

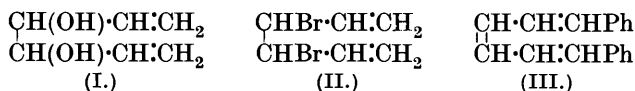
CCCXCII.—*Properties of Conjugated Compounds.*
Part III. The Bearing of Hexatriene Chemistry
on the Reactive Form of Conjugated Hydrocarbons.

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THE chemistry of hexatriene is of fundamental importance from two standpoints. First, although a simple conjugated hydrocarbon, its additive behaviour is at variance, according to van Romburgh's observation, with the requirements of the Thiele hypothesis, and secondly its structure allows the anticipation of two geometrical isomerides, one of which, approaching so closely the Kekulé representation of benzene, has been a subject of speculation in respect of a possible valency connexion between the terminal carbon atoms.

With van Romburgh's hexatriene the evidence for 3 : 4-addition

is, apparently, convincing. The formation of the hydrocarbon from Griner's *s*-divinylglycol (I) (the reduction product of acraldehyde, *Ann. Chim. Phys.*, 1892, **26**, 368) through the 3 : 4-dibromide (II)



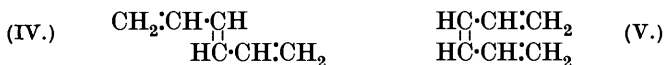
would appear quite normal ; further the crystalline product obtained by adding bromine to the hydrocarbon, since it is identical with the parent dibromide (II), would be naturally regarded as a 3 : 4-dibromide. At the outset of this investigation this series of reactions appeared to offer an attractive method for testing the generality of the 3 : 4-additive mode in the hexatriene series. Thus it was found with a 1 : 6-diphenylhexatriene (III) synthesised from cinnamaldehyde through stages analogous to (I) and (II), that out of the very numerous geometrical, stereo-, and position isomerides theoretically possible the additive dibromide actually obtained was identical with the parent dibromide ; with 1 : 6-dimethylhexatriene and 2 : 5-dimethyl-1 : 6-diethylhexatriene, which were also synthesised, polymerisation took place too rapidly to allow of satisfactory bromination.

Derivation of Hexatriene Bromides.

Re-examination of the *s*-divinylglycol from acraldehyde showed that, contrary to Griner's opinion, it was a mixture of *meso* and *racemic* forms : on reduction, it yielded two forms of *s*-diethylglycol, each oxidisable to propionic acid. On replacement of hydroxyl by bromine with phosphorus tribromide under Griner's conditions—conditions under which much hydrogen bromide was liberated—the product, so far from being homogeneous, consisted of solid and liquid bromides boiling over a considerable range. Excluding the highest-boiling fraction consisting of a tribromohexene (the formation of which was reduced to a minimum by modifying Griner's method), the material consisted of a liquid and a solid, designated for convenience (A) and (B). Of these, the solid (B) was the compound utilised by van Romburgh for generating hexatriene, whilst (A), an impure liquid dibromide, undoubtedly suffered progressive conversion into the isomeride (B), the active agent in the conversion being in all probability the hydrogen bromide liberated during distillation. Although in purifying this unstable substance repeated fractionation involving considerable loss of material was necessary, large quantities of it were prepared. On treatment with zinc it yielded a new hydrocarbon closely approach-

ing van Romburgh's compound in physical properties and superficially indistinguishable therefrom. Whereas the new hydrocarbon yielded an oily dibromide (C) (by far the most stable of the liquid dibromohexadienes encountered) and on further bromination an oily tetrabromide, the dibromide and tetrabromides (two) from van Romburgh's hydrocarbon were all crystalline.

To this second hydrocarbon, differing entirely in its additive bromides from dihydrobenzene, must be attributed the hexatriene structure, the only feasible relationship with the known hexatriene being one of *cis-trans* isomerism as in (IV) and (V).

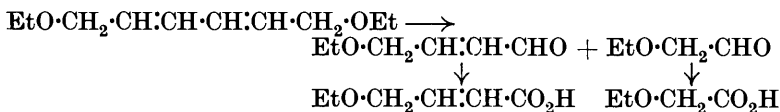


The different chemical behaviour of these substances was discovered at a very early stage, but trustworthy evidence as to which was the *trans*- and which the *cis*-form was difficult to secure. A series of oxidations undertaken in the hope of retaining the $\gamma\delta$ -carbon atoms in recognisable products such as maleic or tartaric acid proved fruitless. Attention was therefore centred on the dibromides (A), (B), and (C), structural discrimination between which represented the only apparent approach towards the elucidation of hexatriene chemistry. Of hexatriene dibromides which demand consideration, there are, excluding improbable 1 : 3-, 2 : 4-, and 2 : 5-forms, seven structures (geometrical, stereo-, and position isomerides) theoretically derivable from *trans*-hexatriene and an additional one from *cis*-hexatriene. Here again in the assignation of formulæ, direct oxidation methods had to be abandoned; some thirty oxidations of the various dibromides with different reagents were carried out and, except in one important particular mentioned later, yielded little useful information.

Structural Relationship of Hexatriene Dibromides.

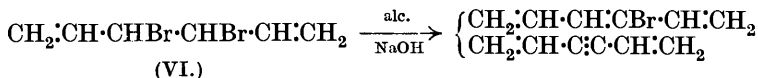
Griner had observed that the solid dibromide (B) gave a diethoxyhexadiene with alcoholic potash. This conversion was found to be almost quantitative when sodium ethoxide was used, and the homogeneous product had the advantage, unusual in this series, of considerable stability. On catalytic hydrogenation it yielded diethoxyhexane, which was successively convertible by usual processes into di-iodohexane, dicyanohexane, and a dibasic acid. The last proved to be suberic acid, indicating that the substituents at each stage occupied the 1 : 6-positions. Evidence as to the position of the double bonds in diethoxyhexadiene was obtained by

ozonisation: the ozonide yielded with water γ -ethoxycrotonaldehyde, ethoxyacetaldehyde, and the corresponding acids.



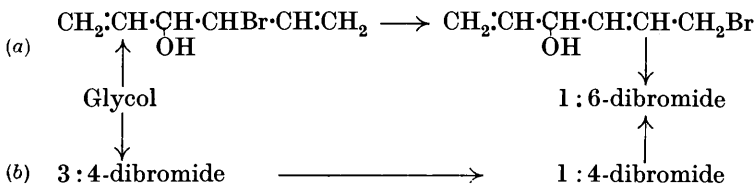
The constitution of the parent dibromide follows from that of its diethoxy-derivative. It is true that change of substituent position during the transformation with sodium ethoxide is not entirely out of the question, but this possibility is discounted by several considerations. Not only was there no positive indication of such change, but degradation of the ozonide of the dibromide repeatedly failed to yield any recognisable trace of formaldehyde or of formic acid; the high boiling point of the dibromide compared with those of its isomerides was also in keeping with the 1:6-constitution. Thus a 3:4-glycol yields a 1:6-dibromide and the hydrocarbon derived from the latter adds bromine terminally.

