100. *Addition of Hydrogen Bromide to Double Bonds. Undecenoic Acid.*

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The use of 11-bromoundecoic acid in synthetic work in this laboratory made it essential to investigate closely the addition of hydrogen bromide to undecenoic acid. From the literature it appeared that the addition gave either 11- or 10-bromoundecoic acid in an arbitrary manner, but some similar problems had been dealt with by Kharasch and his co-workers (*J. Amer. Chem. Soc.*, 1933, **55**, 2468, 2521, 2531; 1934, **56**, 244), who showed that with vinyl bromide and allyl bromide the direction of addition of hydrogen bromide was influenced by a " peroxide effect " owing to the presence of peroxides or even of oxygen in the reacting system. This hitherto unrecognised peroxide factor had obviously been the cause of many conflicting results; some olefinic substances, however, were not affected by oxygen but only by actual peroxide. For instance, propylene which added hydrogen bromide in presence or absence of air to yield exclusively *iso*propyl bromide gave *n*-propyl bromide if benzoyl peroxide was added to the reacting mixture. Usually, therefore, addition to propylene is covered by the Markownikoff rule (*Annalen*, 1870, **153**, 256). Kharasch investigated the effect of solvents, temperature, and light on the addition of hydrogen bromide to allyl bromide and concluded that the peroxide factor was the most important one in determining the orientation. On the other hand, Boorman, Linstead, and Rydon (J., 1933, 568), who studied the addition of hydrogen bromide to lower members of the olefinic acids, found that the solvent was a very important factor, as Walker and Lumsden (J., 1901, **79**, 1191) had observed with undecenoic acid. Recently (*Nature*, 1933, **132**, 643) Linstead and Rydon stated that the direction of addition of hydrogen bromide to allylacetic acid in hexane (in which δ-bromovaleric acid was formed) could not be reversed by exclusion of air to give the γ-isomeride, that " the importance of the peroxide effect varies with different acids and that it cannot account for the influence of the solvent on the addition of hydrogen bromide to allylacetic acid."

When the action of hydrogen bromide on commercial samples of undecenoic acid was investigated (*Nature*, 1933, **132**, 447) in the light of Kharasch's observations, it was found that in ligroin or hexane solution in presence of air the product was almost entirely 11-bromoundecoic acid; in absence of air the 10-bromo-acid was the main product. Purification of the undecenoic acid finally produced samples the reactions of which with hydrogen bromide were insensitive to oxygen, yielding the 10-bromo-acid. When, however, the solvent was changed to benzene or toluene, the purest undecenoic acid was still sensitive to oxygen.

TABLE I.

Addition of hydrogen bromide to impure undecenoic acid.

Expt. No.	Acid used.	Solvent.	In presence of	Product; mols. % of 11-bromo-acid.	Remarks.
1	B.D.H. (m. p. 19—21°)	Ligroin (purified)	Air	80—90	10—25% Soln. at − 15° to 0°. Several experiments.
2	,,	,,	Hydrogen	10—25	
3	,,	,,	$H_2 + Ph_2NH$	7—15	5 Mols. % of Ph_2NH dissolved in the ligroin. Passed HBr immediately.
4	,,	,,	Air + Ph_2NH	8	
5	,,	Toluene	Air	85—95	
6	Distilled (m. p. 22—23°)	Ligroin	Air	80	
7	,,	,,	Hydrogen	17	
8	,,	Toluene	Air	84	
9	,,	AcOH	Air	17	99% AcOH distilled from CrO_3.
10	,,	AcOH, 90%	,,	31	
11	,,	,, , 75%	,,	29	
12	,,	Ether	,,	11	The ether gave a slight reaction for peroxide.
13	Crystallised (m. p. 23·7°)	Ligroin	,,	Mainly 10-	
14	,,	,,	Air stream	Mainly 11-	Air was passed in through a tube.

