

782. *The Dimerisation of Mesityl Oxide. A Novel Type of Diene Addition.**

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Mesityl oxide (I) dimerises exothermally under the influence of lithium, to give 2-acetyl-1 : 3 : 3 : 5-tetramethylcyclohex-5-en-1-ol (II) besides other products. The reaction can be regarded as a diene addition between the enolate (Ia), formed on the metal surface and acting as diene, and the ketone (I) acting as dienophil. The structure of the dimer (II), which contains a highly hindered carbonyl group, has been deduced from spectroscopic evidence and degradative reactions, including conversion into 2 : 3 : 4 : 6-tetramethylacetophenone (XI).

THE work described in this paper arose from the observation ¹ that the reaction of mesityl oxide with *isobutenyl*-lithium yields, besides the expected alcohol, a high-boiling, crystalline product, m. p. 73°. This compound showed no high-intensity light absorption in the near-ultraviolet and did not yield a 2 : 4-dinitrophenylhydrazone, and it was at first taken to be a bimolecular reduction product such as has been reported to be formed from mesityl

* Submitted in honour of the seventieth birthday of Sir Ian Heilbron, D.S.O., F.R.S.

¹ Braude and Coles, *J.*, 1952, 1425.

oxide by the action of magnesium or other metals.² A product of this kind might have conceivably arisen by a reducing action of the lithium alkenyl.³

The analytical data, however, showed that the compound was a dimer of mesityl oxide and the comparatively large amount obtained suggested that its formation was brought about by a catalytic effect of traces of lithium metal present in the reaction mixture. This was confirmed when it was found that mesityl oxide undergoes an exothermic reaction when added to a suspension of lithium in ether, to give a mixture from which the solid dimer, $C_{12}H_{20}O_2$, identical with that obtained earlier, was isolated. The infrared spectrum of the dimer indicated the presence of a hydroxyl group (ν_{\max} , 3475 cm^{-1}) and of an isolated keto-group (ν_{\max} , 1700 cm^{-1}) which appeared to be intramolecularly hydrogen-bonded since the absorption bands in carbon tetrachloride were sharp and independent of concentration, a behaviour typical of α - and β -, but not of γ -, ketols.⁴ The presence of a keto-group was supported by a weak ultraviolet absorption band near 2900 Å, but the failure of the dimer to yield a derivative with Brady's reagent suggested that this group was highly hindered.

Catalytic hydrogenation of the dimer with platinum oxide in ethyl acetate gave a dihydro-derivative which according to the infrared spectrum still contained the intramolecularly hydrogen-bonded hydroxyl and carbonyl functions, indicating that one ethylenic bond was originally present and that the dimer was monocyclic. Catalytic hydrogenation in acetic acid gave a liquid product, $C_{12}H_{22}O$, the infrared spectrum of which indicated the presence of a non-bonded keto-group (ν_{\max} , 1711 cm^{-1}) and the absence of a hydroxyl group; under these conditions, hydrogenolysis as well as saturation of the ethylenic bond had evidently taken place, suggesting that the hydroxyl group was originally in an allylic position and probably tertiary. This was confirmed by the ready dehydration of the dimer when heated with a trace of iodine, which furnished a dehydro-derivative, $C_{12}H_{18}O$, showing ultraviolet absorption characteristic of a conjugated, semicyclic diene (λ_{\max} , 2360 Å; ϵ 9000).

At this stage only the position of the carbonyl function relative to that of the ethylenic and hydroxyl groups remained to be established, and a clue to this was provided by dehydration with oxalic acid which, besides the diene obtained above, also yielded a second diene containing a conjugated dienone chromophore (λ_{\max} , 3020 Å; ϵ ca. 2000). This result showed that the dimer must contain the system $C=C\cdot CMe(OH)\cdot CH\cdot CO$, giving either $C=C\cdot C(=CH_2)\cdot CH\cdot CO$ or $C=C\cdot CMe=C\cdot CO$ on dehydration.

