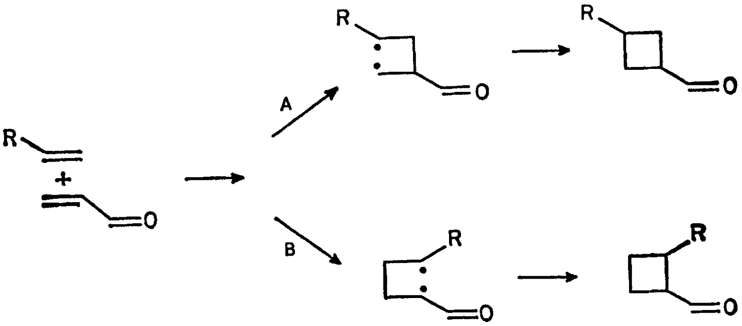
Photochemistry of Substituted Cyclic Enones. Part 2.[1] 5-[Prop-2-enyl]-cyclopentenones

By **Gopala Gowda** and **T. Brian H. McMurry,*** University Chemical Laboratory, Trinity College, Dublin 2, Ireland

The preparation of 5-(prop-2-enyl)-3,4,4-, and -2,4,4-trimethylcyclopentenones is described. Both isomers undergo an intramolecular Eaton–de Mayo photochemical reaction to give the appropriate trimethyltricyclo-$[3,2,1,0^{3,6}]$octan-2-ones. The reaction appears to proceed *via* a singlet excited state.

The tricyclo-octanones can be oxidised under Baeyer–Villiger conditions to afford the expected lactones, and the 6,7,7-trimethyl isomer on treatment with acid gives 6-*exo*-7,7-trimethylbicyclo[3.2.1]oct-3-en-2-one. The 3,7,7-trimethyl ketone has been reduced to the corresponding alcohol. Quantitative europium-shift measurements have been used to determine the structure of these compounds.

THE photochemical addition of olefins to αβ-unsaturated ketones (Eaton–de Mayo reaction) is now well known.[2] It had been suggested that the mode of addition of an unsymmetrical olefin to the enone system is such that the initially formed exiplex collapses to a diradical in which the new bond links the ene to the α-position of the enone.[3] The most stable diradical is formed, which subsequently collapses to the four-membered ring (Path A, Scheme 1). This has been interpreted in terms of ' frontier orbital theory '.[3b] However in looking at intramolecular cyclisations, exceptions to the general rule abound. We leave aside the cases of cyclisation [4] where the enone and ene are held rigidly close to each other, and where the electronic factors can play no part in controlling the regio-specificity. However, in the many examples where free rotation of the olefin is possible, the factors controlling the mode of ring-closure are less clear.[5] For example, while isopiperitenone (1) [6] undergoes photo-cyclisation to give the predicted compound (2),[2] carvone (3a) [7] affords (4a), and cryptomerion (3b) [8] yields (4b). Furthermore the 4-allylcyclopentenone (5) [9] affords (6). In these latter cases, the alternative and predicted [2] product [*e.g.* (7) instead of (6)] contains two fused cyclobutane rings and the transition state in forming this type of ring system may be too strained. In the case of 6-allylcyclohexenones (8a—d),[10,11] products (10a), (9b) and (10b), (9c) and (10c), and (10d) are obtained in varying yields from the respective enones. Clearly steric factors must control the ratio of the products formed in these cases.



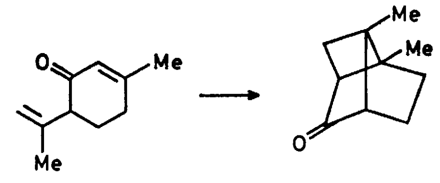
We wished to investigate the photolysis of 5-(prop-2-enyl)cyclopent-2-enones, and we now report on the synthesis and photochemistry of 5-(prop-2-enyl)-3,4,4- and -2,4,4-trimethylcyclopent-2-enones (12a) and (12b). Very recently, Pattenden *et al.*[12] have reported photolysis studies of 3-acetoxy-5-allylcyclopentenones and our results parallel theirs.

RESULTS AND DISCUSSION

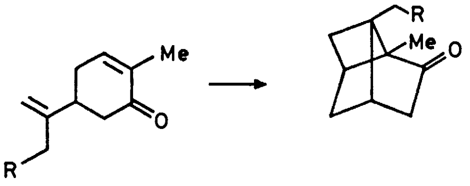
Synthesis.—3,4,4- and 2,4,4-Trimethylcyclopentenones (11a) and (11b) were already available from another study.[1] Synthesis of the 5-allyl derivatives was achieved by the route shown (Scheme 2) and was unexceptional, but it is worth noting that *Z*- and *E*-isomers of the *O*-allyl derivatives of 2,4,4-trimethylcyclopentenone were obtained but that only the *E*-isomer was obtained from 3,4,4-trimethylcyclopentenone. The stereochemistry of the isomers was inferred from the position of the n.m.r. peak due to the hydrogen attached to the 5-methylene group. The literature suggests that this lies at lower field in the *E*- than in the *Z*-isomer.[13,14] We attempted to decarbonylate the 5-allyl-5-formyl-2,4,4-trimethylcyclopentenone using Wilkinson's catalyst.[15] While this gave the required product, a second compound, probably (13), was also obtained, whose stereochemistry was assigned by analogy with the n.m.r. spectra of related compounds.[16] The two compounds required separation, and the route was not pursued.

Photolysis.—Photolysis of (12a) using a medium-pressure mercury lamp produces a single photo-product. From the fact that it is also formed in the presence of ferrocene,[17] but not in the presence of propiophenone, suggests that the singlet excited state of the enone is involved in the reaction.

