Photochemical Oxetan Formation: The Paterno–Büchi[1] Reaction of Aliphatic Aldehydes and Ketones with Alkenes and Dienes

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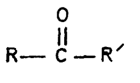
The photochemistry of four aldehydes (acetaldehyde, pivalaldehyde, and cyclopropane- and cyclobutane-carbaldehyde) and two ketones (isopropyl and cyclopropyl methyl ketone) in the presence of various alkenes, *viz.* (*Z*)- and (*E*)-penta-1,3-diene, 2,3-dimethylbut-2-ene, (*Z*)-but-2-ene, (*E*)-1,2-dicyanoethylene, styrene, cyclopropylethylene, 1,1-dicyclopropylethylene, and dicyclopropylmethylenecyclopropane upon irradiation at 310 nm has been studied. With the aldehydes, oxetan formation dominates over other reactions, such as alkene (*Z*)–(*E*) isomerization alkene dimerization, aldehyde dimerization with formation of an acyloin, and abstraction of allylic hydrogens from the alkene by the aldehyde with formation of a hydroxy-compound. Twenty-nine oxetans have been identified. The mechanism of oxetan formation has been discussed with special emphasis on (i) the nature of the reacting excited state (the reacting excited state is the ^1n–π^* state of the carbonyl compound), (ii) the intermediacy of exciplexes and 1,4-diradicals, (iii) the stereospecificity, (iv) the regiospecificity, and (v) the absence of cyclopropyl ring opening.

CONJUGATED dienes are well known quenchers of the T_1 state of carbonyl compounds.[2] In recent photochemical studies of cycloalkanecarbaldehydes[3] attempts to quench the aldehyde T_1 state with (*Z*)-penta-1,3-diene were always complicated by the formation of new products, presumably oxetans. We have now studied the formation of these products for several aldehyde–alkene and aldehyde–diene systems.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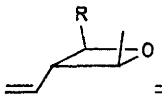
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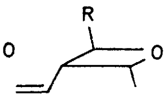
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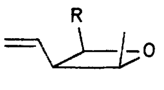
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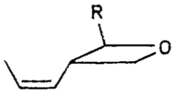
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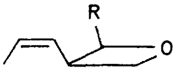
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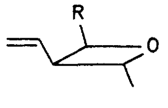
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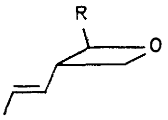
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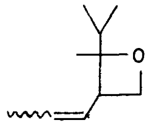
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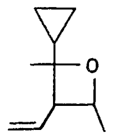
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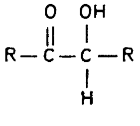
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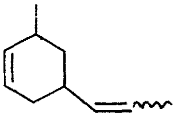
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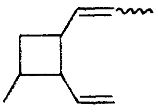
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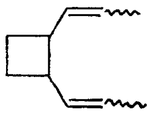
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a; R = Me, R′ = H
b, R = Bu^t, R′ = H
c, R = c-C_3H_5, R′ = H
d, R = c-C_4H_7, R′ = H
e, R = Pr^i, R′ = Me
f, R = c-C_3H_5, R′ = Me

RESULTS

Irradiation of each of the aldehydes (1a—d) in (*Z*)-penta-1,3-diene (2) with λ 310 nm yields five oxetans, *viz.* (4a)—(8a), (4b)—(8b), (4c)—(8c), and (4d)—(8d), respectively, as the only products. Irradiation of both (1c and d) in (*E*)-penta-1,3-diene (3) with λ 310 nm yields oxetans and acyloins, *viz.* (4c), (9c), (5c), (10c), (13c), and (4d),

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[1] D. R. Arnold, in 'Advances in Photochemistry,' Interscience, New York, 1968, vol. 6, p. 301.

[2] J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, **21**, 499.

[3] (*a*) C. W. Funke and H. Cerfontain, *Tetrahedron Letters*, 1973, 487; (*b*) C. W. Funke and H. Cerfontain, *J.C.S. Perkin II*, 1976, 669; (*c*) C. W. Funke, J. L. M. de Boer, J. A. J. Geenevasen, and H. Cerfontain, *ibid.*, 1976, 1084; (*d*) J. J. I. Overwater, Thesis (in English), University of Amsterdam, 1969, pp. 82—84.

