Photochemistry of 1,2-Diketones. Part 5.[1] Formation of Dihydrodioxines, Oxetanes, Allylic Ethers, and 1,2-Adducts from Alicyclic 1,2-Diketones and Alkenes †

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The photoaddition of five alicyclic non-enolizing 1,2-diketones (1a—e), bipivaloyl, and biacetyl to various simple alkenes has been investigated. The dihydrodioxine formation dominates over the formation of oxetane, α-keto allylic ether, and 1,2-adduct (α-hydroxyketone) for the three cyclic 1,2-diketones (1b—d) that have a *syn*-periplanar (lowest) excited 1,2-diketo configuration. The four-membered ring diketone (1a) photo-fragments prior to its addition to the alkene. Biacetyl with an *anti*-periplanar excited 1,2-diketo configuration does not form dihydrodioxines. No information on the geometry of the excited 1,2-diketo configuration could be obtained with (1e) and (2), as the rate of α-cleavage [with (1e)] or intramolecular hydrogen abstraction of the *anti*-periplanar excited diketo moiety [with (1e) and (2)] greatly exceeds the rate of reaction with the alkene. Thirteen dihydrodioxines, twelve oxetanes, four allylic ethers, and fourteen 1,2-adducts have been identified. The formation of the dihydrodioxine and oxetane formation has been discussed with special emphasis on (i) the nature of the reacting excited state (the reacting state is the lowest triplet n–π* state of the 1,2-diketone), (ii) the intermediacy of exciplexes and 1,4-diradicals, and (iii) the stereospecificity of the dihydrodioxine and oxetane formation.

Since the early report of Schönberg and Mustafa [2] that 9,10-phenanthrenequinone with alkenes in ' Cairo sunlight ' forms cycloadducts this photoreaction has been investigated very extensively.[3] The products are [4 + 2]-cycloadducts (dihydrodioxines, also referred to as dioxenes), [2 + 2]-cycloadducts (oxetanes), and 1,2-adducts (α-hydroxyketones), formed by abstraction of an allylic hydrogen from the alkene by the excited 1,2-diketone and recombination of the two resulting radicals with formation of a carbon–carbon single bond. The relative amounts of these products depend on the structure of the alkene. Comparable results were obtained with other quinonoid 1,2-diketones.[3a,e,4] Acyclic phenyl-conjugated 1,2-diketones, such as benzil and 1-phenylpropane-1,2-dione, form mainly oxetanes.[3a,f,5] Acyclic aliphatic 1,2-diketones, such as biacetyl,[3a,c,6] and α-ketocarboxylates, such as methyl and ethyl pyruvate [7] and diethyl mesoxalate,[8] upon irradiation in the presence of alkenes form oxetanes and, if the alkene contains allylic hydrogen, form, in addition, 1,2-adducts and α-ketoallylic ethers, although the latter two types of products were not reported for mesoxalate.[8] Perfluorobiacetyl with both (E)- and (Z)-1,2-difluoroethene yields ca. 65% dihydrodioxines and 20% oxetanes.[9]

Photoreactions of alicyclic 1,2-diketones with alkenes were reported for camphorquinone,[10] 2,2,5,5-tetramethyltetrahydrofuran-3,4-dione,[11] 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene-2,3-dione,[12] and 3,3,6,6-tetramethylcyclohexane-1,2-dione.[12] As for the quinonoid 1,2-diketones, these substrates form dihydrodioxines, oxetanes, and 1,2-adducts.

We have now studied the photochemistry of a series of five α,α,ω,ω-tetramethylcycloalkane-1,2-dione (1a—e), their acyclic analogue (2), and biacetyl (3) in the presence of some simple alkenes. One of the aims of the present study was to obtain, on the basis of possible variations in the yield of the various types of products, additional evidence for the configuration structure of the reacting excited states of these 1,2-diketones and their mutual differences, as was proposed on the basis of the photochemistry of these substrates proper in both an inert solvent and in propan-2-ol as the solvent.[1]
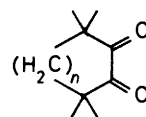
(1) a; n = 0
    b; n = 1
    c; n = 2
    d; n = 3
    e; n = 4

(2) R = Bu^t
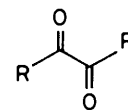
(3) R = Me

Previously it was shown that the irradiation of (1c) in cyclohexene as the solvent leads to products including bicyclohexenyl, 2-hydroxy-3,3,6,6-tetramethylcyclohexanone (7%), two diastereoisomeric 1,2-adducts (in a 3 : 2 ratio, total yield 47%), dihydroxydioxine (7%), and a tetracyclic hydroxy-oxetane (6%), which is a secondary photoproduct from the diastereoisomeric 1,2-adduct formed in excess.[12]

Results

Irradiation of solutions of the α,α,ω,ω-tetramethylcycloalkane-1,2-diones (1a—e) in benzene saturated with ethene, or in benzene with added (E)-1,2-dicyanoethene gave no other products than those found in the absence of the alkene.[1] Irradiation of (1b—d) in benzene saturated with isobutene (IB), or in the presence of added 2,3-dimethylbut-2-ene (DMB) under the same conditions afforded dihydrodioxines, allylic ethers, oxetanes, and 1,2-adducts. The yields of the photoadducts are collected in Table 1.‡ The four-membered ring 1,2-diketone (1a) upon irradiation in neat benzene is fully converted into CO and 2,3-dimethylbut-2-ene without forming any secondary product.[1] Apparently (1a) does not

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† Taken in part from the Thesis (in English) of P. L. Verheijdt, University of Amsterdam, 1981.