Evidence bearing on the change from 3:4-glycol to 1:6-dibromide was furnished by the parent dibromide of the new hexatriene. This lost hydrogen bromide with such facility that the corresponding diacetate, diethoxy-compound, and glycol were unobtainable from it: it yielded a hydrocarbon, C_6H_6 , of strong acetylenic odour and a bromohexatriene—a mode of reaction pointing to the constitution (VI).



This constitution is, moreover, the only one which permits of debromination without necessitating general valency rearrangement. As such rearrangement would lead in all probability to a *trans*-form, the new hydrocarbon, which has the slightly lower boiling point, is regarded as a *cis*-form.

Whether or no the 3:4-dibromide (A) consists essentially of one stereoisomeric form is uncertain. The preferential disappearance



of one stereoisomeric configuration in the change 3:4-glycol \longrightarrow 3:4-dibromide \longrightarrow 1:6-dibromide is conceivable, but there are

indications that to some extent the change proceeds as in scheme (a). Of the alternative scheme (b), which involves complete bromination before isomerisation, it may be said that efforts directed towards detecting the presence of the intermediate 1 : 4-dibromide gave no positive result. The yield of hydrocarbon repeatedly obtained from (A) (30%) was consistent with the presence of a proportion of less readily debrominated dibromide but was equal to that of van Romburgh's hydrocarbon from the homogeneous form (B).

Migration of Bromine.

The formation of the 1 : 6-dibromide from the 3 : 4-glycol has every appearance of involving the migration of bromine. If of common occurrence, the existence of such a facility is a consideration of the utmost importance in arriving at a *generalised* representation of the reactive form of conjugated hydrocarbons. The phenomenon is already known in the saturated hydrocarbon series (Lucas and Jameson, *J. Amer. Chem. Soc.*, 1924, **46**, 2476) and there is accumulating a considerable body of evidence that bromine migration in unsaturated hydrocarbons happens frequently; further, the general tendency of such halogen movement appears to be towards the assumption of terminal position with respect to a previously conjugated unit. Illuminating instances are those of hydrogen bromide addition to isoprene and $\beta\gamma$ -dimethylbutadiene (Claisen, *J. pr. Chem.*, 1922, **105**, 68; Bergmann, *J. Russ. Phys. Chem. Soc.*, 1920, **52**, 37). In both cases, the first-formed tertiary bromide arising by 1 : 2-addition isomerises to a primary bromide, apparently the result of terminal addition; both changes are unexplainable by hydrogen migration. The question as to the primary or secondary nature of an additive product is vital, and if facile change from a primary to a secondary product is prevalent where bromine is the addendum, it is also to be suspected, speaking of hydrocarbons, where hydrogen is the addendum; in the latter case, however, proof is exceedingly difficult for obvious reasons.

The number of well-authenticated instances of 1 : 4-addition to hydrocarbons is very small. The production of a 1 : 4-dibromide from isoprene has recently been established (Bergmann, *loc. cit.*, p. 24; Staudinger, *Helv. Chim. Acta*, 1922, **5**, 756); the formation of a considerable proportion of the 1 : 2-dibromide of butadiene along with the 1 : 4-product is recorded by Straus as a private communication from Thiele (*Ber.*, 1909, **42**, 2872), and the formation of a 1 : 4-dibromide of *cyclopentadiene* is recorded by Thiele (*Annalen*, 1900, **314**, 296). The behaviour of butadiene, isoprene, and *cyclopentadiene* is at present being further examined, but in 1909 Straus (*loc. cit.*) expressed the opinion that whilst 1 : 4-addition

may occur, it is not the rule. He went beyond this in stating that no case was then known, at least among open-chain compounds, where 1:4-addition took place exclusively. Straus's further reflexion concerning the gloomy prospect afforded by the necessity of exhaustively determining the constitution of each single additive product before judging the position of entering halogen atoms suggests either a specific additive mode for each substance, or rather (since the reactive form of the addendum, molecular or atomic, is regarded as a possible contributing feature) that the joint relation of unsaturated hydrocarbon and addendum is specific. Leaving out of consideration the reactive form of the addendum, the formation of two or more additive dibromides for any conjugated hydrocarbon may be viewed in two ways: either the latter has two or more distinct tendencies towards reaction, possibly expressible by an equilibrium between reactive forms (compare Chandrasena and Ingold, J., 1922, **121**, 1312), or one or more of the products arise by secondary process—in the latter case the isomeric change is in no wise dependent on the reactive form of the parent hydrocarbon. For an equilibrium between the reactive forms of hydrocarbons there is no direct experimental evidence (compare Farmer and Healey, this vol., p. 1060).

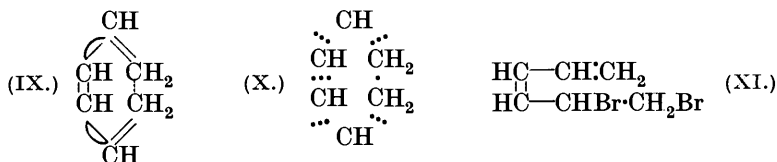
Yet van Romburgh's hexatriene adds bromine terminally. Obviously, if the foregoing considerations hold good, the 1:6-product may be no less a secondary product than the same compound is when formed from a 3:4-glycol. Since free hydrogen bromide and possibly free bromine are promoters of migratory changes, the use of a brominating agent other than commercial bromine is indicated in striving to isolate the primary additive bromide. Gupta and Thorpe (J., 1922, **121**, 1896) have investigated the employment of dibromodimethyldihydroresorcinol as a source of bromine in substitution reactions, and Rosenmund and Kuhnhen (Ber., 1923, **56**, 1262) have used the hydrobromide of quinoline dibromide with success in both substitution and additive reactions. When the quinoline derivative is employed with van Romburgh's hexatriene, instead of complete transformation into the solid dibromide, the latter (B) is replaced to a large extent (usually about 65%) by a new liquid dibromide (D), which is comparatively stable at room temperature but is converted (with slight decomposition and evolution of a little hydrogen bromide) into the



1:6-form (B) on distillation. The only reasonable formula for this substance (D) is (VII), a constitution borne out by its behaviour

with alcoholic alkali. With this reagent, as anticipated, (D) did not yield an acetylenic hydrocarbon, nor did it yield a diethoxy-derivative—a circumstance rendering a *cis-cis*- or *cis-trans*-1 : 6-configuration highly improbable—but conversion into a bromohexatriene readily took place. The further characterisation of the dibromide (VII) and its derivative (probably VIII) was not possible with the material at disposal.