Our results with various samples of the acid are set out in Tables I and II. The products, nearly all of which were free from unsaturated acid, were analysed by the thermal method and the percentages are probably correct to ± 5 units. Unless otherwise stated, the solutions contained 10% of undecenoic acid, and hydrogen bromide was passed in immediately after they were made. Where experiments were done in duplicate, the average percentage is given (*i.e.*, of 11-bromo-acid; the remainder is 10-bromo-).

*Effect of Impurities.**—As the impurities are removed, the undecenoic acid becomes less sensitive to oxygen. At first, with the crude material (f. p. 19—21°) in ligroin solution, very little air or oxygen in the reaction flask will cause addition of hydrogen bromide so as to form mainly 11-bromoundecoic acid (1). Even the material of f. p. 23° readily gives this acid (6), but specimens of f. p. 23·7° need an air stream along with the hydrogen bromide, otherwise the product is mainly the 10-bromo-isomeride (13, 14). Finally, the pure acid, f. p. 24·6°, in ligroin solution needs the addition of perbenzoic acid, or unsaturated aldehyde (29, 30), or water before the 11-bromo-acid can be formed, and these catalysts are not always effective (20—33).

It was of interest to investigate the impurities which appeared to be such powerful oxygen carriers. The preliminary results suggested substances similar to the unsaturated

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* Numbers in parentheses refer to the experiments in Tables I and II.

TABLE II.

Addition of hydrogen bromide to pure undecenoic acid at 0°.

Expt. No.	Solvent.	In presence of	Product; mols. % of 11-bromo-acid.	Remarks.
20	Ligroin (purified)	Air	13	
21	,,	Oxygen	12	
22	,,	Hydrogen	13	
23	,,	Air	15	Stood 1 hr. with H_2O_2 soln. and then decanted before passing HBr.
24	,,	$(Ph\cdot CO\cdot O)_2$ (5 mols. %)	15	Stood 3 hrs. before passing HBr.
25	,,	$Ph\cdot CO_3H$,,	16	,, 3·5 ,, ,, ,,
26	,,	$Ph\cdot CO_3H$,,	85	,, 12 ,, ,, ,,
27	,,	Heptaldehyde (10 mols.)	11	,, 14 ,, ,, ,,
28	,,	Residue from purification of undecenoic acid (5%)	83	,, 12 ,, ,, ,,
29	,,	$C_{14}H_{26}O$* (10 mols. %)	88	,, 30 ,, ,, ,,
30	,,	,, ,,	85	,, 3 mins. ,, ,,
31	,,	Air	12	1 G. acid in 50 c.c. ligroin.
32	,,	Nitric oxide	—	Product mainly 10-bromo-, but not binary. Also with acid, m.p. 22°.
33	,,	Air + water	94	0·3 G. H_2O to 10 c.c. ligroin.
34	,,	H_2 + water	20	1 C.c. H_2O to 16 c.c. ligroin.
40	Hexane	Air	25	Trace of unchanged acid.
41	,,	,,	14	No unchanged acid.
42	,,	$Ph\cdot CO_3H$ (5 mols. %)	87	Allowed to stand 12 hrs.
45	Ether	Air	5	Very slow reaction. Passed HBr for 6 hrs. The ether contained peroxide.
46	,,	$Ph\cdot CO_3H$	14	Stood 14 hrs.
50	AcOH (pure)	Air	9	HBr + air passed in at 30°.
51	,,	$Ph\cdot CO_3H$	7	Stood 12 hrs.
55	H_2O (suspension)	Air	11	At 35°.
60	Toluene	,,	97	
61	Toluene (A.R.)	,,	98	
62	,, ,,	H_2	12	
63	,, ,,	Water + air	92	3 C.c. H_2O to 10 c.c. toluene.
64	Benzene ,,	Air	94	
65	Benzene (m. p. 5·55°)	,,	95	Specially pure acid (m. p. 24·58°) again crystallised twice from pure hexane. 1·5 G. in 15 c.c. benzene.
66	,, ,,	,,	64	2·0 G. in 5 c.c. benzene.
67	,, ,,	,,	29	2·0 G. in 2 c.c. benzene.
68	No solvent	,,	10	Pure acid + HBr; 12 hrs. at 30°.
69	Benzene (m. p. 5·55°)	H_2	12	
70	,,	Air + water	92	0·3 G. water to 10 c.c. benzene.
71	,,	H_2 + water	11	,, ,, ,,

