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## Properties of 4,4-Dimethylcyclopent-2-enone: Methylation of the Enolate Ion: Base-catalysed and Photochemical Dimerisations

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(a) Methylation of the enolate ion of 4.4-dimethylcyclopent-2-enone (IV) occurs through the monocyclic valence tautomer, giving 4,4,5-trimethyl- and 4,4,5,5-tetramethyl-cyclopent-2-enone. The action of triphenylmethyl-sodium on (IV) is not proton abstraction, but Michael addition. A rationalisation for this is proposed. (b) Physical measurements are described which show the dimer of 4,4-dimethylcyclopent-2-enone, formed on treatment with base, to be *endo*-5,5,10,10-tetramethyltricyclo[5,2,1,0<sup>2,6</sup>]decane-3,8-dione (X). Its mode of formation is discussed. (c) Structures for the two photodimers of 4,4-dimethylcyclopent-2-enone are assigned on the basis of physical data and by analogy with the photodimers of cyclopent-2-enone itself.

Methylation of the Enolate Ion.—Methylation of the enolate ion (I) of the cyclohepta-2,4-dienone, eucarvone, is reported <sup>1</sup> to give the bicyclic product (II), $\dagger$  probably via the bicyclic anion (III). Steric hindrance to the

approach of the alkylating agent at C-7 of the monocyclic anion due to the *gem*-dimethyl group at C-6 was proposed as a rationalisation for the preferred reaction through

<sup>1</sup> E. J. Corey and H. J. Burke, J. Amer. Chem. Soc., 1956, 78, 174. <sup>2</sup> A. J. Bellamy and G. H. Whitham, Tetrahedron, 1968, 24,

† It has been shown that (II) is not formed exclusively, but that alkylation at C-7 in eucarvone accounts for up to 25% of the alkylation products.<sup>2,3</sup>

the valence tautomer of (I), *i.e.* the bicyclic anion  $(III).^4$ 



In the light of this, the alkylation of the enolate ion (V) of 4,4-dimethylcyclopent-2-enone (IV), the 5-membered ring analogue of eucarvone, was studied. Alkylation at C-5 in (IV) might be slow owing to the presence of the *gem*-dimethyl group at C-4, and might result in alkylation of the less stable, valence tautomer of (V), *i.e.* the bicyclic anion (VI), giving bicyclo[2,1,0]pentan-2-one derivatives.

However, methylation of the anion (V) was found to proceed through the monocyclic form; no evidence was obtained for the formation of bicyclic derivatives. Treatment of 4,4-dimethylcyclopent-2-enone (IV) with a large excess of sodium hydride and methyl iodide gave initially 4,4,5-trimethylcyclopent-2-enone (VII), which was converted into 4,4,5,5-tetramethylcyclopent-2-enone (VIII). The methylation conditions (see Experimental section) were chosen so as to minimise the base-catalysed dimerisation reaction of (IV) described later; under these conditions methylation of the anion occurs faster than reaction with another molecule of (IV).

The observed results are not unexpected in view of the Woodward-Hoffmann selection rules <sup>5</sup> for concerted electrocyclic reactions. Application of these rules to the cyclopentadiene system predicts that thermal valence tautomerism of cyclopentadiene derivatives into bi-

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cyclo[2,1,0]pentene derivatives by the symmetryfavoured conrotatory process, would be sterically prohibited owing to the small size of the ring.\* Thus (V) would not be expected to isomerise into (VI) under the conditions used.† Nevertheless, the ready formation of (VIII) is surprising, since molecular models suggest that severe non-bonded interactions probably exist between the two gem-dimethyl groups.

In preliminary experiments it was discovered that triphenylmethylsodium reacts with (IV), not as a base, but as a nucleophile. The product, (IX), is formed by the Michael addition of the triphenylmethyl anion to the  $\alpha\beta$ -unsaturated ketone. This is surprising because non-bonded interaction between the C-4 methyl groups and the attacking species would appear to be more severe for nucleophilic attack at C-3 than for nucleophilic attack on a hydrogen at C-5, since closer approach is required for the formation of a C-C bond than for abstraction of a proton.

However, in the transition state for both types of reaction there will be little bond formation, since both processes will be highly exothermic and the transition state structures will resemble the reactants. One rationalisation of the preferred reaction at C-3 is that the site of reaction will be largely entropy-controlled, and that alignment of the dipoles of the  $\alpha\beta$ -unsaturated ketone and the triphenylmethylsodium ion pair prior to reaction will cause the triphenylmethyl anion to be on the C-3 side of the *gem*-dimethyl group. For reaction at C-5 to occur, the triphenylmethyl anion would need to migrate over a C-4 methyl group, and this would increase the energy of the partially stabilised system.

An alternative possibility, that the formation of (V) could be reversible and the formation of (IX) irreversible, is ruled out by the observation<sup>8</sup> that the reaction between the triphenylmethyl anion and a ketone to form an enolate ion is kinetically controlled, *i.e.* irreversible under these conditions, in the absence of excess of ketone.

A further example of the Michael addition of a strong base to an  $\alpha\beta$ -unsaturated ketone occurs in the reaction between fluoroenylsodium and mesityl oxide in ether,<sup>9</sup> although in this case the results suggest that both Michael addition and proton abstraction occur, the latter predominating.

