XX.—*Properties of Conjugated Compounds. Part XI. Addition of Hydrogen Bromide to βγ- and αδ-Dimethylbutadiene.*

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THE mode of addition of hydrogen bromide to βγ-dimethylbutadiene has been studied within the last ten years by Bergmann (*J. Russ. Phys. Chem. Soc.*, 1920, **53**, 37) and Claisen (*J. pr. Chem.*, 1922, **105**, 65), but whereas the former author states that the hydrocarbon yields a stable αβ-compound, $CMe_2Br{\cdot}CMe{:}CH_2$ with one molecule of hydrogen bromide, the latter concludes that, although an unstable αβ-hydrobromide is intermediately formed, the stable product is the αδ-compound $CMe_2{:}CMe{\cdot}CH_2Br$. The αβ ⟶ αδ isomerisation involved in the change from intermediate to stable compound is attributed to the action of heat or the catalytic action of hydrogen bromide.

In arriving at the constitution of βγ-dimethylbutadiene hydrobromide, Bergmann relied on the fact that this substance is hydrolysed by dilute alkali to dimethyl*iso*propenylcarbinol—apparently a derivative of the αβ-hydrobromide—but Claisen (*loc. cit.*) convincingly showed that the stable αδ-hydrobromides of both βγ-dimethylbutadiene and isoprene yield on hydrolysis, not the corresponding primary alcohols [$CMe_2{:}CR{\cdot}CH_2Br \longrightarrow CMe_2{:}CR{\cdot}CH_2{\cdot}OH$], but the isomeric tertiary alcohols [$CMe_2{:}CR{\cdot}CH_2Br \longrightarrow CMe_2(OH){\cdot}CR{:}CH_2$]. Consequently, whilst Bergmann's dimethyl*iso*propenylcarbinol might have been derived from the αβ-hydrobromide of dimethylbutadiene, it might equally have arisen from the αδ-isomeride. Claisen's own evidence for the formation of an αβ-hydrobromide relates to observations as to the way in which the boiling point of the hydrobromination product varies according to the conditions of formation and isolation. The differences in boiling point are assumed to correspond to differences in constitution and are such as to suggest that a low-boiling and labile αβ-compound may be prepared under suitable conditions of working but that it readily changes to its αδ-isomeride.

Claisen's experiments have been repeated many times by the authors, who find it to be true, as is stated, that if the hydrobromide be prepared very carefully with a deficiency of hydrogen bromide at − 20°, and the crude product then distilled over a little freshly ignited sodium carbonate, much of the material has a boiling point lower (up to 15° lower at 10 mm.) than that of the pure αδ-hydrobromide; moreover, if the low-boiling portion be heated for some time on a steam-bath, the boiling point rises to that of the pure αδ-compound. Nevertheless the authors are emphatically of opinion that the observations in question have no constitutional significance in relation to αβ,αδ-isomerism and that the supposed efficacy of solid sodium carbonate in preventing isomerisation is unreal.

The formation of low-boiling samples of the hydrobromide occurs *only* when a deficiency of hydrogen bromide is employed. Claisen apparently observed this and assumed that the deficiency of hydrogen bromide was directly related to the formation of low-boiling samples of the addition product. It seemed none the less possible, however, that the significant feature in relation to the low boiling point of the product was not the deficiency of hydrogen bromide, but the excess of hydrocarbon. It has been found, indeed, that the boiling point of a considerable proportion of the pure αδ-hydrobromide may be deliberately depressed by adding thereto several drops of the original hydrocarbon; * also the original boiling point may be restored by heating the sample for about ½ hour at atmospheric pressure. All the low-boiling samples, when once obtained, may be distilled at the lower temperature no less well in the absence of sodium carbonate than in its presence. Fractional crystallisation of the supposed mixture of isomerides, carried out as efficiently as possible at — 70°, has failed to yield or indicate the presence of an αβ-compound.

