Arylcyclopropane Photochemistry. Part 3.[1] The Photochemistry of 1-Phenyl-4,4,5-trimethyl-3-oxabicyclo[3.1.0]hexan-2-one

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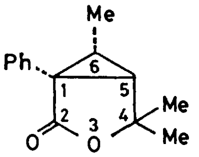
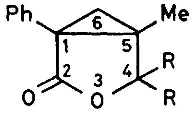
The photochemistry (wavelength of irradiation 254 nm) of the 3-oxabicyclo[3.1.0]hexan-2-ones (2a and b) in benzene and acetonitrile in the presence and absence of an added alkanol has been studied. Product formation is explained in terms of the formation of two intermediate ketens. One, containing an oxiranyl group, is trapped by trimeric methanol (if present) with formation of ester (3b) with simultaneous loss of a carbonyl compound. In the absence of alkanols this oxiranyl keten intermediate reacts in two ways: (i) thermal ring closure with reformation of (2a or b) and (ii) photolysis with formation of carbon monoxide. The other keten intermediate is proposed to be formed from a vibrationally excited ^1S state of (2a and b) by loss of a carbonyl compound. It is trapped by an alkanol (if present) with formation of ester (4). Without added alkanol it is photolysed with formation of carbon monoxide. It is concluded from the ratio of the photoproducts (3) and (4) that the cyclopropane bond of a 1-phenyl-3-oxabicyclo[3.1.0]hexan-2-one to be cleaved is preferentially that which is more highly substituted and which has the better orbital overlap with the π-system of the carbonyl group.

SOME time ago we reported on the formation of a keten upon irradiation of 1-phenyl-4,4,6-*exo*-trimethyl-3-oxabicyclo[3.1.0]hexan-2-one (1).[1a] It was proposed that the keten is formed *via* initial cleavage of the C(1)–C(6) cyclopropane bond, as this bond is weaker than C(1)–C(5) as result of better orbital overlap of the C(1)–C(6) than the C(1)–C(5) bond with the π-system of the carbonyl group.

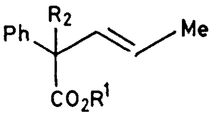
We now report on the photochemistry of 1-phenyl-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (2a) and the homologue (2b), for which the possibility of C(1)–C(5) bond cleavage is relatively enhanced as result of advanced stabilization of the developing radical position on C(5) by the 5-methyl group.



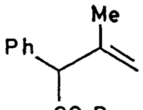
(1)



(2)
a; R = H
b; R = Me



(3)
a; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = CD_3, R^2 = D$
d; $R^1 = Et, R^2 = H$



(4)
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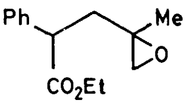
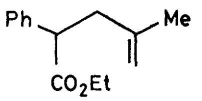
b; R = Me
c; R = Et



(5)



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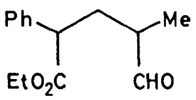

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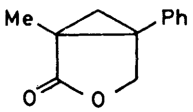


(8)

RESULTS

Synthesis of Compounds (2a *and* b).—These compounds were obtained as depicted in Scheme 1. Michael addition of the anion of methyl α-chlorophenylacetate to ethyl methacrylate afforded the cyclopropane-1,2-dicarboxylate.[2] The lactone (2a) was obtained from the cyclopropane-1,2-dicarboxylate by $LiAlH_4$ reduction and subsequent oxidative ring closure with Ag_2CO_3 on Celite.[3] Reaction of MeMgI with the cyclopropane-1,2-dicarboxylate afforded (2b).

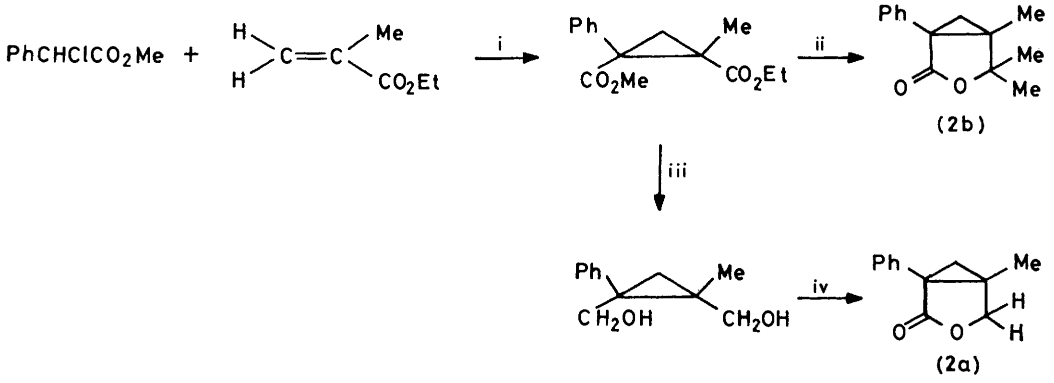
The structural assignment of (2a) was based on a comparison of the chemical shift of the ^1H n.m.r. absorption for the 4-protons of (2a) (δ 4.30) with that of the 4-protons of (8) (δ 4.14) which compound is a by-product from the synthesis of (2a). The structure assignment of (2b) was based on ^1H n.m.r. and a.s.i.s. data (Table 1), especially on those for the methyl attached to the cyclopropane ring. This methyl group is located at C(5) and not at C(1), as its Δδ is even larger than that for the methyl groups at C(4).

