258. *Addition of Hydrogen Bromide to Non-terminal Double Bonds.* iso*Undecenoic Acid.*

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The addition of hydrogen bromide to olefins containing terminal double bonds has been shown to be sensitive to the presence of oxygen or peroxides (Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468, and subsequent papers ; Ashton and Smith, J., 1934, 435, 1308). In almost every case the presence of peroxide has favoured terminal addition of the bromine atom ($CH_2{:}CH\cdot CH_2\cdot \longrightarrow CH_2Br\cdot CH_2\cdot CH_2\cdot$), the one exception being vinylacetic acid (Linstead and Rydon, J., 1934, 2002), where the double bond is under the influence of the carboxyl group.

In the present investigation the addition reactions of *iso*undecenoic acid ($\Delta^{9:10}$-undecenoic acid) have been studied under more powerfully oxidising and anti-oxidising conditions than those effective with $\Delta^{10:11}$-undecenoic acid (Ashton and Smith, *loc. cit.*), and in every case the resulting mixture of 9- and 10-bromoundecoic acids has had substantially the same composition. The slowness of the additions, as well as the composition of the product, indicate that the " normal " uncatalysed reaction is involved, instead of the alternative of a reaction sensitive to traces of peroxide which the anti-oxidant has failed to eliminate. As there is every reason to consider *iso*undecenoic acid as typical of olefins with non-terminal double bonds, it is inferred that the addition of hydrogen bromide to these compounds is not subject to the peroxide effect.

The recent criticism (Lauer and Stodola, *J. Amer. Chem. Soc.*, 1934, **56**, 1215) of the widely-quoted results of Lucas and Moyse (*ibid.*, 1925, **47**, 1459) for the addition of hydrogen bromide to Δ^2-pentene made it advisable to attempt an analysis of the addition products from *iso*undecenoic acid in benzene or ligroin solution. In the absence of a satisfactory synthesis of 9-bromoundecoic acid, it has been assumed that the system of 10- and 11-bromoundecoic acids can be used in the analysis, and the consistency of the results, as well as the many examples in the literature of the behaviour of isomerides (van der Linden, *J. Chim. physique*, 1912, **10**, 465 ; Geerling and Wibaut, *Rec. trav. chim.*, 1934, **53**, 1011), justify this procedure where an error of $\pm 5\%$ is allowable. The mean of the analysis is 43% of 10-bromo- and 57% of 9-bromo-undecoic acid, the known sources of error tending to lower the proportions of the former.

In order to compare the relative influence of methyl and ethyl on a double bond, Lucas and Moyse analysed the products of addition of hydrogen bromide to Δ^2-pentene, finding 78% of 3-bromo- and 22% of 2-bromopentane. This result was confirmed by Kharasch and Darkis (*Chemical Rev.*, 1928, **5**, 590). Lauer and Stodola point out the inaccuracy of the refractometric method and, by a procedure which in our opinion is also open to criticism, find only 53% of 3-bromopentane ($C_2H_5 : CH_3 = 53 : 47$).

In *iso*undecenoic acid the carboxyl group probably exerts little influence, so the effect of the polymethylene chain on the double bond should be at least as great as that of ethyl. Accordingly, on the basis of Lucas and Moyse's results, at least 78% of 9-bromoundecoic acid should be produced instead of the 57% actually found. If the carboxyl group exerts the same influence as in additions to stearolic acid (Robinson and Robinson, J., 1926, 2204), the 78% of 9-bromo-acid will be reduced only to 72%. The results with *iso*undecenoic acid appear, therefore, to fall into line with those of Lauer and Stodola.

Experimental.

Undecolic Acid, $CH_3\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2H$.—10 : 11-Dibromoundecoic acid (the crude product from 90 g. of undecenoic acid), potassium hydroxide (200 g.), and water (120 c.c.) were heated to 170° for 0·5 hr. The product (65 g. ; b. p. 170°/15 mm.) was crystallised from ligroin to m. p. 61° (Krafft and Seldis, *Ber.*, 1900, **33**, 3572 ; Welander, *ibid.*, 1895, **28**, 1448, gave m. p. 59·5°).

