Photochemistry of 4,4,*exo*-6-Trimethyl-1-phenyl-3-oxabicyclo[3,1,0]-hexan-2-one. Formation of a Keten Intermediate

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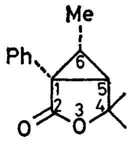
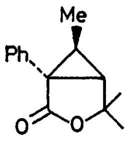
The photochemistry (λ 254 nm) of *exo*-(1) was examined. In nonhydroxylic solvents an αβ-unsaturated lactone (2) was formed. In hydroxylic solvents a βγ-unsaturated ester (3) was also formed, which is proposed to arise from a keten intermediate. Upon acetone-sensitized irradiation of *exo*-(1) only *exo*–*endo* isomerization occurs.

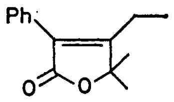
As an extension of our work on the photochemistry of α-aryl acetates[1] we now report a study on the photochemistry of *exo*-(1). During our study some publications appeared on related systems which prompted us to report our results. Flechtner *et al.*[2] reported on the bicyclic anhydride 6,6-diphenyl-3-oxabicyclo[3.1.0]-hexane-2,4-dione and the bicyclic ester 6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-2-one. The anhydride upon irradiation led to the formation of a keten which was trapped by t-butyl alcohol; with the lactone however the only products obtained were explained in terms of photoextrusion of diphenylcarben. The photolysis of diphenylepoxymaleic anhydride was reported by Griffin *et al.*[3] to give among others a keten which was trapped by methanol. The formation of the photoproducts from some 2-arylcyclopropylmethyl acetates and the corresponding hydroxides was explained in terms of a photochemical cyclopropyl–homoallyl rearrangement *via* an ionic intermediate.[4]



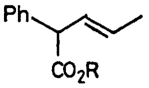
exo-(1)



endo-(1)



(2)



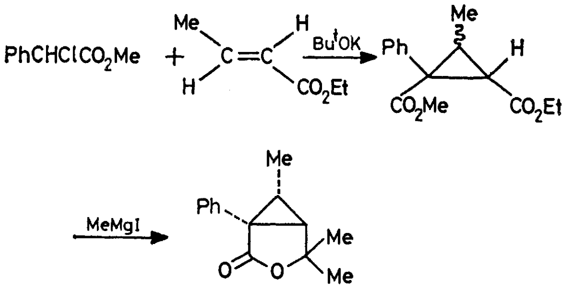
(3)

a; R = Me
b; R = Et
c; R = Pr^i

RESULTS

Synthesis of Starting Material.—4,4,*exo*-6-Trimethyl-1-phenyl-3-oxabicyclo[3.1.0]hexan-2-one [*exo*-(1)] was synthesized from methyl α-chlorophenylacetate as depicted in Scheme 1. The first step is a base-induced Michael type of addition to an αβ-unsaturated ester, which was performed as described by Bonavent *et al.*[5] No attempt was made to separate the mixture of the resulting isomers. After distillation the product was treated with a Grignard reagent to give the lactone after acid hydrolysis.

In the second step (Scheme 1), in principle two isomeric lactones can be formed because of the presence of two ester carbonyl groups which can each be attacked by the Grignard reagent. The structural assignment of the isolated lactone



SCHEME 1

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[1] A. A. M. Roof, H. F. van Woerden, and H. Cerfontain, *Tetrahedron Letters*, 1975, 815; *Tetrahedron*, 1976, **32**, 2967.

[2] Th. W. Flechtner, L. J. Szabo, and L. J. Koenig, *J. Org. Chem.*, 1976, **41**, 2038.

[3] G. W. Griffin, K. Nishiyama, and K. Ishikawa, *J. Org. Chem.*, 1977, **42**, 182.

[4] S. S. Hixson, *J.C.S. Chem. Comm.*, 1974, 681; S. S. Hixson and J. Borovsky, *ibid.*, 1975, 607; S. S. Hixson and R. E. Factor, *Tetrahedron Letters*, 1975, 3111.