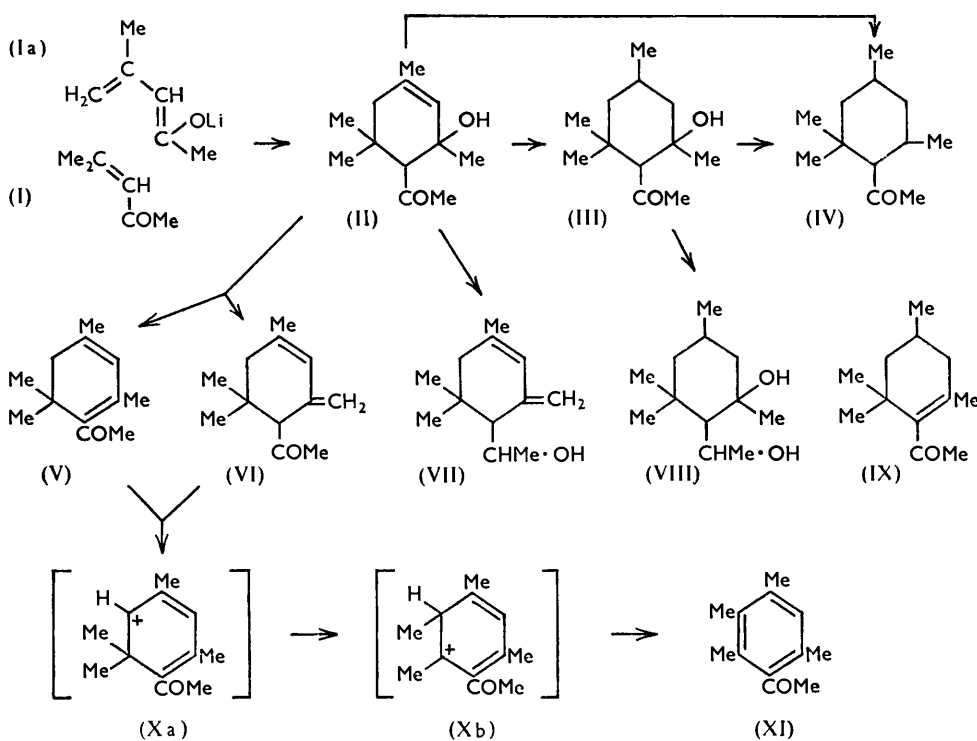
These facts are uniquely explicable by structure (II), 2-acetyl-1 : 3 : 3 : 5-tetramethylcyclohex-5-en-1-ol, for the dimer and by the annexed scheme. The presence of an isolated carbonyl group in the dimer (II) was confirmed by reduction with lithium aluminium hydride which was accompanied by dehydration to give the dienol (VII). The dihydro-derivative (III) is similarly reduced to the diol (VIII) but resists dehydration to the unsaturated ketone (IX). It may be noted that the results of "active hydrogen" (Zerewitinoff) determinations proved somewhat misleading in this series; thus, the dimer, with methylmagnesium iodide, evolved methane corresponding to *two* active hydrogen atoms. The hindered acetyl group evidently behaves as an enolic hydroxyl function and this is confirmed by the fact that the ketone (IV) still shows one active hydrogen by this method. (Values corresponding to 0.1—0.5 active hydrogen atom are obtained with other ketones under similar conditions.) The lack of reactivity of the acetyl group towards Brady's reagent is not surprising since it is flanked by four α -substituents in the dimer and by three in the dehydration products; steric hindrance in this system will be even more severe than in 2 : 2 : 6-trimethylcyclohexanone (which reacts slowly) and 2 : 2 : 6 : 6-tetramethylcyclohexanone (which does not react under comparable conditions). Similar observations have been made for *o*-methylacetophenones (see below) and other examples

² Vogel, *J.*, 1927, 594; Wiemann and Glacet, *Compt. rend.*, 1948, **226**, 923; Glacet, *ibid.*, 1948, **227**, 480; Kolobielski and Wiemann, *ibid.*, 1951, **233**, 691; 1954, **238**, 1039; Kolobielski, *ibid.*, 1953, **237**, 1717; *Ann. Chim. (France)*, 1955, **10**, 271.

