

Photochemistry of 2-(Cycloalk-1-enyl)cycloalkanones. A New Photochemical Reaction of $\beta\gamma$ -Unsaturated Ketones

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On u.v. irradiation 2-(cyclohex-1-enyl)cyclohexanone (2) reacts by γ -hydrogen abstraction by the carbonyl oxygen atom and cyclobutane formation to form tricyclo[6.4.0.0^{2,7}]dodec-6-en-1-ol (4). In contrast, 2-(cyclohept-1-enyl)cycloheptanone (11) or 2-(cyclo-oct-1-enyl)cyclo-octanone (13) undergoes oxetan formation between the two double bonds giving 2-oxatetracyclo[8.5.0.0^{1,9}.0^{3,8}]pentadecane (12) or 2-oxatetracyclo[9.6.0.0^{1,10}.0^{3,10}]heptadecane (14), respectively.

THE photochemistry of $\beta\gamma$ -unsaturated ketones has been widely studied and the most frequently reported transformations have been 1,3- and 1,2-acyl shifts from, respectively, the excited singlet and triplet states.¹ The formation of isomeric cyclobutanols is an important photochemical reaction if there is a γ -hydrogen atom that can be readily abstracted.^{1e,2}

The excited states in $\beta\gamma$ -unsaturated ketones have been recently calculated to be predominantly of $n \rightarrow \pi^*$ character for the lowest singlet and of $\pi \rightarrow \pi^*$ character for the lowest triplet.³ The photoproducts from the two states are consistent with the changes in orbital overlap that occur. The $\pi \rightarrow \pi^*$ character of the lowest triplet state has been supported by the phosphorescence spectra of several $\beta\gamma$ -unsaturated ketones.⁴ In some cases the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states are of similar energy and solvent effects determine which is the lower.⁴ (An alternative explanation for the dichotomy between the singlet and triplet states, where both are assumed to be of $n \rightarrow \pi^*$ character, has been proposed in terms of spin distribution.^{1f})

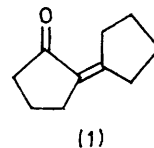
There are many factors which determine the photochemical transformation that is observed for a particular $\beta\gamma$ -unsaturated ketone. In general, intersystem crossing is inefficient for these ketones and direct irradiation gives products from an excited singlet state. 1,3-Acyl shifts commonly occur and such rearrangements are assisted by the overlap of the orbitals on the double bond and the carbonyl group.^{1h,j} This overlap, which depends on the conformation of the molecule, also results in enhancement of the u.v. absorption spectrum ($n \rightarrow \pi^*$ region).^{3,5} The 1,3-acyl shift is assisted by any factors which stabilise the incipient allyl radical, e.g. an aromatic ring.^{1d} Conformational effects also

influence the ease of γ -H abstraction and minor structural changes can radically alter the observed photochemistry.^{1e}

Sensitised irradiation usually results in a 1,2-acyl shift,^{1c,e-i,6} or oxa-di- π -methane rearrangement, but certain $\beta\gamma$ -unsaturated ketones^{1e} are inert under these conditions. Rotational isomerism^{1a} or ring twisting^{1e} may be easier routes for the dissipation of triplet energy rather than the 1,2-acyl shift. In some cases steric factors may preclude the formation of a stable product from a 1,2-acyl shift. The difference in triplet state reactivities could, however, be due to the presence of different low lying triplet states.

This paper reports the photochemical behaviour of a series of 2-(cycloalk-1-enyl)cycloalkanones, usually in equilibrium with their isomeric 2-(cycloalkylidene)cycloalkanones, on direct and sensitised irradiation. The formation of oxetans on irradiation of 2-(cyclohept-1-enyl)cycloheptanone and 2-(cyclo-oct-1-enyl)cyclo-octanones is a new photochemical reaction of $\beta\gamma$ -unsaturated ketones.⁷

The first compound studied, the $\alpha\beta$ -unsaturated ketone, 2-(cyclopentylidene)cyclopentanone (1), was



stable to both direct and acetone-sensitised irradiation. Several other $\alpha\beta$ -unsaturated ketones have been reported to be photochemically stable, including 2-(isopropylidene)cyclopentanone,⁸ a close analogue of (1),

³ K. N. Houk, D. J. Northington, and R. E. Duke, jun., *J. Amer. Chem. Soc.*, 1972, **92**, 6233.

⁴ K. G. Hancock and R. O. Grider, *J.C.S. Chem. Comm.*, 1972, 580.

⁵ E.g. D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. (B)*, 1967, 216; R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 1956, 2302.

⁶ R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, 1971, **93**, 3957, 3963; W. G. Dauben, M. S. Kellog, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, 1970, **92**, 1786; J. Ipaktschi, *Tetrahedron Letters*, 1969, 215; H. Hart and R. K. Murray, *ibid.*, p. 379; S. Domb, K. Schaffner, G. Bozzato, and J. A. Saboz, *Helv. Chim. Acta*, 1969, **52**, 2436; K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron*, 1968, **24**, 6725; J. R. Williams and H. Ziffer, *Chem. Comm.*, 1967, 469; *Tetrahedron*, 1969, **24**, 6725.

⁷ Preliminary report, R. C. Cookson, and N. R. Rogers, *J.C.S. Chem. Comm.*, 1973, 809.

⁸ (a) D. R. Morton, D. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 4349; (b) D. R. Morton and N. J. Turro, *ibid.*, 1973, **95**, 3947.