[5] G. B. Bonavent, M. Causse, M. Guitard, and R. Fraisse-Julien, *Bull. Soc. chim. France*, 1964, 2462.

exo-(1), especially the position of the phenyl group [at C(1) or C(5)] was based on the ^{1}H n.m.r. and aromatic solvent-induced shift data (Table). Of all absorptions the one at δ 2.13 was most affected by the aromatic solvent ($\Delta\delta$ 0.61) and was therefore assigned to 5- and not to 1-H which is closer to the ester carbonyl group. $J_{5,6}$ of 4 Hz illustrates that the hydrogens at C(5) and C(6) are *trans*; thus the methyl group at C(6) is *exo*. The i.r. spectrum showed absorptions at $\nu_{max.}$(CHCl$_3$) 1 750, 1 600, 1 500, 1 385, and 1 370 cm^{-1}.

^{1}H N.m.r. and a.s.i.s. data (p.p.m.) of exo- and endo-(1)

	exo-(1)			*endo*-(1)
	δ(CDCl$_3$)	δ(C$_6$D$_6$)	$\Delta\delta$	δ(CDCl$_3$)
Ph	7.38 (m)	*a*		7.33
5-H	2.13 (d, *J* 4 Hz)	1.52	0.61	2.21 (d, *J* 8 Hz)
6-H	1.5	1.1	0.4	*b*
4-Me	1.57 (s)	1.13	0.44	*b*
	1.46 (s)	1.08	0.38	
6-Me	0.86 (d, *J* 6 Hz)	0.50	0.36	*b*

[a] Not recorded. [b] Obscured by the *exo*-(1) 4-Me singlet.

Irradiations.—The irradiation of *exo*-(1) in dry acetonitrile and also in dry benzene at λ 254 nm gave carbon monoxide, acetone, and an $\alpha\beta$-unsaturated lactone (2) with the following spectral data, δ(CDCl$_3$) 7.43 (5 H, s, Ph), 2.52 (2 H, q, CH$_2$), 1.57 (6 H, s, *gem*-Me$_2$), and 1.14 (3 H, t, CH$_2$*Me*); $\nu_{max.}$(CHCl$_3$) 1 745, 1 655, 1 600, and 1 500 cm^{-1}.

Upon irradiation of *exo*-(1) in the presence of dry methanol, no carbon monoxide, but in addition to (2), a new product (3a) with the following spectral data was detected, δ(CCl$_4$) 7.27 (5 H, s, Ph), 6.1—5.3 [2 H, m, (*E*)-CH=CH], 4.5—4.0 (1 H, m, PhC*H*), 3.59 (3 H, s, CO$_2$Me), and 1.65 (3 H, m, C=CMe); $\nu_{max.}$(CHCl$_3$) 1 720, 1 600, and 1 500 cm^{-1}. The *E*-assignment of (3a) was based on comparison with the n.m.r. data of (*E*)-2,2-dimethyl-4-phenylhept-5-en-3-one, kindly supplied by Dr. A. J. A. van der Weerdt.[6]

Upon irradiation of *exo*-(1) in the presence of ethanol the ester (3b) was formed. In order to obtain information on the possible formation of a keten intermediate, *exo*-(1) (*ca.* 1 mmol) was irradiated in acetonitrile (3 ml) for 5 h at λ 254 nm. G.l.c. analysis immediately after the termination of the irradiation showed the absence of (3a), but upon the immediate addition of methanol (0.5 ml) after photolysis the presence of some (3a) was observed. When the irradiation of *exo*-(1) was carried out in propan-2-ol as a (possible hydrogen donating) solvent, (2) and (3c) and no other or additional products were found.