³ Cf. Braude in "Progress in Organic Chemistry" (J. W. Cook, Ed.), Vol. III, Chapter 4, Butterworths, London, 1955.

⁴ Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068; Sheehan, O'Neill, and White, *ibid.*, 1950, **72**, 3376; Duculot, *Compt. rend.*, 1955, **241**, 1738; Lüttke, *Chem. Ber.*, 1950, **83**, 571.

of this type have been described in the steroid field.⁵ Steric hindrance is undoubtedly also the cause of the exceptionally weak absorption of the dienone (V) (see above) since the carbonyl group will be prevented from becoming coplanar with the diene system; closely analogous cases are 1-acetyl-2 : 6 : 6-trimethylcyclohexene⁶ and dehydro- β -ionone.⁷ It is interesting that the ratios of the ϵ values for the trialkylated compounds to those found or



expected for the unsubstituted parent compounds are about 0.1 in each case, corresponding⁸ to an interplanar angle of 70° . The fact that dehydration of the dimer gives predominantly the exocyclic (VI) rather than the homocyclic dienone (V) provides another indication of the fact that the additional conjugation in the latter is comparatively weak. A preference for systems containing the 1-methylcyclohex-2-enol grouping as such to undergo exocyclic dehydration has been noted in other cases.⁹ Thus Dr. O. H. Wheeler has found that 1 : 3-dimethylcyclohex-2-en-1-ol with phosphorus oxychloride in pyridine gives 1-methyl-3-methylenecyclohexene showing ultraviolet absorption typical of a semicyclic diene (λ_{\max} , 2270 Å; ϵ 9500).*

Structure (II) was confirmed by treatment of the dimer with tetrachloro-1 : 2-benzoquinone, which has been shown¹⁰ to effect aromatisation of *gem*-alkylated hydroaromatic

* *Added, July 5th, 1956.*—On the other hand, 1 : 3-dimethylcyclohexa-1 : 3-diene is obtained with sulphuric acid (Meinwald and Grossman, *J. Amer. Chem. Soc.*, 1956, **78**, 992), showing that the course of dehydration depends on the conditions. Interconversion of the dienes, as in the α : β -phellandrene system, may also occur and this matter is being investigated further.

⁵ Ruzicka, Jeger, Grob, and Hösli, *Helv. Chim. Acta*, 1943, **26**, 2283; Barnes, Barton, Cole, Fawcett, and Thomas, *J.*, 1953, 571; Elks, Evans, Long, and Thomas, *J.*, 1954, 451.

⁶ Henbest and Woods, *J.*, 1952, 1150; Braude and Timmons, *J.*, 1955, 3766.

⁷ Henbest, *J.*, 1951, 1074.

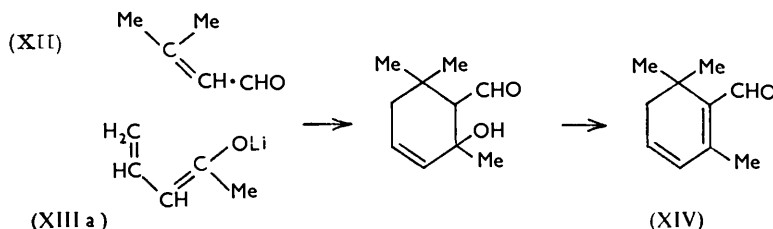
⁸ Braude, *Experientia*, 1955, **11**, 457; Braude and Sondheimer, *J.*, 1955, 3754; Braude and Timmons, *J.*, 1955, 3766.

⁹ Bann, Heilbron, and Spring, *J.*, 1936, 1274; Mukherji and Bhattacharyya, *J. Amer. Chem. Soc.*, 1953, **75**, 4698; cf. Novello, Christy, and Sprague, *ibid.*, 1954, **76**, 738.

