Photochemistry of 2-(Prop-2-enyl)cyclopent-2-enones

By **Michael J. Bullivant** and **Gerald Pattenden,*** Department of Chemistry, The University, Nottingham NG7 2RD

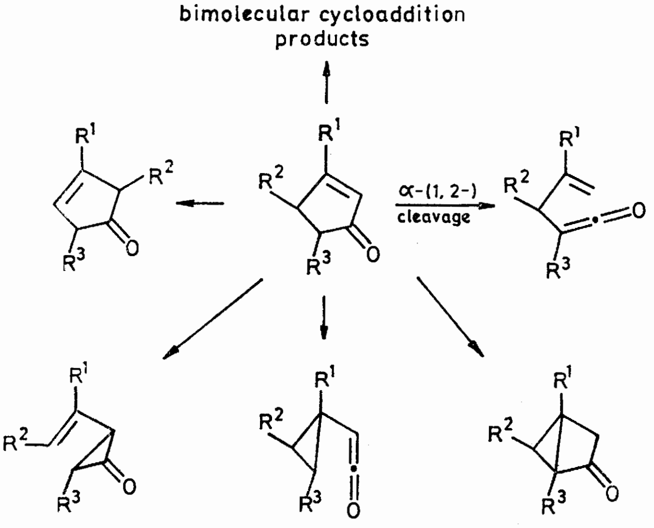
The photochemistry of several substituted 2-(prop-2-enyl)cyclopent-2-enones has been examined. The 2-(prop-2-enyl)cyclopent-2-enones (2a; R = OMe or OAc), (6a), and (21) undergo di-π-methane rearrangement to vinylcyclopropanes [(3a and b), (7), and (29), respectively], whereas the side-chain substituted analogues (2b: R = OMe or OAc), (2c; R = OAc), and (6b), under similar conditions, undergo *Z*–*E* isomerisation. Sensitisation and quenching experiments with (2a; R = OAc) suggest that (3) is derived from a triplet excited state of (2a). The reactivity differences between (2a), (6a), and (21), and (2b), (2c), and (6b) are rationalised on the basis of dissipation of triplet energy by ' free-rotor ' effects in the (prop-2-enyl) side chains of the molecules.

Irradiation of cyclopent-2-enones (13) and (22), under conditions similar to those used in the photolyses of (2a), (6a), and (21), gave no products expected from di-π-methane rearrangement.

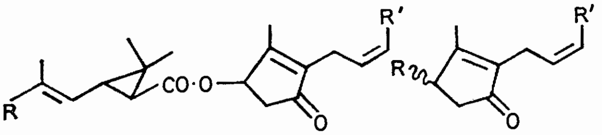
Substitution of the methane portion of the di-π-methane system, as in (33), results in a dramatic increase in efficiency of the di-π-methane rearrangement [to (34)] over that observed for the conversions (2a) ⟶ (3), (6a) ⟶ (7), and (21) ⟶ (29). These data suggest that the latter rearrangements most probably proceed *via* a radical process involving hydrogen migration.

Photolysis of the pyrethrin insecticides (1; R = Me, R' = H) and (1; R = Me, R' = Et) produces the vinylcyclopropane (35) and *E*-alkene (39), respectively, in high yields.

SEVERAL studies of the photochemistry of substituted cyclopent-2-enones have been reported. Cyclopent-2-enone itself and many 3-alkylcyclopent-2-enones commonly undergo a variety of photo-induced bimolecular cycloaddition reactions,[1] whereas 4- and 5-alkyl substituted cyclopent-2-enones produce photoproducts resulting largely from intramolecular [2 + 2] cycloadditions (see Scheme 1).[2] Cycloaddition reactions involving H-transfer processes are also well known,[3] and the photochemical α-(1,2-)cleavage of a cyclopent-2-enone has been described.[4] The photochemistry of cyclopent-2-enones bearing substituents containing chromophores in addition to the intact enone chromophore has received little attention. In connection with studies on the photodecomposition of the pyrethrin insecticide [*viz.* (1)] we have examined the solution photochemistry of simple derivatives of the 2-(prop-2-enyl)cyclopent-2-enone units [*viz.* (2)] present in these compounds.[5] We report here the results of these studies and of similar studies with closely related cyclopent-2-enones.



SCHEME 1



(1)

(2) a; R' = H
b; R' = Me
c; R' = Et

We first examined the photolysis of derivatives of the 4-hydroxycyclopent-2-enones (2a—c; R = OH). The cyclopent-2-enone (2a; R = OH) is readily available, and both (2b; R = OH) and (2c; R = OH) were synthesised as described previously.[6] Acetate derivatives (2a—c; R = OAc) were prepared from the alcohols by straightforward methods, whereas the methyl ethers (2a—c; R = OMe) were obtained either from the corresponding semicarbazone derivatives of (2a—c; R = OH) by treatment with methanol–acid mixtures or *via* a Wittig reaction approach.[6a]

Irradiation of the methyl ether (2a, R = OMe) in hexane through quartz or Pyrex resulted in the slow production of a photostationary equilibrium mixture of (2a; R = OMe) and a single photoproduct corresponding to *ca.* 83% conversion. Preparative g.l.c. purification

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[1] (*a*) W. L. Dilling, *Chem. Rev.*, 1966, **66**, 373; (*b*) P. G. Bauslaugh, *Synthesis*, 1970, **2**, 287; (*c*) P. de Mayo, *Accounts Chem. Res.*, 1971, **4**, 41.

[2] (*a*) W. C. Agosta and A. B. Smith, *J. Amer. Chem. Soc.*, 1971, **93**, 5513; (*b*) W. C. Agosta, A. B. Smith, A. S. Kende, R. G. Eilerman, and J. Benham, *Tetrahedron Letters*, 1969, 4517; (*c*) S. Wolff and W. C. Agosta, *J.C.S. Chem. Comm.*, 1972, 226; (*d*) R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, *J. Amer. Chem. Soc.*, 1972, **95**, 4346; (*e*) H. E. Zimmerman and R. D. Little, *J.C.S. Chem. Comm.*, 1972, 698.

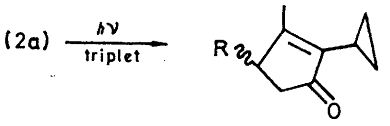
[3] (*a*) R. Reinfried, D. Bellus, and K. Schaffner, *Helv. Chim. Acta*, 1971, **54**, 1517; (*b*) G. Mark, H. Matthaus, F. Mark, J. Leitich, D. Henneberg, G. Schomburg, I. Wilucki, and O. E. Polansky, *Monatsh.*, 1971, **102**, 37; (*c*) J. L. Ruhlen and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1967, **89**, 4944.

[4] B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1963, **46**, 2473.

[5] Preliminary communication, M. J. Bullivant and G. Pattenden, *J.C.S. Chem. Comm.*, 1972, 864.

[6] (*a*) G. Pattenden and R. Storer, *J.C.S. Perkin I*, 1974, 1603; (*b*) L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc.* (*C*), 1969, 1016.