The chemical evidence obtained by the degradation of a number of distilled and undistilled specimens of the addition product points unmistakably to the fact that the *primarily formed* hydrobromide (even when addition is effected at — 20° in the absence of excess of hydrogen bromide) *is the αδ-compound*; furthermore, so far as degradation experiments can indicate, it is the *sole product*, although the complete absence of very small proportions of the αβ-isomeride could not be asserted. The decomposition of its ozonide to yield acetone and bromoacetone proceeds fairly smoothly and with excellent yields from both distilled and undistilled specimens, but in no experiment could the presence of formaldehyde, formic acid, or methyl bromo*iso*propyl ketone (arising from an αβ-form) be distinguished by the most delicate tests.

The behaviour of βγ-dimethylbutadiene in thus yielding directly a non-mobile hydrobromide of terminal character is quite different from that of αδ-dimethylbutadiene, which gives a mixture of products. The hydrobromination of the latter does not appear to have

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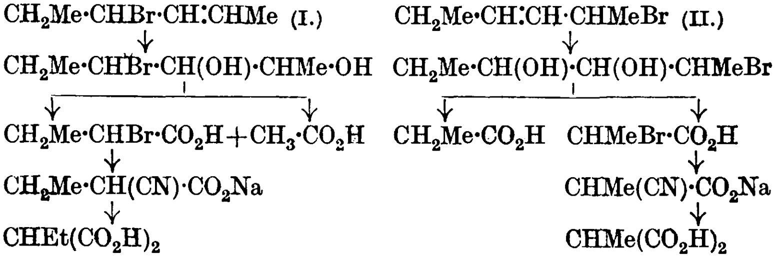
* The hydrocarbon constitutes up to 20% of the crude hydrobromination mixture under Claisen's conditions of addition. Although the bulk of this is readily removed, the last minute traces considerably affect the boiling point, and are, apparently, not rapidly expelled.

been previously studied, but there can be no doubt that the product contains both the αβ-hydrobromide (I) and its αδ-isomeride (II), since by gentle permanganate oxidation it yields a mixture of glycols which is in turn convertible into a mixture of mono- and di-basic acids as shown in the scheme :



Methylsuccinic acid, which, along with acetic acid, should be formed from the third theoretically possible hydrobromide,

$$CHMeBr\cdot CH_2\cdot CH{:}CHMe,$$

were it present, could not be isolated even when the degradation was carried out on a considerable scale. This absence of a third isomeride is interesting as showing that αβ-addition takes place in only one of two possible ways.

By separating and weighing the acetic and propionic acids produced from a large quantity of the hydrobromide, it has been possible to arrive at a rough estimate of the αβ,αδ-ratio, but owing to the laborious nature of the process it has been necessary to confine attention to undistilled samples of the hydrobromide which have been thoroughly freed from volatile impurity. The mixed acids have been obtained in about 91% yield and, on the assumption that the original proportion of the two acids is not affected by the experimental losses, it has been computed that the proportion of αβ-hydrobromide in the hydrobromination product amounts to 90% of the whole—a figure which agrees roughly with the highest estimate of the proportion of acetaldehyde produced by ozonolysis of the hydrobromide.

With respect to the mobility of the αδ-dimethylbutadiene hydrobromides no definite statement can be made. The boiling point of the addition product fluctuates (within limits) so irregularly, changing a little at each distillation, that no constant-boiling fractions could be obtained. It was evident that the addition product contained more than one hydrobromide, but although the variability of the boiling point could have been regarded as indicating the occurrence of some isomerisation during distillation, and even on standing, a prolonged study of distillation phenomena in connexion with refractivity and density determinations failed to show any great probability in this direction.

From the two examples here discussed, it is clear that the manner in which the alkylbutadienes add hydrogen bromide varies, as it does for other symmetrical and unsymmetrical addenda, with the position of substituent groups in the unsaturated chain. At present, however, there is nothing to indicate the order of events in the two-fold process of addendum-attachment and addendum-partition.

EXPERIMENTAL.

A. *Addition to βγ-Dimethylbutadiene.*

Method of Hydrobromination.—The hydrogen bromide was prepared by the interaction of carefully purified hydrogen and bromine in the presence of heated platinised asbestos. For this purpose the hydrogen issuing from a purifying train was slowly bubbled through the exact amount of bromine to be used in the experiment, and the resulting gaseous mixture conducted through a quartz tube containing the catalyst (compare Claisen and Eisleb, *Annalen*, 1913, **401**, 21). The hydrogen bromide was passed over red phosphorus into a reaction flask maintained at, or below, — 20° by immersion in a freezing mixture. Quantities of from 5 g. to 30 g. of the hydrocarbon were treated at one time, the period of conversion for 20 g. being about 4 hours. The proportion of hydrogen bromide relative to the amount of hydrocarbon taken, as also the temperature of addition and the manner of working up the product, was varied in the different experiments.

