# 442. *Investigation of the Olefinic Acids. Part XV. The Effect of Peroxides on the Orientation of the Addition of Hydrogen Bromide to Vinyl- and Allyl-acetic Acids.*

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IN a recent paper (Boorman, Linstead, and Rydon, J., **1933**, 568) it was shown that the direction of the addition of hydrogen bromide to vinyl- and allyl-acetic acids was determined by the nature of the solvent. The bromine atom attached itself to the carbon atom nearer the carboxyl group (proximate addition *) under the following conditions: in the absence of solvent, in the presence of water, or in solution in acetic acid or ether; if, however, the acid was dissolved in a hydrocarbon solvent, this orientation was reversed (distant addition *). In investigations on similar additions to unsaturated bromides and hydrocarbons, Kharasch and Mayo (*J. Amer. Chem. Soc.*, **1933**, **55**, 2468) and Kharasch, McNab, and Mayo (*ibid.*, pp. 2521, 2531, and subsequent papers) showed conclusively that the presence of peroxides was of vital importance in determining the orientation; for instance, allyl bromide underwent distant (1 : 3) addition in the presence of added peroxide, oxygen, or oxygen-containing solvents but proximate (1 : 2) addition in the presence of anti-oxidants, or when the pure material was allowed to react in an atmosphere of hydrogen. Kharasch and his co-workers observed that distant addition preponderated in hydrocarbon solvents but not in acetic acid, a fact which was attributed to the anti-oxidant properties of the latter.

It therefore seemed possible that the reversal of addition observed with unsaturated acids was due to the same cause, particularly as the solvent effects were similar. This possibility appeared to be strengthened by Smith's observation (*Nature*, **1933**, **132**, 447) that the usual orientation of the addition of hydrogen bromide to undecenoic acid in petroleum was substantially reversed in the presence of anti-oxidants. Ashton and Smith's more recent results (this vol., p. 435) indicate that undecenoic acid, unless highly purified, contains traces of material which readily forms an active peroxide.

The behaviour of vinyl- and allyl-acetic acids has now been re-examined with the following results: (1) The direction of addition to both acids in hexane (normally distant)

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* These terms have the advantage over "terminal" and "non-terminal" that they can be used for additions to other than terminal double bonds, the term *distant* being applied to the carbon atom further removed from the characteristic atom or group (carboxyl, bromine, etc.).

is *not* reversed by the presence of anti-oxidants (hydrogen, quinol, diphenylamine). (2) Addition to vinylacetic acid in the absence of solvent (proximate) is unchanged in the presence of 1% of benzoyl peroxide. (3) Addition to freshly prepared allylacetic acid without solvent occurs in the same direction (proximate) as that to old samples which contain peroxide. (4) Admixture of 1% of benzoyl peroxide, however, *reverses* the normal addition to allylacetic acid in the absence of solvent, and this provides the only difference from our previous observations.

These experiments gave unambiguous results, and homogeneous solid bromo-acids were obtained except in two experiments (see below) where the orientation was determined indirectly. Addition did not proceed in both directions simultaneously to any appreciable extent.

It is clear that peroxides exert a much smaller influence on additions to these unsaturated acids than on those to unsaturated bromides and the orienting effects of solvents cannot in this case be due to variations in the peroxide effect. The previous generalisations (J., 1933, 569) may be amplified as follows. The normal addition (which follows the Markownikoff rule) may be completely masked by the effect of the carboxyl group and the presence of peroxides. It is necessary from the results of Ashton and Smith to recognise that the direct effect of the carboxyl group ceases to operate when the number of methylene groups intervening between the carboxyl and the double bond is increased from 2 to 8. The point of inflexion can only be found by experimental study of intermediate acids. The importance of the *peroxide effect* is variable and the results so far obtained indicate that it decreases as the double bond approaches the carboxyl group.

## EXPERIMENTAL.

Vinyl- and allyl-acetic acids were prepared and purified by methods already described (J., 1933, 560, 582). The additions of hydrogen bromide were carried out by the standard procedure (J., 1933, 568). Redistilled sodium-dried *n*-hexane was used as solvent.

*Addition to Vinylacetic Acid.*—(i) *In hexane in an atmosphere of hydrogen.* Air was expelled from the apparatus by means of hydrogen. Reaction was complete in ½ hour. After removal of the solvent the product solidified in ice, and had m. p. 31°, mixed m. p. with γ-bromobutyric acid, 32°.

(ii) *In hexane in the presence of quinol* (1%). Reaction was complete in ½ hour. The product solidified in ice; m. p. 31°, mixed m. p. 32°.

(iii) *In hexane in the presence of diphenylamine* (1%). The reaction was complete in 20 minutes. The product solidified in ice; m. p. 32°, mixed m. p. 32—33°.

(iv) *In the presence of benzoyl peroxide without a solvent.* Benzoyl peroxide (1%) was added to the acid. Five saturations on successive days were necessary for the completion of the reaction. The product solidified immediately in a freezing mixture and had m. p. 14—18° On analysis by the method previously used (Boorman, Linstead, and Rydon, *loc. cit.*) it was shown to contain only 0·4% (corr.) of the γ-bromo-acid (Found: equiv., by titration with baryta, 164·1. Calc., 167·1).

*Addition to Allylacetic Acid.*—(i) *In hexane solution in an atmosphere of hydrogen.* Air was first displaced by hydrogen. The product on removal of the solvent had m. p. 40°, unchanged on admixture with authentic δ-bromovaleric acid.

(ii) *In hexane in the presence of quinol* (1%). This experiment was duplicated. The product had m. p. and mixed m. p. 40°.

(iii) *In hexane in the presence of diphenylamine* (1%). This experiment was duplicated. During the addition, about 50% of the product was deposited in crystalline form (m. p. 39°, mixed m. p. 39°). The remainder solidified readily on removal of the solvent at room temperature and had m. p. and mixed m. p. 40°.

(iv) *To stale acids without a solvent.* A year-old specimen, giving a positive thiocyanate reaction (Kharasch, *et al., locc. cit.*), was used. The addition proceeded normally, but the product did not solidify in a freezing mixture. Esterification by the usual method gave a poor yield (54%) of bromo-ester, b. p. 109—110°/18 mm., there being a considerable amount of acrid high-boiling residue. The bromo-ester, on malonation, hydrolysis, and decarboxylation, gave a 90% yield of dicarboxylic acid. The solid that separated first had m. p. 92°, mixed m. p. with β-methyladipic acid, 93°. After complete solidification the solid had m. p. 90°. On recrystallisation from benzene it melted at 94°, unchanged on admixture with authentic β-methyladipic acid.

(v) *Addition in the presence of benzoyl peroxide* (1%). On removal of the reaction vessel from the ice-bath (after the passage of hydrogen bromide) a violent exothermic reaction occurred. The product did not solidify in a freezing mixture, and on esterification gave an 80% yield of a product, b. p. 101—110°/19 mm. This, on malonation, hydrolysis, and decarboxylation, gave a 90% yield of dicarboxylic acid, m. p. 95°. Recrystallisation from benzene raised the m. p. to 104°, not depressed on admixture with authentic pimelic acid. Repetition of the experiment led to a similar result.

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