‡ All the irradiations of the five-, six-, and seven-membered cyclic 1,2-diketones in the presence of alkenes yielded, besides the photoadducts, small amounts (<10%) of the photoproducts, which are also present in the absence of the alkenes and were discussed previously.[1]

Table 1. Photoadducts from the 1,2-diketones (1)—(3) and some simple alkenes with benzene as solvent

| 1,2-Diketone | $\bar{\Phi}$ (°) [a] | Alkene [b] | Triplet sensitizer [c] | Yield (%) (structure) | | | | $\dfrac{(D + AE + O)}{1,2\text{-}A}$ |
				Dihydrodioxine (D)	Allylic ether (AE)	Oxetane (O)	1,2-Adduct (1,2-A)	
(1a)	0	DMB		0	0	0	0	
(1b)	0	IB		25 (4b)	10 (6b)	11 (8b)	14 (10b)	3.3
		DMB		61 (5b)	0	2 (9b)	18 (11b)	3.5
(1c)	42	IB		46 (4c)	3 (6c) [d]	6 (8c)	33 (10c)	1.7
		DMB		46 (5c)	0	0	31 (11c)	1.5
(1d)	82	IB		9 (4d)	2 (6d)	17 (8d)	12 (10d)	2.3
		DMB		48 (5d)	0	4 (9d)	23 (11d)	2.3
(1e)	98	IB		0	0	0	0	
		DMB		0	0	0	5 (11e)	
(2)	122	IB		0	0	0	0	
		DMB		0	0	0	0	
(3) [e]	160	IB [f]		0	17 (12)	5 (14d)	18 (15)	1.2
		DMB		0	61 (13)	0	15 (16); 6 (17)	2.9
(1b)		cP		7 (cis-19)	0	8 (21)	29 (23-1); 25 (23-2) [g]	0.28
		cH		2 (cis-20); [d] 2 (trans-20) [d]	0	4 (22)	28 (24-1); 21 (24-2) [g]	0.16
(1c) [h]		cH		7			28 + 6; 19 [g]	0.13
(1b)		(Z)-B		40 (cis-25b); 3 (trans-25b)	0	7 (26b); 15 (27b)	7 [(Z)-28b]	9
		(E)-B		4 (cis-25b); 40 (trans-25b)	0	1 (26b); 4 (27b)	10 [(E)-28b]	5
(1d)		(Z)-B		4 (cis-25d); 4 (trans-25d)	0	18 (26d); 21 (27d)	16 [(Z)-28d]	2.9
		(E)-B		1 (cis-25d); 7 (trans-25d)	0	8 (26d); 16 (27d)	16 [(E)-28d]	2.0
(1b)		DMB	3-MAP	61 (5b)	0	2 (9b)	17 (11b)	3.7
			4-BBP	62 (5b)	0	1 (9b)	18 (11b)	3.3
		(Z)-B	4-BBP	41 (cis-25b); 3 (trans-25b)	0	6 (26b); 14 (27b)	8 [(Z)-28b]	8
		(E)-B	4-BBP	4 (cis-25b); 40 (trans-25b)	0	$\simeq 1$ (26b); 5 (27b)	6 [(E)-28b]	8

