2. *Synthesis of Polymethylnaphthalenes.*

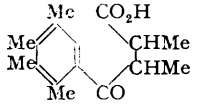
By B. J. Abadir, J. W. Cook, and D. T. Gibson.

1 : 2 : 3 : 4-Tetramethylbenzene (prehnitene) was used as the starting point in the synthesis of 1 : 2 : 3 : 4 : 6-penta-, 1 : 2 : 3 : 4 : 5 : 6-, 1 : 2 : 3 : 4 : 5 : 7-, and 1 : 2 : 3 : 4 : 6 : 7-hexa-, and 1 : 2 : 3 : 4 : 5 : 6 : 7-hepta- and octa-methylnaphthalenes. With a large excess of maleic anhydride four of these hydrocarbons underwent Diels–Alder addition, yields ranging from 45 to 68%. Polymethylanthracenes were formed as by-products when tetrachloro-ethane was used as solvent in Friedel–Crafts condensations in which *p*-xylene or prehnitene formed one reactant. With *p*-xylene one of these by-products was probably 1 : 2 : 4-trimethylanthracene.

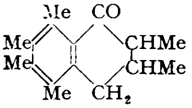
Very few fully substituted naphthalene derivatives are known. *peri*-Substituents in the naphthalene molecule are liable to overlap in the absence of molecular distortion, and it was thought that this effect might be accentuated in a completely substituted naphthalene. The primary purpose of the present investigation was the synthesis of octamethylnaphthalene for examination of its physical characteristics. This has been accomplished by several routes and *X*-ray crystallographic examination of the hydrocarbon has shown that the congestion of methyl groups is such as to produce actual distortion of the naphthalene rings (see following paper). Suitable modification of the synthetic procedures enabled us to prepare also a pentamethylnapthalene, three hexamethylnaphthalenes, and a heptamethylnaphthalene. Until recently the most highly methylated naphthalene described in the literature was a pentamethyl compound. Since our experiments were completed, Mosby (*J. Amer. Chem. Soc.*, 1952, **74**, 2564) recorded the synthesis of a new pentamethylnaphthalene and a new hexamethylnaphthalene.

The most satisfactory route to octamethylnaphthalene involved the intermediate formation of 1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethylnaphthalene (III), which was converted into the 8-chloromethyl derivative and this submitted to catalytic hydrogenation over palladised charcoal, whereby octamethylnapthalene was formed (cf. Hewett, *J.*, 1940, 293). For the preparation of the heptamethylnaphthalene, prehnitene was condensed with αβ-dimethylsuccinic anhydride in presence of aluminium chloride to give γ-keto-αβ-dimethyl-γ-prehnitylbutyric acid (I). Hydrogenation of its sodium salt over copper chromite led to αβ-dimethyl-γ-prehnitylbutyric acid which was cyclised by hydrogen fluoride to 1 : 2 : 3 : 4-

tetrahydro-1-keto-2 : 3 : 5 : 6 : 7 : 8-hexamethylnaphthalene (II). This ketone reacted normally with methylmagnesium iodide and the resulting crude alcohol was submitted to dehydration and then dehydrogenation, giving the heptamethylnaphthalene (III).



(I)



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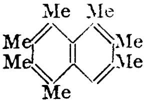
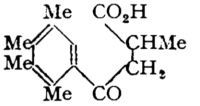


(III)

A possible variant of the above synthesis of octamethylnaphthalene would have involved introduction of one of the two final methyl groups at an earlier stage by treating the methyl ester of (I) with one molecular proportion of methylmagnesium iodide. Not unexpectedly, however, the carbonyl group proved too hindered for preferential attack by the Grignard reagent and no acidic product was formed after hydrolysis. Similar failure attended an attempt to condense methyl α-bromo-αβ-dimethylsuccinate with acetylprehnitene by the Reformatsky reaction. However, this ketone reacted with the usual carbonyl reagents.

Reduction of the tetrahydroketohexamethylnaphthalene (II) by Clemmensen's method or by the Huang-Minlon procedure gave, in poor yield, the corresponding tetrahydrohexamethylnaphthalene, and catalytic hydrogenation of (II) followed by dehydration gave a good yield of the corresponding dihydrohexamethylnaphthalene. Both these hydrocarbons were smoothly dehydrogenated to 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene (XIII).

Prehnitene was condensed with methylsuccinic anhydride in presence of aluminium chloride to give in 85% yield the homogeneous γ-keto-α-methyl-γ-prehnitylbutyric acid (IV). This readily gave a 2 : 4-dinitrophenylhydrazone and was easily reduced by Clemmensen's method to α-methyl-γ-prehnitylbutyric acid. In both these respects the behaviour of the keto-acid (IV) was in marked contrast to that of its homologue (I), which supports the view that methylsuccinic anhydride had reacted to give the α-methylbutyric acid rather than the β-methyl acid. α-Methyl-γ-prehnitylbutyric acid was cyclised by hydrogen fluoride to 1 : 2 : 3 : 4-tetrahydro-1-keto-2 : 5 : 6 : 7 : 8-pentamethylnaphthalene, which was converted by standard reactions into 1 : 2 : 3 : 4 : 6-pentamethylnaphthalene and 1 : 2 : 3 : 4 : 5 : 6-hexamethylnaphthalene (V). The compound (VI) formed by addition of maleic anhydride to this hexamethylnaphthalene (see below) was oxidised to benzene-1 : 2 : 3 : 4-tetracarboxylic acid, which confirms the structures assigned to (IV) and (V). If the isomeric β-methylbutyric acid derivative had been formed this would have led to 1 : 2 : 3 : 4 : 5 : 7-hexamethylnaphthalene, the maleic anhydride adduct of which would have been oxidised to benzene-1 : 2 : 3 : 5-tetracarboxylic or to mellitic acid.



