223. *The Formation of Diene Hydrocarbons. Part I. Principles relating to the Course of Reaction in the Dehydration of Unsaturated Alcohols. The Co-formation of* αα- *and* αγ-*Dimethylbutadiene.*

By Reginald G. R. Bacon and Ernest Harold Farmer.

It is known that, when a secondary alcohol of the type $R\cdot\dot{C}H\cdot\dot{C}(OH)\cdot\dot{C}HR'$ is dehydrated, there may in general be formed two olefins, $R\cdot\dot{C}{:}\dot{C}\cdot\dot{C}HR'$ and $R\cdot\dot{C}H\cdot\dot{C}{:}\dot{C}R'$. Analogously, from tertiary alcohols $CRR'R''\cdot OH$, three olefins may in general be formed, provided that the first carbon atoms of the groups R, R′ and R″ possess the necessary hydrogen atom for elimination.* Church, Whitmore, and McGrew (*J. Amer. Chem. Soc.*, 1934, **56**, 176), as the result of quantitative experiments with twenty-two alkylcarbinols, arrange the commoner alkyl radicals in the order of their tendency to contribute a hydrogen atom for elimination with hydroxyl: this order ($Et > Bu^{\alpha} > n\text{-}C_5H_{11} > Me$) agrees, except in the case of methyl, with that recorded by Ingold (J., 1927, 997) for the tendency to contribute hydrogen for elimination with the basic group in the somewhat analogous Hofmann degradation:

$$R\cdot CH(H)\cdot CH_2\cdot\overset{\oplus}{N}Me_2\cdot CH_2\cdot CH(H)\cdot R' \begin{array}{l} \nearrow R\cdot CH{:}CH_2 + \overset{\oplus}{N}HMe_2\cdot CH_2\cdot CH_2R' \\ \searrow R'\cdot CH{:}CH_2 + \overset{\oplus}{N}HMe_2\cdot CH_2\cdot CH_2R \end{array}$$

The dehydration of alcohol systems $R\cdot\dot{C}H\cdot\dot{C}(OH)\cdot\dot{C}H\cdot\dot{C}{:}CR'R''$ and $R\cdot\dot{C}H\cdot\dot{C}(OH)\cdot CH{:}CR'R''$, which already contain one double bond, has fairly generally been assumed to yield a single homogeneous diene in each case, and the same applies to certain diols which give up their hydroxyl groups successively or simultaneously to form conjugated dienes. Yet in these examples also, theoretical considerations point clearly to the possibility that dehydration at each secondary alcohol centre may occur in either or both of two directions, so that, from an alcohol such as dimethylallylcarbinol (I),

$$\underset{\text{(III.)}}{CMe_2{:}CH\cdot CH{:}CH_2} \longleftarrow \underset{\text{(I.)}}{CH_3\cdot CMe(OH)\cdot CH_2\cdot CH{:}CH_2} \longrightarrow \underset{\text{(II.)}}{CH_2{:}CMe\cdot CH_2\cdot CH{:}CH_2}$$

either the non-conjugated diene (II) or its conjugated isomeride (III), or both, may be produced. These courses of reaction take no account of "abnormal" shifts of double

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* Eliminations which are made possible by the migration of alkyl groups, such as occur during the dehydration of *tert.*-butylcarbinol (Whitmore, *J. Amer. Chem. Soc.*, 1933, **55**, 1106, 3721), are not here considered.

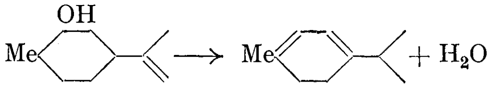
bonds, such as have been reported by Dumoulin (*Compt. rend.*, 1926, **182**, 974) and Merling (*Annalen*, 1891, **264**, 342) respectively to occur in the pyrolytic eliminations (1) and (2),

$$(1)\quad \mathrm{CH_2{:}CH{\cdot}CH(OH){\cdot}C_3H_7 \longrightarrow CH_2{:}CH{\cdot}CH{:}CHEt + CHMe{:}CH{\cdot}CH{:}CHMe}$$

$$(2)\quad \mathrm{CH_2{:}CH{\cdot}[CH_2]_4{\cdot}NMe_3{\cdot}OH \longrightarrow CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CH{:}CH_2 + CHMe{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2}$$

or of the seemingly erratic movements of double bonds which are a feature of certain terpene dehydrations, as, for instance, that represented in (3), and of various dehydrative ring-closures described by Bogert (*J. Amer. Chem. Soc.*, 1935, **57**, 151) exemplified in (4). If an " abnormal " double bond displacement of this kind were to occur in dimethylallylcarbinol, a third diene hydrocarbon, $\mathrm{CH_2{:}CMe{\cdot}CH{:}CHMe}$ (IV), could arise, but it is difficult in reviewing recorded examples to discriminate between degrees of abnormality, *i.e.*, to judge how far such displacements are the direct result of deep-seated molecular disturbance occasioned by high temperatures, or are normal features of specific dehydrative mechanisms. The displacement of the double bond shown in (3) does not occur when dehydration is accomplished by the xanthic ester method, and there is no evidence to show that the principles of reaction which govern eliminations effected under mild conditions remain trustworthy for the very numerous dehydrations which can be brought about at comparatively high temperatures in the presence of contact reagents; moreover it is not established that the different " mild " dehydrating agents of the ordinary types, each acting with its own degree of ease or success, give exactly the same product or mixture of products for the same alcohol. It appears very necessary, therefore, in attempting to trace the influence of structure on the course of dehydration to have due regard to the experimental process employed, and for this reason comparisons in this paper are restricted to dehydrations which result from the employment of a single experimental procedure (*viz.*, refluxing the alcohol with a few drops of concentrated hydrobromic acid), although later it is hoped to investigate and compare the results of other procedures.

(3)



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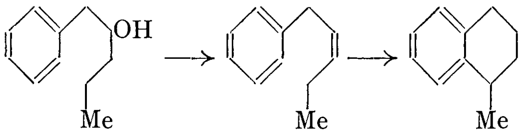
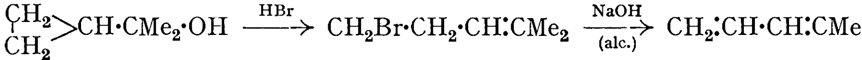


Although dimethylallylcarbinol (I) itself does not appear to have been dehydrated previously, M. and A. Saytzew (*Annalen*, 1877, **185**, 151) obtained a hydrocarbon C_6H_{10} by the action of alcoholic potash on the corresponding chloride, and Ljubarsky (*J. pr. Chem.*, 1900, **62**, 657) prepared a hydrocarbon (b. p. 60—78°) by the same method and suggested that the essential elimination product was either (II) or (III). Diels and Alder (*Annalen*, 1929, **470**, 62) prepared a hydrocarbon by Saytzew's method and obtained therefrom a small yield of the maleic anhydride derivative of $\alpha\gamma$-dimethylbutadiene (IV).

The product of dehydration of dimethylallylcarbinol, with hydrobromic acid as catalyst, has been found by us to consist entirely of diene hydrocarbons C_6H_{10}. From the mixture, a substantially complete separation of a relatively low-boiling, non-conjugated hydrocarbon (b. p. 57—58°/766 mm.) can be effected without difficulty by fractionation, and this by reason of its physical properties, chemical reactivity, and the nature of its degradation products (see p. 1072) can be definitely identified as β-methyl-$\Delta^{\alpha\delta}$-pentadiene (II). The residue is still heterogeneous, the physical properties of its fractions changing progressively over a boiling range of 4° (b. p. 73·0—76·7°; $n_D^{13.5°}$ 1·4464—1·4513).

