194. *Addition of Hydrogen Bromide to Non-terminal Double Bonds. Effect of the Alkyl Groups.*

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PRELIMINARY experiments (Harris and Smith, J., 1935, 1108) showed that the product of the action of hydrogen bromide on *iso*undecenoic acid [$CH_3 \cdot CH\colon CH \cdot (CH_2)_7 \cdot CO_2H$] contained approximately 57% of 9-bromoundecoic acid and that the true percentage would probably be lower.

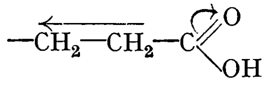
This result was more in harmony with that of Lauer and Stodola (*J. Amer. Chem. Soc.*, 1934, **56**, 1215), who found 53% of 3-bromopentane in the product of the addition of hydrogen bromide to Δ^2-pentene, than with the results of Lucas and Moyse (*ibid.*, 1925, **47**, 1459) and Kharasch and Darkis (*Chem. Reviews*, 1928, **5**, 590), who found 79% of 3-bromopentane.

By the synthesis of 9-bromoundecoic acid and use of the binary system with 10-bromoundecoic acid it has been possible to make a more accurate analysis of the products from *iso*undecenoic acid. The reaction in hexane solution was very slow and also in acetic acid (considering the high solubility of hydrogen bromide in acetic acid), but the figures given in Table I show that the analyses steadily approach 50% of the 10-bromo-acid as the olefin is eliminated.

A further attempt (compare Harris and Smith, *loc. cit.*) to detect a " peroxide " effect by carrying out simultaneously an experiment in which strongly " oxidant " conditions prevailed and a second with rigorously " antioxidant " conditions showed that the variation in composition of the products was within the margin of error. Kharasch and McNab (*Chem. and Ind.*, 1935, **13**, 990) similarly failed to detect a "peroxide" effect with non-terminal double bonds. If the " abnormal or peroxide catalysed reaction " is one which involves a reversal of orientation of addition, the reversal would scarcely be detected when the "normal" reaction gave the isomerides in the proportion 50 : 50 or 51 : 49. (With *terminal* double bonds a " normal " reaction yielding 90% of $CH_3{\cdot}CHBr{\cdot}[CH_2]_n{\cdot}$ is replaced by a more rapid " abnormal " reaction yielding 90% of $CH_2Br{\cdot}CH_2{\cdot}[CH_2]_n{\cdot}$.) It is possible that the high rate of the reaction in benzene despite the low concentration of hydrogen bromide is connected with the fact that benzene is a solvent which favours the " abnormal " reaction (compare Ashton and Smith, J., 1934, 437).

At the time when the addition products of *iso*undecenoic acid were thought to contain approximately 43% of the 10-bromo-acid it was represented to us that the proportion of 10-bromo-acid had been raised by the influence of the terminal carboxyl group, and that our assumption of the equivalence of $\cdot[CH_2]_7{\cdot}CO_2H$ and $\cdot[CH_2]_7{\cdot}CH_3$ was unjustified. As the difficulties of carrying out a similar investigation with an olefin $CH_3{\cdot}CH{:}CH{\cdot}[CH_2]_n{\cdot}CH_3$ were insuperable, it was decided to alter the end group of *iso*undecenoic acid in two ways. A change of carboxyl to amido was not expected to have any appreciable effect on the composition of the addition product, but the amide as a high-melting solid would give valuable confirmation of the results from the acid. The slightly lower percentages of 10-bromo-acid observed (46% and 47%) were due to impurities introduced by the extra processes involved.

Reduction of the carboxylic acid to the alcohol and addition of hydrogen bromide to the latter would be a severer test, since in the alcohol there should be no opposition by the end group to any general effect in the alkyl chain :



$$-\overleftarrow{\mathrm{CH_2-CH_2}}-\mathrm{CH_2-O-H}$$

Oxidation of the mixture of bromo-alcohols gave the bromo-acids slightly contaminated with by-products which were not removed by fractional distillation. The melting points from the binary system show that the mixtures must contain at least 44% of the 10-bromo-acid, and on the assumption that the impurities have molecular weights of 100—300, the ratio of the bromo-acids must be very near to 50 : 50; the same ratio should hold for the bromo-alcohols before oxidation.

