252. 1 : 2 : 3 : 4 : 5 : 6- *and* 1 : 2 : 3 : 4 : 5 : 7-*Hexamethylnaphthalene.*

By W. CARRUTHERS and J. D. GRAY.

The two hexamethylnaphthalenes named in the title have been synthesised. The " 1 : 2 : 3 : 4 : 5 : 6 "-hexamethylnaphthalene prepared by Abadir, Cook, and Gibson [2] is shown to be the 1 : 2 : 3 : 4 : 5 : 7-isomer. Treatment of 3-methyl-5-(2 : 3 : 4 : 5-tetramethylphenyl)hexan-2-one with hot polyphosphoric acid affords 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene and an oil which appears to consist mainly of a derivative of indene.

UNTIL recently very few polysubstituted naphthalene derivatives were known, but lately Mosby [1] and Abadir, Cook, and Gibson [2] have synthesised a number of polymethyl derivatives, including the octamethyl compound which was shown to be non-planar by Donaldson and Robertson [3] by *X*-ray crystallographic analysis. We have obtained the two hexamethylnaphthalenes named above in the course of unsuccessful attempts to prepare derivatives of octamethylnaphthalene suitable for optical resolution.

Reaction of prehnitene (1 : 2 : 3 : 4-tetramethylbenzene) with ethyl 2-methylpent-4-enoate in presence of aluminium chloride, after the method of Colonge and Grimaud,[4] afforded the ester (I) and hence, by hydrolysis and cyclisation of the acid chloride with stannic chloride, the hexamethyltetralone (II). This was smoothly converted into 1 : 2 : 3 : 4 : 5 : 7-hexamethylnaphthalene (III), m. p. 78—80°, by Clemmensen reduction and dehydrogenation of the tetrahydronaphthalene by palladium, or, better, by successive treatment with lithium aluminium hydride, potassium hydrogen sulphate, and palladium in boiling trichlorobenzene.

A hexamethylnaphthalene regarded as the 1 : 2 : 3 : 4 : 5 : 7-isomer has already been described by Abadir, Cook, and Gibson [2] who, however, recorded m. p. 140°; another hydrocarbon, m. p. 80°, was considered to be 1 : 2 : 3 : 4 : 5 : 6-hexamethylnaphthalene. We find that the latter is identical with our 1 : 2 : 3 : 4 : 5 : 7-isomer. The infrared spectra were superposable, and there was no depression of m. p. on admixture of our hydrocarbon and several of its derivatives with the original specimens, which were kindly put at our disposal by Dr. Cook. In conformity with the behaviour of other polyalkylnaphthalenes, our 1 : 2 : 3 : 4 : 5 : 7-hexamethylnaphthalene underwent a Diels–Alder reaction with maleic anhydride in hot benzene.[2, 5] The adduct was oxidised by alkaline potassium permanganate to benzene-1 : 2 : 3 : 5-tetracarboxylic acid and this series of reactions proves the orientation of the methyl groups. The adduct of 1 : 2 : 3 : 4 : 5 : 6-hexamethylnaphthalene would have afforded benzene-1 : 2 : 3 : 4-tetracarboxylic acid on oxidation. In addition, we synthesised 1 : 2 : 3 : 4 : 5 : 6-hexamethylnaphthalene by standard procedures from ω-bromoacetylprehnitene and diethyl methylmalonate and showed that, in fact, it had m. p. 48—50°. An attempt to prepare the 1 : 2 : 3 : 4 : 5 : 7-isomer by a similar route failed because α-bromopropionylprehnitene and diethyl malonate in methanolic or ethanolic sodium alkoxide afforded only the α-ketol ethers (IV; R = Me or Et), while with diethyl sodiomalonate in benzene no reaction took place.