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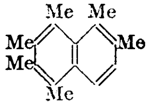

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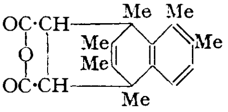
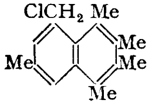


(VI)

1 : 2 : 3 : 4 : 5 : 7-Hexamethylnaphthalene was, in fact, obtained from 1 : 2 : 3 : 4 : 6-pentamethylnaphthalene by chloromethylation to (VII) followed by catalytic dechlorination. The structure (VII) follows from the fact that the hexamethylnaphthalene formed from it was distinct from both 1 : 2 : 3 : 4 : 5 : 6- and 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene. A fourth hexamethylnaphthalene (1 : 2 : 3 : 4 : 5 : 8-) has been described by Mosby (*loc. cit.*). The failure of 1 : 2 : 3 : 4 : 6-pentamethylnaphthalene to undergo chloromethylation at position 5, which would have been expected by analogy with simpler derivatives of 2-methylnaphthalene, is possibly due to the steric influence of the methyl group at position 4. It was hoped that 1 : 2 : 3 : 4 : 5 : 6-hexamethylnaphthalene also would undergo chloromethylation at position 8 to give a product which could be reduced to give a second heptamethylnaphthalene. Curiously, substitution took place at the alternative β-position to give (VIII) which was converted by catalytic dechlorination into 1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethylnaphthalene.

In our earlier experiments on the synthesis of polymethylnaphthalenes αβ-dimethylsuccinic anhydride was treated with durene. The acid (IX) was reduced to γ-duryl-αβ-dimethylbutyric acid, and this underwent rearrangement and cyclisation under the influence of hydrogen fluoride (cf. Badger, Carruthers, and Cook, *J.*, 1949, 2044; Aitken, Badger, and Cook, *J.*, 1950, 331) to produce the ketone (II) in 50% yield. The initial Friedel–Crafts reaction was complicated by the fact that methyl migration took place to some extent in this stage also, so that the γ-duryl acid (IX) was accompanied by about a quarter of its weight of the γ-prehnityl acid (I). These were separated by taking advantage of the sparing water-solubility of the sodium salt of the latter; their structures were shown by oxidation with sodium hypobromite and hydrolysis with hydrochloric acid in a sealed tube to the appropriate substituted benzoic acids and hydrocarbons respectively. In subsequent Friedel–Crafts reactions with αβ-dimethylsuccinic anhydride it was more convenient to use prehnitene, formed from a mixture of durene and *iso*durene by the Jacobsen reaction.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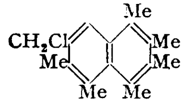
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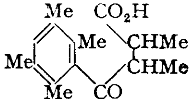
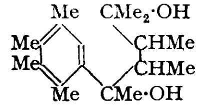

(IX)

In another approach to the synthesis of octamethylnaphthalene methyl γ-keto-αβ-dimethyl-γ-prehnitylbutyrate (cf. I) was treated with excess of methylmagnesium iodide to give an oil which evidently contained the desired diol (X) as on treatment with hydrogen fluoride (cf. Kloetzel, *J. Amer. Chem. Soc.*, 1940, **62**, 3405) it gave a very small yield of octamethylnaphthalene (isolated through its complex with 2 : 4 : 7-trinitrofluorenone).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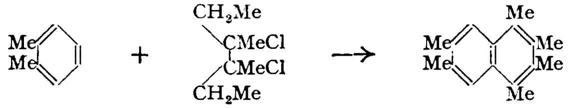
(XI) (XII) (XIII)

Bruson and Kroeger (*J. Amer. Chem. Soc.*, 1940, **62**, 36) have shown that ditertiary 1 : 4-diols, and also the 1 : 4-dichlorides and the conjugated dienes related to them, undergo a double condensation with aromatic compounds (" cycli-alkylation ") under the influence of aluminium chloride to give fused-ring hydroaromatic compounds. In all cases the dienes may well be intermediates and this probably applies also to the reaction of 3 : 4-dichloro-3 : 4-dimethylhexane (XII) with benzene, which was found by Sisido and Nozaki (*ibid.*, 1947, **69**, 961) to give 1 : 2 : 3 : 4-tetramethyltetralin. These reactions suggested yet another route to the higher polymethylnaphthalenes. Unfortunately, aluminium chloride caused loss and migration of methyl groups so that mixtures were formed. *o*-Xylene (XI) and (XII) gave 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene (XIII), together with an oil from which was isolated, after selenium dehydrogenation, 1 : 2 : 3 : 4 : 5 : 7-hexamethylnaphthalene (cf. VII) (probably as a result of initial isomerisation of *o*- to *m*-xylene). Prehnitene reacted with 3 : 4-dichloro-3 : 4-dimethylhexane (XII) at 40° to give, after dehydrogenation, a mixture containing 1 : 2 : 3 : 4 : 6 : 7-hexamethyl-, 1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethyl-, and octamethyl-naphthalene. Another experiment at 60° gave, in addition to the hepta- and octamethylnaphthalene, a hydrocarbon, m. p. 236°, having the ultra-violet absorption of an anthracene derivative and the composition of a hexamethylanthracene. Chromic acid oxidation gave a hexamethylanthraquinone, so that the *meso*-positions of the hydrocarbon are unsubstituted.

Condensation of *p*-xylene with 2 : 3 : 4 : 5-tetramethylhexane-2 : 5-diol gave as the only isolable solid product an anthracene hydrocarbon which, from its composition and m. p. (241°), and the m. p. of the quinone, appeared to be 1 : 2 : 4-trimethylanthracene. Probably the tetrachloroethane used as a solvent in the Friedel–Crafts reaction played a part in the formation of this hydrocarbon. A lower-boiling liquid fraction gave, after selenium dehydrogenation, a red picrate, m. p. 185°, which was also obtained under similar conditions from the condensation product of prehnitene with 2 : 5-dimethylhexane-2 : 5-

diol. The derived hydrocarbon, m. p. 125—128°, had the absorption characteristics of a polymethylnaphthalene. The prehnitene condensation also yielded an anthracene hydrocarbon, m. p. 236°, which has not been identified.

While this synthetic work was in progress Kloetzel, Dayton, and Herzog (*ibid.*, 1950, **72**, 273) reported that 1 : 2 : 3 : 4-tetramethylnaphthalene undergoes a Diels–Alder addition of maleic anhydride in the substituted ring, and with a large excess of the reagent they obtained a 90% yield of adduct. Lower homologues were subsequently found to give similar adducts, but in much smaller yield (Kloetzel and Herzog, *ibid.*, p. 1991).