The photo product, from (12a), should have either the structure (14a) or (15a). The n.m.r. spectrum showed three methyl singlets at τ 8.80, 9.10, and 9.20, supporting either structure. The compound had an i.r. carbonyl



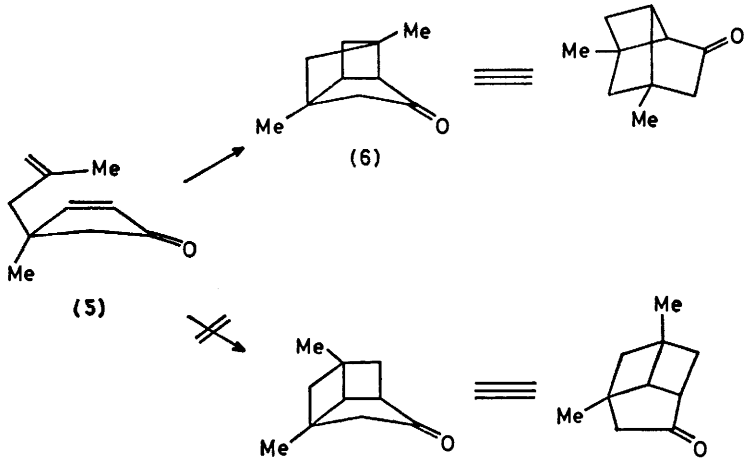
(1) **(2)**



(3) **(4)**

a; R = H

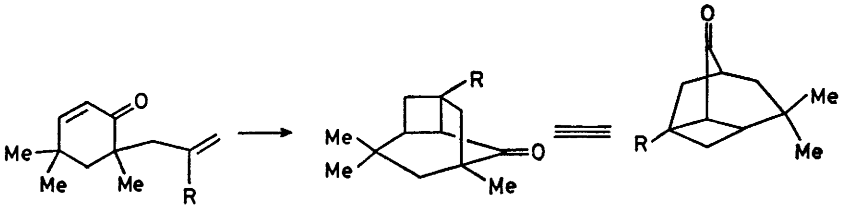
b; R = $CH_2CH = CMe_2$



(6)

(5)

(7)



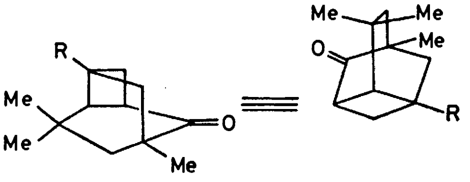
(8) (9)

a; R = H

b; R = Me

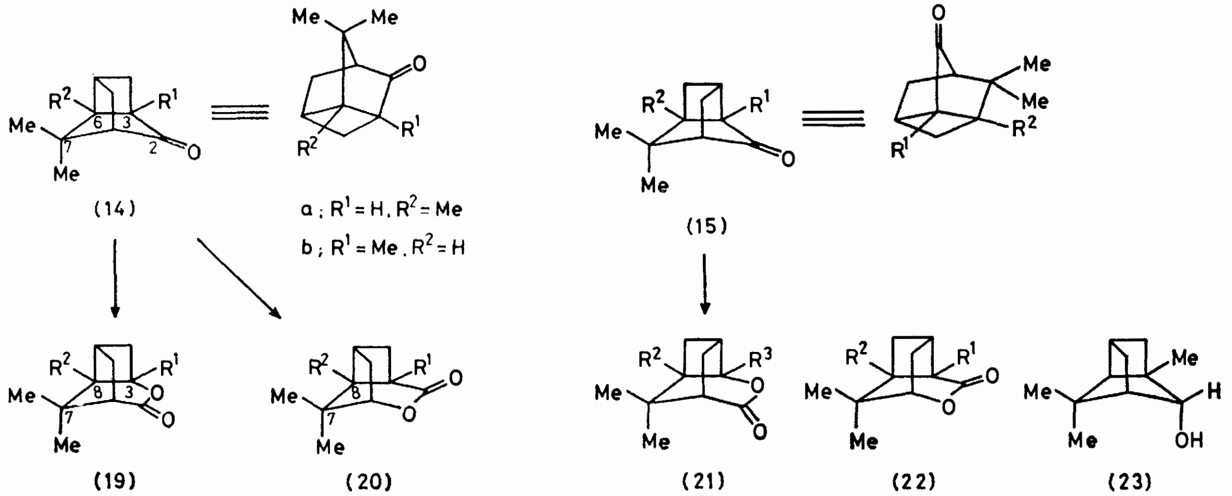
c; R = $CHMe_2$

d; R = Cl



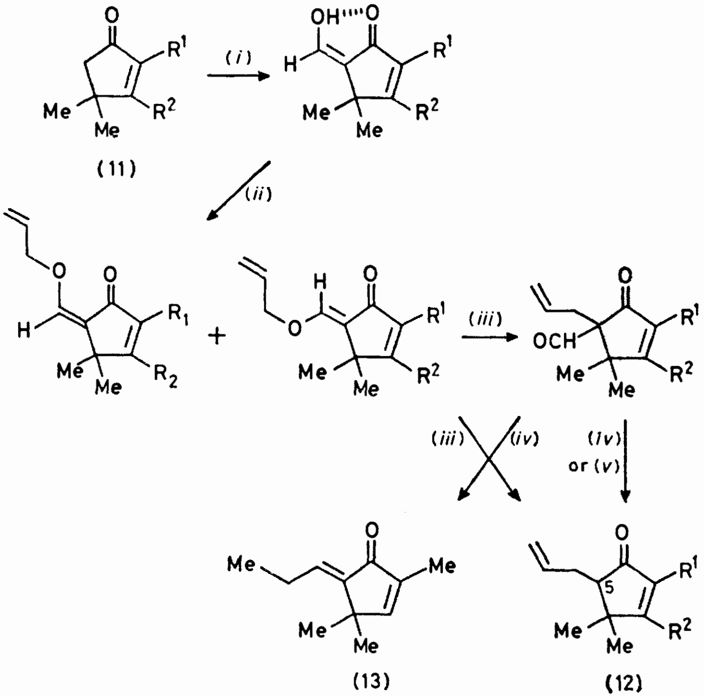
(10)

band at 1 741 cm^{-1}. Model compounds suggest that (14a) should show an i.r. band around 1 750 cm^{-1},[18] while (15a) should give a band around or above 1 760 cm^{-1}.[19,20] The spectroscopic and chemical evidence outlined below also favours (14a), and we shall assume in further discussion that this is correct, pointing out, however, where the formulation as (15a) is unsatisfactory.



