

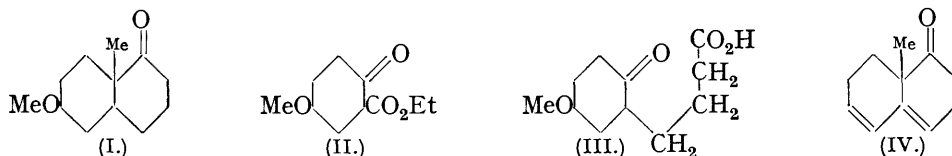
### 15. *The Synthesis of Polyterpenoid Compounds. Part IV.*

By J. W. COOK and C. A. LAWRENCE.

It has been shown already that the authors' modification of the Darzens reaction, whereby ring closure is effected in a *cyclohexene* derivative containing a carboxylated side chain, can be used for the synthesis of 1-ketodecahydronaphthalene derivatives containing an "angular" methyl group. This has been extended in the hope of synthesising 1-keto-6-methoxy-9-methyldecahydronaphthalene, from which a sterol-like molecule might be elaborated. This line of attack was eventually abandoned, as several intermediate stages gave poor yields and ring closure was accompanied by loss of methyl alcohol. Another synthetic route to decahydronaphthalene derivatives has been explored, and several examples are given of the "diene-synthesis" with 1-vinyl- $\Delta^1$ -*cyclohexene* and its 2-methyl derivative, methods of preparation of which are described.

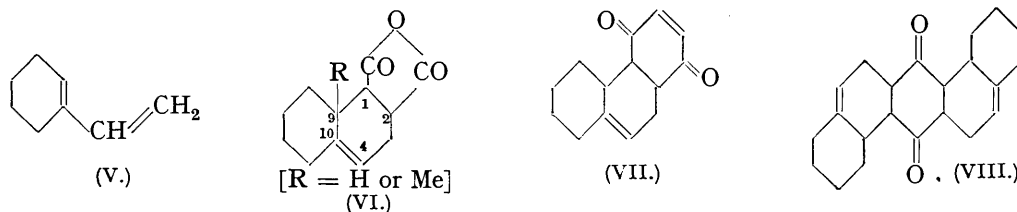
A COMPOUND which might prove of service in the synthesis of members of the sterol group is 6-methoxy-9-methyl-1-decalone (I), and attempts have been made to synthesise this

ketone by extension of the reactions described in Part III (Cook and Lawrence, J., 1937, 817). 4-Methoxycyclohexanone, obtainable from quinol monomethyl ether (Helfer, *Helv. Chim. Acta*, 1924, 7, 953), was condensed with ethyl oxalate to give *ethyl 4-methoxycyclohexanone-2-glyoxylate*, which underwent thermal degradation to *ethyl 4-methoxycyclohexanone-2-carboxylate* (II). The ensuing condensation with  $\gamma$ -iodobutyronitrile gave an 80% yield of *ethyl 4-methoxy-2- $\gamma$ -cyanopropylcyclohexanone-2-carboxylate*, but this on hydrolysis gave only a 25% yield of  $\gamma$ -(2-keto-5-methoxycyclohexyl)butyric acid (III), so that



the yield was about 5% with respect to the 4-methoxycyclohexanone. Methylmagnesium iodide interacted with the carbonyl group of the ethyl ester of the keto-acid (III) and the product was hydrolysed, dehydrated, and the unsaturated acid cyclised in the customary way. The reaction was accompanied by elimination of methyl alcohol and the only ketonic derivatives isolated from the products were shown by analysis to be derived from a ketomethylhexahydronaphthalene, for which formula (IV) may be suggested by analogy with the known tendency for double bonds to become conjugated and distributed between two condensed six-membered rings. No material improvement could be effected in the yields of the intermediate products in this synthesis, so further development was considered impracticable at present, although a different type of method for the synthesis of the keto-acid (III) is under investigation.

