58. *Mechanism of Polymerisation. Part III. Experiments relating to the Constitution of the Solid Dimeride and the Liquid Trimeride of βγ-Dimethylbutadiene.*

By Ernest Harold Farmer and Robert C. Pitkethly.

The solid camphor-like dimeride formed together with various liquid dimerides by the action of the Bertram–Walbaum reagent on βγ-dimethylbutadiene appears from its behaviour towards additive reagents and on oxidation to be a mono-olefinic dicyclic hydrocarbon containing a reactive methylene group. Its behaviour with chromic acid and ozone is highly characteristic and is reminiscent of that of α-fenchene and of camphene with the same reagents. Consideration of the ways in which methylene-bicyclanes could be formed *directly* and simply from the monomeride suggest that the dimeride is either a trimethylmethylene*bicyclo*[2 : 2 : 2]octane or a tetramethylmethylene*bicyclo*[1 : 2 : 2]heptane.

The trimeric material from βγ-dimethylbutadiene is heterogeneous in constitution, but a fraction (30%) of constant refractive index can be isolated. This, on the basis of its additive behaviour, its behaviour on oxidation, and the fact that it gives a naphthalenic hydrocarbon on dehydrogenation, is thought to consist substantially of an alkenylhydronaphthalene, which may well be pentamethyl*iso*propenyloctahydronaphthalene.

The Solid Dimeride.

βγ-Dimethylbutadiene, when polymerised in an acid medium, gives a liquid monocyclic dimeride, a solid camphor-like dimeride, $C_{12}H_{20}$ (m. p. 66°), and probably two liquid dicyclic dimerides (this vol., p. 11). Although the solid dimeride can be made to react with 2 mols. of bromine when treated with pyridine perbromide, it is definitely mono-olefinic as determined by hydrogenation at atmospheric pressure and by reaction with perbenzoic acid; moreover, its dihydride is unreactive towards bromine. This behaviour, taken together with the way in which the dimeride reacts with oxidising agents (below), leaves little doubt that it is dicyclic in character.

Oxidation of the dimeride with chromic acid gives at once a crystalline monobasic acid, $C_{12}H_{20}O_2$, the reaction involving mere incorporation of oxygen atoms in the molecule and simulating that which occurs with two well-known methylene-dicyclanes, α-fenchene and camphene :
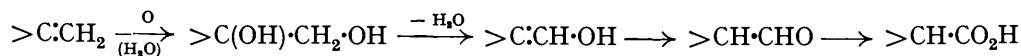
$$C_8H_{14}{>}C{:}CH_2 \xrightarrow{2O} C_8H_{14}{>}CH{\cdot}CO_2H \quad \text{(I.)}$$
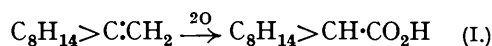
Treibs and Schmidt (*Ber.*, 1928, **61**, 459) showed that α-fenchene passes on treatment with chromic acid into a mixture of fenchenylanic acid (I) and fenchenylanaldehyde, $C_8H_{14}{>}CH{\cdot}CHO$ (II) (together with some α-fenchocamphorone, $C_8H_{14}{>}CO$); and Komppa and Roschier (*Ann. Acad. Sci. Fennicæ*, 1917, *A*, **10**, xviii, 1; *Annalen*, 1929, **470**, 129) showed that it gives on ozonolysis a mixture of this same acid and ketone. The latter authors have suggested that the acid is formed from the ozonide by the unusual rearrangement :
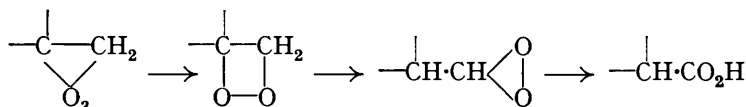
In the oxidation of α-fenchene by chromic acid, the aldehyde (II) seems to be the primary product, and the acid (I) to be formed from it by secondary reaction. Now it has been found in the case of a third well-known methylene-dicyclane, β-pinene, that conversion of the methylene-hydrocarbon into the aldehyde can be conducted in two distinct stages, *viz.*, by transformation first into the corresponding glycol with permanganate, and thence into the aldehyde (with some pinol as by-product) by the action of hot dilute acids :
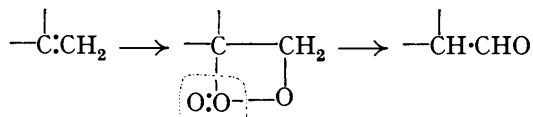
$$C_8H_{14}{>}C{:}CH_2 \longrightarrow C_8H_{14}{>}C(OH){\cdot}CH_2{\cdot}OH \longrightarrow C_8H_{14}{>}CH{\cdot}CHO$$
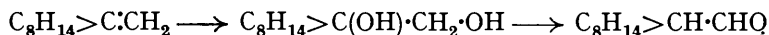
Another example of this two-stage oxidation is afforded by the conversion of β-phellandrene into phellandral under similar conditions. Hence we suggest that the course of oxidation in acid media of *all* the above-named terpenic methylene compounds is the following :