¹ (a) K. G. Hancock and R. O. Grider, *Tetrahedron Letters*, 1971, 4281; 1972, 1367; (b) D. I. Schuster and D. H. Sussmann, *ibid.*, 1970, 1661; (c) J. Ipaktschi, *ibid.*, 1969, 2153; 1970, 3179; (d) H. Sato, K. Nakinishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, 1973, **29**, 275; (e) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1972, **94**, 4356, 9252; (f) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *ibid.*, 1971, **93**, 4309; (g) E. Baggolini, K. Schaffner, and O. Jeger, *Chem. Comm.*, 1969, 1103; (h) J. R. Williams and G. M. Sarkisian, *ibid.*, 1971, 1564; (i) R. G. Carlson, R. L. Coffin, W. W. Cox, and R. S. Givens, *J.C.S. Chem. Comm.*, 1973, 501; (j) N. P. Peet, R. L. Cargill, and J. W. Crawford, *J. Org. Chem.*, 1972, **38**, 1222; (k) L. A. Paquette, R. E. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, 1970, **90**, 5753.

² (a) N. C. Yang and D. Thap, *Tetrahedron Letters*, 1966, 3671; (b) E. F. Keifer and D. A. Carlson, *ibid.*, 1967, 1617; (c) R. C. Cookson, J. Hudec, G. E. Usher, and A. Szabo, *Tetrahedron*, 1968, **24**, 4353; (d) J. C. Dalton and H.-F. Chan, *J. Amer. Chem. Soc.*, 1973, **95**, 4085.

whereas others readily undergo isomerisation to the $\beta\gamma$ -isomer⁹ or even oxeten formation.¹⁰ The lack of isomerisation of (1) may reflect an unfavourable distance between the carbonyl group and the γ -H to be abstracted compared with its homologues (see below) or it may be due to rapid thermal isomerisation back to the exocyclic double bond isomer.

Intersystem crossing is efficient for $\alpha\beta$ -unsaturated ketones and the excited state involved is generally the lowest triplet state. Rotational isomerism is often observed in irradiation^{8b,9,11} and this represents an important route for loss of triplet energy for both $\alpha\beta$ - and $\beta\gamma$ -unsaturated ketones. Rotational isomerism of (1) does not give rise to a new product and would continue unobserved; *cis-trans* isomerism of *trans*-2-ethylidenecyclododecanone was, however, found to occur. Direct or acetone-sensitised irradiation of *trans*-2-ethylidenecyclododecanone resulted in the formation of 50:50 *cis:trans* mixture as well as a cyclobutanol from transannular γ -H abstraction. The isomerisation was not accompanied by detectable formation of the $\beta\gamma$ -unsaturated isomer, 2-vinylcyclododecanone.

It is interesting to note that had the $\beta\gamma$ -isomer of (1) been formed by photochemical deconjugation it might have been expected to undergo a 1,3-acyl shift. The closely related 2-methyl-2-(cyclopent-1-enyl)cyclopentanone,¹⁴ 3-methyl-3-(cyclopent-1-enyl)butan-2-one,¹⁴ and 2-isobutenylcyclopentanone¹⁴ underwent 1,3-acyl shifts on direct irradiation.

An equilibrium mixture of 2-(cyclohex-1-enyl)cyclohexanone (2) (*ca.* 90%) and 2-(cyclohexylidene)cyclohexanone (3) (*ca.* 10%), readily available from the acid-catalysed self-condensation of cyclohexanone,¹² on irradiation gave the cyclobutanol (4) as the major photoproduct (80% yield).

The formation of the cyclobutanol (4) on irradiation of (2) has been confirmed by an independent study.¹³ Compound (4), a white crystalline solid, m.p. 84–85° (waxy if impure), was identified on the basis of spectral evidence and its thermal (at *ca.* 100°) or acid-catalysed rearrangement to (2).^{*} Recently a different route to (4) has been described¹⁴ but only one stereoisomer (4a) was isolated. This was converted back into (2) by strong base. Slight differences in the physical and spectral properties of (4) and (4a) suggest that the photoproduct (4) was a mixture of stereoisomers.

The decomposition of the cyclobutanol (4) and related compounds can give rise to two different products depending on the direction of ring opening. The decomposition of (4), either acid or base catalysed, gave predominantly (2) and none of the isomer (5), whereas thermal rearrangement of (6)^{2c} gave the ring