We thereupon turned our attention to an application of the "diene-synthesis" involving compounds of the type of 1-vinyl- $\Delta^1$ -cyclohexene (V), a hydrocarbon which was obtained without difficulty by dehydration of 1-vinylcyclohexanol formed by partial hydrogenation of 1-ethylcyclohexanol, despite the subsequent report of Bergmann and Bergmann (*J. Amer. Chem. Soc.*, 1937, 59, 1446) that they were unable to interrupt the hydrogenation at the desired stage. The diene (V) condensed normally with maleic anhydride, and the *adduct* (VI; R = H) was hydrolysed by water to the corresponding carboxylic acid, which was isomerised by alkali and gave a saturated *lactonic acid*.\* 1-Vinyl- $\Delta^1$ -cyclohexene also reacted with *p*-benzoquinone, giving, according to the conditions, 1:4-diketodecahydrophenanthrene (VII) or 9:10-diketo-octadecahydro-1:2:5:6-dibenzanthracene (VIII). The ring system present in the latter compound was established by its dehydrogenation to 1:2:5:6-dibenzanthracene. 1-Vinyl- $\Delta^1$ -cyclohexene does not appear to have been obtained previously with certainty, although the product obtained by Egorova (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1122) by isomerisation of vinylidenecyclohexane probably consists of this hydrocarbon. 1-Vinyl- $\Delta^3$ -cyclohexene, which is the principal thermal dimeride of butadiene, was found by Slobodin (*J. Gen. Chem. Russ.*, 1936, 6, 129) to be isomerised by heated floridin to a mixture of conjugated dienes which reacted with maleic anhydride; this mixture contained chiefly 1-ethylidene- $\Delta^2$ -cyclohexene and was apparently free from 1-vinyl- $\Delta^1$ -cyclohexene.



\* At this stage of our work it was stated at a Meeting of the Society that a similar condensation had been carried out with 1-methyl-2-vinyl- $\Delta^1$ -cyclohexene by Meggy and Robinson, who used a different type of method for the preparation of the diene (*Chem. and Ind.*, 1937, 56, 512; see also Meggy and Robinson, *Nature*, 1937, 140, 282).

Although Meggy and Robinson (*loc. cit.*) had anticipated us in the logical extension of our work to 1-methyl-2-vinyl- $\Delta^1$ -cyclohexene, nevertheless for comparative purposes we prepared this diene by our own method and condensed it with maleic anhydride. The resulting adduct (VI; R = Me) and the corresponding dicarboxylic acid had m. p.'s which tallied approximately with those cited by Meggy and Robinson, and in this case alkali did not produce isomerisation.

In the meantime the synthesis of an oestrogenic hormone by the types of reaction with which we have been concerned has been brought several stages nearer fulfilment by the appearance of two interesting papers (Dane *et al.*, *Annalen*, 1937, **532**, 29, 39) in which it is shown that 6-methoxy-1-ethynyl-3 : 4-dihydronaphthalene and 1-methyl- $\Delta^1$ -cyclopentene-4 : 5-dione can function as components in the Diels-Alder reaction, although the crucial experiment of combining them with each other does not yet appear to have been attempted. In view of the publication of these papers we are not continuing our experiments in this direction.

#### EXPERIMENTAL.

*Ethyl 4-Methoxycyclohexanone-2-glyoxylate*.—4-Methoxycyclohexanone was prepared by oxidation of 4-methoxycyclohexanol (Helfer, *Helv. Chim. Acta*, 1924, **7**, 953). We are indebted to Messrs. Howards and Sons, Ltd., for their kindness in hydrogenating quinol monomethyl ether to 4-methoxycyclohexanol.