TABLE 1

^1H N.m.r. and a.s.i.s. data of (2b)

	δ ($CDCl_3$)	δ (C_6D_6)	Δδ
Ph	7.3 (m)		
4-Me	1.46 (s)	1.09	0.37
	1.38 (s)	1.01	0.37
6-H	1.4	0.95 (d, *J* 5 Hz)	0.45
	1.4	0.88 (d, *J* 5 Hz)	0.50
5-Me	0.98 (s)	0.51	0.47

Irradiations.—Irradiation (λ 254 nm) of a solution of (2b) (0.10M) in benzene–methanol (1 : 1 v/v) led to the formation of (3b) and acetone as the only products. Irradiation of (2b) in dry benzene did not lead to the formation of either (3b) or acetone and the only monomeric product detected was carbon monoxide, which compound was not formed upon irradiation of (2b) in benzene–methanol. Irradiation (λ 254 nm) of (2b) in benzene–CD_3OD and in benzene–ethanol led to the formation of the esters (3c and d), respectively. Irradiation of (2b) in dioxan–water (1 : 1 v/v) afforded (3a). A special search for (4a) showed it to be absent within the ^1H n.m.r. limits of detection which is thought to be 3%. Irradiation of (2a) as well as of (2b) in dry ethanol gave (3d) and (4c) in a ratio of 10 : 1. The esters (3d) and (4c) were also formed upon irradiation of both (2a and b) in acetonitrile–ethanol (1 : 1 v/v). The irradiation of (2a) in dry methanol gave (3b) and (4b), as concluded from the ^{1}H n.m.r. spectrum of the resulting product mixture which showed vinyl proton absorptions characteristic of (3) and (4). Close g.l.c. monitoring of the photoreaction of (2a) in ethanol showed that (3d) and (4c) are primary photoproducts. Separate irradiation of (3d) in ethanol did not lead to the formation of (4c).



SCHEME 1 Reagents: i, Bu^tOK; ii, MeMgI; iii, $LiAlH_4$; iv, Ag_2CO_3–Celite

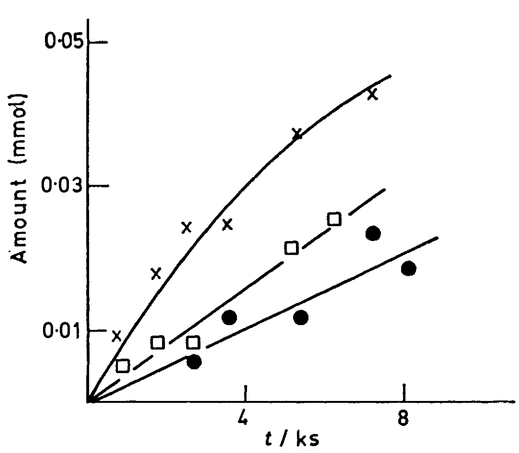


FIGURE 1 Dependence of conversion of (2b) on the irradiation time: ●, $[MeOH]_{stoich}$ 0; □, $[MeOH]_{stoich}$ 0.36; ×, $[MeOH]_{stoich}$ 1.23M

These results point to the occurrence of a keten as intermediate. In order to obtain information on the possibility that this keten intermediate reverts to the starting compound, we have examined the photochemistry of (2b) in the presence of various concentrations of methanol. The rate of conversion of (2b) (0.10M) in benzene upon irradiation at 254 nm proved to increase with increasing methanol concentration (Figure 1). The dependence of the amount of (3b) formed upon irradiation of (2b) (0.095M) in benzene on the irradiation time appeared to be linear * for various methanol concentrations (Figure 2). The slopes of the linear graphs were taken to be the rates of formation of (3b); they are given in Table 2.