Base-catalysed Dimerisation.—During the study of the alkylation of the enolate ion of 4,4-dimethylcyclopent-2-enone, it was found that those conditions which only slowly converted the free ketone into its conjugate base resulted in the formation of a complex mixture. Only one of the products has been isolated and characterised.

- <sup>6</sup> J. I. Brauman and D. M. Golden, J. Amer. Chem. Soc., 1968, 90, 1920. 7 J. J. Brauman, L. E. Ellis, and E. E. van Tamelen, J. Amer.
- <sup>7</sup> J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, J. Amer. Chem. Soc., 1966, **88**, 846.
- <sup>8</sup> H. O. House and B. M. Trost, J. Org. Chem., 1965, **30**, 1341.
  <sup>9</sup> H. France, P. Maitland, and S. H. Tucker, J. Chem. Soc., 1937, 1739.

<sup>\*</sup> The symmetry-' forbidden' thermal disrotatory isomerisation of bicyclo[2,1,0]pentene into cyclopentadiene is reported to have an activation energy of 26 kcal./mole in the gas phase ( $t_1$  40 hr. at room temp.). Relief of strain in the transition state is suggested to be responsible for the fast isomerisation rate compared with those of bicyclo[3,2,0]hept-6-ene and bicyclo[4,2,0]oct-7-ene.<sup>6</sup> The rules predict that both the reverse and forward disrotatory reactions would be symmetry-' allowed' in the excited state, and experimental verification of the reverse (photochemical) reaction has been reported.<sup>7</sup>

<sup>&</sup>lt;sup>†</sup> The thermal interconversion of (I) and (III), a disrotatory process, would not be sterically restricted.

<sup>&</sup>lt;sup>4</sup> E. J. Corey, H. J. Burke, and W. A. Remers, J. Amer. Chem. Soc., 1956, 78, 180.

<sup>&</sup>lt;sup>5</sup> For discussion see S. I. Miller, *Adv. Phys. Org. Chem.*, 1968, **6**, 185.

Treatment of 4,4-dimethylcyclopent-2-enone with either potassium t-butoxide in t-butyl alcohol at  $25^{\circ}$  or sodium hydride in boiling dioxan gave *endo*-5,5,10,10-tetra-methyltricyclo[5,2,1,0<sup>2,6</sup>]decane-3,8-dione (X) in  $40^{\circ}_{0}$  yield.

The molecular weight (mass spectrum) indicated that (X) was a dimer of 4,4-dimethylcyclopent-2-enone. The i.r. spectrum showed the presence of two cyclopentanone carbonyl groups [ $\nu_{max}$ . (Nujol) 1745 and 1725 cm.<sup>-1</sup>;  $\nu_{max}$ . (CCl<sub>4</sub>) 1750 cm.<sup>-1</sup>], together with two bands assigned to different methylene groups adjacent to carbonyl groups [ $\nu_{max}$ . (CCl<sub>4</sub>) 1435 and 1420 cm.<sup>-1</sup>]. The latter had disappeard after base-catalysed deuterium exchange. Camphor has  $\nu_{max}$ . (Nujol) 1742 cm.<sup>-1,10</sup> The intensity of the u.v. absorption also suggested the presence of two carbonyl groups:  $\lambda_{max}$ . (EtOH) 300 mµ ( $\varepsilon$  57). Camphor has  $\lambda_{max}$ . (EtOH) 290 mµ ( $\varepsilon$  32),<sup>11</sup> and cyclopentanone has  $\lambda_{max}$ . (EtOH) 288—291 mµ ( $\varepsilon$  19).<sup>12</sup>

Structures considered for the dimer were (X), (XI), (XII), and (XIII), which might be formed by a double Michael reaction, and (XIV) and (XV), resulting from a

Diels-Alder reaction between a cyclopentadiene, the enolate ion of 4,4-dimethylcyclopent-2-enone, and the free ketone.

Structures (XI)—(XV) were eliminated by measurement of the dipole moment of the dimer:  $3.31 \pm 0.07$  D. In the calculation of the expected dipole moment for the structures (X)-(XV) (Dreiding models), the group moment of the carbonyl group was taken  $^{13}$  as 2.91 D, and all other bond moments were ignored. The following slight simplifications were made. For structures (X) and (XIV), the bonds C(2)-C(6) and C(8)-C(9)were taken as parallel, and the planes C(1)C(7)C(8)C(9)and C(2)C(3)C(5)C(6) were assumed to meet in a line parallel to C(2)-C(6). Also the ring C(2)-C(6) was assumed to be flat. For structures (XI) and (XV), the planes C(1)C(7)C(8)C(9) and C(2)-C(6) were assumed to be parallel, with the ring C(2)-C(6) flat. Also the bonds C(2)-C(6) and C(8)-C(9) were taken as parallel. Similar approximations were made for structure (XII). The calculated dipole moments were: (X)  $3.17 \pm 0.10$ (XI) 1.94, (XII)  $4.19 \pm 0.15$ , (XIII) 0.0 (centre of symmetry), (XIV) 5.42  $\pm$  0.02, and (XV) 4.77  $\pm$  0.06 p. The only structure with calculated dipole moment in agreement with the experimental value is (X). Structures (XII) and (XIII) are also inconsistent with the i.r. data, and with the methyl <sup>1</sup>H n.m.r. peaks (3 singlets; 3H, 3H, and 6H).