$$>\!C\!:\!CH_2 \xrightarrow[(H_2O)]{O} \; >\!C(OH)\!\cdot\!CH_2\!\cdot\!OH \xrightarrow{-H_2O} \; >\!C\!:\!CH\!\cdot\!OH \longrightarrow \; >\!CH\!\cdot\!CHO \longrightarrow \; >\!CH\!\cdot\!CO_2H$$

and that the aldehyde $C_{12}H_{20}O$ in the present work is produced from the solid dimeride of dimethylbutadiene in exactly this way.

If this is correct and the solid dimeride has an extracyclic methylene group, the dimeride should give on ozonolysis formaldehyde and a cyclic ketone (as do the methylene-hydrocarbons β-pinene and selinene : Brus and Peyresblauques, *Compt. rend.*, 1928, **187**, 194 ; Schmidt, *Z. angew. Chem.*, 1929, **42**, 126 ; Ruzicka and Stoll, *Helv. Chim. Acta*, 1922, **5**, 926), provided reaction follows a normal course. In practice, however, we have been able to obtain only a very small yield of formaldehyde from the ozonolysis product, but on the other hand have obtained approximately a 50% yield of a monocarbonyl derivative, $C_{12}H_{20}O$ (not a dicarbonyl derivative as would be expected from a dicyclene in contradistinction to a methylene-dicyclane) ; in other words, ozonolysis brings about oxidation without loss of any carbon atoms of the molecule, and this can only mean that the carbonyl derivative $C_{12}H_{20}O$ is the aldehyde corresponding to the saturated acid ($C_{12}H_{20}O_2$) produced by chromic acid oxidation of the dimeride (above), and is formed by some such mechanism as :

$$-\!\overset{|}{C}\!:\!CH_2 \longrightarrow -\!\overset{|}{\underset{\overset{\displaystyle |}{O\!:\!O\!-\!-\!O}}{C}}\!\!-\!\!CH_2 \longrightarrow -\!\overset{|}{C}H\!\cdot\!CHO$$

In the formation of a methylene-dicyclane by dimerisation of an open-chain diene the first step is with little doubt the production of an open-chain dimeric structure, which subsequently undergoes two stages of cyclisation. Now it is possible that the monocyclic dimeric kation (III), which we regard as the probable precursor of the ordinary liquid
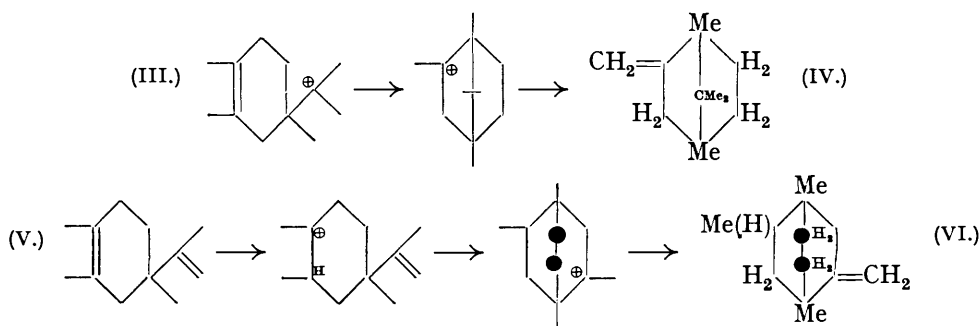
dimeride (V) (see this vol., p. 11) * passes in part by transannular addition directly into the methylene-dicyclane (IV) ; on the other hand, the solid dicyclic dimeride may well be formed directly from (V) and may thus have the formula (VI). Of the formulæ (IV) and (VI),† we consider (VI) probably to represent the solid dimeride, since existing

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* Free-radical structures equivalent in their essential characteristics to the primarily formed, open-chain dimeric kation and to the derived monocyclic kation (III) could be postulated as intermediates in the case of thermal polymerisations (compare Harkness, Kistiakowsky, and Mears, *J. Chem. Physics*, 1937, **5**, 691), but are hardly likely to appear in acid-catalysed polymerisations in solution. It may be remarked here that the experimental evidence advanced by Harkness and his collaborators (*loc. cit.*) as indicating the non-formation of any proportion of cyclic dimeride during the thermal dimerisation of gaseous butadiene is hardly more convincing than Vaughan's earlier evidence to the contrary (*J. Amer. Chem. Soc.*, 1932, **54**, 3863 ; 1933, **55**, 4109).

