370. *Addition of Hydrogen Bromide to Triple and to Double Bonds. Undecynoic, Undecenoic, and* 10 : 11-*Epoxyundecoic Acids.*

By P. L. Harris and J. C. Smith.

Because of the differences between acetylenes and olefins it was not predictable that with a triple bond a " peroxide effect " (Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468) would cause terminal addition of the bromine from hydrogen bromide. Experiments with Δ^{10}-undecynoic acid (dehydroundecylenic acid; Krafft and Seldis, *Ber.*, 1896, **29**, 2232) have shown that terminal addition of bromine occurs in presence of " oxidants," and the reverse in presence of " anti-oxidants." Compared with the corresponding olefin, the acetylene reacts slowly and the addition of only the first molecule of hydrogen bromide has been studied. Apparently in presence of halogen acid any *cis*-11-bromoundecenoic acid initially formed is converted into the *trans*-acid.

Identification of the products of the reactions depends on the constitution of the bromo-acid, m. p. 41·5°, assumed by Krafft and Seldis to be *trans*-11-bromoundecenoic acid. Although the bromine atom in this compound is eliminated during catalytic reduction, it cannot be replaced by acetoxyl and thus a determination of the constitution by this method is not feasible. The following considerations, however, give a clear indication of the constitution.

(i) The product of incomplete catalytic reduction does *not* contain 10-bromoundecoic acid, and although 11-bromoundecoic acid has not been isolated in substance, its presence is indicated by the cryoscopic behaviour of the mixture.

(ii) Removal of the bromine atom by hydrogenation would be expected if the first stage was reduction to 11-bromoundecoic acid. The bromine atom in the 10-bromo-acid is very difficult to reduce.

(iii) The formation of solid solutions (Type I System) with 11-bromo- and of a eutectic system with 10-bromo-undecoic acid indicates greater similarity of structure with the 11-bromo-acid.

Further experiments on the " peroxide effect " with undecenoic acid extending those of Ashton and Smith (J., **1934**, 437) show that additions of hydrogen bromide in carbon disulphide, chloroform, and carbon tetrachloride are sensitive to " oxidants " (compare Kharasch and Mayo, *loc. cit.*). The example of chloroform is instructive, since unless traces of alcohol are removed the solvent acts as an anti-oxidant.

The experiments of Ashton and Smith (*loc. cit.*, p. 437, Nos. 29, 30, 25, 26) indicated that, although α-heptenylheptaldehyde and air produced a " peroxide effect " without any delay, yet perbenzoic acid was ineffective until 12 hours had elapsed after the making-up of the solution. This result is now found to be due to the use of an ethereal solution of perbenzoic acid : in ligroin solution perbenzoic acid immediately catalyses the reaction with hydrogen bromide and air.

It is necessary to emphasise that *in the absence of air* the catalysts perbenzoic acid, benzoyl peroxide, 10 : 11-epoxyundecoic acid, and α-heptenylheptaldehyde have a very small influence on the composition of the product from hydrogen bromide and undecenoic acid. At least with this olefin molecular oxygen is essential for the " peroxide effect," and catalysts such as perbenzoic acid have a supplementary action. In the experiments of Kharasch and Mayo on allyl bromide (*loc. cit.*), Kharasch, McNab, and Mayo on vinyl bromide (*ibid.*, p. 2522), and Kharasch and Hannum on vinyl chloride (*ibid.*, 1934, **56**, 712), no precautions were taken to ensure that oxygen was not formed from the " oxidants " present, and this is especially important in view of the long duration of the reactions.

EXPERIMENTAL.

Δ^{10}-*Undecynoic Acid*, $CH⋮C\cdot[CH_2]_8\cdot CO_2H$.—The acid of m. p. 43° (Krafft and Seldis, *loc. cit.*) had iodine number (Hanuš) 138 (theory for addition of 1 mol. of IBr, 139).