A complete analysis of the <sup>1</sup>H n.m.r. spectrum (100 MHz) of the non-deuteriated dimer (X) was not attempted; the main structural information was obtained from the  ${}^{1}H$  n.m.r. spectra of the products of deuterium exchange. The product obtained after treatment with boiling sodium methoxide in [2H]methanol for 20 hr. consisted mainly of  $[^{2}H_{5}]$ -species (86%) with only 2%  $[^{2}H_{6}]$ -species. In view of the simplicity of the  $^{1}H$  n.m.r. spectrum of this product, and the spin-decoupling results, by far the major  $[{}^{2}H_{5}]$ -species must be (XVI). The methyl groups gave three singlets at  $\tau$  9.00 (3H), 8.95 (3H), and 8.85 (6H). The remaining three protons gave signals at  $\tau$  7.77 [1H, q,  $J_{6.7}$  4.7,  $J_{1.7}$  1.8 Hz, C(7)-H], 7.68br [1H, C(1)-H,  $W_{\frac{1}{2}}$  3.8 Hz; coupling with H-7 only observed as broadening due to coupling of H-1 with deuterium], and 7.34br [1H, d,  $J_{6.7}$  4.7 Hz, C(6)-H]. The assigned coupling was confirmed by the appropriate spin-decoupling experiments. In particular, irradiation of the broad singlet at  $\tau$  7.68 caused the quartet at  $\div$  7.77 to collapse to a doublet ( $J_{6.7}$  4.7 Hz), confirming the long-range coupling between H-1 and H-7 (see ref. 14 for examples of long-range coupling in similar environments). The magnitude of the coupling constant between H-6 and H-7 further confirms the endo-configuration of the C(2)-C(6) ring in (X).\* Models indicate that the dihedral angle between the exo-hydrogen at



<sup>\*</sup> Reduction of (X) gave a single diol, as might be expected for the *endo*-isomer, but not for the *exo*-isomer (XI).

<sup>&</sup>lt;sup>10</sup> J. Modiano, Ann. Chim. (France), 1955, **10**, 563.

<sup>&</sup>lt;sup>11</sup> S. F. Marsocci and S. MacKenzie, J. Amer. Chem. Soc., 1959, **81**, 4513.

<sup>&</sup>lt;sup>12</sup> J. M. Conia, C. Nevot, and P. Gosselin, *Bull. Soc. chim. France*, 1959, 1511.

<sup>&</sup>lt;sup>13</sup> F. V. Brutcher, T. Roberts, S. J. Barr, and N. Pearson, J. Amer. Chem. Soc., 1959, **81**, 4915.

<sup>&</sup>lt;sup>14</sup> S. Sternhell, Rev. Pure Appl. Chem. (Australia), 1964, 14, 15.

C-6 and the bridgehead hydrogen at C-7 in structure (X) is  $40^{\circ}$ , and from the relation between dihedral angle and coupling constant shown by Karplus,<sup>15</sup> the expected coupling constant between these two hydrogens is 4.7 Hz, as observed. For the exo-isomer (XI), in which the corresponding dihedral angle would be 80°, the expected coupling constant is 0 Hz. The coupling constants between the bridgehead hydrogen and the adjacent exoand endo-hydrogens in camphane derivatives are 4.0-4.4 and 0 Hz, respectively (dihedral angles 44 and 79° respectively).<sup>16</sup>

Deuterium exchange for a much longer period (1770 hr.) resulted in the incorporation of six deuterium atoms (78%). The <sup>1</sup>H n.m.r. spectrum of the product showed that the quartet at  $\tau$  7.77, observed after 20 hr. exchange, had almost completely disappeared. Thus the sixth deuterium was positioned at C-7. The lower field spectrum then became two singlets at  $\tau$  7.68 [1H, C(1)-H,  $W_{\frac{1}{2}}$  2·4 Hz] and 7·36 [1H, C(2)-H].

A probable mechanism for the formation of (X) from 4,4-dimethylcyclopent-2-enone on treatment with base involves two Michael addition reactions, without isomerisation of the intermediate anion, as shown in the Scheme:



Since (X) was isolated in only 40% yield, and the nature of the other products was not investigated, it would be unwise to speculate on reasons for the formation of the observed stereochemistry. The incorporation of deuterium at C-7 probably occurs by a reversal of the second step in the formation of (X), *i.e.* (XVIII)  $\rightarrow$  (XVII), rather than direct enolisation of the 8-carbonyl group towards C-7, violating Bredt's rule. Exchange of the hydrogen at C-7 while in the open form (XVII), followed by recyclisation to (XVIII), appears more reasonable.

Photodimerisation.-Ultraviolet irradiation of 4,4-dimethylcyclopent-2-enone gave two photodimers, with structures analogous to the two photodimers of cyclopent-2-enone itself.<sup>17</sup> Structures (XIX) and (XX), assigned to the photodimers m.p. 171.5-173.5° and 93—94° respectively, are supported by the following The i.r. spectrum for both isomers showed a data.

strong carbonyl absorption,  $\nu_{max.}$  1750 cm.  $^{-1},$  characteristic of a saturated cyclopentanone, together with a band at 1420 cm.<sup>-1</sup> assigned to a methylene adjacent to a carbonyl group. Base-catalysed deuterium exchange of (XIX) and (XX) resulted in the incorporation of a maximum of six deuterium atoms. The band at 1420 cm.<sup>-1</sup> was absent from the spectrum of the exchange products. The molecular weights of (XIX) and (XX) were twice that of 4,4-dimethylcyclopent-2-enone.