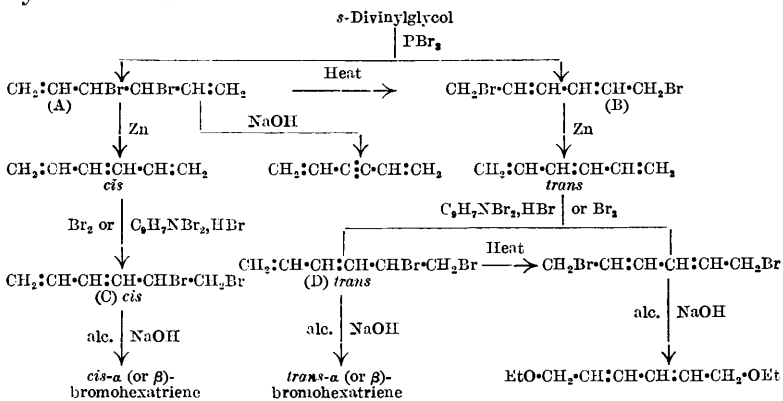
Turning to *cis*-hexatriene, residual valency or electronic formulæ such as (IX) and (X) automatically disappear with the denial of an activated form in which the three unsaturated centres of the chain are fused.



But whether the reactive form of the hydrocarbon is an open-chain or pseudo-cyclic structure, the formation of a 1 : 6-dibromide would be expected to result in the appearance of the solid (B), since the necessary valency adjustment consequent on addition should lead to the assumption of the *trans-trans*-configuration no less than in the case of addition to *trans*-hexatriene. Both hexatrienes being regarded as open-chain forms, then of those additive modes which would tend to destroy differentiation between the respective additive products there are 1 : 6 (compelling valency reorganisation), 3 : 4 (removing the double bond which is the seat of geometrical isomerism) and 1 : 4 (compelling valency reorganisation). Neglecting 1 : 3-, 3 : 5-, etc., forms, there is left only the 1 : 2-form, so that the only distinction between the 1 : 2- dibromides from the two hydrocarbons should be one of spatial distribution as in (VII) and (XI).

It was found by experiment that the dibromide (C) from the new hexatriene behaved in quite different fashion from the known 1 : 6- and 3 : 4-forms. It was not convertible into an acetylenic hydrocarbon or a diethoxy-derivative, but, like the labile product (D) from van Romburgh's hexatriene, readily yielded with alkali a bromohexatriene. The great difference between the forms (C) and (D) is the tendency towards bromine migration in the latter contrasting with the high degree of stability of the former. This difference is quite compatible with the widely different steric conditions in the two compounds and it is noteworthy that the dibromide (C) obtained by using commercial bromine appeared in every

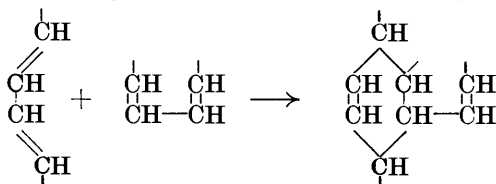
respect identical with that obtained by using quinoline dibromide hydrobromide.



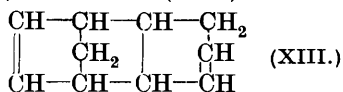
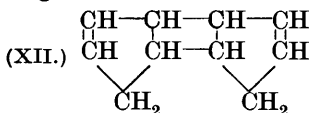
The halogen atoms of certain of the additive dibromides of this series possess marked lability: *e.g.*, the dibromide of 1:6-diphenylhexatriene reverts to the hydrocarbon on treatment with diethylamine or pyridine, whilst the dibromides (A) and (B) readily liberate iodine from potassium iodide acidified with acetic acid. This lability, which has not as yet been extensively examined, varies considerably with the nature, and possibly the spatial distribution, of the groups R, R' in the complex R·CHBr·R'. For instance, whilst diphenylhexatriene dibromide loses its bromine with pyridine as noted above, the solid hexatriene dibromide (B) yields a stable pyridinium salt of type PyBr-CH₂·CH:CH:CH:CH-CH₂-PyBr and analogous compounds with diethylamine and aniline. Evidence on the subject of bromine migration is furnished by Prévost in two papers which escaped the authors' notice until a late stage in the investigation. It is shown (*Compt. rend.*, 1926, **183**, 1292) that erythrol, CH₂·CH·CH(OH)·CH₂·OH, when treated with phosphorus tribromide in pyridine solution, yields not the expected 1:2-dibromo-Δ³-butene, but 1:4-dibromo-Δ²-butene, CH₂Br·CH:CH·CH₂Br. Thus the transformation already known to take place when the hydroxyl groups of substituted vinylcarbinols are replaced by bromine, R·CH(OH)·CH:CH₂ $\xrightarrow{\text{PBr}_3}$ R·CH:CH·CH₂Br, is repeated with vinylglycol (erythrol). Consequently the suspicion arose that *s*-divinylglycol might behave similarly, and this author enumerates (*Compt. rend.*, 1927, **184**, 458) certain observations of Griner (*loc. cit.*) that are inconsistent with a 3:4-constitution for solid hexatriene dibromide. In support of this view, he succeeded in obtaining from the latter a glycol and the corresponding diacetate which differed in properties from *s*-divinylglycol and its diacetate;

moreover, the molecular exaltations of these two derivatives are consistent with the constitutions $\text{HO}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{AcO}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{OAc}$ respectively.

The chemistry of hexatriene is intelligible on the basis of bromine migration in a non-conjugated system, but although it is clear that a terminal additive product is by no means the necessary outcome of primary additive reaction, and although it may be demonstrable that a terminal product may arise merely by isomerisation of a different additive form, there is as yet no certainty that it may not also arise as a primary product of addition. Thus whilst there can be no other conclusion than that the attempts which have been made from time to time (compare Allsop and Kenner, *J.* 1923, **123**, 2296) to retain the Thiele hypothesis by restricting its scope to conjugated hydrocarbons cannot stand when bromine and hydrogen bromide are the addenda considered, it is possible that the modern extension of the Thiele hypothesis which allows of two or more types of polarisation, one or more of which may come into play as determined by the nature and reactive condition of the addendum, may cover the experimental observations. At the same time, the extent to which addition to an unsaturated compound and addendum separately is by no means clear. In this respect polymerisation processes are of great interest. If butadienoid compounds in general polymerise in the manner suggested by Lebedef (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249) it would seem



that the forms $\cdot\overset{\cdot\cdot}{\text{C}}\text{H}:\text{CH}:\text{CH}:\overset{\cdot\cdot}{\text{C}}\text{H}$ and $\text{CH}:\overset{\cdot\cdot}{\text{C}}\text{H}:\overset{\cdot\cdot}{\text{C}}\text{H}:\text{CH}$ (or their electronic equivalents) may co-exist and that additive mode is determined by the reactive state of each particular addendum. The usual co-existence of such forms would account for the difference between the recorded tendencies towards polymerisation of open-chain butadienes and *cyclopentadiene*, the latter yielding under the exigencies of spatial configuration a dimeride (XII) (Staudinger, *Helv. Chim. Acta*, 1924, **7**, 23) rather than (XIII).