It seemed of interest, therefore, to examine the behaviour of some of our polymethylnaphthalenes in this reaction. The hydrocarbon was heated in benzene solution with 30 mols. of maleic anhydride. Adducts were formed in all of the 5 cases investigated, and the figures in parentheses give the yield of adduct obtained after 48 hours : 1 : 2 : 3 : 4 : 6-pentamethyl (50%); 1 : 2 : 3 : 4 : 5 : 6-hexamethyl (68%); 1 : 2 : 3 : 4 : 6 : 7-hexamethyl (45%); 1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethyl (60%); octamethyl (62%). In each case the hydrocarbon was regenerated quantitatively when the adduct was heated above its m. p. under reduced pressure. For the two hexamethylnaphthalenes it was shown that maleic anhydride had been added to the fully substituted ring, for the adduct (VI) from 1 : 2 : 3 : 4 : 5 : 6-hexamethylnaphthalene was oxidised by alkaline permanganate to prehnitic acid and that from 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene to pyromellitic acid. The absorption spectra of the adducts had the expected benzenoid character.

EXPERIMENTAL

Light petroleum had b. p. 40—60°, ligroin b. p. 100—120°.

Condensation of αβ-*Dimethylsuccinic Anhydride with Durene.*—Durene was prepared by bischloromethylation of commercial xylene followed by reduction with zinc dust and sodium hydroxide (von Braun and Nelles, *Ber.*, 1934, **67**, 1094); (±)-αβ-dimethylsuccinic anhydride was obtained as described by Fieser and Daudt (*J. Amer. Chem. Soc.*, 1941, **63**, 782). Durene (3·3 g.) and αβ-dimethylsuccinic anhydride were added in small portions, during 40 minutes, to a stirred ice-cold suspension of powdered anhydrous aluminium chloride (10 g.) in carbon disulphide (70 c.c.). Stirring was continued for 4 hours and the reaction mixture kept at room temperature overnight. The solvent was decanted and the residue decomposed with ice and hydrochloric acid. The resinous product was boiled with sodium carbonate solution and extracted with ether to remove surplus durene. The aqueous solution was evaporated to 15 c.c. and kept in the refrigerator overnight. A sparingly soluble sodium salt (0·8 g.) separated. Acidification of this gave *γ-keto-*αβ*-dimethyl-γ-prehnitylbutyric acid* (I) which crystallised from benzene–light petroleum in needles, m. p. 151—152° (Found : C, 73·6; H, 8·55. $C_{16}H_{22}O_3$ requires C, 73·3; H, 8·4%). The *methyl* ester (prepared with methanol and sulphuric acid) formed plates (from methanol), m. p. 88° (Found : C, 73·6; H, 8·85. $C_{17}H_{24}O_3$ requires C, 73·9; H, 8·7%).

A solution of the acid (100 mg.) in acetic acid (3 c.c.) and acetic anhydride (0·2 c.c.) was saturated with hydrogen chloride, then kept overnight, and evaporated, and the residue twice evaporated with benzene. The resulting unsaturated *lactone* formed needles (from benzene–light petroleum), m. p. 114·5° (Found : C, 78·7; H, 7·9. $C_{16}H_{20}O_2$ requires C, 78·65; H, 8·2%). The same lactone was formed when a solution of the acid in hydrogen fluoride was kept for 30 hours.

The alkaline filtrate from which the sodium salt of (I) had separated was acidified. The precipitate (2·4 g.) crystallised from dioxan to give thick needles, m. p. 147—148°, of *γ-duryl-γ-keto-*αβ*-dimethylbutyric acid* (IX) (Found : C, 73·7; H, 8·7. $C_{16}H_{22}O_3$ requires C, 73·3; H, 8·4%). Its *methyl* ester formed prisms (from methanol), m. p. 103° (Found : C, 73·85; H, 8·5%), and the acid was converted by hydrogen chloride and acetic anhydride in acetic acid into the corresponding unsaturated lactone, m. p. 119° (Found : C, 78·8; H, 7·8. $C_{16}H_{20}O_2$ requires C, 78·65; H, 8·0%).

The same two acids (60% yield) were obtained when the Friedel–Crafts reaction was carried out in cold tetrachloroethane. The proportion of (IX) to (I) was then 10 : 1.

Structures of the Acids (I) *and* (IX).—(*a*) A solution of the acid (200 mg.) in ice-cold 10% sodium hypobromite (20 c.c.) was heated slowly to 100°, and the temperature kept thereat for 4 hours. The product, isolated as usual, was crystallised from ligroin. (I) thus gave 2 : 3 : 4 : 5-tetramethylbenzoic acid, m. p. 166—168° alone or mixed with an authentic specimen (lit., 169°);

the amide had m. p. 220° (lit., 222°). The acid (IX) similarly gave 2 : 3 : 5 : 6-tetramethylbenzoic acid, m. p. 176—178°, not depressed by an authentic specimen (lit., 179°).

(*b*) The acid (500 mg.) was heated in a sealed tube with concentrated hydrochloric acid for 5 hours at 150°. The acid (I) gave prehnitene, b. p. 202°/760 mm. (lit., 204°), whereas (IX) gave durene, m. p. and mixed m. p. 79—80° (from methanol).

5-*Acetylprehnitene.*—A mixture of durene and *iso*durene (Smith, *Org. Synth.*, 1930, **10**, 32) was converted into prehnitene by the Jacobsen reaction (Smith and Lux, *J. Amer. Chem. Soc.*, 1929, **51**, 2994; Smith and Cass, *ibid.*, 1932, **54**, 1614). 5-Acetylprehnitene, prepared by the Friedel–Crafts reaction with acetyl chloride, formed a yellow oil, b. p. 145°/15 mm. (cf. Claus and Föhlisch, *J. pr. Chem.*, 1888, **38**, 231). It gave an orange 2 : 4-*dinitrophenylhydrazone*, m. p. 155—156° (Found: N, 15·4. $C_{18}H_{20}O_4N_4$ requires N, 15·7%), an *oxime*, m. p. 122° (Found: N, 7·0. $C_{12}H_{17}ON$ requires N, 7·3%), and a *semicarbazone*, m. p. 203° (Found: N, 18·2. $C_{13}H_{19}ON_3$ requires N, 18·0%).