(14) (15) (19) (20) (21) (22) (23)

Treatment of the photo-ketone with boron trifluoride–ether in refluxing methylene dichloride afforded a product whose i.r. and u.v. spectra showed that it contained an αβ-unsaturated cyclohexenone ring. In addition to two coupled vinyl protons at τ 2.6 and 4.13, there were two methyl singlets at τ 8.93 and 9.02, and a methyl doublet at τ 8.95. A dihydro-derivative prepared by hydrogenation shows the characteristic i.r. peak of a cyclohexanone ($\nu_{max.}$ 1 700 cm^{-1}). The spectroscopic evidence favours the bicyclo[3.2.1]octenone structure (16)[21] for the acid rearrangement product and (17) for its dihydro-derivative. The gross structure, and the assigned stereochemistry to (16) is confirmed by lanthanide shift measurements, and also by oxidation of (16) by permanganate to afford what we believe to be the trimethylcyclopentanedicarboxylic acid (18). This has the same m.p. as that reported for a compound[22] with the stereochemistry as shown in (18). The diacid isomeric at the 5-position has a different m.p.[22] Compound (16) can be formed by the route A (Scheme 3) from (14a). Compound (15a) would only yield (16) by the very unlikely route B, which involves the formation of a secondary from a tertiary carbonium ion.

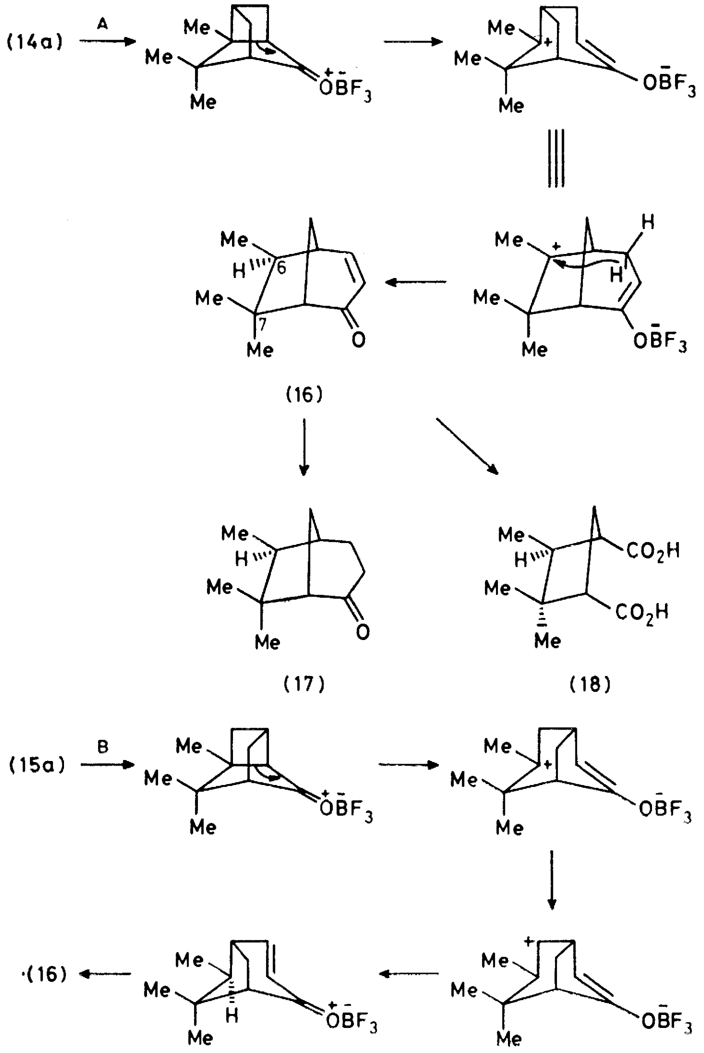


(11) (13) (12)

a; R = H, R^2 = Me b; R^1 = Me, R^2 = H

SCHEME 2 (*i*) EtO_2CH, OMe^-; (*ii*) $CH_2{=}CHCH_2Br$, K_2CO_3, acetone; (*iii*) heat, 250 °C; (*iv*) $(Ph_3)_3RhCl$; (*v*) OH^-

Europium shift measurements were used to assign the methyl and also the 1-H signal in the n.m.r. spectrum of (16). The 7-*exo*-methyl proved to have the signal at highest field, presumably because it is shielded by the αβ-unsaturated ketone. Using the standard methods [23] we found that the best fit occurred when the europium atom lies on an extension of the C–O axis at a distance of 3.5 Å from oxygen and when the 6-methyl was *endo*.



SCHEME 3

Oxidation of the photo-product from (12a) with 90% hydrogen peroxide–boron trifluoride [24] afforded a mixture of two lactones. The less-polar product had a carbonyl absorption at 1 735 cm^{-1}, indicative of a six-membered lactone. The n.m.r. spectrum showed three methyl singlets, and a double double doublet at τ 5.66 (*J* 9, 3.5, and 1.5 Hz), indicative of a proton on carbon also linked to the oxygen of the lactone ring. The rest of the spectrum is complex, but addition of europium shift reagent enabled us to pick out the hydrogen next to the carbonyl group as a doublet (*J* 6 Hz). The more polar product had carbonyl absorption at 1 720 cm^{-1}, and the n.m.r. spectrum showed three methyl singlets and a broad doublet at τ 5.65 (*J* 5 Hz). Europium shift measurements indicated that the signal due to the hydrogen next to carbonyl was a double double doublet.