Figure 1 shows the dependence of photoproduct formation on irradiation time with *exo*-(1) (0.29 mmol) in benzene–acetonitrile (2 : 3 v/v; 2 ml), both in the presence and absence of methanol (0.1 ml). The rate of disappearance of *exo*-(1) and of the formation of (2) are both independent of the presence of methanol. The formation of (2) and (3a) accounts for *ca.* 70% of converted starting material.* Irradiation of the lactone (2) (0.1 mmol) in acetonitrile–methanol (1 : 1 v/v; 2 ml) at λ 254 nm led to a rapid conversion of (2) and the formation of some unidentified products but not to the formation of (3a) or *exo*-(1). A solution of *exo*-(1) (0.27 mmol) in acetonitrile–methanol (1 : 1 v/v; 15 ml) was irradiated at λ 254 nm for 12 h. The recovered lactone (1) contained, according to ^{1}H n.m.r., 25% *endo*-(1).† The n.m.r. absorptions assigned to *endo*-(1) are listed in the Table. A solution of *exo*-(1) (0.50 mmol) in a mixture of acetone (5 ml) and methanol (0.5 ml) was irradiated at λ 300 nm for 30 h. G.l.c. analysis showed the absence of (2) and (3a). The recovered lactone (1) contained, according to ^{1}H n.m.r., 33% *endo*-(1). Irradiation of *exo*-(1) in benzene–methanol (1 : 1 v/v) saturated with xenon ‡ did not affect the rate of formation of (2) and (3a).

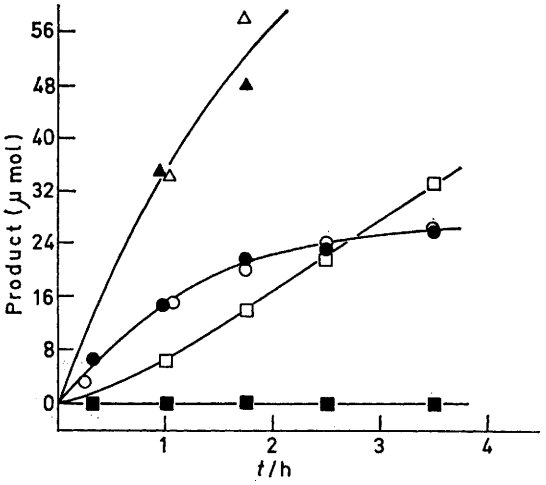

FIGURE 1 Dependence of product formation on irradiation time: △,▲ consumed (1); ○,● (2); □,■ (3a); △, ○, □ in the presence of methanol; ▲, ●, ■ in the absence of methanol

DISCUSSION

The photoformation of (3a and b) from *exo*-(1) in the presence of methanol or ethanol indicates the intermediacy of a keten. This intermediate can also account for the formation of carbon monoxide in non-hydroxylic solvents.[9] The ester (3a) is only present *after* the addition of methanol to the irradiated mixture and not *before*. Accordingly (3a) is not formed by reaction of methanol with the excited state of *exo*-(1) but with the postulated keten intermediate. Keten formation is irreversible because of the observed insensitivity of the rate of substrate conversion to methanol concentration. The rate of formation of (2) is the same in the presence and absence of methanol (Figure 1). Thus (2) is not formed from an intermediate which is trapped by methanol.

The formation of the observed photoproducts of *exo*-(1) can be explained in terms of the mechanism shown in Scheme 2. Products (2) and (3) are thought to result from the singlet excited state, as they are not formed upon acetone, *i.e.* triplet photosensitization.

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* The initial upward curvature for the formation of (3a) can be explained in terms of the relatively slow reaction of the keten with methanol.[7]

† In a dark experiment it was shown that no epimerization occurs under the g.l.c. conditions.

‡ Xenon is known to enhance spin–orbit coupling by a heavy atom effect and thus the rate of intersystem crossing of aromatic hydrocarbons.[8]

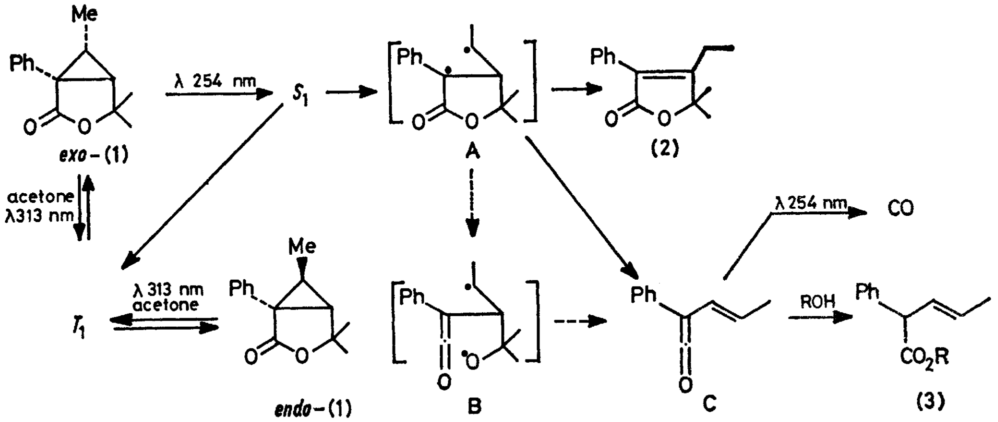
[6] A. J. A. van der Weerdt, H. Cerfontain, J. P. M. van der Ploeg, and J. A. den Hollander, *J.C.S. Perkin II*, 1978, 155.

