PHOTOCHEMISTRY IN SOLUTION
XV: DIECKMANN ESTER AND RELATED COMPOUNDS

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Summary

Substituted Dieckmann esters I and their corresponding six-membered ring homologues II yield the aldehydo esters III and IV respectively by UV irradiation. The reaction involves a triplet n,π^* excited state and occurs with reasonable quantum yields ($\geqslant 0.22$) for the cyclopentanones I and cyclohexanones II, except when the latter can undergo the Norrish type II reaction with the substituent of the carbon atom α to the carbonyl group.

For both series of keto esters the singlet excited state shows a small reactivity compared with that of the triplet excited state, the difference in lifetime being at least one order of magnitude. The lifetime of the intermediate biradical BR which leads to the aldehyde IIIb is of the order of 1 μs.

The aldehydes III are photostable whilst the aldehydes IV are photolabile and undergo a Norrish type II reaction from the excited singlet state as well as E–Z isomerization from the triplet state.

The intersystem crossing efficiency, measured by triplet energy transfer to piperylene, is of the order of 0.7 - 1.0 in the four examples investigated. This reaction, which leads to new compounds, is of interest only for the five-membered ring series.

1. Introduction

Reference should be made to Part XIV [1]. The photochemical behaviour of cycloalkanones is well documented [2 - 4] and the Norrish type I reaction has recently been used in multiple-step syntheses of natural products [5]. The respective 2-substituted-2-ethoxycarbonylcycloalkanones can be easily obtained by alkylation of the Dieckmann ester [6] and of 2-ethoxycarbonylcyclohexanone [7]. This presents possibilities for the preparation of unsaturated aldehydo esters.

As well as the products expected from α cleavage, the irradiation of 2-cyanocyclohexanone and 2-cyanocycloheptanone gives ring-enlargement

products which react with the solvent (water or methanol) to yield cyclic imides [8]. Recently, 2-cyanocycloalkanones and 2-ethoxycarbonylcyclo-alkanones (five- to seven-membered ring ketones) have been examined under prolonged (70 h) irradiation in alcoholic solutions [9]. Very poor chemical yields of the δ-, ϵ- or ω-cyanoesters or diesters are reported and it is not very clear whether the photochemical reaction mixture contains other products after such a long irradiation period. This contrasts with our observation for the five-membered ring series, e.g. 2-ethoxycarbonylcyclopentanone Ia (Fig. 1) essentially forms the photostable E and Z isomers of ethyl 6-oxo-2-hexenoate IIIa when irradiated in benzene solution. 2-Methyl-2-methoxy-carbonylcyclohexanone has been reported recently to form the E and Z isomers of methyl 7-oxo-2-methyl-2-heptenoate together with dimethyl-2-methylsuberate by irradiation in methanol solution [10].

2-Methyl-2-ethoxycarbonylcyclopentanone Ib has been used as the starting material in a multiple-step synthesis of natural products [11]. In this work our results on the photochemical behaviour of a series of 2-alkyl-2-ethoxycarbonylcyclopentanones I and of a series of their six-membered ring homologues II in hydrocarbon solution are presented. The chemical nature of the reaction has been described elsewhere [12].

2. Results and discussion

2.1. Emission

The fluorescence of compounds I and II, recorded at room temperature in cyclohexane solution, has a broad structureless band with a maximum at about 410 nm, as expected for cyclic ketones [3]. The fluorescence quantum yields, determined by comparison with the known values of ϕ_f of 0.93×10^{-3} for acetone [13] and 0.90×10^{-3} for 4,4-dimethylcyclohexa-none [3], are given in Table 1. The singlet lifetimes of the keto esters I and II were measured from the quenching of the fluorescence by biacetyl [14] in cyclohexane solution and by the single-photon counting technique. The values obtained by the two methods are in good agreement (Table 1).

The radiative deactivation constant of the singlet state is of the order of 7×10^5 s^{-1} for the five-membered ring series I , except Ia for which $k_f = 3.6 \times 10^5$ s^{-1}. In the six-membered ring series II, k_f decreases regularly from 7.3×10^5 to 4.1×10^5 s^{-1} as the number of carbon atoms of the side chain R increases.

The phosphorescence emission, obtained at 77 K in ether—isopentane—ethanol (EPA) solution, has a broad structureless band with a maximum at about 440 nm. The phosphorescence lifetime at this temperature is of the order of 2 ms (Table 1). These results are consistent with the $\pi^* \rightarrow n$ transition of a carbonyl group [15].

