4. *Mechanism of Polymerisation. Part II. Dimerisation of βγ-Dimethylbutadiene in Presence of an Acid Catalyst.*

By Ernest Harold Farmer and Robert C. Pitkethly.

Polymerisation of βγ-dimethylbutadiene by sulphuric acid dissolved in acetic acid gives dimeric, trimeric and other low-molecular products, but the nature of the product varies somewhat with the experimental conditions.

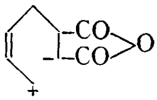
The dimeric product consists mainly of a monocyclic (*cyclo*hexenic) hydrocarbon, but under suitable conditions a solid, camphor-like (dicyclic) dimeride is also formed. There is evidence also that the *cyclo*hexenic dimeride is contaminated by a third liquid (dicyclic) dimeride.

The *cyclo*hexenic dimeride is identical with that which has frequently been obtained by the action of heat on βγ-dimethylbutadiene, but Lebedev's preparation of the latter appears to have contained also a fourth (dicyclic) dimeride. The *cyclo*hexenic dimeride has been synthesised.

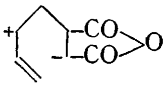
The formation of both monocyclic and dicyclic dimerides, as also the formation of the *cyclo*pentenic dimeride obtainable from α-phenylbutadiene, is readily representable on the basis of Whitmore's hypothesis.

LITTLE is known at present as to how many courses of reaction even the simplest of *low-molecular* polymerisation processes can follow. In the case of *high-molecular* polymerisations, according to the Staudinger conception, reaction both for olefins and for conjugated diolefins pursues normally a uniform course with formation of products which in a given example differ only in the degree of polymerisation (and hence in the chain length of the molecules) attained; and even in those examples where uniform head-to-tail arrangement of the molecules seems to be disturbed by some degree of 1 : 2- or of head-to-head/tail-to-tail linking, the habit of forming essentially linear " polymer-homologous " products is retained. But with low-molecular polymerisations there is little information as yet to show whether reaction promoted by heat necessarily yields the same product or products at each polymeric stage as reaction promoted by chemical reagents or by electric discharge, nor has the range of isomerism which can occur with any particular polymerising agency at the different polymeric stages been determined.

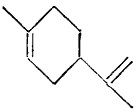
The published evidence at the time this investigation was begun indicated that conjugated diene hydrocarbons yielded on polymerisation either low-molecular products which consisted mainly or wholly of cyclic dimerides, or high-molecular products which were more or less rubber-like in character. It seemed that the formation of the dimeric substances, whether promoted by heat or by catalysts, followed invariably a single course, *viz.*, one which was formally analogous to the Diels–Alder reaction between conjugated dienes and maleic anhydride. Consideration, however, of the analogy between the two types of additive reaction led to the conclusion that the resemblance between the reactions could only be purely superficial in character, since the Diels–Alder reaction with little doubt depended for its initiation on the dissimilar polar character of the reactants [anionoid hydrocarbon and kationoid addendum as suggested by R. Robinson, " Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," p. 29], whereas in the dimerisation reaction no pronounced tendency to interaction on the part of two hydrocarbon molecules, *both* normally anionoid, could be envisaged, unless activation of one of the molecules had supervened whereby its polar character became altered. By the normal mechanism of the Diels–Alder reaction as pictured by Robinson the formation of only *cyclo*hexene- or alkenyl*cyclo*butane-derivatives could be expected, since the first stage of addition would yield an open-chain polar complex such as (I) or (II) (from butadiene and maleic anhydride); and present experience shows that the *cyclo*hexenic compounds are invariably the favoured products.* Departure, however, from the Diels–Alder mechanism at once removes this restriction on the form of the dimeric products and opens up the possibility of the formation of either open-chain or cyclic compounds, the latter of which may be *cyclo*hexenic, *cyclo*pentenic or conceivably *cyclo*butenic in character.



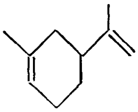
(I.)



(II.)



(III.)



(IV.)

With the foregoing possibilities in view work was initially begun by one of us with Mr. H. Brunner on the low-molecular polymerisation of β-phenylbutadiene. The work on the constitution of the dimeric constituent of the low-molecular product, which was a re-examination of the earlier results of Lebedev (*Chem. Zentr.*, 1914, i, 1407; 1923, i, 1539), was, however, forestalled by Bergmann (J., 1935, 1359), who showed that Lebedev's *cyclo*hexenic formula for the dimeride was incorrect and the latter had in fact a *cyclo*pentenic constitution. This result (although we reject Bergmann's tentative suggestion as to the mechanism of reaction) fulfilled at once one of the expectations set out above,

---

* On the other hand, in the apparently analogous additions of diphenylketen to conjugated olefins, four-carbon rings seem to be the rule.

viz., that the *cyclo*hexenic form was not a necessary consequence of dienic dimerisation. The following results connected with the low-polymerisation of βγ-dimethylbutadiene not only serve to confirm the distinctive natures of the Diels–Alder and the dimerisation reactions but throw new light on the mechanism of reaction.