According to Lillford and Satchell, ketens in the presence of methanol are trapped exclusively by trimeric methanol.[4] In order to interpret quantitatively the observed dependence of the rate of formation of (3b) and the rate of conversion of (2b) on the methanol concentration, the equilibrium constant, K_{trimer}, for $3(MeOH)_1 \rightleftharpoons (MeOH)_3$ in benzene as a solvent was determined using i.r. spectroscopy.

TABLE 2

Rate of formation v of (3b) in benzene at various methanol concentrations

[MeOH]/M	10^3 v/mmol k s^{-1}
0.18	1.14
0.36	2.36
0.54	3.2
0.74	3.8
1.23	4.2

For a stoicheiometric methanol concentration of 0.41M the i.r. spectrum shows three absorptions at 3 605, 3 500, and 3 380 cm^{-1} which were assigned to the methanol monomer $(MeOH)_1$, dimer $(MeOH)_2$, and trimer $(MeOH)_3$, respectively.[5] At low stoicheiometric methanol concentrations (*i.e.* ⩽ 0.18M) only the monomer and a relatively weak dimer absorption are observed. With increasing methanol

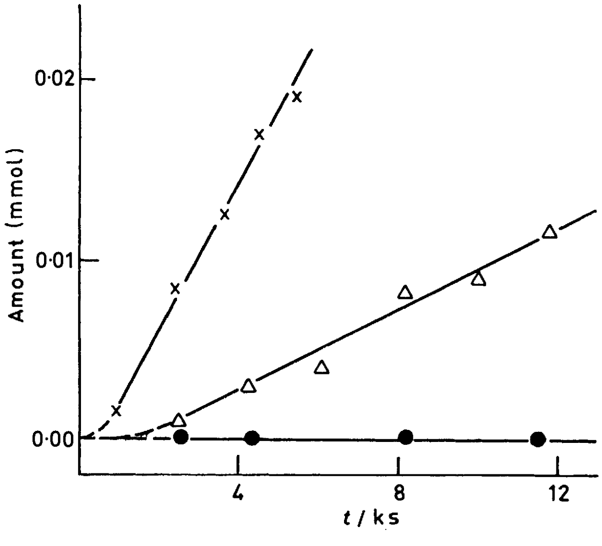


FIGURE 2 Dependence of formation of (3b) from (2b) on the irradiation time: ●, $[MeOH]_{stoich}$ 0; △, $[MeOH]_{stoich}$ 0.18; ×, $[MeOH]_{stoich}$ 1.23M

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* The initial curvature is thought to reflect the initial non-steady state condition.

concentration the trimer absorption appears and increases strongly, the monomer absorption decreases relatively and the dimer absorption decreases even more readily than the monomer absorption. The monomer concentrations calculated from the optical density E at 3 605 cm^{-1} are collected in Table 3. For the calculation of K_{trimer} it was assumed that $[(MeO)_2H] = 0$, which approximation is at least correct for the higher methanol concentrations employed. Accordingly, equation (1) applies and may be rewritten as (2).

$$[(MeOH)_3] = K_{\text{trimer}}[(MeOH)_1]^3 = \tfrac{1}{3}\{[MeOH]_{\text{stoich}} - [(MeOH)_1]\} \quad (1)$$

$$\{[MeOH]_{\text{stoich}}/[(MeOH)_1]\} - 1 = 3K_{\text{trimer}}[(MeOH)_1]^2 \quad (2)$$

TABLE 3

I.r. measurements of methanol in benzene

$[MeOH]_{\text{stoich}}$/M	0.16	0.41	0.63	0.94	1.35	1.57	1.93
E(3 605 cm^{-1})	0.11	0.24	0.28	0.35	0.40	0.40	0.45
$[(MeOH)_1]$/M	0.11	0.24	0.28	0.35	0.40	0.40	0.45