The hydrocarbons to be expected in the residue are of course $\alpha\alpha$- and $\alpha\gamma$-dimethylbutadiene (III and IV), both of them conjugated. The molecular refraction of the residue was in fact sufficiently high to point to a wholly conjugated (albeit heterogeneous) constitution, but since reasonably efficient separation of the components by the best columns and with the bulk of material at disposal proved to be out of the question the course was adopted of examining the mixture side by side with a series of heterogeneous products, all somewhat different in physical properties, obtained by dehydration of various alcohols and glycols which from their structure might have been expected to yield the αα-hydrocarbon. The results obtained with the latter are described below (p. 1070) in detail; it is sufficient here to state that the products in *all* these cases consisted of mixtures in different proportions of two conjugated dienes differing little in boiling point. In the dimethylallylcarbinol product one of the hydrocarbons was easily identifiable as αγ-dimethylbutadiene by the formation of its characteristic unimolecular derivative with maleic anhydride and an approximate estimate of its proportion in the mixture could be made from the yield of this derivative when formed at room temperature in benzene solution * (compare Farmer and Warren, J., 1931, 3234).

The identification of the remaining hydrocarbon as the αα-compound was rendered difficult by the fact that the four † preparations of this hydrocarbon described in the literature, although undoubtedly all of essentially dienic constitution and agreeing fairly closely in boiling point, yet differed from one another materially in their other physical properties and all remained uncharacterised by the formation of a crystalline derivative. Three of these, however, were derived by different workers (Bruylants, *Bull. Acad. roy. Belg.*, 1908, 1044; van Keersbilck, *Bull. Soc. Chim. Belg.*, 1929, **38**, 205; Farmer and Warren, *loc. cit.*, p. 3221) from the tertiary alcohol (V) *via* a bromide of the reputed constitution (VI), and there can be slight doubt that the main product in each case, whether the αα-hydrocarbon or not, was the same substance.



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!CH{\cdot}CMe_2{\cdot}OH \xrightarrow{HBr} CH_2Br{\cdot}CH_2{\cdot}CH{:}CMe_2 \xrightarrow[\text{(alc.)}]{NaOH} CH_2{:}CH{\cdot}CH{:}CMe_2$$

(V.) (VI.) (III.)

The fourth preparation, due to Krestinski (*Ber.*, 1922, **55**, 2754), was obtained in very small amount by the dehydration with acetic anhydride of what was unquestionably mainly the alcohol (VII) (synthesised from *iso*butenylmagnesium bromide and acetaldehyde) ‡ and this may well have resembled the other three as regards the main component, but have

$$CMe_2{:}CH{\cdot}MgBr + CH_3{\cdot}CHO \longrightarrow \text{(VII)}\ CMe_2{:}CH{\cdot}CHMe{\cdot}OH \longrightarrow \text{(III)}$$

differed therefrom in the proportion of other hydrocarbons present. Of the three preparations derived from the alcohol (V), the most satisfactory as regards freedom from foreign hydrocarbons and impurities is probably that obtained in considerable quantity by one of us (Farmer and Warren, *loc. cit.*). It differed in boiling point from its αγ-isomeride by 1° and was unique among the seven monomethyl- and dimethyl-butadienes in giving only a polymeric (amorphous or microcrystalline) derivative with maleic anhydride.

In the present case the crude maleic anhydride derivative obtained from the residual mixture of conjugated hydrocarbons contained, in addition to the characteristic crystalline derivative of the αγ-hydrocarbon, a quantity (at least 20%) of waxy polymeric anhydride, and the oxidation products from various fractions of the conjugated residue contained in notable proportions acetone and oxalic acid (in addition to formic and acetic acids) which could only have been derived from the αα-hydrocarbon. Since the hydrogenation figures obtained experimentally precluded the possibility that a completely foreign hydrocarbon was also present in significant quantity, we must conclude that the conjugated portion of the dehydration product of dimethylallylcarbinol consisted of a mixture of αα- and αγ-dimethylbutadienes.

Thus all the courses of dehydration foreshadowed above, including that in which the original double bond of dimethylallylcarbinol becomes displaced, are realised in practice, and since the hydrocarbons (II), (III), and (IV) are formed in roughly the proportions 50%, 10%, and 40%, it seems clear that, although in the system $CH_2{:}CH{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH_3$ elimination can occur in both of the possible directions, *i.e.*, by removal of the hydroxyl

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* The maleic anhydride derivative of αγ-dimethylbutadiene undergoes polymerisation on long standing.

† This number does not include several preparations described as the αα-compound which it is now clear must have consisted almost entirely of the αγ-hydrocarbon (see below).

‡ For the synthesis of this alcohol by a more reliable method and its dehydration by hydrogen bromide, see below.

group with a proton from either C_3 or C_5, yet owing to the influence (electron-donating) of the adjacent vinyl group the hydrogen atom on C_3 is so firmly held that removal of the proton from C_5 becomes capable of proceeding on preferential terms. But this relatively difficult removal (C_5 being part of a terminal methyl group) only succeeds at the expense of provoking a molecular disturbance sufficiently intense to allow the inherent conjugative tendency of the molecules (involving double-bond shift) to assert itself.

In addition to the principles of dehydration considered above, comprising (1) elimination of the elements of water in all the normally possible directions and (2) a capacity in certain cases for the occurrence of some degree of " abnormal " double bond displacement directed towards the achievement of conjugation, there is a third principle of elimination to be taken into account. This concerns the capacity of structures containing the group $C{:}C{\cdot}CX$, where $X = OH, Br$, etc., to undergo $\alpha\gamma$-change, and results in the phenomenon of certain alcohols behaving on dehydration partly or wholly as their isomeride. Our experience has already shown that this third principle is of great practical importance, and in extreme cases (extreme from the standpoint of reactivity) it is responsible for a secondary or tertiary alcohol behaving as an isomeric primary alcohol. A good example for investigation appeared to be ε-methyl-Δ^{β}-hexen-δ-ol (VIII), which in its isomeric form would be the β-methyl-Δ^{γ}-hexen-ε-ol (IX). Having regard to the activation value of the groups

$$\begin{tikzcd}
\text{(VIII.) } CHMe_2{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH_3 \arrow[r, "\alpha\gamma\text{-change}"] \arrow[d, "-H_2O"] & CHMe_2{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_3 \text{ (IX.)} \arrow[d, "-H_2O"] \\
\text{(X.) } CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CH_3 & CHMe_2{\cdot}CH{:}CH{\cdot}CH{:}CH_2 \text{ (XI.)}
\end{tikzcd}$$

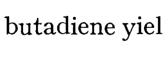
(Pr^{β} and Me) substituting the basic 3-carbon system of (VIII), the anion of (VIII) might be expected to pass largely (> 50%) into that of (IX) with the result that a mixture of ααδ-trimethylbutadiene (X) and α-*iso*propylbutadiene (XI), the latter compound preponderating, would ultimately appear on dehydration.

According to Reif (*Ber.*, 1908, **41**, 2739) the alcohol (VIII) is dehydrated by potassium hydrogen sulphate to give in very poor yield a hydrocarbon, b. p. 97—99°, regarded as (X). We have found, however, that dehydration proceeds very efficiently in presence of hydrobromic acid to give a hydrocarbon, b. p. 99—112°. This hydrocarbon was wholly dienoid in character, but all the fractions obtained on distillation consisted of mixtures of two different hydrocarbons, the one concentrated towards the lower-boiling limit and the other towards the upper. The former of these was recognised as α-*iso*propylbutadiene (XI) and the latter as ααδ-trimethylbutadiene (X). Both hydrocarbons (X) and (XI) are capable of exhibiting geometrical isomerism, so four stereo-forms were probably present in the mixture, thus rendering a clear-cut separation of the two structural isomerides impossible on the scale of working used. The identity of the two hydrocarbons rests on analysis, hydrogen or bromine value, and the following evidence :

(1) All the fractions yielded formic acid (from XI) and all yielded acetone (from X) on oxidation; moreover the yield of acetone increased markedly on passing from the lower- to the higher-boiling fractions.