Abadir, Cook, and Gibson [2] prepared their supposed 1 : 2 : 3 : 4 : 5 : 6-hexamethylnaphthalene from the acid obtained in high yield by Friedel–Crafts reaction of prehnitene and methylsuccinic anhydride in ethylene chloride solution. This acid was regarded by them as the α-methyl acid (V; Ar = C_6HMe_4), but clearly to account for the formation of 1 : 2 : 3 : 4 : 5 : 7-hexamethylnaphthalene in the subsequent reactions, it must, in fact,

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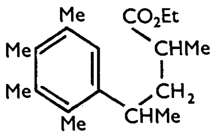
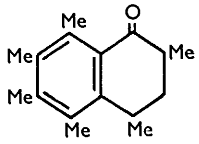
[1] Mosby, *J. Amer. Chem. Soc.*, 1952, **74**, 2564.
[2] Abadir, Cook, and Gibson, *J.*, 1953, 8.
[3] Donaldson and Robertson, *ibid.*, p. 17.
[4] Colonge and Grimaud, *Bull. Soc. chim. France*, 1951, 439, 857.
[5] Kloetzel, Dayton, and Herzog, *J. Amer. Chem. Soc.*, 1950, **72**, 273; Kloetzel and Herzog, *ibid.*, p. 1991.

be the β-methyl isomer (VI; Ar = C_6HMe_4). This is supported by the fact that the corresponding butyric acid is not identical with the α-methylbutyric acid which we synthesised. Friedel–Crafts reactions with methylsuccinic anhydride and aromatic hydrocarbons in nitrobenzene solution are generally held to give rise to the α-methyl-acid (V) in preponderant amount,[6] but it seems to be the case that different proportions of the two possible isomers are obtained when, instead, methylene or ethylene chloride is employed as solvent.[7] We confirmed that reaction of prehnitene and methylsuccinic anhydride in ethylene chloride led to the acid (VI; Ar = C_6HMe_4) almost exclusively; in nitrobenzene solution, on the other hand, a mixture was obtained from which the isomer (V) was isolated in moderate yield.

Attempts to convert the tetralone (II) into the unknown 1 : 2 : 3 : 4 : 5 : 6 : 8-heptamethylnaphthalene by reaction with methylmagnesium iodide or methyl-lithium were unsuccessful. The ketone was always recovered, even when reaction was continued for 40 hr. in boiling xylene or di-*n*-butyl ether. The complete resistance to reaction contrasts with the behaviour of the analogue (VII) and may possibly be ascribed to the " buttressing effect " [8] of the 4-methyl group of the ketone (II).



(I)



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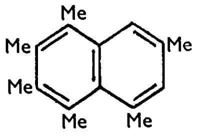

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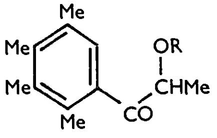
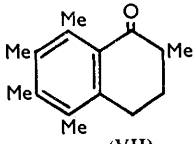
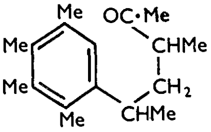


(IV)

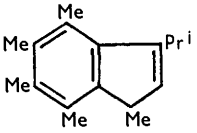
(V) $Ar{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$ $Ar{\cdot}CO{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$ (VI)



(VII)



(VIII)



(IX)

In other experiments, the ketone (VIII), obtained from prehnitene and 3-methylhex-5-en-2-one [9] in presence of aluminium chloride, was treated with polyphosphoric acid at 125—130°. An oily mixture was produced, from which a naphthalene hydrocarbon, m. p. 143—144°, was obtained directly in 30% yield. This was not the expected 1 : 2 : 3 : 4 : 5 : 6 : 8-heptamethyl derivative, however; it was identified as 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene by mixed m. p.s of the hydrocarbon and of three derivatives with authentic specimens.[2] The formation of the hexamethylnaphthalene from the ketone (VIII) requires migration of one methyl group and elimination of another, and it seems likely that these processes take place after the formation of the highly sterically hindered heptamethyl compound. Migration of alkyl groups attached to the benzene ring in presence of hot polyphosphoric acid has already been noted by Mosby.[1,10] The remaining oily part of the reaction product was unsaturated. On oxidation with nitric acid it afforded mellitic acid, and this showed that it was a product of cyclisation, but it could not be dehydrogenated to a naphthalene derivative by palladium or with selenium. This fact, together with the ultraviolet absorption spectrum, which closely resembles that of indene,[11] suggests that the oil consists largely of one or more derivatives of indene (for example, IX), which may be envisaged as arising by rearrangement in the protonated ketone (VIII). The elementary analysis of the oil, and the somewhat reduced

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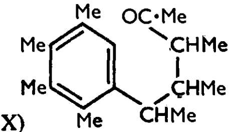
[6] Berliner, " Organic Reactions," John Wiley & Sons, Inc., New York, 1949, Vol. V, p. 242.
[7] Baddar, Fahim, and Fleifel, *J.*, 1955, 2199.
[8] Westheimer and Reiger, *J. Amer. Chem. Soc.*, 1950, **72**, 19; Chien and Adams, *ibid.*, 1934, **56**, 1787.
[9] Colonge and Pichat, *Bull. Soc. chim. France*, 1941, 853, 855.
[10] Mosby, *J. Org. Chem.*, 1953, **18**, 485.
[11] Morton and de Gouveia, *J.*, 1934, 911.