From the overlap of the absorption and fluorescence curves, the energies of the lowest excited states of the ketones I and II are estimated to be 85 and 87 kcal mol^{-1} respectively. From the phosphorescence spectra, the

TABLE 1

The absorptions, emissions and singlet lifetimes of ketones I and II

Compound	Ia	Ib	Ic	Id	Ie	I (R = allyl)	IIa	IIb	IIc	IId	IIe	II (R = allyl)
Absorption												
$\lambda_{max}^{cyclohexane}$ (nm)	255	300	303	302	303	303	255	290	290	290	290	290
ϵ (1 mol^{-1} s^{-1})	600	40	47	47	61	56	800	21	27	21	28	28
Fluorescence												
$\lambda_{max}^{cyclohexane}$ (nm)	410	410	410	410	410	410	440	410	410	410	410	410
$\phi_f \times 10^3$ [a]	1.1	2.3	2.1	1.8	1.2	1.3		2.4	1.3	0.7	0.7	0.9
$\tau_S \times 10^9$ (s) [a,b]	3	3.4	2.9	2.0	1.7	1.5	1.3	3.3	2.1	1.5	1.7	2.5
$\tau_S \times 10^9$ (s) [a,c]		3.4	3.7	2.4	1.7			3.3	2.2		1.9	
$k_f \times 10^{-5}$ (s^{-1}) [d]	3.6	6.7	7.2	9.0	7.0	8.0	1.4	7.3	6.2	4.7	4.1	3.6
$k_q \tau_S$ (1 mol^{-1}) [e]	4.2	5.1	4.2	3.0	2.3	2.3		2.2	0.8	0.6	0.2	—
$k_q \tau_S$ (1 mol^{-1}) [f]	3.8	4.6	4.4	4.8	3.2			1.8	0.8	0.6	0.2	—
Phosphorescence												
λ_{max}^{EPA} (nm)		440	440	440	440	440		445	445	445	445	
τ_{ph} (ms) [g]		2.6	2.7	2.0	2.5			1.5	1.6	1.5	2.4	

[a] ±10%.
[b] Determined from the slope of the Stern–Volmer plot of the inhibition of the fluorescence in cyclohexane solution using biacetyl as quencher ($k_q = 1.3 \times 10^{10}$ 1 mol^{-1} s^{-1}).
[c] Obtained by the single-photon counting technique.
[d] ±20%.
[e] Slope of the quenching of the fluorescence by 2,5-dimethyl-2,4-hexadiene in cyclohexane solution.
[f] Slope of the quenching of the fluorescence by 2,5-dimethyl-2,4-hexadiene in pentane solution.
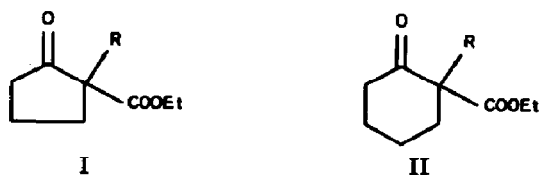[g] Phosphorescence lifetime at 77 K.

Fig. 1. The compounds investigated: a, R = H; b, R = CH_3; c, R = C_2H_5; d, R = n-C_3H_7; e, R = iso-C_4H_9.

energy of the lowest excited triplet state is deduced to be of the order of 73 kcal mol^{-1} for the six-membered ring ketones and 76 kcal mol^{-1} for their five-membered ring homologues.

2.2. Quantum yields

The quantum yields for product formation (Table 2) were measured in degassed pentane solution at 313 nm by comparison with the known values of 0.12 and 0.26 for the Norrish type I reactions of camphor [16] and 2,2,4,4-tetramethylcyclohexanone [3] respectively.

The quantum yields for aldehyde formation decrease as the size of the substituent R increases. This phenomenon is more pronounced for the six-membered ring series II than for the lower homologues I; in the latter series the efficiency for aldehyde formation of Ib is unexpectedly lower than that of Ia and Ic. The regular decrease in ϕ_{ALD} can be attributed to the Norrish type II reaction which occurs essentially from the singlet state [3]. This reaction is known to occur more efficiently as the energy of the γ C—H bond of the abstracted hydrogen is lowered [17] and when this hydrogen lies in the plane of the carbonyl group [18]. Consequently, the semi-axial position of the alkyl substituent R of the five-membered ring series is not very favourable for giving the Norrish type II reaction. This reaction is more favourable in the cyclohexanone series where the substituent R can take the more favourable equatorial position. Although a methoxycarbonyl group gives a smaller steric hindrance than a methyl group [19], the R alkyl group of II must remain longer in the axial position during the chair—chair inter-conversion since the Norrish type II reaction is a less important process in this case than when the ethoxycarbonyl group is absent; consequently, the efficiency for aldehyde formation becomes one order of magnitude higher for IId and IIe compared with their homologues without the ester group [3].