If the photo-ketone has the structure (14a), then the structures of the two lactones are (19a) and (20a). On the other hand, if the photo-ketone were (15a), then the lactones are (21a) and (22a). It is known that a ketone having the same ring system as (15a), but lacking the methyl substituents, is oxidised to afford *one* lactone [related to (21)] whose i.r. carbonyl band occurs at 1 770 cm^{-1}.[19] As we obtain *two* lactones, neither of which shows a band at 1 770 cm^{-1}, the structure (15a) is excluded for the photo-ketone. Our preference for (14a) is also supported by examination of models which suggest that the two lactones mentioned above are (19a) and (20a) respectively, but not (21a) and (22a). In particular the 3-H in each case is coupled to 2-H$_2$ [$J_{\text{calc.}} > 8.3$ and 3.0 Hz for (19a); 8.0 and 3.2 Hz for (20a)], and by long range coupling with 1-H. The 6-H is coupled with one of the 9-H (J *ca.* 6 Hz), but only slightly with the second ($J < 0.5$ Hz). These assignments are confirmed by quantitative europium shift measurements, which also enable us to assign the methyl signals in (19a) and (20a). In each case the 7-*exo*-methyl lies at lower field than the 7-*endo*, and the 8-methyl at still lower field. Curiously, the best fit for the shift results occurs if we assume that (19a) and (20a) exist as the conformations shown.

There is only one photo-product formed during the photolysis of (12b). As in the case of (12a), the reaction proceeds in the presence of ferrocene [17] but no product is formed on photolysis in the presence of propiophenone, indicating that a singlet excited state of (12b) is probably involved in the reaction. By analogy with the previous reaction, the photo-product should possess the structure (14b) and this is supported by an i.r. band at 1 740 cm^{-1}. In this case the photo-ketone did not rearrange with boron trifluoride, presumably because the carbonium ion which would be formed on ring-opening of the cyclobutane ring is secondary and not tertiary.

Oxidation of the ketone with boron trifluoride–hydrogen peroxide affords, as expected, a single lactone (19b), which lacks a C*H*–O signal. Europium-shift measurements enable us to identify the 6-H signal as a doublet (J 4 Hz) and also show that the 7-*exo*-methyl signal is at lower field than the 7-*endo*-methyl signal. Quantitative measurements support the structure (19b) with the conformation shown (europium atom on C–O axis 3 Å from oxygen) though (21b) is not too unsatisfactory. However, quantitative measurements on the alcohol obtained by borohydride reduction of the photo-ketone, and presumably formed by attack of the hydride from the less hindered side, strongly supports the structure (23) for this compound, and hence structure (19b) follows for the ketone.

Europium-shift measurements; values of 10^3 $(3\cos^2\chi^{-1}/r^3)$ are given in parentheses

	$\frac{-\Delta\tau}{[\mathrm{Eu(fod)_3}]/[\mathrm{Compound}]}$					
Compound	1-H	3-H	4-H	6-Me	7-*exo*-Me	7-*endo*-Me
(16)	10.6	7.9	2.3	1.6	5.3	2.5
	(10)	(9.5)	(2.9)	1.9	(6.4)	(3.1)
	3-H	6-H	7-*exo*-Me	7-*endo* Me	8-Me	
(19a)	3.5	8.9	3.9	2.0	1.7	
	(4.4)	(9.0)	(5.0)	(2.5)	(2.3)	
(20a)	8.4	3.5	3.38	1.63	1.60	
	(8.5)	(4.4)	(4.2)	(2.1)	(2.2)	
	3-Me	6-H	7-*exo*-Me	7-*endo* Me		
(19b)	2.8	11.2	5.1	2.4		
	(2.9)	(9.0)	(5.0)	(2.5)		
	1-H	3-Me	7-*exo*-Me	7-*endo* Me		
(23)	10.3	9.4	11.4	3.5		
	(9.0)	(6.0)	(7.4)	(2.3)		

These results and those of Pattenden *et al.*[12] show that, unlike the 4-(prop-2-enyl)cyclopentenone,[9] the 5-(prop-2-enyl)cyclopentenones undergo ring-closure in the expected manner.[2] There can be nothing unique about prop-2-enylcyclopentenones which cause them to react in the ' abnormal ' manner. The factors involved in the cyclisation of the 4-(prop-2-enyl)cyclopentenone (5) must be special for this system, and, as suggested above, must be steric in origin.

EXPERIMENTAL

For general methods, see Part 1.[1] Photolyses were carried out at room temperature under nitrogen using a 250-W Hanovia medium-pressure lamp through a Pyrex window.

5-*Hydroxymethylene*-3,4,4-*trimethylcyclopentenone*.—3,4,4-Trimethylcyclopentenone (10 g), ethyl formate (9.5 ml), and sodium methoxide (7 g) in anhydrous benzene (100 ml) under an atmosphere of nitrogen were set aside with stirring for 24 h at room temperature. Water (100 ml) was added, and the aqueous layer separated, washed with ether, and then acidified with hydrochloric acid. This aqueous solution was extracted with ether (3 × 30 ml), and the combined ether layers washed with water, and dried ($MgSO_4$). Removal of the ether afforded 5-(*hydroxymethylene*)-3,4,4-*trimethylcyclopentenone* (4 g) which was purified by preparative t.l.c. and sublimation, m.p. 88 °C (Found: C, 71.3; H, 7.85. $C_9H_{12}O_2$ requires C, 71.0; H 7.95%); $\nu_{max.}$ 1 670 and 1 610 cm^{-1}; $\lambda_{max.}$ 285 and 245 nm (log ε 3.90 and 4.08); τ 2.94 (5-methylene-H), 4.05 (br, 2-H), 8.0 (d, J 1.3 Hz, 3-Me), and 8.8 (4-Me_2).