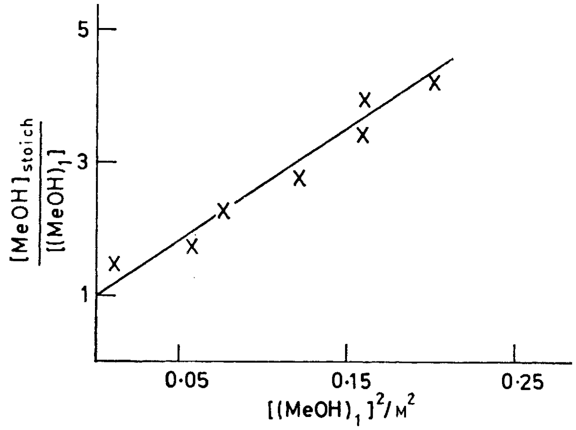
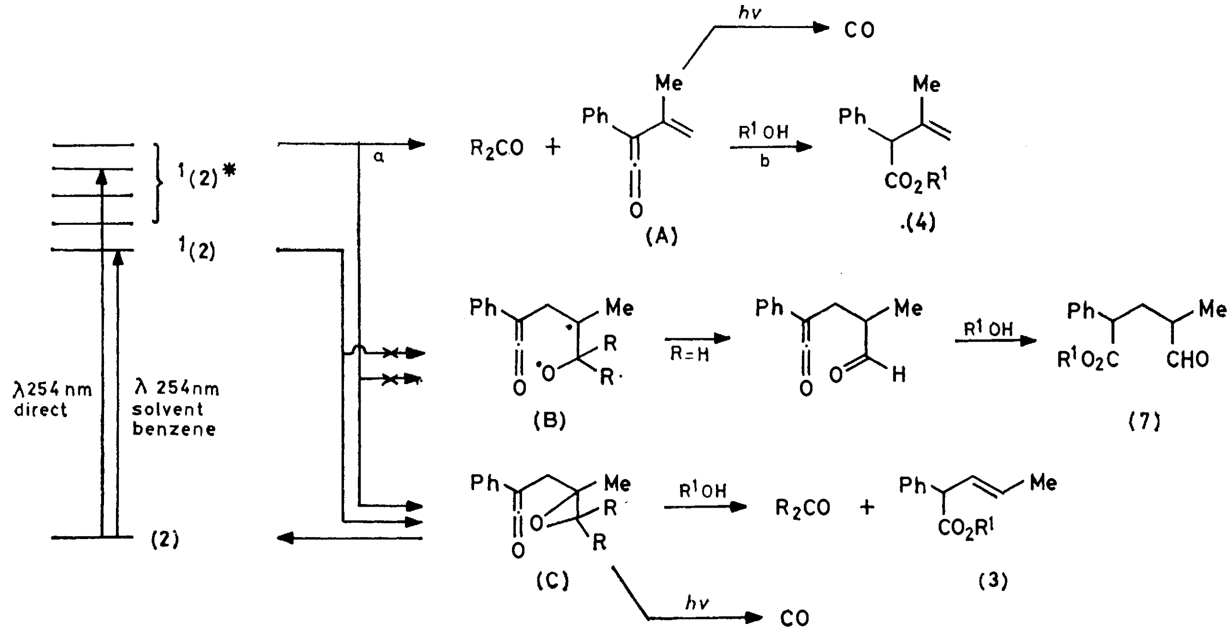


FIGURE 3 The association of methanol in benzene

The dependence of $[MeOH]_{\text{stoich}}/[(MeOH)_1]$ on $[(MeOH)_1]^2$ is linear (Figure 3), as required by equation (2). K_{trimer} was calculated from the slope of the graph to be $5.5\ l^2\ mol^{-2}$.

It soon became apparent that oxiranylketens should be considered as potential intermediates in the photoreaction of (2a and b). Therefore compound (5), which was expected to result from the reaction of ethanol with the oxiranylketen [possibly formed from photo-excited (2a)] was synthesized by epoxidation with *m*-chloroperbenzoic acid of (6) which is the main product from irradiation at 254 nm of ethyl 1-phenyl-2,2-dimethylcyclopropanecarboxylate.[6] The oxiran (5) did not survive the g.l.c. conditions used for the analysis of the mixture resulting from irradiation of (2a), and rearranged to the aldehyde (7). Irradiation (λ 254 nm) of (5) (70 mg) in dry ethanol (3 ml) resulted in the rapid disappearance of (5), as concluded indirectly by g.l.c. analysis from the relative decrease of the decomposition product (7). The g.l.c. analysis of the resulting photolysis mixture did not show the presence of any sufficiently volatile product. Upon irradiation at 254 nm of (7) in ethanol, subsequent g.l.c. analysis showed the presence of large amounts of products which are all different from those formed upon irradiation of (2a) in ethanol, and further, only a trace of (3d). Accordingly, neither (5) nor (7) are intermediate in the photoconversion of (2a).

Lactone (2b) upon irradiation (λ 300 nm) in acetone as solvent and photosensitizer in the presence of methanol proved to be photostable. The acetone sensitized irradiation of (1) leads to epimerization at C(6).[1b] Thus it is concluded that products (3) and (4), upon direct irradiation of (2b) at 254 nm, are formed by reaction from the singlet excited state of (2b).



