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Stereospecific Photoisomerisations of 6-Acetoxy-2,3,4,5,6-pentamethylcyclohexa-2,4-dienone

By M. R. Morris and A. J. Waring,* Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

U.v. irradiation of 6-acetoxy-2,3,4,5,6-pentamethylcyclohexa-2,4-dienone in ether or methanol gives *exo*-6-acetoxy-1,3,4,5,6-pentamethylbicyclo[3,1,0]hex-3-en-2-one, whose structure is established by degradation to tetramethylcyclopent-2-enone derivatives. Low-temperature spectroscopy and trapping experiments show the dienone to suffer stereospecific photochemical ring opening to a keten, which can be trapped by cyclohexylamine, and may isomerise to the bicyclohexenone in a stereospecific thermal bond-crossing reaction, or to the dienone by a thermal and probably also a photochemical reversion. The latter processes are strongly solvent-dependent.

In the preceding paper ¹ we showed that a 6-acetoxypenta-alkylcyclohexa-2,4-dienone undergoes photorearrangement to a bicyclo[3,1,0]hex-3-en-2-one by a highly stereoselective skeletal rearrangement. We now consider in more detail the analogous rearrangement of 6acetoxypentamethylcyclohexa-2,4-dienone (pentamethyl-o-quinol acetate) (I).

The quinol acetate (I) was made by lead tetra-acetate acetoxylation of pentamethylphenol in chloroform.² It has been reported to be obtained from a similar reaction in acetic acid.³ U.v. irradiation, through Pyrex glass, in dry or wet ether, or methanol solution, and isolation by careful crystallisation gave up to 80% of photoproduct (II). Analysis by g.l.c. of the crude photomixture from irradiations in wet ether indicated a yield of (II) greater than 70% at 90% conversion, but is complicated by the finding that (I) undergoes partial thermal rearrangement to its *para*-isomer (III) † under the g.l.c. conditions used. The volatile impurities are pentamethylphenol, unchanged quinol acetate, and two unidentified products (*ca.* 4%). Analyses by n.m.r.



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 $^{^+}$ Dienone (III) was prepared by acid-catalysed isomerisation of (I) (see Experimental section). It was previously obtained in the preparation of (I).³

and u.v. spectroscopy suggest 80-95% yields of (II). Irradiations in methanol gave about 70% of (II), 25% of (III), and traces of pentamethylphenol.

The bicyclo[3,1,0]hex-3-en-2-one structure of (II) is shown by its u.v. and i.r. spectra, and supported by the n.m.r. spectrum. Quartets (J ca. 1 Hz) at τ 7.98 and 8.43 are due to the 4- and 3-methyl groups, homoallylically coupled together, and a sharp peak at 7.98 due to acetate. The three remaining sharp peaks, at τ 8.73, 8.82, and 8.86, are assigned to the 6-, and 1- or 5-methyl groups.* Our assignments are supported by solventshift studies which will be reported separately.

It is necessary to locate the acetoxy-group in (II). Hydrolysis with dilute acid gave the ketone (IV) as the major product. I.r. peaks at 1652, 1710 cm⁻¹, and the u.v. spectrum $[\lambda_{max}, 241 \text{ nm} (\log \epsilon 3.94)]$ support the cyclopentenone structure. N.m.r. peaks at τ 8.12 and 8.24 (with homoallylic coupling), 8.18, 8.67, and 9.01 (d, I 7.5 Hz) are assigned to methyl groups at positions 3 and 2, acetyl, and the 4- and 5-methyl groups.⁺ Deuteriation with sodium carbonate in hexadeuterioacetone exchanges the 3-methyl and acetyl protons, but does not appreciably affect the 5-proton (τ 7.74, J 7.5 Hz). Our evidence for a 4- rather than 5-acetyl structure follows shortly. Hydrolysis of (II) under Zemplen conditions ¹² was carried out in the hope of producing the bicyclohexenol. This could not be isolated, but compound (IV) and its isomer (V) were given in a ca. 2:3ratio: the latter is shown by its spectra to be another acetyl-2,3,4,5-tetramethylcyclopent-2-enone, which could be a positional or geometric isomer of (IV). Interconversion of compounds (IV) and (V) occurred on (separate) treatment with a trace of sodium methoxide in methanol, giving a 5:4 ‡ equilibrium mixture. Although this result is consistent with the isomers being a *cistrans* pair it does not preclude the possibility that (V) is a 5-acetylcyclopent-2-enone (VI) which might equilibrate with (IV) as shown in the Scheme. Cyclopropyl acetates have been made by acetic anhydride trapping of the (formal) cyclopropoxide ions formed in this sort of way.¹³ However, the identical mass spectra of (IV) and (V) suggest stereoisomerism, and our later