* From heptaldehyde.

aldehyde, $C_{14}H_{26}O$, formed by the action of alcoholic potash on heptaldehyde (Perkin, J., 1883, **43**, 45), and this was a powerful catalyst (29, 30). The heptaldehyde formed during the distillation of ricinoleic acid (castor oil) must be the origin of the catalytic impurities in commercial undecenoic acid.

Effect of Solvents.—In the absence of oxygen (presence of hydrogen or diphenylamine) undecenoic acid, molten or dissolved in any of the solvents, adds hydrogen bromide to form 10-bromoundecoic acid. In the presence of oxygen the molten acid yields 10-bromoundecoic acid (68) and so also do solutions in hexane, ligroin, ether, or acetic acid (100, 90, or 75% acid) (20, 21, 31, 41, 45, 50); but in benzene or toluene the main product is the 11-bromo-acid (60, 61, 64, 65, 66). If the concentration of undecenoic acid in benzene solution is increased, the proportion of the 10-bromo-acid formed increases, a 55% solution giving 71%, the 100% solution (pure acid) giving 90% of 10-bromoundecoic acid (66, 67, 68).

In acetic acid or in ethereal solution, 12 hours' standing with perbenzoic acid fails to make undecenoic acid add hydrogen bromide to give the 11-bromo-acid as the main product, although in ether a small increase in the proportion of this acid is noticed (45, 46).

The effect of a solvent, therefore, is to allow or to impede the action of oxygen or peroxide on the reaction with hydrogen bromide. There is little influence on the proportion of isomerides formed *in the absence of oxygen, i.e.*, in the normal reaction.

The Peroxide Effect.—First, it should be noted that in some cases the peroxide effect may not operate because of the shape of the vessel. Solutions which had reacted in a flask with hydrogen bromide to give 11-bromoundecoic acid, when placed in a test-tube gave mainly the 10-bromo-acid because (*a*) the liquid surface exposed to the air was too small and (*b*) a sudden rush of hydrogen bromide could remove the air immediately above the liquid surface.

In all cases where air, oxygen, or peroxide influences the reaction, the effect is to increase the proportion of the 11-bromo-acid. This is true whether the solvent is hexane, ligroin, benzene, toluene, or ether. The peroxide effect, therefore, is one which reverses the normal direction of addition.

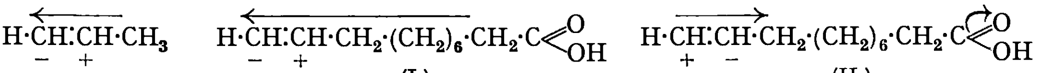
Kharasch investigated the influence of other gases and found that only oxygen had a peroxide effect. We have found similarly that an atmosphere of nitric oxide has much the same effect as one of hydrogen (32).

Effect of Moisture.—Expts. No. 33, 34, 63, 70, and 71 show that, although water has no apparent influence on the normal reaction (formation of 10-bromoundecoic acid in absence of air), yet it makes the peroxide effect possible with *air* where the dry solution would require the addition of an oxygen carrier (21, 26, 28).