In *iso*undecenoic acid, therefore, the observed composition of the addition product is not the combined result of a tendency of the alkyl chain to produce excess of 9-bromo-acid and of an opposite tendency of the carboxyl group exactly balanced. (If the carboxyl group had any influence, this should vary greatly in such different solvents as hexane and acetic acid. A better test for the transmission of the influence of end groups through a chain or a solvent would be an investigation of the nuclear reactions of quinol ethers $MeO{\cdot}C_6H_4{\cdot}O{\cdot}[CH_2]_n{\cdot}CO_2H$; compare Robinson and Smith, J., 1926, 392; Bradfield and Jones, J., 1928, 1011.)

Although it would not be justifiable to assume the equivalence of carbon atoms 9 and 10 of *iso*undecenoic acid in other circumstances, yet in the particular reaction studied—the addition of hydrogen bromide in solvents of widely different nature—these carbon atoms appear to be equally activated, just as do carbon atoms 2 and 3 in Δ^2-pentene (Lauer and Stodola, *loc. cit.*). It would appear, therefore, that in a homologous series,

$CH_3 \cdot CH{:}CHR$, there is no appreciable change in the relative activity of the unsaturated carbon atoms. It is of interest to compare this result with those of measurements of reactivity in other homologous series, and the following classification has been found to group the most carefully studied series into only three types. In the majority of reactions there is a great *decrease* in reactivity in passing from the first member (1 CH_2 group) to the third member and then a slower decrease along the series: Type I of Homologous Series Reactivity. Examples are the reactions of *n*-alkyl halides with trimethylamine, sodium methoxide or sodium benzyloxide; the hydrolysis of esters and the esterification of alcohols (for bibliography, see Haywood, J., 1922, **121**, 1904; Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 263).

When some unsaturated group or atom is present, large *alternations* in reactivity for the first three or four members are shown, followed by a gradual decrease in reactivity (Type II). Examples are the reactions between $CH_3 \cdot CO \cdot O \cdot [CH_2]_n \cdot Cl$ or $CH_3 \cdot CO \cdot [CH_2]_n \cdot Cl$ and potassium iodide (Conant, Kirner, and Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 488); $Ph \cdot S \cdot [CH_2]_n \cdot OH$ and hydrogen bromide (Bennett and Mosses, J., 1931, 2956); the hydrolysis of aliphatic amides (Crocker, J., 1907, **91**, 593); and possibly the dissociation constants of *n*-aliphatic acids.

In a few reactions there is an *increase* of reactivity with increase in length of the carbon chain (Type III). Examples are the relative directive powers of alkoxy-groups as shown by the nitration of *p*-alkoxyanisoles (Robinson and Smith, *loc. cit.*); the rate of chlorination of alkyl ethers of phenol (Bradfield and Jones, *loc. cit.*); and the rate of conversion of alkylamine acetates into amides (Musselius, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 29). In the reactions of the ethers mentioned above, the results could also be interpreted as showing a *decreasing* effect of a longer alkyl chain on the oxygen atom (Type II).

The addition of hydrogen bromide to a series of olefins with non-terminal double bonds shows a new kind of Homologous Series Reactivity, Type IV: constant reactivity with increasing alkyl chain. Apparently the carbon atoms joined by the double bond are not activated by such a small disturbance as the difference between the general effect of an alkyl chain and that of a methyl group, and the reaction with hydrogen bromide is the result of a collision between a hydrogen bromide molecule and an olefin molecule with sufficient vibrational energy in the double bond.