† Other structures (" meta "-bridged) could be formulated, but are not considered likely to be produced.

evidence indicates that the ease of formation and freedom from strain of *bicyclo*[1 : 2 : 2]-heptanes is inferior to that of *bicyclo*[2 : 2 : 2]octanes; but it is to be borne in mind that the conversion at will of the ordinary dimeride (V) into the solid dimeride has not yet been effected.

The Liquid Trimeride.

The trimeric fraction, when separated by distillation from dimeric, tetrameric, and higher polymeric material, was evidently not homogeneous in constitution, since its sub-fractions differed considerably in physical properties. A portion of the trimeric fraction of nearly constant refractive index was separated by systematic fractionation and this was used for investigation. The analytical figures, molecular weight (in benzene), and molecular refractivity of this portion agreed with the values required for a diolefinic *dicyclic* trimeride, $C_{18}H_{30}$.

Although only one double bond in the trimeric molecule could be saturated by catalytic hydrogenation at atmospheric pressure and room temperature, yet the trimeride absorbed two molecules of bromine, and its dihydride one molecule of bromine. With permanganate the trimeride underwent rapid oxidation at room temperature, but its dihydride was attacked only very slowly. On ozonolysis the trimeride gave formaldehyde (0·2 mol.) together with a ketonic oil, and other materials which have not been investigated. The formation of the formaldehyde points to the presence of a methylene group in at least one-fifth of the material ozonised.

On dehydrogenation with selenium the trimeride gave a mixture of hydrocarbons, from which could be isolated *via* its *picrate* a crystalline aromatic hydrocarbon, $C_{17}H_{22}$, m. p. 111°. With this proportion of carbon to hydrogen the hydrocarbon can hardly be other than a substituted naphthalene ($C_{10}H_8 + 7CH_2$) and, since it is impossible to construct an anthracene or phenanthrene nucleus by union of three molecules of βγ-dimethylbutadiene, the mere fact of the formation of a picrate lends strong support to this conclusion.

It is uncertain whether the dicyclic trimeride which gives the naphthalenic hydrocarbon on dehydrogenation is to be regarded as derived by two stages of cyclisation from a preformed open-chain trimeric structure (hydrocarbon or kation) or by the addition of dimethylbutadiene to the ordinary dimeride (V) or to a kationic form thereof. If the former mechanism is correct, the open-chain structure would have the structure (VII) and would yield a dicyclic derivative having the skeleton (IX) [compare the conversion of farnesene (VIII) into dicyclic *iso*cadinene; Henderson and Robertson, J., 1926, 2811]; but if the latter is correct, the dicyclic derivative might have any one of the skeletons

(VII.)   (VIII.)   (IX.)

(X.)   (XI.)   (XII.)
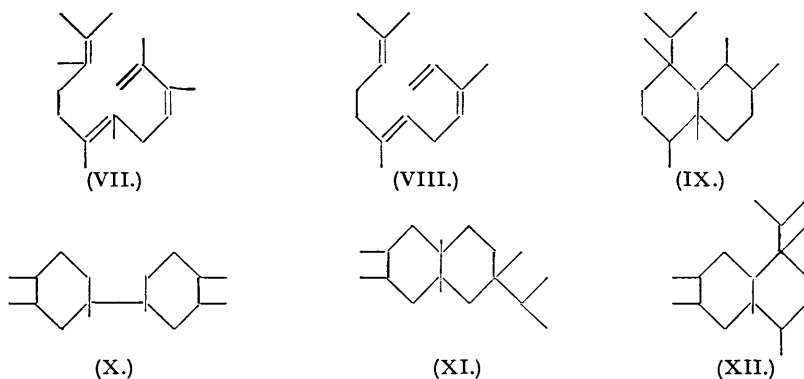
(IX)—(XII). Substances having the skeletons (X) and (XI) would only arise if dimethyl-butadiene were to add to one or to the other bond of the dimeride in the way (Diels–Alder type of reaction) that *cyclo*pentadiene is reputed to add to di*cyclo*pentadiene (Alder, Stein, and Finzenhagen, *Annalen*, 1931, **485**, 223; Alder and Stein, *ibid.*, 1932, **496**, 197, 204). This we hold to be extremely unlikely, since on the one hand (XI) would be the product of addition occurring at the endocyclic double bond of the dimeride, which is the less

reactive bond of the two, and on the other hand the formula (X) clearly cannot apply because a substance having this skeleton would give a derivative of diphenyl on dehydrogenation and hence would not yield a picrate.