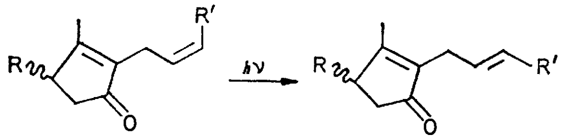
gave a solid, m.p. *ca.* 22°, isomeric with (2a; R = OMe), whose spectroscopic properties (Experimental section) showed that structural modifications had taken place in only the prop-2-enyl side chain. The n.m.r. spectrum showed no absorption corresponding to olefinic and vinyl-methylene protons, and instead displayed three groups of multiplets (ratio 1 : 2 : 2) centred at τ 8.57, 8.94, and 9.27, associated with cyclopropyl ring protons; the i.r. spectrum revealed no olefinic C–H out-of-plane absorption bands. These data were consistent with the cyclopropane formulation (3a) arising from photochemical di-π-methane rearrangement of (2a; R = OMe). Similarly, irradiation of the corresponding acetate (2a; R = OAc) led to (3b), the structure of which was also apparent from its spectral properties.



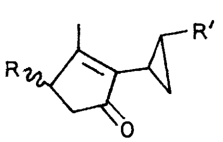
(3) a; R = OMe
b; R = OAc

Irradiation of (2a; R = OAc) in hexane in the presence of either acetophenone or chlorobenzene as sensitizer, under conditions where essentially all the light was absorbed by the sensitizer, did not enhance the yield of photoproduct. In addition, analysis of mixtures from irradiation of (2a; R = OAc) quenched by 2,5-dimethylhexa-2,4-diene failed to reveal the presence of (3b), and starting material was recovered almost quantitatively. Since direct irradiation and sensitised irradiation of (2a; R = OAc) result in the formation of (3b), and the latter is not observed during quenched irradiations, it seems likely that (3) is derived from a triplet excited state of (2a).

By contrast to the rearrangement (2a) ⟶ (3), photolysis of the *Z*-isomers of the methyl ether (R = OMe) and acetate (R = OAc) derivatives of (2b) and (2c) produced only the corresponding *E*-isomers (4a and b) respectively; no evidence was obtained for the co-formation of cyclopropane photoproducts [*viz.* (5)] resulting from a di-π-methane rearrangement of (2b and c). In all cases photoequilibrium mixtures of the *Z*- and *E*-isomers were produced, and the *E*-isomers were separated and purified by chromatography; the structures of the *E*-isomers followed from their spectral data (Experimental section).

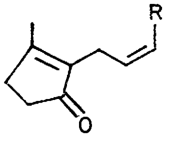


(4) a; R' = Me

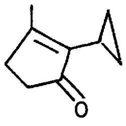


(5) a; R' = Me

The dichotomous photoreaction pathways followed by (2a) and (2b and c) were unexpected, but in separate studies with other cyclopent-2-enones were shown to be general for this type of substituted (prop-2-enyl)cyclopent-2-enone. Thus, photolysis of (6a) led exclusively to the di-π-methane rearrangement product (7), whereas the related cyclopent-2-enone (6b), under identical conditions, gave the *E*-alkene (8).



(6) a; R = H
b; R = Me



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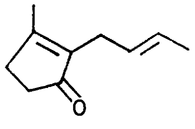
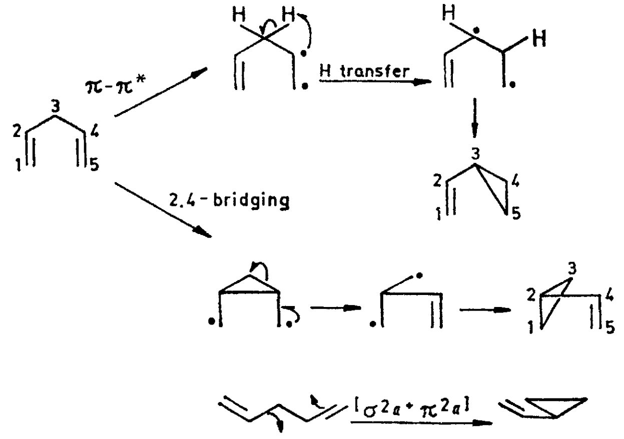


(8)

There is considerable interest in the details of the mechanism of the photochemical di-π-methane rearrangement.[7] In general terms, the rearrangement can be depicted as proceeding *via* a stepwise radical process involving either H-migration from the central methylene group or initial 2,4-bridging and no H-migration (see Scheme) or alternatively as a [$_{\sigma}2_a + _{\pi}2_a$] process involving addition of one σ-bond across an electronically excited π-bond (see Scheme 2). Extensive investigations on structure–multiplicity relationships in the di-π-methane rearrangement have led to the general conclusion that acyclic di-π-methane systems [*e.g.* (10)] rearrange preferentially by way of their singlet excited states, whereas di-π-methane systems in a sterically constrained situation [*e.g.* (11)] do so by way of their triplet states. These observations have been rationalised on the basis of the presence or absence of structural features within the molecule undergoing rearrangement, which provide alternative means for dissipating excitation energy; for extensive discussion on this topic see reference 7.



Scheme 2

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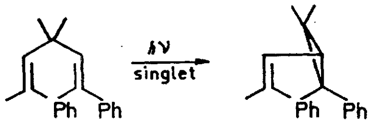
[7] See S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531, and references cited therein.

The di-π-methane system in (2) is special in that it is neither acyclic [*cf.* (10)] nor particularly constrained [*cf.* (11)]; it rearranges inefficiently (estimated quantum yield <0.01) *via* a triplet excited state to only (3). In the light of contemporaneous studies on the di-π-methane rearrangement, the dichotomous photo-reaction pathways followed by (2a) and (2b and c) are best rationalised in terms of the different capacities of the molecules to scatter their triplet energies by ' free-rotor ' effects about the side chain double bonds. In (2b and c) and (6b), free rotation about the excited side-chain π-bonds leads to efficient deactivation of the triplet, and π-geometrical isomerisation takes precedent over di-π-methane rearrangement. In (2a) and (6a), although deactivation of the triplet excited state by rotation about the excited π-bond is also possible, π-geometrical isomerisation cannot be manifested in these structures and instead they undergo inefficient di-π-methane rearrangements.



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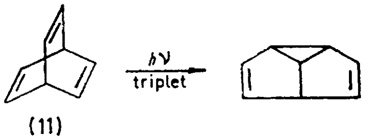
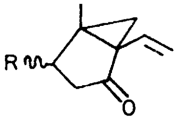


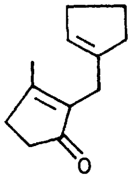
(11)

The selective formation of only one of the two *a priori* possible di-π-methane rearrangement products [*i.e.* (3)/(7) and (12)], is difficult to rationalise. Studies by Zimmerman and his co-workers[7] have led to the conclusion that in most di-π-methane rearrangements the less conjugated π-bond preferentially migrates to the more conjugated π-chromophore, the controlling factor being maintenance of maximum odd-electron stabilisation during the three-membered ring opening step, if the reaction proceeds *via* the 2,4-bridging process (see Scheme 2). By analogy and inference, the cyclopentenones (2a) and (6a) would be expected to produce largely (12a or b) and (12c) respectively, but this was not observed. These data might suggest that the radical pathway *via* the 2,4-bridging process (see Scheme 2) is not followed by (2)/(6) and that the H-migration process is more applicable. Alternatively, steric constraining effects could operate in the sequence leading from (2)/(6) to (12), and instead (3)/(7) is produced.