Isolation of 9-*ketoundecoic acid* from the mixture obtained by hydration of undecynoic acid was achieved by making use of the fact that the 10-keto-acid as a methyl ketone gave a sodium bisulphite addition compound, while the ethyl ketone remained unaffected. The substance isolated by Myddleton and Barrett (*J. Amer. Chem. Soc.*, 1927, **49**, 2258) by a tedious series of crystallisations and thought to be 9-ketoundecoic acid (m. p. 43·5°) was actually the eutectic mixture of the two acids.

9-*Hydroxy*- and 9-*bromo-undecoic acids* had lower melting points than the corresponding 10-substituted compounds, but otherwise were very similar and there was no evidence of conversion of 9- into 10-bromo-acid during the addition reactions.

EXPERIMENTAL.

9- *and* 10-*Ketoundecoic Acids*.—$\Delta^{9:10}$-Undecynoic acid (12 g.), m. p. 60°, added to ice-cold sulphuric acid (150 c.c. of 85%), yielded after 48 hours 11·5 g. of distilled keto-acids, m. p. 44—45° (compare Myddleton and Barrett, *loc. cit.*).

Separation of the Keto-acids.—The keto-acid mixture (20 g.) in benzene (150 c.c.) was shaken with concentrated sodium bisulphite solution (400 c.c.) during 70 hours. The bisulphite compound of the 10-keto-acid, filtered off, washed with benzene, and warmed with dilute hydrochloric acid, yielded 9 g. of keto-acid, m. p. 53—55°; this crystallised from benzene–light petroleum in plates (6 g.), m. p. 59°. The semicarbazone melted at 135—136° (Chuit, Boelsing, Hausser, and Malet, *Helv. Chim. Acta*, 1926, **9**, 1074, give m. p. 134—135°).

9-*Ketoundecoic Acid*.—The filtrate from the sodium bisulphite compound of the 10-keto-acid gave on concentration 10 g. of crystals, m. p. 55—57°. After two crystallisations from light petroleum these melted at 58—59° (plates); yield, 7 g. (Found: C, 65·8; H, 9·9. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%). The *semicarbazone* crystallised from alcohol in prisms, m. p. 161° (Found: N, 16·2. $C_{12}H_{23}O_3N_3$ requires N, 16·3%).

Because of the similarity in the melting points the following mixed m. p.'s were taken:

9-*keto-acid* (m. p. 58—59°) with $\Delta^{9:10}$-undecynoic acid (m. p. 61°) gave a mixed m. p. 43—47°; 9-keto-acid with 10-keto-acid, mixed m. p. 43—45°; 10-keto-acid with undecynoic acid, 43—47°.

9-*Hydroxyundecoic Acid.*—Reduction of the 9-keto-acid in alcoholic solution with sodium amalgam (2—4%) was slow, and amalgam from highly purified mercury was almost without action on the ketone. Reduction of the keto-ester with *iso*propyl alcohol and aluminium *iso*propoxide (Ponndorf, *Z. angew. Chem.*, 1926, **39**, 138) gave good results. Methyl 9-ketoundecoate (15 g., from the keto-acid and methyl alcohol in presence of sulphuric acid), aluminium *iso*propoxide (10 g.), and *iso*propyl alcohol (200 c.c.) were heated in a flask provided with an efficient fractionating column so that liquid very slowly distilled during 2 hours. After the solvent had been evaporated, some of the hydroxy-ester was extracted with ether, but much was still mixed with the aluminium compounds. Concentrated hydrochloric acid was then added, and superheated steam passed until no more oily drops distilled. The total yield of hydroxy-ester (and hydroxy-acid) was then hydrolysed with alcoholic potassium hydroxide and gave 10·5 g. of crude hydroxy-acid, m. p. 26°. After two crystallisations from benzene–light petroleum the *acid* melted at 34—35° (Found: C, 65·3; H, 10·8. $C_{11}H_{22}O_3$ requires C, 65·3; H, 10·9%).

