219. *Mechanism of Polymerisation. Part IV. Experiments relating to the Constitution of the Solid Dimeride and the Liquid Trimeride of βγ-Dimethylbutadiene, and to the Separation of the Higher Polymerides.*

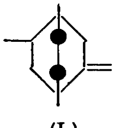
By Ernest Harold Farmer and John F. Martin.

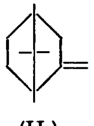
The solid dimeride, $C_{12}H_{20}$, previously reported to be formed by the acid-catalysed polymerisation of βγ-dimethylbutadiene, yields with lead tetra-acetate a mixture of acetates. The *monoacetate*, $C_{12}H_{19}{\cdot}OAc$, gives on hydrolysis a *ketone*, $C_{12}H_{20}O$, which is oxidised by nitric acid to a dibasic *acid*, $C_{12}H_{20}O_4$. By considering (1) the reactivity of the ketone, and (2) the structures of all the bicyclic dimeric products to which simple additive mechanisms could give rise, it is possible to correlate all experimental observations on the basis that the dimeride is one of two methylenotetramethyl*bicyclo*heptanes (or, less probably, a methylenotrimethyl*bicyclo*octane) which forms a monoacetate capable of undergoing Wagner–Meerwein rearrangement involving ring enlargement.

The trimeric, tetrameric, and pentameric portions of the polymeride have been separated from one another by molecular distillation, leaving as residue a highly viscous liquid of mainly hexameric complexity. The trimeric portion, $C_{18}H_{30}$, gives on dehydrogenation in the liquid phase with selenium an increased yield of the naphthalenic hydrocarbon, $C_{17}H_{22}$, previously reported, but the main bulk of the trimeric fraction is apparently incapable of dehydrogenation in this way; the residue from selenium dehydrogenation, however, when submitted as a vapour to the action of hydrogen and palladised charcoal, gives an isomeric naphthalenic hydrocarbon, $C_{17}H_{22}$, whereas the original dimeride gives a mixture of both isomerides. The first of these naphthalenic hydrocarbons is readily oxidised to a *quinone*, $C_{17}H_{20}O_2$.

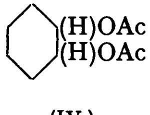
Accordingly, although the trimeric portion almost certainly comprises a mixture of isomeric hydrocarbons, that portion which gives rise in turn to the naphthalenic hydrocarbon and the quinone is probably pentamethyl*iso*propenyloctahydronaphthalene (XXI).

The solid camphor-like dimeride formed by the action of the Bertram–Walbaum reagent on βγ-dimethylbutadiene (Farmer and Pitkethly, J., 1938, **16**, 290) has now been obtained in considerably increased yield (total 4%). This substance, for which a bicyclic methyleno-structure (I or II) was suggested, was shown to resemble certain known methylenoterpenes in not readily undergoing scission of the methylene group under the action of ozone or chromic acid. In order to obtain more direct evidence of the methyleno-constitution and at the same time to enable discrimination to be made between various


(I.)

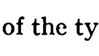

(II.)

(III.)

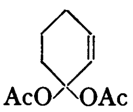


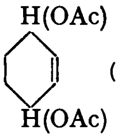
(IV.)

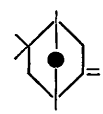
possible formulæ, the action on the dimeride of permanganate and of lead tetra-acetate has now been studied. The former of these reagents has but slight action either in warm aqueous or in boiling acetone solution, but the latter has given unexpected results.