$\Delta^{9:10}$-*Undecenoic Acid* (iso*Undecenoic Acid*).—Attempts to reduce the triple bond of the foregoing acid to a double bond by means of nascent hydrogen or catalytically have not yet led to a homogeneous product. Krafft and Seldis prepared *iso*undecenoic acid by first adding hydrogen bromide (1 mol.) to undecolic acid, and then reducing the bromine atom (by sodium amalgam in alcohol). It was found better to reduce the iodide in acid solution, as follows.

To a well-stirred solution of undecolic acid (20 g.) in warm acetic acid (50 c.c.), cold hydrogen iodide (14 g.) in acetic acid was slowly added. A rise in temperature occurred, and the mixture was left for several hours. It was poured into water, ether added, and the ethereal extract washed with dilute sodium bisulphite solution, several times with water to remove acetic acid, and dried (sodium sulphate). After evaporation of the ether, the residue was distilled, first at 15 mm. while acetic acid passed over. Almost all the remainder boiled at 166—170°/0·6 mm., and was redistilled to a colourless or light yellow liquid. At the commencement of each distillation a little iodine was liberated. The mixture of iodoundecoic acids would not crystallise.

Reduction.—To a warm solution of the iodides (17 g.) in propionic acid (150 c.c.), a small amount of zinc dust was added, and the mixture boiled under reflux for 24 hrs. with occasional additions of zinc (compare Carey and Smith, J., **1933**, 346). If too much zinc had been added, the zinc propionate which separated after some hours could be redissolved by the *cautious* addition of a few c.c. of water. The hot liquid was poured into water (500 c.c. containing 5 c.c. of concentrated sulphuric acid), and the flask and zinc washed three times with boiling dilute sulphuric acid, the washings being added to the main bulk. The ligroin (b. p. 40—60°) extract of this mixture was washed six times with water in order to remove propionic acid; it was then dried and evaporated. After a little propionic acid had distilled, the liquid boiled constantly at 130°/1 mm., and was free from iodine. The yield was 8—9 g. (80—90%) and the m. p. varied from 9° to 13°. The iodine number (Hanuš) (average, 112; calc., 138) indicated the presence of saturated impurities.

It was thought that the presence of a lower-melting (*cis* ?) isomeride of *iso*undecenoic acid might be detected by the action of nitrous acid. Under the same conditions under which oleic acid was rapidly converted into elaidic acid, the crude *iso*undecenoic acid, m. p. 8°, was unchanged, and after two hours had m. p. 7°.

Distillation of a large quantity of *iso*undecenoic acid (m. p. 10°) raised the m. p. of the main fraction only to 11·4°, b. p. 129—130°/1 mm. All fractions were free from halogen. After two crystallisations from acetone, a specimen originally of m. p. 10° melted at 17° (yield 30%), and several further crystallisations raised the m. p. to 19·1° (in a capillary tube, 20°). Krafft and Seldis (*loc. cit.*) give m. p. 18—19°. The iodine number (Hanuš) was 134 (calc., 138), and the amide melted at 99° (Found : N, 7·7. Calc.; N, 7·7%). Chuit, Boelsing, Hausser, and Malet (*Helv. Chim. Acta*, **1926**, **9**, 1074) and also Krafft and Seldis (*loc. cit.*) obtained high yields of azelaic acid on oxidation, showing that the double bond was in the 9 : 10-position.

10-*Bromoundecoic Acid.*—The method of analysis adopted for mixtures of 9- and 10-bromoundecoic acid necessitated replotting with greater accuracy one portion of the system 10- and 11-bromoundecoic acids.