A mixture of 4-methoxycyclohexanone (12.8 g.) and ethyl oxalate (16 g.) was cooled in a freezing mixture and treated gradually with a well-cooled solution of sodium (2.5 g.) in alcohol (50 c.c.). After being kept at 0° for 48 hours, the reaction mixture was decomposed with ice-cold dilute sulphuric acid, and the product extracted with ether. The crude ester remaining after removal of the solvent from the washed and dried extract was used for thermal degradation. An analytical sample of the glyoxylic ester was purified through its cupric derivative, which separated when a mixture of the ester and saturated aqueous cupric acetate was kept overnight. The cupric compound crystallised from alcohol in light green, microscopic, diamond-shaped plates, m. p. 161—163° (decomp.) [Found: C, 51.05; H, 5.9; Cu, 12.2. (C<sub>11</sub>H<sub>15</sub>O<sub>5</sub>)<sub>2</sub>Cu requires C, 51.0; H, 5.8; Cu 12.3%]. *Ethyl 4-methoxycyclohexanone-2-glyoxylate* was isolated from the cupric compound by shaking with ether and ice-cold dilute sulphuric acid, and formed a colourless viscous liquid, b. p. 116°/0.4 mm., which gave a cherry-red colour with alcoholic ferric chloride (Found: C, 57.3; H, 7.2. C<sub>11</sub>H<sub>16</sub>O<sub>5</sub> requires C, 57.9; H, 7.1%). The bis-2 : 4-dinitrophenylhydrazone formed thin, orange-yellow, microscopic needles (from aqueous dioxan), m. p. 224—227° (decomp.) (Found: C, 46.9; H, 4.3; N, 18.9. C<sub>25</sub>H<sub>24</sub>O<sub>11</sub>N<sub>8</sub> requires C, 46.9; H, 4.2; N, 19.0%).

*Ethyl 4-Methoxycyclohexanone-2-carboxylate* (II).—The crude glyoxylic ester was boiled under reflux until a test portion gave a purple colour with alcoholic ferric chloride (about 20 minutes), and the product was distilled in a vacuum. The yield of pure *ethyl 4-methoxycyclohexanone-2-carboxylate* (II), b. p. 131—133°/10 mm., was about 25% (Found: C, 60.3; H, 8.3. C<sub>10</sub>H<sub>16</sub>O<sub>4</sub> requires C, 60.0; H, 8.05%). Its 2 : 4-dinitrophenylhydrazone formed thin golden-yellow plates (from alcohol), m. p. 129—131° (decomp.) (Found: C, 50.6; H, 5.4; N, 14.9. C<sub>16</sub>H<sub>20</sub>O<sub>7</sub>N<sub>4</sub> requires C, 50.5; H, 5.3; N, 14.7%).

*Ethyl 4-methoxy-2- $\gamma$ -cyanopropylcyclohexanone-2-carboxylate* was obtained in 80% yield when a mixture of  $\gamma$ -iodobutyronitrile (8.2 g.) and the sodio-compound prepared from the keto-ester (II) (8.4 g.) and powdered sodium (0.95 g.) in benzene (40 c.c.) was heated on the water-bath for 24 hours. It formed a colourless viscous liquid, b. p. 155°/0.2 mm. (Found: C, 62.8; H, 8.1. C<sub>14</sub>H<sub>21</sub>O<sub>4</sub>N requires C, 62.9; H, 7.9%), and gave a 2 : 4-dinitrophenylhydrazone which crystallised from methyl alcohol in yellow parallelogram-shaped plates, m. p. 123—126° (Found: C, 53.7; H, 5.6; N, 15.9. C<sub>20</sub>H<sub>25</sub>O<sub>7</sub>N<sub>5</sub> requires C, 53.7; H, 5.6; N, 15.65%).

$\gamma$ -(2-Keto-5-methoxycyclohexyl)butyric Acid (III).—Ethyl 4-methoxy-2- $\gamma$ -cyanopropylcyclohexanone-2-carboxylate (11.8 g.) was heated on the water-bath for 3 hours with aqueous potassium hydroxide (9 g. in 250 c.c.). Neutral material was extracted with ether, and the alkaline solution was acidified, saturated with sodium chloride, and extracted with ether twelve times. The dried extract was distilled and two fractions collected: (i) b. p. 175—185°/0.6 mm. (2.2 g.); (ii) b. p. 260—275°/0.6 mm. (4.75 g.). Fraction (i) was the desired  $\gamma$ -(2-keto-5-methoxycyclohexyl)butyric acid (III), which was purified through the semicarbazone and then formed a colourless viscous liquid, b. p. approx. 185°/1 mm., which had not crystallised after several months (Found: C, 62.3; H, 8.7. C<sub>11</sub>H<sub>18</sub>O<sub>4</sub> requires C, 61.7; H, 8.5%). Its semicarbazone