When heated in an acetic acid medium the dimeride ($C_{12}H_{20}$) gave with lead tetra-acetate a mixture of acetates of which 43% consisted of a *monoacetate*, $C_{12}H_{19}{\cdot}OAc$. The molecular refraction of this compound denoted the presence therein of one double bond, and hydrolysis of the acetate with alkali gave a camphoraceous, pasty solid from which a crystalline *semicarbazone* (m. p. 255°) could readily be obtained. From this semicarbazone, by hydrolysis with oxalic acid, the corresponding carbonyl *compound*, $C_{12}H_{20}O$, was obtained as a crystaline solid (m. p. 180°) closely resembling camphor in odour and appearance. This compound was quite different from the aldehyde, $C_{12}H_{20}O$ (semicarbazone, m. p. 224°), previously obtained from the dimeride (Farmer and Pitkethly, *loc. cit.*). It passed on oxidation with nitric acid into a dibasic *acid* $C_{12}H_{20}O_4$ (m. p. 161°). The production of such a dibasic acid without loss of any carbon atom pointed at once to a formula for the carbonyl compound of the type  $C_{10}H_{18}{<}\begin{smallmatrix}CH_2\\ CO\end{smallmatrix}$, and in order to explain the formation of such a ketone from a mono-olefinic methylene hydrocarbon we make the following suggestion.

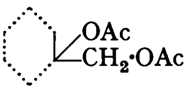
*cyclo*Hexene is known to yield with lead tetra-acetate a mixture of the monoacetate (III) and the diacetates (IV)—(VI) (Criegee, *Annalen*, 1930, **48**, 263); various terpenes, including pinene, dipentene, α-terpinene, and terpinolene, also behave similarly (Ward, *J. Amer. Chem. Soc.*, 1938, **60**, 325). Now there are three bicyclic dimeric structures which by the simple additive processes previously discussed are capable of being formed directly from monomeric dimethylbutadiene. These are (I), (II), and (VII), and with any of these lead

(V.) 

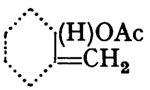
 (VI.)

 (VII.)

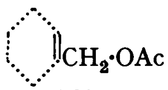
tetra-acetate might be expected to give compounds of the types (VIII) and (IX) in which the dotted structures are intended to represent any one of the bicyclic ring systems present in (I), (II), and (VII). The previous and the present observations concerning the chemistry



(VIII.)



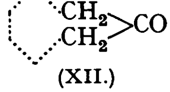
(IX.)



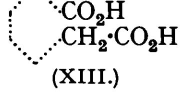
(X.)

(XI.)

of the solid dimeride appear to be capable of correlation *only* if the monoacetate first formed from the dimeride is (IX); for since the hydrolysis of any ester to yield a ketone may be interpreted as denoting that the alcoholic component of the ester is the enolic form of a ketone, and since the ketone in this particular case must contain the grouping $\cdot CH_2\cdot CO\cdot$, it is reasonable to suppose that a monoacetate (IX) is first formed and this immediately passes into its anionotropic form (X) under the prevailing conditions,* and is later transformed (owing to the acidity of the medium) by Wagner–Meerwein rearrangement into (XI). The ketone formed by hydrolysis of the acetate would then be (XII)



(XII.)



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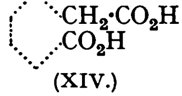

(XIV.)

and this would be capable of passing on oxidation without loss of carbon atoms into a dibasic acid (XIII) or (XIV). This postulated course of reaction seems more likely to be the true course in view of the fact that all other Wagner–Meerwein isomerisations which could occur with monoacetates normally derived from (I), (II), and (VII) by the action of lead tetra-acetate are found on inspection to lead to ketones of the type $\cdot CHR\cdot CO\cdot CHMe\cdot$,

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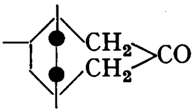
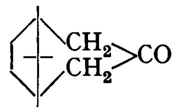
* Alternatively (X) is derived by loss of acetic acid from the diacetate (VIII).

and these, of course, could not be oxidised to dibasic acids without loss of one or more carbon atoms.

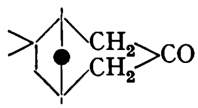
The formation of the ketone of formula (XII) [which, written fully, is actually one or other of the three forms (XV), (XVI), or (XVII)] thus involves a ring enlargement, and



(XV.)



(XVI.)



(XVII.)