Addition of Hydrogen Bromide.—(i) *In presence of an " oxidant."* A slow stream of hydrogen bromide containing air was passed for 3 hours into an ice-cold solution of Δ^{10}-undecynoic acid (10 g.) and perbenzoic acid (1 g.) in benzene (30 c.c.). Evaporation of the benzene left an oil (iodine number 9), which was dissolved in ether, shaken with dilute ammonia solution to remove benzoic acid, then with water, and dried (sodium sulphate), and the solvent evaporated. After removal of unchanged undecynoic acid and dibromo-acids by fractional distillation, the main fraction (7 g., b. p. 148—156°/0·1 mm.) had *M* 267 (calc. for $C_{11}H_{19}O_2Br$, 263) and m. p. 18·6°. It could not be recrystallised without great loss. Treatment with nitrous acid caused the m. p. to fall to 17°.

(ii) *In presence of an " anti-oxidant."* A stream of hydrogen was passed for 15 minutes through an ice-cold solution of Δ^{10}-undecynoic acid (10 g.) and diphenylamine (1 g.) in benzene (30 c.c.). Hydrogen bromide (free from air) was then passed for several hours, the diphenylamine hydrobromide filtered off, and after evaporation of the solvent the iodine number of the product determined. The mixture was made up again by addition of diphenylamine and benzene, and the process continued. After 3 hours 33%, 5·5 hours 27%, and 8 hours 18% of acetylenic acid remained. After 8 hours the product was worked up, yielding a main fraction

(8 g.), b. p. 151—157°/0·1 mm., and very little dibromo-acid. The main fraction, m. p. 12·1°, had *M* 266 (calc., 263). Nitrous acid caused no change in m. p.

Equal weights of products (i) and (ii), mixed and cooled to − 10°, would not crystallise until seeded with solid from (i). When the mixture was allowed to warm, all but a trace of solid melted at − 6° and a clear liquid was obtained at + 3°. Products (i) and (ii) were therefore of widely different composition.

Addition of 11-*Bromoundecenoic Acid.*—This acid (see below) was added in weighed amounts to the products (i) and (ii), and the change in m. p. noted. Product (i) with 4% of 11-bromo-acid crystallised more readily and the m. p. was raised 2·3°; with 7% of 11-bromo-acid, the change was + 4·3°.

Product (ii), mixed with 3·5% and 6% of 11-bromo-acid, melted 1·1° and 2·0° lower than originally.

Product (i) had therefore as its main constituent 11-bromoundecenoic acid.

Bromoundecenoic Acid.—Krafft and Seldis (*loc. cit.*) by the action of alcoholic potassium hydroxide solution on 10 : 11-dibromoundecoic acid obtained as a by-product a monobromoundecenoic acid, m. p. 41·5°, and suggested that it was the *trans*-form of 11-bromoundecenoic acid. It has now been prepared in larger quantities, but the yield is poor. The fraction, b. p. 150—158°/0·1 mm., m. p. about 33°, melts after two crystallisations from ligroin at 40·5—41° and finally at 41—42° (41·4° with thermometer in the liquid) (Found: *M*, 263. Calc. for $C_{11}H_{19}O_2Br$, 263). Heating at 150° for 7 days with sodium acetate and acetic acid removed only part of the bromine and the product appeared to polymerise. No acetate could be isolated.

Mixtures of Bromoundecenoic Acid with 11-*Bromoundecoic Acid.*—The specimens used had been crystallised to constant m. p. (thermometer in the liquid) and the mixtures formed an unbroken series of solid solutions (Type I).

Bromoundecenoic acid, mols. %	100	96·6	93·8	88·8	82·0	72·5	56·7	0·0
M. p. (clearing point)	41·4°	41·4°	41·45°	41·7°	41·9°	42·6°	43·8°	49·2°

Mixtures of Bromoundecenoic Acid with 10-*Bromoundecoic Acid.*—Sufficient points were determined to show that the system was of the eutectic type.