formed microscopic needles (from alcohol), m. p. 178—178.5° after slight sintering (Found : C, 53.3; H, 7.8.  $C_{12}H_{21}O_4N_3$  requires C, 53.1; H, 7.8%). Fraction (ii), the major product, appeared to be an *anhydride* of a  $\gamma$ -2-ketocyclohexenylbutyric acid resulting from elimination of methyl alcohol. After redistillation it formed a very viscous, brownish liquid, b. p. 251—260°/0.4 mm. (Found : C, 69.2, 69.2; H, 7.9, 8.0.  $C_{20}H_{26}O_5$  requires C, 68.9; H, 7.5%). On hydrolysis with alkali this anhydride yielded an acid, which was distilled at 0.6 mm. from a bath at 200° and then gave a *semicarbazone* which crystallised from alcohol in short colourless needles, m. p. 219—220.5° (Found : C, 55.3; H, 7.4.  $C_{11}H_{17}O_3N_3$  requires C, 55.2; H, 7.15%). When the anhydride was heated with a little baryta at 280—290° in a vacuum, it gave a distillate which formed a *semicarbazone*, apparently of an isomeric  $\gamma$ -2-ketocyclohexenylbutyric acid, which crystallised from alcohol in rosettes of microscopic plates, m. p. 213.5—215° (decomp.), depressed by the isomeric semicarbazone (Found : C, 55.4; H, 7.4; N, 17.6.  $C_{11}H_{17}O_3N_3$  requires C, 55.2; H, 7.15; N, 17.5%). The yield of the desired keto-acid (III) was not improved when the hydrolysis of the cyano-ester was carried out with concentrated hydrochloric acid.

1-Keto-9-methylhexahydronaphthalene (IV?).— $\gamma$ -(2-Keto-5-methoxycyclohexyl)butyric acid (5.7 g.) was esterified with alcohol (30 c.c.) and concentrated sulphuric acid (0.7 c.c.), giving an ethyl ester which formed an almost colourless oil, b. p. 145°/0.2 mm. This ester (4.7 g.) was condensed with methylmagnesium iodide exactly as described in Part III (J., 1937, 821) for the ester of  $\gamma$ -2-ketocyclohexylbutyric acid, and the resulting  $\gamma$ -(5-methoxy-2-methyl- $\Delta^1$ -cyclohexenyl)butyric acid (1.6 g.; b. p. 160—165°/0.8 mm.) was submitted to the general procedure for cyclisation described in Part II (J., 1935, 1637). The neutral product (0.65 g.; b. p. 150°/30 mm.) gave small yields of a 2 : 4-dinitrophenylhydrazone, which crystallised from aqueous dioxan in microscopic, vermilion, diamond-shaped plates, m. p. 224° (decomp.) (Found : C, 59.7; H, 4.8.  $C_{17}H_{16}O_4N_4$  requires C, 59.6; H, 5.3%), and a *semicarbazone*, which formed a microcrystalline powder (from dilute dioxan), m. p. 214—216° (decomp.) in a preheated bath (Found : C, 65.4; H, 7.5.  $C_{12}H_{17}ON_3$  requires C, 65.7; H, 7.8%). The analytical figures indicate that these are derivatives of 1-keto-9-methylhexahydronaphthalene.

#### “ Diene ” Condensations.

1-Vinylcyclohexanol.—1-Ethylcyclohexanol was prepared from cyclohexanone and acetylene as described by Pinkney, Nesty, Wiley, and Marvel (*J. Amer. Chem. Soc.*, 1936, **58**, 974) and had b. p. 85—87°/28 mm. Its *p*-nitrobenzoate formed small lath-shaped crystals (from aqueous methyl alcohol), m. p. 64—64.5° (Found : C, 65.95; H, 5.6.  $C_{15}H_{15}O_4N$  requires C, 65.9; H, 5.5%), and its 3 : 5-dinitrobenzoate formed thin irregular plates (from ethyl alcohol), m. p. 104.5—106° (Found : C, 56.5; H, 4.5.  $C_{15}H_{14}O_6N_2$  requires C, 56.6; H, 4.4%).