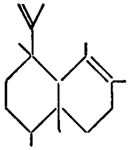
in this respect closely parallels the ready formation of *cyclo*heptanone and *cyclo*octanone from *cyclo*hexanone (Mosettig and Burger, *J. Amer. Chem. Soc.*, 1930, **52**, 3456; Robinson and Smith, J., 1937, 371). In support of the formula (XII) it may be mentioned (i) that the ketone forms a semicarbazone with the greatest ease, whereas ketones in which one of the α-carbon atoms is both quaternary in character and carries a methyl group (*e.g.*, camphor, fenchone, and various substituted *cyclo*hexanones; Wallach, *Annalen*, 1907, **353**, 209; Cornubert and Sarkis, *Compt. rend.*, 1932, **195**, 252) form semicarbazones with more or less marked difficulty; and (ii) that when the ketone is reduced by the Kishner–Wolff method to yield the corresponding *hydrocarbon*, $C_{12}H_{22}$, the latter (m. p. 146°) is quite different from the direct hydrogenation *product* (m. p. 78°) of the original dimeride.

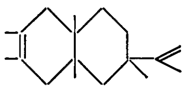
Since the dimeride and the derived ketone very closely resemble corresponding members of the camphor group in their physical attributes, we are inclined to dismiss formula (XV) from consideration as offering a suitable representation of the ketone. The choice is thus between (XVI) and (XVII) for the ketone and between (II) and (VII) for the parent dimeride. At present, however, we have insufficient evidence to permit of decision between the rival formulæ for each.

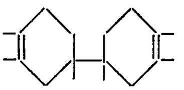
The Trimeric and Higher Polymeric Fractions.—When the proportion of sulphuric acid in the Bertram–Walbaum reagent was 1—1·8% the yield of polymerides was: dimeride, 29·0; trimeride, 19·5; tetrameride, 18·4; pentameride, 15; higher polymerides, 17%. The oily trimeric, tetrameric, and pentameric fractions were sharply separated by high-vacuum fractionation in a continuous molecular still, the residue (mainly hexameric) being too viscous to flow over the evaporating surface of the still.

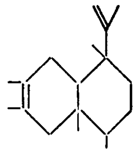
By exhaustive systematic fractionation of the trimeric portion at reduced pressure, a fraction (25% of the whole) of practically constant refractive index was isolated. This fraction gave formaldehyde as the volatile oxidation product with ozone, and formic acid that with permanganate. The supplementary ketonic fission product obtained with ozone was isolated by means of the Girard "T" reagent (semicarbazone, m. p. *ca.* 260°) but in too small a yield to permit of its adequate study. Dehydrogenation of this constant-boiling fraction with selenium gave a maximum yield of 6·5% of the crystalline naphthalenic hydrocarbon, $C_{17}H_{22}$ (m. p. 111°; picrate, m. p. 156°; trinitrobenzene derivative, m. p. 183°), which Farmer and Pitkethly (*loc. cit.*) have reported to be obtainable in small amount from the trimeride; about the same yield of this hydrocarbon could, however, be obtained from a higher-boiling fraction of the trimeride. The non-crystalline residue of the dehydrogenated constant-boiling fraction was deemed, after prolonged fractionation and examination, to consist mainly of undehydrogenated trimeride, but this residue gave no further quantity of the crystalline naphthalenic hydrocarbon when retreated with selenium. Hence it appears that a very large proportion of the trimeride is incapable of dehydrogenation with selenium as catalyst.