In dehydrogenation reactions with selenium the methyl groups of the quaternary carbon groupings >CMeR and $\geqslant$CMe are usually eliminated (*e.g.*, in selinene, ionene, the sterols, and various synthetic compounds). The structure (XI) has three such groupings, and (IX) and (XII) have two; but as only one methyl group is lost in practice, it follows that one or two methyl groups (presumably situated in bridge-head positions) must escape elimination by migration. Recent work by Linstead and his collaborators on 9-methyloctalin and 4 : 9-dimethyloctalin (J., 1937, 1146) has shown that a methyl group can migrate from a bridge-head position to an adjacent carbon atom when sulphur is the dehydrogenating agent. We suggest, therefore, that the aromatic hydrocarbon isolated from the trimeride is a *tetramethylisopropylnaphthalene* derived from a trimeride having the carbon skeleton (IX), (XI) or (XII), but most likely from one having the skeleton (IX) or (XII). Up to the present it has not been possible to distinguish between these formulæ.

Without doubt other hydrocarbons are present in the trimeric fraction and it is probable that the tetrameric and higher fractions also represent mixtures of isomeric hydrocarbons. It is hoped later to resume the study of the trimeric and the tetrameric products of acid-catalysed polymerisation.

<div align="center">EXPERIMENTAL.</div>

The Solid Dimeride.—This was obtained in 1·6% yield by treatment of βγ-dimethylbutadiene with a Bertram–Walbaum reagent containing 1% of concentrated sulphuric acid (this vol., p. 11). It absorbed only 1 mol. of hydrogen (Found : 0·986 mol.) when exhaustively hydrogenated (Adams's catalyst) in acetic acid; furthermore, when it was treated at room temperature in pure chloroform with perbenzoic acid, and the excess of reagent determined after periods ranging from 5 minutes to 24 hours by means of potassium iodide and standard thiosulphate solution, it was found that the unsaturation–time relationship could be represented by a smooth curve in which the observed unsaturation increased asymptotically to a maximum of 1·0 double bond. When, however, the dimeride was treated with bromine under Rosenmund and Kuhnhenn's conditions (*Z. Unters. Nahr. Genuss.*, 1923, 46, 154), 2 mols. of halogen were absorbed (Found : 2·02, 2·015), the second molecule apparently by substitution.

When the solid dimeride was melted with an equimolecular quantity of maleic anhydride, a yellow coloration developed, and was especially marked in the anhydride layer. No combination, however, took place, nor could any combination be effected in benzene solution.

Oxidation. The hydrocarbon (0·5 g.), dissolved in glacial acetic acid (15 c.c.), was treated very slowly (2 hours) at 80° with chromic acid (1·65 g.) dissolved in 50% acetic acid (10 c.c.). The product was heated on a steam-bath for 2 hours and then kept overnight at room temperature; afterwards it was diluted with water (150 c.c.) and the flocculent precipitate which separated was filtered off, dried, and extracted with light petroleum. The solid (0·1 g.) recovered from the solvent was an acid, which, after reprecipitation from solution in sodium carbonate solution and crystallisation from light petroleum, formed colourless leaflets, m. p. 119°. This substance, for reasons already given (p. 288), is considered probably to be 1 : 2 : 4-*trimethyl*-1 : 4-endo*ethylene*cyclo*hexane*-5-*carboxylic acid* [Found : C, 73·7 ; H, 9·9 ; M (monobasic), 193·6. $C_{12}H_{20}O_2$ requires : C, 73·4 ; H, 10·25% ; M, 196·2]. From the aqueous oxidation liquor a small amount of intractably gummy material was recovered.

Ozonolysis. The solid dimeride (0·5 g.), dissolved in pure *alcohol-free* chloroform (90 c.c.), was ozonised at 0°. The solution of the ozonide was refluxed for 1½ hours with water, and the chloroform layer then separated and washed with water. The aqueous solution and washings, when tested with 2 : 4-dinitrophenylhydrazine, gave only a trace of formaldehyde-2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 162°).

The chloroform layer contained no acidic material : it was accordingly dried and evaporated, yielding a rather intractable, pasty mass of camphor-like odour. This material coloured Schiff's reagent, but was not oxidised at room temperature by permanganate : it gave a *semicarbazone*, probably that of 5-*aldehydo*-1 : 2 : 4-*trimethyl*-1 : 4-endo*ethylene*cyclo*hexane*, which after several recrystallisations from methyl alcohol melted at 224° (Found : C, 65·9 ; H, 9·7 ; N, 17·9. $C_{13}H_{23}ON_3$ requires C, 65·85 ; H, 9·7 ; N, 17·7%).