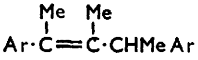
intensity of ultraviolet absorption, indicate that the corresponding indanes are also present, probably produced from the indenes by hydrogen transfer[12] involved in the formation of the hexamethylnaphthalene.

In another approach reduction of the ketone (VIII) with lithium aluminium hydride and treatment of the alcohol with concentrated sulphuric acid gave a liquid hydrocarbon which was not converted into a naphthalene by palladium or with selenium.

Before the nature of the product formed on cyclisation of ketone (VIII) was recognised, an attempt was made to prepare the homologue (X) (and thence possibly octamethylnaphthalene) by way of the reaction of 3-methylpentane-2 : 4-dione with the Grignard reagent or lithio-compound prepared from 1-prehnitylethyl bromide. The only product isolated was the hydrocarbon (XI ; Ar = C_6HMe_4), formed by cleavage of the diketone and reaction with two molecules of the organometallic compound. The structure (XI) is assigned on analogy with similar recorded reactions of β-diketones with Grignard reagents,[13]



(X)



$\mathrm{Ar{\cdot}\overset{\displaystyle Me}{\overset{|}{C}}{=}\overset{\displaystyle Me}{\overset{|}{C}}{\cdot}CHMe\,Ar}$

(XI)

and is supported by the ultraviolet absorption spectrum, which is similar to that of α-2 : 4 : 6-tetramethylstyrene.[14] The same product was obtained when the monoketal or monohemithioketal was employed in the reaction in place of the diketone.

EXPERIMENTAL

Ultraviolet absorption spectra were measured in 95% ethanol, on a " Unicam " spectrophotometer.

α-Methyl-γ-(2 : 3 : 4 : 5-tetramethylphenyl)valeric Acid.—Ethyl 2-methylpent-4-enoate (45·3 g.) was added dropwise to a stirred mixture of prehnitene (45·6 g.) and aluminium chloride (64·5 g.) at 35°. After 4 hr., ice and hydrochloric acid were added, and the mixture extracted with ether. The *valerate* (77·6 g.) obtained had b. p. 198—200°/23 mm. (Found: C, 78·4; H, 10·0. $C_{18}H_{28}O_2$ requires C, 78·2; H, 10·2%).

The ester (77·6 g.) was hydrolysed by potassium hydroxide (20 g.) in boiling aqueous ethanol (200 c.c., 1 : 1) for 5 hr. The *acid* (70 g.) had m. p. 76—90° (Found: C, 77·2; H, 9·8. $C_{16}H_{24}O_2$ requires C, 77·4; H, 9·7%). Oxidation of the acid (200 mg.) with concentrated nitric acid (1·5 c.c.) and water (3 c.c.) at 175—180° for 6 hr. gave benzenepentacarboxylic acid, identified by conversion into the pentamethyl ester, m. p. and mixed m. p. 143—146°.

1 : 2 : 3 : 4-*Tetrahydro*-2 : 4 : 5 : 6 : 7 : 8-*hexamethyl*-1-*oxonaphthalene.*—A mixture of the foregoing acid (53 g.) and phosphorus pentachloride (47·7 g.) in benzene (220 c.c.) was kept at room temperature for 1 hr., then heated on the steam-bath for 5 min. The solution was cooled to 0° and stannic chloride (52 c.c.) in benzene (52 c.c.) added dropwise with stirring. After ¾ hr. the mixture was decomposed with ice and hydrochloric acid, and the benzene layer separated and washed with sodium hydroxide and water. The *tetralone* distilled as a colourless oil at 212°/26 mm. (39 g.) and crystallised from methanol in colourless prisms, m. p. 62—63° (Found: C, 83·4; H, 9·5. $C_{16}H_{22}O_2$ requires C, 83·4; H, 9·6%). The ketone did not react with semicarbazide acetate, but slowly formed a 2 : 4-*dinitrophenylhydrazone*, orange-red needles, m. p. 167—168° (Found: N, 13·9. $C_{22}H_{26}O_4N_4$ requires N, 13·7%).

