

283. Addition of Hydrogen Bromide to Double Bonds. Ethyl Undecenoate, Undecenol, and Undecenyl Acetate.

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It has been shown (this vol., p. 435) that the "normal" addition of hydrogen bromide to undecenoic acid gives rise to 10-bromoundecoic acid, whereas the "peroxide-catalysed" addition yields the 11-bromo-isomeride. Similar conditions are now found to govern the reaction between hydrogen bromide and ethyl undecenoate in dilute benzene or ligroin solution: esterification of the carboxyl group has had no appreciable effect on the reaction.

The behaviour of undecenol towards hydrogen bromide has been investigated by Chuit, Boelsing, Hausser, and Malet (*Helv. Chim. Acta*, 1926, **9**, 1074), who found that the product was 10-bromoundecanol or 1:10-dibromoundecane according to the temperature. Owing to the importance of 1:11-dibromoundecane in the synthesis of dicarboxylic acids, several attempts were made by Chuit and his co-workers to prepare this dibromide from undecenol. On analogy with undecenoic acid and ester, the presence of a peroxide should favour terminal addition of the bromine atom to undecenol, but because of the counter-effect of the hydroxyl group, neither perbenzoic acid nor α -heptenylheptaldehyde exerted the desired influence. Obviously, the use of an ester should avoid this difficulty, and it was found that undecenyl acetate in the presence of a peroxide catalyst readily yielded the required 11-bromo-compound; furthermore, addition of hydrogen bromide in presence of hydrogen gave the 10-bromo-isomeride.

From these experiments it appears that the discovery of the "peroxide factor" (Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468) should solve the preparative difficulties involving orientation of addition of hydrogen bromide to compounds with terminal double bonds.

The results are summarised in the table.

Expt.	Substance.	Solvent.	In presence of	Main product.	Remarks.
(a)	Et undecenoate	Benzene	Air + C ₁₄ H ₂₆ O *	11-Bromo-	
(b)	" "	"	H ₂ + NHPh ₂	10- "	
(c)	" "	Ligroin	Air	11- "	Catalytic impurity from undecenoic acid still present.
(d)	" "	"	H ₂ + NHPh ₂	10- "	
(a)	Undecenol	Benzene	Air + Ph·CO ₃ H	10-Bromo-	
(b)	" "	"	Air + C ₁₄ H ₂₆ O	10- "	
(c)	" "	Ligroin	" "	10- "	
(d)	" "	"	H ₂ + NHPh ₂	10- "	
(a)	Undecenyl acetate	Benzene	Air + C ₁₄ H ₂₆ O	11-Bromo-	Passed HBr immediately.
(b)	" "	"	" "	11- "	Left 36 hrs. before passage of HBr.
(c)	" "	"	H ₂	10- "	
(d)	" "	Ligroin	Air + C ₁₄ H ₂₆ O	11- "	Rapid reaction with HBr.
(e)	" "	"	H ₂ + NHPh ₂	10- "	Slow reaction with HBr.

* α -Heptenylheptaldehyde.

EXPERIMENTAL.

11-Bromoundecoic Acid.—This important compound has previously been made only from impure undecenoic acid; after several crystallisations from ligroin it did not melt sharply in a capillary tube (50° in some specimens, 51° in others, softening some degrees below). Undecenoic acid (3 g. of f. p. 24.4°) was dissolved in pure benzene (20 c.c.), water (0.5 c.c.) added, and hydrogen bromide passed at 0° to saturation. After standing for 10 mins., the solution was evaporated in a

vacuum, leaving a product of m. p. 46.5°. 15 G. of bromo-acid (m. p. 46—47°) obtained as above, on crystallisation from purified ligroin (120 c.c.) at 0° gave 11.5 g. after removal of solvent. The m. p. was now 48.8°, and in a capillary tube the substance softened at 45°, melting at 48.5—50°. Recrystallisation from ligroin (220 c.c.; b. p. 60—80°) gave 9.1 g., m. p. 49.05—49.1° (in a capillary, soft at 48°, m. p. 49.5—51°). Recrystallised from carbon tetrachloride (40 c.c.) at 0°, the 9 g. gave 4.6 g., m. p. 49.25°. Distillation at 0.4 mm. followed by crystallisation from ligroin failed to alter this m. p. (Found: Br, 30.3. Calc.: Br, 30.2%). In a capillary tube the glistening plates softened at 49.5° and melted at 51°, but if much material was taken, or if the heating was rapid, m. p.'s of 52° were observed. The lower-melting form previously indicated (this vol., p. 440) is probably stabilised by traces of impurity, so that low softening points are observed and the solubility greatly increased.

Some large-scale preparations of 11-bromoundecic acid from undecenoic acid of m. p. 21—22° in purified ligroin solution with a stream of hydrogen bromide mixed with air were carried out at temperatures up to 40°. The mixture with excess of hydrogen bromide was kept over-night, then cooled to -10°, and filtered (yields 80—85%). This procedure avoided the tendency of the product to crystallise early and block the delivery tube.