¹⁰ Beames, Braude, Jackman, and Linstead, *Chem. and Ind.*, 1954, 1174; Braude, Linstead, and Lowe, unpublished work.

systems with 1 : 2 migration, rather than loss, of one of the substituents. 2 : 3 : 4 : 6-Tetramethylacetophenone (XI), identical in infrared absorption with a specimen prepared by acetylation of *isodurene*, was obtained in 59% yield; the course of the reaction probably involves initial dehydration to the dienes (V) and (VI), followed by dehydrogenation *via* the unstable carbonium-ion intermediates (Xa and b). Since the ketone (XI) is a liquid and, like the dimer (II), does not easily yield carbonyl derivatives owing to steric hindrance,¹¹ its identity was confirmed by oxidation to 2 : 3 : 4 : 6-tetramethylbenzoic acid. The strong steric hindrance in 2 : 3 : 4 : 6-tetramethylacetophenone is borne out by the ultraviolet light absorption ($\lambda_{\text{infl.}}$ 2450 Å; ϵ 2000; cf. acetophenone,⁸ $\lambda_{\text{max.}}$ 2430 Å, ϵ 13,000); the interplanar angle between the phenyl and the carbonyl group indicated by these data is about 70°, as for the dienone (V) (see above).

It seems highly probable that formation of the dimer (II) involves a diene addition between one molecule of mesityl oxide (I), acting as dienophile, and another in the form of the enolate (Ia), acting as diene. The characteristics of the reaction, which shows an



induction period until the lithium assumes a bright, metallic appearance, suggest that the dimerisation takes place at the metal surface and that the enolate is produced by chemisorption of the ketone. An analogous dimerisation of $\beta\beta$ -dimethylacetaldehyde (3-methylbut-2-enal) under basic conditions, *e.g.*, under the influence of sodamide, was observed by Fischer and Löwenberg¹² and was interpreted by them as a diene addition, but it was later suggested¹³ that a Michael addition may be involved. We have now effected the dimerisation by lithium of $\beta\beta$ -dimethylacetaldehyde (XII), which is accompanied by dehydration to the diene aldehyde (4-formyl-1 : 5 : 5-trimethylcyclohexa-1 : 3-diene), and under such conditions this reaction, like that of mesityl oxide, almost certainly proceeds by diene addition. As would be expected, pent-3-en-2-one also appears to undergo lithium-catalysed dimerisation, but the products in this case proved difficult to separate and purify and, as none could be obtained crystalline, they were not further examined. It is interesting that if "mixed" additions of this type could be effected, they would provide a new route, which could conceivably have biosynthetic significance, to monocyclic terpenes; thus $\beta\beta$ -dimethylacetaldehyde with the enolate (XIIIa) of pent-3-en-2-one might yield the hydroxy-derivative shown and thence dehydrocyclocitral (XIV).

EXPERIMENTAL

Analytical data were determined in the organic microanalytical (Mr. F. H. Oliver and staff) and spectroanalytical (Mr. R. L. Erskine and Mrs. A. I. Boston) laboratories of this Department. Some of the infrared spectroscopic data were obtained in the laboratories of the British Rubber Producers' Research Association, by courtesy of Dr. G. Gee, F.R.S. Intensities of infrared absorption bands are indicated qualitatively by the symbols vs (very strong), s (strong), m (medium), and w (weak).

Dimerisation of Mesityl Oxide.—(a) Mesityl oxide (15 g.) was added to a stirred suspension of finely cut lithium (14 g.) in dry ether under nitrogen. The lithium rapidly assumed a bright, metallic appearance and a vigorous reaction commenced within about 10 min. More mesityl oxide (85 g.) was then added at such a rate that the ether continued to reflux gently. After a

¹¹ Pearson and Greer, *J. Amer. Chem. Soc.*, 1955, **77**, 1294, 6649.