Polymerisation by the Bertram–Walbaum Reagent.—Hydration of compounds containing isolated double bonds has often been effected by sulphuric acid in acetic acid since this reagent was first introduced by Bertram and Walbaum. The only previously recorded instance of its action on conjugated dienes, however, is due to Wagner-Jauregg (*Annalen*, 1932, **496**, 52), who transformed isoprene into a complex mixture of products containing two *cyclo*hexenic dimerides (III) and (IV) in addition to trimeric material (apparently partly monocyclic) and various mono- and sesqui-terpenic alcohols. The complexity of Wagner-Jauregg's product suggested the necessity for a detailed investigation of the simplest diene, *viz.*, butadiene, but its relative inaccessibility in pure form made it more practicable to study βγ-dimethylbutadiene, the symmetrical structure of which restricts the possibilities of isomerism in the products of polymerisation. The relative polymerisabilities of butadiene, isoprene, and βγ-dimethylbutadiene are indicated in Table I, and are in agreement with those expected on constitutional grounds.*

TABLE I.

Polymerisation of Dienes (Bertram–Walbaum Reagent).

	Conc. of H_2SO_4 in reagent.	Time (days).	Extent of polymerisation (%).		Conc. of H_2SO_4 in reagent.	Time (days).	Extent of polymerisation (%).
Butadiene ...	4	3	25	βγ-Dimethylbutadiene	0·1	3	44
" ...	4	9	58	"	0·1	4	57
Isoprene † ...	0·3	3	30	"	1	4	85
				"	4	4	90

† Figures due to Wagner-Jauregg (*loc. cit.*).

The products of the polymerisation of βγ-dimethylbutadiene with the Bertram–Walbaum reagent were freed from alcohols and then subjected to systematic fractional distillation, and Table II shows that the composition of the polymerisation mixture varied with the concentration of sulphuric acid in the reagent. The present communication is concerned only with the study of the dimeric products, and it was found that, whereas the use of 0·1% sulphuric acid in acetic acid led to an apparently homogeneous terpenic liquid dimeride, when the concentration was 1% there was formed a similar but not entirely homogeneous terpenic liquid dimeride (showing appreciable variations in the physical properties of its fractions on distillation) as well as a camphor-like solid dicyclic dimeride (1·5% yield) the constitution of which is being investigated. Very narrow limits of concentration are requisite for the formation of this solid dimeride, which, moreover, could not be obtained at will by the action of sulphuric acid on the liquid dimeride.

TABLE II.

Variation in Composition of Polymerisation Products.

Concn. of H_2SO_4 (%).	Vol. (c.c.) of reagent per g. of hydrocarbon.	Time (days).	Total yield (%).	Composition.		
				Dimeride (%).	Trimeride (%).	Higher polymerides (%).
0·1	3·0	4	56	52	34	14
1	4·4	4	93	28	24	43
4	13·6	4	95	19	35	44

Constitution of the liquid dimeride. The liquid dimeride obtained by the use of low concentrations of sulphuric acid (about 0·1%) was doubly unsaturated, as was shown by quantitative additive experiments with bromine, hydrogen chloride, and hydrogen. The addition compounds were liquid, as also were those resulting from the action of nitrosyl

---

* Experiments made several years ago by Mr. R. G. R. Bacon show that αγ-dimethylbutadiene polymerises as readily as, and αδ-dimethylbutadiene considerably less readily than, βγ-dimethylbutadiene in a reagent containing 0·3% of H_2SO_4.

chloride, nitric oxide, and nitrogen peroxide. Saturation of the two double bonds by hydrogen occurred at markedly different rates, so that a dihydride could be isolated in substantially pure condition. The dibromide of this dihydride deposited 12% of an easily decomposed, crystalline dibromide, m. p. 57°, probably one of the four possible stereoisomeric dibromides.

The additive reactions of the liquid dimeride, apart from the isolation of the dihydride and its dibromide, have been described previously for the liquid dimeride obtained by thermal polymerisation of βγ-dimethylbutadiene (five authors) and by heat-degradation of dimethylbutadiene-rubber (Richards). The physical constants of the thermal dimerides, together with those of our material, are cited in Table III, from which it is seen that, although the values for the different preparations show appreciable variations, those for our dimeride obtained with 0·1% sulphuric acid agree with the values observed by Kogerman and by Lebedev, although the latter author had been able to obtain only a monohydrochloride.