Effects on the reaction in toluene, at that time attributed to the action of water, were observed in this laboratory (compare report of Chemical Society Discussion, *J. Soc. Chem. Ind.*, 1933, **52**, 219) by Dr. Urushibara working in collaboration with Professors Barger and Robinson. Professor Robinson (private communication) has, however, pointed out that " traces of water " were introduced merely by exposing the contents of the flask to moist air, and on the subsequent appearance of the paper of Kharasch and Mayo it was clear that further experiments were required before it could be decided whether the active catalyst was indeed water or, as hitherto unsuspected, the oxygen of the air.

The result with an aqueous suspension of undecenoic acid (55) is readily understood. The liquid acid, dry or moist, is not sensitive to oxygen, nor is its solution in water. In Expt. No. 33 it is the *ligroin* solution which is rendered susceptible to air by the water.

Interpretation of Results.—As the normal addition of hydrogen bromide to pure undecenoic acid either alone or in solution yields mainly 10-bromoundecoic acid, the orientation follows the Markownikoff rule. Just as with propylene, addition is orientated by the relative charges on the carbon atoms united by the double bond (I) (compare Lucas and Moyse, *J. Amer. Chem. Soc.*, 1925, **47**, 1459):



$$\overleftarrow{\mathrm{H{\cdot}\underset{-}{C}H{:}\underset{+}{C}H}}\mathrm{{\cdot}CH_3} \qquad \overleftarrow{\mathrm{H{\cdot}\underset{-}{C}H{:}\underset{+}{C}H{\cdot}CH_2{\cdot}(CH_2)_6}}\mathrm{{\cdot}CH_2{\cdot}C}{<}^{\mathrm{O}}_{\mathrm{OH}} \qquad \overrightarrow{\mathrm{H{\cdot}\underset{+}{C}H{:}\underset{-}{C}H{\cdot}CH_2{\cdot}(CH_2)_6{\cdot}CH_2{\cdot}C}}{<}^{\curvearrowright\mathrm{O}}_{\mathrm{OH}}$$

(I.) (II.)

No evidence exists in support of the view that the distant carboxyl group can influence the orientation in additions to undecenoic acid (II). The Δ^{α}-, Δ^{β}-, and Δ^{γ}-acids studied by Boorman, Linstead, and Rydon present a more complex problem because of the influence of the carboxyl group on the double bond. This influence should be weak with the Δ^{γ}-acids, and the peroxide effect should be detectable; Linstead and Rydon (*Nature, loc. cit.*) found that the addition of hydrogen bromide to allylacetic acid (without solvent) could be reversed in the presence of benzoyl peroxide, the product then being δ-bromovaleric acid.

	" Normal " addition.	Peroxide catalysed.
$CH_2{:}CH{\cdot}CH_3$	$CH_3{\cdot}CHBr{\cdot}CH_3$	$CH_2Br{\cdot}CH_2{\cdot}CH_3$.[1]
$CH_2{:}CH{\cdot}CH_2Br$	$CH_3{\cdot}CHBr{\cdot}CH_2Br$	$CH_2Br{\cdot}CH_2{\cdot}CH_2Br$.[2]
$CH_2{:}CH{\cdot}Br$	$CH_3{\cdot}CHBr_2$	$CH_2Br{\cdot}CH_2Br$.[3]
$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	($CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$) ?	$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.[4]
$CH_2{:}CH{\cdot}(CH_2)_8{\cdot}CO_2H$	$CH_3{\cdot}CHBr{\cdot}(CH_2)_8{\cdot}CO_2H$	$CH_2Br{\cdot}CH_2{\cdot}(CH_2)_8{\cdot}CO_2H$.
$CH_2{:}CH{\cdot}CH_2{\cdot}CMe_3$	$CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CMe_3$	$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_3$.[5]

[1] Kharasch, McNab, and Mayo. [2] Kharasch and Mayo. [3] Kharasch, McNab, and Mayo.
[4] Linstead and Rydon. [5] Kharasch, Hannum, and Gladstone.

