12. *Addition of Hydrogen Bromide to Non-terminal Double Bonds. The* iso*Propylidene Group. Crotonic Acid.*

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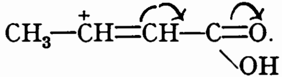
The effect of oxygen or of peroxides in reversing the normal addition of hydrogen bromide, well established in the case of terminal double bonds ($CH_2{:}CH{\cdot}CH_2{\cdot} \xrightarrow[O]{HBr} CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}$), has been detected also in olefins with sufficiently polar non-terminal double bonds ($CMe_2{:}CH{\cdot} \xrightarrow[O]{HBr} CHMe_2{\cdot}CHBr{\cdot}$); but where there is conjugation with a carbonyl group as in crotonic acid, no reversal is observed. The stability of the *iso*propylidene group is discussed. 2-*Methylnonadecoic acid* and 2-*methylnonadecanol* have been synthesised.

IT was shown by Abraham, Mowat, and Smith (J., 1937, 948) that additions of hydrogen bromide to the system $CH_3{\cdot}CH{:}CHR$ gave a 50/50 mixture of the two bromides and that the composition was uninfluenced by the presence of oxygen or peroxides. The absence of a peroxide effect was attributed to the approximate equality of activation of both unsaturated carbon atoms by *n*-alkyl groups of whatever chain length. These views have since been confirmed by Kharasch, Walling, and Mayo (*J. Amer. Chem. Soc.*, 1939, **61**, 1559).

It was thought, however, that in a system ($CMe_2{:}CH{\cdot}[CH_2]_n{\cdot}$) containing the *iso*propylidene group there should be sufficient polarity in the double bond for the manifestation of a peroxide effect. Owing to the use of unsuitable conditions the effect was not at first detected (*Chem. and Ind.*, 1938, **16**, 466), but during the last year (Thesis, J. B. Guy, Oxford, June, 1939) quite definite results have been obtained with 2-methyl-Δ^2-nonadecene, $CMe_2{:}CH{\cdot}[CH_2]_{15}{\cdot}Me$. This olefin by the normal addition of hydrogen bromide gives 2-*bromo*-2-*methylnonadecane*, $CMe_2Br{\cdot}[CH_2]_{16}{\cdot}Me$, identical with the bromide made from dimethylheptadecylcarbinol. In presence of peroxides addition of hydrogen bromide yields a product much more stable to heat than the tertiary bromide. That this must be the 3-bromo-isomeride is shown by its non-identity with 1-*bromo*-2-*methylnonadecane*, which was prepared by the malonic ester synthesis from pure heptadecyl iodide :

$$C_{17}H_{35}I \longrightarrow C_{17}H_{35}{\cdot}CH(CO_2Et)_2 \longrightarrow C_{17}H_{35}{\cdot}CMe(CO_2Et)_2 \longrightarrow C_{17}H_{35}{\cdot}CHMe{\cdot}CO_2H \longrightarrow C_{17}H_{35}{\cdot}CHMe{\cdot}CH_2{\cdot}OH \longrightarrow C_{17}H_{35}{\cdot}CHMe{\cdot}CH_2Br$$

Since the completion of our investigation Walling, Kharasch, and Mayo (*J. Amer. Chem. Soc.*, 1939, **61**, 1711, 2693) have shown that 2-bromo-Δ^2-butene, $CHMe{:}CMeBr$, and trimethylethylene (Michael and Weiner, *J. Org. Chem.*, 1939, **4**, 531) also yield " abnormal " addition products. It is well established, therefore, that non-terminal, as well as terminal double bonds can show the peroxide effect.

Crotonic acid provides an interesting special case because the double bond is part of a katio-enoid system,  $\mathrm{CH_3{-}\overset{+}{C}H{=}CH{-}\underset{\diagdown OH}{C}{=}O}$. The α-carbon atom does not acquire electrons and consequently should not be liable to attack by bromine *atoms* with the formation of α-bromobutyric acid ("abnormal " addition of hydrogen bromide). Even under the most favourable peroxidic conditions the addition of hydrogen bromide gave only β-bromobutyric acid (compare Walling, Kharasch, and Mayo, *loc. cit.*, p. 2696).