TABLE 1

Photoproducts from the aldehydes and ketones (1a—f) and (*E*)- and (*Z*)-penta-1,3-diene

Aldehyde		Penta-1,3-diene		Temp.	Product ratio											
Structure	Molarity	Configuration	Molarity	(°C)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(15)[a]	(16)[a]
(1a)	0.75	*Z*	10	20	6	54	12	24	4							
(1b)	1.0	*Z*	10	20	5	53	14	23	5							
(1c)	1.0	*Z*	10	20	8	53	19	17	3							
(1d)	0.75	*Z*	10	20	6	54	13	23	3							
(1d)	0.75	*Z*	0.25[b]	20	11	55	13	19	2					79		
(1d)	0.75	*Z*	10	65	8	51	15	23	3							
(1c)	1.0	*E*	10	20	58	0.5				18	24			0.5		
(1d)	1.0	*E*	10	20	56					13	24			6		
(1e)	0.8	*Z*	10	20								15			30	55
(1f)	1.0	*Z*	10	20									20		30	50

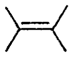
[a] The limit of detection is 3%. [b] In 2,2-dimethylbutane as solvent, (*Z*)-penta-1,3-diene is converted in *ca.* 5% into the (*E*)-isomer.

TABLE 2

Product formation from cyclopropanecarbaldehyde and various alkenes

[Aldehyde]	(Temp.)		Alkene		
M	°C	λ/nm	Structure	Molarity	Products[a]
0.2	20	310	(17)	8 (neat)	(25) 99, (26) 1 [b]
0.1	−30	>300	(18)	11 (neat)	(27) 50, (28) 50
0.3	20	310	(19)[c]	1.5 (in CH_3CN)	(20) 84, (29) 8, (30) 8
0.3	20	310	(21)[c]	8.5 (neat)	(31) ≃50, (32) ≃50[d]
0.5	8	310	(22)	neat	(33)[d]
1.0	20	310	(23)	neat	(34)[d]
1.0	20	310	(24)	neat	(35)[d]

[a] Data without parentheses give the relative yields of the products. [b] Two other products were formed in a yield of 4 and 10% relative to (27) + (28). I.r. and g.l.c. suggest that these are oxetan isomers of (27) + (28). (*E*)-But-2-ene was not detected, the upper limit being 0.5% of (*Z*)-but-2-ene. [c] These compounds absorb slightly in the 310 nm region. [d] Minor products were formed in a yield of <25% relative to the listed product.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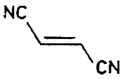

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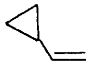
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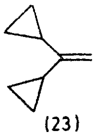
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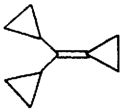
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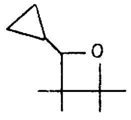

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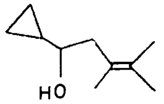

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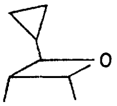

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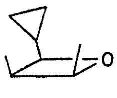

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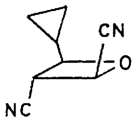

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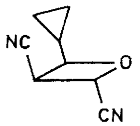

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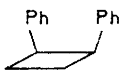

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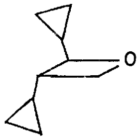

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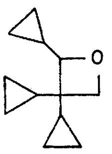

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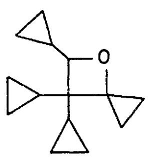

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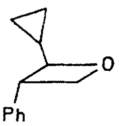

(36)

(9d), (10d), and (13d), respectively, and small amounts of the penta-1,3-diene dimer (14). The reaction conditions and product ratios for the two series of photoreactions are listed in Table 1. Worth noticing is the similarity of the oxetan ratios in each of the series for the various aldehydes.

Irradiation of isopropyl methyl ketone (1e), (1M) in neat (*Z*)-penta-1,3-diene (10M) with λ 310 nm at 20° yields the oxetan (11) and the penta-1,3-diene dimers (15) and (16) *

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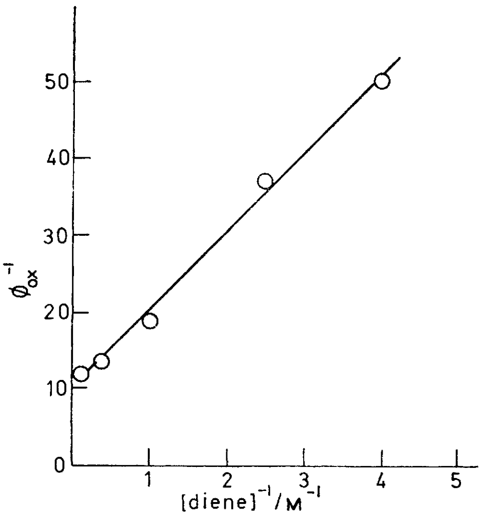
* The complexity of the (13)–(16) g.l.c. region suggests the presence of several stereoisomers of (15) and (16).

in a ratio of *ca.* 15 : 30 : 55. Under the same conditions cyclopropyl methyl ketone (1f) yields the oxetan (12), and the dimers (15) and (16) † in a ratio of *ca.* 20 : 30 : 50.