The <sup>1</sup>H n.m.r. spectrum (60 MHz) of (XIX) in deuteriochloroform showed peaks at  $\tau$  8.80 and 9.05 (each s, 10- and 5-Me), 7.42 and 7.96 [each d,  $J_{gem}$  16.8 Hz,  $C(9)H_2$  and  $C(4)H_2$ ], and a simplified  $A_2X_2$  system  $(J_{1.6} = J_{2.7} = 0): \tau 7.07$  [q,  $J_{2.6}$  6·1,  $J_{1.2}$  3·1 Hz, C(2)and C(7)-H] 7.81 [m, coincident with one of the bands of the 4- and 9-methylene absorption, C(1)- and C(6)-H]. The larger coupling constant was assigned to the ciscyclobutane protons  $[J_{cis}: J_{trans} > 1 \text{ (ref. 18)}].$  Eaton reports 5.4 and 2.7 Hz for the coupling constants between vicinal cyclobutane protons in cis, anti, cis-tricyclo- $[5,3,0,0^{2,6}]$ deca-4,9-diene-3,8-dione.<sup>17a</sup> The absorption due to the protons at C-2, C-4, C-7, and C-9 disappeared on deuterium exchange, leaving the signals of the C-1 and C-6 protons as a singlet at  $\tau$  7.84. In benzene, the absorption due to the protons at C-1 and C-6 still coincided with part of the 4- and 9-methylene absorption.

The <sup>1</sup>H n.m.r. spectrum (60 MHz) of (XX) (in benzene) was simplified by the chemical equivalence of the protons at C-1 and C-2, and C-6 and C-7, and showed peaks at  $\tau$  9.29 and 9.41 (each s, 5- and 8-Me), 7.92 and 8.24 [each d,  $J_{\text{gem}}$  17.6 Hz, C(4)H<sub>2</sub> and C(9)H<sub>2</sub>], and a simplified  $A_2X_2$  system ( $\delta_{AX}$  22 Hz,  $J_{1,2} = J_{6,7} = J_{1,6} = J_{2,7} = 0$ ):  $\tau$  7.70 and 8.10 (each d, 1- and 2-H and 6- and 7-H,  $J_{1.7} = J_{2.6} = 5$  Hz). The absorption due to protons at C-1, C-2, C-4, and C-9 disappeared on deuterium exchange, leaving the signals of the C-6 and C-7 protons as a singlet at  $\tau 8.07$ . In deuteriochloroform, the protons at C-1, C-2, C-6, and C-7 have the same chemical shift  $[\tau 7.49 (s)]$  and hence no coupling was

<sup>&</sup>lt;sup>15</sup> M. Karplus, J. Chem. Phys., 1959, **30**, 11.

<sup>&</sup>lt;sup>16</sup> F. A. L. Anet, Canad. J. Chem., 1961, 39, 789.

P. E. Eaton, J. Amer. Chem. Soc., 1962, 84, (a) 2344; (b)
 2454; (c) P. E. Eaton and W. S. Hurt, *ibid.*, 1966, 88, 5038.
 <sup>18</sup> H. Weitkamp and F. Korte, *Tetrahedron*, 1966, Suppl. 7,

p. 75.

observed. The methyl groups gave two singlets at  $\tau$ 8.86 and 9.05, and the methylene protons gave two doublets ( $J_{\text{gem}}$  17.6 Hz) at  $\tau$  7.49 and 7.97.

Further evidence for the  $\gamma$ -diketone group in (XX) was obtained by treatment with lithium in liquid ammonia, followed by oxidation. Under these conditions the 1,2-bond was broken to give (XXI). The structure of (XXI) was supported by the following data. Its i.r. spectrum showed bands characteristic of a saturated cyclopentanone,  $v_{max}$  1750 cm.<sup>-1</sup>, and of a methylene adjacent to a carbonyl group,  $v_{max}$  1410 cm.<sup>-1</sup>. The latter had disappeared after base-catalysed deuterium exchange. The mass spectrum of the deuteriated product indicated that a maximum of eight deuterium atoms were incorporated. The molecular weight of (XXI) was 222.

The <sup>1</sup>H n.m.r. spectrum (60 MHz) of (XXI) in carbon tetrachloride showed peaks at  $\tau$  8.81 and 9.12 (each s,  $4 \times Me$ ), 7.97 [s, C(4)- and C(4')-H<sub>2</sub>], and 7.90 [s, C(2)and C(2')-H<sub>2</sub> and C(1)- and C(1')-H]. The absorption due to protons at C-4, C-4', C-2, and C-2', had disappeared after deuteration, leaving the methine proton signals as a singlet at  $\tau$  7.89.

The reductive cleavage of the 1,2-bond in (XX) indicated a 1,4-relation of the two carbonyl groups, a suitable orientation of the 1,2-bond for overlap with  $\phi$  orbitals at C-3 and C-10, and strain in the 1,2-bond. Photodimer (XIX) did not undergo a reductive ring cleavage under the same conditions.

By analogy with the photodimers of cyclopent-2-enone,<sup>17a</sup> structures (XIX) and (XX) were assumed to have a cis, anti, cis-configuration. On this assumption, (XXI) would be the (+)-stereoisomer.

## EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were determined either at 100 MHz with a Varian HA 100 spectrometer, or at 60 MHz with a Perkin-Elmer R10 spectrometer. Chemical shifts are relative to tetramethylsilane. Unless otherwise stated, light petroleum refers to the fraction b.p. 40-60°.