(12) a; R = OMe
b; R = OAc
c; R = H

To examine the ' free-rotor ' proposal as a means for energy dissipation in substituted 2-(prop-2-enyl)cyclopent-2-enones, we investigated the photolysis of the cyclopentenylmethylcyclopentenone (13). This incorporates a photosensitive di-π-methane chromophore, which is structurally unable to dissipate excitation energy by free rotation about excited π-bonds. We would expect (13) to undergo triplet di-π-rearrangement to (14) or (15) much more efficiently than (2a) rearranges to (3). The cyclopentenone (13) was synthesised from cyclopent-1-enylmethyl chloride (16) as outlined in Scheme 3. An acetoacetate condensation with (16) first produced the ketone (17), which with diethyl carbonate gave the β-oxo-ester (18). Condensation between (18) and bromoacetone led to the dione (19), which was cyclised by base, with concomitant hydrolysis, to the enone (20); decarboxylation of (20) then led to (13).



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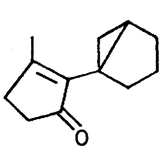

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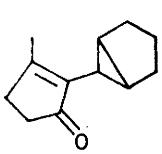

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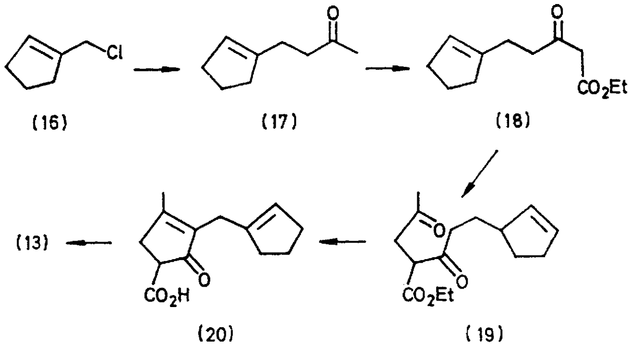

SCHEME 3

In numerous attempts we did not observe photorearrangement of (13) to (14)/(15) or indeed to any other photoproducts; all such attempts led only to polymeric material. Unprecedented steric demands, either in the transition states leading to (14)/(15) or in the products of reaction, could have accounted for these observations. Accordingly, we examined the photolysis of the less substituted cyclopentenones (21) and (22).

The cyclopentenone (21), which lacks a methyl substituent at C-3, was synthesised from cyclohexane-1,3-dione as shown. Reaction between allyl bromide and the carbanion obtained from cyclohexane-1,3-dione produced (23), which with t-butyl hypochlorite was then converted into the chloro-dione (24). Heating (24) in xylene in the presence of potassium carbonate effected simultaneous ring contraction and decarbonylation and gave the cyclopentenone (21).[8] Attempts were also

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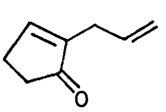
[8] *Cf.* G. Büchi and B. Egger, *J. Org. Chem.*, 1971, **36**, 2021.

made to synthesise (21) from cyclopentane-1,2-dione (25).[9] A Grignard reaction between the isobutyl ether (26) derived from (25), and allylmagnesium bromide gave the alcohol (27), but hydrolysis and dehydration of (27) in acid led only to the positional isomer (28) of (21).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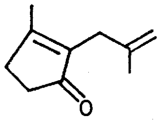
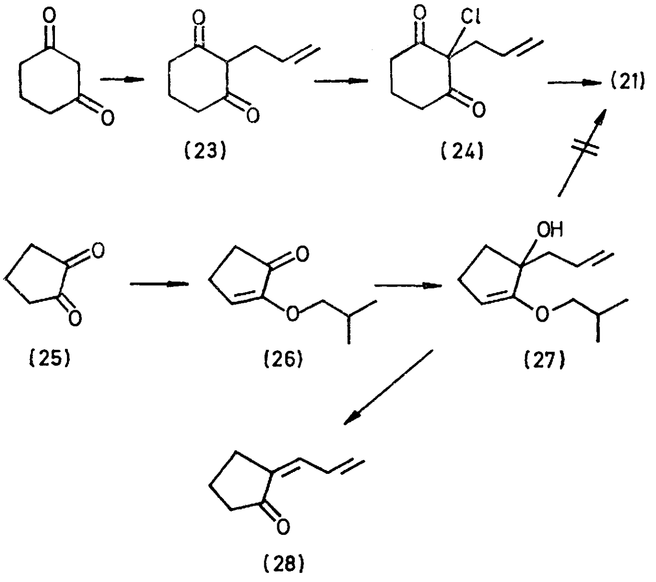
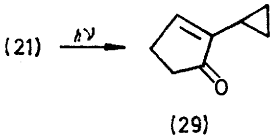
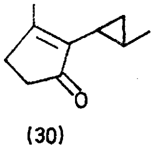

(22)

Photolysis of (21) in hexane produced the expected vinylcyclopropane (29), and at a rate comparable with that observed in the formation of (3) from (2a); These data then suggested that the methyl substituent at C-3 in (2a) has little effect, sterically or otherwise, on the efficiency of the di-π-methane rearrangement in these systems. Photolysis of (22), like that of (13) led to none of the vinylcyclopropane products, *viz.* (30)/(31), to be expected from a di-π-methane rearrangement. Instead in hexane, only polymeric material resulted.



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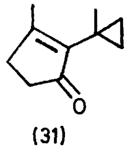
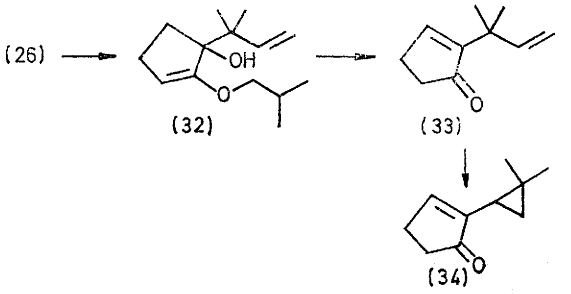

(31)

The general inefficiencies observed for the di-π-methane rearrangements of (2a), (6a), and (21) are probably best rationalised in terms of the radical mechanism involving H-transfer (see Scheme 2). Support for this came from separate studies of the di-π-methane rearrangement of the cyclopentenone (33), a molecule which has the methane portion of the di-π-methane system doubly substituted, which prevents it from undergoing rearrangement *via* H-transfer. The cyclopentenone (33) was synthesised from the keto-ether (26) following reaction with the Grignard reagent from 3,3-dimethylallyl chloride, and hydrolysis and dehydration of the intermediate alcohol (32). Photolysis of (33) in hexane for 3 h resulted in complete conversion into a single volatile product, which after chromatography could be separated in upwards of 60% yield. Spectral data were consonant with the vinylcyclopropane structure (34) expected from di-π-methane rearrangement of (33). Double substitution of the methane unit of the di-π-methane system in (21) [*i.e.* as in (33)] therefore results in more efficient rearrangement [*ca.* 3 h for 100% conversion into (34) against 26 h for 55% conversion into (29)] to the corresponding vinylcyclopropane; this result is similar to observations made by Zimmerman and his colleagues[10] while the present work was in progress. This being so, it is most probable that the di-π-methane rearrangements of (2a), (6a), and (21) to (3), (7), and (29) respectively proceed *via* the radical process involving H-migration rather than by the alternative radical sequence involving initial 2,4-bridging and no H-migration (see Scheme 2).