Upon irradiation of cyclopropanecarbaldehyde (1c) in (the presence of) various alkenes, the oxetan formation is important and no cyclopropane ring-opened products are formed. The results are summarized in Table 2. For the irradiation of cyclobutanecarbaldehyde (1d) with (*Z*)-penta-1,3-diene (2), a plot of the reciprocal of the quantum yield of the total oxetan formation, *i.e.* (4d) + (5d) + (6d) + (7d) + (8d) (ϕ_{ox}^{-1}) against the reciprocal of the diene concentration is linear with an intercept of 10 and a slope of 10 (Figure). A 40-fold variation in the diene concentration hardly affects the ratio of the oxetans (Table 1). The addition of 0.4 and 0.8M (*Z*)-penta-1,3-diene to cyclobutanecarbaldehyde (0.01M) in n-heptane reduces the fluorescence with 32 and 59% respectively.



Effect of the (*Z*)-penta-1,3-diene concentration on the sum of the quantum yields of the oxetans (4d)—(8d)

The identification of the various oxetans was based mainly on ^{1}H n.m.r. data. The assignments of the configurations were based on the vicinal coupling constants of the oxetan ring hydrogens, since $J_{trans} < J_{cis}$.[4] Some relevant data are compiled in Table 3.

TABLE 3

Chemical shifts and coupling constants of oxetan ring hydrogens

	δ			J/Hz			
Oxetan	H-2	H-3	H-4	2,3	3,4	3,4′	4,4
(4a)	4.41	2.48	4.41	6.2	6.2		
(4c)	4.00	2.88	4.52	6.5	6.2		
(4d)	4.29	2.62	4.44	5.2	6.5		
(5a)	4.58	3.09	4.78	6.2	8.0		
(5b)	4.07	3.25	4.63	6.5	8.5		
(5c)	4.13	3.35	4.77	6.5	8.2		
(5d)	4.37	3.06	4.68	5.0	8.5		
(6b)	4.33	3.43	4.83	8.0	8.0		
(6c)	4.03	3.37	4.81	7.5	7.5		
(6d)	4.59	3.35	4.84	7.5	8.0		
(7a)	4.53	3.42	4.22, 4.49	6.5	8.5	6.7	5.7
(7b)	4.05	3.58	4.18, 4.38	6.5	8.5	6.5	5.5
(7c)	3.91	3.57	4.17, 4.42	6.7	8.5	7.0	5.7
(7d)	4.33	3.39	4.24, 4.43	5.0	8.7	7.0	5.7
(8d)	4.64	3.82	4.67, 4.15	8.5	8.7	5.7	5.7
(9c)	4.19	3.19	4.63	8.0	6.0		
(9d)	4.49	3.12	4.47	8.5	6.2		
(10a) [a]	4.53	3.04	4.23, 4.43	6.5	8.5	7.0	5.7
(10c)	4.08	3.82	4.32, 4.48	6.7	8.2	7.0	5.7
(10d)	*ca.*4.4	*ca.*3.1	*ca.*4.4, *ca.*4.4				
(27)	3.81	2.80	4.26	6.3	7.9		
(28)	4.01	2.98	4.88	7.8	*ca.*7		
(29)	4.38	3.79	5.18	7.0	7.0		
(30)	4.43	4.16	5.18	*ca.*8	5.5		
(33)	4.01	2.25	4.26, 4.44	6.5	8.0	6.5	6.0

[a] Compound (10a) was prepared from (1a) and (3).

DISCUSSION

Products.—The data in the Tables 1 and 2 clearly show that, in the presence of a sufficient amount of alkene or diene, oxetan formation dominates over the other aldehyde photoreactions, such as intermolecular hydrogen abstraction with the formation of (13).[3c] The formation of (31) in the photolysis of cyclopropanecarbaldehyde in styrene is no exception to this rule since this product very probably arises from thermal cleavage of the oxetan (36) [5] during the g.l.c. separation (see Experimental section).