Typical 2,3-dimethyleyclopent-2-enones have ν_{max} . 1650— 1695 and 1700—1720 cm⁻¹, and λ_{max} . 234—240 nm (log ε 4.04— 4.16), with n.m.r. peaks at τ 7.93—8.03 (3-Me), 8.30—8.40 (2-Me), 8.77—8.98 (4-Me), and 8.87—9.04 (5-Me).^{9,10} The high τ values of the acetyl and methyl peaks for (IV) and (V) deserve comment. Molecular models suggest that the acetyl protons should be shielded by the olefinic bond, over which they lie in some conformations. Similar shielding of isopropyl methyl protons (and the introduction of marked non-equivalence) in 4-isopropylcyclopent-2-enones has been discussed by Sorensen.11 In its more stable conformations the acetyl group should also shield the 3-methyl protons.

‡ Ratios are obtained from unstandardised g.l.c. peak areas, and are only approximate.

⁴ H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem.* Soc., 1966, 88, 1005; H. Hart and D. W. Swatton, *J. Amer. Chem. Soc.*, 1967, 89, 1874; D. W. Swatton and H. Hart, *J. Amer.* Chem. Soc., 1967, 89, 5075.

work supports this view. De Puy has shown that acidcatalysed ring-opening of cyclopropanols generally occurs with retention of stereochemistry at the newlyformed tetrahedral centre, whereas alkaline cleavage often occurs with inversion.¹⁴ Our finding that (IV) is the kinetic product from acid cleavage, and is slightly



more stable than (V), but that (V) is the predominant product of alkaline cleavage, suggests that (IV) is the cis(Ac,H)- and (V) the trans-isomer.

Vigorous alkaline hydrolysis of photoproduct (II) gave two major products in a ca. 9:1 ratio. The main, lower-boiling component was isolated and shown to be trans-2,3,4,5-tetramethylcyclopent-2-enone, identical with an authentic sample made by Nazarov cyclisation.¹⁵ The hydrolysis experiments show that the acetoxygroup in (II) occupies the 6-position. Removal of acetate to give (VII), then (IV) and (V), can be followed by cleavage of the β -diketone or vinylogous β -diketone function to give the tetramethylcyclopentenone. Hydrogenation of (IV) gave a mixture of three acetyltetramethylcyclopentanones which did not suffer acetyl loss, even under much more vigorous hydrolysis conditions than those used to convert (II) into tetramethylcyclopentenone. Thus compounds (IV) and (V) must be vinylogous, rather than genuine, β-diketones; the 4acetyl structures seem assured, and interconversion of

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⁹ H. N. Al-Jallo and E. S. Waight, J. Chem. Soc. (B), 1966, 73; A. J. Bellamy, J. Chem. Soc. (B), 1969, 449; W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, J. Org. Chem., 1968, 33, 566 4060.

¹⁰ (a) T. S. Sorensen, J. Amer. Chem. Soc., 1967, **89**, 3782; (b) P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, J. Amer. Chem. Soc., 1969, 91, 6404.