[a] Ground state intercarbonyl dihedral angles from ref. 14. [b] DMB, IB, cP, cH, and B stand for 2,3-dimethylbut-2-ene, isobutene, cyclopentene, cyclohexene, and but-2-ene, respectively. [c] 3-MAP and 4-BBP stand for 3-methoxyacetophenone (E_T = 303 kJ mol⁻¹) and 4-benzoylbiphenyl (E_T = 254 kJ mol⁻¹), respectively. [d] Identified tentatively on the basis of its g.l.c. retention time. [e] Ryang reported a product yield ratio for (12) : (14) : (15) of 16 : 10 : 41 and for (13) : (a mixture of unspecified alcoholic photoadducts) of 70 : 12.[6b] Turro recently showed that the yields of the photoadducts of biacetyl and DMB vary markedly with the polarity of the solvent and the temperature.[6d] [f] Besides (12), (14), and (15) 22% of the dihydrodimer of biacetyl (18) (lit. 13% [6b]) was isolated by g.l.c. (at 110 °C). [g] Two diastereoisomers. [h] Ref. 12.
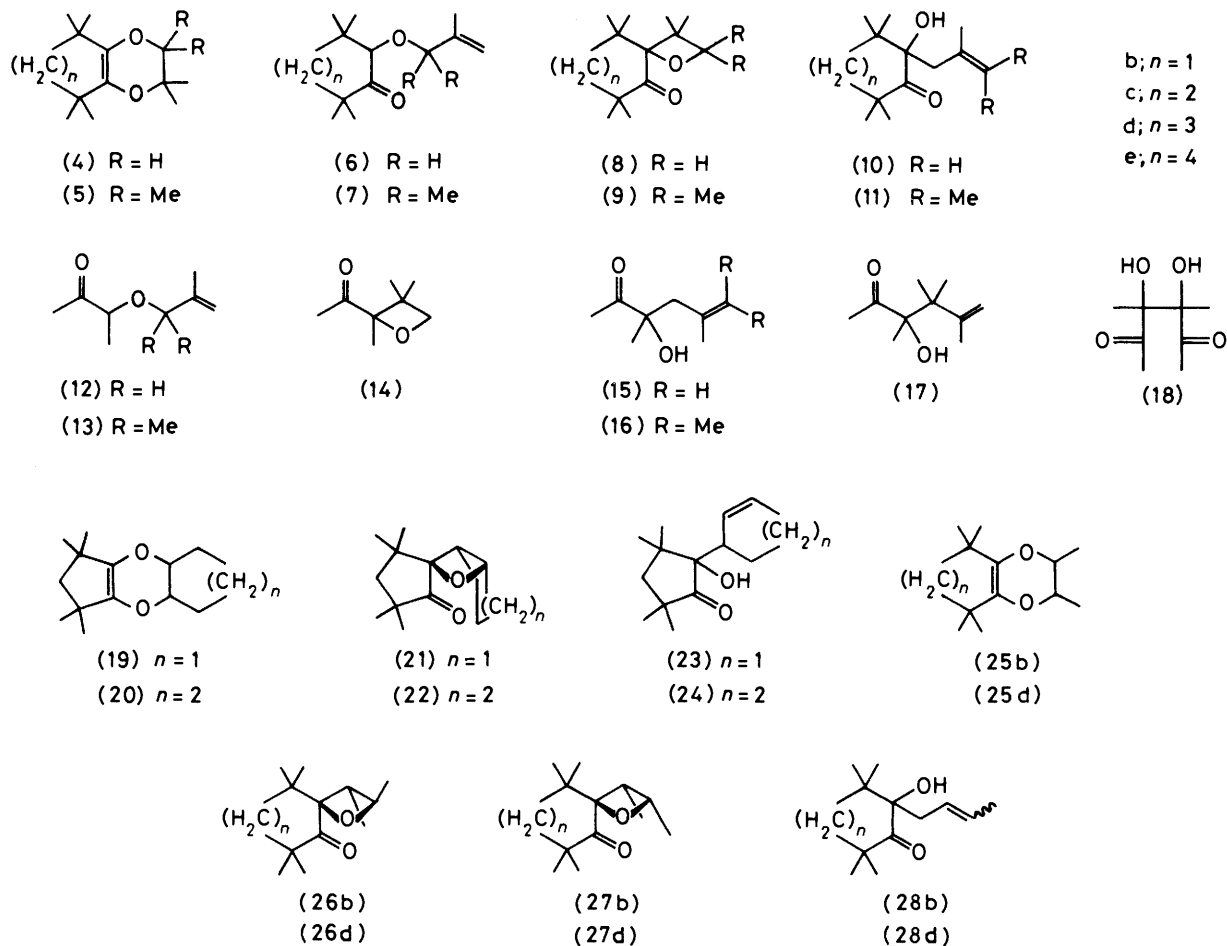
photoreact with the DMB produced. The eight-membered ring 1,2-diketone (1e) and bipivaloyl (2) do not form any significant amount of photoadducts, but instead the same photoproducts in the same ratio, as observed in the absence of the alkene resulting from Norrish type I and II processes.[1,13] These two diketones are ground-state transoid, 1,2-diketones, *i.e.* their time-averaged intercarbonyl dihedral angle $\bar{\Phi}$ is >90° (*cf.* Table 1), of which the (luminescing) lowest singlet and triplet excited states have an *anti*-periplanar diketo moiety.[13,14] Therefore the photoreaction of biacetyl (3) (another ground-state transoid 1,2-diketone, but without γ-hydrogens rendering intramolecular hydrogen abstraction and subsequent cyclization impossible) was also studied. From (3) and both IB and DMB photoadducts are formed with the exception of dihydrodioxines (Table 1).

Upon irradiation of (1b) in the presence of cyclopentene (cP) and of cyclohexene (cH), or of (1b) and (1d) with (E)- or (Z)-but-2-ene [(E)- and (Z)-B] dihydrodioxines, oxetanes and 1,2-adducts are formed, but no allylic ethers. The structures of the photoadducts reveal that there is some loss of the stereochemical integrity of the but-2-ene upon forming the dihydrodioxines, but not of the 1,2-adducts.