The carbonyl triplet sensitized excitation of butadiene and isoprene yields dimers analogous to (14)—(16) with the latter two dominating.[6] Triplet sensitized (*Z*)-penta-1,3-diene yields the (*E*)-isomer and (15) and (16).[7]

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[4] (*a*) D. H. Williams and I. Fleming, ' Spectroscopic Methods in Organic Chemistry,' McGraw-Hill, London, 1966, p. 109; (*b*) A. Balsama, G. Ceccarelli, P. Crotti, and Fr. Macchia, *J. Org. Chem.*, 1975, **40**, 473.

[5] G. Jones, S. B. Schwartz, and M. T. Marton, *J.C.S. Chem. Comm.*, 1973, 374.

[6] (*a*) W. L. Dilling and R. D. Kroenig, *Tetrahedron Letters*, 1968, 5101; (*b*) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1965, **87**, 3406.

[7] J. Saltiel, D. E. Townsend, and A. Sykes, *J. Amer. Chem. Soc.*, 1973, **95**, 5968.

The present formation of (15) and (16) therefore probably proceeds *via* triplet energy transfer from the ketones (1e and f) to (*Z*)-penta-1,3-diene, followed by attack of triplet excited diene on a ground-state diene molecule. The present formation of (14) is neither accompanied by the formation of (15) and (16), nor by (*Z*)—(*E*) isomerization of the diene. Accordingly, for the formation of (14), a route *via* the T_1 state of the diene can be ruled out. The S_1 state of the diene can be excluded as intermediate in the formation of (14)—(16) since this state can neither be reached directly, nor sensitized (see later). The present formation of (14) therefore probably proceeds *via* a ' hot ' ground state of (*Z*)-penta-1,3-diene. The known thermal formation of (14) from a mixture of (*Z*)- and (*E*)-penta-1,3-diene[8] and orbital symmetry arguments[9a] support this proposal. The formation of the alcohol (26) upon irradiation of cyclopropanecarbaldehyde (1c) in 2,3-dimethylbut-2-ene (17) is obviously the result of intermolecular hydrogen abstraction of the excited aldehyde from (17), followed by combination of the resulting radical pair [reactions (1) and (2)].

$$(1c)^* + (17) \longrightarrow \overline{c\text{-}C_3H_5\dot{C}HOH\ \ H_2\dot{C}(CH_3)C{=}C(CH_3)_2} \quad (1)$$

$$\overline{c\text{-}C_3H_5\dot{C}HOH\ \ H_2\dot{C}(CH_3)C{=}C(CH_3)_2} \longrightarrow (26) \quad (2)$$

The low value of the (26) : (25) ratio (0.01) illustrates that hydrogen abstraction is of minor importance relative to oxetan formation, despite the low strength of the allyl–hydrogen bond.[10] This conclusion is supported by the absence of allyl hydrogen abstraction from but-2-ene and the two penta-1,3-dienes by excited (1a—d). The (*E*)-(*Z*) isomerizations of (19) and (20) in the photoreaction with acetone proceed *via* triplet energy transfer from acetone to the alkenes, *i.e. via* the T_1 state of the alkenes.[11] The present photoisomerization of (*E*)-1,2-dicyanoethylene in the presence of cyclopropanecarbaldehyde probably proceeds similarly.

The direct irradiation of styrene yields mainly *cis*-1,2-diphenylcyclobutane (32).[12] Thermolysis of styrene yields, together with polymers and other dimers, some *trans*-1,2-diphenylcyclobutane, which is the major dimerization product of triplet sensitized styrene.[13] The stereospecific formation of the *cis*-isomer in the present experiment may be explained by attack of directly singlet photoexcited styrene (see Table 2, footnote *c*) on a ground-state styrene molecule which reaction is orbital symmetry allowed.[9b]