SCHEME 2

DISCUSSION

The photochemical reactions of (2a and b) may be explained in terms of the mechanism shown in Scheme 2. The superscript 1 denotes the multiplicity of the excited state and the asterisk in $^1(2)^*$ a vibrationally excited state of $^1(2)$. The photoformation of (4) from the ^1S

state of both (2a and b) is suggested to occur *via* initial C(1)–C(6) bond cleavage giving keten (A) and R_2CO (step a), followed by reaction of keten (A) with alcohol (if present) (step b), *i.e.* by the same mechanism as proposed before [1b] for the formation of (3) upon irradiation at 254 nm of (1) in hydroxylic solvents. In the absence of an alkanol the intermediate (A) is probably photolysed with formation of carbon monoxide.[7] Reversion of the keten intermediate (A) to starting compound is unlikely in view of the results with lactone (1) from which it could be concluded that such a process does not occur.[1b]

It is proposed that (A) [and thus (4)] results from a vibrationally excited ^1S state of (2a and b) as will now be explained. Upon irradiation of (2b) in benzene, the solvent absorbs all the incident radiation (*cf.* Figure 4).

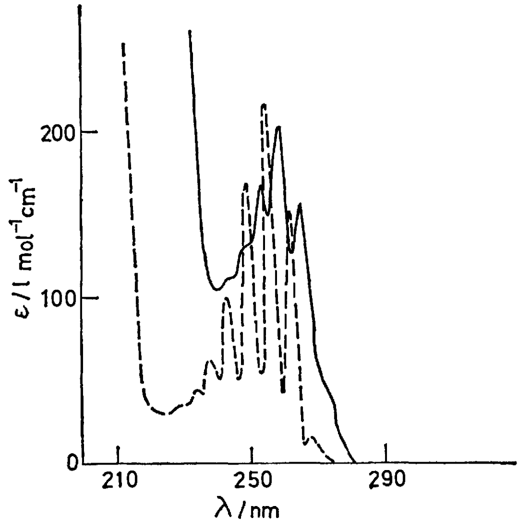


FIGURE 4 U.v. absorption of (2b) (——) and benzene (— — —) in cyclohexane

Energy transfer to (2b) occurs from photoexcited benzene at its lowest vibrational level. This can be compared energetically with the direct excitation of (2b) with $\lambda \geqslant 262$ nm (*cf.* Figure 4), leading to population of the lowest vibrational level of the ^1S state of (2a and b). Direct irradiation (λ 254 nm) of (2a and b) leads to population of upper vibrational levels of the ^1S state of (2a and b) (*cf.* Figure 4) which are thought to undergo chemical reaction with formation of intermediate (A) and vibrational relaxation to the lowest vibrational level of ^1S which can only form intermediate (C).[†] The preceding reasoning suggests that the acid (4a) would be formed on irradiation of (2b) in dioxan–water as solvent, but this was not observed. It should be realized however, that the rate of relaxation of $^1(2)^*$ to $^1(2)$ may depend on the solvent properties. Since the esters (4b and c) are formed from photoexcited (2a) in methanol and ethanol respectively, we feel quite sure that (A) results from $^1(2)^*$.

The photoformation of (3) from (2) may be explained in terms of formation of keten (C) as intermediate from the ^1S state of (2), and subsequent conversion in the presence of an alkanol. As (3b) is also produced upon addition of methanol just after the termination of the irradiation of (2b), (3) is not formed by attack of R^1OH on the ^1S state of (2). It is proposed that the keten intermediate contains an oxiranyl group as in (C) and not the 1,3-diradical structure as in (B). For, in the case of (2a) as substrate this diradical would undergo a 1,2-hydrogen shift to the carbon atom bearing the radical position [9] to give a keten-aldehyde which upon reaction of its keten part with ethanol would yield (7).

The observed product dependence on the methanol concentration (Table 2) can also be explained more easily in terms of intermediate (C) than (B). The photoreactions of (2b) may be described by steps (3)—(7).

$$(2b) + {}^1(C_6H_6) \longrightarrow {}^1(2b) \qquad (3)$$

$$^1(2b) \xrightarrow{k_4} (C;\ R = Me) \qquad (4)$$

$$(C;\ R = Me) \xrightarrow{k_5} (2b) \qquad (5)$$

$$(C;\ R = Me) + {}^1(C_6H_6) \xrightarrow{k_6} CO \qquad (6)$$

$$(C;\ R = Me) + (MeOH)_3 \xrightarrow{k_7} (3b) \qquad (7)$$

Carbon monoxide is thought to result from the photolysis of keten (A),[7] as it is formed upon irradiation of (2b) in benzene in the absence of methanol, but not in the presence of methanol.