11-Iodoundecic Acid.—11-Bromoundecic acid (10 g., m. p. 50°) was added to a solution of sodium iodide (10 g.) in acetone (60 c.c.), and the mixture boiled under reflux for 1 hr. After removal of the solvent and addition of water, the iodide was extracted with ether. The acid, 11.6 g. of m. p. 66°, crystallised from ligroin in flat plates, m. p. 66°; recrystallised from carbon tetrachloride, it still had m. p. 66°, and in the Beckmann apparatus had f. p. 65.6°, m. p. 65.6° (Found: I, 40.5. $C_{11}H_{21}O_2I$ requires I, 40.7%).

10-Hydroxyundecic Acid.—During the preparation of 10-bromoundecic acid (this vol., p. 439), it was noticed that the olefin reacted completely only after some hours at room temperature, indicating the slowness of the "normal" reaction. The product was pure enough to be crystallised from ligroin without previous purification by partial freezing. By the action of potassium acetate and acetic acid, followed by hydrolysis, 10-bromoundecic acid m. p. 35° gave the hydroxy-compound (together with some olefin) which, twice crystallised from benzene-ligroin, had m. p. 49—49.5° (softening at 47°). There is also a metastable form of m. p. approx. 34°. Chuit *et al.* (*loc. cit.*) give m. p. 49.5°.

Addition of Hydrogen Bromide to Ethyl Undecenoate.—Hydrogen bromide was prepared as previously described and was not dried. The benzene was of A.R. quality, and the ligroin (b. p. 60—80°) was free from olefins (this vol., p. 439). As reaction vessels for 10—20 g. quantities of the olefins, conical flasks (150—250 c.c.) were used. α -Heptenylheptaldehyde was prepared as before from heptaldehyde; in acetic acid solution it yielded a semicarbazone (m. p. 77°, from ligroin), which rapidly decomposed on standing and gave low values for nitrogen on analysis.

Undecenoic acid, f. p. 22.5°, gave an almost quantitative yield of the ethyl ester, b. p. 130—134°/15 mm. (Grün and Wirth, *Ber.*, 1922, 55, 2208). The specimen probably retained some of the catalytic impurity present in undecenoic acid, but for the present purpose further purification was unnecessary.

(a) Hydrogen bromide was passed into a solution of the ester (10 g.) and α -heptenylheptaldehyde (1 g.) in pure benzene (50 c.c.) at 0° for 40 mins. After removal of the solvent, 11 g. of the residual bromo-ester were converted through the acetate into the hydroxy-acid (yield 7 g., m. p. 50—55°). Once crystallised from benzene, the substance melted at 65—66° and, again crystallised from benzene, at 67—68°, either alone or when mixed with a specimen of 11-hydroxyundecic acid, m. p. 67—68°, prepared from the pure 11-bromo-acid (compare Walker and Lumsden, *J.*, 1901, 79, 1191).

(b) The ester (15 g.) and diphenylamine (0.1 g.) were dissolved in benzene (60 c.c.) at 0°. After the air had been displaced by a stream of hydrogen, hydrogen bromide was passed for 40 mins., and the flask then left for 3 hrs. at room temperature. The bromo-ester as in (a) was converted into hydroxy-acid, and the product distilled. Approx. 4 g. of unsaturated ester distilled at 130—165°/0.4 mm. and 10 g. at 165—174°. The second fraction, which only slowly reduced permanganate solution, melted partly at 28—30°, resolidified, and then melted at 43°. Twice crystallised from benzene-ligroin, it gave 4 g. of m. p. 48°, or mixed with 10-hydroxyundecic acid (m. p. 49°) at 48—49°. The production of olefin during the conversion of secondary bromide into the hydroxy-compound was also observed by Chuit (*loc. cit.*).

(c) Into a solution of the ester (10 g.) in ligroin (50 c.c.) at 0°, hydrogen bromide mixed with air was passed for 30 mins., and then for 10 mins. at 15°. The bromo-ester was converted into hydroxy-acid (8 g., m. p. 56°) which, once crystallised from benzene, melted at 66° or at 67° when mixed with a specimen of 11-hydroxyundecic acid.

(d) To a solution of ester (20 g.) in ligroin at 0°, diphenylamine (0.2 g.) was added, and the air displaced with hydrogen. Hydrogen bromide free from air was passed for 40 mins., and the mixture left over-night, air being excluded. The hydroxy-acid from the product melted at *ca.* 17° and, recrystallised from benzene–ligroin, at 47° (yield 12 g.) (Found: C, 65.4; H, 10.9. Calc. for C₁₁H₂₂O₃: C, 65.3; H, 10.9%). Mixed with 10-hydroxyundecanoic acid, m. p. 49°, it melted at 48–49°, and with the 11-hydroxy-isomeride at 38–42°.