A solution of 1-ethylcyclohexanol (31.1 g.) in ethyl alcohol (250 c.c.) was shaken with hydrogen in presence of palladium-black (0.3 g.) until 5.5 l. had been absorbed at 24.5° and 772 mm. The resulting colourless liquid (26 g.; b. p. 76—79°/25 mm.) gave a *p*-nitrobenzoate crystallising in long colourless needles (from aqueous methyl alcohol), m. p. 101—102° (Found : C, 65.7; H, 6.4.  $C_{15}H_{17}O_4N$  requires C, 65.4; H, 6.2%), and a 3 : 5-dinitrobenzoate, which formed thin irregular plates, m. p. 122—123° (from alcohol) (Found : C, 56.4; H, 5.1.  $C_{15}H_{16}O_6N_2$  requires C, 56.2; H, 5.0%). 1-Vinylcyclohexanol, obtained by hydrolysis of the dinitrobenzoate, formed a colourless liquid, b. p. 67—68°/10 mm., which absorbed approximately the calculated amount of bromine (Found : C, 75.4; H, 11.5.  $C_8H_{14}O$  requires C, 76.1; H, 11.2%).

For comparative purposes the esters of 1-ethylcyclohexanol (Wallach, *Annalen*, 1908, **360**, 50; Sabatier and Maihle, *Ann. Chim.*, 1907, **10**, 544) were prepared. Its *p*-nitrobenzoate formed long slender needles (from aqueous methyl alcohol), m. p. 73—74° (Found : C, 65.1; H, 7.0.  $C_{15}H_{19}O_4N$  requires C, 64.95; H, 6.9%), and its 3 : 5-dinitrobenzoate formed thin irregular plates (from alcohol), m. p. 127—127.5° (Found : C, 55.9; H, 5.8.  $C_{15}H_{18}O_6N_2$  requires C, 55.9; H, 5.6%). Clearly these esters suffice to characterise the three carbinols and to establish the individuality of the vinyl compound, although mixed m. p.'s of corresponding esters showed no depressions.

1-Vinyl- $\Delta^1$ -cyclohexene (V).—1-Vinylcyclohexanol (4.2 g.), purified through its *p*-nitrobenzoate, was heated with potassium hydrogen sulphate (5 g.) at 180° for an hour in an atmosphere of nitrogen. The resulting 1-vinyl- $\Delta^1$ -cyclohexene formed a colourless mobile liquid, b. p. 145°, with an odour resembling that of butadiene (Found : C, 88.1; H, 11.2.  $C_8H_{12}$  requires C, 88.8; H, 11.2%).

$\Delta^4$ :<sup>10</sup>-Octahydronaphthalene-1 : 2-dicarboxylic Anhydride (VI; R = H).—A mixture of 1-vinyl- $\Delta^1$ -cyclohexene (0.5 g.), maleic anhydride (0.35 g.), and xylene (3 c.c.) was warmed until a

clear solution was obtained and then kept overnight at room temperature. The solvent and unreacted diene were removed in a vacuum at 80°. The residual viscous liquid crystallised in the ice-chest and was drained on a tile and washed with water to remove maleic anhydride. The product (0.6 g.; m. p. 47—49°) was recrystallised from light petroleum and gave imperfect needles of  $\Delta^4:10$ -octahydronaphthalene-1:2-dicarboxylic anhydride (VI; R = H), m. p. 52—53° (Found: C, 69.7; H, 6.7.  $C_{12}H_{14}O_3$  requires C, 69.9; H, 6.8%).  $\Delta^4:10$ -Octahydronaphthalene-1:2-dicarboxylic acid, formed by prolonged hydrolysis of the anhydride with hot water, crystallised from water in microscopic plates, m. p. 131—132.5° (Found: C, 64.5; H, 7.35; equiv., 114.2.  $C_{12}H_{16}O_4$  requires C, 64.3; H, 7.2%; equiv., 112). A specimen of this acid which had been dried in the air had m. p. 130—131° on rapid heating, but 157—158° (after sintering) on slow heating. The diphenacyl ester formed thin needles (from alcohol), m. p. 139.5—140.5° (Found: C, 72.85; H, 6.2.  $C_{28}H_{28}O_6$  requires C, 73.0; H, 6.1%).