The Norrish type II reaction of 2-substituted cycloalkanones has been found [2 - 4] to be essentially a singlet reaction in hydrocarbon solution. Consequently when this reaction occurs, e.g. for IIc - IIe, the intersystem crossing efficiency should decrease, as should the aldehyde quantum yields since they arise from the triplet state. The intersystem crossing efficiency ϕ_{ISC} was measured using Lamola and Hammond's method [20]. The values obtained (Table 2) were corrected for the amount of triplet state of the ketone quenched by the diene in the cases of Ib and IIb - IIe. Only relative

TABLE 2

The quantum yields and rate constants for intersystem crossing (ISC) and aldehyde formation, and the triplet lifetime

| Compound	Ia	Ib	Ic	Id	Ie	IIa	IIb	IIc	IId	IIe
Intersystem crossing										
ϕ_{ISC} (absolute)[a]	0.76	0.85					1	1	0.7	0.8
ϕ_{ISC} (relative)[b]		0.51	0.53	0.45	0.40					
$k_{ISC} \times 10^8$ (s^{-1})[c]		2.6					3.0	4.7	4.7	4.7
Aldehyde formation[d]										
ϕ_{ALDE}[a]	0.30	0.24	0.27	0.22	0.13	0.25	0.17	0.12	0.04	0.05
ϕ_{ALDZ}[a]	0.10	0.05	0.10	0.09	0.09	0.05	0.10	0.10	0.03	0.06
ϕ_{ALDE}/ϕ_{ALDZ}	3	4.8	2.7	2.4	1.4	5	1.7	1.2	1.3	0.8
Triplet lifetime										
$k_q \tau_T$ ($l\ mol^{-1}$)[e]		4.9					5.6	3.7	4.8	2.7
τ_T (ns)[f]		0.4					0.4	0.3	0.4	0.2

[a] ±10%.

[b] By comparison with 2,4,4-trimethylcyclohexanone for which $\phi_{ISC} = 1$; no correction for the amount of triplet quenched was made.

[c] ±20%.

[d] In pentane solution.

[e] ±15%; pentane solution; after correction for the fluorescence quenching by the diene (2,5-dimethyl-2,4-hexadiene).

[f] Deduced from $k_q\tau_T$ by taking k_q to be equal to the diffusion constant of pentane, *i.e.* 1.3×10^{10} $l\ mol^{-1}\ s^{-1}$.

values could be obtained for Ia and Ic - Ie. Since ϕ_{ISC} still remains important for IIc - IIe, the alkyl substituent R assumes mainly the axial configuration; this explains why the quantum yield for aldehyde formation from these compounds decreases only slightly compared with that from IIb.

2.3. Triplet lifetime

The triplet lifetime was deduced from the slope of the Stern–Volmer plot for the quenching of aldehyde formation using 2,6-dimethyl-2,4-hexadiene as quencher in degassed pentane solution (Table 2). These measurements were limited to the six-membered ring series. The triplet lifetime obtained for compound II is of the order of 0.3 ns. The values given in Table 2 were corrected since dienes also quench the fluorescence of the ketones (see Table 1); it should be noted that the fluorescence quenching by dienes is about two orders of magnitude smaller than diffusion. In spite of this difference in rate constants, the quenching of the singlet state by the dienes must be taken into account because of the difference in lifetime of the two excited states. Thus with the six-membered ring series II, the product $k\tau$ corresponding to the slope of the Stern–Volmer plot for the triplet state is about 4.5 l mol^{-1} (after correction)[†] whilst that corresponding to the singlet state is of the order of 1 l mol^{-1}.

The Norrish type I reaction is well documented; it involves the triplet $^3(n,\pi^*)$ state which leads to a biradical BR (Scheme 1) by α cleavage. The lifetimes of the triplet states of the ketones I and II consequently vary with the inverse of the rate constant for ring opening, since this process is the principal deactivation pathway.

Scheme 1.

I (n = 1)
II (n = 2)

III (n = 1)
IV (n = 2)