5-(*Hydroxymethylene*)-2,4,4-*trimethylcyclopentenone*.—Under the same conditions, 2,4,4-trimethylcyclopentenone (2 g) afforded 5-(*hydroxymethylene*)-2,4,4-*trimethylcyclopentenone* (1.3 g) which was purified by preparative t.l.c. and sublimation, m.p. 82 °C (Found: C, 71.2; H, 7.8%); $\nu_{max.}$ 1 670 and 1 610 cm^{-1}; $\lambda_{max.}$ 291 and 247 nm (log ε 3.83 and 3.87); τ 0.26 (OH, exchangeable with D_2O), 2.89 (5-methylene-H), 3.19 (q, J 1.3 Hz, 3-H), 8.18 (d, J 1.3 Hz, 2-Me), and 8.74 (4-Me_2).

E-5-(*prop*-2-*enyloxymethylene*)-3,4,4-*trimethylcyclopentenone*.— 5-(Hydroxymethylene)-3,4,4-trimethylcyclopentenone (1.5 g), allyl bromide (1.65 g), potassium carbonate (2.25 g), and dry acetone (100 ml) were refluxed under nitrogen for 7.5 h. Water (200 ml) was added and the mixture extracted with ether (3 × 40 ml). The combined ether layers were washed with water and dried ($MgSO_4$) to give 5-(*prop*-2-*enyloxymethylene*)-3,4,4-*trimethylcyclopentenone* (1.5 g) which was purified by preparative t.l.c. and distillation, b.p. 120 °C at 9 mmHg (Found: C, 74.6; H, 8.15. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%); $\nu_{max.}$ 1 690, 1 630, and 1 610 cm^{-1}; $\lambda_{max.}$ 285 and 249 nm (log ε 4.0 and 4.02); τ 2.92 (5-methylene-H), 4.1 (q, J 1.5 Hz, 2-H), 4.1—4.7 (m, propenyl vinyl-H), 5.5 (m, propenyl-CH_2), 8.0 (d, J 1.5 Hz, 3-Me), and 8.7 (4-Me_2).

E- *and* Z-5-(*prop*-2-*enyloxymethylene*)-2,4,4-*trimethylcyclopentenone*.— 5-(Hydroxymethylene)-2,4,4-trimethylcyclopentenone (1.5 g) with the same reactants and the same conditions afforded a mixture which could be separated by preparative t.l.c. to give E-5-(*prop*-2-*enyloxymethylene*)-2,4,4-*trimethylcyclopentenone* (990 mg), b.p. 90 °C at 0.3 mmHg (Found: C, 75.1; H, 8.55%); $\nu_{max.}$ 1 695, 1 650, and 1 625 cm^{-1}; $\lambda_{max.}$ 285 and 251 nm (log ε 3.69 and 3.59); τ 2.87 (5-methylene-H), 3.15 (q, J 1.3 Hz, 3-H), 4.2—4.7 (m, propenyl vinyl-H), 5.46 (m, propenyl-CH_2), 8.22 (d, J 1.3 Hz, 2-Me), and 8.71 (4-Me_2); and the Z-*isomer* (100 mg), b.p. 95 °C at 0.3 mmHg (Found: C, 74.6; H, 8.6%);

$\nu_{max.}$ 1 695, 1 650, and 1 625 cm^{-1}; $\lambda_{max.}$ 287 nm and 235 nm (log ε 4.01 and 3.87); τ 3.25 (q, *J* 1.3 Hz, 3-H), 3.61 (5-methylene-H), 4.1—4.7 (m, 3 H, propenyl vinyl-H), 5.57 (m, 2 H, propenyl-CH_2), 8.22 (d, *J* 1.3 Hz, 2-Me), and 8.76 (4-Me_2). The *E*-isomer was the less polar fraction.

5-(*Prop*-2-*enyl*)-3,4,4-*trimethylcyclopentenone* (12a). The corresponding propenyloxymethylene ketone (4 g) was heated in a thin-walled test tube at 250 °C under nitrogen for 15 min. The reaction mixture was cooled, and purified by t.l.c. or by column chromatography to give 5-(*prop*-2-*enyl*)-3,4,4-*trimethylcyclopentenone* (1.5 g), b.p. 115 °C at 10 mmHg (Found: C, 80.6; H, 10.0. $C_{11}H_{16}O$ requires C, 80.4; H, 9.8%); $\nu_{max.}$ 1 700, 1 640, and 1 620 cm^{-1}; $\lambda_{max.}$ 230 nm (log ε 4.14); τ 4.2 (q, *J* 1.3 Hz, 2-H), 4.2—4.9 (m, 3 H, propenyl vinyl-H), 7.2—7.9 (m, 3 H, 5-H and propenyl-CH_2), 8.0 (d, *J* 1.3 Hz, 3-Me), and 8.8 and 8.9 (4-Me_2).

A further fraction (2.0 g) contained a mixture of (12a) and 5-formyl-5-(prop-2-enyl)-3,4,4-trimethylcyclopentenone. Without further purification, this fraction, sodium hydroxide (2.0 g), methanol (50 ml), and water (5 ml) were stirred at room temperature under nitrogen for 30 min; the reaction was monitored by t.l.c. The solvent was removed *in vacuo*, and the residue diluted with water and extracted with ether (3 × 40 ml). The combined ether layers were washed with water, dried ($MgSO_4$), and the ether removed to afford (12a) (1.6 g).