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 ¹² G. Zemplen and E. Pacsu, *Ber.*, 1929, **62**, 1613.
 ¹³ D. P. G. Hamon and R. W. Sinclair, *Chem. Comm.*, 1968, 890

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 ¹⁵ L. de Vries, J. Org. Chem., 1960, 25, 1838; U.S.P. 3,121,752/ 1964 (Chem. Abs., 1964, 60, 11,915h).

^{*} Data on 6-acetoxybicyclo[3,1,0]hexenones are absent from the literature. Polyalkyl analogues have peaks for 1-methyl at τ 8.53–8.90 (usually 8.74–8.90), 3-methyl at 8.29–8.46, 4-methyl τ 7.87–8.15, and 5-methyl at 8.55 to ca. 8.80.4-8

(IV) or (V) with (VII) according to the Scheme is excluded.*

The stereochemistry of (II) was investigated in a variety of ways. The n.m.r. peak assigned to the 6methyl group is at τ 8.73, which is an abnormally high value: the 1-methyl signals in 1-methyl- and 1,2,2trimethylcyclopropyl acetates are at $\tau 8.51-8.53$.¹⁹ We ascribe the high τ value to an *endo*-6-methyl group which is shielded by the olefinic and carbonyl double bonds of the bicyclohexenone ring system. Calculations of this shielding, by use of the assumptions of Tillieu or Pople,²⁰ suggest a value of 0.2-0.3 p.p.m. Analogous shielding of one 6-methyl group relative to the other is found in many 6-methylbicyclo[3,1,0]hex-3-en-2ones 4,8,21 and structurally analogous homofulvenes.22 In all the cases reported it is assumed that the endogroup is specially shielded.[†] The series of stereochemically unambiguous model compounds, the 'lumiproducts' from irradiation of steroidal 1,4-dien-3ones,^{5,23} and their bicyclic analogues ²⁴ all have endomethyl signals at a normal, rather than high, field for methyls attached to cyclopropane (τ 8.78–8.88). However, the other methyls on the bicyclohexenone ring in these model compounds generally absorb at relatively low field, and it may be that their other rings give a general deshielding. To help support the 6-endomethyl structure, compound (II) was reduced to the ketone (VIII) (stereochemistry of reduction unknown).



The 6-methyl n.m.r. signal moved downfield to τ 8.63.[‡] showing some residual shielding by the carbonyl group (calculated as ca. 0.10 p.p.m. by use of the assumptions mentioned above); the 1- and 5-methyl signals were virtually unchanged at 8.88-8.90.

Our attempts to establish the stereochemistry of compound (II) by chemical means would only give positive results if the acetate were endo instead of exo: all gave negative results, and we cannot attach much

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¹⁹ J. P. Freeman, J. Org. Chem., 1964, **33**, 1379; C. H. De Puy, W. C. Arney, and D. H. Gibson, J. Amer. Chem. Soc., 1968, **90**, 1830.

weight to them. However, we believe our n.m.r. deductions, supported by the work in the preceding paper¹ and other studies 26 point strongly to the endo-methyl structure.

The intermediacy of a keten (IX) in the conversion (I) \rightarrow (II) was suggested by trapping experiments and by the stereospecificity of the reaction.²⁷ Irradiation of compound (I) in ether containing cyclohexylamine gave two products in a ratio of ca. 90:1. Isolation by rather inefficient crystallisation gave the amide (X). The i.r. and n.m.r. spectra show the expected groups, and the assignments of structure and stereochemistry are supported in the following paper $^{\mathbf{28}}$ where a series of analogous amides is compared. Cyclohexylamine was shown not to produce the keten (X) by thermal reaction with quinol acetate (I) or photoproduct (II). Although the formation of an amide is consistent with the presence of a keten during the photolysis of (I) it neither unambiguously proves this, nor gives evidence that the keten is involved in the conversion (I) \longrightarrow (II). Lowtemperature irradiations were performed to establish these points. Irradiation of (I) in a clear glass of etherisopentane-ethanol (5:5:2 v/v) at 77 K, with observation of the u.v. spectrum, showed progressive loss of the quinol acetate spectrum and appearance of a new intense absorption below 250 nm. When the glass was warmed the spectrum changed until it was superimposable on that calculated for a 45:55 mixture of (I) and (II). Analysis by g.l.c. showed both compounds to be present, along with an unidentified product which may be the ethyl ester derived from keten (IX). Similar irradiation in a methylcyclohexane-isopentane (1:1) glass gave comparable results, except that on warm-up the spectrum reverted essentially to that of (I). Strong over-irradiation failed to remove all absorption due to (I), and we estimate that up to 40% may remain in this case. Irradiation of a mull of (I) in Nujol at 77 K, with observation of the i.r. spectrum, showed the appearance of a strong keten peak at 2095-2100 cm⁻¹, with diminution of the dienone 1650 peak relative to acetate at 1740 cm⁻¹. A steady state was reached, containing peaks due to both (I) and the keten. On warming the spectrum reverted to that of (I).