[7] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 889.

[8] A. R. Horrocks, A. Kearvell, K. Tickle, and F. Wilkinson, *Trans. Faraday Soc.*, 1966, **62**, 3393.

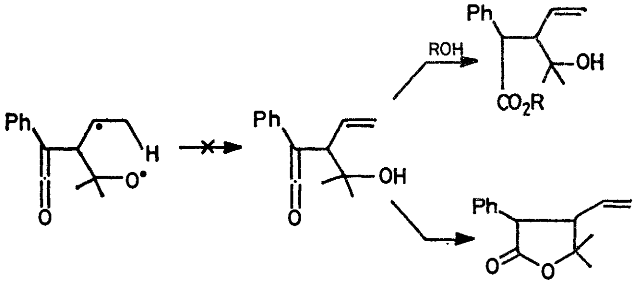
[9] J. G. Calvert and J. N. Pitts, ' Photochemistry ', Wiley, New York, 1966.

Upon λ 254 nm irradiation of *exo*-(1) in benzene as solvent (2) and (3) are also formed. Accordingly, as the solvent absorbs all the incident radiation, it follows that benzene acts as a singlet sensitizer. The first step in the formation of (2) and (3) is cleavage of the C(1)–C(6) bond resulting in the singlet 1,3-diradical A which can react in two different ways, first by a 1,2-hydrogen shift giving (2), and secondly by loss of acetone to yield C. Attack of an alcohol (if present) yields (3), otherwise C is probably photolysed with formation of carbon monoxide.[9] The formation of some *endo*-(1) upon direct irradiation may be explained in terms of reaction from the triplet excited state formed by intersystem crossing from S_1, because *endo*-(1) is also formed upon triplet photosensitization with acetone. The conversion of T_1 to *endo*-(1) occurs possibly *via* a triplet state biradical similar in structure to the singlet biradical A, as sensitized irradiation of pyrazolines results in clean formation of cyclopropanes.[10] A two step mechanism for the formation of C, *i.e. via* B, seems less likely. The reaction of A to B is highly endothermic with the radical position going from a stabilized benzylic position to the non-stabilized oxygen and the simultaneous cleavage of a σ-bond with formation of a relatively weaker π-bond. Accordingly, in order to rationalize the C–O bond cleavage of the diradical A to yield B, it would have to be presumed that A has an excess of (vibrational) energy. Also, one would expect that intermediate B would undergo intramolecular hydrogen transfer from the 6-methyl group to the oxygen radical site *via* a six-membered ring transition state (Scheme 3), especially if the intermediate B results from *endo*-(1) since the methyl group at C(6) is then very close to the ether oxygen (see Figure 2). In fact, no products resulting from intramolecular hydrogen transfer have been detected. Thus either β-scission is very fast relative to *e.g.* the intramolecular 1,5-hydrogen shift, or the acetone expulsion occurs directly from A. The driving force for C–O bond cleavage in A is possibly the ring strain of the five-membered lactone ring of the bicyclic system, as irradiation of alkyl-substituted methyl 1-phenylcyclopropanecarboxylates did not lead to keten-derived products.[11]