Nevertheless the appearance of ready isomerisation among the products of addition to conjugated hydrocarbons is a factor demanding consideration in estimating the significance of current reaction formulæ. It is hoped shortly to submit further evidence on the subject of *primary* additive products.

EXPERIMENTAL.

s-Divinylglycol.

Reduction.—The glycol (prepared in large quantities from the pure stabilised acraldehyde of Messrs. Poulenc Frères by the method of Griner, *loc. cit.*) was reduced at atmospheric pressure and room temperature with palladium and hydrogen. Absorption was rapid and somewhat exceeded the requirements of simple hydrogenation—a fact explained by the formation of some quantity of a volatile alcohol, presumably ethylpropylcarbinol. On working up the product in the usual way, a liquid was obtained; one portion of this (b. p. 87—89°/15 mm.) remained almost completely liquid at —20°, whilst the remainder (b. p. 89—91°/15 mm.) solidified in the receiver of the apparatus. The former, after being freed as far as possible from the latter and redistilled, was obtained as a colourless, mobile oil, b. p. 87—88°/15 mm. (Found: C, 60·6; H, 11·8. $C_6H_{14}O_2$ requires C, 61·0; H, 11·9%). The latter crystallised from light petroleum in white plates, m. p. 88° (Found: C, 60·5; H, 11·8%). Both substances gave good yields of propionic acid (identified as the anilide, m. p. 105°) when carefully oxidised with dilute potassium permanganate. They must therefore be stereoisomeric forms of *s-diethylethylene glycol*.

Bromination.—Numerous methods of halogenation were tested. The most satisfactory reagent was phosphorus tribromide. Griner's procedure (*loc. cit.*, p. 380) was followed, but it was found advantageous to employ a mechanical stirrer and extract the product (after pouring on ice) with ether. The well-washed extract was dried and the main bulk of solvent removed on a steam-bath. The remaining ether was removed at reduced pressure, and the residual oil diluted with light petroleum and cooled in a freezing mixture. The crystals of dibromide (B) (m. p. 85°) which separated were removed and the procedure of cooling and filtering twice was repeated. The ultimate filtrate was freed from solvent as above, and the residual oil fractionated. To avoid gross decomposition, it was necessary to distil the crude liquid, first, at 1 mm. pressure; subsequently three fractions were collected, (a) a small portion boiling below 80°/11 mm., (b) b. p. 80—115°/11 mm., (c) b. p. 115—140°/11 mm. The portion (b), on redistillation, passed over

almost entirely at 80—95°/10 mm.; this material corresponded in composition approximately with hexatriene dibromide, but contained a material which caused considerable carbonisation on standing for a few hours. To obtain some idea of the correct boiling point of the pure dibromide, the sub-fractions indicated were analysed ($C_6H_8Br_2$ requires C, 30.0; H, 3.4; Br, 66.6%).

B. p.	Percentage composition.		
	C.	H.	Br.
80—87°/10 mm.	32.2	4.4	63.4
88—92°/11 mm.	31.0	4.1	—
90—95°/10 mm.	31.1	3.9	65.0
90—96°/11 mm.	30.0	4.0	64.7

Finally, a considerable quantity of a pale yellow oil (A), b. p. 94—96°/11 mm., was obtained, which was used in subsequent operations (Found: C, 30.0; H, 3.6; Br, 66.6%). This substance could not be kept for many days at room temperature owing to the rapidity of carbonisation.

The higher-boiling material, after separation by the above-described method of a quantity of solid dibromide which commenced to crystallise on cooling, consisted mainly of a yellow oil, b. p. 135—140°/11 mm. This was evidently a *tribromohexene* (Found: Br, 73.1. $C_6H_9Br_3$ requires Br, 74.8%). It was subsequently found that the proportion of this substance was greatly reduced when bromination was effected by gradually pouring a chloroform solution of the glycol into a chloroform solution of phosphorus tribromide. With this procedure, however, it was particularly necessary to avoid undue heating of the crude mixture of bromides whilst removing the solvent.

Dibromide (A) and its Derivatives.

γδ-Dibromo-Δ^{αε}-hexadiene.—All attempts to demonstrate the constitution of the dibromide (A) by direct oxidation failed. The assigned formula rests upon the properties of the substance in relation to those of the three isomeric dibromides.

(a) *Isomeric Change.*—It was repeatedly observed during distillation of this liquid that a portion of the material suffered change of boiling point. This was not very marked at pressures of 1—4 mm., degradation (accompanied by liberation of hydrogen bromide) then being slight, but was much more marked at pressures of 10—22 mm., degradation being appreciable. From the higher-boiling portions so produced, crystals of the solid dibromide invariably separated. The loss of material sustained in this way was considerable and in conjunction with the initial low yield of crude bromides rendered

the accumulation of adequate quantities of reasonably pure liquid dibromide very laborious.

(b) *Ease of Hydrogen Bromide Removal.*—Numerous attempts were made to prepare the glycol and the diacetate of the glycol corresponding to this dibromide. In every case, owing to the loss of hydrogen bromide, the product was a mixture of substances of very different boiling point from which no pure substance could be fractionated. With alcoholic sodium ethoxide, loss of hydrogen bromide was still more complete: a $\gamma\delta$ -diethoxyhexadiene was therefore unobtainable.

For rapid removal of hydrogen bromide alcoholic sodium hydroxide was found to be the best reagent. Sodium ($1\frac{1}{2}$ atoms) was dissolved in aqueous alcohol, and the cold solution added gradually, with shaking, to an alcoholic solution of the dibromide (1 mol.). The separation of sodium bromide was completed by heating the mixture for a few minutes on a steam-bath, after which the product was cooled and poured into water. An oil was precipitated: this was well washed with water, dried with calcium chloride, and fractionated. Two fractions were collected, (a) b. p. 80—95° and (b) b. p. 50—60°/22 mm. Redistillation of the former yielded a colourless, mobile hydrocarbon of penetrating, acetylenic odour. The ease with which this substance, doubtless Δ^{α} -hexadien- γ -in, polymerised rendered purification and analysis very difficult, and a detailed study of its properties impossible (Found: C, 91.1; H, 7.2. C_6H_6 requires C, 92.3; H, 7.7%). The fraction (b) yielded a faintly yellow liquid, b. p. 52—55°/20 mm., which could not be completely freed from the polymeric products of the hydrocarbon. This substance, which polymerised completely in 24 hours, resembled, in its very characteristic odour, the bromohexatrienes later described. There can be little doubt that it was γ -bromohexatriene (Found: Br, 49.3. C_6H_7Br requires Br, 50.3%).