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²³ H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, Helv. Chim. Acta, 1962, 45, 2346; C. Ganter, F. Greuter, D. Kägi, K. Schaffner, and O. Jeger.

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^{*} This result confirms the expectation that the ion (VII) should suffer cleavage of the 1,6-rather than the 5,6-bond. 16,17 The opposite result was found for 6-acetoxy-3,5,6-triphenylbicyclo-[3,1,0]hex-3-en-2-one.18

[†] Note added in proof: Strong support for this view is now ailable. The epimer of 4,6-dimethyl-6-trichloromethylbiavailable. cyclo[3,1,0]hex-3-en-2-one which has its 6-methyl group specially shielded has been shown in an X-ray structure determination to have the 6-endo-methyl structure. (D. I. Schuster, K. V. Prabhu, S. Adcock, J. van der Veen, and H. Fujiwara, J. Amer. Chem. Soc., 1971, **93**, 1557.)

Brennan and Hill observed a similar downfield shift of an unambiguously endo-substituent.25

²⁰ The contours were taken from L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 2nd edn.,

DISCUSSION

Irradiation of quinol acetate (I) gives keten (IX) by a highly stereospecific process. Powerful nucleophiles (cyclohexylamine or dimethylamine, but not methanol or water) add to the keten at C-1,C-2. In the absence of such nucleophiles the keten may undergo internal cycloaddition, reverting to (I) or giving the bicyclohexenone (II) by another highly stereoselective process. Both cycloadditions occur thermally, and their relative rates are solvent dependent. The keten also appears to revert to (I) photochemically.

Since our original suggestion that ketens can be involved in the skeletal rearrangement of cyclohexa-2.4-dienones to bicyclo[3,1,0]hex-3-en-2-ones²⁷ experimental proof has been provided by other trapping and low-temperature i.r. studies.²⁹ Ketens are well known in the familiar ring-opening of cyclohexa-2,4-dienones.²⁸ The isolation of a single amide in this and other work ²⁸ could reflect stereospecific ring opening to the single keten (IX), or a non-stereospecific opening (giving both 5Z- and 5E-ketens) followed by preferential trapping of the 5*E*-isomer, or trapping of both ketens followed by photoisomerisation of the mixture of amides to give the more photostable product. Quinkert and his coworkers recently found this last mechanism to apply in the opening of 6-methyl-6-phenylcyclohexa-2,4-dienone: irradiation at 365 nm gave the Z- and E-ketens, then amides, in a ratio of 1:0.55. Although photostable at 365 nm, both amides were interconverted by 313 nm light, to give mainly the 5Z-isomer.³⁰ Our system does not show similar behaviour: the same amide is obtained by irradiation through Pyrex, or through filters which pass light of 366, 334, and 313 nm with relative intensities ca. 100:5:1 and have total cut-off at 310 nm.* It seems unlikely that the stereochemistry of the 5,6-bond should appreciably affect the attack of cyclohexylamine on the keten function in (IX), and the regularity of results in the following paper supports this view. We conclude that the ring-opening of (I) to (IX) is the stereoselective step.