4,4-Dimethylcyclopent-2-enone (IV).---This compound was prepared by the method of Rouse and Tyler.<sup>19</sup> The final step involving dehydration of 2-hydroxy-4,4-dimethylcyclopentanone was accomplished with polyphosphoric acid, but the product was not pure 4,4-dimethylcyclopent-2-enone as reported.<sup>19</sup> 2-Hydroxy-4,4-dimethylcyclopentanone  $(12 \cdot 0 \text{ g.})$  was added with cooling to polyphosphoric acid [172 g.; prepared by heating a mixture of phosphorus pentoxide (90 g.) and 90% orthophosphoric acid (47 ml., 82 g.) at 100° for 36 hr.; a small amount of phosphorus pentoxide remained undissolved] and the mixture was kept at 25° for 12 hr. After 10 hr. at 100°, the mixture was kept at  $25^{\circ}$  for a further 36 hr. Ice (200 g.) was added, and the product (6.9 g., 67%) was isolated with ether (5  $\times$ 75 ml.); it was a mixture of 4,4-dimethylcyclopent-2-enone (61%) and 2,3-dimethylcyclopent-2-enone (39%), which

was separated by preparative g.l.c. The former had  $\nu_{\rm max.}$  (film) 1720 and 1590 cm.<sup>-1</sup>,  $\lambda_{\rm max.}$  (EtOH) 218.5 (e 13,000) and 315 (40) mµ. Cyclopent-2-enone has  $\lambda_{max}$ . (EtOH) 218 mµ (ε 9,500),20 and 311 mµ (ε 26).21 The 2,4-dinitrophenylhydrazone had m.p. 164.5-166° (from ethanol as deep red crystals) (lit.,<sup>19</sup> 163-164°). The <sup>1</sup>H n.m.r. spectrum (60 MHz; CCl<sub>4</sub>) showed peaks at  $\tau$  8.78 [s, C(4)-Me<sub>2</sub>], 7.89 [s, C(5)-H<sub>2</sub>] 4.11 [d, J 5.6 Hz, C(2)-H], and 2.65 [d, J 5.6 Hz, C(3)-H].

The 2,3-dimetnylcyclopent-2-enone had  $v_{max}$  (film) 1700 and 1655 cm.<sup>-1</sup>,  $\lambda_{max}$  (EtOH) 233.5 ( $\epsilon$  14,900) and 299.5 (64) m $\mu$ . The complete i.r. spectrum was identical with that reported.<sup>22</sup> Other reported data are:  $v_{max}$ . (CCl<sub>4</sub>) 1701 and 1656 cm.<sup>-1</sup>,  $\lambda_{max}$ . (EtOH) 234 m $\mu$  ( $\varepsilon$  13,580); <sup>23</sup> and  $\lambda_{max}$  (EtOH) 235 ( $\epsilon$  14,450) and 300 (58) m $\mu$ .<sup>22</sup> The 2,4-dinitrophenylhydrazone had m.p. 224-226° (from chloroform-ethanol as deep red crystals) (lit.,<sup>24</sup> 226-227°; lit.<sup>22</sup> 234-234.5°), and the semicarbazone had m.p. 243-243.5° (from ethanol) (lit.,<sup>22</sup> 246-248°). The <sup>1</sup>H n.m.r. spectrum (60 MHz; CCl<sub>4</sub>) showed absorption at 7 8.38 [m, C(3)-Me], 7.98 [s, C(2)-Me], and 7.35-8.05 [m, C(4)and  $C(5)-H_2$ , identical with that reported,<sup>23</sup> except that no coupling was reported for the C-3 methyl.

Treatment of 4,4-dimethylcyclopent-2-enone with (a)polyphosphoric acid as before, or (b) polyphosphoric acid containing the same proportion of water as would be liberated in the dehydration, did not produce any 2,3-dimethylcyclopent-2-enone. The latter probably arises by dehydration of the allylic alcohol formed by enolisation of 2-hydroxy-4,4-dimethylcyclopentanone, accompanied by migration of the methyl group.

Methylation of 4,4-Dimethylcyclopent-2-enone.-The ketone (110 mg., 1 mmole) in dioxan (1.0 ml.) was added dropwise (2 drops per min.) with stirring under nitrogen to a suspension of sodium hydride (10 mmoles) in dioxan (4.0 ml.) under reflux during 1.5 hr. The mixture was heated under reflux for a further 1.5 hr., and then cooled to 20°. Methyl iodide (1.5 ml., 22.5 mmoles) was added, and the mixture was stirred at 20° for 4 days. More methyl iodide (1.0 ml.) was added after 2 days. Glacial acetic acid (1.0 ml.) was then added, followed by brine (20 ml.), and the product was extracted with ether  $(\times 2)$ . The extract was washed with aqueous sodium hydrogencarbonate, aqueous sodium thiosulphate, and finally brine. Evaporation of the dried solution gave 4,4,5,5-tetramethylcyclopent-2-enone (VIII) as the only product (>99%)(purified by preparative g.l.c.),  $v_{max.}$  (CCl<sub>4</sub>) 1715 cm.<sup>-1</sup>. λ<sub>max.</sub> (EtOH) 220.5 mμ (ε 7900) (Found: C, 77.65; H 10.05. C<sub>9</sub>H<sub>14</sub>O requires C, 78.2; H, 10.2%), M (mass spectrum), 138, as a low-melting solid,  $\tau$  (60 MHz; CCl<sub>4</sub>) 9.04 and 8.93 [each s, C(5)- and C(4)-Me<sub>2</sub>], 4.08 [d, J 5.8 Hz, C(2)-H], and 2.70 [d, J 5.8 Hz, C(3)-H].