(2) From no fraction could *pure* acetic acid be obtained as an oxidation product: it was always contaminated by another acid of higher equivalent, and from the lowest-boiling fraction of hydrocarbon *iso*butyric acid (from XI) was isolated in the form of its silver salt.

(3) The mixture of hydrocarbons yielded two products with maleic anhydride, *viz.*, a new crystalline derivative, $C_{11}H_{14}O_3$, m. p. 90° (A), and a polymeric product (B). The higher-boiling fraction yielded (B) practically exclusively and the lower fractions largely (A), but with an amount of (B) which increased as the boiling point of the fractions rose.


(XII.)

The last observation, taken in conjunction with the oxidation results above, left little doubt that the crystalline derivative was derived from (XI) and was in fact 3-iso*propyl*-Δ^4-*tetrahydrophthalic anhydride* (XII), and the polymeric substance was derived from (X). This deduction is greatly strengthened by the knowledge that αα-dimethyl- as well as ααδ-trimethylbutadiene yields only polymeric addition products with maleic anhydride, and there appears some probability that αα-dialkyl-substitution of butadienes tends generally towards polymeric reactivity.

Although no very accurate estimate could be formed of the proportion of the isomeric dienes obtained from the alcohol (VIII), yet both were evidently produced in substantial amount. The occurrence of αγ-change, of which other examples are given below, must therefore be accepted as a normal concomitant of dehydration in those cases where the structure of the alcohol and the conditions of dehydration permit it. The homogeneity, therefore, of many dienoid hydrocarbons described in the literature which have been derived from precursors susceptible of αγ-change must be regarded with suspicion. It must be borne in mind, however, that in all dehydration processes employing catalysts such as hydrobromic acid and iodine, esterification is usually held to constitute the first stage of reaction (the bromide, iodide or other ester group being more readily ionisable and detachable than the original hydroxyl group) and this mechanism gives free play to the anionotropic tendency; yet under other conditions of reaction it appears possible that elimination may be able to proceed by a more direct route or at least by one which largely or entirely prevents the occurrence of αγ-change.

Although in general the employment of saturated glycols in place of unsaturated alcohols leads normally to an increased degree of structural variation in the dehydration products, yet there is one particular example of glycol dehydration which is of special interest in relation to the foregoing results. Kyriakides investigated the dehydration of β-methylpentane-βδ-diol (XIII) and δ-methyl-Δ^{β}-penten-δ-ol (XIV), using hydrobromic acid as catalyst, and reported that he had obtained αα- and αγ-dimethylbutadiene (III and IV) in the

$$\underset{\text{(XIII.)}}{\mathrm{CMe_2(OH)\cdot CH_2\cdot CHMe\cdot OH}} \longrightarrow \underset{\text{(XV.)}}{\mathrm{CMe_2{:}CH\cdot CHMe\cdot OH}} \longrightarrow \underset{\text{(III.)}}{\mathrm{CMe_2{:}CH\cdot CH{:}CH_2}}$$

$$\text{(XIV.)}\quad \mathrm{CHMe{:}CH\cdot CMe_2\cdot OH} \longrightarrow \mathrm{CHMe{:}CH\cdot CMe{:}CH_2}\quad \text{(IV.)}$$

respective cases (*J. Amer. Chem. Soc.*, 1914, **36**, 993). In the course of the former dehydration an unsaturated alcohol appeared as a by-product (presumably an intermediate product), and this was assumed to consist mainly of the compound (XV), since the formation of the isomeric alcohols $\mathrm{CMe_2(OH)\cdot CH_2\cdot CH{:}CH_2}$ and $\mathrm{CMe_2(OH)\cdot CH{:}CHMe}$, arising by dehydration at the secondary instead of at the tertiary carbinol group, was not considered to be highly probable. It was recognised, however, that the alcohol $\mathrm{CH_2{:}CMe\cdot CH_2\cdot CHMe\cdot OH}$ represented another possible intermediate, and this would finally be dehydrated to produce αγ-dimethylbutadiene, so causing contamination of the main hydrocarbon product. In the case of the second dehydration (XIV ⟶ IV), a pure product was considered to result, since there were no obvious side-reactions.

The product of dehydration of the glycol (XIII), however, appeared on subsequent examination (Diels and Alder, *Annalen*, 1929, **470**, 98; Farmer, Lawrence, and Scott, J., 1930, 511) to be not αα- but αγ-dimethylbutadiene, and to be indistinguishable in its essential chemical behaviour (especially in the formation of the crystalline derivative with maleic anhydride) from the hydrocarbon from (XIV). A little later Whitby and Gallay (*Canadian J. Res.*, 1932, **6**, 280), in publishing the results of a study of the heat-polymerisation of a number of dimethylbutadienes, claimed that the hydrocarbons derivable by the Kyriakides method from the compounds (XIII) and (XIV) were indeed distinct hydrocarbons (*i.e.*, αα- and αγ-dimethylbutadiene respectively), differing in physical properties, in speed of polymerisation, and in the nature of their polymerides. It was admitted that the dehydration product of the glycol might conceivably contain a little of the αγ-hydrocarbon, but it was believed to consist preponderantly of αα-dimethylbutadiene.

The conclusions of the Canadian workers may be criticised in that (1) no direct experimental evidence for the constitution of their hydrocarbons was adduced, (2) their specimens did not differ sufficiently in physical properties to suggest any marked difference in composition, and (3) the polymerisations were carried out with only 10 g. portions of the hydrocarbons, of which 57% polymerised in the case of the supposed αα-compound and 51% in that of the αγ-isomeride. The polymeric products they obtained were separated into dimeric and rubber-like components, which exhibited certain physical differences in the two cases; but, bearing in mind the small quantities of materials employed and how greatly the course of polymerisation may be affected by the presence of traces of impurities, it cannot be claimed that the experiments in question were highly conclusive.

A new detailed study of the dehydration products of the glycol (XIII) and the unsaturated alcohol (XIV) provides adequate evidence for rejecting unhesitatingly the contention of Whitby and Gallay with respect to the main dehydration product from (XIII). The hydrocarbon products from both (XIII) and (XIV) have been obtained again in considerable quantities and submitted to rigid fractionation in Widmer or bead-packed columns. The two products resembled fairly closely the conjugated portions of the dehydration product from dimethylallylcarbinol described above, except that the range of boiling point, and other of the physical properties, differed appreciably in the three individual cases. Since the boiling point was in no instance sharp and the successive fractions obtained by distillation showed progressive small differences in physical properties, it was clear that the dehydration products of (XIII) and (XIV), like that of dimethylallylcarbinol, were mixtures, although that from (XIV) was heterogeneous only in minor degree. The main product in each case was unquestionably αγ-dimethylbutadiene and an approximate estimate of the proportion of this hydrocarbon present could be made by isolating it in the form of its pure maleic anhydride derivative, but no satisfactory separation of the individual hydrocarbons could be made. The residual hydrocarbon, taking into consideration its empirical composition (as judged from that of the total dehydration product), physical properties, its oxidation products and ability to yield only a polymeric additive derivative with maleic anhydride under standard conditions (compare Farmer and Warren, J., 1931, 3234), must be regarded as αα-dimethylbutadiene. On the basis of the quantity of crystalline maleic anhydride derivative of the αγ-compound obtainable directly from the mixture of hydrocarbons and the proportion of oxalic acid (from the αα-compound) obtained by oxidation of the same mixture, the proportions of the two dimethylbutadienes in the dehydration products of (XIII) and (XIV) are estimated to be roughly as follows: (XIII) 90%, 10%, (XIV) 95%, 5%. The appearance of the αα-hydrocarbon from (XIV) is doubtless due to the occurrence of αγ-change in small degree during dehydration :

$$\mathrm{CHMe{:}CH{\cdot}CMe_2{\cdot}OH} \xrightarrow{-\overset{\ominus}{\mathrm{OH}}} \mathrm{CHMe{:}CH{\cdot}\overset{\oplus}{C}Me_2} \rightleftharpoons \mathrm{\overset{\oplus}{C}HMe{\cdot}CH{:}CMe_2} \xrightarrow{-\overset{\oplus}{\mathrm{H}}} \mathrm{CH_2{:}CH{\cdot}CH{:}CMe_2}$$