For steps (5)—(7) equation (8) follows (with $k_6' = k_6[^1(C_6H_6)]$). Combination of (8) and (1) gives (9). A

$$\frac{v_5 + v_6 + v_7}{v_7} = \frac{k_5 + k_6'}{k_7[(MeOH)_3]} + 1 \qquad (8)$$

$$\frac{1}{v_7} = \frac{1}{v_5 + v_6 + v_7} + \frac{k_5 + k_6'}{(v_5 + v_6 + v_7)k_7K_{\text{trimer}}} \times \frac{1}{[(MeOH)_1]^3} \qquad (9)$$

plot of $1/v_7$ (from Table 2) *versus* $[(MeOH)_1]^{-3}$ (obtained by interpolation from the data in Table 3) is linear as required by equation (9) (Figure 5). From the intercept with the vertical axis ($v_5 + v_6 + v_7$) was obtained as 0.0048 mmol ks^{-1} and from the slope $(k_5 + k_6')/k_7$ was calculated to be 0.063 mol l^{-1}. For $[MeOH]_{\text{stoich}}$ 1.23 and 0M the rate of conversion of (2b) is 0.007 8 and 0.002 5 mmol ks^{-1} respectively (see Figure 1). For $[MeOH]_{\text{stoich}}$ 1.23M *ca.* 90 [= 100 × 0.004 2 (see Table 2)/0.004 8]% of the keten intermediates are trapped by trimeric methanol. Accordingly *ca.* 0.008 7 (=0.007 8/0.9) mmol ks^{-1} of ketens are formed. This implies that

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[†] Recently the photochemical *cis–trans* isomerization of some optically *endo*- and *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indenes was reported.[8] For the direct irradiations the isomerization occurs 19% by internal and 81% by external cyclopropane bond fission. The triplet photosensitized isomerization occurs 2% by internal and 98% by external bond fission. It was therefore proposed that the isomerization occurs at least 17 (=19 − 2)% directly from the singlet excited state. In view of the present results with (2) in benzene, it may well be that internal bond fission occurs from a vibrational excited ^1S state, and not from the lowest vibrational level of ^1S.

in the absence of methanol 0.006 2 (=0.008 7 — 0.002 5) mmol ks^{-1} of keten revert to (2b) and 0.002 5 mmol ks^{-1} of keten form carbon monoxide. Thus $k_5/k_6' = 2.5$ and accordingly $k_5/k_7 = 0.045$ mol l^{-1}. The latter datum illustrates that the retroreaction of (C) to (2b) [step (5)] is much slower than the non-catalysed addition of methanol to (C). The rate constant for the addition of methanol to dimethylketen in ether is 0.017 l mol^{-1} s^{-1} [4] and thus k_5 will be *ca.* 0.000 8 s^{-1}. We do not see any obvious reason for such a low rate constant for the retroreaction if the keten has structure (B). It is however conceivable for the oxiranylketen (C), since oxirans are known to react only slowly with ketens with formation of γ-butylrolactones in low yield [10] (the reaction of alcohols with dimethylketen gives esters in high yield! [4]).

The reaction of (C) with ethanol is expected to yield (5). However, it was shown that (5) is not an intermediate upon irradiation of (2a) in ethanol. Accordingly it must at present be concluded that (3) is formed by reaction of an alkanol with (C) with concerted loss of R_2CO.† This unprecedented conclusion stands at present unexplained.

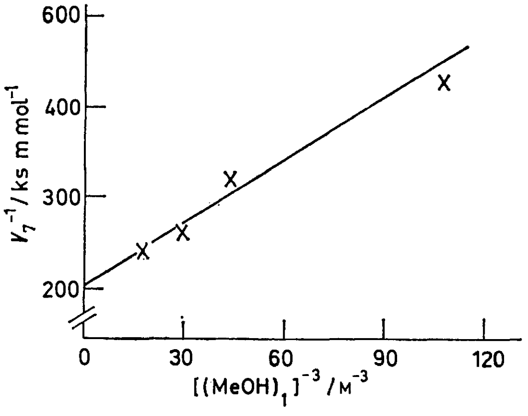

FIGURE 5 Dependence of the rate of formation of (3b) from (2b) on the methanol monomer concentration

With (1), only products resulting from initial C(1)–C(6) bond cleavage are formed.[1b] With (2a and b), however, the photoproducts are formed *via* both initial C(1)–C(6) and C(1)–C(5) bond cleavage, with the latter one dominating.