The formation of a single bicyclohexenone (II) from the keten (IX) represents a stereoselective intramolecular addition, like a 'crosswise' Diels-Alder addition, with bonding of C-1 to C-5, and C-4 to C-6. Although we have no direct evidence on this point, a concerted process is assumed by analogy with other keten cycloaddition reactions.³¹ Molecular models show that the addition should be antarafacial on both the diene-keten and enol acetate components, $[\pi 2a + \pi 4a]$, and should be allowed,

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thermally, by the Woodward-Hoffmann rules.³² To effect the necessary overlap of the π -orbital lobes at C-4 and C-6, and at C-1 and C-5, the keten must be twisted from planarity. This probably explains the findings that only heavily substituted cyclohexa-2,4dienones lead to bicyclo[3,1,0]hex-3-en-2-ones on photolysis.⁴ The increasing ease of the keten-to-bicyclohexenone cyclisation in polar rather than non-polar media, seen in this and other work,²⁹ correlates with the known solvent effects on simple keten cycloadditions.³¹ Even though these are concerted, bonding to the keten carbonyl group is somewhat in advance of the second bond formation, and the transition state is relatively polar.

EXPERIMENTAL

Pentamethyl-o-quinol Acetate (I).-Pentamethylphenol (13.0 g) in chloroform (75 ml) was added slowly, with stirring, to a slurry of lead tetra-acetate (38 g) in chloroform (45 ml), with the temperature kept below 30° . After 1.5 h at 25° the orange solution was washed free of Pb^{II} with water, dried (MgSO₄), and evaporated to an oil. Careful crystallisation from ether at -78° gave the quinol acetate (I) (9.65 g, 68%), m.p. 76-83°. Recrystallisation, or silica-gel chromatography, gave material m.p. 84-86° [Found: C, 70.05; H, 8.15%; M, 222 (mass spec.). Calc. for $C_{13}H_{18}O_3$: C, 70.2; H, 8.2%; M, 222], ν_{max} 1735, 1663, 1640, and 1575 cm⁻¹, λ_{max} 213.5 and 321 nm (log ϵ 3.87 and 3.58) (95% ethanol), λ_{max} 212.5 and 316 nm (log ϵ 3.87 and 3.70) (cyclohexane), consistent with the structure.^{2c,27} The n.m.r. peaks, τ 7.98 (sharp s), 7.98br, 8.12, 8.12, 8.25, and 8.78 are assigned to acetate, and 3-, 2-, 4-, 5-, and 6-methyl groups on the basis of analogy 2c, 27 and solventshift studies. Hydrogenation (PtO₂ in methanol) required 96% of the theoretical volume and gave a quantitative yield of pentamethylphenol.

Irradiation of the Acetate (I) in Ether.-Quinol acetate (I) (6.0 g) in ether (600 ml) saturated with water was irradiated under nitrogen, in a Pyrex flask. Samples were analysed by u.v. spectroscopy and g.l.c. (columns of polypropylene glycol at 205°, polyethylene glycol adipate at 150°, silicone E30 at 150°, or QF1 at 170°), and irradiation was stopped at about 90% conversion. The g.l.c. showed the major photoproduct to represent 90-95% of the volatile materials; n.m.r. analysis of the crude photolysate suggested a yield of ca. 95% of photoproduct (II). Careful crystallisation from petroleum (b.p. $<40^{\circ}$) at -80° gave 6-acetoxy-1,3,4,5,6-pentamethylbicyclo[3,1,0] hex-3-en-2-one (II) (4.05 g, 67%) as off-white crystals, m.p. $43-46.5^{\circ}$ (Found: C, 69.85; H, 8.15. C₁₃H₁₈O₃ requires C, 70.2; H, 8.2%), ν_{max} 1750 (ester), 1690, and 1640 cm⁻¹ (bicyclohexenone). The u.v. spectrum, λ_{max} 207.5, 230, 268, and 325 nm (log ε 3.67, 3.76, 3.53, and 2.58), has a similar shape to those of typical bicyclo[3,1,0]hex-3-en-2-ones.33 The n.m.r. peaks were assigned earlier.