Another alcohol which might be expected to give αα-dimethylbutadiene on dehydration is the β-methyl-Δ^{β}-penten-δ-ol of Krestinski mentioned above, but even here the occurrence of αγ-change during dehydration is rendered possible by the structure of the alcohol, although such change is likely to take place only in minor degree. The alcohol has now been prepared in a way which imports less of structural uncertainty than attaches to Krestinski's compound, *viz.*, from β-methylcrotonaldehyde, $\mathrm{CMe_2{:}CH{\cdot}CHO}$, synthesised by the procedure of Fischer, Ertel, and Löwenberg (*Ber.*, 1931, **64**, 30), by treatment with methylmagnesium bromide.* The dehydration product obtained with hydrogen bromide differed somewhat in boiling point (well defined at 77—78°) from the three mixtures of αα- and αγ-dimethylbutadiene already described. It exhibited a lower density and lower refractive index and optical exaltation than the purest available specimen of the αγ-hydrocarbon. The main product arising from its interaction with maleic anhydride was a wax-like polymeride; also when oxidised with permanganate it gave abundant quantities of acetone, oxalic acid and formic acid : consequently it would appear to consist predominantly of αα-dimethylbutadiene. Nevertheless the occurrence of αγ-change in any degree during dehydration would lead to the production of αγ-dimethylbutadiene, and it was indeed found that the polymeric maleic anhydride derivative from the dehydration product, although it was identical in appearance and general properties with the corresponding material derived by Farmer and Warren (*loc. cit.*) from the supposedly pure αα-dimethylbutadiene formed by Bruylants' method, yet yielded on extraction with petroleum a tiny quantity of crystalline addition product identical in appearance with the highly

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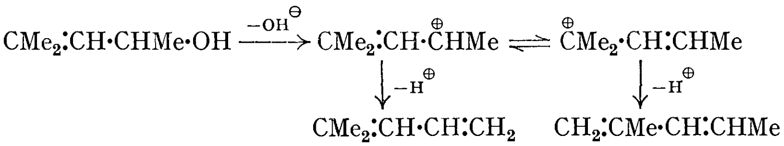
* It is possible that a slight degree of αγ-change occurs even during the preparation of the alcohol.

characteristic derivative from αγ-dimethylbutadiene. This small specimen, however, could not be sufficiently purified for absolute identification, but the presence of a small

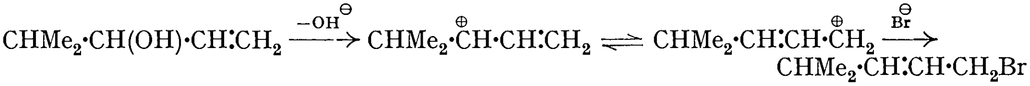
(XV.)


$$\begin{tikzcd} \mathrm{CMe_2{:}CH{\cdot}CHMe{\cdot}OH} \arrow[r, "-\overset{\ominus}{\mathrm{OH}}"] & \mathrm{CMe_2{:}CH{\cdot}\overset{\oplus}{C}HMe} \arrow[r, leftrightharpoons] \arrow[d, "-\overset{\oplus}{\mathrm{H}}"] & \mathrm{\overset{\oplus}{C}Me_2{\cdot}CH{:}CHMe} \arrow[d, "-\overset{\oplus}{\mathrm{H}}"] \\ & \mathrm{CMe_2{:}CH{\cdot}CH{:}CH_2} & \mathrm{CH_2{:}CMe{\cdot}CH{:}CHMe} \end{tikzcd}$$

(IV.)

proportion of αγ-hydrocarbon in the dehydration product was supported by the fact that acetic acid could be definitely recognised among the oxidation products. The hydrocarbon obtained from the alcohol (XV) differed considerably in physical properties from Farmer and Warren's preparations of Bruylants' hydrocarbon, and also from Krestinski's hydrocarbon.

Still another possible method for obtaining the αα-hydrocarbon is the dehydration of δ-methyl-Δ^{α}-penten-γ-ol, $\mathrm{CHMe_2{\cdot}CH(OH){\cdot}CH{:}CH_2}$ (XVI). This alcohol, however, could not be dehydrated at all with hydrogen bromide or iodine—a surprising circumstance in view of the fact that every other alcohol containing a secondary hydroxyl group adjacent to a double bond which had been examined was dehydrated readily in presence of these reagents. Dehydration has been accomplished in analogous structures even where the group supplying the hydrogen atom for elimination with hydroxyl is methyl: when, therefore, as in this example, an *iso*propyl group should discharge this function, elimination might be expected to proceed with great ease. It has already been shown (p. 1068) that the alcohol $\mathrm{CHMe_2{\cdot}CH(OH){\cdot}CH{:}CHMe}$, which is analogous in constitution, is dehydrated with ease in presence of hydrogen bromide: it must be concluded, therefore, that the inactivity of (XVI) arises from the occurrence of essentially complete αγ-change during the dehydration process, the product being a primary alcohol which would not be expected to undergo dehydration under the conditions used:



$$\mathrm{CHMe_2{\cdot}CH(OH){\cdot}CH{:}CH_2} \xrightarrow{-\overset{\ominus}{\mathrm{OH}}} \mathrm{CHMe_2{\cdot}\overset{\oplus}{C}H{\cdot}CH{:}CH_2} \rightleftharpoons \mathrm{CHMe_2{\cdot}CH{:}CH{\cdot}\overset{\oplus}{C}H_2} \xrightarrow{\overset{\ominus}{\mathrm{Br}}} \mathrm{CHMe_2{\cdot}CH{:}CH{\cdot}CH_2Br}$$

Up to the present, therefore, homogeneous αα-dimethylbutadiene has almost certainly never been isolated unless in the instances referred to above where the diene hydrocarbon was derived from dimethyl*cyclo*propylcarbinol by the Bruylants method. The product obtainable by this method requires further examination, but since the procedure involved is expensive and extremely laborious to carry out on a scale large enough to permit of careful fractionation being attempted, the further investigation has been postponed. It appears probable from the present results that dehydration by hydrogen bromide or by iodine is unsuitable for the production of homogeneous hydrocarbons from systems capable of αγ-change, for here the reaction initiated by the catalyst is usually sufficiently slow to permit of the occurrence of extensive isomeric change before the final stage of dehydration (*i.e.*, removal of hydrion) is completed. Successful formation of a homogeneous product (and this conclusion would seem to apply especially to αα-dimethylbutadiene) is more likely to be accomplished by a rapidly proceeding mechanism or one which does not conduce to the intermediate formation of isomerisable kations. A positive indication in this direction is afforded by the apparent absence of αγ-dimethylbutadiene from the dehydration product of dimethylallylcarbinol when the dehydrating agent is phenylcarbimide (p. 1077), but further investigation of the influence of different dehydrating agencies and different elimination reactions on the constitution of the product is proceeding.