(c) *Bromine Addition.*—The dibromide, dissolved in chloroform, absorbed bromine readily at first, but later absorption was slow. After removal of the solvent at reduced pressure and distillation, the tetrabromide (presumably $\alpha\beta\gamma\delta$ -tetrabromo- Δ^{ϵ} -hexene) was obtained as a yellow oil (b. p. 155—158°/11 mm.) which remained liquid at -25° (Found: Br, 79.7. $C_6H_8Br_4$ requires Br, 80.0%).

cis-Hexatriene.—To 3:4-dibromohexadiene, dissolved in 5 times its bulk of 98% alcohol, excess of zinc dust was added in small amounts, the reaction mixture being finally heated for 20 minutes on a steam-bath. The zinc residue was filtered off and the filtrate poured into several times its bulk of water. The oily layer was separated and washed ten times with small quantities of water. Subsequent drying over calcium chloride and distillation yielded a

colourless liquid (b. p. 75—83°) and a considerable quantity of high-boiling material. On redistillation the former boiled at 78.5°/760 mm. Yield 30%. This hydrocarbon resembled van Romburgh's hexatriene in odour and in proneness to polymerisation; the latter property in conjunction with high volatility rendered analysis difficult. The density and molecular exaltation (d_4^{20} 0.7175; n_D^{20} 1.4577; $[R_L]_D$ 30.41) are lower than the latest values recorded by van Romburgh for the isomeric hydrocarbon (Found: C, 88.5; H, 11.6. C_6H_8 requires C, 90.0; H, 10.0%). It is probable that the new hydrocarbon contained van Romburgh's hexatriene to the extent of 2—2½%.

Dibromide (C) and its Derivatives.

cis- $\alpha\beta$ -Dibromo- Δ^7 -hexadiene.—Bromine (2 atoms) was added to a chloroform solution of *cis*-hexatriene kept below 0°. Addition was very rapid. The product, after removal of the solvent at reduced pressure, was a colourless oil (all the other dibromides were yellow in liquid form), b. p. 90—96°/11 mm. (Found: Br, 66.5. $C_6H_8Br_2$ requires Br, 66.6%). There was a very small residue of the solid dibromide (B), representing about 1½—2½% of the hexatriene employed.

A colourless, stable dibromide quite indistinguishable from the above was obtained by employing quinoline dibromide hydrobromide in place of free bromine (method of Rosenmund and Kuhnhenh, *loc. cit.*). The acetic acid solution of the product was poured into ice-water, and the oily dibromide extracted with ether. It was necessary to remove the usual small amount of solid dibromide (B) before distillation.

The corresponding tetrabromide (tetrabromohexene) was obtained by employing 4 atoms of bromine instead of 2 atoms. It consisted of a large proportion of a yellow oil, b. p. 155—158°/11 mm. (Found: Br, 79.8. $C_6H_8Br_4$ requires Br, 80.0%), and a very small proportion of a solid which crystallised from petroleum in colourless needles, m. p. 91° (Found: C, 18.1; H, 2.7; Br, 79.6. $C_6H_8Br_4$ requires C, 18.0; H, 2.0; Br, 80.0%).

cis- α (or β)-Bromohexatriene.—The dibromide (C) (1 mol.) was dissolved in a little alcohol and to it an alcoholic solution of sodium ethoxide (2 mols.) was added drop by drop with shaking. The reaction was completed by heating the mixture for ½ hour on a steam-bath. On cooling and pouring the mixture into water an oil was precipitated. This was extracted with ether and dried, and the solvent removed under a column. The residue, which contained no volatile hydrocarbon, was distilled. An almost colourless liquid possessing the characteristic bromohexatriene odour passed

over at 45—65°/20 mm., leaving much material, apparently the product of extensive polymerisation. On redistillation, the bulk of the distillate boiled at 52—55°/20 mm. (Found : Br, 48.5. C_6H_7Br requires Br, 50.3%). This substance polymerised extensively in 24 hours.

Dibromide (B) and its Derivatives.

$\alpha\zeta$ -Dibromo- Δ^{88} -hexadiene.—Numerous attempts were made to demonstrate the constitution of Griner's solid dibromide (m. p. 85°) directly. As these had little success, the constitution of its diethoxy-derivative (below) was fully examined, the possibility of isomerisation during conversion being discounted by many observations.

The two forms of the corresponding tetrabromide (possibly $\alpha\beta\epsilon\zeta$ -tetrabromo- Δ^{ν} -hexene) are incorrectly described by Griner (*loc. cit.*, p. 383). The less soluble isomeride, after successively crystallising from chloroform and light petroleum, yielded colourless prisms, m. p. 111° (Found : Br, 80.0. Calc. : Br, 80.0%); the more soluble separated from light petroleum in colourless prisms, m. p. 46° (Found : Br, 80.3%). These tetrabromides showed very great stability towards oxidation by ozone and by permanganate.

Behaviour with Organic Bases.—When a dry ethereal solution of pyridine (2 mols.) was added to a dry solution of the solid dibromide (B) a bulky precipitate separated. This substance, which was readily soluble in water, appeared to be quite free from pyridine hydrobromide. It crystallised from alcohol-ether in colourless plates, m. p. 212°, and appeared to be the *dipyridinium* salt, $PyBr \cdot CH_2 \cdot CH : CH : CH : CH \cdot CH_2 \cdot PyBr$ (Found : Br, 41.2. $C_{16}H_{18}N_2Br_2$ requires Br, 40.2%). Analogous compounds were formed with aniline and diethylamine, but were not further investigated. Dry distillation of the dipyridinium compound yielded a large amount of pyridine dibromide and a minute quantity of a liquid with a garlic-like odour.

$\alpha\zeta$ -Diacetoxy- Δ^{88} -hexadiene.—A mixture of the dibromide (50 g.) with glacial acetic acid (50 g.) was added to excess of potassium acetate moistened with glacial acetic acid (50 g.). The whole was heated on a steam-bath for 24 hours. The cooled mass was poured into water, and the product isolated in the usual way. As it still contained bromine, it was heated for a further period with potassium acetate and acetic acid. Finally a product almost free from bromine was obtained. The bulk of this distilled at 155—160°/14 mm. as a colourless oil (Found : C, 60.8; H, 7.0. $C_{10}H_{14}O_4$ requires C, 60.6; H, 7.1%).