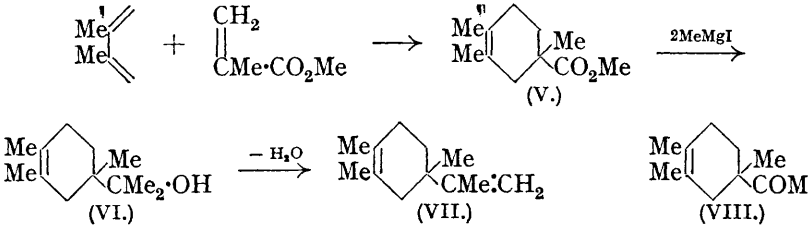
TABLE III.

Dimeric βγ-Dimethylbutadiene.

Author.	Origin.	B. p.	$d_{4°}$.	n_D.
Dalecki [1]	Heat-formed	203·5—205·5°/749 mm.	$0·8628^{19°}$	—
Richards [2]	,,	205/760 mm.	$0·8532^{25°}$	$1·47786^{25°}$
Lebedev [3]	,,	205/750 mm.	$0·8597^{20°}$	1·48074
Aschan [4]	,,	200·5—201·5/760 mm.	$0·8535^{20°}$	$1·47915^{20°}$
Whitby and Crozier [5]	,,	198—200/738 mm.	—	$1·4775^{25°}$
Kogerman [6]	,,	205—206/738 mm.	$0·8592^{20°}$	$1·48107^{20°}$
Present authors	Acid-formed	85/15 mm.	$0·8585^{22°}$	$1·4804^{22°}$
,, ,, ...	Synthetic	206·5—207·5/760 mm.	$0·8626^{16°}$	$1·4823^{16°}$

[1] *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 533. [2] *Compt. rend.*, 1911, **153**, 116. [3] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249, 1379. [4] *Oversikt. Finsk. Vetenskaps. Soc. Forh.*, 1915, **58**, 42; *Chem. Abs.*, 1920, **14**, 3823. [5] *Canadian J. Res.*, 1932, **6**, 218, 280. [6] *Sitzungsber. Naturforsch. Ges. Tartu*, 1935, **41**.

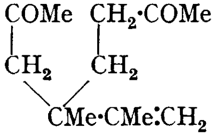
Thus it appears that the dimerides formed by heat- and by acid-treatment are identical as regards the main constituent, a view which is supported by the fact that our hydrocarbon resembled that of Kogerman in undergoing selenium dehydrogenation to an aromatic hydrocarbon (probably 3 : 4-dimethylcumene) which could be oxidised to trimellitic acid. These observations are consistent with the view that the principal dimeric compound has the structure (VII). Confirmation of this view was afforded by the synthesis of (VII) from βγ-dimethylbutadiene and methyl α-methylacrylate according to the scheme:

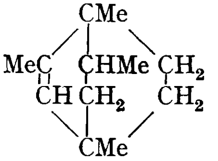


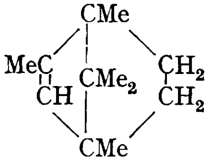
The intermediate ketone (VIII) and a compound $C_{13}H_{24}O$, probably the methyl ether of (VI), were among the by-products of the Grignard condensation. The physical and chemical properties of the synthetic hydrocarbon (VII) resemble closely those of the acid-formed dimeride of βγ-dimethylbutadiene and also the thermal dimeride of Lebedev and of Kogerman (see Table III).

Lebedev reported that his thermal dimeride of βγ-dimethylbutadiene was oxidised by permanganate to a diketone (IX) (about 30% yield), which gave a disemicarbazone, m. p. 228°. Kogerman, on the other hand, obtained formaldehyde by ozonolysis of his dimeride, but could not isolate or identify the major degradation product. Our acid-formed dimeride behaved similarly to Kogerman's compound and gave on ozonolysis a 70% yield of formaldehyde together with a yellow oil from which no solid ketone derivatives could be obtained. By permanganate oxidation we obtained a substantial yield of formic acid together with a neutral product which consisted partly of unattacked hydrocarbon but contained *inter alia* some proportion of a dicarbonyl derivative; the latter gave in small yield a disemicarbazone of the same empirical formula as Lebedev's compound, but of different melting point (m. p. 251°).

The formation of a diketone of formula (IX) from the dimeride (VII), involving as it does attack at the endocyclic double bond in preference to the exocyclic one, is not credible in view of the foregoing observations and of general experience. We therefore conclude from the evidence adduced above that none of the specimens of dimeride is completely homogeneous, but they consist mainly of (VII). We have little doubt that the large proportion of diketone formed by oxidation of Lebedev's dimeride and the small amount of an isomeride from ours arose by fission of mono-olefinic dicyclic compounds * for which the formula (X) (2 stereo-forms), or formulæ (X) and (XI) are tentatively suggested.