Undecenoic acid (37 g., f. p. 24·0°) was dissolved in purified ligroin (200 c.c.); hydrogen was passed for 10 minutes, and then dry hydrogen bromide (free from air) for 2 hours at room temperature. The sealed flask was left over-night, and all the hydrogen bromide had then been absorbed. Again, hydrogen and hydrogen bromide were passed, and the mixture, after having stood for 24 hours, was free from olefin. (Use of diphenylamine as an anti-oxidant makes the reaction even slower.) After the solution had been concentrated to half volume and cooled to − 15°, the solid was removed and then crystallised from ligroin at − 15°. The product (35 g., m. p. 33°) was twice crystallised from ligroin and had m. p. (clearing-point) 35·1° (compare Ashton and Smith, *locc. cit.*, pp. 439, 1309). After distillation (b. p. 165°/0·7 mm.) and two crystallisations from ligroin, the substance still crystallised slowly and had an indefinite m. p. in the Beckmann apparatus; it " cleared " at 35·25°. A change of solvent was therefore tried. After four crystallisations from acetone at a low temperature, the substance had clearing-point 35·7°, a slow rise from 35·2° taking place during 15 minutes while the bath was kept 1° above the melt. The f. p. was still indefinite, and the m. p. in a capillary tube was 36·5°. A further four crystallisations failed to cause any change in m. p. The difficulty of purification above 35° is probably due to the presence of about 3% of the higher-melting 11-bromo-isomeride in solid solution, and the slow crystallisation of the pure 10-bromo-acid is an indication of polymorphism, a transition taking place near the m. p.

A second specimen of 10-bromoundecoic acid was purified to the same constant clearing-point, 35·7°.

Mixtures of 10- *and* 11-*Bromoundecoic Acids.*—The following values replace those previously given (Ashton and Smith, *loc. cit.*, p. 440) :

10-Bromoundecoic acid, mols. %	100	87·4	78·0	67·9	66·8	57·7
M. p. (clearing point)	35·7°	32·8°	30·2°	27·1°	26·5°	30·2°

Addition of Hydrogen Bromide.—For the addition reactions, 2—10 g. of *iso*undecenoic acid were taken, and the technique was the same as that used previously (*idem, loc. cit.*), but as the reactions were much slower than with compounds having terminal double bonds, the flasks were sealed and left for 24 hours. If olefin could still be detected, hydrogen (or air) and hydrogen bromide were passed again for 1 hour, and the apparatus re-sealed. When reaction was complete, or when only a trace of olefin was left (1—4 days), the solvent was evaporated (after being filtered if diphenylamine had been used), and the yellow to dark-brown residue distilled. Usually there was a small fraction, b. p. 119—130°/0·2 mm., and the main fraction boiled at 140—160°/0·2 mm. The very small residue contained the high-boiling catalyst.

Redistillation gave a colourless to light-yellow main fraction, b. p. 145—159°/0·2 mm., which had an analysis in agreement with that for monobromoundecoic acid (yield 80—90%), and a lower fraction containing only traces of bromine. Any added perbenzoic acid was eliminated as benzoic acid in the lower fraction. In experiments in which the reaction had gone to completion and there was no catalyst to be removed (Expt. A), the distillation caused a rise of less than 2° in the m. p. An attempt to separate the monobromo-acids, and especially to isolate the 9-bromo-acid by fractional distillation, failed owing to the closeness of the b. p.'s.

The products from all the addition experiments exhibited the same behaviour on crystallisation. On cooling in a freezing mixture, they yielded a solid of m. p. $-$ 6° to $-$ 4°. When the semi-solid mass was stirred at 0°, a change of crystal form occurred, and the m. p. now became 14—18°. Examination of the binary systems showed that it was unlikely that the m. p. of mixtures with the *normal* form of 10-bromoundecoic acid (m. p. 35·7°) could be depressed to $-$ 5°, and a lower-melting form was probably involved. The 9-bromo-acid may also be polymorphous.

Analysis of the Products.—The mixtures of 9- and 10-bromoundecoic acids from most of the experiments were analysed by addition of successive weighed amounts to a known weight of pure 10-bromo-acid, followed by a determination of the m. p. On the assumption that the depression in m. p. of 10-bromoundecoic acid by the 9-bromo-acid would be the same as by an equal number of molecules of the 11-bromo-isomeride, the composition of the new mixture could be read off, and that of the original mixture calculated. Additional details of the following experiments are given in the table.

Expt. A. *iso*Undecenoic acid (m. p. 19°, 2·5 g.) yielded 3·4 g. (95%) of a brown oil, m. p. 15·7°; distilled, this had m. p. $-$ 5° and + 17°; *M* 261 (calc., 265). Addition of a trace of 10-bromo-acid raised the m. p. to 18°.