The Trimeric Fraction.—For the production of trimeric βγ-dimethylbutadiene in quantity the polymerisation of the hydrocarbon was conducted preferably with a reagent containing 1% of sulphuric acid. The polymeric material remaining after the dimeride fraction had been distilled (this vol., p. 16) gave on continued distillation a fairly definite, trimeric fraction (b. p. 120°/20 mm.—120°/1 mm.); the boiling point then rose continuously to 180°/0·5 mm. and a large residue remained. Distillation of the residue could be continued in a molecular still until only a black viscous resin (solid when cold) remained.

The crude trimeric fraction was refractionated slowly (controlled reflux ratio) at 0·5 mm. pressure under a 45 cm. vacuum-jacketed column, packed with a nichrome wire spiral, the progress of distillation being followed by determining the refractive index of each fraction and plotting these values against the total proportion (%) of material distilled at the end of each fraction. Five fractions were at first collected and these were subdivided in subsequent series of distillations, the individual fractions obtained being combined or segregated according to the correspondence or otherwise of their refractive indices. At the sixth series of distillations nearly 30% of the material distilled had a practically constant refractive index. This portion had $n_D^{24·5°}$ 1·49345, $d_4^{24·5°}$ 0·8952, $[R_L]_D$ 80·04 (calc. for $C_{18}H_{30}|_2^=$, 79·99), M (in benzene) 252, 250 (calc. 246·2), and was used in the following experiments.

When brominated by the method of Rosenmund and Kuhnhenn, the trimeride took up 2 mols. of bromine (Found : 1·99, 1·99), but when hydrogenated at room temperature (Adams's catalyst) in either alcohol or acetic acid, it took up only 1 mol. of hydrogen (Found : 1·01, 1·01). Towards permanganate the trimeride was very unstable, and the aqueous oxidation product after neutralisation readily reduced warm silver nitrate solution.

The *dihydride* obtained by hydrogenation of 5 g. of trimeride distilled at 140—149°/12 mm., but on redistillation a third of the material distilled at 139·5—141·5°. This had $n_D^{17°}$ 1·4878, $d_0^{17°}$ 0·88815, $[R_L]_D$ 80·57 (calc. for $C_{18}H_{32}|_1^=$, 80·46) (Found : C, 86·9; H, 12·85. $C_{18}H_{32}$ requires C, 87·0; H, 13·0%). The dihydride absorbed 0·98 mol. of bromine when treated with pyridine perbromide under the conditions of Rosenmund and Kuhnhenn, but was not attacked by permanganate at room temperature.

Ozonolysis. The trimeride was ozonised in chloroform, and the solution refluxed with water. The aqueous solution so obtained contained formaldehyde and this was isolated in the form of its 2 : 4-dinitrophenylhydrazone, m. p. 162° (yield, 0·2 mol.). The chloroform solution yielded an oil, which was treated with the Girard reagent " T " in order to isolate the ketonic component. The latter, regenerated from combination with the reagent, was an oil which gave with semicarbazide hydrochloride a very small quantity of a solid derivative. The nature of this derivative and of the remaining ozonolysis products has not been determined.

Dehydrogenation of the Trimeride.—The trimeride (6 g.), when dehydrogenated at 340° ± 10° for 40 hours with selenium (10 g.), gave a dark brown, slightly fluorescent oil (5 g.), which was first distilled and then refluxed for some time with sodium in ether. The product was freed from the reagent and fractionated. Six fractions boiling between 260° and 300° were collected, and each of these was separately treated with a solution of picric acid in methyl alcohol. Five of the fractions gave some proportion of orange crystals, and these crystals when combined and recrystallised several times from methyl alcohol formed bright orange needles (0·75 g.), m. p. 156°. This was the *picrate* of a hydrocarbon $C_{17}H_{22}$ (Found : C, 60·45, 60·7; H, 5·6, 5·45. $C_{17}H_{22},C_6H_3O_7N_3$ requires C, 60·65; H, 5·5%).

When heated for 15 minutes at 100° with 10% caustic soda solution, the picrate gave an oil which solidified on cooling. This was a *hydrocarbon*, apparently (although not certainly) tetramethyl*iso*propylnaphthalene, which formed colourless needles, m. p. 111°, when twice crystallised from methyl alcohol (Found : C, 90·1; H, 9·65. $C_{17}H_{22}$ requires C, 90·26; H, 9·7%).

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