Condensation of αβ-*Dimethylsuccinic Anhydride with Prehnitene.*—Prehnitene (16·5 g.) and freshly powdered anhydrous aluminium chloride (50 g.) were added during an hour to an ice-cold stirred mixture of (±)-αβ-dimethylsuccinic anhydride (16 g.) and tetrachloroethane (120 c.c.). Stirring was continued for 6 hours. Next morning, the reaction mixture was treated with ice and hydrochloric acid, and steam-volatile material removed. The resinous residue was extracted with sodium carbonate solution and the filtered solution acidified. The resinous precipitate, which gradually solidified (m. p. 140—160°; 29 g.), was separated by fractional crystallisation from mixtures of various proportions of benzene and light petroleum into 2 stereoisomers (cf. Fieser and Daudt, *loc. cit.*). The principal component was γ-keto-αβ-dimethyl-α-prehnitylbutyric acid, m. p. 151—152°, described above (Found: C, 73·0; H, 8·2%). The isomeric *acid* formed small plates, m. p. 167—168° (Found: C, 73·4; H, 8·3%). For the subsequent stages the crude mixture, m. p. 140—160°, was used.

αβ-*Dimethyl*-γ-*prehnitylbutyric Acid.*—Attempted reduction of the keto-acid (I) by Clemmensen's method led to its recovery unchanged. A solution of the sodium salt of the acid (10 g.) in water (150 c.c.) was stirred and heated with copper chromite catalyst (6 g.) and hydrogen in a steel autoclave. The initial pressure at 140° was 130 atm. The temperature was slowly raised to 240° and kept thereat for 15 hours. The still warm solution was filtered from catalyst, evaporated to 50 c.c., and kept in the refrigerator overnight. The sodium salts which crystallised were redissolved in water, the solution acidified, and the precipitate extracted twice with ether (50 c.c.). The undissolved αβ-*dimethyl*-γ-*prehnitylbutyrolactone* (0·6 g.), which was insoluble in sodium carbonate solution, crystallised from methanol in prisms, m. p. 131—132° (Found: C, 77·85; H, 9·1. $C_{16}H_{22}O_2$ requires C, 78·1; H, 8·9%). Evaporation of the ethereal extract gave αβ-*dimethyl*-γ-*prehnitylbutyric acid* (6 g.) which crystallised from benzene in rosettes of needles, m. p. 135—136° (Found: C, 77·2; H, 9·6. $C_{16}H_{24}O_2$ requires C, 77·4; H, 9·7%). The original aqueous filtrate gave on acidification unchanged keto-acid (1 g.) of m. p. (165—166°) corresponding with that of the higher-melting component of the mixture. There was no depression on mixing.

1 : 2 : 3 : 4-*Tetrahydro*-1-*keto*-2 : 3 : 5 : 6 : 7 : 8-*hexamethylnaphthalene* (II).—(*a*) A solution of dimethylprehnitylbutyric acid (3 g.) in hydrogen fluoride (70 c.c.) was kept for 30 hours. The neutral product, freed from acidic material, distilled at 180°/4 mm. (2·4 g.). This *ketone* (II) crystallised from ligroin in stout needles, m. p. 120° (Found: C, 83·2; H, 9·3. $C_{16}H_{22}O$ requires C, 83·4; H, 9·55%).

(*b*) The same acid (3 g.) was converted into its chloride by treatment with phosphorus pentachloride (3 g.) in benzene (10 c.c.) followed after addition of the pentachloride by a further 30 c.c. Volatile material was removed at 60—70° under reduced pressure, and evaporation with benzene was thrice repeated. A solution of the residual acid chloride in dry benzene (20 c.c.) was added dropwise to a stirred suspension of aluminium chloride (35 g.) in benzene (50 c.c.). After 5 hours' stirring the complex was decomposed with ice and hydrochloric acid. The resulting ketone (II) (2 g.), crystallised from light petroleum, had m. p. 120°, undepressed by a sample prepared as described under (*a*). The ketone was oxidised with dilute nitric acid (1 part of conc. acid, 1 part of water) in a sealed tube at 175° to mellitic acid, identified by preparation of its methyl ester, m. p. 184—186° alone or mixed with an authentic sample.

5 : 6-*Dihydro*-1 : 2 : 3 : 4 : 6 : 7-*hexamethylnaphthalene.*—A solution of the aforesaid ketone (1 g.) in acetic acid (30 c.c.) was hydrogenated over Adams's platinum catalyst (2 hours). The crude alcohol was dehydrated by treatment with formic acid (2 hours at room temperature) or by distillation (200°/4 mm.), and the resulting hydrocarbon purified by passage of its solution in benzene–light petroleum through a column of alumina. 5 : 6-*Dihydro*-1 : 2 : 3 : 4 : 6 : 7-

hexamethylnaphthalene formed needles (0·7 g.) (from methanol), m. p. 117°, depressed to 104° by admixture with the tetrahydro-compound (below) (Found : C, 89·4; H, 10·3. $C_{16}H_{22}$ requires C, 89·65; H, 10·35%).

5 : 6 : 7 : 8-*Tetrahydro*-1 : 2 : 3 : 4 : 6 : 7-*hexamethylnaphthalene*.—(*a*) A mixture of the ketone (II) (0·5 g.), amalgamated zinc (5 g.), concentrated hydrochloric acid (25 c.c.), toluene (4 c.c.), and ethanol (1 c.c.) was boiled for 36 hours. More amalgamated zinc (2 g.) and hydrochloric acid (5 c.c.) were then added and boiling continued for 12 hours more. The product, recovered by ether-extraction, gave needles (0·1 g.) (from methanol) of 5 : 6 : 7 : 8-*tetrahydro*-1 : 2 : 3 : 4 : 6 : 7-*hexamethylnaphthalene*, m. p. 111° (Found : C, 88·9; H, 10·95. $C_{16}H_{24}$ requires C, 88·8; H, 11·2%).

(*b*) Reduction of the ketone (II) (0·5 g.) by the Huang-Minlon procedure gave the same hydrocarbon (0·3 g.).

