199. Photo-CIDNP. Investigation of β,γ-Unsaturated Ketones: Evidence for Temperature-dependent S_1 *vs.* T_2 Reactivities of Cyclopent-2-enyl Methyl Ketones

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Dedicated to Professor *Egbert Havinga* on the occasion of his 70th anniversary

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Summary

On ultraviolet irradiation of the cyclopent-2-enyl methyl ketones **1a–c** at $-54° \leq t \leq 139°$, photo-CIDNP. effects of the starting ketones, the 1,3-acetyl shifted isomers (**2**), and radical disproportionation and combination products (**4–7**) were observed. These effects show a unique dependence of the polarization phase on temperature which is a novel feature in photo-CIDNP. studies. The results of the investigation, which also included experiments using triplet quenchers, triplet sensitizers and radical scavengers, are rationalized in terms of *Schemes 2* and *3.*

α-Cleavage is a major excited-state reaction of **1a–c** on direct irradiation. Temperature-activated α-cleavage ($k_a^S(t)$) to the radical pair $\mathbf{R} \cdot \cdot \mathbf{R}'^1$ and inter-system crossing (k_{isc}) to the T_2 state are among the competing S_1 deactivation processes. The T_2 state in turn cleaves ($k_a^{T_2}$) to $\mathbf{R} \cdot \cdot \mathbf{R}'^3$. A 'low-temperature range' with $k_{isc} \gg k_a^S(t)$ and a 'high-temperature range' with $k_a^S(t) \gg k_{isc}$ exhibiting preferential reactivity from the T_2 and S_1 states, respectively, can be defined for all three β,γ-unsaturated ketones **1a–c**.

Introduction. - Most β,γ-unsaturated ketones predominantly undergo two characteristic photoreactions: an allylic 1,3-acyl shift on direct irradiation, and a triplet sensitized oxadi-π-methane rearrangement *(Scheme 1)*[2]). These results clearly showed from the beginning that at least two excited states are reactive. It has been universally accepted that the oxadi-π-methane rearrangement occurs from the lowest-lying triplet (T_1), and that this state is predominantly π,π^* in nature[3]). The

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[2]) See [1] for comprehensive reviews of β,γ-unsaturated ketone photochemistry, and [2] for a progress report on cyclopent-2-enyl methyl ketones.

[3]) For experimental identifications of $T_1(\pi,\pi^*)$ as the oxadi-π-methane-reactive state, see [3–5].

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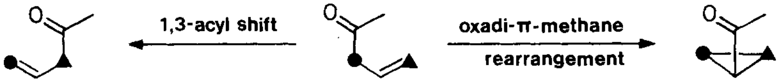
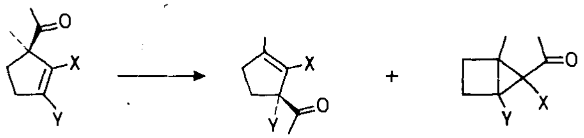
Scheme 1. *Allylic 1,3-acyl shift and oxadi-π-methane rearrangement of β,γ-unsaturated ketones*



reactive state assignment of the 1,3-acyl shift, however, has persisted as a prominent matter of debate [1b] [2]. Early proposals that the 1,3-acyl shift is a singlet-excited state (S_1) process [6] [7], initially found general consensus, and a symmetry-allowed concerted nature was considered likely [6] [8], *e.g.*, in the case of the cyclopent-2-enyl methyl ketone **1a** [6]. The triplet nature of a few 1,3-acyl shifts appeared exceptional [9] [10]. Among these, the 1,3-acyl shift of cyclopent-2-enyl phenyl ketones proceeds *via* a radical pair mechanism and originates predominantly from the n,π^* triplet, which is the lowest-lying excited state in these compounds [10].

More recently, a short-lived T_2 state of prevalent n,π^* character has also been considered as a possible origin of the 1,3-acyl shift in β,γ-unsaturated ketones with a $T_1(\pi,\pi^*)$ state [1b] [2] [11] [12]. The results of fluorescence studies were inconclusive on this point [11] [12]. However, we have recently shown unequivocally that the 1,3-acyl shift can indeed occur from the $T_2(n,\pi^*)$ state of one β,γ-unsaturated ketone, **1c**, when T_2 is selectively generated by thermal cleavage of a dioxetane precursor, and that yet the contribution by a singlet 1,3-acyl shift on direct photoexcitation of **1c** is appreciable [4]4). CIDNP. effects have been taken as evidence for all three of the views currently held on the 1,3-acyl-shift mechanism [2] [10] [14] [15]. We now report photo-CIDNP. results on the β,γ-unsaturated

Table 1. *Quantum yields for direct irradiation and triplet sensitization of* **1a–c**a)b)