The Hydrobromide as prepared by Claisen.—The product obtained by using $\frac{2}{3}$ mol. of hydrogen bromide per molecule of hydrocarbon at — 20° was kept alone for 10 minutes and then in contact with a mixture of calcium chloride and potassium carbonate for a further 30 minutes (Claisen, *loc. cit.*, p. 77). The resultant, pale brown liquid contained free hydrocarbon. Most of this evaporated when the pressure in the containing flask was reduced, but the residual oil did not then distil constantly. Three fractions were collected : (i) below 45°/20 mm. (4 g.), (ii) 45—48°/20 mm. (14 g.), (iii) 48—52°/20 mm. (10 g.), but the combined fractions distilled completely between 51° and 54°/20 mm. after being heated on a steam-bath at atmospheric pressure for $\frac{1}{2}$ hour. (In all distillations of hydrobromides a water-bath maintained at about 15° above the b. p. of the material was employed. This allowed distillation to proceed uniformly at the rate of about 2 drops per second.) The fraction of b. p. 51—54°/20 mm. was a pure hydrobromide (Found : Br, 49·4. $C_6H_{11}Br$ requires Br, 49·3%), but the low-boiling portion, after the first few drops of the distillate had been rejected, had almost the correct bromine content (Br, 48·9%). The freshly prepared hydrobromide, when freed from volatile impurities by thorough agitation at greatly reduced pressure, was practically pure monohydrobromide (Br, 49·8%).

To the distillate of b. p. 51—54°/20 mm., 0·5 g. of βγ-dimethylbutadiene was added, and the mixture redistilled. Although the bulk of added impurity at once evaporated when the pressure was reduced, and the last traces might well have been expected to disappear whilst the hydrobromide was being heated to its b. p., yet more than a third of the material now boiled below 50°/20 mm. and the remainder at 51—54°/20 mm. The first fraction could for the most part be redistilled at the lower temperature, but when the combined fractions were heated on a steam-bath for ½ hour, the original b. p. (51—54°/20 mm.) was restored. When this latter distillate was in its turn treated with a little hydrocarbon, the b. p. of a considerable proportion thereof was again depressed below 50°/20 mm.

The Hydrobromide prepared under Conditions differing from those of Claisen.—(i) *Using a slight excess of hydrogen bromide.* Slightly more than 1 mol. of hydrogen bromide per molecule of hydrocarbon was employed at — 20°. The product solidified when cooled to — 70°, but no separation into structurally distinct compounds could be achieved by fractional crystallisation either in the undiluted state or from solution in *n*-hexane, light petroleum, or chloroform. The solid hydrobromide melted at — 32° both before and after recrystallisation from petroleum, and distilled completely at 68—70°/35 mm. (53—55°/20 mm.).

(ii) *Using a slight deficiency of hydrogen bromide at* — 20°. The material thus obtained melted at — 32° and boiled at 53—55°/20 mm. after recrystallisation. A large proportion of similarly obtained, but unpurified, material boiled at 32—45°/20 mm.

(iii) *Using a slight deficiency of hydrogen bromide at* — 72°. Since the contents of the reaction vessel solidified as the addition proceeded, the hydrogen bromide was conducted on to the surface of the constantly agitated hydrocarbon. The solid so obtained melted to a pale pink liquid which darkened on standing. After the excess of hydrocarbon had been removed by a stream of air bubbles at reduced pressure, it boiled practically constantly at 54°/20 mm.

Degradation of the Hydrobromide.—Since neutral permanganate and dichromate proved unsatisfactory as oxidising agents, the former giving apparently a mixture of hydroxy- and bromo-acetone, reliance was placed on ozonolysis. This process was applied to all fractions of the distilled hydrobromide, and also to samples of the hydrobromide which had been purified merely by removal of the excess of hydrocarbon at reduced pressure. In all cases identical results were obtained.