The photosensitized irradiations of (1b) with DMB and (Z)- and (E)-B yield the same products in essentially the same ratio as the direct irradiations (Table 1).

Discussion

Mechanism of Formation of the Photoadducts.—The formation of the various photoadducts may be discussed in terms of the mechanism shown in the Scheme for the cyclic 1,2-diketones (1b—d) and IB (R = H) or DMB (R = Me) as typical reactants (yielding the even- and odd-numbered products for IB and DMB, respectively). This mechanism is in fact an extension of that proposed for the photoreaction of biacetyl [6b] and quinonoid 1,2-diketones [3a] with alkenes. Irradiation of the 1,2-diketone leads to a singlet excited- and, subsequently to a triplet excited-state with *syn*- or *anti*-periplanar diketo geometry, depending on whether the intercarbonyl dihedral angle of the ground-state 1,2-diketone is less than or greater than 90°, respectively.[13,14] Subsequently two chemical pathways can be discerned, *viz.* abstraction of an allylic hydrogen of the alkene [route (a)] with subsequent recombination of the resulting semidione and allylic radicals,

(4) R = H
(5) R = Me

(6) R = H
(7) R = Me

(8) R = H
(9) R = Me

(10) R = H
(11) R = Me

b; n = 1
c; n = 2
d; n = 3
e; n = 4

(12) R = H
(13) R = Me

(14)

(15) R = H
(16) R = Me

(17)

(18)

(19) n = 1
(20) n = 2

(21) n = 1
(22) n = 2

(23) n = 1
(24) n = 2

(25b)
(25d)

(26b)
(26d)

(27b)
(27d)

(28b)
(28d)

to yield the 1,2-adduct (10, 11) and electrophilic attack of the triplet excited 1,2-diketone on the double bond of the ground-state alkene [route (b), possibly *via* an exciplex (see later)] to yield the diradical intermediate (I). This diradical may undergo 1,4- or 1,6-ring closure with formation of the oxetane (8, 9) or dihydrodioxine (4, 5), respectively, a [1,5]-H shift with formation of the allylic ether (6, 7),* or homolytic C–O bond cleavage (see later). Step (b) resembles that for the stepwise [2 + 2]-cycloaddition of monoketones with alkenes. Our observations that the cyclic 1,2-diketones form photoadducts with alkenes having an electron-rich double bond (Table 1), but not with electron-deficient alkenes such as (*E*)-1,2-dicyanoethene, substantiate the electrophilic character of the excited diketone addition.

Monoketones upon excitation in the presence of alkenes are thought to form an exciplex prior to the formation of the 1,4-diradical intermediate leading to the oxetane.[6d,15,16] Exciplex formation was also proposed to occur in the photoaddition of (i) 9,10-phenanthrenequinone to phenylallenes,[17] (ii) glyoxal[18] and biacetyl[6d] to alkenes, and (iii) methyl pyruvate to DMB.[7b] Therefore the exciplex route (c) is added as an additional route for the formation of the 1,4-diradical (I) (see Scheme).

The formation of only one oxetane on using IB, *viz.* (8), is in line with the stepwise mechanism proposed for the formation of the oxetanes. This oxetane results from the more stable of the two possible 1,4-diradicals, *i.e.* the one formed by terminal addition of the excited 1,2-diketone to IB.

Upon irradiation of the cyclic 1,2-diketones with (*E*)- or (*Z*)-B both the *cis-* and *trans*-dihydrodioxines and the *endo,-cis-* and *endo, trans*-oxetanes are formed (Table 1). The yields illustrate loss of the stereochemical integrity of the but-2-ene isomer in the formation of the cyclo-adducts, vindicating the diradical mechanism depicted in the Scheme. Rotation around the $C(sp^3)$–$C(sp^2)$ bond in the side chain of the diradical intermediate (I) prior to the 1,4- and 1,6-cyclization explains the formation of the observed oxetanes and dihydrodioxines.

Dihydrodioxine Formation.—With (1b) the formation of dihydrodioxine proceeds highly stereospecific. With (1d) the stereospecificity is far less and the formation of the *trans*-isomer is apparently favoured (Table 1). The photoreactions of 9,10-phenanthrenequinone with both but-2-ene[3c,19] and 1,2-dichloroethene[3k] are non-stereospecific and the formation of the *cis*-dihydrodioxine is favoured, the *cis-* to *trans*-isomer ratio being 6 : 4 independent of the geometry of the starting but-2-ene and 7 : 3 and 8 : 2 for (*E*)- and (*Z*)-1,2-dichloroethene, respectively.