In an extension to our studies, we examined the photolysis of the insecticidal cyclopentenone derivatives (1; R = Me, R′ = H) and (1; R = Me, R′ = Et). Irradiation of (1; R = Me, R′ = H), under conditions similar to those used in the photolysis of the derivatives (2a; R = OMe or OAc) resulted in almost complete conversion (> 95%) into the vinylcyclopropane product (35)[11] expected from di-π-methane rearrangement. We were unable to detect either of the esters [36; R ≡ (2a)] or [37; R ≡ (2a)] or the lactone (38) in the photolysis products; these molecules have previously been shown to be the principal products from photolysis of simple alkyl esters of *trans*-chrysanthemic acid[12] [*i.e.* the acid

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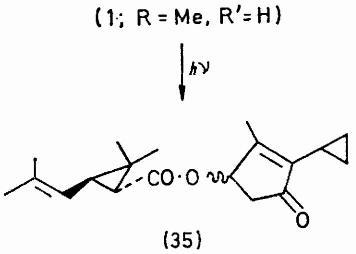
[9] *Cf.* M. F. Ansell and J. W. Ducker, *J. Chem. Soc.*, 1959, 329.

[10] H. E. Zimmermann and J. A. Pincock, *J. Amer. Chem. Soc.*, 1973, **95**, 2957.

[11] M. J. Bullivant and G. Pattenden, *Tetrahedron Letters*, 1973, 3679.

[12] M. J. Bullivant and G. Pattenden, *Pyrethrum Post*, 1971, **11**, 72.

unit in (1) when R = Me]. The vinylcyclopropane (35) was not observed during quenched irradiations of (1; R = Me, R′ = H) with 2,5-dimethylhexa-2,4-diene, which suggests that it arises from a triplet state of (1; R = Me, R′ = H). Photolysis of (1; R = Me, R′ = Et), like photolyses of derivatives of (2c), led almost exclusively to the *E*-isomer (39).



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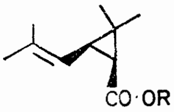

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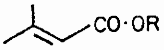

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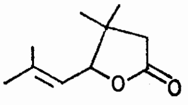

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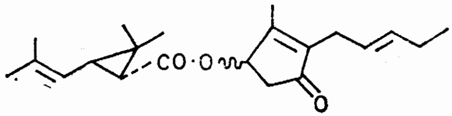

(39)

EXPERIMENTAL

^{1}H N.m.r. spectra were determined with a Perkin-Elmer R10 spectrometer with tetramethylsilane as internal standard. Bands were singlets except where stated otherwise; splittings (*J*) are in Hz. Molecular weights were determined from mass spectra, measured with a A.E.I. MS 902 spectrometer.

4-Acetoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone (2a; R = OAc).—The acetate was prepared from the corresponding alcohol, and had b.p. 95—99° at 0.3 mmHg, n_D^{25} 1.4918 (lit.,[13] b.p. 96—97° at 0.5 mmHg, n_D^{25} 1.4902), $\lambda_{max.}$ (EtOH) 228 nm, (ε 13 250), $\nu_{max.}$ (film) 1 742 and 1 715 cm^{-1}, τ 4.31 (ddt, *J* 18, 10, and 7, CH$_2$·CH:CH$_2$), 4.41br (CHO), 4.94—5.18 (m, : CH$_2$), 7.07 (d, *J* 7, C*H*$_2$·CH:), 7.24 (dd, *J* 18 and 6, C*H*H·CO), 7.86 (dd, *J* 18 and 2, CH*H*·CO), 7.89 (COMe), and 7.98 (:CMe), M^+ 194, and was homogenous in g.l.c. analysis (5% SE30; 105 °C).

(±)-(Z)-*4-Acetoxy-3-methyl-2-(pent-2-enyl)cyclopent-2-enone* (2c; R = OAc).—A solution of (±)-(*Z*)-4-hydroxy-3-methyl-2-(pent-2-enyl)cyclopent-2-enone (2c; R = OH) (2.1 g) and sodium acetate (20 mg) in acetic anhydride (5 ml) was stirred at 25 °C for 3 days, and then heated at 100 °C for 0.5 h. The acetic anhydride was removed *in vacuo* and the residue was dissolved in light petroleum (b.p. 40—60°; 50 ml). The solution was washed successively with aqueous sodium carbonate solution (2 × 20 ml) and water (5 × 15 ml), and then dried. Distillation gave the *acetate* (2.4 g, 92%), b.p. 80—83° at 0.2 mmHg, $\lambda_{max.}$ (EtOH) 227 nm (ε 11 000), $\nu_{max.}$ (film) 1 744, 1 714, and 1 659 cm^{-1}, τ 4.39br (·CH·O·), 4.5—5.0 (m, 2 × :CH), 7.1 (d, *J* 6, :C·C*H*$_2$·CH:), 7.26 (dd, *J* 6 and 18, C*H*H·CO), 7.89 (dd, *J* 2 and 18, CH*H*·CO), *ca.* 7.86 (obscured, C*H*$_2$·CH$_3$), 7.96 (COMe), 8.02 (:CMe), and 9.01 (t, *J* 7, CH$_2$·C*H*$_3$) (Found: C, 69.9; H, 8.5%; *m/e* 222. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.2%; *M*, 222), which was homogenous in g.l.c. analysis (10% PEGA; 150 °C).

(±)-(Z)-*4-Acetoxy-3-methyl-2-(but-2-enyl)cyclopent-2-enone* (2b; R = OAc).—The ester, prepared from the corresponding alcohol as described for (2c; R = OAc),[14] had b.p. 110° at 5 × 10^{-2} mmHg, n_D^{20} 1.4919, $\lambda_{max.}$ (EtOH) 228 nm (ε 10 050), $\nu_{max.}$ (film) 1 738, 1 709, 1 654, and 710 cm^{-1}, τ 4.34br (d, *J ca.* 6, C*H*·OAc), 4.47—5.04 (m, CH:CH), 7.07 (d, *J* 6, :C·C*H*$_2$), *ca.* 7.2 (dd, *J ca.* 6 and 18, CH*H*·CO), 7.8 (dd, *J ca.* 2 and 18, C*H*H·CO), 7.91 (OCOMe), 7.97 (:CMe), and 8.32 (d, *J* 6, :CH·C*H*$_3$), M^+ 208.

Photochemical Reactions.—General procedure. Irradiations were carried out using a water-cooled immersion well with quartz-filtered light from a 100 W medium-pressure mercury vapour lamp (Hanovia type). Solutions were purged with nitrogen before irradiation, and all solvents used were of analytical reagent quality. Reactions were monitored by removing samples at intervals and analysing by g.l.c. Photolyses were usually continued until photoequilibria were established or until extensive decomposition became evident. After removal of the solvents by distillation *in vacuo*, photoproducts were isolated and purified by chromatography.

2-Cyclopropyl-4-methoxy-3-methylcyclopent-2-enone (3a).—By the general procedure, photolysis of 4-methoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone (2a; R = OMe)[6a,15] (3 g) in hexane (1 000 ml) for 10 days, led to a 5 : 1 mixture (by g.l.c. on 5% SE-30; 90 °C) of photoproduct and starting material. Chromatography (25% SE-30; 170 °C) gave the *cyclopropane* (eluted second), m.p. 20—22°, $\lambda_{max.}$ (EtOH) 230 nm (ε 10 250), $\nu_{max.}$ (film) 1 709 and 1 645 cm^{-1}, τ 5.76br (CH·O), 6.64 (OMe), 7.44 (dd, *J* 6 and 18, CH*H*·CO), 7.82 (dd, *J* 2 and 18, C*H*H·CO), 7.91 (:CMe), 8.57 (1 H, m), 8.94 (2 H, m), and 9.27 (2 H, m) (Found: C, 72.3; H, 8.6%; *m/e*, 166. $C_{10}H_{14}O_2$ requires C, 72.3; H, 8.5%; *M*, 166).