9-*Bromoundecoic Acid.*—The hydroxy-acid (4 g.) was heated to 130° during 6 hours while a slow stream of dry hydrogen bromide was passed through the liquid. The product was dissolved in ether, and the ethereal solution washed, dried and evaporated. The distilled *bromo-acid* melted at 22°, and after one crystallisation from hexane, at 27°; yield, 3 g. After four similar crystallisations it had a constant m. p. 30·0° (thermometer in the liquid) and m. p. 31° in a capillary tube (Found: C, 49·7; H, 7·9. $C_{11}H_{21}O_2Br$ requires C, 49·8; H, 7·9%).

Mixtures of 9- *and* 10-*Bromoundecoic Acids.*—These all crystallised slowly and the m. p.'s (clearing points) were taken in the Beckmann apparatus. Mixtures containing 45—57% of the 9-bromo-acid showed a decided arrest at —6° to —4° on heating and often melted completely at this point, but stirring at —5° or seeding with the 10-bromo-acid (m. p. 35·7°) produced the higher-melting form. The eutectic point (16·5° from the curves) was rather indefinite.

As was assumed by Harris and Smith, the curve for the depression of m. p. of 10-bromoundecoic acid by the 9-bromo-acid exactly covers the curve for depression by the 11-bromo-acid.

9-Bromo-acid, mols. %	100	88·8	79·4	71·9	66·1	62·7	59·7	57·5	55·25	53·2	51·05	48·1	45·3	37·5	26·05	17·9	10·0	0·0
M. p.	30·0°	26·65°	23·90°	21·45°	19·45°	18·35°	17·3°	16·5°	17·3°	18·55°	19·65°	20·75°	22·05°	24·95°	28·75°	31·30°	33·17°	35·68°

$\Delta^{9:10}$-*Undecenoic Acid* (iso*Undecenoic Acid*).—Reduction of the mixture of 9- and 10-iodoundecenoic acids (Harris and Smith, *loc. cit.*) with zinc turnings and propionic acid was complete in 48 hours. The product, m. p. 11—13°, was crystallised to m. p. 19·2° (thermometer in the liquid) and iodine number (Hanuš) 138 (calc., 138). For experiments I to M it was necessary to use the purest *iso*undecenoic acid.

Catalytic reduction of $\Delta^{9:10}$-undecynoic acid (hydrogen with colloidal palladium or with nickel) gave products melting at 0—8° and in each case the m. p. was raised 2—3° by allowing the liquid to stand with nitrous acid. This probably indicated a change of *cis*- into *trans*-*iso*-undecenoic acid, but, as saturated impurities were always present, purification was so tedious that the catalytic method was abandoned.

Addition of Hydrogen Bromide.—In the addition experiments of Harris and Smith (*loc. cit.*, p. 1110) the products usually contained a trace of olefin, and, as the analyses and determinations of the equivalents showed, this was not eliminated by distillation. In the present experiments the time for complete saturation of the double bond, especially when hexane was used as solvent, was much greater than had been anticipated. With benzene as solvent, completely saturated products were finally obtained, and after distillation without any attempt at fractionation these gave correct analyses; repeated distillation caused no change in m. p. All the products showed a lower m. p. (— 6° to — 4°), but the eutectic arrest (near + 16°) was very indefinite (as with mixtures of the synthetic acids) and could not be used as a criterion of purity. Addition of a known weight of 10-bromoundecoic acid and redetermination of the m. p. showed on which branch of the curve the product lay, and also confirmed the composition given by the original m. p.

Expts. A—H. The products of experiments A—H (Harris and Smith) had been mixed. As the mixture appeared more strongly reducing than would be accounted for by the presence of any of the catalysts used, 5 g. of it were dissolved in acetic acid (50 c.c.), and the solution kept saturated with hydrogen bromide during 9 days. The solution then reduced very dilute permanganate–sodium carbonate solution only after 3 hours. The product, isolated by dilution with water and extraction with hexane, distilled at 150—157°/0·2 mm. and had *M*, 264, m. p. 19·9° (49·5% of 10-bromoundecoic acid).