It is important to note that in all cases where the peroxide effect has been observed the double bond is in a terminal position. Until it is known whether double bonds in other positions show the peroxide effect in their reactions, a possible constitutional factor is undetermined. It has been noted, however, that oxygen has an effect on other reactions; *e.g.*, it retards the chlorination of benzene (Luther and Goldberg, *Z. physikal. Chem.*, 1906, **56**, 43) and accelerates the side-chain bromination of 2 : 2′-ditolyl (Hannon and Kenner, this vol., p. 138). Other examples are given by Lenher (*J. Amer. Chem. Soc.*, 1931, **53**, 3763), and the anticatalytic effect of traces of oxygen on the combination of hydrogen and chlorine is well known.

EXPERIMENTAL.

Undecenoic Acid.—The commercial acid (f. p. 19—21°) was fractionally distilled, most of the impurity being low boiling. The main fraction (b. p. 119°/0·4 mm., f. p. 22—23°) was crystallised four times from ligroin at − 14°, and the f. p. was then constant at 24·57°, m. p. 24·58°, m. p. in a capillary tube 25·5°. The yield was 8 g. of pure acid from 30 g. of acid of f. p. 22·5°. For some experiments material of f. p. 24·57° was recrystallised twice from purified ligroin. After standing for some hours the acid melted at 24·42°, but again at 24·58° after being heated in a vacuum. Krafft (*Ber.*, 1877, **10**, 2035) gives m. p. 24·5°.

Hydrogen bromide was prepared by the action of bromine on hot tetralin, washed by passing twice through cold tetralin and over moist red phosphorus, then dried (if necessary) with phosphorus pentoxide.

Ligroin. The commercial product (b. p. 60—80°) contained olefins. It was shaken with three successive quantities of oleum (30% SO_3), washed with sodium hydroxide solution, then with water, dried (sodium sulphate), and distilled.

11-*Bromoundecoic Acid.*—This acid was conveniently made from *partly* purified undecenoic acid. Hydrogen bromide (undried) was passed rapidly into a solution of the acid (m. p. 22°; 50 g.) in purified ligroin (350 c.c.) at 0° in a 600—800 c.c. conical flask. The size of the delivery tube did not seem important, and the flask could be open to the air or closed with a calcium chloride tube. After 20—30 minutes a solid appeared, and the flask was shaken frequently for a further 20 minutes while the gas was passed in. The solid, which became pink, was filtered off after cooling to − 12°, and transferred to a porous plate. When dry it was almost colourless, m. p. (capillary tube) 45—48° (yield, 45—53 g.). It is necessary to observe the conditions carefully. As was shown in Expts. 20, 33, pure undecenoic acid will need addition of water (or peroxide). Crude acid (f. p. 19—20°) gives a product of m. p. *ca.* 44°, which is not easily purified. If the temperature is below 0° at the beginning, undecenoic acid may crystallise and delay the reaction. Unless the apparatus has been generating hydrogen bromide for a long time the gas should contain sufficient air, but in order to make certain, the wash-bottles should be opened for a few seconds before the reaction flask is connected. Use of unpurified ligroin greatly reduces the yield of 11-bromoundecoic acid, and moreover, the product is difficult to purify.

The crude product, m. p. 45—48°, was crystallised three times from ligroin and then had f. p. 49·23°, m. p. 49·25° (in a capillary tube 50°). Walker and Lumsden (*loc. cit.*) gave m. p. 51°.

If benzene is used as the solvent in this preparation, it should be removed in a vacuum, and the product crystallised from ligroin.

10-*Bromoundecoic Acid.*—Dry hydrogen bromide was passed into a solution of *pure* undecenoic acid (f. p. 24·5°, 7 g.) in purified ligroin (25 c.c.) for 40 mins.; no precipitate appeared. After the mixture had stood for 2 hrs. the solvent was removed in a vacuum at 60°. The residue was allowed to solidify slowly, and when about one-tenth remained liquid this was drained off. The solid (m. p. 33°, 7 g.) was crystallised 3 times from ligroin at − 15° and then melted at 35·1° (capillary tube, 35·5—36°). Brunner (*Ber.*, 1886, **19**, 2226) gave m. p. 35°. The substance crystallises much more slowly than the 11-bromo-acid.