The high stereospecificity with (1b) indicates that the rotation around the –OC(HMe)–ĊHMe bond in (I) is slow relative to the rate of ring closure to give the dihydrodioxine. The loss of stereospecificity with (1d) and 9,10-phenanthrenequinone illustrates that the lifetime of the 1,4-diradical (I) is sufficiently long to allow rotation around the $C(sp^3)$–$C(sp^2)$
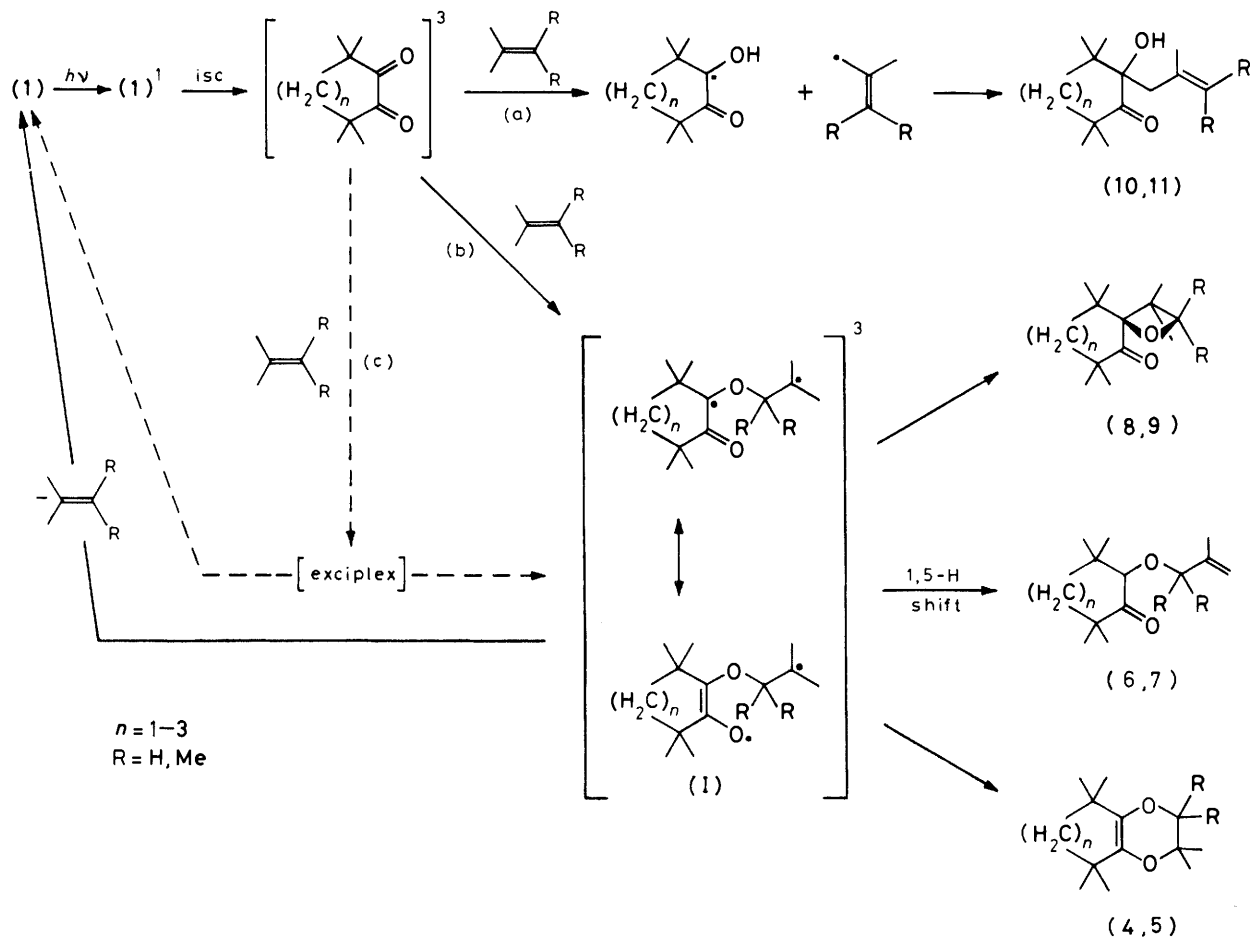
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* The formation of (11) and the absence of the 2,3-dimethylbut-2-enyl ether isomer on reaction of (1) with DMB render the alternative mechanism for the formation of (10) from (1) and IB, *viz. via* initial abstraction of an allylic hydrogen from IB by the excited 1,2-diketone and subsequent recombination of the resulting radicals to yield the enolic 1,4-adduct followed by ketonization, highly improbable.

n = 1—3
R = H, Me

Scheme.

bond of the side chain prior to the 1,6-cyclization. The lifetime and thus the loss of stereospecificity will be substantially greater for a triplet than for a singlet 1,4-diradical in view of the required spin inversion with the triplet species before the ring closure can occur. The 4-benzoylbiphenyl triplet-sensitized photoaddition of (1b) to each of the two but-2-enes yields the same products in essentially the same ratio as in the direct irradiation (Table 1). This illustrates that the photoaddition of the cyclic 1,2-diketones upon direct irradiation also proceeds from the (lowest) excited triplet state. The ratio in which the cis- and trans-dihydrodioxine are formed from the 1,4-diradical (I) is then further determined mainly by steric factors.