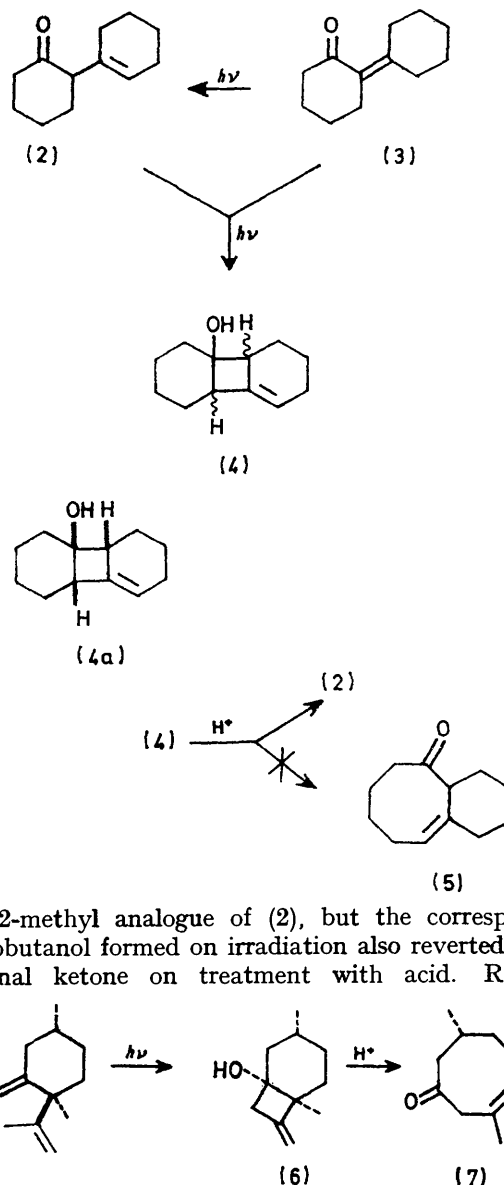
* Further support for the structure was given by the results of hydrogenation and ozonolysis (see Experimental section).

⁹ N. C. Yang, and M. J. Jorgenson, *Tetrahedron Letters*, 1964, 1203; A. Marchesini, G. Pagnoni, and U. M. Pagnoni, *ibid.*, 1973, 1041.

¹⁰ L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, 1969, **91**, 7204.

¹¹ E. G. V. Ramamurthy and R. S. H. Lui, *Tetrahedron Letters*, 1973, 441.

expanded ketone (7) as the major product. The presence of the 4-methyl group in (6) led us to synthesise



the 2-methyl analogue of (2), but the corresponding cyclobutanol formed on irradiation also reverted to the original ketone on treatment with acid. Recently

the base catalysed rearrangement of analogues of (4) has been shown to be susceptible to solvent and steric effects.¹⁴ [The ketones (5) and (7) would be, of course, the products of direct 1,3-acyl shifts from the original ketones.]

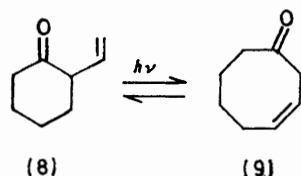
Though 1,3-acyl shifts occur on direct irradiation of compounds analogous to (2), *e.g.* (8) \rightarrow (9)¹⁵ these usually have no γ -H atoms at a suitable distance from the carbonyl oxygen to be abstracted. Compounds like (2) and (8) often have little or no enhancement of

¹² K. K. Kelly and J. S. Matthews, *J. Chem. Eng. Data*, 1969, **14**, 271; W. S. Rapson, *J. Chem. Soc.*, 1941, 1254.

¹³ B. Odell, personal communication.
¹⁴ P. Caubere and J. J. Brunet, *Tetrahedron*, 1972, **28**, 4835, 4847.

¹⁵ L. A. Paquette and R. E. Eizember, *J. Amer. Chem. Soc.*, 1967, **89**, 6205; J. K. Crandall and J. P. Arrington, *ibid.*, p. 6208.

their u.v. absorption which indicates poor orbital overlap between the carbonyl oxygen and the double bond; consequently there is little assistance for a concerted 1,3-shift [apparent exceptions are 2-methyl-2-(cycloprop-1-enyl)cyclopentanone¹⁴ and 2-(isobutenyl)cyclopentanone¹⁵]. When 1,3-acyl shifts do occur in this type of compound the photostationary states generally



lie on the side of the vinyl isomer [e.g. (8)]^{14,15,16} and the presence of biradical intermediates has been indicated.¹⁵

In addition to the studies on the equilibrium mixture of (2) and (3) the photochemistry of pure 2-(cyclohexylidene)cyclohexanone (3) was also examined. On direct irradiation it gave (4) as the major photoproduct.* The most likely route to (4) on direct irradiation of (3) is initial isomerisation to (2), *via* the lowest excited triplet state, followed by a singlet state reaction of (2). This concept was supported by the faster rate of formation of (4) in methanol than in non-polar solvents, suggesting the enhanced triplet state reactivity in a polar solvent,¹⁷ and by the isomerisation of (3) to (2) on acetone-sensitised irradiation. Monitoring the direct irradiation of (3) by recording the carbonyl region of the i.r. spectrum at intervals showed the slow build up of (2) (and/or other $\beta\gamma$ -unsaturated or saturated ketones) which indicated isomerisation to (2) followed by rapid rearrangement to (4). A very small amount of (4) was detected after the acetone-sensitised irradiation of (2) or (3).

A remarkable change in photochemical behaviour occurred when the seven- or eight-membered ring analogues of (2) were irradiated. A mixture of 2-(cycloheptylidene)cycloheptanone (10) (~60%) and 2-(cyclohept-1-enyl)cycloheptanone (11) (40%) was used but 2-(cyclo-oct-1-enyl)cyclo-octanone (13) was obtained containing little of the $\alpha\beta$ -unsaturated isomer.† The major photoproducts on direct irradiation were shown to be the unstable oxetans (12) or (14): though oxetans have been formed intramolecularly from $\delta\gamma$ -unsaturated ketones¹⁸ and even oxetens from $\alpha\beta$ -unsaturated ketones¹⁰ these are the first examples from $\beta\gamma$ -unsaturated ketones.‡