1a X = Y = CH_3 **2a** (≈**1a**) **3a**
1b X = CH_3, Y = H **2b** **3b**
1c X = Y = H **2c** **3c**

Compound	Direct irradiationc)d)				Sensitization with acetonec)e)				Lit.
	ϕ_{-1}	ϕ_2	ϕ_3	ϕ_2/ϕ_3	ϕ_{-1}	ϕ_2	ϕ_3	ϕ_2/ϕ_3	
1af)	0.12	0.088	0.0084	10.5	0.54	0.083	0.35	0.24	[17]
1b	0.52	0.14	0.0086	16.3	0.28	0.038	0.18	0.21	[3] [17]
1c	0.65	0.20	0.04	5.0	0.70	0.015	0.46	0.033	[4]g)

a) Racemic forms of all ketones were used. b) For a further evaluation of these data on the basis of the CIDNP. results reported in this paper, see 'Results'. c) All runs at 20–25°. d) Cyclohexane or 2-methylheptane solutions, 313 nm. e) 254 nm. f) 1,3-Acyl shift **1a** → **2a** measured by NMR. using 1-trideuteriomethyl-2,3-dimethyl-cyclopent-2-enyl methyl ketone; exper. error ±20% for Φ_{-1a} and Φ_{2a}, and ±10% for all other measurements. g) See [18] for the first photochemical study of **1c**, for which we thank Prof. *R. S. Givens*.

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4) For a recent case where the 1,3-acyl shift occurs on thermal activation [13a], direct irradiation and triplet sensitization, see [13b].

ketones **1a-c** which allow the assembly of a more coherent mechanistic picture of the S_1 *vs.* T_2 reactivity of these ketones[5]). Previously published data on the characteristic photochemical features of these β,γ-unsaturated ketones are summarized in *Table 1*.

Experimental. - The synthesis and characterization of the following compounds have been reported [3]: **1a,b**, **2b** and **3a,b**. Those of **1c**, **2c** and **3c** [4] will be described in a forthcoming paper (see also [18]). Tentative structural assignments of the dienes **5a**, **5b** (*cf.* [10]) and **6a** are based on the appearance of the appropriate olefinic proton signals in the NMR. spectrum. Tributyl-stannane *(purum)* was purchased from *Fluka AG* and all other chemicals from *Merck AG* in the highest purity grades available. (D_{14}) Diglyme was dried by vacuum distillation over sodium, and CD_3CN by treatment with $CaCl_2$ and subsequent distillation.

The NMR. spectra were run with solutions degassed by flushing with argon and contained in tubes sealed with septa [19]. Sample purity and chemical conversion were monitored by NMR. and by GC. on an OV 101 capillary glass column (length 100 m). GC./MS. analyses were carried out with an OV 101 column (length 30 m) coupled to a *Varian* CH5 mass spectrometer.

All CIDNP. measurements were performed on a *Bruker* WH 90 FT. NMR. spectrometer, using a ^1H-probe modified for irradiation with a lens-light pipe arrangement [20]. The light of a 1000 W *Hanovia* 977B Xe-Hg lamp was filtered through a 3 cm path length of a ($NiSO_4/CoSO_4$)-solution [21] in order to isolate the 260-350 nm wavelength region. The sample temperatures ($\pm 2°$) were either measured with a NiCrNi thermocouple or obtained from the chemical shifts in methanol and ethylene glycol samples [22]. The spectra in *Figures 1-3* were obtained from *Fourier* transformations of 3 or 4 free induction decays recorded with *ca.* 30° flip angle and 10 s pulse delay. The spin lattice relaxation times were measured with a $180°\text{-}\tau\text{-}90°$ pulse sequence [23]. The CIDNP. enhancement factor for $CH_3C\mathit{H}O$ was determined with a relaxation time of 2.1 s and a small flip angle of 20°; see [24].

Results. - 1. *1,2,3-Trimethyl-cyclopent-2-enyl methyl ketone* (**1a**). *Figure 1B* shows the CIDNP. effects observed during the irradiation of **1a** in CD_3OD at 45°. The assignments of the signals, the phases of the CIDNP. effects and their temperature dependence are given in *Table 2*. Enhanced absorptions or emissions were exhibited by the starting ketone **1a**, acetaldehyde (**4**), and the dienes **5a** and **6a**.

The CIDNP. effects exhibited no major changes up to 100°, but they decreased continuously on lowering the temperature from 45° to 10°. Below 8°, the polarization phases of the acetaldehyde (**4**) and of the CH_3CO group of **1a** were inverted, and those of all other signals inverted on further reduction of the temperature to below $-18°$. Biacetyl (**7**) exhibited an appreciable polarization only at temperatures $\lesssim 10°$. The sense of this polarization was opposite to that of $C\mathit{H}_3CHO$ *(Fig. 1A)*.