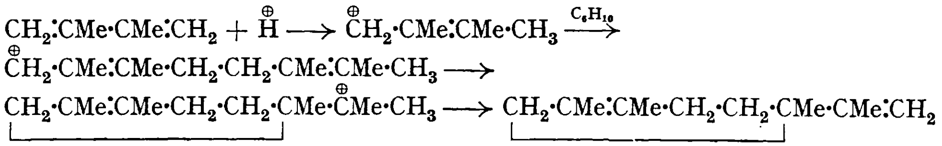

(IX.)


(X.)

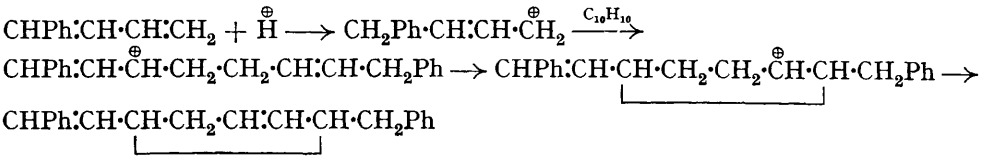

(XI.)

Vaughan (*J. Amer. Chem. Soc.*, 1932, **54**, 3868; 1933, **55**, 4009) has already suggested, without adducing convincing evidence, that dicyclic forms may accompany the ordinary *cyclo*hexenic dimeride in heat-polymerised butadiene.

The formation of the monocyclic and dicyclic dimerides, like that of the *cyclo*pentenic dimeride of α-phenylbutadiene referred to above, can readily be represented on the basis of the Whitmore hypothesis: thus the formation of the first of these may be represented in scheme (A) and that of the last in scheme (B):

(A)


$$CH_2{:}CMe{\cdot}CMe{:}CH_2 + \overset{\oplus}{H} \longrightarrow \overset{\oplus}{C}H_2{\cdot}CMe{:}CMe{\cdot}CH_3 \xrightarrow{C_6H_{10}} \overset{\oplus}{C}H_2{\cdot}CMe{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CMe{\cdot}CH_3 \longrightarrow \underbrace{CH_2{\cdot}CMe{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe}{\cdot}\overset{\oplus}{C}Me{\cdot}CH_3 \longrightarrow \underbrace{CH_2{\cdot}CMe{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe}{\cdot}CMe{:}CH_2$$

(B)


$$CHPh{:}CH{\cdot}CH{:}CH_2 + \overset{\oplus}{H} \longrightarrow CH_2Ph{\cdot}CH{:}CH{\cdot}\overset{\oplus}{C}H_2 \xrightarrow{C_{10}H_{10}} CHPh{:}CH{\cdot}\overset{\oplus}{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2Ph \longrightarrow CHPh{:}CH{\cdot}\underbrace{CH{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\oplus}{C}H}{\cdot}CH{\cdot}CH_2Ph \longrightarrow CHPh{:}CH{\cdot}\underbrace{CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH}{\cdot}CH_2Ph$$

EXPERIMENTAL.

Polymerisation of βγ-Dimethylbutadiene with the Bertram–Walbaum Reagent.—With a 0·1% *reagent.* The hydrocarbon, prepared by dehydration of pinacol hydrate (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 987), was washed with water, dried over calcium chloride, and rectified under a Widmer column (b. p. 69°/760 mm.) just before use. A portion (160 g.) was dissolved in the reagent (500 c.c.) containing 0·1 g. of concentrated sulphuric acid per 99·9 g. of glacial acetic acid. After 96 hours the solution was stirred into 1½ l. of water, and the product extracted with ether. The extract was washed with sodium carbonate solution until neutral and with water, dried over anhydrous sodium sulphate, and freed from solvent under a metre-long Vigreux column and from unchanged dimethylbutadiene (10 g.) by partial distillation under a shorter column. The residual oily liquid (96 g.; 64%) was refluxed for 4 hours with 2N-methyl-alcoholic potassium hydroxide (500 c.c.); most of the alcohol was then distilled, and the residue poured into water. The hydrolysis product was extracted in ether, dried

---

* The fact that Lebedev's dimeride would not combine with 2 mols. of hydrogen chloride (see above) is a further indication of the (substantially) dicyclic character of his product.

(sodium sulphate), freed from solvent, heated on a steam-bath for 4 hours with boric acid (20 g.), and finally divided into the following fractions by distillation: (i) 60—120°/20 mm. (47 g.; colourless), (ii) 120°/20 mm.—120°/1 mm. (35 g.; faint yellow), (iii) 120—140°/1 mm. (6 g.; yellow), (iv) yellow viscous residue.

The residue was basified with sodium hydroxide and steam-distilled: a fragrant oil (0·5 g.), consisting of the alcohols formed by the Bertram–Walbaum reagent, distilled.