SCHEME 2

The photochemical ring opening of phenylcyclopropanes is directed by the substitution pattern,[12] and it is the cyclopropane bond between the most highly substituted carbon atoms which is cleaved preferentially with formation of alkenes in which the double bond is out of conjugation with the phenyl group. It is surprising therefore that with the present substrate only products resulting from initial C(1)–C(6) bond cleavage are formed. The preference of this bond cleavage over C(1)–C(5) cleavage, which is equally possible on the basis of the degree of substitution, may be explained in terms of the enhanced weakening of the C(1)–C(6) bond as a result of overlap with the π-system of the lactone carbonyl group. This explanation is congruent with the



SCHEME 3

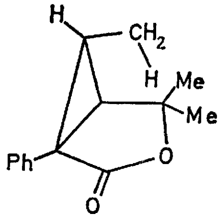


FIGURE 2

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[10] Y. S. Rao, *Chem. Rev.*, 1976, **76**, 625 and references cited therein.

[11] P. C. M. van Noort and H. Cerfontain, unpublished results.

[12] P. H. Mazzochi and R. S. Lustig, *J. Amer. Chem. Soc.*, 1975, **97**, 3714.

one advanced by Dauben *et al.*[13] for the photoproducts obtained from some bicyclo[3.1.0]hexan-2-ones.

The double bond in (2) is conjugated both with the phenyl and the carbonyl group which is contrary to the tendency to deconjugation observed in the photochemistry of phenylcyclopropanes.[11] However, the formation of an endocyclic double bond was also observed for the formation of $\Delta^{\alpha,\beta}$-butenolides upon reaction of diazoalkanes with $\Delta^{\alpha,\beta}$-butenolides.[10]

The absence of any effect of xenon on the photolysis of *exo*-(1) is thought to indicate that either the reaction of singlet excited *exo*-(1) to the intermediate A is fast relative to the xenon-collisionally-induced enhanced rate of intersystem crossing, or more likely that the spin-orbit coupling is much larger in *exo*-(1) than in simple aromatic hydrocarbons[8] due to the presence of a carbonyl group.

In conclusion, irradiation of *exo*-(1) gives a keten and acetone by cleavage of the C(1)–C(6) and C(2)–O bonds, which is to our knowledge the first example of photochemical keten formation from a lactone. So far keten formation with the simultaneous formation of CO_2 has only been reported for some structurally related anhydrides.[2,3] Investigations of the scope of this reaction are in progress.

EXPERIMENTAL

Irradiations.—Direct irradiations were carried out in a Rayonet photochemical reactor with four RUL 253.7 nm lamps in quartz fingers. The acetone photosensitized reactions were carried out in a Rayonet photochemical reactor with eight RUL 300 nm lamps in Pyrex vessels. The solvents used were distilled and dried over molecular sieves 4A. G.l.c. analysis was done with a 3.5 m × 3/8 in copper column, 12% OV-225 on Chromosorb W-AW 60—80 mesh. The photoproducts were isolated with the same column. Quantitative analysis was performed with the aid of a Varian CDS 111C digital integrator using hexadecane as internal g.l.c. standard.

Synthesis of Compound exo-(1).—Ethyl methyl 1-phenyl-3-methylcyclopropane-1,2-dicarboxylate was obtained as described.[5] A solution of the cyclopropanedicarboxylate (18.5 g) in ether (50 ml) was treated at ambient temperature with methylmagnesium iodide [from magnesium (2.5 g) and methyl iodide (14 g)] in ether (75 ml). After 30 min at reflux the mixture was treated with dilute aqueous HCl until the solid material had dissolved. Work-up by extraction with ether gave a brown oil (13 g) which was distilled at 1 mmHg. The fraction distilling at 110—140° was collected (9.2 g). The addition of n-pentane (*ca.* 5 ml) resulted in the precipitation of 4,4,exo-6-*trimethyl*-1-*phenyl*-3-*oxabicyclo*[3,1,0]*hexan*-2-*one* (2.33 g, 16%), m.p. 111—113 °C (Found: C, 77.85; H, 7.55; O, 14.6. $C_{14}H_{16}O_2$ requires C, 77.8; H, 7.4; O, 14.8%).

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[13] W. G. Dauben, L. Schulte, G. W. Shaffer, and R. B. Gagosian, *J. Amer. Chem. Soc.*, 1973, **95**, 468.