1 : 2 : 3 : 4 : 5 : 7-*Hexamethylnaphthalene.*—(*a*) The above ketone (1 g.) was reduced with lithium aluminium hydride (0·17 g.) in refluxing ether for 2 hr. Next morning the alcohol (0·93 g.) was isolated in the usual way, and dehydrated by fused potassium hydrogen sulphate (90 mg.) at 160° for 10 min. The product was distilled and the dihydronaphthalene (0·74 g.) obtained as crystals, m. p. 38—39°. This material (0·33 g.) was dehydrogenated with 20%

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[12] Cf. Gutsche, Saha, and Johnson, *J. Amer. Chem. Soc.*, 1957, **79**, 4441.

[13] Kohler and Erickson, *ibid.*, 1931, **53**, 2301.

[14] Newman and Deno, *ibid.*, 1951, **73**, 3644.

palladium–charcoal in boiling trichlorobenzene under carbon dioxide for 5 hr. 1 : 2 : 3 : 4 : 5 : 7-*Hexamethylnaphthalene* (0·19 g.) was obtained as colourless plates (from *cyclo*hexane), m. p. 78—80° (Found: C, 90·4; H, 9·5. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%). The *picrate* formed red needles, m. p. 169—170° (Found: N, 9·4. $C_{16}H_{20},C_6H_3O_7N_3$ requires N, 9·5%), and the 2 : 4 : 7-trinitrofluorenone complex deep red needles, m. p. 181—182° (from benzene).

(*b*) The foregoing ketone (0·32 g.) and amalgamated zinc (1 g.) were boiled with hydrochloric acid (1·8 c.c.), water (0·75 c.c.), and toluene (1 c.c.) for 24 hr. The cooled mixture was extracted with benzene, and the recovered tetrahydronaphthalene (0·24 g.) dehydrogenated directly by 30% palladium–charcoal (0·1 g.) at about 325° for 2 hr. in an atmosphere of carbon dioxide. The resulting 1 : 2 : 3 : 4 : 5 : 7-hexamethylnaphthalene (0·19 g.), purified through its picrate, crystallised from *cyclo*hexane as colourless plates, m. p. 78—80°, not depressed when mixed with the hydrocarbon obtained as above.

Maleic Anhydride Adduct of 1 : 2 : 3 : 4 : 5 : 7-*Hexamethylnaphthalene.*—A solution of the hydrocarbon (1·6 g.) and freshly distilled maleic anhydride (24 g.) in benzene (32 c.c.) was boiled for 48 hr., and benzene removed under reduced pressure. The residue was worked up by the method of Kloetzel, Dayton, and Herzog,[5] and the crude adduct acid reconverted into the *adduct* anhydride by crystallisation from ethyl acetate containing a few drops of acetic anhydride, giving colourless crystals (1·6 g.), m. p. 147° (Found: C, 77·5; H, 6·8. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·2%).

The adduct (1·6 g.) in 1% sodium hydroxide solution (100 c.c.) was treated dropwise with 8% aqueous potassium permanganate (excess) on the steam-bath for 16 hr. Excess of permanganate was decomposed with methanol, and the hot solution filtered. The residue was thoroughly extracted with hot water, and the combined filtrates were concentrated to 150 c.c., acidified, and extracted with ether. On treatment of the crude acid product with ethereal diazomethane, tetramethyl benzene-1 : 2 : 3 : 5-tetracarboxylate was obtained, having m. p. and mixed m. p. 109—111° (from methanol).

5-*Acetylprehnitene.*—The method of Claus and Föhlisch [15] gave a mixture and we employed the following modification.

A solution of acetyl chloride (6·3 g.) and aluminium chloride (10·1 g.) in methylene chloride (20 c.c.) was slowly added to a stirred solution of prehnitene (10 g.) in methylene chloride (20 c.c.) at 0°. After 1 hr. at room temperature, ice and hydrochloric acid were added and the methylene chloride layer was separated and washed. 5-*Acetylprehnitene* had b. p. 135°/5 mm., n_D^{19} 1·5437 (Found: C, 81·7; H, 8·8. $C_{12}H_{16}O$ requires C, 81·8; H, 9·2%). The 2 : 4-*dinitrophenylhydrazone* formed orange-red needles, m. p. 178—179° (Found: C, 61·1; H, 5·7. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·7%). The semicarbazone had m. p. 210—211° (lit., 209°).