The fraction (i) on redistillation from a Kon flask passed over between 84° and 110° at 24 mm., the b. p.–% distilled curve showing its extensive heterogeneity: reasonably good fractionation could only be achieved by redistillation under a metre-long vacuum-jacketed column, packed with a spiral of copper foil and fitted with a still-head suitable for controlling the reflux-ratio; an apparently homogeneous dimeric *product*, b. p. 85°/15 mm., $n_D^{22°}$ 1·4804, $d_{0°}^{22°}$ 0·8604, was then obtained [Found: C, 87·5; H, 12·1. $(C_3H_5)_2$ requires C, 87·7; H, 12·25%]. The trimeric and higher fractions were saved for subsequent fractionation.

With a 1% *reagent.* A solution of the hydrocarbon (204 g.) in 660 c.c. of a Bertram–Walbaum reagent containing 1% (w/w) of concentrated sulphuric acid was kept for 4 days. The polymerisation product, isolated as before, was a brown mobile liquid which contained no unchanged hydrocarbon. It was refluxed for 1 hour with 7½% (w/w) methyl-alcoholic potassium hydroxide and kept for 24 hours, and the hydrolysis product then worked up as before. The oil obtained (191 g.) was heated on a steam-bath with boric acid (20 g.) for 3 hours and then distilled. The following fractions were collected: (i) 45—75°/20 mm., (ii) 75—120°/20 mm., (iii) 120°/20 mm.—120°/1 mm., (iv) 120—165°/1 mm., and (v) a brown viscous residue.

Fraction (ii) was divided into small fractions by distillation in a specially-constructed vacuum-jacketed column, 40 cm. long, and fitted with a reflux still-head allowing of close control of the reflux-ratio. The column was packed with a single spiral of 16-gauge nichrome wire. The lowest fractions which distilled solidified almost completely when cooled in a freezing mixture. The solid was collected on a cooled sintered-glass filter, drained on a tile, and crystallised from methyl alcohol. The crystals, camphor-like in odour, volatilised rapidly on exposure to air; when distilled on to a cold surface, they gave feathery crystals, m. p. 66° (yield, 1·5 g. or 1·6%). This substance was a *dimeride* of dimethylbutadiene [Found: C, 87·9; H, 12·25; *M* (in benzene), 167, 165. $(C_6H_{10})_2$ requires C, 87·7; H, 12·25%; *M*, 164]. The liquid dimeric material from which the solid had been removed was separately rectified; the final product seemed to be slightly less homogeneous than that from the preceding preparation, as judged by the larger range of boiling point and refractive index.

The trimeric fraction (iii) was intensively refractionated, the above-mentioned packed column being used. Since the thermometer at the head of the column gave no indication of the changing composition of the fractions, refractive index–% distilled curves were plotted after each distillation. The fraction corresponding to the flat portion of the curve in the sixth distillation was selected for subsequent work with *trimeric* βγ-*dimethylbutadiene* [Found: C, 87·8; H, 12·2. $(C_6H_{10})_3$ requires C, 87·7; H, 12·25%]: it had $n_D^{24·5°}$ 1·49345, $d_{0°}^{24·5°}$ 0·8953, $[R_L]_D$ 80·04 (calc. for $C_{18}H_{30}|\overline{2}$, 79·99).

The Liquid Dimeride.—Hydrogenation. In ethyl alcohol with Adams's platinum catalyst reaction ceased when 0·3247 g. of the dimeride had absorbed 48·46 c.c. of hydrogen at 17°/764 mm. This corresponds to an unsaturation of 0·99 double bond per $C_{12}H_{20}$-unit. In acetic acid, with the same catalyst, there was a well-marked break at the point corresponding exactly to the absorption of 1 mol. of hydrogen per mol. of dimeride, but reaction only ceased when 2 mols. of hydrogen had been absorbed. The unsaturation values found at the two stages corresponded to 0·99, 1·01 and 2·03, 2·00 double bonds per $C_{12}H_{20}$-unit respectively.

The half-hydrogenated dimeride obtained by reducing 10 g. of the dimeride in 250 c.c. of rectified spirit (catalyst 0·2 g.) was not homogeneous: it gave on rectification under a short column the fractions: (i) 80—86° (0·9 g.), (ii) 86—91° (1·0 g.), (iii) 91—94° (3·9 g.), and (iv) 94—95° (2·0 g.), of which the third (2 g.) gave with bromine (1 mol.) in carbon disulphide a liquid dibromide. From the latter, after two months, a solid dibromide (0·5 g.; 12·7%) separated. This formed feathery needles, m. p. 57°, from light petroleum (Found: Br, 49·6. $C_{12}H_{22}Br_2$ requires Br, 49·05%). Presumably the solid and the liquid are stereoisomeric forms of 1 : 2-*dibromo*-1 : 2 : 4-*trimethyl*-4-iso*propyl*cyclo*hexane*.