Y

BR

k_{ALD}
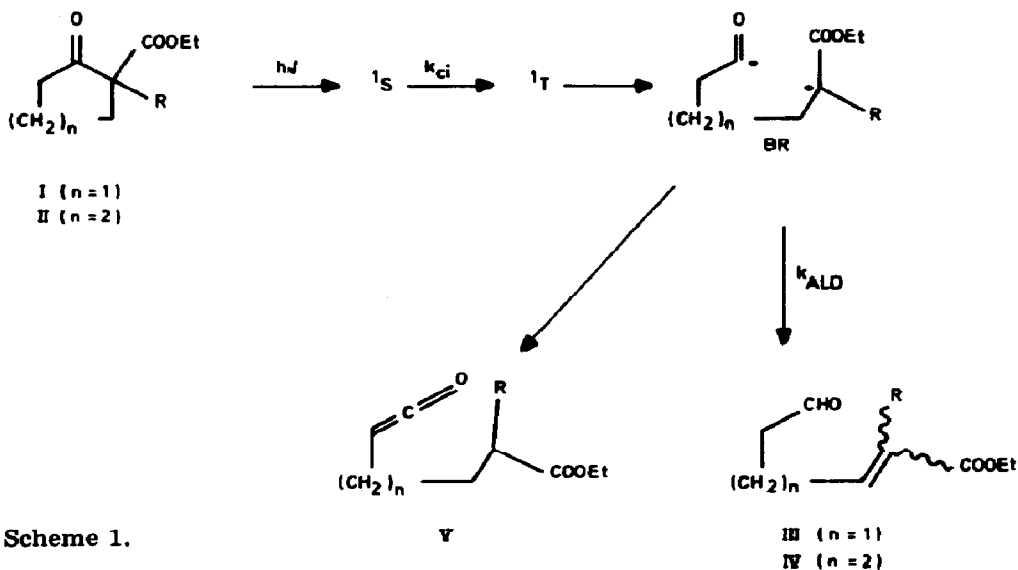
[†]With compound Ib, the slope for triplet quenching before correction is 9.5 l mol^{-1} and that for singlet quenching by the same diene is 4.6 l mol^{-1}.
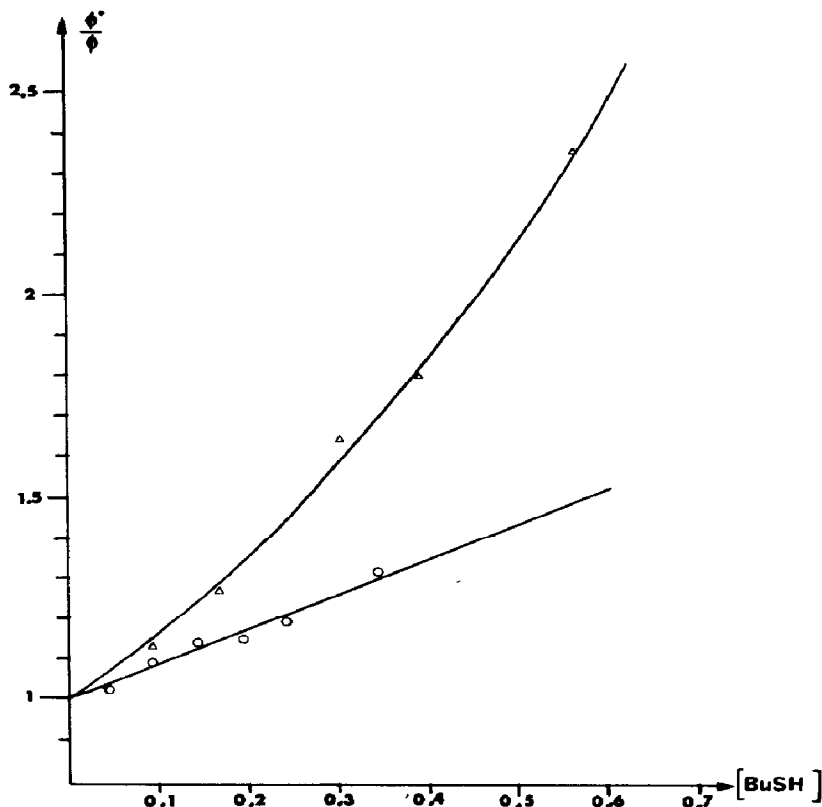
Fig. 2. Stern–Volmer plots of the quenching of the fluorescence (○) of Ib and of the formation of the aldehyde IIIb (△) from the biradical BR using butanethiol as quencher in pentane solution.

The biradical BR leads to a mixture of the E and Z isomers of the aldehyde III when starting from I, or to a mixture of the aldehydes E-IV and Z-IV together with the ketene V when starting from II. In both cases the biradical BR can undergo ring closure back to the starting ketone and this process will probably determine the lifetime of the biradical BR.

In the five-membered ring ketone series I, where ketene formation is negligible, the efficiency of ring closure from BR is the difference between the efficiencies of intersystem crossing and aldehyde formation. The rate constants k_{-NI} and k_{ALD} can be obtained when the lifetime of the biradical BR is known. This was determined for the ketone Ib by inhibition of the aldehyde formation using butylmercaptan as radical scavenger. The kinetic analysis gave a curved plot as shown in Fig. 2. Since butanethiol slightly inhibits the fluorescence of the ketone Ib, two intermediate species must be quenched, one of which is the carbonyl singlet excited state. Wagner and coworkers have shown [21] that butanethiol has little effect on the phosphorescence of acetophenone (300 times less efficient as a quencher than dienes) but intercepts triplet biradicals [22] with a rate constant of 10^6

l mol^{-1} s^{-1}. The $^3(n,\pi*)$ excited state of the ketone Ib is too short lived (0.4 ns) to be quenched by the thiol; consequently the second species quenched in the formation of IIIb from Ib is the intermediate biradical BR. Kinetic treatment of the quenching yields the relation

$$\phi^0_{ALD}/\phi_{ALD} = (1 + k_q^{BR}\tau_{BR}[BuSH])(1 + k_q^S\tau_S[BuSH]) \qquad (1)$$

where ϕ^0_{ALD} and ϕ_{ALD} are the quantum yields for aldehyde formation in the absence and presence of butanethiol respectively, τ_{BR} and τ_S are the biradical and singlet lifetimes respectively in the absence of quencher, and k_q^{BR} and k_q^S are the quenching rate constants of the biradical and of the singlet state by butanethiol of concentration [BuSH]. The product $k_q^S\tau_S$ was obtained from the quenching of the fluorescence and has a value of 0.95 l mol^{-1}. Equation (1) gives $k_q^{BR}\tau_{BR}$ = 0.9 l mol^{-1} and, thus, the lifetime of the biradical BR is 0.9 ± 0.2 μs. The rate constants $k_{ALD\,E}$ and $k_{ALD\,Z}$ for the formation of the E and Z isomers of the aldehyde IIIb as well as that k_{-NI} for the back reaction are found to be