^{*} The amide absorption above 300 nm is so weak ($\varepsilon < 2$) that even with an amide-to-quinol acetate ratio of 100:1, the amide would absorb less than 20% of the total absorbed light. Quin-kert's amide contains a styrene-type chromophore, which should be photolabile above 300 nm.

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Irradiation of the Acetate (I) in Methanol.—Irradiation of compound (I) (4.0 g) in dry methanol (400 ml) gave an oily mixture. Analysis by n.m.r. and g.l.c. suggested a mixture of ca. 4 : 1 of (II) and quinol acetates (o- and p-, which are indistinguishable under the g.l.c. conditions employed). Column chromatography on silica allowed pentamethylphenol (ca. 5%) and some (II) to be separated. Other fractions contained (II) and pentamethyl-p-quinol acetate (III), analysed by u.v. spectroscopy and g.l.c. We estimate that the mixture contains ca. 70% of (II) and 25% of (III).

Pentamethyl-p-quinol A cetate(III).-Pentamethyl-oquinol acetate (I) $(2 \cdot 0 \text{ g})$ in ether (100 ml) was treated with distilled boron trifluoride-ether complex (4 ml) for 1 h at 25°. Addition of water, neutralisation with sodium hydrogen carbonate, extraction with ether, and evaporation of the dried extract gave a yellow oil containing both the o- and p-isomers. Crystallisation from ether and petroleum (b.p. $<40^{\circ}$) at -80° gave white crystals (1.02 g, 50%) of the p-quinol acetate, m.p. 100-102°. (Found: C, 70·35; H, 8·15. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·2%). The i.r. spectrum, v_{max} . 1755 and 1643 cm⁻¹, is typical of p-quinol acetates,^{2c, 27} but the peak at 1670 cm⁻¹ is abnormally weak. The u.v., λ_{max} . 204 and 250.5 nm (log ε 3.70 and 4.11) and n.m.r. spectra, τ 7.98 (OAc), 8.17 (four allylic Me), and 8.62 (4-Me), are consistent with the structure; the 3and 5-methyl groups must be shielded by the acetate group.34

Irradiation of the Acetate (I) in the Presence of Cyclohexylamine.—A solution of the acetate (I) (0.5 g) and 10 equiv. of redistilled cyclohexylamine in dry ether (25 ml) was irradiated through Pyrex glass. Monitoring by g.l.c. (E30 column at 190°) showed the quinol acetate to be replaced by two new compounds (ratio ca. 90:1) with long retention times. The solution was washed free of amine with 0.5N-hydrochloric acid, then water, dried, and evaporated to a pale yellow oil (0.75 g, ca. 100%). Crystallisation from petroleum (b.p. 30-40°) at -80° gave 3Z,5E-Ncyclohexyl-6-acetoxy-2,3,4,5-tetramethylhepta-3,5-dienamide

(X) (0.44 g, 61%) as white crystals, m.p. $72 \cdot 5$ — $73 \cdot 5^{\circ}$ (Found: C, 70.8; H, 10.1; N, 4.5. $C_{19}H_{31}NO_3$ requires C, 71.0; H, 9.75; N, 4.35%). The i.r. [3380, 1670 (amide), and 1738 cm⁻¹ (enol acetate)] and u.v. [end absorption at 208 nm (log ε 3.75)] spectra are similar to those of analogous amides.²⁸ N.m.r. peaks were observed at τ 3.92br (NH), 6.52 (cyclohexyl methine), 6.95 (q, J 7.5 Hz, 2-H), 7.86 (Ac), and 8.92 (d, J 7.5 Hz, further split by *ca*. 2.5 Hz, 2-Me). Three signals which overlap at *ca*. τ 8.31, and a fine multiplet at τ 8.48 are due to the 3-, 4-, 5-, and 6-methyl groups; the 8.48 peak is assigned to the 5-methyl, on the basis of comparison with analogues. The amide is believed to be the 3Z,5E (3-*cis*,5-*trans*) isomer.²⁸