Mechanism of Formation of the Oxetans (4)—(10).—The oxetans (4)—(10) are formed upon irradiation of an aldehyde A [(1a—d)] in the presence of a diene D [(2) and (3)] with λ 310 nm. The dienes are transparent in the 310 nm region. Accordingly, the u.v. irradiation is exclusively absorbed by the aldehyde. The ${}^1A$ thus formed (3) may react *via* (4)—(6), but not *via* (7), since this step is highly endothermic.* On the other hand, energy transfer from ${}^3A$ to D [reaction (8)] is highly exothermic and therefore diffusion controlled (k_8 *ca.* 10^{10} l mol^{-1} s^{-1}). ${}^3D$ would mainly exhibit (*Z*)-(*E*) isomerization [reaction (9)] and would also yield dimers [reaction (10)]. Except for the experiment with low (*Z*)-penta-1,3-diene concentration (0.25M), the latter processes have not been detected (see Table 1). This renders ${}^3A$ and ${}^3D$ unlikely as intermediates in the formation of (4)—(10), and suggests instead that ${}^1A$ is the most likely reacting excited species. This suggestion is supported by the concomitant formation of (13) which is known to be a ${}^1A$ product.[3c] Singlet excited carbonyl compounds were also proposed before as intermediates in the oxetan formation from aliphatic ketones and conjugated dienes[16] and from aliphatic aldehydes and alkenes.[17] The present formation of (25), (27), (28), and (33)—(36) from cyclopropanecarbaldehyde and the

$$A \xrightarrow{h\nu} {}^1A \tag{3}$$

$${}^1A \longrightarrow A + h\nu' \tag{4}$$

$${}^1A \longrightarrow {}^3A \tag{5}$$

$${}^1A + A \longrightarrow (13) \tag{6}$$

$${}^1A + D \not\longrightarrow A + {}^1D \tag{7}$$

$${}^3A + D \longrightarrow A + {}^3D \tag{8}$$

$${}^3D \longrightarrow (Z)\text{- and } (E)\text{-D} \tag{9}$$

$${}^3D + D \longrightarrow \text{dimers } [\textit{e.g. } (15), (16)] \tag{10}$$

$${}^1A + D \longrightarrow {}^1[\text{exciplex}] \tag{11}$$

$${}^1[\text{exciplex}] \longrightarrow {}^1[\text{1,4-diradical}] \tag{12}$$

$${}^1[\text{exciplex}] \longrightarrow A + D^* \tag{13}$$

$${}^1[\text{1,4-diradical}] \longrightarrow \text{oxetan} \tag{14}$$

$${}^1[\text{1,4-diradical}] \longrightarrow A + D^* \tag{15}$$

$$D^* + D \longrightarrow (14) \tag{16}$$

* Asterisk denotes excess of vibrational energy.

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* The excitation energies are in kcal mol^{-1}: ${}^1A$ *ca.* 84, ${}^3A$ *ca.* 78,[2] where acetone was taken as model for A, and ${}^1D$ *ca.* 110,[14] ${}^3D$ *ca.* 57.[15]

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alkenes (17), (18), and (21)—(24) probably also proceeds *via* ^{1}A (see later).

Considering that exciplexes and 1,4-diradicals (see later) are generally proposed as intermediates in the photoreaction of excited carbonyl compounds with electron-rich alkenes and dienes,[16,18] the formation of (4)—(10) may be explained in terms of the steps (3), (11), (12), and (14). For the set of reaction steps (3)—(15), equation (17) can be derived for the oxetan quantum yield. Thus a plot of $\phi_{ox}{}^{-1}$ against $[D]^{-1}$ is linear

$$\varphi_{ox}{}^{-1} = \left(1 + \frac{k_4 + k_5 + k_6}{k_{11}[D]}\right)\left(\frac{k_{12} + k_{13}}{k_{12}}\right)\left(\frac{k_{14} + k_{15}}{k_{14}}\right) \quad (17)$$

with an intercept of $(k_{12} + k_{13})(k_{14} + k_{15})/k_{12}k_{14}$ and a slope of $(k_4 + k_5 + k_6)(k_{12} + k_{13})(k_{14} + k_{15})/k_{11}k_{12}k_{14}$. In fact, for the formation of (4d)—(8d) from (1d) and (2), the relation between $\phi_{ox}{}^{-1}$ and $[D]^{-1}$ is linear with an intercept of *ca.* 10 and a slope of *ca.* 10 (Figure), and hence $(k_{12} + k_{13})(k_{14} + k_{15})/k_{12}k_{14}$ *ca.* 10 and $(k_4 + k_5 + k_6)/k_{11}$ *ca.* 1. Apparently, because of the exciplex and/or the 1,4-diradical decay to ground-state A and D [steps (13) and (15)], the fraction of exciplex species forming oxetans is only 0.1. The rate constant for exciplex formation k_{11} can be calculated from equation (17). The fluorescence of carbonyl compounds is generally weak;[2] accordingly $k_4 \ll k_5$.