$$k_{ALD\,E} = 2.5 \times 10^5\,s^{-1}$$

$$k_{ALD\,Z} = 5 \times 10^4\,s^{-1} \qquad k_{-NI} = 5 \times 10^5\,s^{-1}$$

The ratio $\phi_{ALD\,E}/\phi_{ALD\,Z}$ of the quantum yields for aldehyde formation varies with the substituent R (Table 2) and decreases from 4.8 (R = methyl) to 1.4 (R = isobutyl) in the five-membered ring series, and from 5 (R = H) to 0.8 (R = isobutyl) in the homologous six-membered ring series. This trend towards unity as the size of the substituents increases seems to depend on the conformation of the starting molecule. (This point, which involves the geometry of the starting molecule and the evolution of the biradical, will be discussed elsewhere.)

From a synthetic point of view [12], the ethyl ϵ-oxo-2-alkenoates formed from the alkylated Dieckmann esters I are relatively stable under irradiation and can be isolated with chemical yields of about 80% for over 90% conversion. In contrast, these yields are lower (20 - 40% only) for the six-membered ring ketones because of the photosensitivity of the aldehydes formed. This was examined for the E and Z isomers of the aldehydes IIIb and IVb. Also for the six-membered ring series, the formation of the ketene V is a pathway which leads to a diester when the irradiation is carried out in alcoholic solution; the corresponding quantum yield has been found [10] to be one fifth of that for the aldehyde of IIb. In hydrocarbon solution the ketene perturbs the normal course of aldehyde formation to a certain extent and therefore the synthetic interest in the six-membered ring series is lowered.

2.4. Photoreactivity of aldehydes IIIb and IVb

The aldehydes III and IV absorb in the same region as the ketones from which they are formed. Their olefinic double bond gives an absorption maximum at about 217 nm, and irradiation of aldehydes IIIb and IVb with

TABLE 3

Photoreactivity of aldehydes IIIb and IVb

| Compound	E-IIIb	Z-IIIb	E-IVb	Z-IVb
Absorption[a]				
λ_{max} (ϵ)	215(11500)	217(9000)	217(8600)	217(7300)
	290(38)	290(33)	290(sh)	290(35)
Fluorescence[a]				
λ_{max} (nm)	400	400		
ϕ_f	$\approx 10^{-4}$	$\approx 10^{-4}$		
τ_S (ns)[b]	1.5	1.4		
Quantum yields[c]				
$\phi_{E \to Z}$	0.02		0.035	
$\phi_{Z \to E}$		0.006		0.03
ϕ_{VIIb}			$\begin{cases} E\ 0.06 \\ Z\ 0.002 \end{cases}$	$\begin{cases} E\ 0.003 \\ Z\ 0.03 \end{cases}$

[a]In cyclohexane solution.
[b]$\pm 10\%$; determined from the slope of the Stern–Volmer plot of the inhibition of the fluorescence using biacetyl as quencher ($k_q = 1.3 \times 10^{10}$ l mol^{-1} s^{-1}).
[c]In pentane solution; $\pm 15\%$.

a Corex cut-off leads to E–Z isomerization with an E–Z photostationary equilibrium of 1.6 for IIIb and 1.2 for IVb.

Selective excitation of the carbonyl group of IIIb by irradiation at 313 nm gives essentially E–Z isomerization with low efficiency (Table 3) and small quantities ($\phi < 10^{-3}$) of an unsaturated alcohol VI which probably results (Scheme 2) from the thermal rearrangement of an oxetane, as has been observed previously [23].
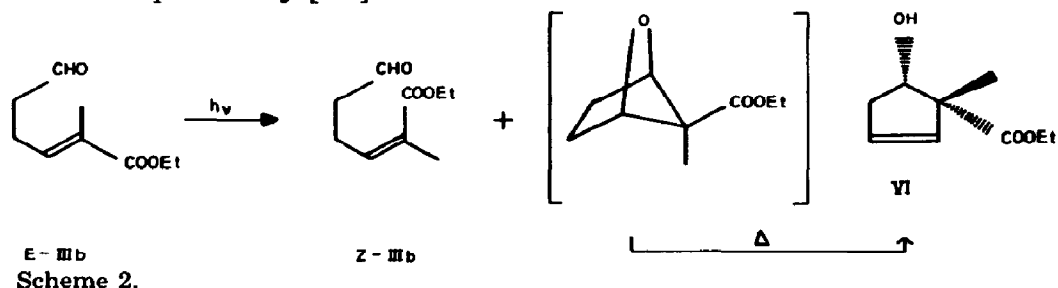
E - IIIb   Z - IIIb
Scheme 2.