¹² Fischer and Löwenberg, *Annalen*, 1932, **494**, 263; Fischer and Hultszsch, *Ber.*, 1935, **68**, 1726; cf. Braude and Evans, *J.*, 1955, 3334.

¹³ Jones and Koch, *J.*, 1942, 393.

further 1 hour's stirring, unchanged lithium (8 g.) was filtered off and 10% aqueous ammonium chloride (600 g.) was added. The ether layer was separated, dried (Na_2SO_4), and fractionated, giving some unchanged mesityl oxide (9 g.), a range of fractions (total 60 g.), b. p.s 60—90°/0.2 mm., and a high-boiling residue (16 g.). The intermediate fractions, when kept at 0° for several days, deposited crystals which were filtered off and recrystallised from pentane, giving 2-acetyl-1 : 3 : 3 : 5-tetramethylcyclohex-5-en-1-ol (II) (4 g.) as needles, m. p. 73° [Found : C, 73.1; H, 10.2%; M (in camphor), 198. $\text{C}_{12}\text{H}_{20}\text{O}_2$ requires C, 73.4; H, 10.3%; M , 196]. The m. p. was undepressed on admixture with the product, m. p. 74°, obtained by Braude and Coles.¹ Ultraviolet light absorption : λ_{max} , 2550 Å (ϵ 40) and 2900 Å (ϵ 30 in EtOH). Infrared absorption : (i) As paraffin mull, ν_{max} , 3450 (m, hydrogen-bonded O-H stretching), 1700 (vs, C=O stretching), 1158 (s, C-O stretching), 829 and 808 cm^{-1} (m, >C=CH- bending); (ii) in CCl_4 (LiF prism), ν_{max} , 3578 (w, free O-H stretching) and 3475 cm^{-1} (m, hydrogen-bonded O-H stretching). With methylmagnesium iodide in ether, the dimer evolved methane corresponding to 1.03% (2.02 atoms) of "active" hydrogen. Microhydrogenation (acetic acid-platinic oxide) resulted in the uptake of 1.04 mols. of hydrogen. No 2 : 4-dinitrophenylhydrazone was formed on treatment with Brady's reagent, even after 2 days at room temperature. The dimer readily reacted with bromine in chloroform, but no solid products could be isolated.

(b) Finely cut lithium (3.5 g.) was added to a stirred solution of mesityl oxide (100 g.) in ether (500 ml.) under nitrogen. After about 10 min., a vigorous, exothermic reaction occurred. When this had subsided, the mixture was heated under reflux for 3 hr. and then worked up as above. A somewhat higher yield of solid dimer (10.7 g.), m. p. 73°, together with a similar mixture of liquid products was obtained.

Catalytic Hydrogenation of the Dimer.—(a) The dimer (1.0 g.) in ethyl acetate (30 ml.) was shaken with platinic oxide (50 mg.) in hydrogen. The uptake ceased when 124 ml. at 17°/760 mm. (Calc. for 1 mol., 123 ml.) had been absorbed. Removal of the catalyst and solvent gave 2-acetyl-1 : 3 : 3 : 5-tetramethylcyclohexan-1-ol (III) which crystallised from aqueous methanol in needles (0.6 g.), m. p. 76°, depressed to 67° on admixture with the starting material (Found : C, 72.8; H, 11.2. $\text{C}_{12}\text{H}_{22}\text{O}_2$ requires C, 72.7; H, 11.2%). Infrared light absorption (in CCl_4) : ν_{max} , 3475 (m, O-H stretching), 1700 (vs, C=O stretching), 1458 (s), 1404 (s), 1373 (s), 1360 (s), 1335 (s), 1196 (s), and 1147 (s) cm^{-1} . An attempted dehydration of the hydroxyketone (III) by iodine at 80°/10 mm. gave, after distillation, mainly unchanged starting material.