The methylation at 20° was followed by g.l.c. of a mixture of the ketone, sodium hydride, and methyl iodide in dioxan, in the proportions used before, but without prior formation of the enolate anion. After 70 hr. the mixture contained 4,4-dimethyl-, 4,4,5-trimethyl-, and 4,4,5,5tetramethylcyclopent 2-enone in the ratio 1:11:8. The mixture was worked up at this stage, and 4,4,5-trimethylcyclopent-2-enone (VII),  $\nu_{max}$  (CCl<sub>4</sub>) 1715 cm.<sup>-1</sup>, was iso-

<sup>&</sup>lt;sup>19</sup> R. S. Rouse and W. E. Tyler, J. Org. Chem., 1961, 26, 3525. <sup>20</sup> W. M. Schubert and W. A. Sweeney, J. Amer. Chem. Soc., 1955, **77**, 2297.

<sup>&</sup>lt;sup>21</sup> H. S. French, J. Amer. Chem. Soc., 1952, 74, 514.

 <sup>&</sup>lt;sup>22</sup> W. Keller-Schierlein, M. Lj, Mihailovic, and V. Prelog, *Helv. Chim. Acta*, 1958, **41**, 220.
 <sup>23</sup> H. N. A. Al-Jallo and E. S. Waight, *J. Chem. Soc.* (B), 1966,

<sup>24</sup> S. Dev and C. Rai, J. Indian Chem. Soc., 1957, 34, 266.

lated by preparative g.l.c.;  $\tau$  (60 MHz; CCl<sub>4</sub>) 8.98 and 8.78 [each s, C(4)-Me<sub>2</sub>], 8.96 [d, J 7.3 Hz, C(5)-Me], 8.00 [q, C(5)-H], 4.06 [d, J 5.6 Hz, C(2)-H], and 2.70 [d, J 5.6 Hz, C(3)-H].

Methylation at ca.  $100^{\circ}$  with a mixture of sodium hydride and methyl iodide (10 and 15 mmoles respectively) also gave 4,4,5,5-tetramethylcyclopent-2-enone (96%).

Treatment of (IV) with Triphenylmethylsodium.-4,4-Dimethylcyclopent-2-enone (110 mg., 1 mmole) in dry ether (20 ml.) was added dropwise under nitrogen to a stirred solution of triphenylmethylsodium in ether (50 ml.; containing 6-7 mmoles of triphenylmethylsodium) at  $0^{\circ}$ during 30 min. The solution was kept at 0° for a further 1 hr., then poured into ether [25 ml.; containing acetic acid (0.5 ml.)]. Chloroform was added and the solution was shaken with 10% aqueous sodium carbonate then water. Evaporation of the dried solution left a yellow syrup which was chromatographed on alumina. Elution with benzeneether (49:1) gave triphenylmethane. Elution with benzene-ether (4:1) then ether gave 3,3-dimethyl-4-triphenylmethylcyclopentanone (IX) (332 mg., 94%), m.p. 155-155.5° [from light petroleum (b.p. 60–80°)],  $v_{max.}$  (CCl<sub>4</sub>) 1745 (C=O) and 1412 (CH<sub>2</sub> adjacent to C=O) cm.<sup>-1</sup>,  $\lambda$ (cyclohexane) 230 (£ 9800), 240 (7200), and 250 (2400) mµ,  $\lambda_{infl}$  260 ( $\epsilon$  1022) and 265 (910) mµ,  $\lambda_{sh}$  272 mµ ( $\epsilon$  575) (Found: C, 88.3; H, 7.9. C<sub>26</sub>H<sub>26</sub>O requires C, 88.1; H, 7.4%), M (mass spectrum) 354.

The same product was obtained, again in almost quantitative yield, by adding slightly more than 1 mmole of triphenylmethylsodium in ether to 4,4-dimethylcyclopent-2-enone in ether at 0°.

The ketone (IX) (90 mg.) was treated with a boiling solution of sodium methoxide in [<sup>2</sup>H]methanol [3·0 ml.; from sodium (30 mg.)] for 22 hr. Deuterium oxide (2·0 ml.) was added, and the methanol was evaporated at 20° *in vacuo*. The product was isolated with benzene. Evaporation of the dried extract gave the deuterium exchange product (85 mg.), m.p. 154·5—155·5°. The product showed new i.r. bands at  $v_{max}$ . (CCl<sub>4</sub>) 2230 and 2160 cm.<sup>-1</sup>, and the band at 1412 cm.<sup>-1</sup> in the spectrum of the original ketone was absent. The mass spectrum showed the following deuteriated species: [<sup>2</sup>H<sub>2</sub>] (5%), [<sup>2</sup>H<sub>3</sub>] (15%), [<sup>2</sup>H<sub>4</sub>] (80%).