The fully-hydrogenated dimeride, 1 : 2 : 4-*trimethyl*-4-iso*propyl*cyclo*hexane*, obtained in small amount by reduction of the dimeride in acetic acid solution, was also obtained by heating the dimeride (12·5 c.c.) with concentrated hydriodic acid (17 c.c.) and red phosphorus (1 g.) at 250° for 9 hours. The turpentine-like hydrocarbon, after refluxing over sodium, distilled mainly between 125° and 132°; after fractionation it was obtained as a mobile liquid, b. p. 177° (Found: C, 85·55; H, 14·55. $C_{12}H_{24}$ requires C, 85·6; H, 14·4%). It had $n_D^{20^\circ}$ 1·4636, d^{20° 0·8375, $[R_L]_D$ 55·42 (calc., 55·42).

Dibromide. When treated with bromine by the method of Rosenmund and Kuhnhenn (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154), the dimeride absorbed the equivalent of 2 mols. of bromine (unsaturation value 81·75, 81·45. $C_{12}H_{20}\,|^{=}_{2}$ requires 82·15). When bromine (2 mols.) was added to the dimeride in ether–amyl alcohol (method of Baeyer and Villiger, *Ber.*, 1894, **27**, 448), in chloroform, or in carbon disulphide, the bromine was completely absorbed but only a liquid bromide was formed; in ether, hydrogen bromide was evolved and more than 2 mols. of bromine were taken up.

Dihydrobromide. An ethereal solution of the dimeride at − 15° was saturated with dry hydrogen bromide (phosphoric oxide). A heavy brown oily layer separated and afterwards redissolved. The product, after being freed from ether by a current of dry air, gave an oily dihydrobromide (1·410 g. of dimeride absorbed 1·36 g. of hydrogen bromide. Calc. for $C_{12}H_{20}|^{=}_{2}$, 1·39 g.), from which no solid component could be obtained.

An exactly similar result was obtained when hydrogen chloride replaced hydrogen bromide (1·83 g. of dimeride absorbed 0·94 g. of hydrogen chloride. Calc. for $C_{12}H_{20}\,|^{=}_{2}$, 0·95 g.).

Nitrosate. The nitrosate formed by means of amyl nitrite and acetic acid was a yellow oil.

Dehydrogenation. Heated with powdered selenium at 280—300° for 21 hours, the dimeride gave principally a yellow oil, b. p. 160—170°: this on boiling for 8 hours with excess of 3% permanganate solution containing sodium carbonate gave, on being worked up, a solid acid, m. p. 206—209°, and 217—218°, after several crystallisations from ethyl acetate. This acid was identified as trimellitic acid, m. p. 219°, mixed m. p. 217—218°; equiv., 70·1, 70·45 (Calc. for $C_9H_6O_6$, 70·05).

Ozonolysis. The dimeride (1 g.) was ozonised in pure chloroform (90 c.c.) which itself gave no formaldehyde when successively treated with ozone and water. The colourless solution was refluxed with water for 18 hours; the chloroform layer was then washed with water, dried and freed from solvent by evaporation. The clear yellow oil obtained, when treated *without distillation* with semicarbazide hydrochloride and sodium acetate, yielded no semicarbazone. The aqueous liquor and washings gave 0·7 g. (70% yield) of formaldehyde-2 : 4-dinitrophenylhydrazone, m. p. (after one crystallisation from alcohol) and mixed m. p. 162°.

Oxidation. To the dimeride, suspended in water and vigorously stirred, a solution of potassium permanganate (32 g. in 1070 c.c. of water) was slowly added. The mixture, after standing overnight, was just decolorised with sulphurous acid and then worked up in the usual way. The neutral product of the oxidation was carefully fractionated: examination of the fractions showed it to be composed largely of the unchanged dimeride, but partly of a substance of lower specific refractivity than the latter. Treatment of the fractions with semicarbazide acetate gave very slowly and in small yield gritty crystals of a semicarbazone. This was the *disemicarbazone* of a dicarbonyl compound, $C_{12}H_{20}O_2$, the latter being with little doubt derived by fission of the double bond in a dicyclic form of the dimeride (see p. 15) (Found: C, 53·95; H, 8·4. $C_{14}H_{26}O_2N_6$ requires C, 54·2; H, 8·4%).

The aqueous mother-liquor was shown by numerous tests and derivatives to contain a considerable quantity of formic acid.

Synthesis of Liquid Dimeride.