EXPERIMENTAL.

Preparation of Dimethylallylcarbinol (*δ-Methyl-Δ^{α}-penten-δ-ol*).—The preparation from magnesium turnings and an ethereal solution of acetone (1 mol.) and allyl bromide (1 mol.) as recommended by Jaworski (*Ber.*, 1909, **42**, 436) proved unsatisfactory. The following procedure, which incorporates Gilman and McGlumphy's precautions for the conduct of organometallic reactions where the halide is olefinic (*Bull. Soc. chim.*, 1928, **43**, 1322), was used with invariable success for the preparation in good yield of large quantities of the carbinol : Finely powdered magnesium of good quality (73 g.; 3 mols.) was covered with ether (200 c.c.), and allyl bromide (121 g.; 1 mol.), dissolved in ether (570 c.c.), added with vigorous stirring during 4 hours; the solvent continued in gentle ebullition throughout the reaction. The Grignard reagent was treated with acetone (1 mol.) at − 10° in the usual manner. From the product, after working up, a liquid was obtained most of which distilled without dehydration at 32—36°/12 mm. (yield, 60—65%), and the remainder, a more viscous, deep yellow liquid, without marked break at 70—140°/12 mm. The lower-boiling liquid was dimethylallylcarbinol, and after further rectification at atmospheric pressure boiled at 117—119°/775 mm. It was a colourless liquid of characteristic and pleasant odour, $d_{4^\circ}^{17\cdot0^\circ}$ 0·8326, $n_{\mathrm{D}}^{17\cdot0^\circ}$ 1·4277; whence $[R_L]_{\mathrm{D}}$ 30·90 (calc., 30·97).

Dehydration with Hydrobromic Acid.—The following procedure is of general application to alcohols which undergo dehydration on heating with hydrobromic acid; in some cases, however, reaction proceeds very slowly. The alcohol was refluxed with concentrated hydrobromic acid (usually 1 c.c. per 100 g. of alcohol) in a flask surmounted by a long column of rod-and-disc or Lessing-ring type. Heating was so adjusted that the unchanged alcohol condensed in the column and returned to the flask while the mixture of hydrocarbon and water distilled over (see Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 987). The hydrobromic acid was renewed from time to time, as some was slowly lost by distillation, the aqueous distillate being found to give the reactions of a bromide, and a further part was used up in subsidiary reactions which produced a little tarry material. When all distillable material had been driven over, the organic layer of the distillate was returned to the cleaned flask, the hydrocarbon fraction distilled over, and the residue submitted afresh to dehydration with more hydrobromic acid. After two such re-treatments dehydration had usually reached its limit. Iodine could generally be substituted for hydrogen bromide (compare Hibbert, *J. Amer. Chem. Soc.*, 1915, **37**, 1749) with almost identical results; possibly the former is slightly the less efficient, but the difference is extremely small.

The dehydrated product was roughly dried and the crude hydrocarbon separated from it by distillation was shaken (usually 20 times) with water to remove the residual traces of alcohol, kept overnight with sodium, and finally distilled over sodium, preferably in an atmosphere of nitrogen.

Dehydration Products of Dimethylallylcarbinol.—Dehydration attained at least 90% completion after three treatments with hydrobromic acid. The hydrocarbon on distillation through an 18-inch fractionating column packed with glass beads gave a total yield of 70%, of which 54% distilled at 62—69° and 46% at 69—77°. The hydrocarbon was redistilled through a Widmer column and collected in seven fractions each of approximately 2° range, the whole passing over between 62° and 77°. These fractions were distilled separately through the above-mentioned 18-inch column, whereon it became evident that the dehydration product consisted of a considerable proportion of a hydrocarbon boiling below 60° mixed with a second hydrocarbon boiling above 73°. When the fractionation had been repeated four times, the material had been separated into three portions : (1) Low-boiling hydrocarbon (b. p. 55—60°), 37%; (2) intermediate fraction (b. p. 60—73°), 20%; (3) high-boiling hydrocarbon (b. p. 73—75·8°), 43%. Further distillation of the fractions (1) and (3) indicated that the boiling points of their major components were 57—58°/766 mm. and 74·5—75·5°/766 mm. respectively.

Low-boiling hydrocarbon. The material of b. p. 57—58° took up, on exhaustive hydrogenation, 1·99 mols. of gas per mol. (82 g.) of hydrocarbon. It also absorbed 2 mols. of bromine in 1—2 hours, giving a colourless oily bromide, when treated with the reagent in chloroform at 0°. A satisfactory bromine figure could not, however, be obtained by the method of Rosenmund and Kuhnhenn (*Ber.*, 1923, **56**, 1262) : the total absorption of bromine increased with prolongation of the period of treatment; *e.g.*, 2·86 atoms of bromine per molecule were absorbed in 2 mins., and 3·35 atoms in 2 hours.

The hydrocarbon had $d_{4^\circ}^{17\cdot0^\circ}$ 0·6960 and $n_{\mathrm{D}}^{17\cdot0^\circ}$ 1·4081, whence $[R_L]_{\mathrm{D}}$ 29·10 (calc. for C_6H_{10}, 28·97). It was clear, therefore, that the double bonds in the molecule were not conjugated. This conclusion was confirmed by the fact that the hydrocarbon would not react at all with maleic anhydride under the usual conditions of addition.

Oxidation of the hydrocarbon was conducted by adding 3% permanganate solution (10 atoms of oxygen) to a vigorously stirred aqueous suspension thereof at 0°. The product, after being kept for several hours at room temperature, was freed from manganese mud by filtration, and the alkaline filtrate distilled. The distillate was collected in small fractions until no more organic material passed over. The absence of acetone (which usually passes over completely in the first 100 c.c. of distillate) and of other volatile carbonyl compounds from these fractions was shown by means of 2 : 4-dinitrophenylhydrazine. The volatile liquid acids produced by oxidation were obtained by acidifying the alkaline liquor with sulphuric acid and distilling the product until solid began to be deposited in the flask. The distillate was neutralised with caustic soda and evaporated to dryness and from the solid residue the free fatty acids were liberated by careful acidification. The acids were conveniently identified by addition of silver nitrate to a portion of the neutralised liquor. The white precipitate thus formed in good yield was filtered off quickly : it blackened on standing. The blackening, due to the production of silver from silver formate, was completed by suspending the precipitate in water and boiling. The hot solution, freed from silver by filtration, deposited characteristic lustrous plates of silver acetate (Found : Ag, 64·6. Calc. for $C_2H_3O_2Ag$: Ag, 64·65%). Confirmation of the formation of formic acid was obtained by reducing a portion of the mixed volatile acids with magnesium and hydrochloric acid and applying the usual tests to the formaldehyde produced. The non-volatile acid produced by oxidation, in this case oxalic acid, was obtained in good yield (nearly 1 mol.) by precipitation as the calcium salt from a portion of the oxidation liquor from which the volatile acids had been removed. The precipitate, containing some calcium sulphate, was estimated in the usual way with permanganate and sulphuric acid.

The three acids formed by oxidation were those to be expected from a substance (II), the acetic and oxalic acids being the normal degradation products of the first-formed acetoacetic acid. The hydrocarbon is therefore identified as *β-methyl-$\Delta^{\alpha\delta}$-pentadiene* (Found : C, 87·3; H, 12·7. C_6H_{10} requires C, 87·7; H, 12·3%).