Expt. B. Acid of m. p. 19° yielded a light yellow oil, m. p. 15°. Redistilled, this had m. p.'s $-$ 5° and 17°, raised by addition of 10-bromo-acid. A mixture of A and B (1 : 1) had m. p. 17°.

Expt. C. M. p. 16°, *M* 262 (calc., 265). 1·001 G. of 10-bromoundecoic acid mixed with 0·254, 0·614, and 1·056 g. of the product in this experiment had m. p.'s 33·0°, 30·2°, and 27·9° respectively, whence 10-bromo-acid in the mixtures = 88·2, 78·0, and 70·3%; in product C, 41·8, 42·1, and 42·1%.

Expt. D. M. p. 16°, *M* 260 (calc., 265). 1·004 G. of 10-bromo-acid mixed with 0·314 and 0·822 g. of the product had m. p.'s 32·4° and 28·8° respectively, whence there were 86·0 and 73·8% of 10-bromo-acid in the mixtures; 41·2 and 41·8% in product D.

Expt. E. M. p. 18°, *M* 262. Mixed with D (1 : 1), m. p. was 17°. 1·001 G. of 10-bromo-acid mixed with 0·509 and 0·914 g. of product E had m. p.'s 31·1° and 28·9° respectively; whence 81·3 and 73·7% of 10-bromo-acid in the mixtures; 44·5 and 44·9% in product E.

Expt. F. M. p. 17°, *M* 263. 1·319 G. of 10-bromo-acid mixed with 0·340, 0·7075, and 1·343 g. of product F had m. p.'s 32·9°, 30·8°, and 28·0° respectively; whence 88·0, 80·0, and 71·0% of 10-bromo-acid in the mixtures; 41·4, 42·7, and 42·4% in F.

Expt. G. The product had been collected in two fractions: G (i) 2·1 g., b. p. 140—154°/0·2 mm., m. p. 17·5°; Br, 27·8 (calc., 30·2%); G (ii), 3·1 g., b. p. 154—157°/0·2 mm., m. p. 19·5°; Br, 29·8%; *M*, 263.

G (i). 1·002 G. of 10-bromo-acid mixed with 0·320, 0·753, and 1·056 g. of G (i) had m. p. 32·3°, 29·4°, and 28·2° respectively; whence 85·7, 75·5, and 71·5% of 10-bromo-acid in the mixtures and 40·9, 42·8, and 44·4% in G (i), the variation being due to impurity.

G (ii). 1·0025 G. of 10-bromo-acid mixed with 0·409 and 0·985 g. of G (ii) had m. p. 32·2° and 29·0° respectively; whence 85·0 and 74·0% of 10-bromo-acid in the mixtures; 48·1 and 47·5% in G (ii). The mean content of product G is approx. 46%.

Expt. H. The undecenoic acid was kept for 24 hrs. in benzene with perbenzoic acid (10 mols. %) before passage of hydrogen bromide. The distilled product had m. p. 14°, *M* 257, and was slightly unsaturated.

1·015 G. of 10-bromo-acid mixed with 0·504 and 1·000 g. of H had m. p.'s 30·6° and 27·8° respectively; whence 79·5 and 70·3% of 10-bromo-acid in the mixtures, and 39·7 and 40·1% in H.

Addition of Hydrogen Bromide to iso*Undecenoic Acid.*

Expt.	Solvent.	In presence of	M. p.	Product: mols. % of 10-bromo-acid.
A	Benzene	Air + water	17°	—
B	,,	Hydrogen	17	—
C	,,	Air + $Ph\cdot CO_3H$	16	42
D	Ligroin	H_2 + $NHPh_2$	16	41·5
E	Benzene	Air + $C_{14}H_{26}O$ *	18	45
F	Ligroin	Air + water	17	42
G	,,	H_2 + $NHPh_2$	17·5 and 19·5	46
H	Benzene	Air + $Ph\cdot CO_3H$	14	40
			Mean composition	42·7

* Peroxide catalyst, α-heptenylheptaldehyde.

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