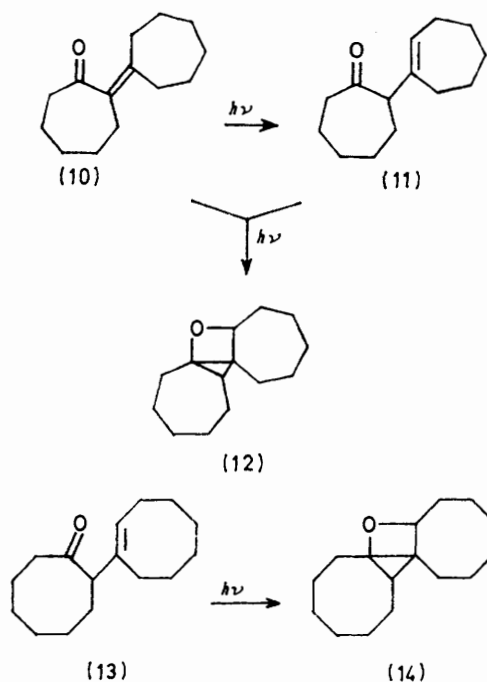
The $\alpha\beta$ -unsaturated isomer (10) is deconjugated to the $\beta\gamma$ -isomer (11) on direct or acetone-sensitised irradiation [cf. isomerisation of (3) to (2)]. No oxetans were formed on sensitised irradiation. The direct irradiation was conveniently monitored by observing the relative

* A number of minor photoproducts were detected (see Experimental section).

† N.m.r. indicated that <25% of the $\alpha\beta$ -isomer was present; i.r. and u.v. spectra indicated very small amounts.

‡ An oxetan analogous to (10) was once postulated as an intermediate in the oxa-di- π -methane rearrangement.

intensities of the two carbonyl peaks in the i.r. spectrum (1680 and 1700 cm^{-1}) and by t.l.c. In benzene (Figure 1)



the $\alpha\beta$: $\beta\gamma$ ratio rapidly increased, accompanied by the formation of oxetans (t.l.c.), over a short period and then both the ratio and oxetan formation changed slowly.

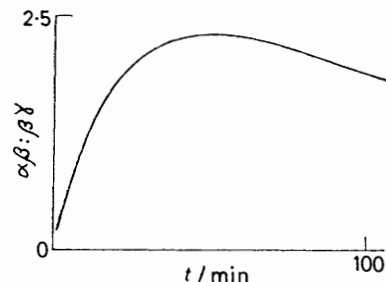


FIGURE 1 Change with time in ratio of $\alpha\beta$ - (10) to $\beta\gamma$ -unsaturated ketone (11) on irradiation in benzene

This is probably due to the rapid consumption of $\beta\gamma$ -unsaturated isomer to form the oxetan competing with a slow deconjugation of the $\alpha\beta$ - to the $\beta\gamma$ -unsaturated isomer. In methanol (Figure 2) there was a more gradual increase of the $\alpha\beta$: $\beta\gamma$ isomer ratio accompanied by steady oxetan formation. The difference of behaviour with solvent may reflect the enhanced isomerisation of (10) to (11) in the more polar solvent owing to enhanced triplet state activity [cf. (3) \rightarrow (2)]. There was no evidence of oxetens.

¹⁶ R. G. Carlson and D. E. Henton, *Chem. Comm.*, 1969, 374; R. G. Carlson and J. H. Bateman, *Tetrahedron Letters*, 1967, 4161.

¹⁷ J. C. Dalton and M. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, 21, 499.

¹⁸ S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, 1972, 94, 507; J. R. Scheffer, K. S. Bhandari, Y.-M. Ngan, and P. K. Schmidt, *Tetrahedron Letters*, 1973, 1413.

The t.l.c. of the crude reaction mixture from irradiation of (10)/(11), or (13), showed two major products and these could be separated by column chromatography. Both products were shown to be oxetans and each product was indicated (by n.m.r.) to consist of a mixture of two stereoisomeric oxetans, so that all

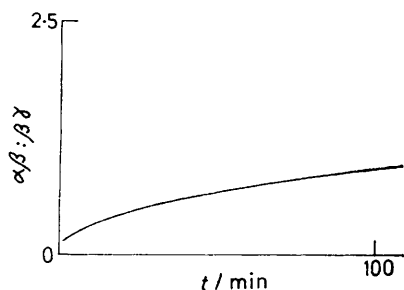
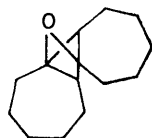


FIGURE 2 Change with time in ratio of $\alpha\beta$ - (10) to $\beta\gamma$ -unsaturated ketone (11) on irradiation in methanol

four possible stereoisomers of (12) [and (14)], were obtained. The n.m.r. spectra of these products showed signals at δ 0.5 [for both 'products' from (10)/(11)] and at 0.39 and 0.65 [for the two 'products' from (13)] which ruled out the alternative structural type (15).



(15)

Equal amounts of stereoisomers were not formed and the major product had the higher R_F value. In the case of (12) this mixture of stereoisomers rearranged cleanly to the more polar (lower R_F value) mixture of isomers on heating at 70° but in the case of (14) both mixtures were thermally stable with respect to each other.* In the presence of acid both (12) and (14) were converted back into starting material. The steric strain involved in molecules (12) and (14) is quite considerable, particularly for the isomers containing a *trans*-configuration about the cyclopropane ring, and it is likely that the corresponding oxetan from (2) would be extremely unstable if it were formed (molecular models).