At 25°, the CIDNP. effects observed in CD_3OD and CD_3CN were of identical polarization and similar magnitude, whereas much smaller effects were found in C_6D_{12}. Some of the latter were of opposite polarization (*Table 2:* $CH_3(\mathit{d})$ of **1a**, and both signals of **4**), but these inverted when the irradiation was carried out in the presence of the free-radical scavenger tributyl-stannane.

When **1a** was subjected to triplet sensitization by irradiation at 260-350 nm at RT. in (D_6)acetone, the *endo-* and *exo*-oxadi-π-methane products **3a** were readily detected by GC. and NMR. However, only very small CIDNP. effects were observed for **1a** and **3a** in this run. The effects observed for **1a** were opposite to those seen in CD_3OD and CD_3CN on direct irradiation at the same temperature.

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[5]) Part of this work has been published in a preliminary communication [16a] and it was presented in lectures given (autumn 1978) under the auspices of the *Japanese Society for the Promotion of Science* [16b].

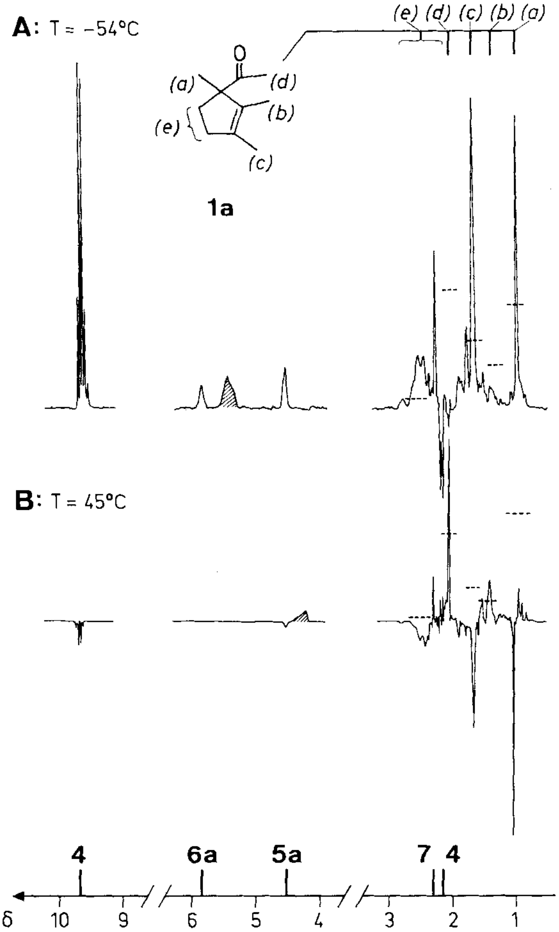


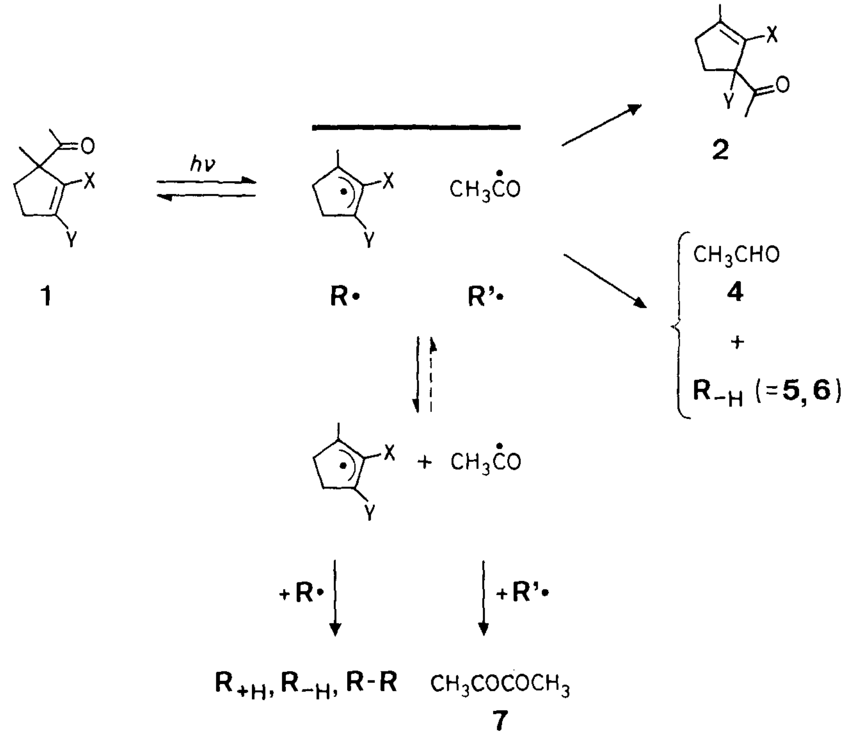
Fig. 1. *Photo-CIDNP. effects on irradiation of* 0.1M *solutions of* **1a** *at* −54° *(A) and* 45° *(B) in* CD_3OD. Dotted lines denote spin-equilibrated NMR. intensities after irradiation, shaded areas solvent signals.