Bromoundecenoic acid, mols. %	100	94·5	87·7	77·4	57·8	0·0
M. p. (clearing point)	41·4°	40·05°	38·1°	35·2°	28·5°	35·7°

Catalytic Reduction.—Bromoundecenoic acid (3·0 g. of m. p. 41—42°) in aqueous alcohol (40 c.c. of 55%), shaken with hydrogen (Pd/$BaSO_4$), absorbed 280 c.c. (1 mol.) in 2·5 hours. The reaction continued without any break in the time–volume curve and when 1·5 mols. had been absorbed the product was isolated. On fractional distillation it yielded undecoic acid (m. p. 29°) and a small fraction, b. p. 150—160°/0·1 mm., m. p. 36·5—38·5°. Redistilled, the higher fraction melted at 39—40°.

Similarly, bromoundecenoic acid (6·0 g.), after having absorbed hydrogen (680 c.c., 1·33 mols., in 220 mins.), yielded fraction (i) 3 c.c., b. p. 125—127°/0·1 mm., m. p. 27°; fraction (ii) 0·5 c.c., b. p. 127—150°, m. p. 33—34°; and fraction (iii) 1·2 g., b. p. 150—156°, m. p. 38—40° (thermometer in liquid, 39·7°), *M* 257. Fraction (iii) was redistilled three times (rejecting the first two drops) and the m. p. was thus raised to 41·8° (thermometer in liquid). Addition of bromoundecenoic acid of m. p. 41·4° gave a mixture of m. p. 41·7°, and admixture with 11-bromoundecoic acid (m. p. 49·2°) raised the m. p. to 45°.

An attempt to crystallise fraction (iii) from ligroin in a freezing mixture gave a small quantity of crystals, m. p. 42·0°. These observations indicate that fraction (iii) is a mixture of unreduced bromoundecenoic acid with about 15% of 11-bromoundecoic acid. 10-Bromoundecoic acid must be absent, as even a small amount of it would depress the m. p. below 41°.

Expt.	Solvent.	In presence of	M. p.	Product : mols. % of 11-bromo-acid.
A	Ligroin	Air	45°	84
B	Carbon disulphide (washed)	Air	45	84
C	,, ,,	Hydrogen	29	26
D	Carbon tetrachloride (tech.)	Air	44	80
E	Carbon tetrachloride (tech.)	Hydrogen	29°	26
F	Chloroform (unwashed)	Air	20	mainly 10-bromo
G	Chloroform (washed)	Air	44	80
H	,,	Hydrogen	27	31

The same apparatus, technique, and part of the same preparation of catalyst being used, 11-bromoundecoic acid was completely reduced to undecoic acid in 2 hours, whereas two specimens of 10-bromoundecoic acid after 4 hours had absorbed only 0·3 and 0·2 mol. of hydrogen.

Addition of Hydrogen Bromide to Undecenoic Acid in Various Solvents.—The sample of undecenoic acid used (m. p. 23·1°) retained a convenient amount of the catalytic impurity (Ashton and Smith, *loc. cit.*, p. 436).

Action of Perbenzoic Acid.—The preparation of perbenzoic acid (Lewin, *J. pr. Chem.*, 1930, **127**, 81) was modified : after removal of ethyl benzoate by extraction with ether the solution of sodium perbenzoate was acidified and then extracted three times with ligroin (b. p. 40—60°, free from olefins). The first extract was usually a 0·5*N*-solution of perbenzoic acid and the total yield was 70—80%. A pure specimen of undecenoic acid (m. p. 24·6°) yielded 10-bromoundecenoic acid when its solution in ligroin was treated with hydrogen bromide and air. To a solution of this undecenoic acid (2 g.) in ligroin (7 c.c. free from olefins), perbenzoic acid (0·1 g. in 5 c.c. of ligroin) was added. The mixture was cooled to 0° and hydrogen bromide and air were passed. Within 15 minutes 11-bromoundecoic acid crystallised, showing that perbenzoic acid in the absence of ether had, without long standing, brought about the peroxide effect.