Mixture of high-boiling hydrocarbons. The fraction (3) on further distillation under an 18-inch column showed progressive change in the refractive index of the fractions [(a) b. p. 73·0—74·5°, $n_{\mathrm{D}}^{13\cdot5^\circ}$ 1·4464; (b) 74·5—75·2°, $n_{\mathrm{D}}^{13\cdot5^\circ}$ 1·4477; (c) b. p. 75·2—75·7°, $n_{\mathrm{D}}^{13\cdot5^\circ}$ 1·4493; (d) b. p. 75·7—76·3°, $n_{\mathrm{D}}^{13\cdot5^\circ}$ 1·4506; (e) b. p. 76·3—76·7°, $n_{\mathrm{D}}^{13\cdot5^\circ}$ 1·4513]. A large proportion of the material boiled between 74·2° and 75·0°, and this fraction gave the values $d_{4^\circ}^{17\cdot2^\circ}$ 0·7179 and $n_{\mathrm{D}}^{17\cdot2^\circ}$ 1·4486, whence $[R_L]_{\mathrm{D}}$ 30·64; Σ 1·67. No satisfactory separation of either of the components could, however, be effected, nor could fractions very rich in the minor component (as indicated by the production of high yields of acetone on oxidation) be isolated.

For the preparation of derivatives and for quantitative oxidation experiments, samples were taken from the united fractions (b. p. *ca.* 74—76°). Reactions with maleic anhydride in benzene solution at room temperature did not proceed to completion, even after a week. The solid product after removal of maleic anhydride (about 75% yield) consisted to at least 20% of a polymeric addition product (only slightly soluble in petroleum); the remainder crystallised from petroleum in the network of silky needles, m. p. 58° (mixed m. p. 58°), which is characteristic of the 3 : 5-dimethyl-Δ^4-tetrahydrophthalic anhydride derived from αγ-dimethylbutadiene.

Various samples of the hydrocarbon mixture were oxidised with permanganate, under the conditions described above. All gave acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°) in considerable yield. Acetic acid also was obtained (Found for the silver salt : Ag, 64·5. Calc., 64·65%). The presence in all the oxidation products of considerable amounts of formic and oxalic acids (from 0·15 to 0·2 mol.) was demonstrated as above.

When submitted to exhaustive hydrogenation, the mixture took up 2·0 mols. of gas. Towards bromine it behaved as a conjugated substance : the first molecule of the reagent was absorbed rapidly, and the second much more slowly, addition being still incomplete (in benzene solution) after 2 days. The bromides were colourless oils.

Dehydration with iodine. Three distillations of dimethylallylcarbinol with small quantities of iodine resulted in 80% dehydration. The hydrocarbon obtained boiled at 58—78° (yield, 70%) and on careful fractionation gave non-conjugated and conjugated portions as above. The conjugated portion (b. p. 72—76°) gave formic, acetic, and oxalic acids on oxidation and behaved towards maleic anhydride very similarly to the corresponding portion of the dehydration product obtained with hydrobromic acid.

Dehydration Products of ε-Methyl-Δ^β-hexen-δ-ol.—Preparation of ε-methyl-Δ^β-hexen-δ-ol. Crotonaldehyde (105 g.), dissolved in ether (800 c.c.), was added below — 10° to *iso*propylmagnesium bromide (243 g.) contained in 1400 c.c. of ether (compare Reif, *Ber.*, 1908, **41**, 2739). The product after hydrolysis with ice-water was worked up in the usual way but without addition of acid or ammonium chloride. The crude alcohol (85 g.) was obtained in 50% yield and distilled without decomposition at 52—61°/18 mm., mainly at 55—58°. After two fractionations at atmospheric pressure it still showed rather a wide boiling range (145—150°); therefore it was fractionated once more at reduced pressure, the fraction of b. p. 55—57°/18 mm. being accepted (Reif records b. p. 139—140°/760 mm.). A specially selected sample, b. p. 55—56°/18 mm., had $d_{4^\circ}^{21\cdot4^\circ}$ 0·8372 and $n_{\mathrm{D}}^{21\cdot4^\circ}$ 1·4377, whence $[R_L]_{\mathrm{D}}$ 35·76 (calc., 35·58).

The residue in the flask gave on distillation an intermediate fraction of indefinite b. p. and a well-defined fraction which boiled without decomposition mainly at 164—167°/18 mm. (yield, 30 g.). The latter, after two fractionations at reduced pressure, boiled for the most part at 164—166°/21 mm. ($d_{4^\circ}^{25\cdot1^\circ}$ 0·9324, $n_D^{25\cdot1^\circ}$ 1·4707). It was a neutral, colourless, unsaturated liquid which reacted violently with sodium with evolution of hydrogen (Found : C, 72·2; H, 12·05. $C_6H_{12}O$ requires C, 71·9; H, 12·1%). The molecular weight, determined cryoscopically in benzene, was 259 (calc. for $C_{12}H_{24}O_2$: *M*, 200). On hydrogenation the high-boiling alcohol absorbed 1 mol. of hydrogen per 194 g. of substance, the absorption being steady but slow; on bromination, however, a lower degree of unsaturation or higher molecular weight was indicated, 1 mol. of halogen being absorbed by 247 g. of the alcohol. The molecular refraction, $[R_L]_D$ 59·98 (calc. on the assumption that the substance contains one double bond and two hydroxyl groups, 60·20), agrees fairly well with the formula $C_{12}H_{24}O_2$, but the precise constitution and the mechanism of formation of the by-product have not been determined.

Dehydration. The alcohol (48 g.) was dehydrated with great ease in the presence of hydrobromic acid, the decomposition being practically complete in one operation. A hydrocarbon, b. p. 95—115°, was obtained in 75% yield. After preliminary distillation and thorough washing in the usual manner, the hydrocarbon was redistilled (Found : C, 87·0; H, 12·4. Calc. for C_7H_{12} : C, 87·4; H, 12·6%) and then fractionated in a Widmer column. Four fractions, *viz.*, (1) b. p. below 99°, (2) b. p. 99—105°, (3) b. p. 105—108°, and (4) b. p. 108—112°, were separated, of which (2) and (3) constituted the chief portion of the material.

A sample of each fraction was kept with a solution of maleic anhydride in benzene for over a week. On evaporation of the solvent and removal of unchanged maleic anhydride with water, the addition product from fractions (1) and (2) crystallised, but those from (3) and (4) were of a sticky or gummy nature. The crystals from (1) and (2) were soluble in petroleum and separated therefrom in lustrous plates, m. p. 90° (Found : C, 67·95; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%), which must be regarded as 3-iso*propyl*-Δ^4-*tetrahydrophthalic anhydride* (XII), but in both cases (more particularly in the product from fraction 2) the crystals were accompanied by a quantity of polymeric additive compound. A little of the crystalline derivative was present in the addition product from (3), but the bulk of this product and the whole of that from (4) were composed of polymeric material.