(b) The dimer (2.0 g.) in acetic acid (20 ml.) was shaken with platinic oxide in hydrogen. The uptake ceased after 6 hr. when 482 ml. at 18°/754 mm. (Calc. for 2 mol., 496 ml.) had been absorbed. The catalyst was filtered off and the solution was diluted with water (80 ml.) and extracted with ether. The ether extract was washed with aqueous sodium hydrogen carbonate, dried (K_2CO_3), and evaporated, giving 1-acetyl-2 : 2 : 4 : 6-tetramethylcyclohexane (IV) (1.4 g.) b. p. 94—96°/13 mm., n_{D}^{25} 1.4559 [Found : C, 78.8; H, 12.1%; M (in camphor), 176. $\text{C}_{12}\text{H}_{22}\text{O}$ requires C, 79.1; H, 12.2%; M , 182]. Infrared absorption (in CCl_4) : ν_{max} , 1711 (vs, C=O stretching), 1449 (s), 1417 (m), 1380—1340 (s), 1230 (s), 1197 (s), and 1154 (s) cm^{-1} . With methylmagnesium iodide in anisole, the ketone evolved methane corresponding to 0.55% (1.00 atom) of "active" hydrogen. Under similar conditions, the following results were obtained with other ketones : cyclopentanone, 0.15; cycloheptanone, 0.53; isophorone, 0.28; 1-acetylcyclohexene, 0.31.

Dehydration of the Dimer.—(a) An intimate mixture of the dimer (0.77 g.) and anhydrous oxalic acid (1.54 g.) was heated for 2 hr. on the steam-bath and then extracted with ether. The ether solution was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and distilled, giving a mixture [of 1-acetyl-2 : 4 : 6 : 6-tetramethylcyclohexa-1 : 3-diene (V) and 4-acetyl-1 : 5 : 5-trimethyl-3-methylenecyclohexene (VI)], b. p. 98°/12 mm., n_{D}^{25} 1.4892 (Found : C, 80.3; H, 10.2. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.8; H, 10.2%). Ultraviolet light absorption in EtOH : Max. at 2360 (ϵ 4000), 2800 (ϵ 2000), and 3020 Å (ϵ 1000). Taking ϵ at 2360 Å as 9000 for pure (VI) (see below), this corresponds to a mixture of about 55% of (V) and 45% of (VI).

(b) The dimer (2.0 g.) and a trace of iodine were heated at 0.2 mm. As soon as the dimer had melted, a vigorous reaction took place and the mixture was distilled at ca. 75°. The product was dissolved in ether, washed with aqueous sodium thiosulphate, and dried (Na_2SO_4). Distillation gave 4-acetyl-1 : 5 : 5-trimethyl-3-methylenecyclohexene (VI) (1.2 g.), b. p. 104°/15 mm., n_{D}^{17} 1.4942, λ_{max} , 2360 Å (ϵ 9000 in EtOH) (Found : C, 80.3; H, 10.2%).

4-1'-Hydroxyethyl-1 : 5 : 5-trimethyl-3-methylenecyclohexene (VII).—The dimer (0.5 g.) in ether (20 ml.) was treated with lithium aluminium hydride (1.1 g.) in ether (20 ml.) at room

temp. After 3 hr., saturated aqueous ammonium chloride (15 ml.) was added, the precipitate was filtered off and washed with ether, and the combined ether solution was dried (Na_2SO_4) and distilled, giving the *alcohol*, b. p. $76^\circ/15$ mm., n_D^{25} 1.4770, λ_{max} 2360 Å (ϵ 8000 in EtOH) (Found : C, 79.7; H, 11.2. $\text{C}_{12}\text{H}_{20}\text{O}$ requires C, 79.9; H, 11.2%). Infrared absorption (liquid film) : ν_{max} 3380 (s, hydrogen-bonded O-H stretching), 1647 (m, C=C stretching), 882 (s, >C=CH_2), 828 (m), and 792 (m, >C=CH^-) cm^{-1} .