Oxidation of acetylprehnitene with sodium hypoiodite [16] afforded prehnitic acid, m. p. 165—169° (lit., 165°, 169°), which when heated with soda-lime was reconverted into prehnitene, identified by comparison of its infrared spectrum with that of an authentic specimen.

ω-*Bromoacetylprehnitene.*—A solution of bromine (8·6 g.) in carbon tetrachloride (30 c.c.) was slowly added at room temperature to a stirred solution of 5-acetylprehnitene (9·5 g.) in carbon tetrachloride (20 c.c.). Then the solution was kept for ¼ hr. and washed with sodium carbonate solution and with water. The crude product distilled at 148—150°/1·5 mm., and solidified (13 g.). Crystallisation from light petroleum (b. p. 40—60°) gave ω-*bromoacetylprehnitene*, m. p. 54—55° (Found: C, 56·8; H, 5·9. $C_{12}H_{15}OBr$ requires C, 51·8; H, 5·9%). Oxidation of the compound with sodium hypobromite gave prehnitic acid, m. p. 170°.

α-*Methyl*-γ-*oxo*-γ-(2 : 3 : 4 : 5-*tetramethylphenyl*)*butyric Acid.*—α-Bromoacetylprehnitene (13 g.) in ethanol (15 c.c.) was gradually added at 60° to a stirred solution prepared from sodium (1·3 g.) and diethyl methylmalonate (8·9 g.) in ethanol. After 2 hr. most of the ethanol was removed on the steam-bath, water was added, and the mixture was extracted with ether. The washed and dried solution was evaporated, and the product distilled as a colourless oil (9·1 g.) at 172°/0·3 mm. This was hydrolysed with potassium hydroxide (5·1 g.) in 1 : 1 aqueous ethanol (50 c.c.), and the resulting malonic acid was decarboxylated at 180° (until evolution of carbon dioxide ceased). The crude *acid* was distilled and crystallised from benzene–light petroleum (b. p. 40—60°) in blades, m. p. 129—130° (Found: C, 72·6; H, 7·95. $C_{15}H_{20}O_3$ requires C, 72·55; H, 8·1%).

α-*Methyl*-γ-(2 : 3 : 4 : 5-*tetramethylphenyl*)*butyric Acid.*—A solution of the above keto-acid

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[15] Claus and Föhlisch, *J. prakt. Chem.*, 1888, **38**, 230.

[16] Fuson and Tullock, *J. Amer. Chem. Soc.*, 1934, **56**, 1638.

(1·5 g.), sodium hydroxide (0·9 g.), and 90% hydrazine hydrate (0·9 c.c.) in diethylene glycol (20 c.c.) was boiled for ¾ hr. The temperature was then raised to 200° by distilling off water, and boiling continued 4 hr. The cooled mixture was poured into water and acidified, and the product extracted with ethyl acetate. The *butyric acid* (1·2 g.) obtained had m. p. 77—78° [from light petroleum (b. p. 40—60°)] (Found: C, 77·1; H, 9·2. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%).

1 : 2 : 3 : 4-*Tetrahydro*-2 : 5 : 6 : 7 : 8-*pentamethyl*-1-*oxo-naphthalene*.—The foregoing butyric acid (0·9 g.) was cyclised as described above for a similar case, using phosphorus pentachloride (0·84 g.) and stannic chloride (0·9 c.c.). The *product* crystallised from light petroleum in prisms, m. p. 57—58° (Found: C, 83·5; H, 9·2. $C_{15}H_{20}O_2$ requires C, 83·3; H, 9·3%).

1 : 2-*Dihydro*-3 : 4 : 5 : 6 : 7 : 8-*hexamethylnaphthalene*.—A solution of the preceding ketone (0·56 g.) in ether (5 c.c.) was added under nitrogen to a stirred solution of methyl-lithium, prepared from methyl iodide (7 g.) and lithium (0·7 g.). After 6 hr. most of the ether was removed, benzene (20 c.c.) was added, and the mixture boiled for 3 hr. The cooled mixture was poured on ice and hydrochloric acid, and the product isolated in the usual way. The *dihydronaphthalene* was obtained as crystals, m. p. 89—90°, from ethanol (Found: C, 89·5; H, 10·4. $C_{16}H_{22}$ requires C, 89·65; H, 10·35%).