5-(*Prop*-2-*enyl*)-2,4,4-*trimethylcyclopentenone* (12b).—(*a*) The corresponding *E*-(propenyloxymethylene)cyclopentenone (130 mg) was heated in a thin-walled test tube at 250 °C under nitrogen for 30 min. The reaction mixture was cooled, diluted with ether, and purified by preparative t.l.c. to afford 5-(*prop*-2-*enyl*)-2,4,4-*trimethylcyclopentenone* (12b) (20 mg), b.p. 48 °C at 0.6 mmHg (Found: C, 80.8; H, 9.9%); $\nu_{max.}$ 1 710 and 1 625 cm^{-1}; $\lambda_{max.}$ 230 nm (log ε 4.03); τ 2.99 (q, *J* 1.3 Hz, 3-H), 3.7—4.9 (m, propenyl vinyl-H), 7.2—8.0 (m, 5-H and propenyl-CH_2), 8.27 (d, *J* 1.3 Hz, 2-Me), 8.79, and 8.94 (4-Me_2): and 5-formyl-5-(prop-2-enyl)-2,4,4-trimethylcyclopentenone (65 mg), b.p. 106 °C at 2.5 mmHg (Found: C, 74.6; H, 8.15%); $\nu_{max.}$ 1 725, 1 700, and 1 640 cm^{-1}; $\lambda_{max.}$ 231 nm (log ε 3.79); τ 0.45 (C*H*O), 2.81 (q, *J* 1.3 Hz, 3-H), 3.9—4.75 (m, 3 H propenyl vinyl-H), 7.4 (m, 2 H, propenyl-CH_2), 8.2 (d, *J* 1.3 Hz, 2-Me), and 8.78 (4-Me_2).

(*b*) Similar pyrolysis of the *Z*-isomer afforded the same products.

(*c*) The above 5-formyl derivative (130 mg) and tris-(triphenylphosphine)rhodium chloride (200 mg) were refluxed under nitrogen in benzene (10 ml) for 10 min. The solvent was removed, ethanol (15 ml) was added, and the *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) collected at the pump. Ethanol was removed from the filtrate and the residue chromatographed (t.l.c.) to give 5-(prop-2-enyl)-2,4,4-trimethylcyclopentenone (12b) (50 mg), starting material (40 mg), and a compound which was probably 5-propylidene-2,4,4-trimethylcyclopentenone (10 mg); $\nu_{max.}$ 1 695, 1 650, and 1 635 cm^{-1}; $\lambda_{max.}$ 256 (log ε 3.76); τ 3.13 (q, *J* 1.3 Hz, 3-H), 4.05 (t, *J* 7 Hz, 5-methylene-H), 7.2 (dq, *J* 7 and 7 Hz, propylidene-CH_2), 8.22 (d, *J* 1.3 Hz, 2-Me), 8.8 (4-Me_2), and 8.9 (t, *J* 7 Hz, 5-propylidine-Me).

(*d*) The formyl ketone (3 g), sodium hydroxide (3 g) methanol (100 ml), and water (10 ml) were stirred at room temperature under nitrogen for 30 min. The solvent was removed under reduced pressure, and the residue diluted with water and extracted with ether (3 × 40 ml). The combined ether layers were washed with water and dried ($MgSO_4$). The ether was removed, and the residue chromatographed to give 5-(prop-2-enyl)-2,4,4-trimethylcyclopentenone (12b) (2 g) identical with the sample described above.

Photolysis Experiments

Photolysis of 5-(*Prop*-2-*enyl*)-3,4,4-*trimethylcyclopentenone* (12a).—(*a*) 5-(Prop-2-enyl)-3,4,4-trimethylcyclopentenone (500 mg) in benzene (520 ml) was irradiated with u.v. light for 7 h. The solvent was removed under reduced pressure and the residue separated by column chromatography on silica to give 6,7,7-*trimethyltricyclo*[3.2.1.0^{3,6}]*octan*-2-*one* (14a) (400 mg) as rhombs, m.p. 165 °C (from hexane) (Found: C, 80.0; H, 9.8%); $\nu_{max.}$ 1 740 cm^{-1}; τ 7.5—8.5 (m), 8.8 (6-Me), 9.1 (7-*endo*-Me), and 9.2 (7-*exo*-Me).

(*b*) The same allyl cyclopentenone (200 mg), sublimed ferrocene (1 g), and benzene (520 ml) were irradiated with u.v. light for 1 h. The solvent was removed under reduced pressure and the tricyclic ketone (14a) (180 mg) isolated by column chromatography.

(*c*) The allylcyclopentenone (200 mg), propiophenone (4 g), and benzene (520 ml) were irradiated for 7 h. T.l.c. showed that no tricyclic ketone was formed, but that most of the product was polymeric.

Photolysis of 5-(*Prop*-2-*enyl*)-2,4,4-*trimethylcyclopentenone* (12b).—(*a*) This ketone (12b) (500 mg) in benzene (520 ml) was irradiated for 3 h, monitoring the reaction by t.l.c. The solvent was removed under reduced pressure, and the residue chromatographed to give 3,7,7-*trimethyltricyclo*-[3.2.1.0^{3,6}]*octan*-2-*one* (14b) (450 mg), b.p. 40 °C at 0.5 mmHg (Found: C, 80.3; H, 10.0%); $\nu_{max.}$ 1 741 cm^{-1}; τ 7.5—8.5 (m), 8.87 (3-Me), and 9.09 (7-*endo*- and *exo*-Me).

(*b*) The allyl ketone (200 mg), and sublimed ferrocene (1 g) in benzene (520 ml) were irradiated for 5 h. The solvent was removed under reduced pressure, and the residue chromatographed on silica to give the tricyclo-ketone (14b) (180 mg).

