloride was still extremely slow.

10-Iodoundecoic Acid.—Pure 10-bromoundecoic acid, m. p. 35.7° (capillary tube, 36.5° ; Harris and Smith, J., 1935, 1109), was necessary for this preparation. The bromo-acid (4 g.) was refluxed in acetone (50 c.c.) containing sodium iodide (7.5 g.) for 6 hours, and the solvent removed in a vacuum. Hexane was added, and the resulting solution washed with water, dilute sulphurous acid, and water, and dried. Evaporation of the solvent left a colourless *product* (m. p. 20°) and repeated crystallisation from hexane raised the m. p. to $22.0-22.5^{\circ}$ (capillary tube $22-23^{\circ}$) (Found: I, 40.6. $C_{11}H_{21}O_2I$ requires I, 40.7%).

Mixtures of 10- and 11-Iodoundecoic Acids.—The curve shows that mixtures containing more than 14% of 11-iodoundecoic acid have a higher m. p. than that of the pure 10-iodo-acid.

10-Iodo-acid, mols. %	100	97	92	89	84	80
M. p.	22.0°	21.2°	20.2°	18.7°	25.5°	30.4°

11-Iodoundecoic acid melts at 66° (Ashton and Smith, J., 1934, 1309).

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Addition of Hydrogen Iodide.—(i) Hydrogen iodide containing air was passed into a solution of undecenoic acid (5 g., m. p. 23°, containing catalytic impurity) in benzene (50 c.c.). When the solution appeared saturated with the gas, the flask was sealed and left overnight. After removal of the solvent the product (free from iodide) melted at 18° (Found : *M*, 306. Calc., 312).

(ii) Pure undecenoic acid, m. p. 24.6°, and hydrogen iodide in hexane in presence of air gave a product, m. p. 20—21° (Found : *M*, 308). Crystallisation from hexane raised the m. p. to 22—23° (capillary tube).

(iii) Hydrogen iodide was passed into a solution of undecenoic acid (5 g., m. p. 23°) and 10 : 11-epoxyundecenoic acid (0.25 g., 5 mols. %) (J., 1935, 1575) in purified light petroleum (100 c.c.). The product had m. p. 17—18° (Found : *M*, 305).

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[Received, October 2nd, 1936.]