Oxetane Formation.—The occurrence of the triplet 1,4-diradical (I) is also supported by the observation that (1b) with both (E)- and (Z)-but-2-ene forms the same two oxetane isomers with the endo,trans-isomer (26) in excess to the sterically less favoured endo,cis-isomer (27). Whereas the loss of stereospecificity of the oxetane formation can be ascribed to steric effects, the origin of the high stereospecificity of the dihydrodioxine formation is not directly clear. It may be related to restricted rotational freedom in the conformation of the 1,4-diradical, which leads to the (4 + 2)-cycloadduct.

Both (1b) and (1d) with each of the two but-2-enes yield only one 1,2-adduct, in which the geometry at the double bond is the same as in the starting but-2-ene. This illustrates the absence of (E)–(Z) isomerization of the but-2-ene during the irradiation. Since the only potential route for the but-2-ene

isomerization would be via rotation in the diradical intermediate of type (I), it is concluded that homolysis of (I) into the starting compounds is of no importance for the two but-2-enes.

Product Ratio Determining Factors.—The ratios in which the four types of photoadducts are formed and in which the stereoisomers for a given type of photoadduct are formed depend on both the 1,2-diketone and the alkene employed. For (1b) the ratio {[dihydrodioxine (D) + allylic ether (AE) + oxetane (O)] to 1,2-adduct (A)} increases in the order cH < cP ≪ IB ≃ DMB < (E)- and (Z)-B, whereas the order for (1d) is IB ≃ DMB ≃ (E)- and (Z)-B (cf. Table 1). The lower ratios for cH and cP as compared with the other alkenes are ascribed mainly to a higher rate of step (a), *i.e.* the abstraction of the allylic hydrogens from cH and cP, which are secondary, as compared with those from the other alkenes which are primary.* The variations in the [(D + AE + O)/1,2-A] ratio within the two series of alkenes containing primary and secondary allylic hydrogens may then be explained in terms of steric restrictions in (i) the formation of the 1,4-diradical (I), (ii) the formation of the various rotamers of (I), and (iii) the conversion of these rotamers into the products D, AE, and O.

A lower rate of conversion of the 1,4-diradical (I) into the three types of products would only lead to a lower [(D +

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* Szwarc established that the rate of abstraction of allylic hydrogens from alkenes by methyl radicals is *ca.* 10 times greater per active hydrogen for secondary than primary hydrogens.[20]

Table 2. Conditions and data for the irradiations and g.l.c. analyses

Substrate	Alkene[a]	Sensitizer[a]	λ/nm	Internal standard	G.l.c. conditions[b] Column[c]	Temperature (°C)
(1b)	DMB		>420	Pentadecane	A	175
(1b)	IB		>420	Tetradecane	A	140
(1b)	(E)-B		>420	Pentadecane	A	145
(1b)	(Z)-B		>420	Pentadecane	A	145
(1b)	cP		>420	Hexadecane	A	170
(1b)	cH		>420	Octadecane	A; B	185 (A); 190 (B)
(1b)	DMB	4-BBP	310	Pentadecane	A	170
(1b)	DMB	3-MAP	310	Pentadecane	A	170
(1b)	(E)-B	4-BBP	310		A	160
(1b)	(Z)-B	4-BBP	310		A	160
(1c)	DMB		403	Undecane	A	175
(1c)	IB		403	Undecane	A	170
(1d)	DMB		>345	Hexadecane	A	170
(1d)	IB		>345	Octadecane	A	200
(1d)	(E)-B		>345	Octadecane	A	170, after 20 min 2 °C min⁻¹
(1d)	(Z)-B		>345	Octadecane	A	170, after 20 min 2 °C min⁻¹
(1e)	DMB		>345	Tetradecane	A; C	205 (A); 200 (B)
(3)	DMB		403		D; E	140 + 1 °C min⁻¹ (D); 100 + 2 °C min⁻¹ (E)
(3)	IB		403		A	80 + 2 °C min⁻¹

[a] See subscripts [b] and [c] of Table 1. [b] He was used as carrier gas at a flow rate of 40 ml min⁻¹. [c] ¼ in copper tubing: A, 5 m, 15% SE-30 on Chromosorb W-AW 45—60 mesh; B, 4 m, 12% OV-225 on Chromosorb W-AW 60—80 mesh; C, 4 m, 15% DC-550 on Chromosorb W-AW 60—80 mesh; D, 5 m, 10% Carbowax-20M on Chromosorb W-AW 45—60 mesh; E, 4 m, 15% Reoplex-400 on Chromosorb W-AW 60—80 mesh.

AE + O)/1,2-A] ratio, provided that there is an escape route for the intermediate (I) that does not lead to reaction products. Accordingly it is suggested that the intermediate (I) as a fourth mode of reaction reverts to the starting compounds by homolysis of the C–O bond for the alkenes other than the two but-2-enes (see before).