In the following experiments hydrogen bromide, not specially dried or freed from air, was passed for 1 hour into a solution (usually 30 c.c.) of pure *iso*undecenoic acid (2 g., m. p. 19·2°) at 0°. The flask was then sealed and kept at room temperature.

Expt. I. Hexane. After 15 hours (50 c.c. of hexane being used instead of 30 c.c.) the solution still reduced permanganate and the product had m. p. approx. 17°. After having stood 50 hours, the hexane solution on evaporation gave 2·64 g. (92% yield) of bromo-acids, *M*, 262 (calc., 265) and m. p. 18·3° (46·2% of 10-bromo-acid). Confirmation : 0·5307 g. of product I, mixed with 0·4142 g. of 10-bromoundecoic acid, had m. p. 27·6°, whence 70·0% yield of 10-bromo-acid in the mixture and 46·6% in product I. The remainder of I was treated with hydrogen bromide in hexane for a further 8 days and then had *M*, 264, m. p. 19·0° (47·6% of 10-bromo-acid).

Expt. J. Acetic acid. After 24 hours, the product appeared free from olefin but had *M*, 264 (calc., 265); the m. p. was 19·1° (47·8% of 10-bromo-acid). 0·2366 G. of 10-bromo-acid, mixed with 0·9981 g. of the product J, had m. p. 23·4°, whence 58·0% of 10-bromo-acid in the mixture and 48·1% in J.

Expt. K. Acetic acid. After 5 days the product had *M*, 264, m. p. 19·2° (48·0% of 10-bromo-acid). 0·3165 G. of 10-bromo-acid, mixed with 0·8417 g. of product K, had m. p. 24·9°, whence 62·0% of 10-bromo-acid in the mixture and 47·8% in K. The remainder of K was kept for a further 18 days with hydrogen bromide in acetic acid and then had *M*, 264, Br, 29·8 (calc., 30·2%) and m. p. 19·7° (49·0% of 10-bromo-acid).

Expt. L. Benzene. After 5 days the solution did not reduce permanganate and the product (yield 96%) had *M*, 265, Br, 30·0% and m. p. 20·05° (49·8% of 10-bromo-acid). Subjected to the action of hydrogen bromide in benzene solution for a further 5 days, this gave product L, which had *M*, 265, m. p. 20·05°. 0·6345 G. of product L, mixed with 0·2856 g. of 10-bromo-acid, had m. p. 26·0°, whence 65·1% of 10-bromo-acid in the mixture and 49·4% in L.

Expt. M. Benzene. After 5 days the product had m. p. 20·1° (50·0% of 10-bromo-acid). After 17 days, product M had *M*, 265, m. p. 20·05° (49·8% of 10-bromo-acid), Br, 30·2 (calc., 30·2%).

Expt. N. Hydrogen was passed for 30 minutes through a solution of diphenylamine (0·05 g.) and *iso*undecenoic acid (1·0 g., m. p. 18·7°) in pure benzene (20 c.c.) at 5°. Hydrogen bromide free from air was then passed for 1 hour (air being excluded) and the flask was sealed for 9 days. While the benzene was being evaporated in a vacuum diphenylamine hydrobromide crystallised and was removed. The product (1·3 g., m. p. 18·4°) was distilled and had m. p. 18·45° (46·5% of 10-bromo-acid). 0·6409 G. of product N, mixed with 0·3014 g. of 10-bromo-acid, had m. p. 25·5°, whence 63·7% of 10-bromoundecoic acid in the mixture and 46·7% in N.