The product structures and the appearance of substantial photo-CIDNP. effects are readily explainable in terms of *Scheme 2* which corresponds to the accepted reaction scheme for aliphatic ketones [25]. It starts with photolytic α-cleavage of ketone **1** to an acyl-allyl radical pair, $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}$, from which pair and free-radical reactions ensue.

The detailed interpretation of the CIDNP. effects was based on *Kaptein*'s rules [26], using the parameters $g(CH_3\dot{C}O)=2.0005$, $a_H(CH_3\dot{C}O)=+0.40$ mT [27] [28], g(cyclopentenyl)$\approx g$(allyl)≈ 2.0026 [29]. The signs of the cyclopent-2-enyl ESR. hyperfine coupling constants were assumed to be identical with those of allyl radicals [29] [30] and are compiled in *Table 3*.

The calculated and observed CIDNP. effects (in CD_3OD, CD_3CN, and (D_{14})-diglyme) match when the following mechanistic model is adopted: at $t > 8°$,

Scheme 2. *Photoreaction scheme for ketones* **1a–c**.
Products of type $\mathbf{R}_{+\mathrm{H}}$ (3-methylcyclopentenes) and **R – R** (bis(cyclopent-2-enyl) derivatives; *cf.* [6] [10]) could be detected by GC./MS. analyses, but could not be identified with any certainty by NMR. analysis of the photolyzed solutions.



products **1a**, **4**, **5a**, and **6a** arise predominantly from singlet pairs, $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{1}$, formed from the excited singlet state, whereas at $t < -18°$ these products are formed from radical pairs of triplet or free-radical origin, $\mathbf{R}\cdot + \mathbf{R}'\cdot$. Biacetyl (**7**) carries the polarization of acetyl radical precursors that have escaped from $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{3}$ pairs. This unique temperature effect indicates that, with decreasing temperature, the formation of $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{3}$ or of free radicals increasingly competes with and ultimately overrides the singlet state cleavage to form $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{1}$.

In principle, the observed CIDNP. effects do not directly discriminate between reaction within $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{3}$ and reaction of free radicals diffused from $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{1}$. However, any major contribution to CIDNP. by free radicals from $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{1}$ should respond to temperature changes in a way opposite to that observed, as diffusion from $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{1}$ would be reduced at lower temperatures and increased viscosities [26] [31] [32]. The temperature dependence of the CIDNP. must therefore reflect an increase of $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}^{3}$ formation with decreasing temperature. In agreement with this, a CIDNP. enhancement factor of 5400 was found for $CH_3C\mathit{H}O$ at $-54°$ in CD_3OD, which corresponds in magnitude to factors measured for well-established triplet reactions of radical pairs with similar *g*-value difference and hyperfine splitting constants [21].

Table 2. *CIDNP. effects on irradiation of* **1a**

Compound[a])	Signal[b])	Solvent (0.1 M solutions); Temperature								
		CD_3OD	CD_3OD	CD_3OD	CD_3OD	CD_3OD, CD_3CN	C_6D_{12}	C_6D_{12} + 0.05–0.1 M Bu_3SnH	C_6D_{12}	(D_{14}) diglyme
		+25°	−73°, −54°[c]), −43°	−18°	−8°	+25°, +45°[d])	+25°	+25°	+72°	+100°
		δ	CIDNP. phases[e])							
1a	CH_3(*a*)	1.10	A	E	E	E	E	E	E	E
	CH_3(*b*)	1.50	E	A	A	A	A	A	A	A
	CH_3(*c*)	1.71	A	E	E	E	E	E	E	E
	CH_3(*d*)	2.04	E	E	[f])	A	E	A	A	A
	$(CH_2)_2$(*e*)	2.30 −2.60	A	E	E	E	E	E	E	E
4	CH_3	2.16	E	E	[f])	A	E	A	A	A
	CHO	9.70	A	A	[f])	E	A	E	E	E
5a	$=CH_2$	4.62	A	A	[f])	E	E	E	E	E
6a	$=CH-$	5.68	A	A	[f])	E	E	E	E	E
7	CH_3	2.23[g])	A	A	[f])	[f])	[f])	[f])	[f])	[f])

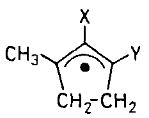
[a]) For the structural formulae see *Table 1, Scheme 2,* and the following:

5a..Y = CH_3 } (=R_{-H})...**6a**
5b..Y = H

[b]) The denotations (*a*)-(*e*) refer to the signal assignments in *Figure 1.* [c]) *Cf. Figure 1A.* [d])*Cf. Figure 1B.* [e]) A = enhanced absorption, E = emission. [f]) Negligible CIDNP. effect. [g]) in CD_3OD at −54°.