Oxidation. Equal quantities of the four hydrocarbon fractions were oxidised with permanganate at 0°. The neutral distillates from the oxidation products gave in every case with 2 : 4-dinitrophenylhydrazine a copious precipitate of the acetone derivative, m. p. 125—126° (mixed m. p. 125—126°); moreover the quantity of this derivative obtained increased markedly and progressively in the successive fractions 1—4, being very considerable in the case of (4). The volatile acidic products from the fractions were neutralised and precipitated with silver nitrate. The white mixtures of silver salts so obtained all blackened on standing, and on boiling with water suffered very considerable decomposition with separation of silver. From each of the decomposition products, however, an undecomposed silver salt was extracted by the boiling water and these were examined separately. That from fraction (1) crystallised in white flakes which differed from silver acetate in appearance and probably consisted of nearly pure silver *iso*butyrate (Found : Ag, 55·8. Calc. for $C_4H_9O_2Ag$: Ag, 55·35%). The silver salts similarly obtained from fractions (2), (3), and (4) separated in needle-like crystals. Their silver contents corresponded with those that would be given by silver acetate admixed with a proportion of the silver salt of an acid of higher equivalent, *e.g.*, the expected *iso*butyric acid [Found : (2) Ag, 64·3; (3) Ag, 63·3; (4) Ag, 63·8. Calc. for $C_2H_3O_2Ag$: Ag, 64·65%]. When portions of the volatile acidic oxidation products were reduced with magnesium and hydrochloric acid, the presence of formaldehyde could readily be demonstrated in the case of the hydrocarbon fractions (1) and (2).

Hydrocarbons from δ-Methyl-Δ^β*-penten-δ-ol.—Preparation of δ-methyl-*Δ^β*-penten-δ-ol* (XIV). Hydracetylacetone was prepared by Claisen's method (*Annalen*, 1899, **306**, 324) and dehydrated to ethylideneacetone by distillation with a trace of sulphuric acid (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 534). Wohl and Maag's method (*Ber.*, 1910, **43**, 3284) was much less satisfactory.

The reaction of ethylideneacetone with methylmagnesium iodide was carried out at − 10°. The product, which distilled without dehydration, was collected at 35—43°/14 mm. (yield, 70%). There remained a liquid by-product, b. p. above 100° (some decomp.). The methylpentenol was rectified through a short column at atmospheric pressure. It was a colourless liquid, b. p. 122°/755 mm., 37°/13 mm., $d_{4^\circ}^{17\cdot0^\circ}$ 0·8319, $n_D^{17\cdot0^\circ}$ 1·4285; $[R_L]_D$ 30·97 (calc., 30·97).

Dehydration. This was accomplished with either aniline hydrobromide or hydrobromic acid, 75% dehydration occurring in the first operation (see p. 1072) and 90% in two operations. The crude hydrocarbon was distilled. The fraction boiling below 80° was purified (p. 1072), and had finally b. p. 74—77°/751 mm. (Found: C, 87·7; H, 12·25. Calc. for C_6H_{10}: C, 87·7; H, 12·3%). It took up 2·0 mols. of hydrogen in presence of platinum, but its reaction with bromine (2 mols.) was still incomplete after 2 days. Yield, 65%.

Maleic anhydride derivative. When the hydrocarbon was mixed with maleic anhydride (1 equiv.) in benzene, some heat was evolved but no pronounced yellow colour developed. The crude derivative, allowed to form at room temperature for a week, dissolved readily in light petroleum, *leaving no appreciable residue of polymeric product.* On cooling, the solution was filled with a very characteristic thick and voluminous network of minute, silky, interlacing crystals. This addition product (3 : 5-dimethyl-Δ^4-tetrahydrophthalic anhydride), first reported by Diels and Alder as the derivative from αγ-dimethylbutadiene, melted sharply at 58°. It showed a pronounced tendency, even when pure, to pass on long keeping into a sticky amorphous material of low m. p.; a similar change, resulting in the separation of a jelly-like material, occurred slowly in petroleum solutions of the derivative. This (apparently polymeric) change does not occur with the pure crystalline derivatives of other simple alkylbutadienes. The yield of total solid derivative, always higher than that from the hydrocarbons derived from β-methylpentane-βδ-diol and δ-methyl-Δ^α-penten-δ-ol (below), amounted to about 95%.

Fractionation. Intensive fractionation with an 18-inch column packed with glass beads showed that the hydrocarbon was heterogeneous. The following refractivities for fractions of different b. p. (at 774 mm. pressure) were observed: (1) b. p. 75·4—75·7°, $n_D^{13\cdot5^\circ}$ 1·4485; (2) b. p. 75·7—76·1°, $n_D^{13\cdot5^\circ}$ 1·4489; (3) b. p. 76·1—76·5°, $n_D^{13\cdot5^\circ}$ 1·4490; (4) b. p. 76·5—77·0°, $n_D^{13\cdot5^\circ}$ 1·4490; (5) b. p. 77·0—78·0°, $n_D^{13\cdot5^\circ}$ 1·4489. The chief portion, b. p. 74·8—75·2°, had $d_{4^\circ}^{17\cdot2^\circ}$ 0·7195 and $n_D^{17\cdot2^\circ}$ 1·4466, whence $[R_L]_D$ 30·47; Σ 1·50.

Oxidation. From the high yield of the pure maleic anhydride derivative of αγ-dimethylbutadiene obtained from the dehydration product of δ-methyl-Δ^β-penten-δ-ol it was clear that the amount of subsidiary dehydration products could not amount to more than about 5%. After oxidation of portions of the dehydration product in aqueous suspension with 3% permanganate solution at 0°, the products being worked up in the way described (p. 1072), the neutral distillate always gave a precipitate with 2 : 4-dinitrophenylhydrazine, m. p. *ca.* 126°. This proved on fractional crystallisation to be heterogeneous, consisting mainly of materials (partly unchanged reagent), m. p. 140° and above; indubitable acetone-2 : 4-dinitrophenylhydrazone could, however, not be isolated from it. On the other hand it gave oxalic acid in yields of 3—5%, and on this basis the hydrocarbon mixture is concluded to contain about 5% of αα-dimethylbutadiene. The acidic product of oxidation contained both acetic acid (Found for the silver salt: Ag, 64·6. Calc.: Ag, 64·65%) and formic acid (compare p. 1073) in good yield. In no case has pyruvic acid been obtained as an oxidation product of the αγ-hydrocarbon, the degradation always proceeding further to give acetic acid.

Hydrocarbons from β-*Methylpentane*-βδ-*diol.*—This glycol (b. p. 95—97°/14 mm.) was prepared from diacetone alcohol by electrolytic reduction using lead electrodes (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 994; Farmer, Lawrence, and Scott, J., 1930, 511).

Dehydration. In the presence of hydrobromic acid the diol underwent dehydration to the extent of 90% in two operations. The unsaturated alcohol observed by Kyriakides (see p. 1069) formed part of the distillate in the first operation: this was resubmitted to dehydration in the second operation. The hydrocarbon, purified in the usual way, boiled at 75—77°/775 mm., mainly at 76·0—76·4° (Found: C, 87·3; H, 12·5%). Yield, 50%.

When hydrogenated in presence of platinum, the hydrocarbon took up 2 mols. of hydrogen; towards bromine, however, its behaviour was similar to that of the hydrocarbon from δ-methyl-Δ^β-penten-δ-ol (above).

Maleic anhydride derivatives. The hydrocarbon, when kept for a week with the reagent in benzene, gave a good yield of the characteristic addition product from αγ-dimethylbutadiene (m. p. 58°). A little polymeric material, however, separated from the benzene solution of the reactants while they were standing, and a further quantity of jelly-like substance of very sparing solubility in petrol was separated from the crude crystalline addition product on crystallisation from petroleum. The total solid addition product after the separation of unchanged maleic anhydride was about 85%.

Oxidation. The volatile neutral portion of the product obtained under the standard conditions of oxidation (see above) consisted partly of acetone (2 : 4-dinitrophenylhydrazone, m. p. 125°; mixed m. p. 125°) and partly of other compounds which gave with 2 : 4-dinitrophenylhydrazine a material melting above 160°. The volatile acidic portion of the oxidation product, examined as above, contained both acetic acid, isolated as the silver salt (Found : Ag, 64·6%), and a not inconsiderable proportion of formic acid. The amount of oxalic acid (arising from the αα-hydrocarbon) formed in the oxidation was 0·07—0·1 mol. (estimated volumetrically).