1 : 2 : 3 : 4 : 5 : 6-*Hexamethylnaphthalene*.—The dihydronaphthalene described above (0·11 g.) and 30% palladium–charcoal (0·6 g.) were heated in boiling trichlorobenzene in an atmosphere of carbon dioxide. Evolution of hydrogen was very slow, and after 17 hr. was not complete. The product was isolated through its picrate and distilled. It separated from methanol as a colourless microcrystalline powder (60 mg.), m. p. 48—50° (Found: C, 90·2; H, 9·4. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%), $\lambda_{max.}$ 241, 301, 337 mμ (log ε 4·82, 3·68, 2·74). The s-*trinitrobenzene complex* formed yellow needles, m. p. 186—189° (Found: C, 62·4; H, 5·3. $C_{16}H_{20},C_6H_3O_6N_3$ requires C, 62·2; H, 5·5%). The picrate, m. p. 155—157°, was unstable.

5-*Propionylprehnitene*.—This *ketone* was prepared from prehnitene (5 g.), propionyl chloride (3·5 g.), and aluminium chloride (5 g.) in methylene chloride as described above for acetylprehnitene. It (7 g.) had b. p. 104°/0·2 mm., n_{D}^{23} 1·5345 (Found: C, 82·1; H, 9·2. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%).

α-*Bromo*-5-*propionylprehnitene*.—This was prepared from 5-propionylprehnitene (6·4 g.) and bromine (5·4 g.) in carbon tetrachloride as described for α-bromoacetylprehnitene. The *bromo-compound* (7·7 g.) crystallised from light petroleum (b. p. 40—60°) in colourless plates, m. p. 36·5—37·5° (Found: 57·9; H, 6·6. $C_{13}H_{17}OBr$ requires C, 58·0; H, 6·4%). On oxidation with sodium hypobromite it gave prehnitic acid, m. p. 165—169°.

Reaction of α-*Bromo*-5-*propionylprehnitene and Diethyl Malonate*.—Diethyl malonate (4·6 g.) was added to a solution of sodium ethoxide prepared from sodium (0·66 g.) and ethanol (15 c.c.), and to the resulting solution α-bromo-5-propionylprehnitene (7·7 g.) in ethanol (10 c.c.) was added at 60°. After 2 hr. most of the ethanol was distilled off and the product isolated in the usual way. The *ketol ether* (6·4 g.) obtained had b. p. 104—110°/0·1 mm. (Found: C, 76·2; H, 8·9. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). This product reduced Fehling's solution, and on treatment with boiling aqueous-alcoholic potassium hydroxide afforded prehnitic acid, m. p. and mixed m. p. 165—169°.

Reaction of Prehnitene and Methylsuccinic Anhydride.—(*a*) Methylsuccinic anhydride (4·3 g.) and aluminium chloride (10 g.) in nitrobenzene (30 c.c.) were gradually added to a stirred solution of prehnitene (5 g.) in nitrobenzene (5 c.c.) at 0°. The mixture was kept at room temperature for 1 hr., then ice and hydrochloric acid were added and the nitrobenzene was steam-distilled. A mixture of acids was obtained, from which α-methyl-γ-oxo-γ-(2 : 3 : 4 : 5-tetramethylphenyl)butyric acid (2 g.), m. p. 130—131°, was isolated by crystallisation from methanol and from benzene–light petroleum (b. p. 40—60°). The m. p. was not depressed on admixture with the acid prepared as described above. No other pure component was isolated from the residual mixture.

(*b*) Reaction in ethylene chloride solution, as described by Abadir, Cook, and Gibson,[2] gave β-methyl-γ-oxo-γ-(2 : 3 : 4 : 5-tetramethylphenyl)butyric acid exclusively in 85% yield. In our hands, the pure acid, recovered from the ethyl ester, had m. p. 112° (lit., 131°). On reduction by the Clemmensen method it furnished the butyric acid, m. p. 106—107° (lit., 106—107°).