The E–Z isomerization may occur either by triplet energy transfer from the excited carbonyl group to the olefinic double bond or via an intermediate exciplex (or biradical) resulting from the interaction of the singlet excited carbonyl group with the ground state electron deficient olefin [24]. Using various 4,4-dimethyl-5-hexenals, it has been shown [25] that intramolecular
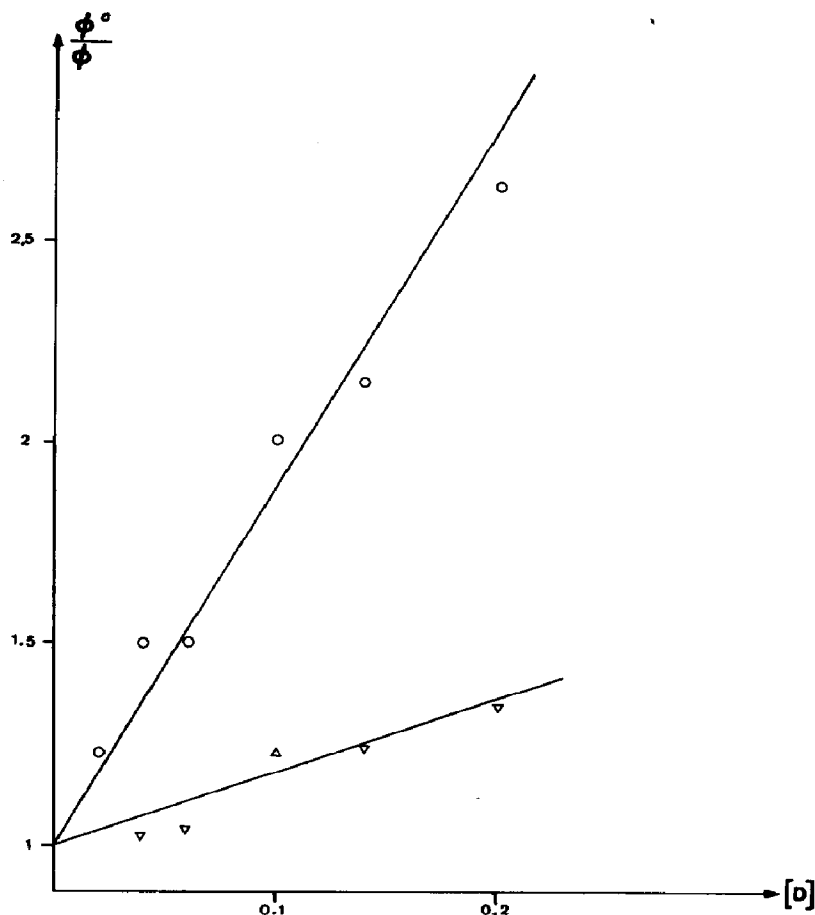
Fig. 3. Stern–Volmer plots of the quenching of the isomerization of the aldehyde E-IVb into Z-IVb (○) and of the formation (△) of the dienic ester E-VII from the aldehyde E-IVb.

oxetane formation arises only from the singlet state whereas E–Z isomerization originates from the triplet state. Also, the cycloaddition of aliphatic ketones to electron deficient double bonds has been shown [26] to proceed through an intermediate exciplex which involves the singlet excited state of the carbonyl group and, when isomerization of the olefin occurs, then a different excited state (probably the triplet) is involved.

When the Norrish type II reaction can occur, as in the case of IV, oxetanes are no longer formed and E–Z isomerization competes with γ hydrogen abstraction. This abstraction is an intramolecular process which is known [27] to involve the singlet state and to be associated with the strength of the γ C—H bond; the main non-radiative decay of the singlet state is the formation of a 1,4 singlet biradical with subsequent reversion to the ground state. The energy of the allylic C—H bond is rather low and of the order of 85 kcal mol^{-1} [28]. As a consequence the singlet lifetime should

decrease significantly, and the absence of fluorescence from E-IVb and Z-IVb is indicative of such behaviour. Irradiation of the aldehyde IV yields E–Z isomerization and the dienic esters VII (Scheme 3). Inhibition of the product formation by 2,6-dimethyl-2,4-hexadiene gives the curves shown in

E - IV   Z - IV   VII (E + Z)
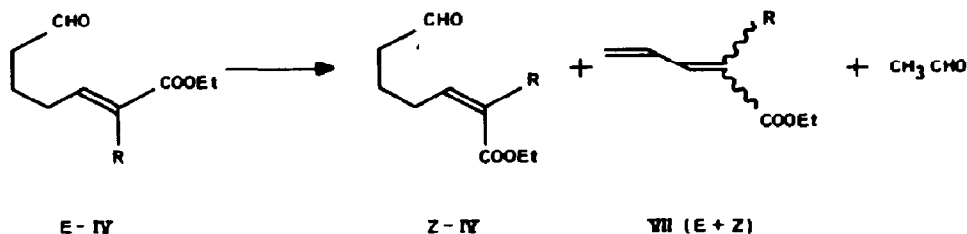
Scheme 3.