1 : 2 : 3 : 4 : 6 : 7-*Hexamethylnaphthalene* (XIII).—This was obtained by dehydrogenation with 20% palladised charcoal of the dihydride at 200—220° or the tetrahydride at 250—300°. Purification by formation and dissociation of the picrate gave 1 : 2 : 3 : 4 : 6 : 7-*hexamethylnaphthalene* as leaflets (from methanol), m. p. 145° (Found : C, 90·6; H, 9·5. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). The *picrate* formed dark red needles (from methanol), m. p. 190·5° Found : N, 9·8. $C_{16}H_{20},C_6H_3O_7N_3$ requires N, 9·5%); the *s*-trinitrobenzene *complex* formed orange needles (from methanol), m. p. 215° (Found : N, 9·9; $C_{16}H_{20},C_6H_3O_6N_3$ requires N, 9·9%); and the 2 : 4 : 7-trinitrofluorenone *complex* formed deep brick-red needles (from acetic acid), m. p. 210° (Found : N, 8·4. $C_{16}H_{20},C_{13}H_5O_7N_3$ requires N, 8·0%).

1 : 2 : 3 : 4 : 5 : 6 :7-*Heptamethylnaphthalene*.—A solution of 1 : 2 : 3 : 4-tetrahydro-1-keto-2 : 3 : 5 : 6 : 7 : 8-hexamethylnaphthalene (II) (0·9 g.) in dry ether (20 c.c.) was added to a Grignard solution from methyl iodide (3·5 g.), magnesium turnings (0·6 g.), and ether (40 c.c.). The ether was removed and replaced by pure benzene (30 c.c.), and the solution boiled for 36 hours. The mixture was decomposed with ammonium chloride solution, the crude alcohol dehydrated with formic acid at room temperature and the liquid product (distilled at 170°/2 mm.) (0·6 g.) dehydrogenated by palladised charcoal in boiling trichlorobenzene (2 hours). The resulting 1 : 2 : 3 : 4 : 5 : 6 : 7-*heptamethylnaphthalene*, purified through its picrate, formed needles (from benzene–methanol), m. p. 134° (Found : C, 90·0; H, 9·5. $C_{17}H_{22}$ requires C, 90·2; H, 9·8%). Its dark brown *picrate* had m. p. 184·5° (Found : N, 9·5. $C_{17}H_{22},C_6H_3O_7N_3$ requires N, 9·5%); its orange-red *s*-trinitrobenzene *complex*, m. p. 210° (Found : N, 9·55. $C_{17}H_{22},C_6H_3O_6N_3$ requires N, 9·5%); its dark red *styphnate* (from methanol), m. p. 168° (Found : N, 9·1. $C_{17}H_{22},C_6H_3O_8N_3$ requires N, 8·9%); and its brownish-black 2 : 4: 7-trinitrofluorenone *complex*, m. p. 212° (Found : N, 7·5. $C_{17}H_{22},C_{13}H_5O_7N_3$ requires N, 7·75%).

Octamethylnaphthalene.—(*a*) Hydrogen chloride was passed into a suspension of paraformaldehyde (0·1 g.) in acetic acid (3 c.c.) until dissolution was complete. The heptamethylnaphthalene (0·3 g.) was then added and the suspension shaken for 24 hours. More hydrogen chloride was led in and shaking continued for a further 24 hours. Ice was added, and the product extracted with ether. The extract was washed with sodium hydrogen carbonate solution and dried and the ether distilled off. The residual oil, which could not be distilled without decomposition, did not crystallise. Nevertheless, it was substantially 8-chloromethyl-1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethylnaphthalene, of which it gave the *s*-trinitrobenzene *complex* as dark red needles, m. p. 160° (decomp.), when the components were mixed in hot benzene solution (Found : N, 8·8. $C_{18}H_{23}Cl,C_6H_3O_6N_3$ requires N, 8·6%).

A solution of the crude chloromethylheptamethylnaphthalene (0·1 g.) in *cyclo*hexane (15 c.c.) was shaken with hydrogen and 20% palladised charcoal (50 mg.) for ½ hour. The filtered solution was evaporated and the residue treated with picric acid in hot methanol. The recrystallised picrate was passed in benzene through a column of alumina. The *octamethylnaphthalene*, obtained in this way free from the strongly adsorbed picric acid, crystallised from benzene–light petroleum in elongated plates (25 mg.) with a greenish tinge and had m. p. 174° (Found : C, 89·9; H, 10·2. $C_{18}H_{24}$ requires C, 89·9; H, 10·1%). The *picrate* formed almost black needles, m. p. 193°, after previous softening (Found : N, 9·1. $C_{18}H_{24},C_6H_3O_7N_3$ requires N, 8·9%); the *s*-trinitrobenzene *complex* formed dark red prisms (from benzene), m. p. 192—193° (Found : C, 63·5; H, 6·2. $C_{18}H_{24},C_6H_3O_6N_3$ requires C, 63·6; H, 6·1%); and the black 2 : 4 : 7-trinitrofluorenone *complex* (from acetic acid) had m. p. 209° (Found : N, 7·7. $C_{18}H_{24},C_{13}H_5O_7N_3$ requires N, 7·6%).

(*b*) Methyl γ-keto-αβ-dimethyl-γ-prehnitylbutyrate (2 g.) was added to a large excess of methylmagnesium iodide, and the mixture (with ether replaced by benzene) boiled for 60 hours. The magnesium complex was decomposed with ammonium chloride solution, and the ethereal layer evaporated. The resulting oil (1·5 g.) was added to hydrogen fluoride (40 c.c.), and the solution kept for 36 hours. The product, dissolved in acetic acid, was treated with 2 : 4 : 7-trinitrofluorenone. The black crystalline complex (30 mg.) had m. p. 207—209°, and from this was regenerated, by reduction with stannous chloride in hydrochloric acid and acetic acid, octamethylnaphthalene (5 mg.), m. p. 172—173°, not depressed by admixture with a sample prepared as under (*a*). The *s*-trinitrobenzene complex had m. p. 192—193°. A further quantity (6 mg.) of octamethyl naphthalene was obtained by selenium dehydrogenation of the oil recovered from the mother-liquors from which the trinitrofluorenone complex had been obtained.