Thermal reactions with Cyclohexylamine.—Treatment of quinol acetate (I) with cyclohexylamine (20 equiv.) in boiling ether showed no change (by g.l.c.) within 20 h; normal irradiation experiments are complete in 2 h. Photoproduct (II) with cyclohexylamine in boiling benzene showed no significant loss [of (II)] and no production of the amide (X) within 72 h.

Acid Hydrolysis of the Bicyclohexenone (II).—A solution of photoproduct (II) (200 mg) in 0.02N-sulphuric acid (30 ml) was heated under reflux for 1.5 h, neutralised with sodium hydrogen carbonate, and extracted with ether. The dried extracts were evaporated to an oil. G.l.c.

34 Ref. 27, p. 239.

(QF1 column at 150 or 170°) showed ca. 70% conversion into a hydrolysis product, contaminated by two minor impurities, which increased with longer reaction times. Separation of the major hydrolysis product by preparative g.l.c. gave cis(Ac,H)-4-acetyl-2,3,4,5-tetramethylcyclopent-2enone (IV) (99% pure), as an oil or white solid, m.p. between 0 and 10° (Found: C, 73·1; H, 8·7. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%). The spectral data are discussed earlier.

Zemplen Hydrolysis of the Bicyclohexenone (II).-Compound (II) (1.10 g) was added to sodium methoxide [from sodium (ca. 10 mg)] in anhydrous methanol (75 ml). After 2 days at 20° reaction was complete (g.l.c.; E30 column at 150°). Extraction with ether, drying, and evaporation gave a yellow oil which was separated by preparative g.l.c. Material eluted first (ca. 40%) (>95% pure) was shown to be compound (IV) by its i.r., u.v., n.m.r., and g.l.c. properties. Material eluted later (ca. 60%) (>95% pure) was the isomeric trans(Ac,H)-4-acetyl-2,3,4,5-tetramethylcyclopent-2enone (V), m.p. between 0 and 10°. I.r. peaks at 1650 and 1710 cm⁻¹ and a u.v. curve $[\lambda_{max}, 240 \text{ nm} (\log \epsilon 3.97)]$ with similar shape to that of (IV) show the similarity of the two isomers. N.m.r. peaks at τ 8.15 and 8.32 (homoallylically coupled), 8.07, 8.88, and 8.97 (d, J 7.2 Hz) are assigned to 3- and 2-Me, Ac, and 4- and 5-Me. The methine proton gives a multiplet, τ 7.6–8.0. The mass spectra of ketones (IV) and (V) are identical $[M^+ 180;$ base peak m/e 138(loss of keten)].

Equilibration Experiments on Cyclopentenones (IV) and (V).—Samples of compounds (IV) and (V), purified as just described, were separately treated under the Zemplen hydrolysis conditions, and analysed at intervals by g.l.c. with the results mentioned earlier. Other materials gradually appeared; one of these disappeared again in an irregular way, and is suspected to be a relatively stable enol form, on the basis of its spectra.