The temperature where CIDNP. inversion occurs is characterized by a delicate balance between CIDNP. effects from singlet pairs, $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}{}^1$, and opposite effects from triplet pairs, $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}{}^3$, and pairs of free radicals. The latter originate from the initial singlet and triplet pairs by diffusive separation [26]. Solvent dependence of the diffusive parameters of radical pairs may well explain the changes observed in C_6D_{12} *vs.* CD_3CN and CD_3OD [26] [30]. In accord with this explanation, trapping of the free radicals in C_6D_{12} regenerated the singlet effects observed also in the latter two solvents *(vide supra).*

Table 3. *Signs of ESR. hyperfine coupling constants in* **R**· [a])



R·	X	Y	$a_H(CH_3)$; $a_H(CH_2)$	$a_H(X)$	$a_H(Y)$
a	CH_3	CH_3	>0	<0	>0
b	CH_3	H	>0	<0	<0
c	H	H	>0	>0	<0

[a]) The signs are assumed to be identical with those of allyl radicals [29] [30].

We further note *(Table 2)* that the CIDNP. effects of CH_3CO in **1a** and of **4** inverted in phase at higher temperatures than those of the cyclopentene moiety of **1a**. Possibly the signals of **1a** partly overlap with corresponding resonances of $\mathbf{R}_{+H}$ and $\mathbf{R}-\mathbf{R}$. The signals of these latter products carry the escape CIDNP. polarization [26]. These polarizations are opposite to their counterparts in molecules of **1a** which have been regenerated from the primary cage $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}$[3]. As a consequence, partial cancellations of polarizations of **1a** may occur. However, this problem has not yet been studied in full detail.

The substantial CIDNP. effects exhibited by **1a**, **4**, **5a**, and **6a** at $t \leq -20°$ and $t \geq 45°$ suggest that α-cleavage to $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}$ is a major excited-state reaction of **1a** on

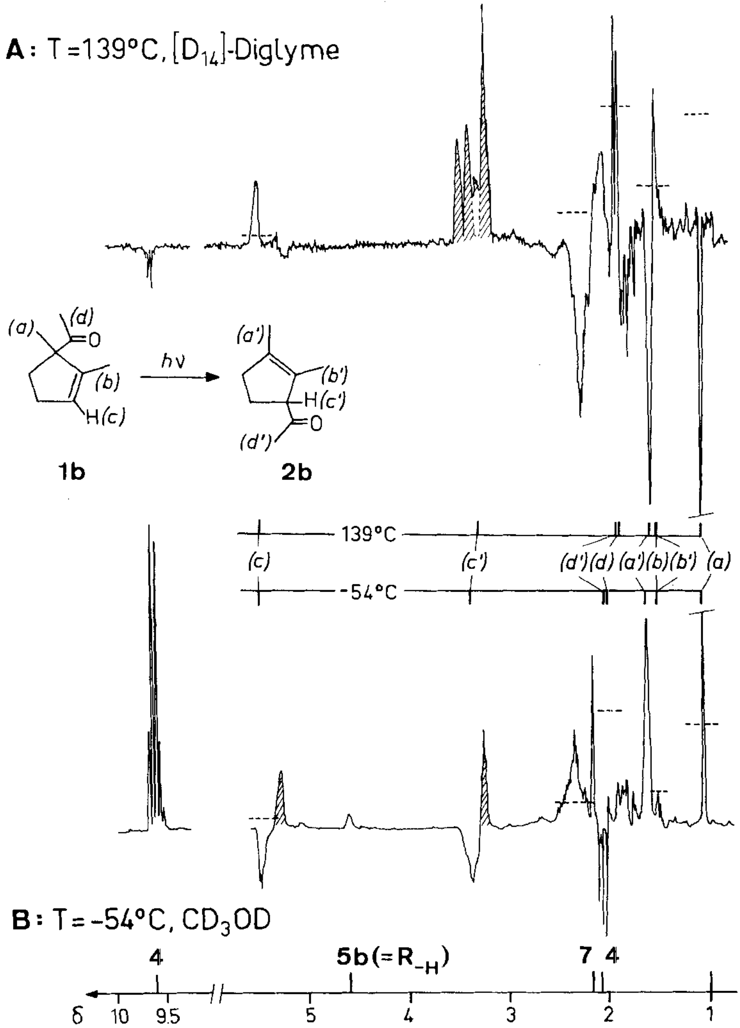


Fig. 2. *Photo-CIDNP. effects on irradiation of* 0.1M *solutions of* **1b** *at* 139° *in (D$_{14}$)diglyme (A) and* −54° *in* CD_3OD *(B).* Dotted lines denote spin-equilibrated NMR. intensities, shaded areas solvent signals.

direct excitation. Although direct evidence for a degenerate 1,3-acyl shift from the radical pair in this β,γ-unsaturated ketone is unobtainable by way of CIDNP., its occurrence is compatible with these data and is, furthermore, strongly supported by the results for **1b** and **1c** described below.