2-1'-Hydroxyethyl-1 : 3 : 3 : 5-tetramethylcyclohexanol (VIII) (with D. HUGHES).—2-Acetyl-1 : 3 : 3 : 5-tetramethylcyclohexan-1-ol (0.5 g.) was reduced with lithium aluminium hydride (1.1 g.) in ether at room temperature. After 3 hr., saturated aqueous ammonium chloride (15 ml.) was added and the ether layer was separated, washed with *N*-sulphuric acid and water, dried (Na_2SO_4), and evaporated, giving the *diol* (0.47 g.), m. p. 101–102°, raised to 104° by crystallisation from light petroleum (b. p. 60–80°) (Found : C, 71.9; H, 12.2. $\text{C}_{12}\text{H}_{24}\text{O}_2$ requires C, 71.95; H, 12.1%).

2 : 3 : 4 : 6-Tetramethylacetophenone (XI).—(a) The dimer (0.80 g.), tetrachloro-1 : 2-benzoquinone (5.0 g.), and dry benzene (6 ml.) were heated under reflux for 20 hr. Light petroleum (30 ml.; b. p. 40–60°) was then added and the mixture was kept overnight at room temperature and filtered. The solution was concentrated to about 10 ml. and chromatographed on alumina, with benzene as eluant. Distillation of the eluate gave 2 : 3 : 4 : 6-tetramethylacetophenone (0.42 g., 59%), n_D^{25} 1.5256, λ_{max} 2150 Å (ϵ 10,500), λ_{inf} 2450 (ϵ 2000) and 2780 Å (ϵ 800 in EtOH). The infrared spectrum was indistinguishable from that of the authentic specimen described below. Oxidation of the ketone (0.23 g.) with potassium hypochlorite followed by hydrolysis, as below, gave unchanged material (0.16 g.) and 2 : 3 : 4 : 6-tetramethylbenzoic acid (0.03 g., 15% or 43% on unrecovered ketone), m. p. and mixed m. p. 165°.

(b) Acetic anhydride (14 g.) was added slowly to a stirred mixture of *isodurene* (15 g.; b. p. 84–87°/17 mm., n_D^{25} 1.5112, prepared¹⁴ from mesitylene), carbon disulphide (45 ml.), and freshly ground aluminium chloride (33 g.). After 30 min. at 80° the mixture was added to excess of ice, the carbon disulphide was allowed to evaporate, and the residue was extracted with ether. The ether extract was washed successively with water, 2*N*-sodium hydroxide, and water, dried (Na_2SO_4), and distilled, giving 2 : 3 : 4 : 6-tetramethylacetophenone (12 g., 61%), b. p. 135–137°/16 mm. After redistillation, it had b. p. 74°/0.3 mm., n_D^{21} 1.5248, λ_{max} 2160 Å (ϵ 10,500), λ_{inf} 2450 (ϵ 2000) and 2780 Å (ϵ 800) in EtOH (Found : C, 81.7; H, 9.2. Calc. for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.8; H, 9.15%) (Smith and Guss¹⁵ give b. p. 135–137°/16 mm.). Infrared absorption (liquid film) : ν_{max} 3360 (w, C=O stretching overtone), 2915 (s, C-H stretching), 1731 (vs, C=O stretching), 1604 (w), 1565 (w), 1447 (m), 1418 (m), 1400 (m), 1379 (m), 1350 (s), 1293 (m), 1255 (s), 1141 (s), 955 (m), 863 (m), and 742 (w) cm^{-1} .