An important point in the use of 2-methyl-Δ^2-nonadecene as an example of an olefin with a non-terminal double bond was the possibility of a tautomeric change,

$$CMe_2{:}CH{\cdot} \rightleftharpoons CH_2{:}CMe{\cdot}CH_2{\cdot},$$

either on standing or under the conditions of the reaction. The dehydration product of dimethylheptadecylcarbinol appeared from oxidation to be largely, if not entirely, in the Δ^2-(*iso*propylidene) form. Evidence from the addition reactions supported this: if the *iso*propenyl form had been present, its terminal double bond would certainly have reacted with hydrogen bromide in presence of peroxides to yield 1-bromo-2-methylnonadecane:

$$CH_2{:}CMe{\cdot}[CH_2]_{16}{\cdot}Me \xrightarrow[O]{HBr} CH_2Br{\cdot}CHMe{\cdot}[CH_2]_{16}{\cdot}Me$$

In the naturally occurring terpenes where the same constitutional question arises (for references, see Kuhn and Roth, *Ber.*, 1932, **65**, 1285; Bradfield, Penfold, and Simonsen, J., 1935, 311) it has been concluded by Dupont (*Bull. Soc. chim.*, 1937, **4**, 2016) from Raman spectra that most of the liquid terpenes are β-(*iso*propylidene) forms. Citronellal, however, contains a small proportion of the α-(*iso*propenyl) form.

EXPERIMENTAL.

Addition of Hydrogen Bromide to Crotonic Acid.—To solutions of crotonic acid (10—20 g.) in pure benzene (200 c.c.), benzoyl peroxide or perbenzoic acid or ascaridole (2—5 mols.) was added. Hydrogen bromide with or without oxygen was passed for several hours, and the mixtures left for 1—10 days at room temperature. After the solvent had been removed, the products were distilled: in every case the b. p. (121°/16 mm.) and the m. p.'s (14° to 18·5°) agreed with those of β-bromobutyric acid given in the literature (b. p. 120°/16 mm., m. p. 17—18°). Addition of hydrogen bromide in absence of oxygen gave β-bromobutyric acid, m. p. 18—19°. It was obvious from the high yields and the m. p.'s that in no case could more than a trace of α-bromobutyric acid (b. p. 108°/16 mm., m. p. − 4°; Lespieau, *Compt. rend.*, 1904, **139**, 739) have been present.

In an early attempt to find a series of compounds containing the *iso*propylidene group and with relatively large depressions of m. p. it was thought that 13-methyl-Δ^{12}-tetradecenoic acid, $CMe_2{:}CH{\cdot}[CH_2]_{10}{\cdot}CO_2H$, would be a suitable olefin, but the necessary hydroxy-acid proved too difficult to prepare, the Grignard reagent attacking both the keto- and the ester group of 13-ketotetradecoic ester.

13-*Ketotetradecoic Acid.*—Ethyl 11-bromoundecoate (Ashton, Robinson, and Smith, J., 1936, 284) was converted into ethyl α-acetylbrassylate (G. M. Robinson, J., 1934, 1544). The main fraction (b. p. 184—186°/0·4 mm.), hydrolysed with aqueous alcoholic potassium hydroxide, yielded the required acid, m. p. 75° (hydrolysis with acid was unsatisfactory). The ethyl ester had b. p. 153°/0·5 mm. and m. p. 36°.

13-*Methyl*-13-*hydroxytetradecoic Acid.*—Methylmagnesium iodide, from magnesium (1·6 g.) and methyl iodide (4·1 c.c.) in ether (30 c.c.), was added with stirring to 13-ketotetradecoic ester in ether (10 c.c.). The product, after hydrolysis with alcoholic potassium hydroxide, melted at 41—59° and contained both neutral and acidic products. From the solution in ether 1% potassium hydroxide solution extracted a mixture of acids, b. p. 173—179°/0·4 mm., m. p. 52—54°, *M* 248. Mixed with a little 13-ketotetradecoic acid, it melted at 59° and was obviously a mixture of the keto-acid with the desired 13-methyl-13-hydroxytetradecoic acid. After heating with semicarbazide acetate, followed by extraction with light petroleum, the mixture yielded the *hydroxy-acid*, m. p. 61° (depressed by admixture with the keto-acid to 46°) (Found: C, 70·2; H, 11·4. $C_{15}H_{30}O_3$ requires C, 69·8; H, 11·6%). The overall yield was poor.