Condensation of Methylsuccinic Anhydride with Prehnitene.—Prehnitene (12 g.) was slowly added to a stirred ice-cold suspension of anhydrous aluminium chloride (40·5 g.) and methylsuccinic anhydride (10 g.) (Dev and Guha, *J. Indian Chem. Soc.*, 1948, **25**, 13) in tetrachloroethane (100 c.c.). Stirring at 0° was continued for 5 hours; the reaction mixture was treated with ice and hydrochloric acid, and the solvent removed in steam. The residue was extracted with sodium carbonate solution, and the filtered solution acidified. The precipitated gum soon became solid (18 g.). Crystallisation from benzene gave *γ-keto-α-methyl-γ-prehnitylbutyric acid* (IV) as prisms, m. p. 130—131° (Found : C, 72·55; H, 8·1. $C_{15}H_{20}O_3$ requires C, 72·55; H, 8·1%). The *ethyl* ester, obtained with ethanol and sulphuric acid, crystallised from ethanol in short rods, m. p. 68·5° (Found : C, 73·5; H, 8·9. $C_{12}H_{22}O_3$ requires C, 73·8; H, 8·8%), and gave on hydrolysis the keto-acid of unchanged m. p. Oxidation of the acid with sodium hypobromite, as described above for the homologue, gave prehnitenecarboxylic acid, m. p. 165—168°, from which was prepared the amide, m. p. and mixed m. p. 220—222°.

α-Methyl-γ-prehnitylbutyric Acid.—This was obtained in 85% yield by reduction of the keto-acid (IV), by using Martin's modification of the Clemmensen method. It formed leaflets (from methanol), m. p. 106—107° (Found : C, 76·6; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%).

1 : 2 : 3 : 4-*Tetrahydro*-1-*keto*-2 : 5 : 6 : 7 : 8-*pentamethylnaphthalene.*—This was obtained by cyclisation of the aforesaid acid with hydrogen fluoride (in 83% yield) or by the action of aluminium chloride on the acid chloride (in 75% yield). The *ketone* formed small needles (from ligroin), m. p. 78·5° (Found : C, 83·2; H, 9·2. $C_{15}H_{20}O$ requires C, 83·4; H, 9·3%). It was oxidised by dilute nitric acid in a sealed tube to mellitic acid, identified as its methyl ester, m. p. 186°.

1 : 2 : 3 : 4 : 6-*Pentamethylnaphthalene.*—The cyclic ketone (1·2 g.) described in the preceding paragraph was hydrogenated in acetic acid over Adams's platinum catalyst, and the crude alcohol dehydrated with formic acid to give, after chromatographic purification, 7 : 8-*dihydro*-1 : 2 : 3 : 4 : 6-*pentamethylnaphthalene* which formed needles (0·63 g.) (from methanol), m. p. 64° (Found : C, 89·7; H, 10·1. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%). This was dehydrogenated by 20% palladised charcoal at 200—220° (2 hours) to 1 : 2 : 3 : 4 : 6-*pentamethylnaphthalene* which formed rhombohedra (from methanol), m. p. 85° (Found : C, 90·7; H, 9·35. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%). Its light red *picrate* had m. p. 176° (Found : N, 10·0. $C_{15}H_{18},C_6H_3O_7N_3$ requires N, 9·8%); its yellow *s*-trinitrobenzene *complex*, m. p. 187° (Found : N, 10·0. $C_{15}H_{18},C_6H_3O_6N_3$ requires N, 10·2%); and its red 2 : 4 : 7-trinitrofluorenone *complex*, m. p. 174° (Found : N, 8·4. $C_{15}H_{18},C_{13}H_5O_7N_3$ requires N, 8·2%).

1 : 2 : 3 : 4 : 5 : 6-*Hexamethylnaphthalene* (V).—1 : 2 : 3 : 4-Tetrahydro-1-keto-2 : 5 : 6 : 7 : 8-pentamethylnaphthalene was treated with excess of methylmagnesium iodide as described above for an analogous case. The oil, b. p. 170°/4 mm., obtained by dehydration of the crude alcohol was dehydrogenated by 20% palladised charcoal in boiling trichlorobenzene (2 hours). The resulting 1 : 2 : 3 : 4 : 5 : 6-*hexamethylnaphthalene*, purified through its picrate, formed needles (from methanol), m. p. 81·5° (Found : C, 90·3; H, 9·4. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). Its dark red *picrate* had m. p. 167—168° (Found : N, 9·6. $C_{16}H_{20},C_6H_3O_7N_3$ requires N, 9·5%); its orange *s*-trinitrobenzene *complex*, m. p. 186° (Found : N, 9·8. $C_{16}H_{20},C_6H_3O_6N_3$ requires N, 9·9%); and its 2 : 4 : 7-trinitrofluorenone *complex*, m. p. 181° (Found : N, 7·8. $C_{16}H_{20},C_{13}H_5O_7N_3$ requires N, 8·0%).

1 : 2 : 3 : 4 : 5 : 7-*Hexamethylnaphthalene.*—1 : 2 : 3 : 4 : 6-Pentamethylnaphthalene was chloromethylated as described for the heptamethylnaphthalene (III). The crude chloromethyl compound (VII), an oil which rapidly became coloured, was dechlorinated when its *cyclo*hexane solution was shaken with hydrogen and palladised charcoal. Purification through the picrate then gave 1 : 2 : 3 : 4 : 5 : 7-*hexamethylnaphthalene* as cubes (from methanol), m. p. 140° (Found : C, 90·45; H, 9·45%). Its m. p. was depressed by admixture with 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene. The dark red *picrate* had m. p. 188° (Found : N, 9·75%); the *s*-trinitro-

benzene *complex*, m. p. 207° (Found : N, 9·9%) ; and the 2 : 4 : 7-trinitrofluorenone *complex* m. p. 199° (Found : N, 7·85%).

1 : 2 : 3 : 4 : 5 : 6 : 7-*Heptamethylnaphthalene from* 1 : 2 : 3 : 4 : 5 : 6-*Hexamethylnaphthalene* —The hexamethylnaphthalene was chloromethylated to give a liquid chloromethyl compound (VIII) characterised as its dark red *picrate*, m. p. 178—180° (decomp.) (Found : N, 8·9. $C_{17}H_{21}Cl,C_6H_3O_7N_3$ requires N, 8·6%), and its red *s*-trinitrobenzene *complex*, m. p. 188° (decomp.) (Found : N, 9·1. $C_{17}H_{21}Cl,C_6H_3O_6N_3$ requires N, 8·9%). The oil was submitted to catalytic hydrogenation over palladised charcoal and gave 1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethylnaphthalene, m. p. 134° (picrate, m. p. 184·5°; 2 : 4 : 7-trinitrofluorenone complex, m. p. 212°). In all three cases there was no depression on admixture with samples prepared as described above.