2. *1,2-Dimethyl-cyclopent-2-enyl* (**1b**) *and 1-methyl-cyclopent-2-enyl* (**1c**) *methyl ketones.* Representative photo-CIDNP. effects of ketone solutions in CD_3OD at $-54°$ and in (D_{14})diglyme at 139° are shown in *Figures 2* and *3*. Assignments of the signals and CIDNP. effects at these and other temperatures are summarized in *Tables 4* and *5*. The CIDNP. effects exhibited again a strong temperature dependence in the range $-54° \leq t \leq 139°$ which qualitatively resembled the results obtained for **1a**. However, the inversion of the effects now set in at considerably higher temperatures ($t \simeq 80°$). At 25°, all effects in CD_3OD, CD_3CN and C_6D_{12} were of similar magnitude.

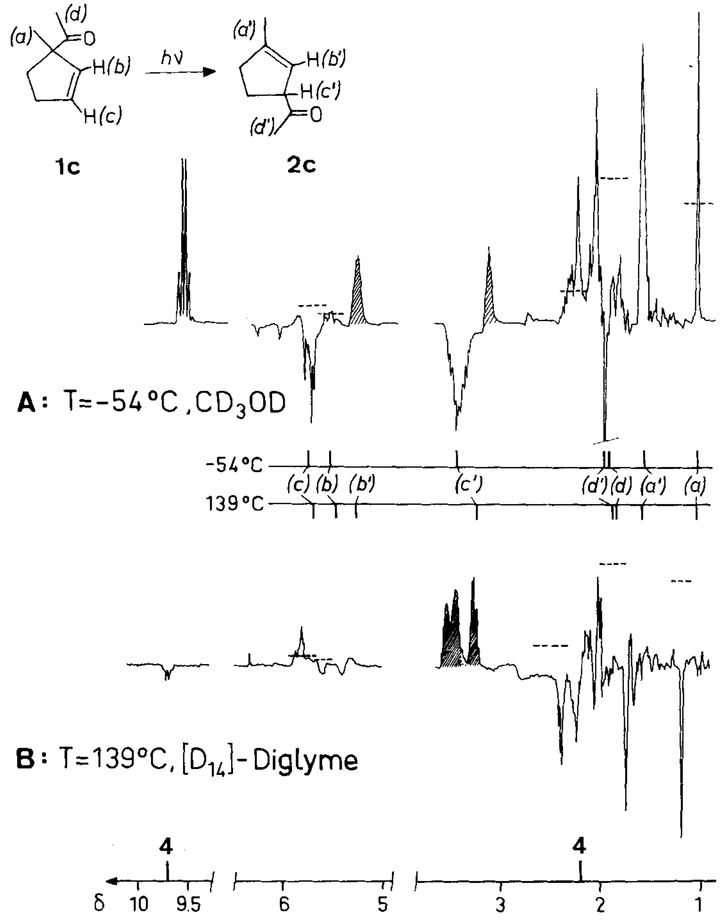


Fig. 3. *Photo-CIDNP. effects on irradiation of* 0.1M *solutions of* **1c** *at* $-54°$ *in* CD_3OD *(A) and* 139° *in* (D_{14})*diglyme (B).* Dotted lines denote spin-equilibrated NMR. intensities, shaded areas solvent signals.

Table 4. *CIDNP. effects on irradiation of* **1b**

Compound[a]	Signal[b]	Solvent (0.1 M solutions) Temperature						
		(D$_{14}$)diglyme	CD$_3$OD	CD$_3$OD, CD$_3$CN, C$_6$D$_{12}$	C$_6$D$_{12}$	C$_6$D$_{12}$	(D$_{14}$)diglyme	(D$_{14}$)diglyme
		+120°	−54°[c]	+25°	+48°	+72°	+100°, +110°	+139°[d]
		δ	CIDNP. phases[e]					
1b	CH$_3$(*a*)	1.16	A	A	[f]	E	E	E
	CH$_3$(*b*)	1.60	E	E	E	[f]	[g]	A
	H (*c*)	5.50	E	E	E	[f]	A	A
	CH$_3$(*d*)	2.02	E	E	[f]	A	A[h]	A[h]
	(CH$_2$)$_2$	2.15 −2.56	A	A	[f]	E	E	E
2b	CH$_3$(*a'*)	1.66	A	A	[f]	E	E	E
	CH$_3$(*b'*)	[g]	[g]	[g]	[g]	[g]	[g]	[g]
	H(*c'*)	*ca.* 3.30	E	E	[f]	[f]	A	A
	CH$_3$(*d'*)	2.04[h]	E	E	[f]	A	A[h]	A[h]
4	CH$_3$	2.08[i]	E	[h]	[h]	[h]	[h]	[h]
	CHO	9.61	A	A	[f]	E	[f]	E
5b	=CH$_2$	4.60[i]	A	[f]	[f]	[f]	[f]	[f]
7	CH$_3$	2.23[i]	A	[f]	[f]	[f]	[f]	[f]