The formation of oxetans between carbonyl compounds and electron deficient olefins is thought to proceed *via* a singlet state complex^{18a} which can either decompose back to reactants or proceed to products. Qualitative consideration of orbital overlap using the model proposed by Houk³ for *trans*-hex-4-en-2-one but with 180° rotation about the 2,3-bond suggests that oxetan formation from the lowest excited n, π^* singlet state of $\beta\gamma$ -unsaturated ketones is electronically favourable. The n electron is initially promoted to the higher ($\pi^*_{CO} - \pi^*_{CO}$) level with an anti-bonding interaction be-

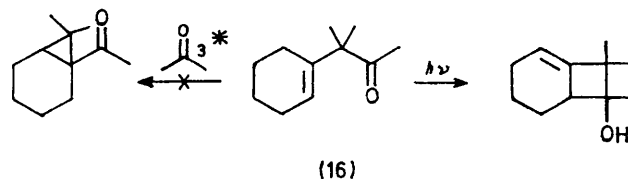
* Though (14a) did not give any of the isomer (14b) at 70° it did form other products, including the original ketone (13).

tween both ends of the C=C and C=O groups. It seems reasonable that this state should rapidly undergo conversion to the lower ($\pi^*_{CO} + \pi^*_{CO}$) level with bonding interactions between the two double bonds, from which oxetan formation can occur.

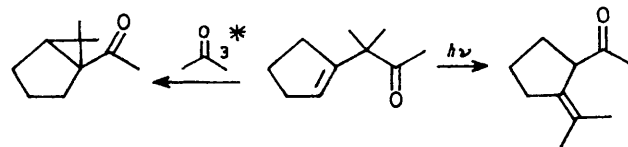
Minor photoproducts of the direct irradiation of (10)/(11) or (13) were alcohols, thought to be isomeric cyclobutanols analogous to (4). The decrease of cyclobutanol formation and increase of oxetan formation with increasing ring size has a precedent in the *intermolecular* photoadditions of cycloalkenes with acetone.¹⁹ Cyclobutanols were formed with cyclohexene and oxetans with cyclo-octene. Similarly the analogous quenching of the triplet state of phenyl ketones by cycloalkenes, proceeding by oxetan formation, decreases in the order $C_8 > C_7 > C_4 > C_5 > C_6$.²⁰

The distance between the carbonyl oxygen and the γ -H to be abstracted has been suggested as an important factor in determining the change of photochemical behaviour of $\beta\gamma$ -unsaturated ketones^{1e} with ring size [*e.g.* (16), (17)]. An unfavourable distance in (17) may prevent cyclobutanol formation so that on direct irradiation a 1,3-acyl shift occurs. The case of cyclobutanol formation from (16) and (2) and the case of isomerisation of (3) and (10) may reflect favourable distances. The lack of 1,2-acyl shifts on acetone-sensitised irradiation of (2), (11), (13), and (16) may reflect preferential loss of triplet energy by ring twisting^{1e} or a different inactive lowest triplet state.

A combination of steric and electronic factors presumably determines the particular photoreaction of a $\beta\gamma$ -unsaturated ketone that is observed. The balance between γ -H abstraction, 1,3-acyl shift, and oxetan formation on direct irradiation is sensitive to minor structural changes.



(16)



(17)

EXPERIMENTAL

The irradiations were carried out with a 450 W medium pressure mercury arc lamp (Hanovia) and a silica or a Pyrex immersion well. The compound to be irradiated was dissolved (1–2% w/v) in solvent (300 ml) and the solution

¹⁹ K. Shima, Y. Sakai, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1971, **44**, 255.

²⁰ I. E. Kochevar and P. L. Wagner, *J. Amer. Chem. Soc.*, 1972, **94**, 3859.

flushed with nitrogen for 1 h before use. A nitrogen atmosphere was maintained during irradiation. Solvents used were cyclohexane (BDH special for spectroscopy), benzene (BDH AnalaR), methanol (BDH AnalaR), and acetone (BDH AnalaR).†

The reactions were monitored by t.l.c. using Keisegel G nach Stahl and by vapour phase chromatography (v.p.c.) using 5 or 10% diethylene glycol succinate (D.E.G.S.) 5 ft glass columns on a Pye series 104 chromatograph. Reaction products were generally isolated and purified by column chromatography on silica gel (100–200 mesh; 50–100 × weight of mixture to be separated) with petroleum-ether as eluant.

The products are characterised by their i.r. (Unicam SP 200, liquid film unless otherwise stated), u.v. (Unicam SP 800), n.m.r. (60 MHz on a Varian A60 or Perkin-Elmer R 12, deuteriochloroform), and mass (A.E.I. MS 12) spectra. Nearly all reaction products were unstable oils unsuitable for elemental analysis. Mass spectral fragments connected to the molecular ion by a metastable are marked with an asterisk.

Irradiation of 2-(Cyclopentylidene)cyclopentanone (1).—2-(Cyclopentylidene)cyclopentanone²¹ (5.0 g) was dissolved in cyclohexane and irradiated for 1.5, 3, and 48 h. No change was observed by t.l.c. or i.r. spectroscopy and after removal of solvent the starting material was recovered (90%) unchanged. Similarly irradiation of (1) in methanol for 21 h or in acetone for 4 h did not lead to rearrangement (t.l.c., i.r.).