2-*Methyl*-Δ^2-*nonadecene.*—Dimethylheptadecylcarbinol was prepared by the method of Ryan and Dillon (*Proc. Roy. Irish Acad.*, 1912, **29**, *B*, 235) from methyl stearate (f. p. 37·6°), but it was found advantageous to use 4 mols. of methylmagnesium iodide to 1 of ester and to reflux the mixture for 4 hours. The carbinol, crystallised from light petroleum, melted at 45·5° (yield, 85%).

Heated with twice its weight of anhydrous oxalic acid at 180—200° for 1 hour, the carbinol gave an 80% yield of olefin, b. p. 212—215°/25 mm., f. p. 12·5°, iodine value (Hanuš) 89·6 (calc., 90·1). Messer (*Chem. News*, 1929, **138**, 292) gives m. p. 11—12°. Fractional distillation, recrystallisation, or chromatographic adsorption failed to change the m. p. The olefin reacted extremely slowly with aqueous permanganate.

Ozonolysis. The olefin (5 g.) in dry carbon tetrachloride (250 c.c.) was subjected to a stream of ozone and oxygen for 10 hours at 0—5°. After the reaction mixture had been left for 24 hours in the open flask and the solvent then evaporated, the product melted at 58°. After three crystallisations from light petroleum it melted at 61°, or at 61—62° when mixed with pure margaric acid, m. p. 62° (in a capillary tube). In another experiment the olefin (5 g.) in carbon tetrachloride was ozonised for 10 hours, the issuing gas being passed through a trap of ice-water; evaporation of the carbon tetrachloride gave a residue, m. p. 35—38°. When this crude ozonide was decomposed with water, and the total yield of acetone estimated (Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39), only 0·55 g. (50—55%) of the calculated amount was found, but there was some loss in dealing with the carbon tetrachloride solution. The non-volatile product (4·5 g.) melted at 49° and readily gave acid, m. p. 58°, on recrystallisation from light petroleum. Combined yields of the acid were crystallised from alcohol, acetone and benzene until the m. p. (thermometer in the liquid) reached 60·8° (Found: C, 75·6; H, 12·5; *M*, 271. Calc. for $C_{17}H_{34}O_2$: C, 75·6; H, 12·6%; *M*, 270). Owing to the difficulty of identifying long-chain compounds by the ordinary methods of m. p.'s in capillary tubes the identity of the acid with margaric acid was proved as follows: (*a*) The acid, m. p. 60·8°, with an equal amount of synthetic margaric acid, m. p. 61·6°, gave a mixture, m. p. 60·9° (thermometer in the liquid). (*b*) To 0·463 g. of the acid, palmitic acid (0·471 g., m. p. 62·6°) was added; the ozonolysis product being assumed to be pure margaric acid, the mixture should contain 48·3 mols. of margaric acid and from the mixed m. p. curve (Smith, J., 1936, 625) should melt at 57·0°; found, 56·8°. (*c*) To 0·464 g. of the acid, stearic acid (0·469 g., m. p. 69·4°) was added; the mixture should have contained 51·0 mols. % of margaric acid and melted at 62·3°; found, 62·2°.

2-Bromo-2-methylnonadecane.—Dry hydrogen bromide was passed through dimethylheptadecylcarbinol (10 g.) at 120° for 4 hours; the product melted at 19° (Found: Br, 21·5. $C_{20}H_{41}Br$ requires Br, 22·1%). A second preparation from the carbinol (5·0 g.) and phosphorus tribromide (2 c.c.) at 20—30° also gave a product, m. p. 19°. This tertiary *bromide* could not be distilled at 0·1 mm. without decomposition. Two crystallisations from hexane at − 25° gave a colourless product, m. p. 19·5° (thermometer in the liquid) (Found: Br, 22·0%).