Fig. 3 for E–Z isomerization and for the formation of VII. From a kinetic treatment the lifetime of the excited species responsible for the E–Z isomerization is found to be about 0.6 ns (taking $k_d = 1.3 \times 10^{10}$ l mol^{-1} s^{-1} for pentane) whereas the species which leads to the dienic esters VII* has a lifetime of about 0.1 ns. We attribute the former value to the triplet state and the latter to the excited singlet state.

3. Conclusion

The formation of the unsaturated aldehydes III and IV from the cyclo-alkanones I and II is a process which occurs from the excited triplet state with reasonable efficiency. It occurs via an intermediate triplet biradical which has a lifetime of approximately 1 μs. The important feature of these ketones is a very short-lived triplet state (approximately 0.3 ns) compared with their singlet excited state (1.5 - 3.7 ns). The aldehydes III resulting from the five-membered ring ketone I are photostable, whilst the aldehydes IV subsequently undergo a Norrish type II reaction from the excited singlet state and an intramolecular triplet energy transfer from the carbonyl group to the ground state double bond which induces E–Z isomerization.

4. Experimental

IR spectra were obtained with a Perkin–Elmer 357 model spectrophoto-meter and UV spectra were recorded on a Varian-Techtron 635. The nuclear

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*The E-IVb isomer leads essentially to the E-VII diene; when the quenching is carried out for more than 10% conversion of the starting E-IV isomer, then the Z-VII diene formed with low efficiency is quenched with a slope almost equal to that of the E–Z isomerization. This indicates that Z-VII is formed from E-IV through the intermediate of Z-IV.

TABLE 4

NMR data in $CDCl_3$ for the dienic esters[a]

Chemical shift δ

Ethyl 2-methyl penta-2(Z), 4-dienoate VIIb (Z)[b]

1.33	(t, J = 7 Hz, 3H)
2.0	(s, 3H)
4.1	(q, J = 7 Hz, 2H)
5.33	(broad d, J = 10 Hz, 1H)
5.36	(broad d, J = 16 Hz, 1H)
6.45	(dq, J = 10.0 and 1.0 Hz, 1H)
7.4	(m, 1H)

Ethyl 2-methyl penta-2(E), 4-dienoate VIIb (E)[c]

1.30	(t, J = 7 Hz, 3H)
2.0	(s, 3H)
4.2	(q, J = 7 Hz, 2H)
5.47	(broad d, J = 9.0 Hz, 1H)
5.50	(broad d, J = 16 Hz, 1H)
6.7	(m, 1H)
7.25	(dq, J = 11.0 and 1.0 Hz, 1H)

Ethyl 2-ethyl penta-2,4-dienoates VIIc (E) + VIIc(Z)[d]

1.13	(t, J = 7 Hz, 3H, $E + Z$)
1.40	(t, J = 7 Hz, 3H, $E + Z$)
2.37	(q, J = 7 Hz, 2H, E or Z)
2.50	(q, J = 7 Hz, 2H, E or Z)
4.27	(q, J = 7 Hz, 2H, $E + Z$)
5.50	(m, 2H, $E + Z$)
6.30	(broad d, J = 10 Hz, 1H, Z)
6.80	(m, 1H, E)
7.10	(broad d, J = 10 Hz, 1H, E)
7.50	(m, 1H, Z)

Ethyl 2-propyl penta-2,4-dienoates VIId(E) + VIId(Z)[e]

0.90	(t, J = 7 Hz, 3H, $E + Z$)
1.30	(t, J = 7 Hz, 3H, $E + Z$)
1.47	(sext, J = 7 Hz, 2H, $E + Z$)
2.33	(t, J = 7 Hz, 2H, E or Z)
2.43	(t, J = 7 Hz, 2H, E or Z)
4.30	(q, J = 7 Hz, 2H, $E + Z$)
5.33	(broad d, J = 10 Hz, 1H, Z)
5.40	(broad d, J = 16 Hz, 1H, Z)
5.50	(broad d, J = 10 Hz, 1H, E)
5.53	(broad d, J = 16 Hz, 1H, E)
6.30	(broad d, J = 10 Hz, 1H, Z)
6.80	(m, 1H, E)
7.2	(broad d, J = 10 Hz, 1H, E)
7.40	(m, 1H, Z)

TABLE 4 *(continued)*

Chemical shift δ

Ethyl 2-isobutyl penta-2(E), 4-dienoate VIIe (E)[f]

0.90	(d, J = 7 Hz, 6H)
1.3	(t, J = 7 Hz, 3H)
1.8	(m, 1H)
2.3	(d, J = 7 Hz, 2H)
4.2	(q, J = 7 Hz, 2H)
5.50	(broad d, J = 10 Hz, 1H)
5.57	(broad d, J = 18 Hz, 1H)
6.8	(m, 1H)
7,35	(dq, J = 11 Hz and 1 Hz, 1H)

Ethyl 2-isobutyl penta-2(Z), 4-dienoate VIIe (Z)

0.9	(d, J = 6 Hz, 6H)
1.35	(t, J = 7 Hz, 3H)
1.8	(m, 1H)
2.25	(d, J = 6 Hz, 2H)
4.3	(q, J = 7 Hz, 2H)
5.35	(broad d, J = 10 Hz, 1H)
5.45	(broad d, J = 16 Hz, 1H)
6.3	(qd, J = 11 Hz and 1 Hz, 1H)
7.3	(m, 1H)

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[a] s, singlet; d,doublet; t, triplet; q, quadruplet; sext, sextuplet; m, multiplet.