4-Acetoxy-2-cyclopropyl-3-methylcyclopent-2-enone (3b).—By the general procedure, photolysis of 4-acetoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone (2a; R = OAc) (1.1 g) in hexane (1 000 ml) for 5 days led to a 1 : 1 mixture (by g.l.c. on 5% SE-30; 105 °C) of photoproduct and starting material. Chromatography (25% SE-30; 183 °C) gave the *cyclopropane* (eluted second), $\nu_{max.}$ 1 744, 1 712, and 1 645 cm^{-1}, τ 4.44br (C*H*·OAc), 7.3 (dd, *J* 7 and 18, C*H*H·CO), 7.93 (dd, *J* 2 and 18, CH*H*·CO), 7.96 (OCOMe), 7.99 (:CMe), 8.61 (1 H, m), 8.87 (2 H, m), and 9.28 (2 H, m) (Found: C, 68.05; H, 7.6%; *m/e*, 194. $C_{11}H_{14}O_3$ requires C, 68.0, H, 7.3%; *M*, 194).

Sensitised Irradiations of 4-Acetoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone (2a; R = OAc).—(a) *By acetophenone.* A solution of the acetate (1 g) and acetophenone (4.52 g) in hexane (1 000 ml) was irradiated for 49 h. Removal of the solvent and chromatography of the residue (5.16 g) in chloroform on silica gel produced a mixture (0.95 g) of acetate (2a; R = OAc) and cyclopropane (3b) in the proportions 88 : 12 (by g.l.c.). Direct irradiation of (2a; R = OAc) in hexane for 49 h produced an 87 : 13 mixture of (2a; R = OAc) and (3b).

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(b) *By chlorobenzene*. A solution of the acetate (1 g) and chlorobenzene (11.3 g) in hexane (1 000 ml) was irradiated for 59 h. Removal of the solvent and analysis of the residue by g.l.c. (10% Apiezon L; 160 °C) showed that (2a; R = OAc) and (3b) were present in the proportions 76 : 24. Direct irradiation of (2a; R = OAc) in hexane for 59 h produced a 78 : 22 mixture of (2a; R = OAc) and (3b).

2,5-Dimethylhexa-2,4-diene-quenched Irradiation of 4-Acetoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone (2a; R = OAc).—A solution of the acetate (0.2 g) and 2,5-dimethylhexa-2,4-diene (4.6 g) in hexane (200 ml) was irradiated for 64 h with Pyrex-filtered light. Removal of the solvent, and purification of the residue by chromatography in 5 : 95 ether–light petroleum (b.p. 40—60°) on silica gel, gave starting material only. No evidence for the formation of cyclopropane (3b) was obtained.

(±)-(E)-4-*Acetoxy-3-methyl-2-(pent-2-enyl)cyclopent-2-enone* (4b; R = OAc).—By the general procedure, photolysis of (*Z*)-4-acetoxy-3-methyl-2-(pent-2-enyl)cyclopent-2-enone (2c; R = OAc) (1.5 g) in hexane (1 000 ml) for 66 h led to a 73 : 27 mixture (by g.l.c. on 10% PEGA; 150 °C) of photoproduct and starting material. Chromatography (25% PEGA; 200 °C) gave the (E)-*olefin* (eluted first), a liquid, n_D^{18} 1.4913, $\lambda_{max.}$ (EtOH) 227 nm (ε 11 050), $\nu_{max.}$ (film) 1 744, 1 716, 1 660, and 970 cm^{-1}, τ 4.38 (d, *J* 6, C*H*·OAc), 4.52—4.92 (m, CH:CH), 7.16 (d, *J* 6, :C·C*H*$_2$·CH:), 7.25 (dd, *J* 6 and 18, C*H*H·CO), 7.87 (dd, *J* 2 and 18, CH*H*·CO), 7.96 (O·COMe), 8.03 (:CMe), *ca.* 8.0 (obscured, C*H*$_2$·CH$_3$), and 9.03 (t, *J* 7, CH$_2$·C*H*$_3$) (Found: C, 70.2; H, 8.05%; *m/e*, 222. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.2%; *M*, 222).

Photolysis of (±)-(*E*)-4-methoxy-3-methyl-2-(pent-2-enyl)cyclopent-2-enone under identical conditions produced a 70 : 30 mixture of *Z*- and *E*-isomers.

(±)-(E)-4-*Acetoxy-3-methyl-2-(but-2-enyl)cyclopent-2-enone* (4a; R = OAc).—By the general procedure, photolysis of (*Z*)-4-acetoxy-3-methyl-2-(but-2-enyl)cyclopent-2-enone (2b; R = OAc) (0.55 g) in hexane (600 ml) for 2 h led to a 60 : 40 mixture (by g.l.c. on 10% Apiezon L; 160 °C) of photoproduct and starting material. Chromatography (25% Apiezon L; 165 °C) gave the (E)-*olefin* (eluted first) a liquid, $\lambda_{max.}$ (EtOH) 227 nm (ε 8 500), $\nu_{max.}$ (film) 1 736, 1 708, 1 653, and 971 cm^{-1}, τ 4.42 (d, *J* 6, C*H*·OAc), 4.52—4.76 (m, CH : CH), 7.19 (d, *J* 6, :C·C*H*$_2$·CH:), *ca.* 7.3 (dd, *J* 6 and 18, C*H*H·CO), *ca.* 7.94 (dd, *J* 2 and 18, CH*H*·CO), 7.98 (OCOMe), 8.05 (:CMe), and 8.38 (d, *J* 4, :CHMe) (Found: *m/e*, 208.1099. $C_{12}H_{16}O_3$ requires *M*, 208.1099).

2-Cyclopropyl-3-methylcyclopent-2-enone (7).—By the general procedure, photolysis of 3-methyl-2-(prop-2-enyl)-cyclopent-2-enone [6a, 16] (1.17 g) (6a) in hexane (1 000 ml) for 72 h led to a 31 : 4 : 65 mixture (by g.l.c. on 10% Apiezon L; 132 °C) of photoproducts (eluted second and third) and starting material. Chromatography (30% SE-30; 200 °C) gave the *cyclopropane* (eluted third), a liquid, $\lambda_{max.}$ 242 nm (ε 9 300), $\nu_{max.}$ (film) 1 700 and 1 648 cm^{-1}, τ 7.3—8.0 (m, CH$_2$·CH$_2$·CO), 7.89 (:CMe), and 8.3—9.5 (5 H, m) (Found: *m/e*, 136.0879. $C_9H_{12}O$ requires *M*, 136.0888).