Addition of Hydrogen Bromide to Undecenol.—Ethyl undecenoate from undecenoic acid, f. p. 22.5°, was reduced to undecenol, b. p. 130°/14 mm., in 76% yield (Grün and Wirth, *loc. cit.*).

Preliminary experiments showed that the addition of hydrogen bromide to undecenol in the presence of perbenzoic acid or of diphenylamine gave the same product, the crude 3 : 5-dinitrobenzoates melting in each case at about 10°. It appeared preferable, however, to identify the bromo-compounds by conversion into the glycols in order to take advantage of the great difference in physical properties between undecane-1 : 10- and -1 : 11-diol.

The products from experiments (a), (b), and (c) (Table I) were converted into glycols which, after fractional distillation to remove olefins, melted at 27–34°, a metastable form of m. p. *ca.* 8° separating first on cooling. Crystallisation (from benzene–ligroin, and other solvents) was difficult, the glycol usually separating as an oil. Eventually the m. p. in each case was raised to 44–47°, not depressed on admixture with the 1 : 10-diol from (d) below.

(d) Undecenol (10 g.) was dissolved in ligroin, the air displaced with hydrogen, and hydrogen bromide passed in for 30 mins. at 0°. After the mixture had been kept for 3 hrs. at 0°, two layers were present, and the solvent was removed in a vacuum. Fractional distillation of the acetate from this product yielded 4.5 g., b. p. 125–150° (strongly unsaturated), and 7.1 g., b. p. 160–165/0.6 mm. (saturated). The second fraction hydrolysed to glycol, m. p. 39°, raised by crystallisation from benzene–ligroin to 47–48° (Found: C, 70.1; H, 12.7. Calc. for C₁₁H₂₄O₂: C, 70.2; H, 12.8%). Chuit *et al.* (*loc. cit.*, p. 1080) give 48.5° as the m. p. of undecane-1 : 10-diol.

Addition of Hydrogen Bromide to Undecenyl Acetate.—(a) To a solution of the acetate (10 g., b. p. 140–142°/15 mm.) in benzene (50 c.c.), α -heptenylheptaldehyde (1 g.) was added, and a stream of hydrogen bromide containing air passed in for 30 mins. at 0°. The product was converted into diacetate, and hydrolysis with aqueous-alcoholic potassium hydroxide gave a product which crystallised on dilution of the alkaline liquid. Recrystallised from benzene (150 c.c.), it yielded 6 g., m. p. 61–62°, alone or mixed with a specimen of undecane-1 : 11-diol, m. p. 62°, obtained by reduction of 11-hydroxyundecanoate, m. p. 19°.

(b) Quantities as in (a); for details, see table. The product was refluxed for 5 hrs. with hydrogen bromide solution (*d* 1.5), and gave 8.5 g. of dibromide, b. p. 190–192°/18 mm. By heating the dibromide with a solution of sodium iodide (10 g.) in acetone (60 c.c.), a di-iodide was obtained, m. p. 20°, raised by two crystallisations from ethyl alcohol to 29–30°. Mixed with 1 : 11-di-iodoundecane, m. p. 31°, it melted at 30–31°.

(c) Acetate (7 g.) in benzene (30 c.c.). Hydrogen was passed in, and then hydrogen bromide at 0°. The mixture was left for 1 hr. at 15°, and the product converted into glycol as usual. Much undecenol was recovered (again showing the slowness of the “normal” reaction), and 3 g. of glycol, m. p. 27°. Twice crystallised from benzene, it melted at 42° (0.5 g.), and at 43–44° when mixed with the 1 : 10-diol.

(d) A solution of acetate (7 g.) and α -heptenylheptaldehyde (0.7 g.) in ligroin (40 c.c.) was treated with hydrogen bromide and air for 20° mins. at 0°, and the solvent removed almost immediately. The crude glycol from this was a yellow solid, m. p. 40°. Crystallised from benzene, it gave 3 g., m. p. 55°, and after a second crystallisation, 1 g., m. p. 61°.

(e) A solution of acetate (10.5 g.) in ligroin (40 c.c.) was treated with hydrogen and then with hydrogen bromide; after 1 hr. at 0°, two layers were present. The product (by the usual process) was mainly undecenol, and only 1 g. of a glycol fraction. This yielded 0.4 g. of glycol, m. p. 40–42°, depressed to 36–39° by addition of a small amount of the 1 : 11-glycol and raised to 44–45° by admixture with the 1 : 10-glycol.

1 : 11-Di-iodoundecane.—Dry hydrogen bromide was passed into undecylene glycol (4.5 g., m. p. 62°) at 130°. The resulting dibromide, b. p. 185°/13 mm., heated with a solution of sodium iodide in acetone, yielded the di-iodide, m. p. 29–30°, and 31° after recrystallisation from ethyl alcohol (Found: I, 61.9. Calc.: 62.2%). von Braun and Danziger (*Ber.*, 1912, 45, 1977) describe this substance as an oil.