In this preparation the essentials are *pure* undecenoic acid and the use of ligroin as solvent; the presence of air has no effect, unless some water is added (compare Expts. 20 and 33 above). Slightly impure acid will need the addition of diphenylamine (3—5 mols. %) or displacement of the air with hydrogen. It was found much less satisfactory to use undecenoic acid freezing below 23°, because the low-melting products were then purified with great loss.

Mixtures of 10- *and* 11-*Bromoundecoic Acid.*—As the mixtures crystallised rather slowly, m. p.'s (clearing points) were recorded instead of f. p.'s. The low values of the clearing points obtained when mixtures of 54·5, 50·7, and 42·4% of 11-bromo-acid are heated quickly after freezing may indicate polymorphism of this acid. Otherwise, the system is of the simplest eutectic type.

11-Bromo-acid, mols. %	100	96·2	91·4	82·8	73·3	59·7	54·5	50·7	42·4
Clearing point	49·25°	48·32°	47·21°	45·13°	42·57°	38·36°	36·37° (32·2°)	34·92° (30·4°)	31·35° (?25·0°)
11-Bromo-acid, mols. %	37·1	34·1	31·5	29·7	24·7	16·5	8·4	3·7	0
Clearing point	28·09°	25·53°	26·25°	27·05°	28·34°	30·74°	32·95°	34·14°	35·07°

Eutectic temp. 25·5° at 34% 11-bromoundecoic acid.

Addition of Hydrogen Bromide.—Most of the small-scale experiments, the results of which are given in Tables I and II, were carried out as follows : 1—2 g. of undecenoic acid were weighed into a 100-c.c. distilling flask, and the solvent (10—25 c.c.) added. An inlet tube (3 mm. internal diameter) passed through a rubber stopper and led the hydrogen bromide below the surface of the solution. A calcium chloride tube was attached to the side tube, and the flask was immersed in ice-water. The apparatus was exposed to the ordinary laboratory daylight. After the solvent had been removed in a vacuum (usually at 50°), the weight of hydrogen bromide absorbed could be ascertained, and as a check the product was tested with permanganate. Most of the diphenylamine was removed by rapid filtration after the reaction; for the presence of the other addenda corrections were applied, the effect of addition of a second amount of the substance having been determined. Although many factors were not controlled, this technique gave quite consistent results.

Impurities in Undecenoic Acid.—Distillation of 50 c.c. of early fractions (b. p. 80—120°/ 0·4 mm.) of commercial acid through a long column gave only 12 c.c. of b. p. 89—105°/0·5 mm. (Found : C, 73·8; H, 11·4. Calc. for $C_7H_{14}O$: C, 73·7; H, 12·3. Calc. for $C_{14}H_{26}O_2$: C, 74·3; H, 11·5%), and 6 c.c. of b. p. 105—116°. Apparently the b. p. of the early fractions had risen on keeping. Expt. No. 28 showed that the fraction of b. p. 89—105°/0·5 mm. was a peroxide catalyst.

Heptaldehyde (b. p. 152—153°) was polymerised (condensed) with alcoholic potassium hydroxide (Perkin, *loc. cit.*), the product washed with water, and dried with sodium sulphate (Expts. 29, 30). Further work is being done on this substance and its catalytic activity.

SUMMARY.

Addition of hydrogen bromide to undecenoic acid in any solvent in the *absence* of air gives mainly 10-bromoundecoic acid (following the Markownikoff rule). In the *presence* of air the product varies with the solvent, some solvents favouring and some hindering the " peroxide effect." Impure specimens of undecenoic acid more readily yield 11-bromoundecoic acid than the pure acid does.

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