Addition of Hydrogen Bromide.—(A) The olefin (5 g.) was mixed with acetic acid (150 c.c.), and dry hydrogen bromide passed for 2 hours. After 2 days a solid, m. p. 16°, appeared on the surface. The solid was returned, and the mixture left with hydrogen bromide for a further 10 days. The product had m. p. 17° and iodine value 16 (Found: Br, 20·8. Calc.: Br, 22·1%).

(B) A solution of the olefin (4 g.) in propionic acid with a trace of ferric chloride was kept saturated with hydrogen bromide. After 10 days the mixture separated into two liquids. Water was then added; the solid product, isolated with ether, had m. p. 18·2° (Found: Br, 21·6%).

(C) To a solution of the olefin in benzene (150 c.c.), perbenzoic acid (5 mols. %, in benzene) was added. The mixture was saturated with hydrogen bromide containing oxygen and left for 2 weeks, and the solvent then removed at 40° in a vacuum. The product melted at 2·7° and had iodine value 0·0 [Found: Br, 19·1% (benzoic acid was present)]. The m. p. of the product was depressed to 1·6° on addition of the tertiary bromide (m. p. 18·5°, 4 mols.) and to 1·7° when a total of 9 mols. was present.

(D) To a solution of the olefin (5 g.) in benzene (150 c.c.), ascaridole (5 mols. %; see Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468; Henry and Paget, J., 1921, **119**, 1714) was added, and hydrogen bromide passed in presence of air. After 19 days the product had m. p. 3·1° (Found: Br, 18·1%).

(E) The olefin (8 g.), ascaridole (2 mols. %), benzene (100 c.c.), hydrogen bromide, and air for 21 days gave a product which after distillation at 0·1 mm. had m. p. 4·2° and iodine value 2·0. (It was not possible to distil the tertiary bromide.)

Synthesis of 1-*Bromo-2-methylnonadecane.*—*Heptadecyl iodide.* An especially pure specimen of heptadecyl alcohol (f. p. 53·8°) was available (Carey and Smith, J., 1933, 1350). The alcohol (17 g.), iodine (14 g.), and red phosphorus (1·0 g.), heated to 120° and then at 160° for 1 hour, gave 23·2 g. (96% yield) of colourless iodide, f. p. 33·9°.

Ethyl heptadecylmalonate. To powdered sodium (2·0 g.), benzene (120 c.c.) and ethyl malonate (20 g.) were added, and the mixture refluxed for 5 hours. Heptadecyl iodide (23·2 g.) in toluene (100 c.c.) was then added, and the mixture refluxed for 40 hours. The solution, after having been washed with dilute acetic acid and with water, gave 24·1 g. (92% yield) of distillate, b. p. 198—202°/0·4 mm., m. p. 20° (transparent form), 32—33° (opaque). It was not further purified.

Ethyl methylheptadecylmalonate. A mixture of powdered sodium (1·6 g.), toluene (100 c.c.), and ethyl heptadecylmalonate (24 g.), heated for 1 hour at 90°, gave a clear solution. Addition of methyl iodide produced an immediate precipitate of sodium iodide, in which some of the sodio-derivative was adsorbed. After having been refluxed for 1 day with occasional additions of methyl iodide, the liquid was neutral, but the suspended solid reacted alkaline; a further 4 days' refluxing with methyl iodide failed to produce a neutral reaction of the solid. When the product was poured into water, a few drops of dilute acetic acid rendered the mixture acid. After having been washed with water, the mixture was dried and evaporated. A portion of the residue after distillation (195—197°/0·5 mm.) melted at 11° (transparent form) and 25° (opaque) (Found : C, 73·3; H, 11·7. $C_{25}H_{48}O_4$ requires C, 72·8; H, 11·7%).

Methylheptadecylmalonic acid. The crude ester, hydrolysed with a solution of potassium hydroxide (25 g.) in water (15 c.c.) and alcohol (100 c.c.), yielded the *acid*, m. p. 97—98°; after two crystallisations from benzene this melted at 100—101° (Found : C, 70·8; H, 11·3. $C_{21}H_{40}O_4$ requires C, 70·8; H, 11·2%).