Addition of Methyl α-Methylacrylate to βγ-Dimethylbutadiene.—Methyl α-methylacrylate (b. p. 100°) was obtained in 40% yield by the action of concentrated sulphuric acid on acetone cyanohydrin in presence of copper powder. The ester (65 g.), mixed with the hydrocarbon (65 c.c.), was heated in sealed tubes for 4 hours at 150°. The colourless viscous product, when distilled at 20 mm., gave the fractions of b. p. (i) below 26° (16 g.), (ii) 26—100° (1 g.), (iii) 101—104°, but mostly 102—102·5° (70 g.), and (iv) a residue (18 g.). Fraction (i), when reheated with a further 16 c.c. of hydrocarbon, gave 20 g. of the product of b. p. 101—104°; this was combined with fraction (iii), and the whole redistilled from an Adams flask. Practically the whole passed over at 104·5°/20 mm., with no significant variation in the refractive index, to give a colourless mono-olefinic liquid, b. p. 106°/19 mm. (corr.), $n_D^{16^\circ}$ 1·4679, $d_{4^\circ}^{16^\circ}$ 0·9738, $[R_L]_D$ 52·07 (calc., 51·98), unsaturation value, 179·3 (calc., 182·3). This was *methyl* 1 : 3 : 4-*trimethyl*-Δ^3-*tetrahydrobenzoate* (V) (Found: C, 72·6; H, 10·0. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·95%). 1 : 3 : 4-*Trimethyl*-Δ^3-*tetrahydrobenzanilide*, formed from this ester by the method of Hardy (J., 1936, 398), crystallised from methyl alcohol in colourless needles, m. p. 94·5° (Found: C, 78·9; H, 8·7. $C_{16}H_{21}ON$ requires C, 79·0; H, 8·7%). 1 : 3 : 4-*Trimethyl*-Δ^3-*tetrahydro*-

benzoic acid, obtained by refluxing the ester for 3 hours with 10% excess of alcoholic sodium hydroxide, formed colourless leaflets, m. p. 56°, from alcohol or dilute acetic acid (Found: C, 71·0; H, 9·5. $C_{10}H_{16}O_2$ requires C, 71·35; H, 9·6%).

Ozonolysis of Methyl 1 : 3 : 4-*Trimethyl*-Δ^3-*tetrahydrobenzoate*.—When the ester (2·5 g.) was ozonised in purified ethyl acetate for 5½ hours at 0°, and the product refluxed overnight with water (50 c.c.), the aqueous layer obtained gave no precipitate with 2 : 4-dinitrophenylhydrazine, whereas the ethyl acetate layer yielded, on drying and removal of the solvent, 2 g. of a golden-yellow oil, b. p. 120—170°/14 mm. This gave with semicarbazide hydrochloride and sodium acetate solution 2 g. of the *disemicarbazone* of methyl α-acetonyl-γ-acetyl-α-methylpropionate, m. p. 200° after recrystallisation from aqueous alcohol (Found: C, 47·7; H, 7·55. $C_{13}H_{24}O_4N_6$ requires C, 47·55; H, 7·35%).

1 : 3 : 4-*Trimethyl*-Δ^3-cyclo*hexenyldimethylcarbinol*.—A solution of methyl 1 : 3 : 4-trimethyl-Δ^3-tetrahydrobenzoate (150 g.) in dry ether (150 c.c.) was added with stirring to the Grignard compound derived from methyl iodide (465 g.), magnesium (80 g.), and dry ether (700 c.c.) at such a rate as to promote and maintain gentle refluxing. After ½ hour's stirring, the product was decomposed with ammonium chloride solution and ice. The carbinol was extracted with ether, washed with brine, dried over sodium sulphate, and freed from solvent. The residue was a rather viscous, yellow oil which proved on distillation to be heterogeneous. The distillate (143 g.) also was heterogeneous (b. p. 101—110°, $n_D^{15.5°}$ 1·4927—1·4877, $d_{4°}^{15.5°}$ 0·9264—0·9249) and could not be resolved into its components by fractionation under an 18-inch vacuum-jacketed column; moreover a portion (b. p. 106—109°) dehydrated by twice treating it with potassium bisulphate (see below) gave a crude hydrocarbon containing an oxygen-containing but non-hydroxylic component.

The remaining (undehydrated) fractions of the crude carbinol were united and a part (50 g.) was dissolved in absolute alcohol (316 c.c.) and refluxed with glacial acetic acid (30 g.) and the Girard reagent "T" (25 g.) on a steam-bath for 45 minutes. The resulting solution (a little reagent was undissolved) was poured into ice-water (1670 g.) containing 18 g. of sodium hydroxide. The product, which changed the colour of bromothymol-blue from blue to yellow, was extracted with ether; the extract was dried over sodium sulphate, and the solvent removed, leaving the non-ketonic component of the crude carbinol. The aqueous mother-liquor was acidified with concentrated hydrochloric acid (167 c.c.), kept overnight, and extracted with ether The extract yielded on evaporation a liquid, from which the *semicarbazone* of 1-acetyl-1 : 3 : 4-trimethyl-Δ^3-*cyclo*hexene was prepared; this crystallised from aqueous alcohol in colourless needles, m. p. 151° (Found: C, 64·1; H, 9·35. $C_{12}H_{21}ON_3$ requires C, 64·5; H, 9·45%).