$\alpha\zeta$ -Diethoxy- Δ^{88} -hexadiene.—The solid dibromide (B) was added to the requisite quantity of thoroughly cooled alcoholic sodium

ethoxide. The product was well shaken and gradually heated till ebullition set in. The reaction was completed by heating for $\frac{3}{4}$ hour on a steam-bath. After cooling, the reaction mixture was poured into water, and the precipitated oil extracted with ether. The diethoxy-compound was obtained in almost quantitative yield as a colourless, mobile oil (b. p. $116^{\circ}/20$ mm.) of characteristic odour (Found: C, 70.5; H, 10.8. Calc.: C, 70.6; H, 10.6%). This corresponds to Griner's product (regarded as $\gamma\delta$ -diethoxy- $\Delta^{\alpha\epsilon}$ -hexadiene) obtained by the action of alcoholic potash on the same dibromide (*loc. cit.*, p. 388).

Reduction of $\alpha\zeta$ -Diethoxy- $\Delta^{\beta\delta}$ -hexadiene.—Diethoxyhexadiene (10 g.) was reduced with colloidal palladium and hydrogen at room temperature and atmospheric pressure. Reduction was rather slow at the beginning but became rapid later and was complete in about $3\frac{1}{2}$ hours. The amount of hydrogen absorbed was about 35% in excess of that theoretically required for reducing two double bonds. On pouring the reaction mixture into water and working up in the usual way the product was found to consist of two substances, (a) a colourless liquid of strong odour (b. p. $38-45^{\circ}/14$ mm.), appreciably volatile in ether vapour and very volatile in alcohol vapour, and (b) a less volatile, colourless liquid (b. p. $80-90^{\circ}/14$ mm.). The former (about 5 g.), which was almost certainly α -ethoxyhexane, distilled completely at $42^{\circ}/14$ mm., but was not quite free from the second product (Found: C, 72.2; H, 13.0. $C_8H_{18}O$ requires C, 73.8; H, 13.8%); the latter (about 3 g.), which possessed a faint odour and distilled at $86^{\circ}/14$ mm., was $\alpha\zeta$ -diethoxyhexane (Found: C, 70.2; H, 12.5. $C_{10}H_{22}O_2$ requires C, 70.0; H, 12.6%).

$\alpha\zeta$ -Di-iodohexane.—Diethoxyhexane contained in a Carius tube was saturated with dry hydrogen iodide, the weight of gas absorbed being noted. The tube was sealed and heated at 100° for 16 hours. It was then cooled, opened, and re-treated with hydrogen iodide until the requisite quantity of this gas (2 mols.) had been absorbed. It was again heated for 16 hours. The cooled product consisted of a small, colourless layer which seemed to be mainly alcohol (free from any considerable amount of ethyl iodide) and a heavy, dark brown layer. The latter was dissolved in ether, washed with sodium bicarbonate solution and water, and dried with calcium chloride. This crude di-iodohexane, which was only slightly deficient in iodine, was converted into the corresponding dinitrile without further purification.

$\alpha\zeta$ -Dicyanohexane.—The crude di-iodohexane was converted into the dinitrile with potassium cyanide as described by Hamonet (*Compt. rend.*, 1903, **136**, 244). The dinitrile was isolated by pouring the reaction product into water and extraction with ether. The

dried extract gave a good yield of a pale yellow oil, which differed from the di-iodide in its ready solubility in alcohol.

Suberic acid. When heated with concentrated hydrochloric acid for 1 hour, the crude dinitrile was hydrolysed and gave an excellent yield of suberic acid, which separated from water in colourless needles, m. p. 138°, mixed m. p. 138° [Found : C, 55.2; H, 7.9; *M* (dibasic), 177. Calc. : C, 55.2; H, 8.0%; *M*, 174].

Oxidation of α -Diethoxy- Δ^{88} -hexadiene.—A stream of ozonised oxygen was passed for 14 hours through a chloroform solution of this substance. The solvent was then removed at reduced pressure. The colourless, syrupy ozonide was shaken with 50 c.c. of water, and the mixture warmed until complete decomposition took place (85°). The yellow aldehydic oil was separated from the aqueous layer and dissolved in ether. From the ethereal extract, freed from acidic matter by shaking it several times with dilute bicarbonate solution, and dried with calcium chloride, the aldehyde was obtained as a mobile, pungent-smelling oil; from the alkaline washings a yellow syrupy acid was extracted by ether. This gave an aldehydic reaction, but deposited, on long standing in a vacuum desiccator, a few crystals (long, colourless prisms, m. p. 45°) of a non-aldehydic acid. The combination of melting point, equivalent (micro-titration, 135), unsaturated nature, and its ready solubility in water and petroleum suggested that the latter acid was γ -ethoxycrotonic acid (compare Lespieau, *Compt. rend.*, 1905, **140**, 723). This was subsequently confirmed (below).

The residual syrupy acid was fractionated. The bulk distilled at 106—107°/21 mm. as a colourless, mobile liquid. Since the basicity of this substance was nearly that of ethoxyacetic acid (the degradation product complementary to γ -ethoxycrotonaldehyde), it was converted into the *p*-bromophenacyl ester. An excellent yield of *p*-bromophenacyl ethoxyacetate was obtained therefrom by the method of Judefind and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1047) : this crystallised in colourless plates, m. p. 104.5°, and agreed in properties with the product described by these authors (Found : C, 48.1; H, 4.4. Calc. : C, 47.8; H, 4.3%).

The aldehydic oil was separated into four fractions by distillation, (a) below 75°/21 mm., (b) 75—85°/21 mm., (c) 85—100°/21 mm., and (d) a viscous residue which partly distilled on strong heating to yield a colourless, mobile oil which polymerised to a jelly on standing for several days. Of these fractions, (b) and (c) constituted the bulk of material. The former, which distilled almost completely at 80°/21 mm., did not yield a semicarbazone or phenylhydrazone but corresponded in composition with γ -ethoxycrotonaldehyde (Found : C, 62.8; H, 8.9. C₆H₁₀O₂ requires C, 63.1; H, 8.8%). This

constitution was confirmed by oxidation (below). From fraction (a) a small quantity of impure ethoxyacetaldehyde (b. p. 70°) was isolated. As this was insufficient for adequate fractionation, it was oxidised to ethoxyacetic acid (below).

Oxidation of γ -Ethoxycrotonaldehyde and Ethoxyacetaldehyde.—These oxidations were conducted in almost exactly the way described by Delépine and Bonnet (*Compt. rend.*, 1909, **149**, 39). The former yielded a solid acid which crystallised from light petroleum in colourless prisms, m. p. 45°. This acid was γ -ethoxycrotonic acid [Found : C, 55.2; H, 7.6; *M* (monobasic), 133. Calc. : C, 55.4; H, 7.7%; *M*, 130] and was identical with that formed directly during the decomposition of the ozonide.

The oxidation product of ethoxyacetaldehyde was a liquid. This was identified as ethoxyacetic acid by conversion into the *p*-bromophenacyl ester described above.

trans-Hexatriene.—Van Romburgh's hydrocarbon, regarded as *trans*-hexatriene, was prepared from the dibromide (B) as described for the *cis*-compound.