2-*Methylnonadecoic acid.* After having been heated for 1 hour at 180—210° in a vacuum, the crude dicarboxylic acid ceased to evolve carbon dioxide. On distillation it left a dark residue (2 g.) and gave 15·7 g. of *acid*, b. p. 190—195°/0·2 mm., m. p. 55—56°. This represents an overall yield of 79% calculated on the heptadecyl iodide. After redistillation and then two crystallisations from benzene–light petroleum there remained 12 g., m. p. 57·5° (in a capillary tube), f. p. 56·4° (thermometer in the liquid) (Found : C, 76·9; H, 12·9; *M*, by titration of 1 g., 312, 313. $C_{20}H_{40}O_2$ requires C, 76·9; H, 12·8%; *M*, 312). The crystals collect in plates and are similar to those of pure stearic acid. Morgan and Holmes (*J. Soc. Chem. Ind.*, 1927, **46**, 152T) state that the α-methyl acids are white micro-crystalline powders.

2-*Methylnonadecan*-1-*ol.* Ethyl 2-methylnonadecoate (10·8 g., b. p. 170°/0·12 mm.) in dry ethyl alcohol (30 c.c.), reduced with molten sodium (4·5 g.), yielded 7·1 g. of the *alcohol*, m. p. 39°, b. p. 167°/0·2 mm. Similarly 7·7 g. of ester gave 5·1 g. (75% yield) of the alcohol, m. p. 39—40°. This product is of course a racemic mixture, and in some of its physical properties behaves as would a 50/50 mixture; it sets to a tough semi-transparent mass which changes only slowly to the opaque form. Two crystallisations from methyl alcohol gave very fine needles, which were freed from solvent at 70° in a vacuum; the f. p. was then 40·1° (Found : C, 80·3; H, 14·3. $C_{20}H_{42}O$ requires C, 80·5; H, 14·1%).

1-*Bromo*-2-*methylnonadecane.* The alcohol reacted slowly with hydrogen bromide at 130—150°, and at higher temperatures darkening occurred; under these conditions isomerisation seemed likely.

The action of phosphorus tribromide on the alcohol in presence of pyridine (Juvala, *Ber.*, 1930, **63**, 1989; Ruzicka and Firmenich, *Helv. Chim. Acta*, 1939, **22**, 392) with or without solvent gave rise to much phosphorus ester, from which it was not possible to isolate the pure bromide. When phosphorus pentabromide was used, the amount of ester formed was small and readily eliminated; the reaction occurred at a low temperature and there was no evidence of isomeric change of the bromide (compare Faworsky, *Annalen*, 1907, **354**, 325).

The powdered alcohol (2·0 g.) and phosphorus pentabromide (4·5 g.; 1·5 mols.) were mixed at 0°. No reaction occurred until the mixture was allowed to warm slightly; the mass slowly liquefied and was kept well shaken at 0—10° for 1 hour. It was then dissolved in ether, and ice added; the solution was extracted with ice-water and then with 4% potassium bicarbonate solution. The ethereal layer was filtered from the potassium salt of the phosphoric ester, again washed with cold bicarbonate solution, then with water, and dried. Removal of the ether in a vacuum left 2·1 g. of a light yellow oil, f. p. 13°. A second preparation had f. p. 13·5°. After two crystallisations from hexane at − 35° the *bromide* had f. p. 14·0° and m. p.'s 14·1° and 16·5° (thermometer in the liquid) (Found : C, 66·9; H, 11·4; Br, 22·0. $C_{20}H_{41}Br$ requires C, 66·5; H, 11·4; Br, 22·1%).

Mixtures of 1- *and* 2-*Bromo*-2-*methylnonadecane.*—The mixtures were not sharp-melting and the following approximate values are recorded :

1-Bromo-compound, mols. %	100	67	50	33	20	0
M. p., α	14·1°	12·2°	11·0°	9·8°	10·0°	—
,, β	16·5°	14·3°	13·4°	12·5°	16·0°	19·4°

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