Dehydrogenation in the vapour phase (one treatment) of the hydrocarbon residue from the selenium treatment, platinised charcoal being used as catalyst, gave a small yield of a second hydrocarbon, $C_{17}H_{22}$ (*trinitrobenzene* derivative, m. p. 166°); and it is to be noted that the original trimeride (untreated with selenium) gave under similar conditions of dehydrogenation a product containing *both* of the hydrocarbons $C_{17}H_{22}$ (both trinitrobenzene derivatives isolated). The second of these hydrocarbons, which has not yet been regenerated from its derivative in a satisfactorily high state of purity, must also be a naphthalenic hydrocarbon, and doubtless differs from its isomeride only in the orientation of the groups in the nucleus. Now, taking into consideration that there are four non-linear trimeric substances, (XVIII)—(XXI), capable of being directly formed from the monomeric hydrocarbon by simple addition (polar or free-radical) mechanisms, and of these (XX) would necessarily give rise on dehydrogenation to a diphenyl derivative and the rest to naphthalenic hydrocarbons, it is seen that the naphthalenic dehydrogenation products are likely to be among five tetramethyl*iso*propylnaphthalenes which could reasonably arise from (XVIII), (XIX), and (XXI),* since only one carbon atom is lost during the dehydrogenation. It is found, however, that oxidation of the principal naphthalenic hydrocarbon (m. p. 111°) with chromic acid readily gives rise to a pale yellow *quinone*, $C_{17}H_{20}O_2$ (m. p. 118°), without loss of carbon atoms, and this fact indicates that the trimeride and its dehydrogenation product are unsubstituted in the 1 : 4-positions of one ring, so that three of the five structures, and hence (XVIII) for the trimeride, are excluded.

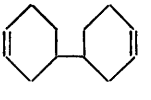

(XVIII.)

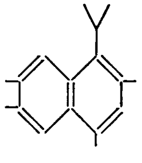

(XIX.)

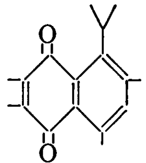

(XX.)


(XXI.)

Of the other three possible forms for the trimeride, (XX) must be absent, or nearly so, for in spite of careful search we have been unable to recognise any trace of a diphenyl derivative† amongst the dehydrogenation products of any fraction of the trimeride. This result is to be contrasted with the observations of Alder and Rickert (*Ber.*, 1938, **71**, 373, 379) that dimeric butadiene (1-vinyl-Δ^3-*cyclo*hexene), when heated with its monomeride in the presence of acetylenedicarboxylic acid (to inhibit polymerisation of the butadiene), adds the monomeride in Diels–Alder fashion at the extracyclic double bond to give some quantity of the trimeride (XXII); and likewise, butadiene under similar conditions becomes added at the extracyclic double bond of styrene or to one of the double bonds of *cyclo*pentadiene to give corresponding hydrodiphenyl derivatives (*loc. cit.*). If these addition compounds may be taken to be the *principal* products of reaction in the respective cases, it appears that the Alder and Rickert type of catalysed thermal addition follows a different course from our acid-catalysed trimerisation, although it seems likely that by employing Alder and Rickert's catalytic procedure it would be possible to obtain a substituted hydrodiphenyl by addition of mono- to di-meric dimethylbutadiene.


(XXII.)


(XXIII.)


(XXIV.)

The trimeric form (XIX) is not very likely to be produced, since its formation would involve the addition of the monomeric hydrocarbon to the endocyclic bond of the ordinary dimeride, despite the fact that this double bond is in all ordinary reactions very markedly less reactive than the extracyclic double bond. Hence it seems most probable that that particular trimeric form which gives rise in turn to the naphthalenic hydrocarbon, m. p. 111°, and the quinone, m. p. 118°, has the formula (XXI), and these last two derivatives are in consequence (XXIII) and (XXIV) respectively. What proportion, however, of the considerable trimeric fraction the form (XXI) constitutes, we are unable on the present evidence to estimate even roughly.

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* Recent published examples show that where quaternary groupings occur in the ring, dehydrogenation may cause either elimination or migration of an alkyl group.

† The expected dehydrogenation product from (XX), *viz.*, 3 : 3′ : 4 : 4′-tetramethyldiphenyl, is a yellow solid, m. p. 76—77° (Crossley and Hampshire, J., 1911, **99**, 726).

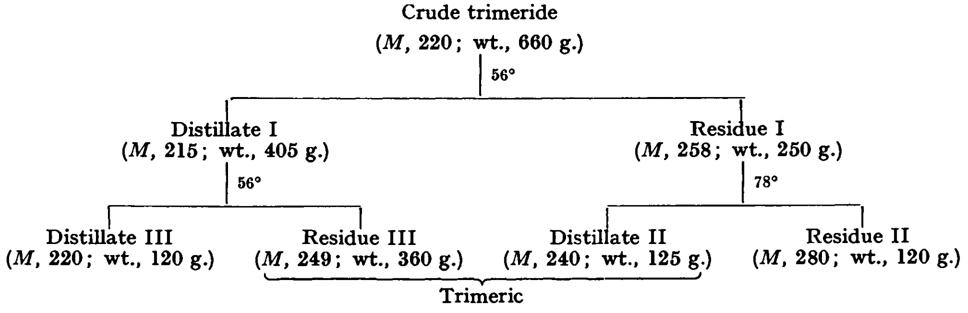
EXPERIMENTAL.