[b] Mixture of the isomers; b.p. = 105 - 110 °C at a pressure of 15 Torr.

[c] From ref. 29: b.p. = 70 - 71 °C at a pressure of 10 Torr; IR, 1692 - 1635 - 995 cm^{-1}.

[d] B.p. = 110 - 115 °C at 12 Torr; IR (film), 3100 - 1705 - 1630 - 1590 - 1370 - 1350 - 1110 cm^{-1}.

[e] B.p. = 130 - 140 °C at 15 Torr; IR (film), 1710 - 1650 cm^{-1}.

[f] Mixture of the two VIIe*E* + VIIe*Z* isomers; b.p. = 130 - 140 °C at 15 Torr.

magnetic resonance (NMR) spectra of the dienic esters VII were obtained on a Varian EM 360 apparatus and the emission spectra were recorded using a Hitachi–Perkin–Elmer MPF 3A equipped with a Tektronix 5130 N oscilloscope for the phosphorescence measurements. Vapour phase chromatography (VPC) was carried out with a Varian-Aerograph 90-P4 for semi-preparative purposes and with the Hi-Fi 1400 model for analytical measurements (the columns were 10 ft in length and contained Chromosorb W impregnated with 30% and 15% Carbowax respectively).

4.1. Preparation of the starting materials

Compounds I and II (R ≠ H) were obtained by alkylation of the sodium salt of the β keto esters Ia [6] and IIa [7]. The synthetic aspect of the photochemical reaction and the spectral characteristics of the aldehydes III and IV have been described previously [12].

4.2. Characterization of the dienic esters

Satisfactory analyses were obtained for all the compounds described (C, ±0.35%; H, ±0.28%). NMR data are summarized in Table 4.

4.3. Irradiation

The photochemical studies were performed using a Philips HPLN 400 medium pressure mercury arc in a water-cooled Vycor jacket. Small scale solutions in Pyrex tubes were degassed using four pumping and freezing cycles on a high vacuum line and sealed. These tubes were used with the classical carousel apparatus [30] for the quantum yield measurements and for the inhibition by dienes. The 3130 Å mercury line was isolated as described in ref. 30. Large-scale irradiation for preparative purposes was carried out with the same lamp using all the light transmitted by the Vycor glass. The ketone, 0.2 - 0.5 M in benzene or cyclohexane solution, was continuously bubbled through with nitrogen for the irradiation period.

4.4. Quantum yields

The quantum yields for product formation were obtained by simultaneous irradiation of compounds I and II (or III and IV) with 2,2,4,4-tetramethylcyclohexanone [3] and camphor [16] used as references. The solutions were adjusted to the same optical density. The percentages of the products formed were deduced from the integrated areas of the corresponding VPC peaks.

The fluorescence quantum yields were measured at right angles in cyclohexane solution of identical optical density (0.5) for all the compounds at the excitation wavelength (290 nm); acetone [13] and 4,4-dimethylcyclohexanone [3] were used as references.

The intersystem crossing quantum yields were evaluated by using the sensitized isomerization of cis-piperylene in pentane solution according to Lamola and Hammond's [20] method. 2,4,4-Trimethylcyclohexanone ($\phi_{ISC} = 1$) [3] was used as a reference.

4.5. Lifetimes

The singlet lifetimes τ_S were determined by quenching the fluorescence with biacetyl. The front surface technique was used to minimize the reabsorption of light by biacetyl. Higher optical densities (1.2 - 1.5) can be used with this method. Excitation was at 310 nm. The quenching rate constant was determined to be 13×10^9 l mol^{-1} s^{-1} from the quenching of the fluorescence of acetone of known lifetime (1.7 ns).

The triplet lifetimes τ_T were deduced from the slope of the Stern–Volmer plot of the quenching of the product formation by 2,5-dimethyl-2,4-hexadiene in degassed pentane solution. The irradiation was carried out with isolation [30] of the 3130 Å mercury line. The quenching rate constant had the same value as the diffusion rate constant, i.e. 1.3×10^{10} l mol^{-1} s^{-1}.

4.6. Phosphorescence

The phosphorescence was characterized at 77 K in EPA glass with excitation at 290 nm. The phosphorescence lifetime τ_{ph} was measured under the same conditions using the classical technique with an oscilloscope.

Acknowledgments

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