Expt. O. A solution of perbenzoic acid (0·06 g.) and *iso*undecenoic acid (1·0 g., m. p. 18·7°) in pure benzene (20 c.c.) was kept for 40 minutes. It was then cooled to 5° while a slow stream of hydrogen bromide containing oxygen was passed for 1 hour. After 7 days the solvent was evaporated and the product (1·5 g.) was distilled, the first few drops (which contained benzoic acid) being rejected. The distillate, m. p. 17·6°, was redistilled and had m. p. 18·1°; again distilled, it had m. p. 18·2° (45·9% of 10-bromo-acid). 0·8257 G. of product O, mixed with 0·2767 g. of 10-bromo-acid, had m. p. 24·05°, whence 59·6% of 10-bromo-acid in the mixture and 46·1% in O.

TABLE I.

Expt.	Solvent.	Time, days.	Mol. wt. (calc., 265).	M. p.	10-Bromo-acid, mols. %.
A—H	Hexane Benzene Acetic acid	>9	264	19·9°	49·5
I	Hexane	2	262	18·3	46·2 (46·6) *
		10	264	19·0	47·6
J	Acetic acid	1	264	19·1	47·8
K	Acetic acid	5	264	19·2	48·0 (47·8)
		23	264	19·7	49·0
L	Benzene	5	265	20·05	49·8 (49·4)
		10	265	20·1	50·0
M	Benzene	5	—	20·1	50·0
		17	265	20·05	49·8
N	Benzene (+ H_2 + $NHPh_2$)	9	—	18·45	46·5 (46·7)
O	Benzene (+ O_2 + $Ph{\cdot}CO_3H$)	8	—	18·2	45·8 (46·1)

* Figures in parentheses are confirmations by addition of 10-bromo-acid.

Addition of Hydrogen Bromide to iso*Undecenoamide.*—Hydrogen bromide was passed through a solution of *iso*undecenoamide (3·0 g., m. p. 99·5°) in benzene (80 c.c.) at 25°, and the temperature gradually brought to 0°. After having stood 5 hours at 0°, the solution did not reduce permanganate; the solvent was removed at 35°. Conversion of the amido- into the carboxyl group was effected as follows: the viscous yellow residue was dissolved in a mixture of acetic acid (12 c.c.) and sulphuric acid (12 c.c. of 60%), and the solution cooled to 0°. While the solution was vigorously stirred, sodium nitrite (5 g. in 10 c.c. of water) was added during 1 hour. The mixture was then stirred for 1 hour at room temperature and finally for 10 minutes at 70°. After water had been added, the mixture was extracted three times with hexane; the bromo-acids were removed from the hexane solution by extraction with potassium hydroxide solution (5%) and liberated by addition of dilute sulphuric acid. The bromo-acids were again dissolved in hexane, the hexane evaporated, and the residue distilled.

Expt. X_1. The treatment with nitrous acid was less prolonged than described above and crystals of unchanged amide appeared in the distillate. These were removed by centrifuging and the clear oil, m. p. 17·4° (yield, 2·5 g.), was distilled. A few drops (b. p. $<$ 150°/0·2 mm.) were rejected; the remainder (product X_1; yield, 2·2 g.) had *M*, 267·5, m. p. 18·0° (45·7% of 10-bromo-acid). 0·8995 G. of product X_1, mixed with 0·3441 g. of the 10-bromo-acid, had m. p. 24·5°, whence 61·0% of 10-bromo-acid in the mixture and 46·1% in product X_1.