Condensation of o-*Xylene with* 3 : 4-*Dichloro*-3 : 4-*dimethylhexane*.—3 : 4-Dichloro-3 : 4-dimethylhexane (18 g.) (Sisido and Nozaki, *loc. cit.*) was added during 2 hours to a stirred mixture of *o*-xylene (80 g.) and anhydrous aluminium chloride (10 g.). The temperature was then raised to 40° and kept thereat for 6 hours, after which the reaction mixture was kept overnight at room temperature and then decomposed with ice and hydrochloric acid. Unchanged reactants were distilled off and the residual oil fractionated at 8 mm. into (i) b. p. 110—130° (5 g.), (ii) b. p. 130—150° (10 g.), and (iii) b. p. 150—170° (7 g.). Fraction (ii) gave, after being heated with selenium, the 2 : 4 : 7-trinitrofluorenone complex of 1 : 2 : 3 : 4 : 5 : 7-hexamethylnaphthalene (40 mg.) from which the impure hydrocarbon (m. p. 133—135°) was recovered by reduction with stannous chloride, and further characterised by preparation of the picrate, m. p. 187—188°. Mixed m. p.s with authentic specimens showed no depression. Fraction (iii) deposited crystals which, after recrystallisation from ligroin and then methanol, had m. p. 145° (300 mg.) and were shown by mixed m. p. and the preparation of the picrate and the 2 : 4 : 7-trinitrofluorenone complex to consist of 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene (Found : C, 90·1; H, 9·75%).

Condensation of Prehnitene with 3 : 4-*Dichloro*-3 : 4-*dimethylhexane*.—(a) *At* 35—40°. 3 : 4-Dichloro-3 : 4-dimethylhexane (15 g.) was added during 2 hours to a mixture of prehnitene (10 g.) and anhydrous aluminium chloride (10 g.). The temperature was raised to 40° and kept at 35—40° for 5 hours. The complex was decomposed in the usual way and unchanged reactants removed. The residue (8 g.) was heated with selenium (8 g.) in a sealed tube at 340° for 24 hours, and the product fractionated at 2 mm. in 4 fractions : (i) b. p. 110—130° (2 g.) ; (ii) b. p. 130—150° (1·5 g.) ; (iii) b. p. 150—160° (1 g.) ; and (iv) b. p. above 160° (0·5 g.). Fraction (ii) gave a red picrate, m. p. 140—141° (40 mg.), which was dissociated into 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene, m. p. 144—145°. Fraction (iii) gave a brownish-black complex (50 mg.), m. p. 210—212°, with 2 : 4 : 7-trinitrofluorenone, which on dissociation gave 1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethylnaphthalene, m. p. 132—133°. Fraction (iv) gave a 2 : 4 : 7-trinitrofluorenone complex (10 mg.), m. p. 207—209°, which was dissociated into octamethylnaphthalene, m. p. 171—173°. In all cases mixed m. p. determinations were made.

(b) *At* 60°. The conditions were as under (a) except that the reaction was carried out at 60° for 7 hours and then at 35—40° for 12 hours, and the selenium treatment was omitted. Fractionation at 1 mm. gave fractions : (i) b. p. 110—130° (2·5 g.) ; (ii) b. p. 130—150° (2 g.) ; (iii) b. p. 150—170° (0·7 g.) ; and (iv) b. p. above 170° (2 g.). Fraction (ii) formed a red picrate, m. p. 184—185° (20 mg.), dissociated to 1 : 2 : 3 : 4 : 5 : 6 : 7-heptamethylnaphthalene. Fraction (iii) gave a black 2 : 4 : 7-trinitrofluorenone complex (30 mg.), dissociated to octamethylnaphthalene. Fraction (iv) deposited crystals which after recrystallisation from benzene formed colourless leaflets, m. p. 236—237°, with the composition of a *hexamethylanthracene* (Found : C, 91·5; H, 8·5. $C_{20}H_{22}$ requires C, 91·5; H, 8·5%). The black *picrate* (from methanol) had m. p. 214° (Found : N, 8·7. $C_{20}H_{22},C_6H_3O_7N_3$ requires N, 8·6%) ; a red *s*-trinitrobenzene *complex* (from benzene), m. p. 224° (Found : N, 8·85. $C_{20}H_{22},C_6H_3O_6N_3$ requires N, 9·0%) ; and a brownish-black 2 : 4 : 7-trinitrofluorenone *complex*, m. p. 228° (Found : N, 7·4. $C_{20}H_{22},C_{13}H_5O_7N_3$ requires N, 7·3%). Oxidation of the hydrocarbon with chromic acid in acetic acid gave a *hexamethylanthraquinone*, m. p. 199° (Found : C, 82·9; H, 7·4. $C_{20}H_{20}O_2$ requires C, 82·2; H, 6·9%). The ultra-violet absorption spectrum of the hydrocarbon in ethanol showed clearly an anthracenoid character (maxima at 3930, 3730, 3610, and 3560 Å, with a more intense peak at 2680 Å).