Fractionation. The hydrocarbon, when distilled slowly at 774 mm. pressure under a good column, gave the following fractions : (1) b. p. 75·4—75·9°, $n_D^{13\cdot5^\circ}$ 1·4500; (2) b. p. 75·9—76·0°, $n_D^{13\cdot5^\circ}$ 1·4500; (3) b. p. 76·0—76·1°, $n_D^{13\cdot5^\circ}$ 1·4501; (4) b. p. 76·1—76·4°, $n_D^{13\cdot5^\circ}$ 1·4503; (5) b. p. 76·4—76·7°, $n_D^{13\cdot5^\circ}$ 1·4503. The bulk distilled at 75·0° ($d_{4^\circ}^{17\cdot2^\circ}$ 0·7190, $n_D^{17\cdot2^\circ}$ 1·4484; whence $[R_L]_D$ 30·58; Σ 1·61).

Hydrocarbons from β-*Methyl*-Δ^β-*penten*-δ-*ol*.—*Preparation of* β-*methyl*-Δ^β-*penten*-δ-*ol* (XV). β-Methylcrotonaldehyde (β-methyl-Δ^α-butenaldehyde) was synthesised from *iso*amyl alcohol (Fischer, Ertel, and Löwenberg, *loc. cit.*). The conversion of the alcohol in turn into *iso*valeraldehyde (b. p. 91—92°), α-bromo-β-methylbutaldehyde, β-methyl-Δ^α-butenal diethyl acetal (b. p. 87—92°/15 mm.), and β-methylcrotonaldehyde (b. p. 129—134°/765 mm.) was carried out with substantially the same results, yields and boiling points as reported by Fischer and his collaborators (who give b. p. 132—133°/730 mm.).

The aldehyde was treated at − 10° with a small excess of methylmagnesium iodide, and the product worked up in the usual manner. The crude alcohol, obtained in 50% yield, distilled at 52—60°/20 mm. (136—142°/768 mm.), mainly at 55°/20 mm.; there was a considerable quantity of liquid residue. The β-*methyl*-Δ^β-*penten*-δ-*ol* required careful fractionation before it could be utilised for dehydration; the greater part, b. p. 137—138°, was a colourless liquid of pleasant but rather musty odour (Found : C, 72·0; H, 12·2. $C_6H_{12}O$ requires C, 71·9; H, 12·1%) and had $d_{4^\circ}^{17\cdot0^\circ}$ 0·8448 and $n_D^{17\cdot0^\circ}$ 1·4318, whence $[R_L]_D$ 30·72 (calc., 30·97).

Hydrogenation showed that the alcohol contained 1·0 double bond per molecule. Oxidation with permanganate at 0° in the usual way gave a copious quantity of acetone (2 : 4-dinitrophenylhydrazone, m. p. 125°; mixed m. p. 125°), and much acetic acid (*p*-bromophenacyl ester, m. p. 84·5°; mixed m. p. 84·5°). Some lactic acid survived in the crude oxidation product as demonstrated by numerous qualitative tests, but the bulk of this primary oxidation product had become oxidised to acetic acid.

Dehydration. The alcohol was dehydrated smoothly and almost completely when twice distilled with small portions of hydrobromic acid. The hydrocarbon, after the usual purification, boiled at 75—80°; almost the whole, however, passed over, on redistillation, at 77—78°/760 mm. ($d_{4^\circ}^{18\cdot2^\circ}$ 0·7163, $n_D^{18\cdot2^\circ}$ 1·4396; $[R_L]_D$ 30·18; Σ 1·21). Several samples of the hydrocarbon arising from different fractions of the parent alcohol gave concordant values for boiling point, density, refractive index, and molecular refraction.

Maleic anhydride derivatives. The product formed as in preceding examples was almost entirely a white, wax-like polymeride, but when removal of the solvent was complete, it was found to be coated with minute feathery tufts of crystalline material identical in appearance with the very characteristic derivative of αγ-dimethylbutadiene. The amount of the latter, however, was so small that it could not be separated by solvent action from the polymeric material, which was itself slightly soluble in hydrocarbon solvents; no satisfactory melting point of the crystalline derivative could therefore be obtained.

Oxidation. Under the usual conditions of oxidation the hydrocarbon yielded much formic acid, oxalic acid, and acetone (2 : 4-dinitrophenylhydrazone, m. p. 124—125°; mixed m. p. 124—125°). The formic acid contained an appreciable proportion of acetic acid, since silver acetate was isolated without difficulty (Found : Ag, 64·2%).

Attempted Dehydration of δ-*Methyl*-Δ^α-*penten*-γ-*ol* (XVI).—The procedure described by Bouis (*Ann. Chim.*, 1928, **9**, 402) for the preparation of this alcohol from acraldehyde and *iso*propylmagnesium bromide, and also several modifications thereof in which the reactants were kept very cold during addition, gave yields of 9% or less. Neither *iso*propyl chloride nor the corresponding iodide proved to be satisfactory substitutes for the bromide. The following procedure, which gave a 20% yield, was the best one discovered.

*iso*Propylmagnesium bromide (1·1 mols.), dissolved in ether (800 c.c.), was treated while still warm with freshly distilled acraldehyde (1 mol.) in ether at such a rate as to maintain gentle ebullition. The ethereal solution, when reaction had ceased, was clear and colourless. The product, after hydrolysis with water, yielded the required alcohol, boiling fairly constantly at 43°/21 mm.; after two further distillations the alcohol had b. p. 124—125°/753 mm., $d_{4^\circ}^{15\cdot6^\circ}$ 0·8412, $n_D^{15\cdot6^\circ}$ 1·4316; $[R_L]_D$ 30·83 (calc., 30·97). The residual liquid was a colourless pleasant-smelling oil, b. p. about 150°/21 mm., leaving a highly viscous residue, undistillable at 10—20 mm. pressure.

The alcohol absorbed 1·01 mols. of hydrogen in presence of platinum and gave on oxidation with permanganate in the usual way much formic acid, a little oxalic acid (0·8 mol.), and unidentified material.

Behaviour with hydrobromic acid and with iodine. The clear orange solution obtained when 1 c.c. of hydrobromic acid was added to the pure alcohol was heated, dehydration apparently occurring since water distilled; this, however, was only that which had been introduced in the hydrobromic acid, and immediately it had passed over the temperature of the distillate rose to the b. p. of the alcohol. No decomposition could be induced by adding further quantities of hydrogen bromide, and no hydrocarbon could be detected in the distillate.

When iodine replaced hydrobromic acid as catalyst, no water at all was evolved and dehydration could not be induced.

Dehydration of Dimethylallylcarbinol with Phenylcarbimide.—The carbinol was heated with phenylcarbimide at 100° for 48 hours. A clear brown solution resulted from which a mixture of hydrocarbon and reagent distilled on heating, leaving diphenylurea in the flask. The impure hydrocarbon was treated with alcohol to remove the reagent, and precipitated by addition of water. The precipitated hydrocarbon, after the customary thorough washing with water, was obtained in 60% yield. On treatment with sodium a vigorous reaction ensued, some constituent being converted into a white solid. The residual hydrocarbon boiled at 60—75° and could be separated by fractional distillation into a non-conjugated and a conjugated portion. When the conjugated portion was oxidised, acetone and formic acid were the only volatile products found; when it was treated with maleic anhydride, much polymeric material was obtained but no crystalline derivative of $\alpha\gamma$-dimethylbutadiene could be isolated.

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