[a] For the structural formulae see *Tables 1* and *2*, and *Scheme 2*. [b] The denotations (*a*)-(*d*) and (*a'*)-(*d'*) refer to the assignments in *Figure 2*. [c] Cf. *Figure 2B*. [d] Cf. *Figure 2A*. [e] A = enhanced absorption, E = emission. [f] Negligible CIDNP. effect. [g] Overlap of the signals CH$_3$(*b*) and CH$_3$(*b'*). [h] CIDNP. polarization ambiguous owing to overlap with solvent lines or emission of undefined origin (in (D$_{14}$)diglyme). [i] In CD$_3$OD at −54°.

The major NMR. signals over the whole temperature range were those of the starting ketones **1b,c**, the 1,3-acyl-shift products **2b,c**, acetaldehyde (**4**), diene **5b**, and biacetyl (**7**; at $t < 0°$ only). Again, this product pattern and the CIDNP. effects can be accommodated by the general reaction mechanism depicted in *Scheme 2*, where $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}$ is predominantly of triplet origin at $t < 48°$ and derives mostly from S$_1$ at $t > 72°$.

The CIDNP. effects of the resonances (*a*), (*b*), (*c*) and (*d*) in the starting ketones **1b** and **1c**, and those of the corresponding signals (*a'*), (*b'*), (*c'*) and (*d'*) in the 1,3-acyl-shift products **2b** and **2c** were of similar magnitude. This shows that the radical pair $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}$ formed both starting ketone and 1,3-acyl-shift product with similar efficiencies, as the relaxation times of (*a*) and (*a'*), (*b*) and (*b'*) *etc.* should not differ significantly. This conclusion follows from previous arguments in the discussion of CIDNP. from competitive radical reactions [33].

GC. analyses of the irradiated solutions of **1b** and **1c** are given in *Table 6*. In all runs small amounts of oxadi-π-methane-rearrangement products (**3b,c**) were also formed on direct irradiation[6]. In addition, several GC. peaks of longer retention

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[6] The formation of the thermally labile [34] oxadi-π-methane-rearrangement products on direct irradiation, which remained below reliable detection limits in the first photochemical study of **1b** [3], has now been demonstrated by the use of improved analytical conditions.

Table 5. *CIDNP. effects on irradiation of* **1c**

Compound[a]	Signal[b]	Solvent (0.1 M solutions) Temperature						
		(D_{14})diglyme	CD_3OD	CD_3OD, CD_3CN, C_6D_{12}	C_6D_{12}	C_6D_{12}	(D_{14})diglyme	(D_{14})diglyme
		+120°	−54°[c]	+25°	+48°	+72°	+100–120°	+139°[d]
		δ	CIDNP. phases[e]					
1c	$CH_3(a)$	1.19	A	A	[f]	E	E	E
	$H(b)$	5.63	A	A	[f]	[f]	E	E
	$H(c)$	5.92	E	E	[f]	[f]	A	A
	$CH_3(d)$	1.98	E	E	E	[f]	A[g]	A[g]
	$(CH_2)_2$	2.10 −2.60	A	A	[f]	E	E	E
2c	$CH_3(a')$	1.74	A	A	[f]	E	E	E
	$H(b')$	5.42	A	[f]	[f]	[f]	E	E
	$H(c')$	*ca.* 3.38	E	E	[f]	[f]	A[g]	A[g]
	$CH_3(d')$	2.00	E	E	E	[f]	A[g]	A[g]
4	CH_3	2.16[h]	E[g]	[f][g]	[f]	[f]	[f][g]	[f][g]
	CHO	9.61[h]	A	A	A	[f]	[f]	E
7	CH_3	2.23[h]	A	[f]	[f]	[f]	[f]	[f]

[a] For the structural formulae see *Tables 1* and *2*, and *Scheme 2.* [b] The denotations (*a*)-(*d*) and (*a'*)-(*d'*) refer to the assignments in *Figure 3.* [c] Cf. *Figure 3A.* [d] Cf. *Figure 3B.* [e] A = enhanced absorption, E = emission. [f] Negligible CIDNP. effect. [g] Overlap with other polarizations of undefined origin. [h] In CD_3OD at −54°.