Condensation of Prehnitene and 3-*Methylhex*-5-*en*-2-*one*.—This ketone (7·3 g.) was added dropwise to a stirred mixture of prehnitene (8·2 g.) and powdered aluminium chloride (12·8 g.) at 35°. After 4 hr. the complex was decomposed with ice and hydrochloric acid, and the organic layer was extracted with ether. 3-*Methyl*-5-(2 : 3 : 4 : 5-*tetramethylphenyl*)*hexan*-2-*one*

(11·2 g.) was obtained as a colourless oil, b. p. 159°/3 mm., n_D^{19} 1·5188 (Found: C, 82·9; H, 10·3. $C_{17}H_{26}O$ requires C, 82·9; H, 10·6%). The *semicarbazone* had m. p. 183—184° (Found: C, 71·3; H, 9·5. $C_{18}H_{29}ON_3$ requires C, 71·3; H, 9·6%). Oxidation with concentrated nitric acid at 175—180° gave benzenepentacarboxylic acid, identified by comparison of the pentamethyl ester, m. p. 144—146°, with an authentic specimen.

3-*Methyl*-5-(2 : 3 : 4 : 5-*tetramethylphenyl*)*hexan*-2-*ol*.—A solution of the hexanone (2 g.) in ether (10 c.c.) was added dropwise to a slurry of lithium aluminium hydride (0·31 g.) in ether. The mixture was boiled for 2 hr., and excess of hydride was then decomposed with ethyl acetate. The *product*, worked up in the usual way, had b. p. 112°/0·07 mm. (Found: C, 82·5; H, 11·0. $C_{17}H_{28}O$ requires C, 82·2; H, 11·4%).

When this alcohol (1·5 g.) was added with stirring to concentrated sulphuric acid (2 g.) at 10°, and the mixture stirred at room temperature for 3 hr., the *product* obtained by addition of ice, was an oil, b. p. 122—123°, with no hydroxyl maximum in the infrared spectrum (Found: C, 88·4; H, 9·8. $C_{17}H_{26}$ requires C, 88·7; H, 11·3%).

Reaction of 3-*Methyl*-5-(2 : 3 : 4 : 5-*tetramethylphenyl*)*hexan*-2-*one with Polyphosphoric Acid*.—The foregoing ketone (11·2 g.) was added dropwise, at room temperature, to stirred polyphosphoric acid prepared from phosphoric oxide (125 g.) and concentrated phosphoric acid (50 c.c.), and the mixture was then heated at 125—130° for 5 hr., with occasional stirring. The cooled mixture was diluted with ice-water, and the organic material was extracted with ether. The product was distilled and two fractions were collected at 100—103°/0·07 mm. (4·2 g.) and 125—130°/0·07 mm. (3·2 g.). The second fraction solidified, and after crystallisation from benzene–light petroleum gave colourless plates of 1 : 2 : 3 : 4 : 6 : 7-hexamethylnaphthalene, m. p. and mixed m. p. 143—144° (Found: C, 90·4; H, 9·5. Calc. for $C_{16}H_{20}$: C, 90·5; H, 9·5%), $\lambda_{max.}$ 237, 293 mμ (log ε 4·90, 3·81). The dark red picrate had m. p. 194—195° (Found: C, 60·4; H, 5·7. Calc. for $C_{16}H_{20},C_6H_3O_7N_3$: C, 60·1; H, 5·2%), and the 2 : 4 : 7-trinitrofluorenone complex, m. p. 205—206° (Found: C, 66·4; H, 4·7. Calc. for $C_{16}H_{20},C_{13}H_5O_7N_3$: C, 66·1; H, 4·7%). Both m. p.s were undepressed on admixture with authentic specimens.

The first fraction above was redistilled and collected as a colourless oil at 140°/0·8 mm., n_D^{22} 1·5441 (Found: C, 88·7; H, 11·0. Calc. for $C_{17}H_{26}$: C, 88·7; H, 11·3. Calc. for $C_{17}H_{24}$: C, 89·5; H, 10·5%), $\lambda_{max.}$ 220, 255,(295) mμ [log ε 4·24, 3·60, (2·96)]. The oil decolorised bromine water and potassium permanganate solution, and gave a yellow-brown colour with tetranitromethane. With dilute nitric acid at 175—180°, it gave benzenehexacarboxylic acid, m. p. and mixed m. p. 185—187°. It was recovered after being heated with selenium in a sealed tube at 310° for 100 hr.; at 360° (70 hr.) charring occurred.