As observed by van Romburgh, when a chloroform solution of bromine (1 mol.) was added to a chloroform solution of the hydrocarbon (1 mol.) at 0°, conversion into the solid dibromide ($\alpha\zeta$ -dibromo- $\Delta^{\beta\delta}$ -hexadiene) was complete.

Dibromide (D) and its Derivatives.

trans- $\alpha\beta$ -Dibromo- $\Delta^{\gamma\epsilon}$ -hexadiene.—When quinoline dibromide hydrobromide (1 mol.) was gradually added at 0° to a well-agitated solution of the *trans*-hydrocarbon in glacial acetic acid, bromination was readily effected. The product was poured into ice-water, and the oily suspension filtered. After removal of a quantity of the solid bromide (B) by filtration the filtrate was extracted with ether. The extract was washed until free from acetic acid and dried, and the ether was evaporated, finally under reduced pressure. The oily residue was dissolved in light petroleum and cooled to -25°; the solid dibromide which separated was filtered off and the cooling and filtering repeated. After removal of the bulk of the solvent by gentle heating and of the remainder under reduced pressure, a yellow oil was obtained (yield, 65%) (Found : Br, 65.2. C₆H₈Br₂ requires Br, 66.6%). A small quantity of this distilled under 1–2 mm. pressure without apparent decomposition. When cautious distillation of a larger portion at 22 mm. pressure was attempted, the distillation of the first few drops (b. p. 107°/21 mm.) was concurrent with a rapid darkening in colour and a slight evolution of hydrogen bromide. Isomeric change had taken place, for further distillation occurred only at a much higher temperature.

On cooling, the contents of the flask, which had previously remained liquid at -25° , set to a solid mass of the dibromide (B). The extent of conversion of the liquid to the solid dibromide was very high.

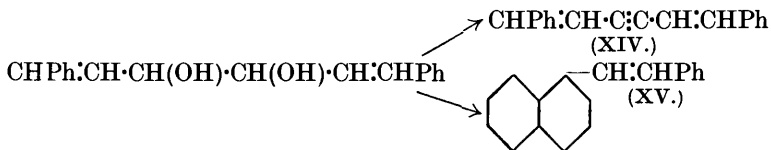
trans- α (or β)-Bromohexatriene.—Removal of hydrogen bromide from the liquid *trans- $\alpha\beta$ -dibromohexadiene* (above) was effected precisely as with the corresponding *cis*-compound (p. 2949). Much polymerisation appeared to have occurred during the reaction, for only a portion of the product was distillable. A faintly yellow liquid, b. p. $53^{\circ}/22$ mm., was obtained which possessed the characteristic odour of bromohexatriene (Found: Br, 48.2. C_6H_7Br requires Br, 50.3%). This substance polymerised the most rapidly of the three isomerides: within 15 minutes of distillation a scaly deposit appeared on the sides of the vessel and within 2 hours the change was complete.

Derivatives of $\alpha\zeta$ -Diphenylhexatriene.

s-Distyrylethylene Glycol (Hydrocinnamoin).—Reduction of cinnamaldehyde was effected by Thiele's method (*Ber.*, 1899, **32**, 1296). Separation of the solid glycol from the viscous oil was best effected by completely dissolving the latter in hot alcohol and cooling the solution in a freezing mixture. The crystals so obtained, when washed with a little ether and recrystallised once from alcohol, attained at once the correct melting point (153 — 154°). Yield 10—12%.

The residual viscous oil was treated with steam to remove volatile matter, cooled, dissolved in ether and dried over sodium sulphate. Removal of the solvent left a transparent jelly, which was kept in an evacuated desiccator for a week. Portions of the substance were examined in the following manner to ascertain whether it contained isomeric distyrylglycols or their corresponding hydrocarbons: (a) *Distillation.* About half the material distilled between 110° and 200° at 3 mm.; the remainder was undistillable (solid distyrylethylene glycol distils readily at 2 mm.). The portion, b. p. 130 — $200^{\circ}/3$ mm., deposited colourless plates, m. p. 206° , which dissolved in ether and benzene to give fluorescent (bluish) solutions. This hydrocarbon had previously been noted by Thiele (*loc. cit.*), and his view that it may be phenyl- α -naphthylethylene appears to be correct: the substance is unimolecular in benzene solution, and of the dehydration products (XIV) and (XV) the latter accounts for our inability to effect any reduction with hydrogen and colloidal palladium (Found: C, 93.9; H, 5.5; *M*, cryoscopic, 225. Calc.: C, 93.9; H, 6.0%; *M*, 230). (b) *Dehydration.* When the material was heated with acetic anhydride for 4 hours at 150° , two substances were obtained, the hydrocarbon (XV) and an oil (more mobile than

the original one) from which no definite product could be isolated. (c) *Attempted benzoylation*. Treatment with benzoyl chloride



(Schotten-Baumann conditions) yielded again the hydrocarbon (XV). (d) *Bromination*. Addition of bromine yielded no identifiable product, but phosphorus tribromide gave a small quantity of the diphenyldibromohexadiene, m. p. 124° , described below, and other non-purifiable products.

Dibromo- $\alpha\zeta$ -diphenylhexadiene.—To phosphorus tribromide (20—25 g.), dissolved in dry ether at 0° , distyrylethylene glycol (5 g.) was added in small amounts, with vigorous shaking. The temperature was allowed to rise during addition and the product was kept at room temperature for $\frac{3}{4}$ hour. The mass was poured on ice and the pale yellow solid which was precipitated was filtered off and washed with ether. The filtrate was extracted with ether, and the extract thoroughly washed and dried. The bulk of the solvent was evaporated and the remainder removed under reduced pressure. The residue was a yellow, sticky mass which was freed from oil by washing with ether. The united solid portions were dried and recrystallised from petroleum, yielding colourless crystals (3.5 g.) of *dibromo- $\alpha\zeta$ -diphenylhexadiene*, m. p. 124 — 125° (Found : Br, 41.0. $\text{C}_{18}\text{H}_{16}\text{Br}_2$ requires Br, 40.8%). The ethereal washings yielded a small amount of a yellow oil, which was very unstable and rapidly caused the decomposition of the solid dibromide if left in contact with it. This substance was probably also a dibromide; mixtures of the two when treated with zinc yielded only the diphenylhexatriene described below.

$\alpha\zeta$ -Diphenylhexatriene.—To the dibromide, m. p. 124 — 125° , dissolved in 50 c.c. of chloroform, zinc dust (1 g.) was added in small portions with thorough shaking. The mixture was then warmed for $\frac{1}{2}$ hour on a steam-bath. The cooled product, diluted with much ether, was washed with dilute sulphuric acid and water, and dried. On concentration and cooling, a crop of shining, yellow leaflets (m. p. 196°) separated. This hydrocarbon, which was crystallisable from chloroform, was undoubtedly the same diphenylhexatriene obtained by Smedley (J., 1908, **93**, 376) through condensing sodium phenylisocrotonate with cinnamaldehyde in presence of acetic anhydride (Found : C, 94.0; H, 6.6. Calc. : C, 93.1; H, 6.9%). Yield 60—65%.