Unchanged ketone was recovered after refluxing with 2 : 4-dinitrophenylhydrazine and hydrochloric acid in aqueous ethanol for 2 hr. (cf. ref. 11) and with hydroxylamine hydrochloride and sodium acetate in aqueous ethanol for 6 hr. An unstable oxime, m. p. 148° (no analytical data), was reported by Claus and Foecking.¹⁶

The ketone (5 g.) was added, with vigorous stirring, to aqueous potassium hypochlorite (9 g.) in water (70 ml.) at 55°. After overnight stirring, the excess of hypochlorite was destroyed by sodium hydrogen sulphite, and the mixture was extracted with ether. The solvent was removed and the residue was refluxed overnight with 2*N*-sodium hydroxide (150 ml.). The unchanged ketone (3.2 g.) was separated and the aqueous layer was acidified with hydrochloric acid. The precipitate was filtered off and extracted with ether. Evaporation and crystallisation from light petroleum (b. p. 60–80°) gave 2 : 3 : 4 : 6-tetramethylbenzoic acid¹⁷ as prisms (0.8 g., 16% or 44% on unrecovered ketone), m. p. 165°.

Dimerisation of 3-Methylbut-2-enal.—The aldehyde (1.8 g.) in ether (25 ml.) was stirred overnight with finely divided lithium (0.07 g.) under nitrogen. Saturated aqueous ammonium chloride was added, the two layers were separated, and the aqueous layer was acidified and extracted with ether. The combined ether solution was dried (Na_2SO_4) and distilled, giving 4-formyl-1 : 5 : 5-trimethylcyclohexa-1 : 3-diene (0.8 g.), b. p. 80°/20 mm.; n_D^{20} 1.5000. This furnished a 2 : 4-dinitrophenylhydrazone which after chromatography on alumina in benzene-ethanol and crystallisation from ethyl acetate-light petroleum (b. p. 80–100°) had m. p. 200–201°, λ_{max} 4030 Å (ϵ 30,000 in CHCl_3) (Found : C, 58.4; H, 5.6; N, 16.8. $\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_4$ requires C, 58.2; H, 5.5; N, 17.0%).

¹⁴ *Org. Synth.*, 1931, **11**, 24, 66.

¹⁵ Smith and Guss, *J. Amer. Chem. Soc.*, 1937, **59**, 804.

¹⁶ Claus and Foecking, *Ber.*, 1887, **20**, 3097.

¹⁷ Gattermann, *Ber.*, 1899, **32**, 1116.

1-Methyl-3-methylenecyclohexene (with Dr. O. H. WHEELER).—3-Methylcyclohex-2-enone¹⁸ (8 g.) in ether (100 ml.) was added to methylmagnesium bromide (from methyl bromide, 6.5 ml., and magnesium, 2.4 g.) in ether (100 ml.) at 0°. After 1 hr. at room temperature, aqueous ammonium chloride was added and the ether layer was separated, dried, and distilled, giving 1 : 3-dimethylcyclohex-2-enol (9.2 g., 100%), b. p. 25—26°/1 mm., n_D^{19} 1.4764 (Found : C, 77.0; H, 11.0. C₈H₁₄O requires C, 76.1; H, 11.2%).

The alcohol (4.2 g.) in dry pyridine (10 ml.) was treated with phosphorus oxychloride (8 ml.) in dry pyridine (20 ml.) with cooling. After the mixture had attained room temperature, it was heated on the steam-bath for 30 min. and then poured on excess of ice. The resulting mixture was extracted with *n*-pentane, and the extract was washed with 2*N*-hydrochloric acid and water, dried (Na₂SO₄), and distilled, giving 1-methyl-3-methylenecyclohexene (2.3 g., 62%), b. p. 135—136°, n_D^{22} 1.4732, λ_{\max} 2280 (ϵ 9500 in EtOH) (Found : C, 88.5; H, 11.4. C₈H₁₂ requires C, 88.8; H, 11.2%). Haworth¹⁹ gives b. p. 135—136°, n_D^{20} 1.4856, for a diene which he obtained directly from the reaction of the ketone with methylmagnesium iodide and formulated as 1 : 3-dimethylcyclohexa-1 : 3-diene.

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¹⁸ Smith and Rouault, *J. Amer. Chem. Soc.*, 1943, **65**, 631; Bowman, Ketterer, and Dinga, *J. Org. Chem.*, 1952, **17**, 563.

¹⁹ Haworth, *J.*, 1913, **103**, 1242.