(*c*) The ketone (12b) (200 mg), propiophenone (4 g), and benzene (520 ml) were irradiated for 3 h. T.l.c. showed that no tricyclo-ketone was formed.

Reaction of 6,7,7-*Trimethyltricyclo*[3.2.1.0^{3,6}]*octan*-2-*one with Boron Trifluoride–Ether*. The photo-ketone (14a) (1 g), boron trifluoride–ether (10 ml) and dry methylene dichloride (25 ml) were refluxed for 6 h. The reaction mixture was cooled, and washed with a 5% solution of sodium hydrogencarbonate and then water. The organic layer was dried ($MgSO_4$), the solvents removed, and the residue chromatographed (preparative t.l.c.) to afford 6-exo-7,7-*trimethylbicyclo*[3.2.1]*oct*-3-*en*-2-*one* (16) (100 mg) as needles, m.p. 40 °C (from ethyl acetate) (Found: C, 80.9; H, 9.9%; $\nu_{max.}$ 1 675 and 1 600 cm^{-1}; $\lambda_{max.}$ 237 nm (log ε 3.80); τ 2.6 (dd, $J_{4,3}$ 9.5, $J_{4,5}$ 7 Hz, 4-H), 4.13 (dd, $J_{3,4}$ 9.5, $J_{3,5}$ 1.4 Hz, 3-H), 8.0 (m), 8.95 (d, *J* 7.5 Hz, 6-*exo*-Me), 8.93 (7-*endo*-Me), and 9.02 (7-*exo*-Me).

6-exo-7,7-*Trimethylbicyclo*[3.2.1]*octan*-2-*one* (17).—The above unsaturated ketone (16) (100 mg), 10% palladium–charcoal (50 mg), and ethanol (10 ml) were stirred in an atmosphere of hydrogen until no more hydrogen was absorbed. The product was purified by preparative t.l.c. to give the *saturated ketone* (17) (90 mg) as rhombs, m.p. 60 °C (from ethyl acetate) (Found: C, 79.9; H, 11.1. $C_{11}H_{18}O$ requires C, 79.5; H, 10.9%) $\nu_{max.}$ 1 700 cm^{-1}; τ 7.5—8.5 (m), 9.0 (d, *J* 7.5 Hz, 6-Me), and 9.05 (7-*exo*- and *endo*-Me).

Oxidation of 6-exo-7,7-*Trimethylbicyclo*[3.2.1]*oct*-3-*en*-2-*one*.—Potassium permanganate (800 mg) was added to a stirred suspension of the enone (250 mg) in water (25 ml) at 70 °C. The mixture was stirred for 3 h, and the manganese dioxide collected at the pump, washing with water. The aqueous solution was acidified with dilute hydrochloric acid, saturated with sodium chloride, and extracted with ether (4 × 40 ml). The combined ether extract was dried ($MgSO_4$) and the ether removed. The solid residue was recrystallised from water to give the cyclopentanedicarboxylic acid (200 mg) as rhombs, m.p. 180 °C (lit.,[19] m.p. 185 °C) (Found: C, 59.95; H, 8.05. Calc. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05%); $\nu_{max.}$ 1 700 cm^{-1}; τ (CD_3OD), 7.76 (m), 9.01 (d, *J* 7 Hz, 5-Me), and 9.01 (4-Me_2).

7,7,8-*Trimethyl*-4-*oxatricyclo*[4.2.1.0^{3,8}]*nonan*-5-*one* (19a) *and* 7,7,8-*Trimethyl*-5-*oxatricyclo*[4.2.1.0^{3,8}]*nonan*-4-*one*(20a).—A mixture of 90% hydrogen peroxide (150 mg) and boron trifluoride–ether (1 g) was added dropwise to a stirred solution of the tricyclic ketone (14a) (500 mg) in ether (5 ml), keeping the temperature of the reaction below 15 °C. The mixture was stirred at 25 °C for 70 h, the reaction being monitored by t.l.c. and g.l.c. The reaction mixture was diluted with ether, washed with 10% sodium hydrogencarbonate solution, and the ether layer dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica to give a mixture of products (300 mg) and unchanged ketone (200 mg). The products were separated by careful preparative t.l.c., using multiple development. The least polar fraction, 7,7,8-*trimethyl*-4-*oxatricyclo*[4.2.1.0^{3,8}]-*nonan*-5-*one* (19a) sublimed without melting at 100 °C; $\nu_{max.}$ 1 735 cm^{-1}; τ 5.66 (ddd, *J* 9, 3.5, and 1.5 Hz, 3-H), 7.5—8.5 (m), 8.8 (8-Me), 9.0 (7-*exo*-Me), and 9.16 (7-*endo*-Me).

The more polar fraction, 7,7,8-*trimethyl*-5-*oxatricyclo*-[4.2.1.0^{3,8}]*nonan*-4-*one* (20a), also sublimed without melting at 100 °C (Found: C, 73.0; H, 8.93. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.9%); $\nu_{max.}$ 1 720 cm^{-1}; τ 5.65 (d, *J* 5 Hz, 3-H), 7.5—8.5 (m), 8.83 (8-Me), 9.08 (7-*exo*-Me), and 9.2 (7-*endo*-Me).

3,7,7-*Trimethyl*-4-*oxatricyclo*[4.2.1.0^{3,8}]*nonan*-5-*one* (19b).—Similar oxidation of the tricyclic ketone (14b) (500 mg) afforded starting material (100 mg) and a single product (19b) (400 mg). The mixture was separated by preparative t.l.c. to give 3,7,7-*trimethyl*-4-*oxatricyclo*[4.2.1.0^{3,8}]*nonan*-5-*one*, b.p. 85 °C at 0.5 mmHg (bath temperature) (Found: C, 73.3; H, 8.99%); $\nu_{max.}$ 1 740 cm^{-1}; τ 7.5—8.5 (m), 8.6 (3-Me), 8.9 (7-*exo*-Me), and 9.1 (7-*endo*-Me).