The <sup>1</sup>H n.m.r. spectrum (60 MHz; CCl<sub>4</sub>) of (IX) showed absorption at  $\tau$  9.06 and 8.76 [each s, C(3)-Me<sub>2</sub>], 9.12 and 8.61 [each d,  $J_{gem}$  ca. 18 Hz, C(2)-H<sub>2</sub>], 7.0—7.8 [m, C(5)-H<sub>2</sub>, AB part of an ABX system,  $J_{gem}$  20,  $J_{4,5}$  9.4 and 2.1 Hz,  $|v_{AB}|$  16.0 Hz], 5.90 [m, C(4)-H, X part of an ABX system], and 2.4—3.1 (m, Ph<sub>3</sub>CH). The absorption due to protons at C-2 and C-5 disappeared on deuteriation, leaving the signal of the methine proton at C-4 as a singlet at  $\tau$  5.93.

endo-5,5,10,10-*Tetramethyltricyclo*  $[5,2,1,0^{2},^{6}]$  decane-3,8dione (X).—(a) Potassium t-Butoxide in t-Butyl Alcohol. 4,4-Dimethylcyclopent-2-enone (1.0 g.) was treated with potassium t-butoxide in t-butyl alcohol [20 ml.; from potassium (0.40 g.)] at 25° for 72 hr. The mixture was poured into ether (100 ml.), and the ethereal solution was washed with water (×2), 4N-hydrochloric acid, and brine. Evaporation of the dried solution gave a viscous liquid (1.02 g.). Extraction with boiling light petroleum (b.p.  $60-80^{\circ}$ ) (×2) effected a preliminary purification. The residue was a yellow gum. The extract was then chromatographed on silica gel (50 g.). Elution with light petroleum-ether (3:2) gave the diketone (0.40 g., 40%), m.p.  $89.5-91^{\circ}$  [from light petroleum (b.p. 60-80],  $\nu_{max}$ . (CCl<sub>4</sub>) 1750br,s, 1435, and 1420m cm.<sup>-1</sup>  $\nu_{max}$  (Nujol) 1745s and 1725s cm.<sup>-1</sup>  $\lambda_{max}$  (EtOH) 300 mµ ( $\varepsilon$  57) (Found: C, 76.8; H, 8.8. C<sub>14</sub>H<sub>20</sub>O<sub>2</sub> requires C, 76.3; H, 9.15%), *M* (mass spectrum) 220, as a white solid, pure by t.l.c. Elution with more polar solvents gave a viscous liquid, which was shown (t.l.c.) to be a mixture of products, and was not investigated further.

(b) Sodium Hydride. A mixture of 4,4-dimethylcyclopent-2-enone (0.25 g.) and sodium hydride (0.11 g.) in dioxan (10.0 ml.) under nitrogen was heated under reflux with stirring for 2.5 hr. It was then cooled and acetic acid (0.3 ml.) was added, followed by brine (100 ml.). The product was extracted with ether ( $\times$ 3), and the extract was washed with aqueous sodium hydrogen carbonate and brine. Evaporation of the dried solution gave the crude product, shown (t.l.c.) to be a mixture. The diketone (0.103 g., 41%), m.p. 91-92°, was isolated by chromatography on silica gel (20 g.).

Dipole moment of  $(\mathbf{X})$ .—The dipole moment was determined for a solution in benzene at 30°, and was calculated from  $\mu^2 = [27kT \ (a_{\epsilon} - a_n) \ M_2]/[4Nd_1 \ (z_1 + 2)^2]$ , where  $M_2$  = molecular weight of solute,  $d_1$  = density of solvent (benzene),  $z_1$  = dielectric constant of solvent,  $a_{\epsilon}$  = slope of  $\varepsilon_{12} - \varepsilon_1$  against  $w_2$  (weight fraction of solute  $4\cdot 3 \times 10^{-3}$  to  $12\cdot 9 \times 10^{-3}$ ),  $a_n$  = slope of  $n^2_{12} - n^2_1$  against  $w_2$  (n = refractive index). In this case  $a_{\epsilon} \gg a_n$ , and  $a_n$  was therefore ignored;  $a_{\epsilon} = 5\cdot 25 \pm 0\cdot 21$ ; thus  $\mu = 3\cdot 31 \pm 0\cdot 07$  D.

5,5,10,10-*Tetramethyltricyclo*[5,2,1,0<sup>2,6</sup>]*decane*-3,8-*diol.*— The diketone (X) (30 mg.) was treated with lithium aluminium hydride (30 mg.) in ether (10 ml.) under reflux for 2 hr. Isolation of the product gave the *diol* (26 mg.), m.p. 184·5—185° (from benzene) (Found: C, 74·5; H, 10·6.  $C_{14}H_{24}O_2$  requires C, 74·95; H, 10·8%), which gave one spot on t.l.c. Oxidation of the diol with 6N-chromic acid in AnalaR acetone for 1 hr. gave back the diketone.