(E)-*2-(But-2-enyl)-3-methylcyclopent-2-enone* (8).—By the general procedure, photolysis of (*Z*)-2-(but-2-enyl)-3-methyl-cyclopent-2-enone [17] (0.38 g) (6b) in hexane (170 ml) for 21 h led to a 64 : 36 mixture (by g.l.c. on 10% Apiezon L; 132 °C) of photoproduct and starting material. Chromatography (15% Apiezon L; 158 °C) gave the E-*olefin* (eluted first), a liquid, $\lambda_{max.}$ (EtOH), 236 nm (ε 10 300), $\nu_{max.}$ (film) 1 694, 1 647, and 974 cm^{-1}, τ 4.6—4.78 (m, CH:CH), 7.23br (C*H*$_2$·CH:), 7.44—7.84 (m, CH$_2$·CH$_2$·CO), 8.0 (:CMe), and 8.38 (d, *J ca.* 4, :CH*Me*) (Found: *m/e*, 150.1040. $C_{10}H_{14}O$ requires *M*, 150.1045).

Cyclopent-1-enylmethyl Chloride (16).—Cyclopent-1-ene-carbaldehyde was prepared (35%) from *cis–trans*-cyclohexane-1,2-diol, largely according to the procedure of Brown *et al*; [18] it had b.p. 55—60° at 20 mmHg, n_D^{24} 1.4848 (lit., b.p. 52° at 20 mmHg, n_D^{17} 1.4892), $\nu_{max.}$ (film) 2 720, 1 681, and 1 616 cm^{-1}, τ 0.26 (CHO), 3.17br (:CH), 7.2—8.4 (6 H, m), M^+ 96.

Reduction of the aldehyde with lithium aluminium hydride in ether produced (75%) cyclopent-1-enylmethanol, b.p. 72—75° at 20 mmHg, n_D^{22} 1.4761 (lit.,[19] b.p. 75° at 20 mmHg, n_D^{20} 1.4760), $\nu_{max.}$ (film) 3 330 cm^{-1}, τ 4.5br (:CH), 5.61 (OH), 5.99br (CH$_2$·OH), and 7.44–8.48 (6 H, m), M^+ 98.

Tri-n-octylphosphine (93 g) was added to a stirred solution of cyclopent-1-enylmethanol (23 g) in carbon tetrachloride (465 ml), and the mixture was stirred vigorously for 0.5 h. The carbon tetrachloride was removed *in vacuo*; chromatography of the residue in pentane on alumina (type H) gave the chloride (*ca.* 20 g), τ 4.37br (:CH), 5.99 (CH$_2$Cl), and 7.4—8.3 (6 H, m), which was used without further purification.

Ethyl 5-(Cyclopent-1-enyl)-3-oxopentanoate (18).—Ethyl acetoacetate (62 g) was added to a cold solution of sodium methoxide (12.8 g) in dry methanol (150 ml), and the solution was then stirred and treated during 0.25 h with cyclopent-1-enylmethyl chloride (20 g). The mixture was heated at 100 °C for 1 h, then cooled and filtered. The filtrate was acidified with acetic acid, then evaporated to dryness *in vacuo*. The vigorously stirred and hot solution of the residue in water (500 ml) was treated, in three portions during 1.5 h, with sodium hydroxide (40 g) in water (300 ml). The mixture was cooled and then extracted with ether (3 × 100 ml). Evaporation of the dried extracts and distillation of the residue gave 4-(cyclopent-1-enyl)butan-2-one (12.3 g), b.p. 84—88° at 15 mmHg, $\nu_{max.}$ (film) 1 710 and 805 cm^{-1}, τ 4.72br (:CH), 7.3—8.0 (10 H, m), 7.93 (COMe), M^+ 138. The ketone (11 g) was added, during 2.5 h, to a stirred mixture of sodium hydride (3.6 g) and diethyl carbonate (17.7 g) in ether (50 ml) maintained under gentle reflux. The mixture was heated under reflux for a further 1 h, then cooled and poured onto ice–water to which glacial acetic acid (12 ml) had been added. The solution was extracted with ether, and the combined extracts were dried and evaporated. Distillation of the residue gave the *oxo-ester* (5.5 g), b.p. 82—90° at 0.2 mmHg, $\nu_{max.}$ (film) 1 737, 1 712, and 1 636 cm^{-1}, τ 4.69br (:CH), 5.85 (q, *J* 7, C*H*$_2$·CH$_3$), 6.59 (CO·CH$_2$·CO), 7.2—8.5 (10 H, m), and 8.73 (t, *J* 7, CH$_2$·C*H*$_3$) (Found: C, 68.9; H, 8.5%; *m/e*, 210. $C_{12}H_{18}O_3$ requires C, 68.5; H, 8.6%; *M*, 210).

2-(Cyclopent-1-enylmethyl)-3-methylcyclopent-2-enone (13).—A solution of the oxo-ester (18) (5.5 g) in dry dioxan (10 ml) was added during 0.2 h to a stirred suspension of sodium hydride (0.65 g) in dioxan (10 ml). The mixture was cooled to −25 °C, and then bromoacetone (5 g) in dioxan (5 ml) was

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added. After warming to 25 °C, the solution was heated at 70 °C for 1 h, treated with 20% sulphuric acid (24 ml), heated at 100 °C for 1 h, cooled, and extracted with ether (3 × 100 ml). Evaporation of the dried extracts left a residue which on distillation gave the *cyclopentenone* (2.32 g, 50%), b.p. 104—105° at 1.5 mmHg, $\lambda_{max.}$ (EtOH), 233 nm (ε 9 610), $\nu_{max.}$ (film) 1 697 and 1 647 cm^{-1}, τ 4.8br (:CH), 7.07br (:C·CH$_2$·C:), 7.28—8.38 (10 H, m), and 7.96 (:CMe) (Found: *m/e*, 176.1202. $C_{12}H_{16}O$ requires *M*, 176.1201).

3-*Methyl*-2-(2-*methylprop*-2-*enyl*)*cyclopent*-2-*enone* (22).—The ketone was prepared as described previously,[20] and showed b.p. 59—62° at 0.2 mmHg (lit., 70—72° at 0.4 mmHg), n_D^{26} 1.4913, $\lambda_{max.}$ (EtOH) 235 nm (ε 11 200), $\nu_{max.}$ (film) 1 698, 1 648, and 898 cm^{-1}, τ 5.41br (:CH$_2$), 7.17 (m, :C·CH$_2$·C:), 7.3—8.0 (4 H, m), 7.99 (:CMe), and 8.39 (H$_2$C:C*Me*), M^+ 150.

2-*Isobutoxycyclopent*-2-*enone* (26).—The vinyl ether was prepared from cyclopentanone, *via* cyclopentane-1,2-dione, as previously described.[9] It had b.p. 66—69° at 0.05 mmHg, m.p. 15—16°, n_D^{22} 1.4798 (lit., b.p. 130—132° at 15 mmHg, n_D^{20} 1.4770), $\lambda_{max.}$ (EtOH) 251 nm (ε 9 700), τ 3.77br (:CH), 6.47 (d, *J* 7, OCH$_2$), 7.46—8.2 (5 H, m), and 9.03 (d, *J* 7, Me$_2$), M^+ 154.