Quantities of 5—20 g., dissolved in chloroform or *n*-hexane, were ozonised for 10 hours at 0°. The ozonide, freed from solvent, was treated with 20—50 c.c. of water and the vapours generated (first in the cold and then on gentle warming) were swept by a stream of carbon dioxide into different reagents. No considerable amount of formaldehyde could have been produced, since β-naphthol and *p*-nitrophenylhydrazine in turn gave no trace of a derivative thereof and numerous sensitive colour tests gave no indication of its presence Dimethyldihydroresorcinol, the most satisfactory reagent known to the authors for detecting the presence of aldehydes amongst the degradation products of butadiene addition products (compare Klein and Livier, *Mikrochemie*, pp. 204—234), gave a very faint precipitate which melted over a range up to 160°. This was neither formaldehyde dimethone, m. p. 187°, nor its anhydride, m. p. 171°; it could conceivably represent a very impure specimen of either of these, but even so would not correspond to more than 1—2% of an αβ-hydrobromide. The aqueous liquor yielded acetone on distillation. This was recognised both by the iodoform reaction and by the formation, under conditions similar to those employed by Robinson in detecting traces of tropinone (J., 1917, **111**, 762), of piperonalacetone, m. p. 105°, mixed m. p. 105·5°. When steam was passed through the aqueous residue, bromoacetone distilled. This substance (b. p. 35—44°/10 mm. on redistillation) gave a semicarbazone, m. p. 142°, and oxime, m. p. 32—34°, which were compared directly with authentic specimens; no higher-boiling bromoketone such as should arise from an αβ-hydrobromide could be isolated in any experiment.

B. *Addition to αδ-Dimethylbutadiene.*

Method of Bromination.—The pure hydrocarbon, prepared by catalytic dehydration of Δ^2-hexen-4-ol both by the method of Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 994) and by distillation in the presence of a few drops of hydrobromic acid, was treated with hydrogen bromide as above described. The product (Found: Br, 49·5. $C_6H_{11}Br$ requires Br, 49·3%), more stable and less lachrymatory than that produced from βγ-dimethylbutadiene, did not distil constantly. The boiling point fluctuated irregularly between 37° and 47°/10 mm. in the same and successive distillations, although care was taken to keep the rate of distillation constant. This happened whether the hydrobromide was worked up in the way described by Claisen for the βγ-hydrocarbon or was freed from unchanged hydrocarbon and volatile impurities merely by subjection to a stream of air bubbles at reduced pressure. The fluctuation in boiling point did not correspond to significant changes in the refractive index or specific gravity of the specimens, since the figures for these, $n_D^{18.9°}$ 1·4760, $d_{4°}^{18.9°}$ 1·199, remained almost constant from fraction to fraction and from specimen to specimen, even after these had been kept for several weeks and distilled many times. The addition product is shown by chemical evidence (see below) to contain two isomeric hydrobromides, *γ-bromo-Δ^{β}-hexene* and *β-bromo-Δ^{γ}-hexene*, but not only could no separation of the isomerides be effected, or indeed their occurrence unmistakably recognised by behaviour on distillation, but the above-mentioned variation of boiling point appeared to be quite unrelated to the progressive occurrence (spontaneously or by action of heat or of catalysts) of isomeric change or serious degradation during distillation (Found, after distillation: Br, 49·0%).

Degradation of the Hydrobromination Product.—(a) *By ozonolysis.* The ozonide was obtained as described above for that of βγ-dimethylbutadiene. It was an explosive liquid which decomposed only very slowly when heated with water. Since it was necessary to determine whether acetaldehyde and propaldehyde, one or both, were formed by its decomposition, considerable attention was paid to the technique of detecting and estimating low concentrations of these substances when produced alone or together with other aldehydes. The well-known β-naphthol test proved wholly untrustworthy as a general method for even the mere detection of acetaldehyde. In many experiments, low concentrations of this substance in carbon dioxide (as derived by passing the gas through a decomposing ozonide or through a dilute solution of genuine acetaldehyde) remained undetected. Dimethyldihydroresorcinol appeared to be generally satisfactory for the detection of acetaldehyde, but under no conditions of working applicable to ozonolysis experiments could the precipitation of the solid acetaldehyde derivative of this reagent (acetaldehyde dimethone, m. p. 139°. Compare Klein and Livier, *loc. cit.*) be brought about quantitatively or in constant ratio (allowing for solubility) to the acetaldehyde present. The figures obtained by the use of this reagent can represent, therefore, only a lower limit for the acetaldehyde produced during ozonolysis.