The non-ketonic portion was submitted to several fractionations at 0·5 mm. pressure (finally under an 18-inch vacuum-jacketed column packed with a spiral of nichrome wire), the progress of fractionation being followed by plotting b. p. and refractive index curves. A reasonably sharp separation into two quite distinct substances was thus made, the highest-boiling fractions (b. p. 105—108°) consisting of practically pure 1 : 3 : 4-*trimethyl*-Δ^3-cyclo*hexenyldimethylcarbinol* (Found: C. 78·95; H, 12·25. $C_{12}H_{22}O$ requires C, 79·05; H, 12·15%), which had $d_{0°}^{17.2°}$ 0·9475, $n_D^{17.2°}$ 1·4956, $[R_L]_D$ 56·20 (calc., 56·47). The lowest-boiling fractions (b. p. 68—71°), after a final redistillation, gave an apparently homogeneous liquid, which had $d_{0°}^{16°}$ 0·8995 and $n_D^{16°}$ 1·4612. This ether-like substance of characteristic odour was mono-olefinic (unsaturation value by hydrogenation, 200·5. Calc., 196·3) and was probably the methyl ether of the carbinol, *viz.*, *methyl* α-1 : 3 : 4-*trimethyl*-Δ^3-cyclo*hexenyl*iso*propyl ether* (Found: C, 79·95, 79·95; H, 12·2, 12·15. $C_{13}H_{24}O$ requires C, 79·5; H, 12·3%).

Dehydration of 1 : 3 : 4-*Trimethyl*-Δ^3-cyclo*hexenyldimethylcarbinol*.—The carbinol (12 g.) was refluxed for 45 minutes with finely powdered potassium bisulphate (20 g.). The cooled product was treated with water, and the suspended hydrocarbon taken up in ether. The ethereal solution was washed with sodium carbonate and with water, dried with calcium chloride, and evaporated. The residue was distilled at 0·5 mm. pressure and the bulk of the distillate (9 c.c.) was refluxed with sodium and finally distilled at 761 mm. pressure over sodium, a 6-inch column filled with glass beads being used. Two fractions were collected: (i) b. p. 200—201·5° (0·2 c.c.) and (ii) 202—203° (7 c.c.), leaving a tiny residue. Fraction (ii) was the synthetic dimeride, 1 : 3 : 4-*trimethyl*-1-iso*propenyl*-Δ^3-cyclo*hexene* (Found: C, 87·35; H, 12·4. $C_{12}H_{20}$ requires C, 87·7; H, 12·3%); it had $d_{0°}^{16°}$ 0·8626, $n_D^{16°}$ 1·4823, $[R_L]_D$ 54·42 (calc., 54·45).

This substance behaved (*a*) on hydrogenation, (*b*) towards bromine, and (*c*) towards amyl nitrite and hydrochloric acid in exactly the same way as the above-described acid-formed dimeride, except that no portion of the dibromide of the half-hydrogenated dimeride has yet been obtained in solid form (compare p. 16).

Addition of Ethyl Crotonate to *βγ-Dimethylbutadiene*.—The hydrocarbon (10 c.c.) and the ester were heated together in a sealed tube for 22 hours at 180°. The product on distillation gave largely a colourless ester, b. p. 127—130°/30 mm. (redistilled, b. p. 127—130°/28 mm.), together with some unchanged ester and a clear yellow viscous residue. The first of these was *ethyl* 2 : 4 : 5-*trimethyl*-Δ^4-*tetrahydrobenzoate* (Found: C, 73·2; H, 10·15. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·25%), which had $n_D^{20°}$ 1·4607, $d_0^{20°}$ 0·9594, $[R_L]_D$ 56·66 (calc., 56·60). 2 : 4 : 5-*Trimethyl*-Δ^4-*tetrahydrobenzanilide*, formed as above from the ester, aniline, and ethylmagnesium bromide, separated in colourless needles, m. p. 162°, from methyl alcohol (Found: C, 79·1; H, 8·6. $C_{16}H_{21}ON$ requires C, 79·0; H, 8·65%). 2 : 4 : 5-*Trimethyl*-Δ^4-*tetrahydrobenzoic acid*, obtained by boiling the ester for 10 minutes with excess of alcoholic potassium hydroxide, formed colourless leaflets, m. p. 137°, from dilute acetic acid (Found: C, 71·3; H, 9·35. $C_{10}H_{16}O_2$ requires C, 71·45; H, 9·6%).

We wish to acknowledge grants from the Royal Society (to E. H. F.) and the Chemical Society (to R. C. P.).

IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, October* 20*th*, 1937.]