When  $\Delta^4:10$ -octahydronaphthalene-1:2-dicarboxylic acid or its anhydride was boiled with sodium hydroxide solution, it was partly isomerised; acidification gave a lactonic acid which, in contrast to the dicarboxylic acid, was readily soluble in cold water; it crystallised from benzene-ligroin in thin irregular plates, m. p. 176—176.5° (Found: C, 64.7; H, 7.3; equiv., 227.4.  $C_{12}H_{16}O_4$  requires C, 64.3; H, 7.2%; equiv., 224). The phenacyl ester formed thin plates (from aqueous alcohol), m. p. 131—131.5° (Found: C, 70.2; H, 6.4.  $C_{20}H_{22}O_5$  requires C, 70.1; H, 6.5%); the m. p. was depressed 10° by admixture with the diphenacyl ester of the dicarboxylic acid.

1:4-Diketodecahydrophenanthrene (VII).—1-Vinyl- $\Delta^1$ -cyclohexene (0.9 g.) was added to a solution of *p*-benzoquinone (0.6 g.) in methyl alcohol (8 c.c.), and the solution kept overnight at room temperature and then boiled for 2 hours. The oil precipitated by addition of water solidified when cooled in a freezing mixture and was twice crystallised from methyl alcohol. The diketone (VII) formed pale yellow, tabular crystals, m. p. 84—85.5°, which darkened on standing (Found: C, 77.8; H, 7.6.  $C_{14}H_{16}O_2$  requires C, 77.7; H, 7.45%).

9:10-Diketo-octadecahydro-1:2:5:6-dibenzanthracene (VIII).—A mixture of 1-vinyl- $\Delta^1$ -cyclohexene (1.2 g.), *p*-benzoquinone (0.5 g.), and tetralin (5 c.c.) was boiled under reflux for 10 minutes and then cooled. The resulting crystals were collected, washed with light petroleum, and recrystallised from toluene. The diketone (VIII) (0.4 g. obtained from 3.7 g. of diene) formed colourless needles, m. p. 200—203° (decomp.) (Found: C, 81.4; H, 8.7.  $C_{22}H_{28}O_2$  requires C, 81.4; H, 8.7%). For dehydrogenation this diketone (45 mg.) was heated at 300—320° for 3 hours with platinum-black (30 mg.) and the sublimate was crystallised from benzene. The resulting yellowish leaflets had m. p. 257—258°, not depressed by 1:2:5:6-dibenzanthracene, and gave a picrate, m. p. 212—213° (lit., 212°).

2-Methyl-1-ethinylcyclohexanol.—This was prepared, by the procedure used by Pinkney *et al.* (*loc. cit.*) for the preparation of 1-ethinylcyclohexanol, from 2-methylcyclohexanone (28 g.), ether (100 c.c.), potassium (10 g.), *tert*-amyl alcohol (130 c.c.), and a saturated (at -15°) ethereal solution of acetylene (100 c.c.). After two distillations the resulting carbinol (22 g.) had b. p. 88—96°/33 mm. For analysis, a portion was repeatedly fractionated, and then had b. p. 83—84°/21 mm. (Found: C, 77.0; H, 10.0.  $C_9H_{14}O$  requires C, 78.2; H, 10.2%). 2-Methyl-1-ethinylcyclohexanol formed a colourless mobile liquid with a camphor-like odour, and did not crystallise on long standing. Its *p*-nitrobenzoate formed small tabular crystals (from methyl alcohol), m. p. 135—136° (Found: C, 66.95; H, 6.0.  $C_{16}H_{17}O_4N$  requires C, 66.9; H, 6.0%), and its 3:5-dinitrobenzoate formed colourless microscopic plates (from aqueous alcohol), m. p. 76.5—79° (Found: C, 57.8; H, 4.9.  $C_{16}H_{16}O_6N_2$  requires C, 57.8; H, 4.85%).