2-*Isobutoxy*-1-(*prop*-2-*enyl*)*cyclopent*-2-*enol* (27).—A solution of 2-isobutoxycyclopent-2-enone (3.1 g) in ether (20 ml) was added to a stirred solution of the Grignard reagent prepared from allyl bromide (3.7 g) and magnesium (0.98 g) in ether (70 ml). The mixture was heated under reflux for 0.75 h, then cooled, and poured into cold saturated ammonium chloride solution. The mixture was diluted with 2N-hydrochloric acid (15 ml) and then thoroughly extracted with ether. Evaporation of the dried extracts left a residue which was distilled to give the *alcohol* (2.1 g, 75%), b.p. 52—53° at 0.05 mmHg, n_D^{21} 1.4841, $\nu_{max.}$ (film) 1 747, 1 643, 1 009, and 931 cm^{-1}, τ 4.26 (ddt, *J* 16, 11, and 6, C*H*:CH$_2$), 4.82—5.1 (m, :CH$_2$), 6.89 (OH), and 7.6—8.4 (8 H, m) (Found: *m/e*, 140.0833. $C_8H_{12}O_2$ requires *M*, 140.0837).

2-*Prop*-2-*enylidene cyclopentanone* (28).—A mixture of 2-isobutoxy-1-(prop-2-enyl)cyclopent-2-enol (27) (1 g) and 6N-hydrochloric acid (10 ml) in ether (5 ml) was shaken vigorously at 25 °C for 64 h, and then extracted with ether (4 × 5 ml). Evaporation of the dried extracts left the diene (0.8 g, 95%) as a liquid, $\lambda_{max.}$ (EtOH) 278 nm, $\nu_{max.}$ (film) 1 714, 1 629, 1 600, 997, 930, and 831 cm^{-1}, τ 3.26 (d, *J* 10, :C*H*·CH:CH$_2$), 3.59 (ddd, *J* 8, 10, and 15, :CH·C*H*:CH$_2$), 4.41 (d, *J* 15, :C*H*H), 4.52 (d, *J* 8, :CH*H*), and 7.2—8.2 (6 H) M^+ 122.

2-(*Prop*-2-*enyl*)*cyclohexane*-1,3-*dione* (23).—Allyl bromide (50 g) was added during 15 min to a cold (0 ± 1 °C) and stirred solution of potassium hydroxide (29 g) and cyclohexane-1,3-dione (50 g) in water (100 ml). The mixture was stirred at 25 °C for 18 h then at 50 °C for 3 h, and cooled to 25 °C. 4N-Sodium hydroxide (250 ml) was added, and the solution was washed with ether (4 × 100 ml) and then poured into hydrochloric acid (200 g) containing crushed ice (200 g). The solid which separated was filtered off, washed, dried, and sublimed to give the *dione* (35 g, 54%), m.p. 120—123°, $\lambda_{max.}$ (EtOH) 261 nm (ε 13 600), $\nu_{max.}$ (CHCl$_3$) 3 250, 1 625, 997, and 935 cm^{-1}, τ 0.56 (OH), 3.75—4.57 (m, C*H*:CH$_2$), 4.82—5.29 (m, :CH$_2$), 6.95 (d, *J* 6, C*H*$_2$·CH:CH$_2$), 7.35—7.8 (m, C*H*$_2$C·OH and C*H*$_2$·CO), and 7.82—8.35 (2 H, m) (Found: C, 70.6; H, 8.2%; *m/e*, 152. $C_9H_{12}O_2$ requires C, 71.0; H, 7.95%; *M*, 152).

2-*Chloro*-2-(*prop*-2-*enyl*)*cyclohexane*-1,3-*dione* (24).— t-Butyl hypochlorite (28 g) was added, during 2 h, to a stirred solution of 2-(prop-2-enyl)cyclohexane-1,3-dione (39.4 g) in dry chloroform (360 ml) at −20 °C under nitrogen. The mixture was stirred at −20 °C for 2 h, then at 25 °C for 0.5 h, and distilled to give the *chloride* (20 g, 40%), b.p. 76—77° at 0.5 mmHg, $\nu_{max.}$ 1 736, 1 713, 1 642, 984, 935, and 786 cm^{-1}, τ 4.31 (ddt, *J* 9, 18, and 6, CH$_2$·C*H*:CH$_2$), 4.68—5.16 (m, :CH$_2$), and 6.57—8.41 (6 H, m) (Found: C, 57.6; H, 6.4%; *m/e*, 186/188. $C_9H_{11}ClO_2$ requires C, 57.9; H, 5.9%; *M*, 186/188).

2-(*Prop*-2-*enyl*)*cyclopent*-2-*enone* (21).—A mixture of 2-chloro-2-(prop-2-enyl)cyclohexane-1,3-dione (10.4 g) and anhydrous potassium carbonate (6 g) in dry xylene (125 ml) was heated under reflux for 17 h, until evolution of gas ceased. Distillation gave the *cyclopentenone* (0.54 g, 8%), b.p. 31—33° at 0.3 mmHg, $\lambda_{max.}$ (EtOH) 227 nm (ε 9 300), $\nu_{max.}$ (film) 1 701, 1 639, 1 008, 926, and 799 cm^{-1}, τ 2.87br (C*H*:C·CO), 4.23 (ddt, *J* 9, 18, and 6, CH$_2$·C*H*:CH$_2$), 4.83—5.13 (m, :CH$_2$), 7.16 (d, *J* 6, C*H*$_2$·CH:), and 7.28—7.79 (4 H, m) (Found: *m/e*, 122.0723. $C_8H_{10}O$ requires *M*, 122.0732), homogenous in g.l.c. analysis (10% SE-30; 104 °C).

2-*Cyclopropylcyclopent*-2-*enone* (29).—By the general procedure, photolysis of 2-(prop-2-enyl)cyclopent-2-enone (21) (0.7 g) in hexane (600 ml) for 26 h led to a 55 : 45 mixture (by g.l.c. on 15% Apiezon L; 140 °C) of photoproduct and starting material. Chromatography (15% Apiezon L; 140 °C) gave the *cyclopropane* (eluted second), a liquid, $\lambda_{max.}$ (EtOH) 236 nm (ε 8 000), $\nu_{max.}$ (film) 1 703, 1 638, and 800 cm^{-1}, τ 3.17br (:CH), 7.34—7.9 (4 H, m), and 8.26—9.4 (5 H, m) (Found: *m/e*, 122.0722. $C_8H_{10}O$ requires *M*, 122.0732).

1-(1,1-*Dimethylprop*-2-*enyl*)-2-*isobutoxycyclopent*-2-*enol* (32).—A solution of 2-isobutoxycyclopent-2-enone (5.2 g) in tetrahydrofuran (10 ml) was added to a stirred solution of the Grignard reagent prepared from 3,3-dimethylallyl chloride (5.3 g) and magnesium (6 g) in tetrahydrofuran (20 ml) under nitrogen. The mixture was stirred at 25 °C for 0.25 h, then poured into cold saturated ammonium chloride solution and extracted with ether. Evaporation of the dried extracts left a residue which was distilled to give the *alcohol* (7.5 g, 95%), b.p. 87—90° at 0.5 mmHg, n_D^{22} 1.4730, $\nu_{max.}$ (film) 3 530, 1 650, 1 003, and 913 cm^{-1}, τ 3.85 (dd, *J* 10 and 18, C*H*:CH$_2$), 4.79—5.18 (m, :CH$_2$), 5.41br (:CH), 6.52 (d, *J* 6, OCH$_2$), 7.76 (OH), 7.8—8.45 (5 H, m), 8.91 (Me$_2$), and 9.04 (d, *J* 6, CH*Me*$_2$), (Found: C, 74.6; H, 10.95. $C_{14}H_{24}O_2$ requires C, 74.9; H, 10.8%).