With the cyclic 1,2-diketones the yield of the allylic ether is moderate [for (1b) with IB] to zero. The low yields of the oxetanes (9b—d) formed with DMB are in line with the high *endo*- (26 + 27) to *exo*-oxetane ratio observed using the 2-butenes as alkene. They are ascribed to steric compression between the methyl adjacent to the spirocarbon pointing away from the carbonyl and the near-by geminal dimethyl moiety upon forming (9b—d).

The present results show that only the 1,2-diketones with a ground-state intercarbonyl dihedral angle $\bar{\Phi} < 90°$ form dihydrodioxines (*cf.* Table 1). In that case the triplet excited state has a *syn*-periplanar 1,2-diketo geometry, which is apparently a prerequisite for the formation of the dihydrodioxines in view of the double-bond character of the intercarbonyl bond in both the triplet excited state and the 1,4-diradical (I), The absence of dihydrodioxines with biacetyl ($\bar{\Phi} = 160°$) is in agreement with this rationale. However, hexafluorobiacetyl with either *cis*- or *trans*-1,2-difluoroethene yields *cis*- and *trans*-dihydrodioxines in addition to three oxetanes [in a ratio of 8.8 : 2.0 : (1.2 + 1.2 + 1.0), respectively].[9] The predominant formation of dihydrodioxines would infer that ground-state hexafluorobiacetyl is present predominantly in a conformation with $\bar{\Phi} < 90°$. In fact, it is to be expected that the $\bar{\Phi}$ of biacetyl ($= 160°$) will decrease upon replacing the hydrogens by fluorine in view of the enhanced steric effect and the enhanced electronic repulsion between the carbonyl oxygen and the fluorines of the CF_3 group bonded to the other carbonyl. In this respect it is of interest that dibromoglyoxal (oxalyl dibromide) at 80 °C contains 58% of the *gauche*-conformation ($\bar{\Phi} = 66°$) and 42. of the single *trans*-formation ($\bar{\Phi} = 180°$).[21]

Experimental

Materials.—The synthesis of the 1,2-diketones [14] and the purification of benzene [1] were described previously. The triplet photosensitizers were from a Photosensitizer and Quencher kit (Baker).

Photochemical Experiments.—The samples to be irradiated were prepared by dissolving the 1,2-diketones in purified benzene (0.10M). Then either the liquid alkene (*ca.* 20 equiv.) was added and the solutions saturated with nitrogen, or the solution was saturated with the gaseous alkene. Thereupon the solutions were irradiated in the wavelength range of the longest wavelength u.v. absorption band of the 1,2-diketone under study,[14] thus avoiding secondary photoreactions. The direct irradiations were carried out in a 2 or a 10 ml tap-water-cooled Pyrex vessel, in general till complete conversion of the coloured [14] 1,2-diketone. The radiation source used was a Philips SP 500 W mercury lamp in combination with a Jena 403 nm interference filter (PAL no. 80332.03), a Schott-Jena GG 345 (2 mm) filter, or a Schott-Jena GG 420 (3 mm) filter to isolate the 403, >345, and >420 nm group of emission bands (*cf.* Table 2), as appropriate.

The triplet-sensitized irradiations have been carried out using equimolar amounts of the 1,2-diketone and the sensitizer (0.10M) in benzene as solvent using $\lambda = 310$ nm (Rayonet PPR 208 photoreactor equipped with eight RUL 3000 lamps). In all experiments >99% of the incident radiation was absorbed by the sensitizer.

The analysis and work-up of the reaction mixtures and the isolation of the photoproducts was as described previously.[1] The g.l.c. columns employed for the analysis and the semi-preparative isolation, and the conditions and internal standards are collected in Table 2. The amounts of the photoproducts were determined from the g.l.c. peak areas with application of response factors, which were corrected for the difference in relative molecular mass of the products.

Table 3. Chemical shifts and coupling constants of the vicinal ring hydrogens of the dihydrodioxines and oxetanes

Dihydrodioxine	Oxetane	H^n, H^{n+1} [a]			Configuration
		δ/p.p.m.		$^3J_{H,H}$/Hz	
		n	$n+1$		
(19)		4.18	4.18	5.0	*cis*
(25b)		4.04	4.04	2.5 [b]	*cis*
		3.62	3.62	5.0 [b]	*trans*
(25d)		3.89	3.89		*cis*
		3.15	3.15		*trans*
	(21)	3.17	5.14	4.0	*endo,cis*
	(22)	3.05	4.8	7.0	*endo,cis*
	(26b)	2.56	4.59	7.5	*endo,trans*
	(26d)	2.71	4.13	7.5	*endo,trans*
	(27b)	3.34	4.9	7.5	*endo,cis*
	(27d)	3.23	4.74	7.5	*endo,cis*

[a] For the dihydrodioxines $n = 5$; for the oxetanes $n = 3$, the spiro-carbon being considered C^2. [b] Estimated by spectral simulation.