Both acetaldehyde and propaldehyde were formed by degradation of the ozonide. Of these, only the latter could be condensed in a series of glass spirals, cooled to − 20°, when the volatile products were swept from the reaction vessel by a stream of carbon dioxide; the yield of crude liquid propaldehyde was too small, however, to allow of more than positive identification. From different samples of the hydrobromide, yields of acetaldehyde dimethone were obtained which pointed to the presence of from 50 to 80% of the hydrobromide $CH_2Me·CHBr·CH{:}CHMe$ in the hydrobromination product. Owing to the untrustworthiness of the method, however, it was not practicable to demonstrate in this way that the undistilled bromination product, as well as all fractions of the distilled product, contained the same high proportion of αβ-addition product.

The bromo-aldehydes obtained in the decomposition were separated from unchanged ozonide by steam distillation—a very necessary procedure if serious accident were to be avoided during subsequent distillation. Since the yellow oil obtained could not be profitably oxidised by permanganate or chromic acid, a different procedure was followed in recognising and estimating the bromine-containing degradation product.

(b) *By permanganate oxidation.* The hydrobromide could not be oxidised satisfactorily to the appropriate mixture of fatty and bromo-fatty acids solely by the action of permanganate in neutral solution. Experiment showed, however, that the hydrobromide, dissolved in acetone, gave a good yield of crude (mixed) bromo-glycols with this reagent; moreover the glycols could be fairly smoothly oxidised to the corresponding acids by the action of a cold dilute potassium dichromate–sulphuric acid solution. The oxidation product, which was very thoroughly extracted with ether, consisted of a low-boiling portion roughly separable into acetic acid and propionic acid fractions, and a bromine-containing portion which could only be distilled satisfactorily at reduced pressure. The acetic and propionic acids, further purified by distillation, were readily obtainable in the form of their *p*-bromophenacyl esters (m. p.'s 85° and 59° respectively), which were compared with authentic specimens. The bromo-acids yielded the corresponding nitriles when heated with potassium cyanide in the usual way: these (not isolated) were convertible into the salts of corresponding acids by boiling with caustic alkali. Of the three dibasic acids which could thus be formed from the three theoretically possible isomeric hydrobromides, only two were obtained. These, methylmalonic acid (m. p. 130°) and ethylmalonic acid (m. p. 112°), were separated by fractional crystallisation and compared with authentic specimens.

The Proportions of αβ- and αδ-Isomerides.

A first approximation to the proportion of αβ- and αδ-isomerides in the original (undistilled) hydrobromination mixture was made possible by oxidising a large quantity of undistilled material in two stages exactly as described above. For this purpose the permanganate oxidation product was not isolated but directly mixed (after removal of manganese mud and the acetone used as solvent) with

40% excess over the amount of cold potassium dichromate–sulphuric acid mixture necessary to ensure complete oxidation to carboxylic acid. The mixture was kept for 36 hours. The two fatty acids were carefully fractionated under a column and weighed. The specimens obtained together represented approximately 91% of the yield theoretically possible (two of the three theoretically possible hydrobromides could yield acetic acid); of this yield, the acetic acid constituted approximately 10·5% and the propionic acid 89·5%.

The bromo-acids, which, although obtained in considerable quantity, were sacrificed somewhat in attaining complete expulsion of propionic acid, were converted into the corresponding malonic acids, but the yield of the latter was not estimated. A careful refractionation of the acid mixture in which ethylmalonic acid was greatly in excess over methylmalonic acid disclosed the presence of no methylsuccinic acid; moreover, subsequent treatment of the mixture with acetyl chloride led to the isolation of no trace of the anhydride of this acid.

The authors desire to thank the Salters' Institute of Industrial Chemistry and the Chemical Society for grants to one of them (F. C. B. M.) which have enabled the investigation to be carried out.

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[*Received, November 12th, 1930.*]