2-Methyl-1-vinylcyclohexanol.—A solution of the foregoing carbinol (16.5 g.) in alcohol (200 c.c.) was shaken with hydrogen in presence of palladium-black (0.3 g.) until 3 l. had been absorbed at 23° and 767 mm. The resulting 2-methyl-1-vinylcyclohexanol (12.9 g.) formed a colourless mobile liquid, b. p. 86.5—90°/30 mm. (Found: C, 76.1; H, 11.3.  $C_9H_{16}O$  requires C, 77.1; H, 11.5%). Its *p*-nitrobenzoate formed small thin plates (from aqueous methyl alcohol), m. p. 71—72° (Found: C, 66.1; H, 7.0.  $C_{16}H_{16}O_4N$  requires C, 66.4; H, 6.6%), and its 3:5-dinitrobenzoate formed small thin plates (from alcohol), m. p. 120—120.5° (Found: C, 57.25; H, 5.7.  $C_{16}H_{16}O_6N_2$  requires C, 57.5; H, 5.4%).

2-Methyl-1-ethylcyclohexanol was prepared for comparative purposes, the following procedure giving a very much better yield than that of Murat (*Ann. Chim.*, 1909, 16, 116): A solution of 2-methylcyclohexanone (18 g.) in ether (50 c.c.) was added to a mechanically stirred Grignard solution prepared from ethyl iodide (25 g.), magnesium (4.2 g.), and ether (170 c.c.), cooled to 0°. After being kept in the ice-bath for  $\frac{1}{2}$  hour, the mixture was allowed to warm to room temperature, then boiled for an hour, and finally kept overnight at room temperature. The

product was decomposed with ice-cold ammonium chloride solution, and the washed ethereal layer was shaken for 2 hours with saturated sodium bisulphite solution to remove unreacted ketone. The ethereal solution was washed, dried (sodium sulphate), and distilled, yielding 17.3 g. (75% yield) of 2-methyl-1-ethylcyclohexanol, b. p. 81—84°/23 mm. Its 3:5-dinitrobenzoate formed thin irregular plates (from aqueous alcohol), m. p. 105.5—107.5° (Found: C, 56.9; H, 6.2.  $C_{16}H_{20}O_6N_2$  requires C, 57.1; H, 6.0%). A crystalline *p*-nitrobenzoate could not be obtained.

1-Methyl-2-vinyl- $\Delta^1$ -cyclohexene.—2-Methyl-1-vinylcyclohexanol (1.4 g.), purified through its *p*-nitrobenzoate, was heated for an hour at 180—185° with potassium hydrogen sulphate (1.5 g.) in an atmosphere of nitrogen. The resulting 1-methyl-2-vinyl- $\Delta^1$ -cyclohexene formed a colourless mobile liquid, b. p. 156—157° (Found: C, 86.7; H, 12.1.  $C_9H_{14}$  requires C, 88.45; H, 11.55%).

9-Methyl- $\Delta^4:10$ -octahydronaphthalene-1:2-dicarboxylic Anhydride (VI; R = Me).—The aforesaid diene (6.2 g.), prepared by dehydration of the crude distilled carbinol (8.3 g.), was added to a mixture of maleic anhydride (5 g.) and xylene (10 c.c.), and the solution heated at 100° for  $\frac{1}{2}$  hour and then kept overnight at room temperature. The adduct partly crystallised and more was isolated from the liquors by vacuum concentration. After washing with water to remove maleic anhydride, 9-methyl- $\Delta^4:10$ -octahydronaphthalene-1:2-dicarboxylic anhydride (VI; R = Me) crystallised from ligroin in thin irregular plates, m. p. 114—114.5° (Meggy and Robinson, *loc. cit.*, give 111.5°) (Found: C, 70.9; H, 7.4. Calc. for  $C_{13}H_{16}O_3$ : C, 70.9; H, 7.3%). The same anhydride resulted when the purified diene was allowed to react with maleic anhydride in benzene at room temperature for 48 hours. The acid obtained by aqueous or alkaline hydrolysis of the anhydride crystallised from water in microscopic prisms, m. p. 179—181° (Meggy and Robinson give 171°) (Found: C, 65.4; H, 7.7. Calc. for  $C_{13}H_{18}O_4$ : C, 65.5; H, 7.6%).

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