Bromination of $\alpha\zeta$ -Diphenylhexatriene.—Addition of bromine (1 mol.) to the hydrocarbon (1 mol.) dissolved in a large bulk of carbon disulphide was effected at -20° . When absorption, which was rather slow, was complete, the product was thoroughly washed and dried. Removal of the solvent yielded a solid which, after being washed with ether, was colourless and needed no further purification. This substance, m. p. $124-125^\circ$, was identical with the solid dibromide (dibromo- $\alpha\zeta$ -diphenylhexadiene) from which the hydrocarbon had been prepared. When thus obtained, it was quite free from the traces of impurities which promoted decomposition (Found : Br, 40.7%).

The *tetrabromide* and *hexabromide* were formed with increasing difficulty by further addition of bromine. The former crystallised in white prisms, m. p. 165° (Found : Br, 58.7. $C_{18}H_{16}Br_4$ requires Br, 57.9%), and the latter in stout needles, m. p. $228-230^\circ$ (Found : Br, 67.8. $C_{18}H_{16}Br_6$ requires Br, 67.4%).

Action of Organic Bases on Diphenylhexatriene Dibromide.—Diethylamine (1 g.) was added to the dibromide (1 g.) dissolved in absolute ether. In 2 days a heavy precipitation (about 1 mol.) of pearly-white diethylamine hydrobromide, m. p. 212° , had taken place. This salt was removed and the ethereal solution was washed with dilute acid and with water and dried. On concentration, it deposited a considerable amount of pure diphenylhexatriene, m. p. 196° .

Pyridine also gave, under similar conditions, the same hydrocarbon.

Derivatives of $\alpha\zeta$ -Dimethylhexatriene [$\Delta^{8\%}$ -Octatriene].

s-Dipropenylethylene Glycol.—Crotonaldehyde was reduced in analogous manner to acraldehyde (compare Charon, *Ann. Chim. Phys.*, 1899, **17**, 266). The glycol, a faintly yellow oil, b. p. $120-122^\circ/9$ mm., was obtained in 50–60% yield.

Bromination of s-Dipropenylethylene Glycol.—The method which gave the best results is the following. The glycol (50 g.), dissolved in dry ether, was added drop by drop to a solution of phosphorus tribromide (200 g.) in dry ether (100 c.c.). At first the temperature was kept below 10° ; later, occasional moderation by cooling kept it in the neighbourhood of room temperature. When addition was complete, the mixture was kept for $\frac{3}{4}$ hour and then poured on ice. After careful washing and drying, the major portion of the solvent was distilled from a steam-bath and the remainder at reduced pressure. No solid bromide was isolable and complete carbonisation of the crude liquid was avoided only by distillation at greatly reduced pressure, all access of air to the hot liquid being prevented.

At 1 mm. a large proportion distilled : this distillate yielded fractions 68—85°/14 mm., 85—100°/14 mm., and 100—120°/14 mm., all of which had nearly the correct bromine content. The substance obviously contained two or more isomeric dibromides along with small amounts of impurity which promoted rapid decomposition at room temperature. As adequate separation of the isomerides was impossible by fractionation, the above fractions were united and redistilled; a portion, b. p. 92—100°/14 mm., was utilised for subsequent experiments. This was an almost colourless liquid which darkened in a few hours and became almost black in 24 hours (Found : Br, 56.3. $C_8H_{12}Br_2$ requires Br, 59.7%).

α-Dimethylhexatriene.—The dibromide (30 g.) yielded with zinc and alcohol (see p. 2948) an oil, much of which distilled between 45° and 112° at 25 mm. Only the portion, b. p. 45—55°/25 mm., was bromine-free: this was redistilled at ordinary pressure and a fraction, b. p. 120—130°, was collected. Thus about 8 c.c. of a somewhat impure, colourless hydrocarbon of distinctive odour were obtained (Found : C, 84.8; H, 11.2. C_8H_{12} requires C, 89.9; H, 11.1%). This, on further fractionation through a small column, yielded 2 c.c. of hydrocarbon, b. p. 125—130° (Found : C, 87.7; H, 11.4%; d_4^{25} 0.8394; n_D^{25} 1.45193; $[R_L]_D$ 34.70). Numerous attempts to obtain purer and larger specimens of the hydrocarbon were made. The rapidity of polymeric and oxidative changes, however, caused great loss both during the debromination process and subsequently; soft, wax-like flakes rapidly appeared on the walls of the vessel containing the hydrocarbon and in a few hours the latter changed into a jelly.

βε-Dimethyl-αζ-diethylhexatriene [*δγ-Dimethyl-Δ^γ-decatriene*].

α-Methyl-β-ethylacraldehyde was prepared from propaldehyde by Döbner and Weissenborn's method (*Ber.*, 1902, **35**, 1144).

δγ-Dimethyl-Δ^γ-decadiene-εζ-diol.—Methylethylacraldehyde was reduced in similar fashion to acraldehyde. The *glycol* was a rather viscous, yellow oil, b. p. 163—165°/23 mm. It was soluble in water and the common organic solvents and did not solidify at -25° (Found : C, 72.8; H, 11.3; d_4^{25} 0.9400; $[R_L]_D$ 59.20. $C_{12}H_{22}O_2$ requires C, 72.7; H, 11.1%).

εζ-Dibromo-δγ-dimethyl-Δ^γ-decadiene.—The glycol (20 g.) was added in drops to an ethereal solution of phosphorus tribromide (100 g.). After 1 hour, the mixture was poured on ice, and the dibromide extracted with ether. The dried ethereal solution yielded, on evaporation, a white, sticky mass: this was taken up in light petroleum and warmed with animal charcoal. After filtration, white

prisms, m. p. 99—100°, separated (Found : Br, 50.2. $C_{12}H_{20}Br_2$ requires Br, 49.4%).

$\beta\epsilon$ -*Dimethyl- $\alpha\zeta$ -diethylhexatriene*.—By the action of zinc on dibromodimethyldecadiene (in alcoholic solution) a product of variable boiling point was obtained. Since even the lowest-boiling fraction still contained bromine, the whole was re-treated with zinc. Much polymeric change attended these operations, waxy scales separating on the sides of the containing vessel. A quantity of unsaturated hydrocarbon of strong odour (colourless liquid, b. p. 65—70°/26 mm.) was obtained, but this still contained traces of bromine and polymerised too rapidly to allow of adequate fractionation. The obvious impurity of this specimen (Found : C, 76.0; H, 11.2. $C_{12}H_{20}$ requires C, 87.8; H, 12.2%) rendered it unsuitable for further use.

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