Polymerised βγ-Dimethylbutadiene.—Polymeric product. The polymerisate obtained by allowing 900 g. of diene to remain dissolved in acetic acid–sulphuric acid (1·8% by weight of H_2SO_4) at room temperature for 96 hours was isolated and freed from traces of esters and of alcohols as before (yield, 820 g.). By distillation at reduced pressure it was resolved into three fractions: (i) dimeric, b. p. 65—120°/18 mm. (160 g., 21%); (ii) trimeric, b. p. 120°/18 mm.—120°/1 mm. (255 g., 29%); (iii) higher polymeric residue (400 g., 50%). By systematic fractionation of (i), through a 60-cm. vacuum-jacketed column packed with a nichrome spiral and with carefully controlled reflux ratio, 25 g. of pure solid dimeride, m. p. 66°, were segregated (*i.e.*, 15% of the dimeric material or 3% of the total polymerides). When the preparation was repeated with 1·5 kg. of hydrocarbon and 1% of sulphuric acid in the mixed acids, the corresponding fractions weighed (i) 465 g., (ii) 410 g., and (iii) 600 g., and from (i), after it had stood for 5 months in the dark, 60 g. of pure solid dimeride were separated.

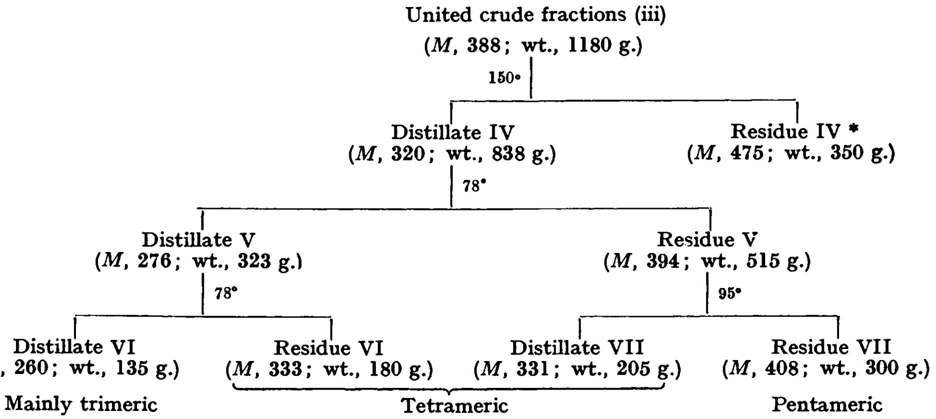
The two crude trimeric fractions so obtained were united and subjected to evaporative distillation in a continuous, vertical, molecular still (see Farmer and Van den Heuvel, *J. Soc. Chem. Ind.*, 1938, **57**, 24). By adjusting the rate of flow on to the evaporating surface and also the temperature of the latter to suitable fixed values, a division of the material into distillable and undistillable portions (*i.e.*, into distillate and residue) was effected. The course of the subsequent evaporative treatments of this first distillate and residue is summarised in the table, the molecular weight (*M*) shown for each fraction being determined cryoscopically (in benzene). The distillates II and VI and residue III were united and again distilled at 78°, a very small first fraction and a very small residue being segregated and rejected, and the main trimeric distillate being collected in several portions. These portions proved to be practically identical in molecular weight (average, 247. Calc.: 246).

The tetrameric, pentameric, and higher polymerides have been stored for future examination.

Isolation of Trimeric Fraction.



Isolation of Tetra- and Penta-meric Fractions.