Irradiation of 2-(Cyclohex-1-enyl)cyclohexanone (2).—2-(Cyclohex-1-enyl)cyclohexanone (2) (ca. 90%) in equilibrium with 2-(cyclohexylidene)cyclohexanone (3) (ca. 10%) was prepared.¹² A solution of the mixture, hereafter referred to as (2), in cyclohexane or methanol was irradiated for 4 h when t.l.c. indicated product formation was complete. Evaporation of solvent gave tricyclo-[6.4.0.0^{2,7}]dodec-6-en-1-ol as a white solid (4) ‡ (80% yield), m.p. 84–85° (after purification by vacuum sublimation), ν_{\max} (CCl₄) 900–1100, 3500, and 3600 cm⁻¹, δ 1.2–2.2 (15H, m), 2.2–2.6 (1.5H, m), 2.9 (0.7H, s), and 5.47 (1H, s): exact proton integrals were difficult to determine because of the overlap and breadth of the signals; OH protons were lost under envelope, *m/e* 178 (*M*⁺), 160, and 149*.

The alcohol (4) rearranged to 2-(cyclohex-1-enyl)cyclohexanone on addition to an ice-cold mixture of methanol and concentrated sulphuric acid, on refluxing in dilute (3*N* in methanol) sulphuric acid in methanol, or on heating (v.p.c.) at 100°, and was reasonably stable to a dilute (0.3*N*) acidic methanol solution at room temperature: irradiation of (2) in such a solution gave (4).

Hydrogenation of (4) (0.92 g) in ethanol (25 ml) with 10% Pd on charcoal (0.1 g) gave a saturated alcohol (0.6 g, 63% yield), ν_{\max} (CCl₄) 910, 3450, and 3550 cm⁻¹, δ 1–2.0 (16H, m) and 2–2.4 (3H, m) [no alkene or -CH(OH)- signals]. Ozonolysis of (4) (ca. 3 g) in n-hexane or methanol at -70° for 3 h followed by work-up with zinc and acetic acid gave an inseparable mixture of products. The crude mixture showed ν_{\max} 1600s, 1710–1720m, and 1770w cm⁻¹.

† All irradiations through a Pyrex filter.

‡ The isomer (4a)¹⁴ had m.p. 91–92°, ν_{\max} 1700 and 3620 cm⁻¹; δ 5.30 (1H, m), 3.30 (1H, s, disappearing on addition of D₂O), 2.9 (1H, m), 2.6 (1H, m), and 1.1–2.2 (14H, stray peak 1.40).

§ Decomposition occurs on the column.

Irradiation of (2) in acetone gave a small amount of the alcohol (4) initially (t.l.c.) but there was no further change on prolonged irradiation.

Irradiation of 2-(Cyclohex-1-enyl)-2-methylcyclohexanone.—A mixture of methylated ketones consisting of >70% 2-(cyclohex-1-enyl)-2-methylcyclohexanone was prepared²² as follows. Sodium *t*-pentylate in benzene (23.7 ml of a 1.5*N* solution) was added to 2-(cyclohex-1-enyl)cyclohexanone (2) (5.9 g) dissolved in benzene. Methyl iodide (4.7 g) in benzene was added dropwise and when addition was complete the mixture was refluxed for 3 h under nitrogen. The mixture was washed with water, extracted with ether, and dried (Na₂SO₄). After chromatography, a mixture (2.5 g, 40% yield) of three isomers (v.p.c., three peaks 70:20:10) was obtained, ν_{\max} 1700 cm⁻¹, δ 1.05 (3H, s), 1.5–2.3 (16H), 5.46 (1H, s) (weak peaks at 0.9–1.0 indicated a doublet, *J* 7 Hz).

Irradiation of the mixture (1.89 g) in cyclohexane gave a mixture of cyclobutanols (1.8 g) which on acid treatment (methanol, concentrated sulphuric acid at 0°) gave the mixture of starting ketones. A purified sample of the mixed cyclobutanols (ca. 25% recovery after chromatography) was obtained; ν_{\max} 900–1400, 1620, 1100, and 3450 cm⁻¹, δ 0.85 (m, weak), 0.98 (s, intense), 1.3–2.6 (m), 2.7–3.1 (m), and 5.3 and 5.4 (each s, equal intensity): overlap of peaks prevented useful integration.

Irradiation of 2-(Cyclohexylidene)cyclohexanone (3).—Pure 2-(cyclohexylidene)cyclohexanone (3) was prepared.²³ Irradiation of (3) (3.0 gm) in cyclohexane for 9 h (t.l.c. indicated complete reaction) followed by removal of solvent, gave a mixture containing principally (t.l.c.) the cyclobutanol (4). Several minor compounds were also detected. Chromatography on silica gel [eluting initially with petroleum-ether 5:1 (v/v) and increasing to 2:1 (v/v)] gave a low yield § of (4) (0.26 g), 2-(cyclohexylidene)cyclohexanone and 2-(cyclohex-1-enyl)cyclohexanone (1.2 g), and four minor compounds (ca. 5–10 mg each, <0.3% yield). Spectral data were insufficient to allow characterisation of the minor compounds though they were all carbonyl compounds (ν_{\max} 1680 and/or 1700 cm⁻¹), two with higher molecular weight (*m/e* 338, 260) than the starting ketone and two with the same molecular weight (*m/e* 178).