10 : 11-*Epoxyundecoic Acid.*—Undecenoic acid (7 g., m. p. 24°) was dissolved in ligroin (200 c.c.) containing perbenzoic acid (7 g., 1·3 mols.), and the solution kept for 24 hours at 30°; only one-fifth of the perbenzoic acid then remained. The reaction mixture was fractionally extracted with dilute ammonia solution, which removed first the benzoic acid and then 10 : 11-*epoxyundecoic acid.* This acid, which did not liberate iodine from potassium iodide, crystallised readily from ligroin as a fine powder (each grain being a cluster of minute prisms), m. p. 45·5° (yield, 25—50%) (Found : C, 66·0; H, 10·0; *M*, 202. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%; *M*, 200). On keeping in a desiccator the crystals changed within 10 days to another form, m. p. 50° (*M* 199).

Action of Hydrogen Bromide.—10 : 11-Epoxyundecoic acid (2 g.) dissolved in ligroin only on warming and crystallised again on cooling. When air and hydrogen bromide (dry or moist) were passed into the warm solution, a heavy oil was quickly precipitated. The oil was sparingly soluble in benzene and when freed from hydrogen bromide it slowly crystallised, m. p. 49—53° (Found : Br, 28·7. $C_{11}H_{21}O_3Br$ requires Br, 28·5%). It is obviously a mixture of bromohydrins and is being further investigated. The easily recognisable 11-bromoundecoic acid was not produced in the above reaction.

A solution of undecenoic acid (0·9 g., m. p. 24·6°) and epoxyundecoic acid (0·6 g.) in ligroin (10 c.c.) at 0° yielded with hydrogen bromide and air an immediate precipitate of oil, followed within 4 minutes by a crystalline precipitate of 11-bromoundecoic acid (m. p. 46°, when separated mechanically). Freed from solvent, the united reaction products were liquid at room temperature.

When hydrogen bromide and air were passed into a solution of undecenoic acid (1·5 g., m. p. 24·6°, which without oxidant yielded 10-bromoundecoic acid) and epoxyundecoic acid (0·08 g., 5 mols. %) in ligroin (16 c.c.), there was an immediate milkiness and within 5 minutes the mixture solidified owing to the formation of 11-bromoundecenoic acid. Epoxyundecoic acid is therefore a powerful " peroxide catalyst," but, as it is itself converted into bromohydrin, the yield of 11-bromoundecoic acid rises as the amount of oxide added is decreased.

Action of Hydrogen Peroxide.—10 : 11-Epoxyundecoic acid in ligroin solution was kept with hydrogen peroxide of various concentrations in the hope of forming a reactive peroxide of undecoic acid. When hydrogen bromide and air were passed into the ligroin solutions, only bromohydrins were formed.

Necessity for the Presence of Molecular Oxygen.—A ligroin solution of undecenoic acid (m. p. 23·1°, retaining some of the oxidant impurity) was freed from air by evaporation of some of the solvent under reduced pressure. When hydrogen bromide (free from air) was passed, the addition was very slow, and after the mixture had stood for 20 hours the product, m. p. 27°, was mainly 10-bromoundecoic acid.

Similar experiments with pure undecenoic acid with addition of 10 molecules % of (a) 10 : 11-epoxyundecoic acid, (b) benzoyl peroxide, and (c) perbenzoic acid also gave products containing 60—90% of 10-bromoundecoic acid.

SUMMARY.

(1) Addition of hydrogen bromide to a terminal triple bond is subject to a " peroxide effect," " oxidants " causing terminal addition of the bromine atom.

(2) In absence of ether, perbenzoic acid has an immediate catalytic effect on addition· to undecenoic acid.

(3) 10 : 11-Epoxyundecoic acid is a powerful catalyst and it is not an intermediate in the formation of 11-bromoundecoic acid.

(4) None of the catalysts is effective in absence of molecular oxygen.

(5) The results of catalytic reduction of the bromoundecenoic acid of m. p. 41·5° justify Krafft and Seldis's assumption that this is the 11-bromo-acid.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

[*Received, October 2nd,* 1935.]