* Largely hexameric. Too viscous to flow at reasonably low temperatures and hence not further separable.

Heterogeneity of the trimeric fraction. The united trimeric portions (Distillate II and VI and Residue III) were redistilled in a molecular still at 45°, the rate of flow being as rapid as the apparatus would allow. A distillate, one-sixth of the whole, was collected, and then at the same temperature but at a reduced rate of flow a second distillate (one-sixth of the whole) was collected. This process was repeated with appropriate changes in the rate of flow until five distillates had been collected and the final sixth of the material remained as residue. The refractive indices of the six portions rose irregularly from 1·4958 to 1·5059 although the molecular weight remained constant.

An attempt was made to isolate substantially homogeneous trimeric forms by submitting the reunited six fractions to systematic fractionation (equilibrium distillation) at 0·5 mm. pressure under the 60-cm. vacuum-jacketed column mentioned above. There was no significant change of b. p. at any point in the fractionation, but the refractive index changed considerably as distillation proceeded. In the fourth series of distillations the refractive index of the fractions rose fairly rapidly from 1·4905 to 1·4940 (0—22% distilled), then remained constant at 1·4938 (22—42% distilled), and finally rose rapidly to 1·5055. The fraction of constant refractive index was subsequently examined (see below) but appeared to be heterogeneous, and hence the trimeric fraction of the polymerisate, with but slight doubt, contains a number of isomeric trimeric forms.

The Solid Dimeride.—Oxidation with lead tetra-acetate. The dimeride (10 g.) was heated at 100° for 3 hours with lead tetra-acetate (35 g.) in glacial acetic acid (200 c.c.). The product was cooled, poured into 3 times its volume of water, and extracted with ether. The ethereal extract was freed from acetic acid, dried (sodium sulphate), and then freed from ether. The mixed acetates were distilled under a 4-inch column at 12 mm., the fractions being: (i) 70—94° (1 g.), (ii) 94—130° (0·5 g.), (iii) 130—138° (6 g.), (iv) 138—170° (2·5 g.), (v) 170—182° (2·5 g.). Fraction (iii), which on redistillation had b. p. 128—135°/12 mm., $d_{4^\circ}^{19^\circ}$ 0·9805, n^{19° 1·47490, $[R_L]_D$ 63·83, represented the *monoacetate* of the dimeride (Found: C, 76·05; H, 10·05; *M*, by saponification, 228. $C_{12}H_{19}{\cdot}OAc$ requires C, 75·7; H, 10·0%; *M*, 222).

Hydrolysis of monoacetate. The fraction (iii) was heated for 1 hour with a small excess of N-alcoholic potash, and then poured into water and extracted with ether. The dried extract yielded on evaporation a pasty solid of strong camphoraceous odour. When a methanol solution of this solid was mixed with semicarbazide hydrochloride dissolved in sodium acetate solution, the *semicarbazone*, m. p. 255°, separated almost immediately (Found: C, 65·85; H, 9·9. $C_{13}H_{23}ON_3$ requires C, 65·8; H, 9·7%). From the united acetate fractions (i), (ii), (iv), and (v) (see above), after hydrolysis, a further substantial amount of this semicarbazone was obtained.

The ketone, $C_{12}H_{20}O$. The semicarbazone was suspended in water containing sufficient oxalic acid for its hydrolysis, and the suspension distilled in a current of steam. The carbonyl compound separated from the distillate as a crystalline solid melting sharply at 180° (recrystallised from methanol, m. p. 180°). It had no observable aldehydic characteristics, was clearly different from the isomeric aldehyde derived by ozonolysis of the dimeride (Farmer and Pitkethly, *loc. cit.*, p. 290), and is probably either 1 : 2 : 2 : 3-*tetramethyl*-1 : 3-endo*ethylene*cyclo*hexan*-5-*one* (XVI) or 1 : 2 : 2 : 4-*tetramethyl*-1 : 4-endo*methylene*cyclo*heptan*-6-*one* (XVII), although 1 : 2 : 4-*trimethyl*-1 : 4-endo*ethylene*cyclo*heptan*-6-*one* (XV) is not altogether excluded (Found: C, 79·9; H, 10·85. $C_{12}H_{20}O$ requires C, 80·0; H, 11·1%). The *oxime* was formed on refluxing the ketone (1 g.) with hydroxylamine hydrochloride (0·38 g.) and alcoholic sodium ethoxide (0·13 g. of Na in 10 c.c. of alcohol) for 8 hours, and precipitating it with water. It crystallised from methanol in plates, m. p. 132° (Found: C, 74·0; H, 10·85. $C_{12}H_{21}ON$ requires C, 73·85; H, 10·75%).