Expt. X_2. The mixture of bromo-acids (2·6 g.) on distillation yielded 2·3 g. of light yellow oil, *M*, 266, m. p. 18·8° (47·1% of 10-bromo-acid). 0·9128 G. of product X_2, mixed with 0·3538 g. of 10-bromo-acid, had m. p. 24·9°, whence 62·0% of 10-bromo-acid in the mixture and 47·3% in X_2.

iso*Undecenol.*—A mixture of *iso*undecenoic acid (15 g., m. p. 18·7°), ethyl alcohol (100 c.c.), and hydrogen chloride (3 g.), heated under reflux during 12 hours, yielded 17 g. of ethyl *iso*undecenoate, b. p. 120°/0·2 mm. Reduction of the ester (15·3 g.) in dry alcohol (50 c.c.) with sodium (11 g.), followed by distillation in superheated steam, gave *iso*undecenol (9·6 g.; yield, 78%), b. p. 92°/0·1 mm. Chuit, Boelsing, Hausser, and Malet (*loc. cit.*, p. 1089) give b. p. 130°/13 mm. (Found: C, 77·6; H, 12·8. Calc.: C, 77·6; H, 12·9%).

Addition of Hydrogen Bromide.—Hexane was chosen as solvent because the mixture of bromoundecanols separated within 5 hours and no conversion of $CH_2{\cdot}OH$ into CH_2Br occurred. The speed of the reaction was surprising in view of the slow addition of hydrogen bromide to *iso*undecenoic acid.

Hydrogen bromide was passed for 30 minutes into an ice-cold solution of *iso*undecenol (4·0 g.) in hexane (70 c.c.). When the mixture had stood for 3 hours at 0°, hydrogen bromide was passed for 10 minutes. After having stood for a total of 5 hours, the mixture had separated into two layers, both of which failed to reduce permanganate solution. The solvent was evaporated under reduced pressure, mainly at 0° and finally at 50°; yield, 5·9 g. A portion was distilled at 0·1 mm. for analysis (Found: Br, 31·9. Calc.: Br, 31·9%). Further preparations gave similar results.

Oxidation.—Nitric acid in any concentration was useless, and alkaline or neutral solutions of potassium permanganate caused loss of bromine. By the use of chromium trioxide in acetic acid in presence of potassium hydrogen sulphate (Willstätter, Mayer, and Hümi, *Annalen*, 1910, **378**, 104) yields of 50—70% were obtained, the loss being due mainly to esterification. Esterification also occurred during oxidation with sodium dichromate and 50% sulphuric acid.

Expt. Z_1. The mixture of bromoundecanols (5·2 g.) was suspended in sulphuric acid (100 c.c. of 50%) and stirred efficiently at 60°. Sodium dichromate (5 g., 1·2 mols.) in warm water (5 c.c.) was added gradually during ½ hour, and the mixture stirred ½ hour longer. The green liquid was extracted three times with hexane, the extract shaken with ice-cold potassium hydroxide solution (three times, each with 20 c.c. of 5% solution, which did not attack the bromine atoms), and the aqueous solution acidified. The bromo-acids, collected by complete extraction with hexane, were distilled (the first 3 drops being rejected), b. p. 149—156°/0·2 mm.; yield, 1·44 g., 26%. The m. p. (17·3°) indicated 44·3% of 10-bromoundecoic acid, but the product was not pure (Found: Br, 29·0; *M*, 266. Calc.: Br, 30·2%; *M*, 265).

Expt. Z_2. A solution of chromium trioxide (2·5 g., 1·2 mols.) in acetic acid (15 c.c.) and water (3 c.c.) was stirred at 50° along with finely powdered potassium bisulphate (3 g.). When the mixture of bromoundecanols (4·0 g., 1 mol.) in cold acetic acid (10 c.c.) was added in one portion, the temperature rose to 80°; it was then maintained at 90° for 10 minutes, dilute sulphuric acid (60 c.c. of 4%) added, and the mixture stirred for 5 minutes at 90°. The bromo-acids had b. p. 151—155°/0·2 mm. (yield, 2·3 g., 54%), *M*, 256·5, and m. p. 16·1°. The product was mixed with that from Z_3 (below).