For a (*Z*)-penta-1,3-diene concentration of 0.25M, $\phi_{(4d)-(8d)}$ is *ca.* 0.02 (Figure), and, since the fraction of exciplex species yielding oxetan is only 0.1 (see before), $\phi_{exciplex}$ is *ca.* 0.2. The ratio (13d) : [(4d)—(8d)] is *ca.* 0.8 (Table 1) and, accordingly, ϕ_{13d} is *ca.* 0.016. This value is in agreement with the value of 0.02, obtained independently from triplet quenching experiments.[1c] Considering the competition between (4)—(6) and (11), and that $k_4 \ll k_5$, it follows that $\phi_{(13d)} = k_6[A]/(k_5 + k_6[A] + 0.25k_{11}) \simeq 0.016$ and that $\phi_{exciplex} = 0.25\ k_{11}/(k_5 + k_6[A] + 0.25k_{11}) \simeq 0.2$. Hence, $k_{11} = k_5 + k_6[A]$ and $k_6[A] = 0.02k_{11}$. Assuming k_5 to be $5 \times 10^8\ s^{-1}$ ($=k_{isc}$ for acetone[11]), it follows that k_{11} is *ca.* $5 \times 10^8\ l\ mol^{-1}\ s^{-1}$ and that $k_6[A]$ is *ca.* $10^7\ s^{-1}$.

As will now be shown, the proposed mechanism agrees with the observed quenching of the fluorescence of cyclobutanecarbaldehyde by (*Z*)-penta-1,3-diene. The dependence of the fluorescence intensity F on the quencher concentration [D] is given by the Stern–Volmer expression $F_o/F = 1 + k_{11}[D]/(k_4 + k_5 + k_6)$ in which F_o is the fluorescence intensity for $[D] = 0$. From the observed $F : F_o$ ratios of 0.68 and 0.41 for 0.4 and 0.8M-diene respectively, k_{11} was calculated to be 6.10^8 and $9.10^8\ l\ mol^{-1}\ s^{-1}$. These values are of the same order of magnitude as determined directly from the Figure 1 (see before).

The diene produced in (13) and (15) probably contains some excess vibrational energy which would explain the 'thermal' dimerization (16) with formation of (14).

Selectivity in the Oxetan Formation.—*A priori*, upon [2 + 2] cycloaddition of the aldehydes (1a—d) with the dienes (2) and (3) 16 oxetans can be formed. Similarly, upon cycloaddition, four oxetans can be formed from (1c) with (18), (19), (21), and (22), and two oxetans from (1c) with (23) and (24). In fact, a smaller number of oxetans is formed in each case. The observed selectivity can be split up into four factors, *viz.* (i) the selection of the carbon–carbon double bond in the diene; (ii) the orientation of the original aldehyde RCHO towards the original olefin $R^1R^2C{=}CR^3R^4$; (iii) the stereochemical configuration of R with respect to R^1, R^2 in the oxetan $\text{RH}\overline{\text{C-O-C}}\text{R}^1\text{R}^2\text{-}\overline{\text{C}}\text{R}^3\text{R}^4$; and (iv) the stereochemical configuration of R^1 and R^2 with respect to R^3 and R^4.

(i) As Table 1 shows, oxetan formation on the C(3)=C(4) bond of (*Z*)- and (*E*)-penta-1,3-diene dominates over that on the C(1)=C(2) bond. This preference for oxetan formation on the C=C bond carrying the greatest number of alkyl substituents has also been observed *e.g.* for cyclobutanone with (2) and (3)[19] and for acetone with isoprene.[16] The preference for oxetan formation on the C(3)=C(4) bond is slightly more pronounced with cyclopropanecarbaldehyde than with the other aldehydes (Table 1). This deviating behaviour of cyclopropyl compounds is more apparent for cyclopropyl methyl ketone (1f) which strongly prefers oxetan formation on the C(3)=C(4) bond with formation of (12), whereas isopropyl methyl ketone yields mainly (11) and apparently prefers the C(1)=C(2) bond (see Table 1), and so does acetone.[20]

For the photoreaction of cyclopropanecarbaldehyde in (*Z*)- and (*E*)-penta-1,3-diene, the relatively high yield of the oxetans (6c) and (9c), which have the cyclopropyl and vinyl substituents in 1,2-*cis* orientation, is especially notable. This preference in orientation may be explained in terms of a through bond stabilizing interaction between these two groups during the approach of singlet excited aldehyde to the ground-state pentadiene.* The analogous interaction between a cyclopropyl and a prop-1-enyl group will be relatively less because of steric hindrance of the methyl group of the latter.