Irradiation of (3) (1.0 g) in methanol was monitored by i.r. spectra and t.l.c. and the reaction to (4) was complete after 2 h. Two minor (<1%) products were present and shown (i.r.) to be neither alcohols nor ketones (*m/e* 338). Irradiation of (3) (1.0 gm) in cyclohexane to give (4) was complete in 6 h.

Irradiation of (3) (1.01 g) in benzene through a Pyrex filter to give (4) was followed by t.l.c. and i.r. spectra and was complete after ca. 7 h. The reaction had proceeded more cleanly to (4) than the previous irradiations in methanol or cyclohexane.

Irradiation of (3) (2.4 g) in acetone gave (2) after 1 h together with a very small amount of (4) and other very minor products.

Irradiation of 2-(Cycloheptylidene)cycloheptanone (10).—The preparation of 2-(cycloheptylidene)cycloheptanone (10) by the method of Rosenfelder and Ginsburg²⁴ gave a

²¹ D. Varch, C. Ouannes, and J. Jacques, *Bull. Soc. chim. France*, 1965, 1662.

²² J. M. Conia, *Bull. Soc. chim. France*, 1954, 943.

²³ J. Reese, *Ber.*, 1942, 75, 384.

²⁴ W. G. Rosenfelder and D. Ginsburg, *J. Chem. Soc.*, 1954, 2955.

product shown (n.m.r. and i.r.) to contain *ca.* 40% 2-(cyclohept-1-enyl)cycloheptanone (11) and *ca.* 60% 2-(cycloheptylidene)cycloheptanone (10), ν_{\max} 1610, 1680, and 1700 cm^{-1} , δ 1.4—1.7 (*ca.* 14H, two peaks at 1.5 and 1.7), 2—2.5 (*ca.* 6H, m), 3.0 (0.35H, two broad peaks), and 5.6 (0.35H, t, J 6 Hz), m/e 206 (M^+).

Irradiation of the mixture (2.5 g) in cyclohexane for 3 h gave two principal and two minor products; very little starting material remained (t.l.c.). The two principal compounds consist of a major one (higher R_F value) (12a) and a minor one (lower R_F value) (12b), stereoisomers of 2-oxatetracyclo[8.5.0.0^{1,9}.0^{3,8}]pentadecane. Evaporation of the solvent under reduced pressure, and chromatography of the residue (2.2 g) on silica gel [200 g; eluting initially with petroleum-ether 98 : 2 (v/v), increasing to 3 : 1 (v/v)] gave in order of elution (12a) (0.53 g, *ca.* 24%), (10) (0.7 g, *ca.* 30%), † (12b) (0.18 g, *ca.* 8%), and a mixture of two alcohols (0.02—0.05 g, 1—2%). Exact ratios of (12a) : (12b) and the yield of alcohols isolated varied slightly. The column fractions containing (12a) were kept in ice-cooled receivers, the solvent was evaporated off, and spectral data were recorded as soon as possible. Isomer (12a) rearranged slowly to (12b) at room temperature and rapidly at 70° (t.l.c.). Both (12a) and (12b) decomposed back to the starting material on treatment with methanol-concentrated sulphuric acid at 0°. Neither (12a) nor (12b) could be reduced by catalytic hydrogenation over Pd on charcoal or Adams catalyst (PtO₂).

The following spectral data were obtained: (12a), ν_{\max} 910, 920, and 980 cm^{-1} , δ (C₆H₆ as internal standard, Me₂Si obscures cyclopropyl region) 0.5 (1H, t, J 6 Hz), 1.2—2.3 (*ca.* 20H, m), and 4.0 (1H, m, very finely split signal containing ten or more peaks), m/e 206, fragmentation pattern identical with that of (12b), see below.

Isomer (12b), ν_{\max} 940 and 980 cm^{-1} , δ (C₆H₆ as internal standard) 0.5 (1H, m, four peaks, possibly two overlapping t), 1.2—2 (ca. 18H, m), 2—2.4 (*ca.* 2H, m), and 4.45 (m, four peaks, possibly two overlapping d, J *ca.* 10 Hz); protons at 0.5 and 4.45 were coupled to signals beneath the envelope and not to each other, m/e 206 (M^+), 177, 163*, 149*, 135, and 108; fragmentation pattern identical with that of (12a) suggesting the transformation (12a) → (12b) on the probe; pattern very similar to that of (10).

The alcohols (minor products) were shown to be two compounds in the ratio 60 : 40 (v.p.c.), ν_{\max} 1040 and 3400 cm^{-1} , δ (poor spectrum), 1.3—2.2 (*ca.* 16 units, m), 2.2—2.7 (~2 units, m), and 5.5 (~0.5 units, m), m/e 206 (M^+), 163, and 119.

Irradiation of (10)/(11) (0.5 g) in methanol after 2 h and irradiation of (10)/(11) (0.5 g) in benzene after 3 h both gave (12). Both irradiations were carefully monitored by t.l.c. and i.r. spectra. The ratio of carbonyl peaks at 1695 and 1675 cm^{-1} was measured at intervals and the results are shown in Figures 1 and 2.

Irradiation of (10)/(11) (0.53 g) in acetone for 2.3 h gave principally (11) together with a very small amount of other more polar products but no oxetans were formed.