5-1′-*Hydroxyethylprehnitene*.—5-Acetylprehnitene (18·5 g.) was added dropwise to a slurry of lithium aluminium hydride (4 g.) in ether (20 c.c.), and the mixture refluxed for 3 hr. The *alcohol* was isolated in the usual manner and had b. p. 121°/1 mm. (14 g.). It crystallised in light petroleum as prisms, m. p. 53—54° (Found: C, 81·2; H, 10·0. $C_{12}H_{18}O$ requires C, 80·9; H, 10·2%).

5-1′-*Bromoethylprehnitene*.—A solution of phosphorus tribromide (3·2 g.) in ether (250 c.c.) was added dropwise at −25° to a stirred solution of the above alcohol (5 g.) and pyridine (0·5 g.) in ether (250 c.c.). The mixture was then stirred at −25° for ½ hr. and next morning poured into ice water, and the ether layer was separated and washed with sodium hydrogen carbonate solution and with water. The crude *bromide* was distilled (b. p. 90°/0·05 mm.; 4·8 g.) and, crystallised from light petroleum (b. p. 40—60°), had m. p. 48° (Found: C, 60·1; H, 7·2. $C_{12}H_{17}Br$ requires C, 59·8; H, 7·1%).

In one experiment the crude bromide from 10·6 g. of alcohol was distilled at 120°/0·15 mm.; hydrogen bromide was evolved and, in addition to a small amount (1·8 g.) of bromide, a hydrocarbon (6·8 g.), b. p. 200°/0·15 mm., was obtained. This hydrocarbon crystallised from benzene in plates, m. p. 169—170°. Its ultraviolet absorption was very similar to that of 9 : 10-dihydroanthracene, and the hydrocarbon is possibly 9 : 10-*dihydro*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*decamethylanthracene*, formed by condensation of two molecules of the bromide (Found: C, 90·2; H, 9·5. $C_{24}H_{32}$ requires C, 89·9; H, 10·1%). It had $\lambda_{max.}$ 230 (infl.), 272 (log ε 4·18, 3·24) and was recovered after being heated with selenium at 310°; at 340° for 50 hr. the product was charred.

Reaction of 1-(2 : 3 : 4 : 5-*Tetramethylphenyl*)*ethylmagnesium Bromide and* 3-*Methylpentane*-2 : 4-*dione*.—The solution prepared from the above bromide (0·49 g.) and magnesium (0·05 g.) in ether (20 c.c.) was added dropwise to a stirred solution of the dione (0·25 g.) in ether (20 c.c.)

at $-80°$. An immediate reaction took place and a complex was precipitated. After 4 hr. the suspension was added slowly to an ice-cold solution of ammonium chloride. The mixture was extracted with ether, and afforded 3-*methyl*-2 : 4-*di*-(2 : 3 : 4 : 5-*tetramethylphenyl*)*pent*-2-*ene* (0·25 g.) as colourless prisms (from benzene), m. p. 220—223° (Found: C, 90·0; H, 10·2. $C_{26}H_{36}$ requires C, 89·6; H, 10·4%), $\lambda_{max.}$ (220), 270, 279 [log ε (4·48), 2·98, 2·94].

Ethylene Monoketal and Ethylene Monohemithioketal of 3-*Methylpentane*-2 : 4-*dione*.—A mixture of the dione (32 g.), ethylene glycol (18·5 g.), and toluene-*p*-sulphonic acid (100 mg.) in dry benzene (400 c.c.) was refluxed (20 hr.) until no more water separated. The *ketal* (25·6 g.) obtained had b. p. 60°/0·1 mm., n_D^{20} 1·4411 (Found: C, 60·3; H, 9·0. $C_8H_{14}O_3$ requires C, 60·7; H, 8·9%).

The *hemithioketal* (17·3 g.), obtained in the same way from the dione (21 g.) and 2-mercaptoethanol (16 g.), had b. p. 56°/0·1 mm., n_D^{23} 1·4860 (Found: C, 55·5; H, 8·4. $C_8H_{14}O_2S$ requires C, 55·2; H, 8·1%).

We are indebted to the Department of Scientific and Industrial Research for a maintenance allowance (to J. D. G.), and to Dr. J. W. Cook, F.R.S., for suggesting this investigation and for his interest in its progress. Microanalyses were by Mr. J. M. L. Cameron and Miss M. Christie.

UNIVERSITY OF GLASGOW.
MEDICAL RESEARCH COUNCIL, CARCINOGENIC SUBSTANCES RESEARCH GROUP,
UNIVERSITY OF EXETER.
[*Received, November* 12*th*, 1957.]