Expt. Z_3. Another portion of the bromoundecanol mixture (5·0 g.), oxidised as in Z_2, gave 3·6 g. of distilled product, m. p. 15°; yield, 68% (the chromate liquor gave a slight reaction for bromide, indicating loss of bromine by hydrolysis). The distilled products Z_2 and Z_3 (5·5 g.) on fractional distillation gave 0·6 g., b. p. 120—151°/0·1 mm., and 4·6 g., b. p. 151—155°, *M*, 261, and m. p. 17·6°. On redistillation the second fraction gave 0·3 g., b. p. 151—152°, and 4 g., b. p. 152—155°, *M*, 261, Br, 29·1%, m. p. 17·6°: thus no separation from the impurity was effected. For a binary mixture of the bromo-acids, m. p. 17·6° corresponds to 45% of the 10-bromo-acid. 0·5161 G. of the mixture, added to 0·5275 g. of 10-bromo-acid, gave a new mixture, m. p. 28·5°, whence 45·2% of 10-bromo-acid in $Z_2 + Z_3$.

TABLE II.

Addition of Hydrogen Bromide to *iso*Undecenoamide in Benzene.

Product converted into 9- and 10-bromoundecoic acids.

Expt.	Yield, %.	Mol. wt. (calc., 265).	M. p.	10-Bromo-acid, mols. %.
X_1	73	267·5	18·0°	45·7 (46·1)
X_2	77	266	18·8	47·3

Addition of Hydrogen Bromide to *iso*Undecenol in Hexane.

Product converted into 9- and 10-bromoundecoic acids.

Expt.	Oxidising agent.	Yield, %.	Mol. wt.	M. p.	10-Bromo-acid, mols. %.
Z_1	$Na_2Cr_2O_7 + H_2SO_4$ aq.	26	267	17·3°	44·3
Z_2	$CrO_3 + AcOH + KHSO_4$	55	261	17·6	45·0 (45·2)
Z_3	,, ,,	68			

SUMMARY.

1. Addition of hydrogen bromide to *iso*undecenoic acid, $CH_3{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2H$, yields 50% each of 9- and 10-bromoundecoic acids.
2. There is no "peroxide effect" * on the orientation, but the reaction appears to be fastest in benzene, a solvent which favours the "peroxide catalysed" reaction with *terminal* double bonds.
3. The solvent has no effect on the orientation of addition.
4. Conversion of the CO_2H group into $CO{\cdot}NH_2$ or even into $CH_2{\cdot}OH$ has no appreciable effect on the proportion of 9- and 10-bromo-compounds formed; the rate of addition, however, is much faster than to the acid.
5. A classification of reactivity in homologous series is given in which the reaction $CH_3{\cdot}CH{:}CHR + HBr$ is classed as Type IV, the reactivity of the unsaturated carbon atoms being independent of the length of the alkyl chain.
6. 9-Ketoundecoic acid has been separated from the acids formed on hydration of undecynoic acid, and melts at 58—59°, not 43·5° (literature).
7. The binary system 9- and 10-bromoundecoic acids has been used for analysis of the addition products.

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* (*Note added, June 4th*, 1937). It has been shown by Harris and Smith (J., 1935, 1573) that with 10 : 11-undecenoic acid "molecular oxygen is essential to the 'peroxide' effect, and catalysts such as perbenzoic acid have a supplementary action." Urushibara and Takebayashi (*Bull. Chem. Soc. Japan*, 1937, **12**, 54) confirm this assertion by experiments with allyl bromide and state that dissolved oxygen is the active catalyst, but by quoting the sentence given above without the words "and catalysts such as perbenzoic acid have a supplementary action" they misinterpret the views of Harris and Smith. Oxygen *alone* will not in *all* circumstances bring about the so-called "peroxide" effect: pure undecenoic acid in hexane, for example, needs the *supplementary* action of such catalysts as water or epoxyundecoic acid. As it is agreed that molecular oxygen is the essential and the active catalyst, further confusion would be avoided by use of the term "oxygen" effect instead of "peroxide" effect.—J.C.S.