Hydrolysis of the Bicyclohexenone (II) to 2,3,4,5-Tetramethylcyclopent-2-enone.—Boiling under reflux of compound (II) (4.05 g) in methanolic potassium hydroxide (1 g in 250 ml) for 3 h led to complete loss of i.r. carbonyl peaks above 1700 cm⁻¹. Neutralisation (dilute H₂SO₄), ether extraction, and washing (NaHCO₃, then water) and evaporation of the extracts gave an oily mixture. G.l.c. (PEGA column, 135°) showed two products in a ca. 9 : 1 ratio. After distillation (54—70° and 10 mmHg) the lower boiling, major component, trans-2,3,4,5-tetramethylcyclopent-2-enone was separated by preparative g.l.c. (PEGA column at 120°), ν_{max} . 1700 and 1650 cm⁻¹, λ_{max} . 236 and 303 nm (log ε 4.08 and 1.79) [lit., ¹⁰⁶ ν_{max} . 1698 and 1649 cm⁻¹, λ_{max} .¹⁵ 236 and 302 nm (log ε 4.14 and 1.99, λ_{max} .¹⁰⁶ 240 nm (log ε 4.04)]. N.m.r. peaks at τ 7.97, 8.30, 8.77 (d), and 8.86 (d) (*J ca.* 7.5 Hz) are assigned to 3-, 2-, 4-, and 5-Me. The spectrum reported ¹⁰⁶ is similar, but slightly shifted upfield (by ca. 0.06 p.p.m.).

2,3,4,5-*Tetramethylcyclopent-2-enone.*— Dibut-2-enyl ketone was cyclised ¹⁵ in formic and phosphoric acids. The product contained two compounds in a *ca*. 9 : 1 ratio, with some minor impurities. The major component, *trans-*2,3,4,5-tetramethylcyclopent-2-enone, was separated by preparative g.l.c. as a liquid, with g.l.c. behaviour and i.r., u.v. and n.m.r. spectra identical with those of the sample prepared before.

Reduction of the Cyclopentenone (IV) and Attempts at Subsequent Cleavage.—Compound (IV) was hydrogenated over platinum oxide in methanol at 25° and 1 atm. The oil remaining after drying and evaporation contained three compounds and had v_{max} . 1740, 1710 cm⁻¹, consistent with the acetylcyclopentanone structures. The mixture was boiled with 1·1 equiv. of methanolic 0·06M-potassium hydroxide for 17 h and worked up as before. The i.r. spectrum showed no loss of acetyl absorption: the carbonyl peaks remained virtually unchanged, small changes in the spectrum being ascribed to stereochemical equilibration.

Hydrogenation of the Bicyclohexenone (II).—Photoproduct (II) was hydrogenated over platinum oxide in ethanol at 20° and 1 atm; uptake 1.0 mol. equiv. Drying and evaporation gave 6-acetoxy-1,3,4,5,6-pentamethylbicyclo[3,1,0]hexan-2-one (VIII) as a yellow oil (Found: C, 68.9; H, 9.05. $C_{13}H_{20}O_3$ requires: C, 69.6; H, 9.0%). Vacuum-distillation or chromatography caused some decomposition, and all studies were performed on the crude material (ca. 95% pure by

* Analogous 'dihydrolumiproducts' derived from steroidal and related bicyclic dienones have n.m.r. peaks for methyls as follows: 6-endo, τ 8·81—8·96; 1-8·65—8·84 or 8·95; 5-8·62—8·84 or 8·95; 4-8·78—8·89; 3-8·99—9·02; $\nu_{\rm max}$. 1695—1720 cm⁻¹, and $\lambda_{\rm max}$. 212—220 nm.^{5,23,24,35}

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g.l.c.); ν_{max} 1755 and 1725 cm⁻¹, λ_{max} 223 nm. N.m.r. peaks at τ 7.98, 8.63, 8.88, 8.90, 8.84(d), and 8.99(d) (J 7.0 Hz) are assigned to acetyl and 6-, 1-, 5-, 4-, and 3-Me, respectively,* partly on the basis of solvent-shift studies.

Low-temperature Irradiations of the Acetate (I).—Quinol acetate (I) in ether-isopentane-ethanol (5:5:2) was degassed by freezing and pumping cycles, and sealed in a quartz cell fitted in a Spectro-Dewar apparatus ³⁶ cooled at 77 K. Irradiation, and recording of the u.v. spectrum, gave the results mentioned earlier. Similar experiments were performed with a frozen glass of (I) in methylcyclohexane-isopentane (1:1). The low-temperature i.r. studies used compound (I) in a Nujol mull.

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