This difference in the photofragmentation of (1) and (2) illustrates once again the importance of orbital overlap of the cyclopropane bond to be broken with the orbitals of the π-system of the carbonyl group.[1b, 11]

In conclusion, our results show that irradiation of (2a and b) at 254 nm gives a keten intermediate containing an oxiranyl group, which either slowly reverts to the starting compound or is trapped by an alkanol under simultaneous loss of a carbonyl compound.‡ A comparison of the results of (2a and b) with those of (1) [1b] further clearly demonstrates that the cyclopropane bond to be cleaved preferentially is that which is more highly substituted and which has the better orbital overlap with the π-system of the carbonyl group.

EXPERIMENTAL

Materials.—Synthesis of (2a). A solution of dimethyl 1-methyl-2-phenylcyclopropane-1,2-dicarboxylate (7.5 g) in ether (20 ml) was slowly added to a stirred suspension of $LiAlH_4$ (4.9 g) in ether (300 ml). After refluxing for 45 min the excess of hydride was removed by the careful addition of water (20 ml), 15% aqueous NaOH (20 ml), and water (20 ml). The precipitate was filtered off with suction. Work-up by extraction with ether and distillation gave 4.0 g (71%) of 1,2-bishydroxymethyl-1-methyl-2-phenylcyclopropane, b.p. 128—130 °C at 0.03 mmHg. A solution of the diol (1.9 g) in dry benzene (300 ml) was refluxed with Ag_2CO_3 (24.8 g) on Celite (22 g) [3] for 2 h. G.l.c. analysis of the crude reaction product showed the absence of diol and the presence of (2a) and its isomer 1-methyl-5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (8) in the ratio 3 : 1. Lactone (2a) and its isomer (8) were isolated by means of preparative g.l.c.

Synthesis of (2b). A solution of dimethyl 1-methyl-2-phenylcyclopropane-1,2-dicarboxylate (12.6 g) [2] in ether (100 ml) was treated at ambient temperature with methylmagnesium iodide [from magnesium (2.5 g) and methyl iodide (14 g)] in ether (75 ml). After refluxing for 1 h the mixture was treated with dilute aqueous HCl until the solid material had dissolved. Work-up by extraction with ether gave a yellow oil (10.6 g) which partially solidified. Careful addition of n-hexane to this oil gave crude solid (2b), which was purified by recrystallization from n-hexane to give (2b) (4 g, 38%), m.p. 104—105 °C.

Synthesis of (5). A solution of (6) (135 mg) in ether (1 ml) was treated with *m*-chloroperbenzoic acid (133 mg) in ether (4 ml) at 0 °C. After stirring for 17 h the acid was removed by washing with a 10% aqueous NaOH solution. The ^{1}H n.m.r. spectrum of the crude product showed the presence of (5) and (6) in about equal amounts. This mixture was used as such for the photochemical and g.l.c. experiments of (5).

Irradiations.—Direct irradiations were carried out in quartz fingers in a Rayonet photochemical reactor with four RUL 253—257 nm lamps. The acetone photosensitized reaction was carried out in a Pyrex vessel in a Rayonet photochemical reactor with eight RUL 300 nm lamps. G.l.c. analysis was done with a copper column, (3.5 m × $\frac{1}{8}$ in, 12% OV-225 on Chromosorb W-AW 60—80 mesh, 190 °C). The photoproducts were isolated with the same column. The quantitative analysis was performed with the aid of a Varian CDS 111C digital integrator using hexadecane as internal g.l.c. standard. The solvents used were distilled and dried over molecular sieves 4A.

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† No search was made for formaldehyde as a photoproduct for irradiation at 254 nm of (2a).

‡ A referee suggested that the observed dependence of the consumption of (2b) on the methanol concentration could also be due to (i) quenching of either (2b) or the sensitizer (benzene) by the keten intermediate, and (ii) an inner light filtering effect by the keten. Both these suggestions imply that the keten concentration should depend on the methanol concentration. However, the keten concentrations at [MeOH] → 0, which were obtained from the intercepts of the linear graphs of Figure 2 with the vertical axis and volume of the irradiated solution (3 ml), are independent of the methanol concentration, *viz.* (6 ± 1) 10^{-4}M over the methanol concentration range 0.18—1.23M. Accordingly, the keten quenching or filter mechanism does not account for the observed dependence of the substrate disappearance on methanol (Figure 1).