Attempts to synthesise the alcohol by using the Grignard reagent from 3,3-dimethylallyl bromide were unsuccessful. The only product isolated was 3,3,6-trimethylhepta-1,5-diene, b.p. 50—55° at 30 mmHg, n_D^{23} 1.4421 (lit.,[21] b.p. 70—71.5° at 49 mmHg, $n_D^{22.5}$ 1.4400), $\nu_{max.}$ (film) 1 644, 1 010, 922, and 848 cm^{-1}, τ 4.18 (dd, *J* 9 and 18, C*H*:CH$_2$), 4.87 (t, *J* 6.5, C*H*:CMe$_2$), 4.93—5.31 (m, :CH$_2$), 8.02 (d, *J* 6.5, C*H*$_2$·CH:), 8.31 (:CMe), 8.41 (:CMe), and 9.03 (CMe$_2$), M^+ 138.

2-(1,1-*Dimethylprop*-2-*enyl*)*cyclopent*-2-*enone* (33).— A mixture of 1-(1,1-dimethylprop-2-enyl)-2-isobutoxycyclopent-2-enol (32) (2 g) and 2N-hydrochloric acid (30 ml) in ether (30 ml) was shaken vigorously at 25 °C for 50 h, and

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[20] L. Crombie, A. J. B. Edgar, S. H. Harper, M. W. Lowe, and D. Thompson, *J. Chem. Soc.*, 1950, 3552.

[21] H. Kwart and R. K. Miller, *J. Amer. Chem. Soc.*, 1954, **76**, 5403.

then extracted with ether (2 × 20 ml). Evaporation of the dried extracts and distillation of the residue gave the *cyclopentenone* (2.7 g, 80%), b.p. 67—71° at 3 mmHg, n_D^{25} 1.4855, $\lambda_{max.}$ (EtOH) 226 nm (ε 7 950), $\nu_{max.}$ 1 702, 1 644, 1 620, 990, 919, and 794 cm^{-1}, τ 2.7br (:CH), 3.91 (dd, *J* 10 and 18, C*H*:CH$_2$), 4.84—5.27 (m, :CH$_2$), 7.3—7.8 (4 H), and 8.7 (CMe$_2$) (Found: *m/e*, 150.1039. $C_{10}H_{14}O$ requires *M*, 150.1045), which was homogenous in g.l.c. analysis (15% Apiezon L; 162 °C).

2-(2,2-*Dimethylcyclopropyl*)*cyclopent*-2-*enone* (34).—By the general procedure, photolysis of 2-(1,1-dimethylprop-2-enyl)cyclopent-2-enone (33) (1 g) in hexane (700 ml) for 3 h resulted in complete conversion into the cyclopropane (by g.l.c. on 15% Apiezon L; 160 °C). Chromatography in benzene–light petroleum (b.p. 60—80) (1 : 1) on silica gel (30 g) gave the *cyclopropane* (0.5 g, 55%) as a liquid, $\lambda_{max.}$ (EtOH) 239 nm (ε 4 850), $\nu_{max.}$ 1 705, 1 634, and 794 cm^{-1}, τ 3.03 (:CH), 7.31—7.84 (4 H, m), 8.84 (CMe), 9.14 (CMe), and 8.24—9.48 (3 H, m) (Found: *m/e*, 150.1035. $C_{10}H_{14}O$ requires *M*, 150.1045).

(±)-3-*Cyclopropyl*-2-*methyl*-4-*oxocyclopent*-2-*enyl* (+)-2,2-*Dimethyl*-trans-3-(2-*methylprop*-1-*enyl*)*cyclopropanecarboxylate* (35).—By the general procedure, photolysis of (±)-prop-2-enylrethronyl (+)-*trans*-chrysanthemate (1; R = Me, R′ = H) (1.52 g) in hexane (1 000 ml) for 20 days led to a 95 : 5 mixture (by g.l.c. on 10% Carbowax 20M; 225 °C) of photoproduct and starting material. Chromatography in hexane on silica gel gave the *cyclopropane* (1.35 g, 90%), an oil, $\nu_{max.}$ (film) 1 723, 1 714, 1 642, and 861 cm^{-1}, τ 4.38br (d, CH·OCO), 5.13 (dm, *J ca.* 7, :CH), 7.31 (dd, *J* 6 and 18, C*H*H·CO), 7.9 (dd, *J* 2 and 18, CH*H*·CO), 7.98 (:CMe), 8.32 (2x : CMe), 8.75 (Me), 8.87 (Me), and 9.1 (2 H, m) (Found: M^+, 302.1880. $C_{19}H_{26}O_3$ requires *M*, 302.1880). A similar result was obtained by using Pyrex-filtered light.

Saponification of the ester (0.25 g) in hot ethanol (10 ml) and water (2.5 ml) containing sodium hydroxide (0.15 g), followed by isolation and purification of the acidic product by chromatography (silica gel; 10 : 1 light petroleum–ether), gave *trans*-chrysanthemic acid, spectrally identical with an authentic sample.

2,5-*Dimethylhexa*-2,4-*diene-quenched Irradiation of* (±)-*Prop*-2-*enylrethronyl* (+)-trans-*Chrysanthemate* (1; R = Me, R′ = H).—A solution of the ester (0.5 g) and 2,5-dimethylhexa-2,4-diene (7.3 g) in hexane (200 ml) was irradiated for 42 h with Pyrex-filtered light. Removal of the solvent left starting material only, homogeneous in g.l.c. analysis (10% Carbowax 20M; 225 °C).

Photolysis of the ester in hexane in the absence of 2,5-dimethylhexa-2,4-diene for the same time led to 20% conversion into the cyclopropane (35).

(±)-2-*Methyl*-4-*oxo*-3-[(E)-*pent*-2-*enyl*]*cyclopent*-2-*enyl* (+)-2,2-*Dimethyl*-trans-3-(2-*methyl-Prop*-1-*enyl*)*cyclopropanecarboxylate* (39).—By the general procedure, photolysis of (±)-(*Z*)-pent-2-enylrethronyl (+)-*trans*-chrysanthemate (1; R = Me, R′ = Et) (0.5 g) in hexane (700 ml) for 1.5 h led to a 2 : 1 mixture (by g.l.c. on 15% Carbowax 20M; 205 °C), of photoproduct and starting material. Chromatography (15% Carbowax 20M; 205 °C) gave the (E)-*olefin* (eluted first), $\nu_{max.}$ (film) 1 720, 1 660, and 861 cm^{-1}, τ 4.4br (CH·O), 4.53—4.85 (m, CH:CH), 5.19 (d, *J* 8, Me$_2$C:C*H*), 7.18 (d, *J* 6, :C·CH$_2$·C:), 7.27 (dd, *J* 6 and 18, C*H*H·CO), *ca.* 7.8 (obscured CH*H*·CO), *ca,* 7.9 (obscured, Me$_2$C:CH·C*H*), *ca.* 7.9 (obscured C*H*$_2$·CH$_3$), 8.03 (:CMe), 8.3 (Me$_2$C:), *ca.* 8.7 (obscured, C*H*·CO), 8.74, 8.76 (Me), 8.86 (Me), and 9.04 (t, *J* 7, CH$_2$·C*H*$_3$) (Found: M^+, 330.2185. $C_{21}H_{30}O_3$ requires *M*, 330.2195).

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