(ii) Tables 1 and 2 show that the oxetan formation with alkenes of the type $R^1R^2C{=}CR^3R^4$ with $R^1,R^2 \neq R^3,R^4$ [*e.g.* (2), (3), (21)—(24)] is regiospecific, *i.e.* only oxetans with one of the two possible $RCHO{-}R^1R^2C{=}CR^3R^4$ orientations are observed as photoproducts. This phenomenon is generally explained in terms of the stability of the intermediate 1,4-diradical [formed by reaction (12)]. With an asymmetric alkene, two 1,4-diradicals can *a priori* be formed, *viz.* $RH\dot{C}{-}O{-}CR^1R^2{-}\dot{C}R^3R^4$ and $RH\dot{C}{-}O{-}\dot{C}R^3R^4{-}\dot{C}R^1R^2$. The relative stability of these two diradicals is determined by the radical

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* The exclusive formation of *cis*-1,2-diphenylcyclobutane from singlet excited styrene may be due to a similar interaction.

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stabilizing properties of R^1—R^4. The radical positions are better stabilized by an adjacent vinyl, prop-1-enyl, phenyl, or cyclopropyl group than by an adjacent methyl, hydrogen, or ethylene substituent. Accordingly, the observed regiospecificity supports the intermediacy of 1,4-diradicals in the formation of (4)—(12) and (33)—(36).

(iii) The photolyses of the aldehydes (1a—d) with (2), (3), (21), and (22) yield mainly oxetans in which the (cyclo)alkyl group of the aldehyde (R) and the vinyl, prop-1-enyl, phenyl, and cyclopropyl group of the alkene (R^1) are situated in the 1,2-*trans*-orientation. This is probably the result of steric repulsion between R and R^1, since this preference is absent for the oxetans obtained from cyclopropanecarbaldehyde and the alkenes (18) and (19) which carry the less bulky methyl and cyano-groups.

(iv) With the alkenes of the type $R^1R^2C{=}CR^3R^4$ for which $R^1 \neq R^2$ and $R^3 \neq R^4$ [*viz.* (2), (3), (18), and (19)], the major part of the oxetans has the same configuration of R^1 with respect to R^3 as the starting alkene. Consequently, only a little bond rotation has occurred in the 1,4-diradical intermediates. Assuming a rotational barrier of 3 kcal mol^{-1} for the $R^1R^2C{-}CR^3R^4$ bond,[21] it follows that k_{rot} is *ca.* 5×10^{10} s^{-1},[22] and hence that oxetan ring closure k_{14} is at least 5×10^{11} s^{-1}. Stereospecificity in oxetan formation has also been observed for other singlet 1,4-diradicals,[17] but is absent for triplet 1,4-diradicals.[23] These results corroborate with theoretical conclusions that the C(1)–C(2) and C(3)–C(4) bond rotational barriers are substantially higher for a singlet as compared with a triplet 1,4-diradical species.[24] The formation of (7), (8), and (10) shows that no (*Z*)-(*E*)-isomerization of the prop-1-enyl group occurs in the intermediate singlet 1,4-diradicals. This retention of configuration is generally observed with radicals which carry at the radical site a (*Z*)-(*E*) isomerizable alk-1-enyl group.[7]

Oxetan Formation with 1,2-*Dicyanoethylene*.—Oxetan formation from acetone and electrophilic alkenes, *e.g.* 1,2-dicyanoethylene (19) does not proceed *via* a 1,4-diradical, but involves singlet exciplex formation, transfer of the carbonyl π^* electron to the lowest unoccupied π-orbital of the alkene within the exciplex, followed by a concerted formation of the two new σ-bonds, which infers stereospecific oxetan formation.[2,25]

For the photoreaction of cyclopropanecarbaldehyde with 1,2-dicyanoethylene such carbonyl π^* electron transfer leads to a positively charged aldehyde function with the electron deficiency concentrated in the highest carbonyl *n* orbital. This orbital is orthogonal with respect to the carbonyl π-system. Accordingly, the positive charge cannot be delocalized to the carbonyl C atom, and thus no cyclopropylcarbinyl–allylcarbinyl cation rearrangement [26] can take place. Hence, for the formation of (29) and (30), no discrimination between the exciplex electron transfer mechanism and the ^1S 1,4-diradical mechanism can be made.