The dibasic acid. The ketone was heated under reflux with excess of nitric acid (*d* 1·42) and the mixture, when evolution of brown fumes had ceased, was poured into an equal volume of water and then extracted with ether. From the ethereal liquor the acidic product was extracted with 10% sodium carbonate and after regeneration was crystallised from hot water. It formed colourless prisms, m. p. 161° (Found: C, 62·85; H, 8·7; equiv., 113·2. $C_{12}H_{20}O_4$ requires C, 63·15; H, 8·8%; equiv., dibasic, 114).

Reduction of ketone. The semicarbazone of the ketone (2·5 g.) was heated with sodium ethoxide in alcohol (1·5 g. of Na in 15 c.c. of alcohol) in a sealed tube at 150° for 16 hours. The product was poured into water and the reduction product separated therefrom by distillation in steam. The hydrocarbon (m. p. 144°) which separated from the distillate (1·2 g.) was collected; after sublimation it melted at 146°. This hydrocarbon is probably 1 : 2 : 2 : 3-*tetramethyl*-1 : 3-endo*ethylene*cyclo*hexane* or 1 : 2 : 3 : 4-*tetramethyl*-1 : 4-endo*methylene*cyclo-

heptane, although 1 : 2 : 4-*trimethyl*-1 : 4-endo*ethylene*cyclo*heptane* is not excluded (Found: C, 86·75; H, 13·1. $C_{12}H_{22}$ requires C, 86·75; H, 13·25%).

Hydrogenation of the solid dimeride. The dimeride (1 g.), in alcohol, when hydrogenated at ordinary temperature and pressure by means of Adams's catalyst absorbed 0·99 mol. of hydrogen per mol. The *dihydride*, after recrystallisation from methanol, melted at 78°. This hydrocarbon is probably 1 : 2 : 2 : 3 : 4-*pentamethyl*-1 : 3-endo*ethylene*cyclo*pentane* (derived from II) or 1 : 2 : 2 : 4 : 5-*pentamethyl*-1 : 4-endo*methylene*cyclo*hexane* (from VII), but 1 : 2 : 4 : 5-*tetramethyl*-1 : 4-endo*ethylene*cyclo*hexane* (from I) is not excluded (Found: C, 86·3; H, 13·5. $C_{12}H_{22}$ requires C, 86·65; H, 13·35%).

Formation of nitrosochloride and hydrochloride. The dimeride (1 g.), in glacial acetic acid (4 c.c.), was mixed with amyl nitrite (1 c.c.) and to the mixture, cooled to − 10°, concentrated hydrochloric acid (2 c.c.) was added dropwise with shaking. After standing for 1 hour, the product was worked up and yielded a crystalline nitrosochloride, which crystallised from light petroleum in colourless prisms, m. p. 115°. When dry hydrogen chloride was passed for several hours through a solution of the dimeride in ether maintained at − 10° a crystalline hydrochloride was formed which after recrystallisation from saturated alcoholic hydrogen chloride melted at 78°.

The Trimeric Fraction.—*Ozonolysis.* The ozonide formed at 0° from 5 g. of the trimeride, dissolved in chloroform, was decomposed by heating with water. From the aqueous portion of the product only formaldehyde was obtained (2 : 4-dinitrophenylhydrazone, m. p. 162°); from the accompanying yellow oil no semicarbazone could be derived directly, but after it had been freed from non-ketonic material by means of Girard "T" reagent, the regenerated oil then gave gritty crystals, m. p. *ca.* 260°, in too small yield for examination.