3,7,7-*Trimethyltricyclo*[3.2.1.0^{3,6}]*octan*-2-exo-*ol* (23).—Sodium borohydride (300 mg) in water (5 ml) was added to the photo-ketone (14b) (550 mg) in methanol (50 ml), and the mixture set aside for 2 h. Removal of the solvent and chromatography of the residue on silica afforded the *alcohol* (23) (270 mg), m.p. 44 °C (Found: C, 79.4; H, 11.1. $C_{11}H_{18}O$ requires C, 79.5; H, 10.9%); $\nu_{max.}$ 3 350 cm^{-1}; τ 6.23 (2-H), 7.99 (m), 8.33 (OH), 8.80 (3-Me), 8.86 (7-*exo*-Me) and 9.13 (7-*endo*-Me).

Europium-shift Measurements.—Europium-shift measurements were carried out by the standard procedure.[23] Successive quantities of the reagent, Eu(fod)$_3$ were added to solutions of the compounds in $CDCl_3$ (n.m.r. tube) (molar ratios 0.19 increasing to 0.65). Plots of chemical shift to molar ratio of Eu(fod)$_3$ gave the values of $-\Delta\tau/[\mathrm{Eu(fod)_3}]$-[compound] recorded in the Table. The expected values were estimated using standard methods.[23] Interatomic and inter-group distances and angles were estimated using Dreiding models. The Europium atom was assumed to be on the axis of the C=O or C–O bond, and the distance of the Eu atom from oxygen were varied to give the optimum fit.

The authors wish to thank the Department of Education (Ireland) for a maintenance award (G. G.).

[9/1314 *Received*, 20*th August*, 1979]

REFERENCES

[1] G. Gowda and T. B. H. McMurry, *J.C.S. Perkin I*, 1979, 274.

[2] *Cf.* W. M. Horspool, ' Photochemistry ', vol. 9, 1978, p. 279, and earlier volumes, Chemical Society Specialist Periodical Reports, Chemical Society, London.

[3] (*a*) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570; T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, 1969, **34**, 509; D. Termont, D. de Keukeleire, and M. Vanderwalle, *J.C.S. Perkin I*, 1977, 2349; (*b*) I. Fleming, ' Frontier Orbitals and Organic Chemical Reactions,' J. Wiley and Son, London, 1976, p. 219.

[4]4. W. Herz, V. Subramanya Iyer, M. G. Nair, and J. Saltiel, *J. Amer. Chem. Soc.*, 1977, **99**, 2704; P. Yates and P. Eaton, *Tetrahedron*, 1961, **12**, 13.

[5] *Cf.* J. R. Scheffer and R. A. Wostradowski, *J. Org. Chem.*, 1972, **37**, 4317; W. L. Dilling, *Chem. Rev.*, 1966, **66**, 373.

[6] W. F. Erman and T. W. Gibson, *Tetrahedron*, 1969, **25**, 2493; W. F. Erman, *J. Amer. Chem. Soc.*, 1967, **89**, 3828.

[7] G. Büchi and I. M. Goldman, *J. Amer. Chem. Soc.*, 1957, **79**, 4741; J. Meinwald and R. A. Schneider, *ibid.*, 1965, **87**, 5218.

[8] G. L. Hodgson, D. F. MacSweeney, and T. Money, *J.C.S. Chem. Comm.*, 1973, 236.

[9] S. Wolff, S. Ayral-Kaloustian, and W. C. Agosta, *J. Org. Chem.*, 1976, **41**, 2947.

[10] W. Fröstl and P. Margaretha, *Helv. Chim. Acta*, 1976, **59**, 2244.

[11] I. Altmeyer and P. Margaretha, *Helv. Chim. Acta*, 1977, **60**, 874.

[12] M. Mellor, D. A. Otieno, and G. Pattenden, *J.C.S. Chem. Comm.*, 1978, 138.

[13] E. W. Garbisch, *J. Amer. Chem. Soc.*, 1963, **85**, 1696.

[14] J. C. Richer and R. Clarke, *Canad. J. Chem.*, 1964, **42**, 2073; G. A. MacAlpine, R. A. Raphael, A. Shaw, A. W. Taylor, and H-J. Wild, *J.C.S. Perkin I*, 1976, 410.

[15] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711; K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, 1968, **90**, 99.

[16] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance in Organic Chemistry,' 2nd edn., Pergamon Press, Oxford, 1969, p. 222.

[17] M. Kikuchi, K. Kikuchi, and H. Kokobun, *Bull. Chem. Soc. Japan*, 1974, **47**, 1331; W. G. Herkstroeter, *J. Amer. Chem. Soc.*, 1975, **97**, 4161.

[18] R. R. Sauers, R. A. Parent, and S. B. Damle, *J. Amer. Chem. Soc.*, 1966, **88**, 2257.

[19] S. A. Monti and S-S. Yuan, *Tetrahedron Letters*, 1969, 3627; *J. Org. Chem.*, 1971, **36**, 3350.

[20] S. D. Larsen and S. A. Monti, *J. Amer. Chem. Soc.*, 1977, **99**, 8015.

[21] H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Amer. Chem. Soc.*, 1961, **83**, 1391.

[22] S. Beckmann and B. Geiger, *Chem. Ber.*, 1962, **95**, 2101.

[23] B. Bleaney, C. M. Dobson, B. A. Levine, R. B. Martin, R. J. P. Williams, and A. V. Xavier, *J.C.S. Chem. Comm.*, 1972, 791.

[24] J. D. McClure and P. H. Williams, *J. Org. Chem.*, 1962, **27**, 24.