Irradiation of 2-(Cyclo-oct-1-enyl)cyclo-octanone (13).—2-(Cyclo-oct-1-enyl)cyclo-octanone (13) was prepared by the method used to synthesise (10)/(11). Cyclo-octanone (15 g, 0.12 mol) dissolved in benzene (25 ml) was added slowly to potassium *t*-butoxide [prepared from potassium

(5.1 g)] in benzene (50 ml) and the mixture was refluxed, under nitrogen, for 12 h. Addition of acetic acid (9.6 ml), water, extraction with ether, and drying (Na₂SO₄) gave after evaporation of solvent and vacuum distillation, (13) [5.1 g, 62% yield (based on recovered cyclo-octanone)], b.p. 138—140° at 0.5 mmHg, ν_{\max} 860, 1460, 1480, and 1690 cm^{-1} , δ 1.4—2.2 (24H, m), 2.9 (~0.8H, m), and 5.6 (~0.8H, t J 8 Hz), m/e 234 (M^+), 205*, 191*, 177*, 163, 149, and 135; λ_{\max} < 230 (intense), 260 (weak), 300 nm (weak).

Irradiation of (13) in cyclohexane for 5 h gave two major and three minor products. Evaporation of solvent followed by column chromatography on silica gel (200 g) [petroleum-ether 90 : 10 (v/v)] separated most of the products in low yield (<25% overall recovery). The two principal products (*ca.* 3 : 1 by t.l.c.) were isomers of 2-oxatetracyclo[9.6.0.0^{1,10}.0^{3,10}]heptadecane (14). The major component (higher R_F value) (14a) had ν_{\max} 940 cm^{-1} , δ 0.39 (1H, m), 1.0—2.3 (24H, m), and 3.8 (1H, m, three peaks) m/e 234 (M^+); pattern similar to that of (13), above. The minor component (lower R_F value) (14b) had ν_{\max} 920 cm^{-1} , δ 0.65 (1H, m), 1—2.3 (24H, m), and 4.52 (1H, m, three peaks), m/e 234 (M^+), 205*, 191*, 177*, and 163* [*cf.* (13)]. Heating (14a) for several h at 70° did not isomerise it to (14b) but both (14a) and (14b) were converted into (13) on treatment with acidic methanol. Attempted catalytic hydrogenations (10% Pd on C or PtO₂) were unsuccessful.

The minor products consisted of a non-polar hydrocarbon [ν_{\max} 910 and 970 cm^{-1} , δ 0.9—2.5 (27H, three peaks) and 4.9—6.1 (4H, m), m/e 206], an alcohol [ν_{\max} 3450 and 1100 cm^{-1} , δ no alkene signal, envelopes 1—2.28], and a carbonyl compound detected as an impurity in a crude sample of (14a) [ν_{\max} 1700 cm^{-1} , δ 2.9 and 5.2]. The best spectral data were obtained for the hydrocarbon and 1-(hept-6-enyl)cyclo-octene is a possible structure.

Irradiation of (13) (2.3 g) in benzene for 6 h gave the oxetans (14) [(14a) : (14b) *ca.* 8 : 1, only *ca.* 8% yield after chromatography, although t.l.c. indicated complete reaction] together with the minor hydrocarbon and alcoholic products noted above. Irradiation of (13) (3.05 g) in methanol for 15 h likewise gave (14) as major product.

Irradiation of (13) (0.83 g) in acetone for 2.5 h did not give the oxetans or isolable photoproducts.

Irradiation of 2-Ethylidenecyclododecanone.—2-(Ethylidene)cyclododecanone was prepared^{25,26} and found to be predominately the 2-*trans*-isomer, δ 1.2 (16H, s), 1.8 (3H, d, J 7 Hz), 2.2—2.7 (4H, m), and 6.5 (1H, q, J 7 Hz). Irradiation of a sample (2.1 g) in cyclohexane for 16 h gave one photoproduct with a slightly higher R_F value than the starting ketone (*ca.* 50 : 50 mixture of this photoproduct and *trans*-2-ethylidenecyclododecanone was indicated) and a more polar photoproduct. Chromatography of the residue (1.9 g) on silica gel [200 g; petroleum-ether 95 : 5 (v/v)] gave, in order of elution, 2-*cis*-ethylidenecyclododecanone (*ca.* 10% yield), ν_{\max} 1660 and 1630 cm^{-1} , δ 1.3 (16H, s), 1.75 (3H, d, J 7 Hz), 2.1—2.7 (4H, m), and 5.6 (1H, q, J 7 Hz), m/e 208 (M^+), 2-*trans*-ethylidenecyclododecanone (*ca.* 10% yield), and a cyclobutanol resulting from transannular γ -H abstraction, ν_{\max} (CCl₄) 1000—1100, 3500, and 3600 cm^{-1} , δ (poor spectrum) 1.4 (*ca.*

²⁵ V. Prelog, L. Ruzicka, and O. Metzler, *Helv. Chim. Acta*, 1947, **30**, 1883.

²⁶ R. A. J. Smith and T. A. Spencer, *J. Org. Chem.*, 1970, **35**, 3220.

† Probably arising from the decomposition of (12a and b) on the column.

20H, s), 2.25 (ca. 5H, m), and 5.35 (ca. 1H, q, J 6 Hz), m/e 208 (M^+) and 190.

The irradiation in cyclohexane was carefully monitored by t.l.c. and after 3 h the major product was the 2-*cis*-isomer but some cyclobutanol formation had occurred. Similarly on irradiation of 2-*trans*-ethylidenecyclohexanone (1.0 g) in benzene for 5.5 h the major photoproduct was

the 2-*cis*-isomer; similarly for irradiation in methanol or acetone.

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