Absence of Cyclopropyl Ring Opening.—Ring opening of cyclopropylmethyl radicals is very fast (*k ca.* 10^8 s^{-1} [27]). It is remarkable therefore that the oxetans obtained from cyclopropanecarbaldehyde all have the cyclopropyl group intact, since their formation is considered to proceed *via* $c\text{-}C_3H_5\dot{C}H\text{-}O\text{-}CR^1R^2\text{-}\dot{C}R^3R^4$ diradical intermediates. The cyclopropyl groups of the alkenes (22)—(24) show the same inertness towards ring opening. Apparently in all these cases the rate of oxetan ring closure of the intermediate (singlet) 1,4-diradicals is very much greater than the rate of cyclopropyl ring-opening, hence $k^{14} > 10^{10}$ s^{-1}. Oxetan formation from aromatic carbonyl compounds and cyclopropylethylene (22) proceeds *via* a relatively long lived cyclopropyl conjugated triplet 1,4-diradical to yield, in addition to the cyclopropyloxetans, considerable amounts of ring-opened products, *viz.* oxepins, formed by ring closure after cyclopropylcarbinyl–allylcarbinyl radical rearrangement of the initial cyclopropyl conjugated triplet 1,4-diradical.[28] The absence of cyclopropyl ring-opening in the present study strongly supports the intermediacy of a singlet 1,4-diradical in the formation of (4c)—(10c), (12), (25), (27), (28), and (33)—(36).

EXPERIMENTAL

Materials.—Compounds (1a) (Merck, zur Analyse), (1b) (Baker, Baker quality), (1e) (Fluka, puriss.), (1f) (Fluka, purum), (17) (Fluka, purum), (18) (Philips, Research Grade), (19) (Fluka, purum), and (21) (Merck, zur Synthese) were used without further purification; (2) and (3) (Fluka, purum) were distilled from $LiAlH_4$ to remove any peroxides.[29] The preparation of (1c and d) has been described.[3b] Compound (22) was prepared by dehydration of 1-cyclopropylethanol,[30] (23) by a Wittig reaction of dicyclopropyl ketone,[31] and (24) by dehydration of tricyclopropylmethanol.[32] The compounds prepared were purified by preparative g.l.c.

Irradiations.—A Rayonet photochemical reactor (Southern New England Ultraviolet Co., model RPR-208) equipped with 300 nm lamps was used as the u.v. radiation source. The radiation penetrating through the Pyrex vessels had $\lambda_{\text{max.}}$ 310 nm. Irradiation of (1c) in (18) was carried out

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with the aid of an immersion medium pressure Hg lamp using a Pyrex vessel to cut off the radiation below 300 nm.

Actinometry.—The absolute light intensity of the Rayonet reactor was determined with the Rayonet merry-go-round attachment (MGR-100) using hexan-2-one as actinometer.[33]

Product Analysis and Isolation.—The irradiation mixtures were monitored by g.l.c., using column A (10 m, diam. 6 mm; 33% dimethylsulpholan–firebrick; 0°) for (2), (3), and (18), column B (6 m, diam. 2 mm; 5% SE 30–Chromosorb W, 100—120 mesh; 50—200°) for (4)—(16) and (25)—(32), and column C (3 m, diam. 6 mm; 15% OV-225–Chromosorb W, 60—80 mesh; 50—200°) for (33)—(35). The products were isolated by means of preparative g.l.c. using column C for (33)—(35) and column D (1.8 m, diam. 6 mm, 20% SF-96–Kieselguhr-3; 50—200°) for (4)—(16) and (25)—(32). Products (3), (4b), (6a), and (8a—c) were not isolated.

Product Identification.—Diene (3) was identified by comparison of its retention time on column A with that of an authentical sample. Oxetans (4b), (6a), and (8a—c) were tentatively identified by comparison of the g.l.c. patterns of (4a)—(8a), (4b)—(8b), (4c)—(8c), and (4d)—(8d) on column B, which were very similar. The other products were identified by means of their i.r., ^{1}H n.m.r., and mass spectra. The spectrometers employed and the spectral data have been described elsewhere.[34]

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