Condensation of p-*Xylene with* 2 : 3 : 4 : 5-*Tetramethylhexane*-2 : 5-*diol*.—The dihydroxy-compound (1·5 g.) (Bruson and Kroeger, *loc. cit.*) was added during 10 minutes to a stirred mixture of tetrachloroethane (15 c.c.), *p*-xylene (4 g.), and anhydrous aluminium chloride (5 g.). The bath-temperature was then raised to 60° and kept there for 5 hours. The mixture was worked up in the usual way and the solvent-free products distilled at 2 mm. The lower fraction, b. p. 140—160° (0·5 g.), was heated with selenium (0·5 g.) in a sealed tube at 330° for 24 hours. Treatment with methanolic picric acid then gave a deep red picrate (8 mg.), m. p. 182—185°, which was dissociated to give a colourless solid, m. p. 125—130°. The higher fraction, b. p. 200°, was semi-solid and after recrystallisation from benzene–ligroin and then benzene, formed yellowish leaflets, m. p. 241—242°, with a strong blue fluorescence in benzene (Found: C, 92·7; H, 7·65. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). The ultra-violet absorption in ethanol was that of an anthracene derivative and the composition suggests a trimethylanthracene. It is not 1 : 2 : 3 : 4-tetramethylanthracene, which has m. p. 136° (Hewett, *loc. cit.*). The hydrocarbon gave a red *s*-trinitrobenzene complex, m. p. 146—148°, and a brownish-black 2 : 4 : 7-trinitrofluorenone complex, m. p. 160—162°, and was oxidised by chromic acid in acetic acid to a yellow quinone, m. p. 155—158°. 1 : 2 : 4-Trimethylanthracene has m. p. 244° and the quinone, m. p. 162—163° (Elbs, *J. pr. Chem.*, 1890, **41**, 121).

Condensation of Prehnitene with 2 : 3 : 4 : 5-*Tetramethylhexane*-2 : 5-*diol*.—Prehnitene (2·3 g.) was treated with the diol (2 g.) and aluminium chloride (8 g.) in tetrachloroethane (20 c.c.) as described for the reaction with *p*-xylene. Distillation of the product at 2 mm. gave (*a*) an oil, b. p. 130—150° (0·8 g.) which, after selenium treatment, yielded the same picrate, m. p. 183—185° (10 mg.), and related solid, m. p. 125—128°, as were obtained in the preceding experiment, and (*b*) a yellow solid, b. p. 200° (0·1 g.), which crystallised from benzene in pale yellow leaflets, m. p. 236—237°, strongly depressed by admixture with the trimethylanthracene described in the previous paragraph. This product also had the ultra-violet absorption of an anthracene derivative; it gave a *s*-trinitrobenzene complex, m. p. 162—164°, and a 2 : 4 : 7-trinitrofluorenone complex, m. p. 183—185°. The amounts were insufficient for analysis.

Ultra-violet Absorption of Polymethylnaphthalenes.—The spectra of the new polymethylnaphthalenes, measured in ethanol, had characteristic naphthalene bands with the strong shift towards the region of longer wave-length which would be expected with such heavy substitution. The Table gives the wave-lengths (in mμ) and extinction coefficients (as logarithms) of the maxima and minima of the two main bands.

	Maxima				Minima	
	(A)		(B)			
Polymethyl derivative	λ	log ε	λ	log ε	λ	log ε
1 : 2 : 3 : 4 : 6-Penta	236	4·87	288	3·69	254	3·20
1 : 2 : 3 : 4 : 5 : 6-Hexa	244	4·86	298	3·87	260	3·19
1 : 2 : 3 : 4 : 5 : 7-Hexa	238	4·82	298	3·85	257	3·14
1 : 2 : 3 : 4 : 6 : 7-Hexa	236	5·13	294	3·73	256	3·24
Hepta	242	4·74	302	3·70	263	3·30
Octa	254	4·70	308	3·70	274	3·31

Maleic Anhydride Addition Compounds of Polymethylnaphthalenes.—The hydrocarbon (0·2 g.) and freshly distilled maleic anhydride (3 g.; *ca.* 30 mols.) in pure dry benzene (4 c.c.) were heated under reflux for 48 hours (somewhat lower yields were obtained after 72 hours). The benzene was removed under reduced pressure and the residue shaken with water until the excess of maleic anhydride had dissolved. The adduct and unchanged hydrocarbon were extracted with ether, and the ether was removed. The residual mixture was boiled for 5 minutes with 5% potassium hydroxide and the unchanged hydrocarbon extracted with ether, the amount being determined after evaporation of the extract. The aqueous solution was acidified and the precipitated acid collected and combined with a further quantity obtained by extraction of the mother-liquor with ether. By dissolving the acid in ethyl acetate containing a few drops of acetic anhydride it was reconverted into anhydride. The Table gives the characteristics of the products.

Polymethyl derivative	Solvent and cryst. form	M. p. of anhydride	Formula	Found (%): C	H	Reqd. (%): C	H
1 : 2 : 3 : 4 : 6-Penta	Acetone (powder)	138—139°	$C_{19}H_{20}O_3$	76·3	7·3	77·0	6·8
1 : 2 : 3 : 4 : 5 : 6-Hexa	Ethyl acetate (prisms)	134—136	$C_{20}H_{22}O_3$	77·15	7·35	77·4	7·15
1 : 2 : 3 : 4 : 6 : 7-Hexa	Ethyl acetate (cubes)	170 (decomp.)	$C_{20}H_{22}O_3$	77·25	7·25	77·4	7·15
1 : 2 : 3 : 4 : 5 : 6 : 7-Hepta	Ethyl acetate (prisms)	160 (decomp.)	$C_{21}H_{24}O_3$	77·65	7·6	77·7	7·45
Octa	Light petroleum (prisms)	176—178 (decomp.)	$C_{22}H_{26}O_3$	77·8	7·8	78·05	7·7

Oxidation of 1 : 4-*Dihydro*-1 : 2 : 3 : 4 : 5 : 6-*hexamethylnaphthalene*-1 : 4-endo-αβ-*succinic Acid.*—Excess of an 8% solution of potassium permanganate was added slowly to a solution of the anhydride (VI) (0·3 g.) in water (20 c.c.) and sodium hydroxide (2 g.). The mixture was stirred and heated on the steam-bath for 16 hours. Methanol (5 c.c.) was added and the mixture warmed until the solution was decolorised. The filtered solution was concentrated, acidified, and extracted with ether. Evaporation of the extract gave a solid which after crystallisation from water was identified as prehnitic acid, m. p. 235—237° alone or mixed with a specimen prepared by oxidation of prehnitene (lit., 238°).

Oxidation of 1 : 4-*Dihydro*-1 : 2 : 3 : 4 : 6 : 7-*hexamethylnaphthalene*-1 : 4-endo-αβ-*succinic Acid.*—This was carried out as in the previous case, and gave pyromellitic acid, m. p. 271—273°, not depressed with a sample prepared by oxidation of durene (lit., 275°).

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