I.r. Analysis of the Methanol–Benzene System.—Spectra were recorded on a Perkin-Elmer 257 grating i.r. spectrophotometer.

Spectroscopic Data.—Compound (2a) has $\nu_{\text{max.}}$ (CHCl$_3$), 1 760, 1 600, and 1 500 cm^{-1}, δ(CCl$_4$) 7.3 (5 H, s), 4.13 (2 H, m), 1.47 (1 H, d, *J* 5 Hz), 1.23 (1 H, d, *J* 5 Hz), and 1.07 (3 H, s); (2b) $\nu_{\text{max.}}$ (CHCl$_3$) 1 760, 1 600, 1 500, 1 385, and 1 375 cm^{-1}, for n.m.r. see Table 1; (3a) δ(CDCl$_3$) 7.27 (5 H, s), 6.0—5.4 (2 H, m), 4.60 and 4.24 (1 H, d, *J* 9 Hz), and 1.65 (3 H, m); (3b) $\nu_{\text{max.}}$ (CHCl$_3$) 1 720, 1 600, and 1 500 cm^{-1}, δ(CCl$_4$) 7.27 (5 H, s), 6.1—5.3 (2 H, m), 4.5—4.0 (1 H, m), 3.59 (3 H, s), and 1.65 (3 H, m); (3c) δ(CDCl$_3$) 7.26 (5 H, s), 5.92 (1 H, d, *J* 15 Hz), 5 64 (1 H, m, *J* 6 and 15 Hz), and 1.75 (3 H, m); (3d) δ(CCl$_4$) 7.21 (5 H, s), 6.0—5.4 (2 H, m), 4.5—4.1 (1 H, m), 4.08 (2 H, q, *J* 8 Hz), 1.69 (3 H, m), and 1.20 (3 H, t, *J* 8 Hz); (4c) $\nu_{\text{max.}}$ (CHCl$_3$) 1 720, 1 600, and 1 500 cm^{-1}, δ(CCl$_4$) 7.27 (5 H, s), 4.91 (2 H, m), 4.20 (1 H, s), 4.16 (2 H, q, *J* 7 Hz), 1.75 (3 H, s), and 1.27 (3 H, t, *J* 7 Hz); (5b) $\nu_{\text{max.}}$ (CHCl$_3$) 1 740 cm^{-1}, δ(CDCl$_3$) 7.27 (5 H, s), 4.09 (2 H, q, *J* 7 Hz,), 3.6 (1 H, m), 2.55 (2 H, m), 1.95 (2 H, m), 1.22 (3 H, s), and 1.12 (3 H, t. *J* 7 Hz); (7) δ(CDCl$_3$) 9.48 (1 H, m), 7.27 (5 H, s), 4.13 (2 H, q, *J* 7 Hz), 3.69 (1 H, m), 2.6—1.6 (3 H, m), 1.16 (3 H, t, *J* 7 Hz), and 1.07 (3 H, m); (8) $\nu_{\text{max.}}$ (CHCl$_3$) 1 760, 1 600, and 1 500 cm^{-1}, δ(CCl$_4$) 7.37 (5 H, s) 4.30 (2 H, s), 1.39 (1 H, d, *J* 5 Hz), 1.25 (1 H, d, *J* 5 Hz), and 1.10 (3 H, s).

We thank Mrs. H. Haak-Ctvrtéckova for carrying out the i.r. measurements.

[8/064 *Received, 16th January,* 1978]

REFERENCES

[1] (*a*) Part 1, P. C. M. van Noort and H. Cerfontain, *Tetrahedron Letters*, 1977, 3899; (*b*) Part 2, P. C. M. van Noort and H. Cerfontain, *J.C.S. Perkin II*, 1978, 757.

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

[3] M. Fetizon, M. Golfier, and J.-M. Louis, *Tetrahedron*, 1975, **31**, 171.

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

[5] D. A. Ibbitson and L. F. Moore, *J. Chem. Soc.* (*B*), 1967, 76.

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

[7] J. G. Calvert and J. N. Pitts, ‘Photochemistry,’ Wiley, New York, 1966, p. 391.

[8] S. S. Hixson and J. Borovsky, *J. Amer. Chem. Soc.*, 1976, **98**, 2840.

[9] D. R. Paulson, A. S. Murray, D. Bennett, E. Mills, V. O. Terry, and S. D. Lopez, *J. Org. Chem.*, 1977, **42**, 1252.

[10] D. Borrmann in ‘Houben-Weyl, Methoden der Organischen Chemie,’ Georg. Thieme Verlag, Stuttgart, 1968, vol. 7/4, p. 185.

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