Dehydrogenation with selenium. The trimeride (30 g.) was heated in the usual way with an equal weight of selenium at 260—270° for 60 hours. The product was extracted with light petroleum, the extract filtered through a column of alumina to remove high-boiling selenium compounds, and then evaporated. The residual yellow oil (27 g.) was treated with alcoholic picric acid, and the picrate collected, dried (orange needles, m. p. 156°), and decomposed with dilute ammonia. The solid naphthalenic hydrocarbon thus regenerated crystallised from methyl alcohol in colourless needles, m. p. 111° (cf. Farmer and Pitkethly, *loc. cit.*, p. 291); its trinitrobenzene derivative crystallised from alcohol in yellow needles, m. p. 183°.

The alcoholic filtrate remaining after separation of the picrate yielded no further amount of picrate; accordingly, it was freed from excess of picric acid and evaporated. The residual hydrocarbon oil (24 g.), which boiled over the range 65—116°/0·4 mm. (residue 5 g.), was intensively fractionated under a good vacuum-jacketed column with controlled reflux. By combination of fractions of similar refractive index, followed by refractionation, a portion (7·5 g.) of b. p. 106—113°/0·5 mm., $n_D^{14\cdot5^\circ}$ 1·49583, $d_4^{14\cdot5^\circ}$ 0·9001, $[R_L]_D$ 80·05, was obtained. This was clearly unchanged trimeric dimethylbutadiene {Found: C, 87·6; H, 12·2. Calc. for $(C_6H_{10})_n$: C, 87·7; H, 12·25%; $[R_L]_D \,|^{=}_{2}$, 79·99}. This unchanged trimeride was re-treated with selenium at 330° for 40 hours, but the product did not contain any picrate-forming hydrocarbon.

Dehydrogenation with platinised charcoal. When the trimeride was vigorously refluxed for 3 hours over platinised charcoal in a stream of carbon dioxide, no gas was evolved, but when it (7·5 g.) was passed as a vapour over platinised charcoal at 335° during 12 hours, 270 c.c. of gas were evolved. The product (6 g.), swept out with hydrogen, was divided into four nearly equal fractions by distillation at 0·5 mm., and each fraction treated with alcoholic trinitrobenzene. The lowest-boiling fraction (b. p. 50—80°) yielded no derivative, but the remaining three each yielded one. The trinitrobenzene derivative from the second and the third fraction melted after one recrystallisation at 181° and readily yielded the pure naphthalenic hydrocarbon, m. p. 111°, and the corresponding picrate, m. p. 156° (mixed m. p. with previously obtained compounds, 111° and 156° respectively), whereas the highest-boiling fraction yielded a mixture of trinitrobenzene derivatives, melting indefinitely about 170° after one recrystallisation from methyl alcohol.

A sample of trimeride (2·75 g.) which had survived dehydrogenation treatment with selenium was passed in vapour form over platinised charcoal at 330° during 6 hours, during which 130 c.c. of gas were evolved. The product (2·15 g.), swept out with hydrogen, formed a *trinitrobenzene* derivative, which melted after recrystallisation from alcohol at 166° and was isomeric with the compound of m. p. 181° [Found: C, 62·8; H, 5·6. $C_{17}H_{22},C_6H_3(NO_2)_3$ requires C, 62·85; H, 5·7%].

Oxidation of the naphthalenic hydrocarbon, m. p. 111°. The hydrocarbon (1·1 g.), dissolved in 20 c.c. of glacial acetic acid, was gradually treated (with stirring) at 60° with chromic acid (3 g.) dissolved in 80% aqueous acetic acid (10 c.c.). After 45 mins. the mixture was heated on the water-bath for 2 hours, and then poured into water. A yellow *quinone* separated, and this was extracted with ether, freed from acetic acid and solvent, and crystallised from methyl alcohol. It formed yellow prisms, m. p. 118°, and was probably a *tetramethyl*iso*propylnaphthaquinone* (XXIV) (Found: C, 79·6; H, 7·75. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·8%).

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