Deuterium Exchange of (X).-The diketone (70 mg.) was treated with sodium methoxide in [2H]methanol [3.0 ml.; from sodium (30 mg.)] under reflux for the required period. Deuterium oxide (2.0 ml.) was added and the methanol was evaporated off at 20° in vacuo. The product was extracted with light petroleum (2  $\times$  10 ml.) and the extract was dried. Evaporation left the diketone (67 mg.), m.p.  $88.5-90.5^{\circ}$  [from light petroleum (b.p.  $60-80^{\circ}$ )]. The product showed new i.r. bands at 2240, 2225, and 2165 cm.<sup>-1</sup>, and the bands at 1435 and 1420 cm.<sup>-1</sup> of the original diketone were absent. The deuteriated species present in the product, determined by mass spectrometry, were as follows after 20 hr.:  $[{}^{2}H_{3}]$  (1%),  $[{}^{2}H_{4}]$  (11%),  $[{}^{2}H_{5}]$  (86%),  $[{}^{2}H_{6}]$  (2%); after 84 hr.:  $[{}^{2}H_{4}]$  (6%),  $[{}^{2}H_{5}]$  (80%),  $[{}^{2}H_{6}]$ (14%); after 1770 hr.;  $[{}^{2}H_{4}]$  (2%),  $[{}^{2}H_{5}]$  (19%),  $[{}^{2}H_{6}]$  $(78\%), [^{2}H_{7}] (1\%).$ 

Photodimerisation of 4,4-Dimethylcyclopent-2-enone.—Neat 4,4-dimethylcyclopent-2-enone (0.5 g.) was irradiated with the sunlight for 3 weeks, after which time the sample was crystalline. The product was separated into two components by chromatography on alumina. Elution with benzene-ether (49:1) gave 5,5,10,10-tetramethyltricyclo-[5,3,0,0<sup>2,6</sup>]decane-3,8-dione (XIX) (0.28 g., 56%), m.p. 171.5—173.5° [from benzene-light petroleum (b.p. 60— 80°)],  $v_{max}$  (CCl<sub>4</sub>) 1750s and 1420m cm.<sup>-1</sup> (Found: C, 76.25; H, 9.1. C<sub>14</sub>H<sub>20</sub>O<sub>2</sub> requires C, 76.3; H, 9.15%), M (mass spectrum) 220, which was pure by t.l.c.

Elution with benzene-ether (19:1-4:1) gave 5,5,8,8tetra methyltricyclo[5,3,0,0<sup>2,6</sup>]decane-3,10-dione (XX) (0.19 g., 39%), m.p. 93-94° (from light petroleum),  $\nu_{max}$  (CCl<sub>4</sub> 1750s and 1420m cm.<sup>-1</sup> (Found: C, 76·4; H, 8·85%), M (mass spectrum) 220, slightly impure by t.l.c. when first isolated.

Deuterium Exchange of (XIX) and (XX).—The diketone (65 mg.) was treated with a boiling solution of sodium methoxide in  $[^{2}H]$ methanol [6·0 ml.; from sodium (60 mg.)] for 16 hr. Deuterium oxide (4·0 ml.) was added, the methanol was evaporated off at 20° in vacuo, and the product was extracted with benzene. The products were purified by recrystallisation.

The mass spectrum of the product from (XIX) showed the following deuteriated species:  $[{}^{2}H_{4}]$  (2%),  $[{}^{2}H_{5}]$  (17%),  $[{}^{2}H_{6}]$  (81%). The i.r. spectrum showed new bands at 2240, 2160, and 2145 cm.<sup>-1</sup>, and the band at 1420 cm.<sup>-1</sup> for the original diketone was absent.

The mass spectrum of the product from (XX) showed the following deuteriated species:  $[{}^{2}H_{4}]$  (2%),  $[{}^{2}H_{5}]$  (18%),  $[{}^{2}H_{6}]$  (80%). The i.r. spectrum showed new bands at 2230 and 2160 cm.<sup>-1</sup>, and the band at 1420 cm.<sup>-1</sup> for the original diketone was absent.

Reduction of (XX) with Lithium in Liquid Ammonia.— The diketone (XX) (79 mg.) in liquid ammonia (50 ml.) was treated with lithium (250 mg.) and the mixture was left for 3 hr. Ammonium chloride was added until the blue colour was discharged, followed by ether (25 ml.) and water (25 ml.). The product was isolated by extraction with ether ( $\times$  2), and the extract was washed with 4N-hydrochloric acid and water. Evaporation of the dried solution gave a The crude product in AnalaR acetone (4.0 ml.) was oxidised with 6N-chromic acid (0.40 ml.) for 1 hr. Isolation of the product gave a viscous liquid (47 mg.). Separation by preparative t.l.c. [1 mm. thick silica gel; developed with chloroform-ethyl acetate (1:1), and detected with iodine] gave diketone (XX) (6 mg.) and 5,5,5',5'-tetramethyl-1,1'-bi(cyclopentyl)-3,3'-dione (XXI) (32 mg.), m.p.  $92\cdot5-94^{\circ}$  (from light petroleum),  $v_{max}$ . (CCl<sub>4</sub>) 1750s and 1410m cm.<sup>-1</sup> (Found: C, 76.0; H, 10.45. C<sub>14</sub>H<sub>22</sub>O<sub>2</sub> requires C, 75.65; H, 9.95%), M (mass spectrum) 222.

Deuterium exchange of (XXI) with sodium methoxide in [<sup>2</sup>H]methanol, as described before, gave a product which was shown by its mass spectrum to contain the following deuteriated species: [<sup>2</sup>H<sub>6</sub>] (7%), [<sup>2</sup>H<sub>7</sub>] (22%), [<sup>2</sup>H<sub>8</sub>] (71%). The i.r. band at 1410 cm.<sup>-1</sup> for (XXI) was absent, and new bands at 2230, 2160, and 2100 cm.<sup>-1</sup> were present.

Diketone (XX) was not reduced by zinc in acetic acid. Diketone (XIX) was recovered unchanged after treatment with lithium in liquid ammonia, followed by oxidation.

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