Analysis and Product Identification.—The photoadducts have been identified on the basis of their spectral data. The spectrometers were described before.[1,13] The n.m.r. spectra have been recorded using $C[^2H]Cl_3$ as solvent and tetramethylsilane as internal standard and the i.r. spectra were recorded using $CHCl_3$. The spectroscopic data have been deposited as Supplementary Publication No. SUP 23666 (10 pp).*

Configurational Assignment of Dihydrodioxines and Oxetanes.—The configurational assignments of the dihydrodioxines and the spiro-oxetanes were based mainly on the chemical shifts and the coupling constants of the vicinal hydrogens of the dihydrodioxines and the spiro-oxetane rings. The methine hydrogens of a *cis*-dihydrodioxine resonate at lower field than those of the *trans*-isomer[3c,22] and the $^3J_{H,H}$ of the vicinal hydrogens will be smaller for a *cis*-dihydrodioxine than its *trans*-isomer (*cf.* for *cis*- and *trans*-2,3-dimethyl-1,4-dioxane $^3J_{H,H} = 3.20$ and 8.46 Hz, respectively[23]). The relevant data are given in Table 3.

The photoreaction of (1b) with cyclopentene yields only one dihydrodioxine, which is considered to be the *cis*-isomer in view of (i) the steric strain that would occur in the *trans*-isomer and (ii) the chemical shift of the methine hydrogens (*cf.* Table 3), which is specific for *cis*-dihydrodioxines.[3g] The chromatogram of the photoproduct mixture resulting from (1b) and cyclohexene contained two small peaks which were ascribed to *cis*- and *trans*-(20) in view of their nearly similar retention times to that of *cis*-(19) and by analogy with the formation of both the *cis*- and *trans*-dihydrodioxine in the photoaddition of 4-oxa-3,3,5,5-tetramethylcyclopentane-1,2-dione[11] and 9,10-phenanthrenequinone[3g] to cyclohexene.

On reaction of (1b) with both cyclopentene and cyclohexene only one oxetane isomer is formed. With cyclopentene only the *cis*-isomer (21) is possible (see earlier). The oxetane (22) is considered also to have the *cis*-configuration by analogy with the oxetane obtained photochemically from 4,6-dimethyl-2,3-dihydrobenzofuran-2,3-dione and cyclohexene, which has the *endo,cis*-configuration.[4] On the basis of the geometry of this oxetane[4] and a (Stuart) molecular-model study of (21) and (22), which revealed less overcrowding in and thus a preference for the *endo*- over the *exo*-configuration, an *endo,cis*-configuration is suggested for both (21) and (22).†

The configurational assignments of the currently obtained oxetanes could not be made simply on the basis of the coupling constant of the vicinal hydrogens (in general $^3J_{cis-H,H} < {}^3J_{trans-H,H}$[24]), since for example the two isomers (26b) and (27b) both have $^3J_{H,H} = 7.5$ Hz. The vicinal coupling constant apparently varies as result of structural and steric factors: for the *cis*-isomers of (21) and (22) $^3J_{H,H} = 4$ and 7 Hz, respectively, whereas $^3J_{H,H} = 6.5$ Hz for both *cis*- and *trans*-2,2,3,4-tetramethyloxetane.[25] A study of the molecular Stuart models of the four geometric oxetane isomers of (26b) revealed that the two oxetanes with the methyl adjacent to the spiro-carbon pointing away from the carbonyl group (*i.e.* the *exo*-isomers) encounter steric compression between this methyl and the near-by geminal dimethyl moiety, whereas those with that methyl pointing towards the carbonyl group (the *endo*-isomers) do not encounter any steric compression (the oxetane methyl adjacent to the ether oxygen is devoid of steric hindrance for all the four oxetane isomers). The two isolated oxetane isomers obtained from both (1b) and (1d) are therefore considered to have all the methyls adjacent to the spiro-carbon pointing towards the carbonyl group and are designated *endo,cis* and *endo,trans*.‡ The assignment of *endo,cis* to (27b) and of *endo,trans* to (26b) is based on the observed chemical shifts of the two methine hydrogens (*cf.* Table 3), since the chemical shifts of the methine hydrogens of the α-keto oxetanes resulting from 9,10-phenanthrenequinone and but-2-ene are smaller for the *trans*- than the *cis*-isomers.[3d] Based on a comparison of the ^1H n.m.r. absorptions patterns and the relative g.l.c. retention times, it was concluded that the isomers (26d) and (27d) have the same geometry as (26b) and (27b), respectively.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1983, Issue 1.

† The lower content of oxetane formation with (1b—d) using DMB compared with both (*E*)- and (*Z*)-B and IB is in accord with the overcrowding argument used for the assignment of the *endo*-configuration to (21) and (22).

‡ The g.l.c. chromatogram of the photoreaction mixture of (1b), but not that of (1d), showed, in addition to the two isolated *endo*-isomers, trace amounts of two other compounds, which on the basis of their g.l.c. retention times are likely to be the two *exo*-isomers.

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