Table 6. *Temperature and solvent effects on relative yields of 1,3-acyl shift* (**1b, c** → **2b, c**) *and oxadi-π-methane rearrangement* (**1b, c** → **3b, c**) *products*

Starting ketone	Solvent	Initial concentration M	Temperature °C	Conversion %[a]	[2]/[3][b]
1b	(D_{14})diglyme	0.11 ± 0.02	90–138	55	> 20
1b	C_6D_{12}	0.10	72	70	9.5
1b	C_6D_{12}	0.10	48	40	7.2
1b	C_6D_{12}	0.15	25	55	6.3
1b	pentane	0.20	25	20	4.2
1b	CD_3CN	0.20	25	10	> 15
1b	CD_3OD	0.10	25	42	> 15
1b	CD_3OD	0.11	−54	42	4.4
1c	(D_{14})diglyme	0.12	> 90	40	> 13
1c[c]	C_6D_{12}	0.10	25	< 20	5
1c	CD_3CN	0.10	25	≤ 20	13.8
1c	CD_3OD	0.11	25	33	19.7
1c	CD_3OD	0.11	−54	67	3.75

[a] GC. or NMR. analysis; error ± 10%. [b] GC. analysis; error ± 10%. [c] Taken from [4].

times in both series could be assigned to bis(cyclopent-2-enyl) products ($\overline{\mathbf{R}-\mathbf{R}}$) by GC./MS. analysis.

The ratio (1,3-acyl shift)/(oxadi-π-methane rearrangement) increased with solvent polarity and, in the same solvent, decreased with decreasing temperature.

These trends appear sufficiently distinct to outweigh possible inaccuracies of the data resulting from the relatively high conversions.

In C_6D_{12} at 25°, the phases of the CIDNP. effects of **1b, c** and **2b, c** were not changed, in contrast to the situation for **1a**. The magnitude of the effects remained essentially insensitive to the presence of triplet quenchers such as 0.1-1.0 M cyclohexa-1, 3-diene and 0.01-0.04 M naphthalene. Addition of 0.05 M and 0.1 M tributyl-stannane to 0.1 M solutions of **1b** in C_6D_{12} reduced selectively the formation of dimers ($\mathbf{R}-\mathbf{R}$) to $\leq 10\%$ of the value in the absence of free-radical scavengers, without affecting the polarization phases. These findings constitute direct evidence that, at 25°, the CIDNP. effects from **1b** and **2b** (and most probably also from **1c** and **2c**) result from $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}{}^3$ rather than from $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}$-born free radicals, and that the triplet α-cleavage is too fast to allow diffusion-controlled quenching of the reactive triplet state.

As with **1a**, only insignificantly small CIDNP. effects were observed during triplet-sensitized irradiations of **1b** and **1c** in (D_6)acetone at RT.

Discussion. - The very pronounced photo-CIDNP. effects exhibited by all three cyclopentenyl methyl ketones **1a-c**, and the 1, 3-acyl-shift products **2b** and **2c** indicate that radical pair formation substantially contributes to the photochemistry of these β,γ-unsaturated ketones on direct irradiation. The results leave no doubt (see preceding section) that the 1, 3-acyl-shift reaction ($\mathbf{1} \rightleftarrows \mathbf{2}$) mostly, if not entirely, derives from this mechanism rather than a concerted one-step process.

In a previous, exploratory photo-CIDNP. study of **1b** [35] the temperature dependence of the photo-CIDNP. had not been taken into account, and the comparatively small effects observed at 25° had been judged mechanistically insignificant. As a consequence, the results were erroneously interpreted in favour of a concerted 1,3-acyl-shift mechanism [3]. The finding that the photoracemization of (*R*)-(+)-**1a** and the 1,3-acyl-shift in a suitably deuteriated derivative of **1a** occur with equal rates [6], is compatible with both a concerted nature of the 1,3-acyl-shift and a radical pair mechanism in which acetyl randomly attacks all four acceptor sites of the cyclopentenyl radical.

The complete, temperature-related inversion of the CIDNP. phases is a novel feature in photo-CIDNP. studies of ketones. A similar influence of temperature on photo-CIDNP. has not been found for other ketones, *e.g.*, pinacolone at $-60° \leq t \leq 25°$ [21] [33] [36], di-*t*-butyl ketone at $-93° \leq t \leq 25°$ [19] [21], and dibenzyl ketone at $-35° \leq t \leq 70°$ [33] [37]. In all these cases the CIDNP. results were compatible with temperature-dependent decarbonylation of the acyl radicals and disproportionation/combination ratios of the radical pairs. No change in the multiplicity of the predominantly triplet-generated radical pairs was reported over the temperature ranges studied[7]).

The temperature effects in our present study are readily rationalized in terms of *Scheme 3*. Temperature activated α-cleavage to $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}{}^1$ (rate constant $= k_a^S(t)$), intersystem crossing (k_{isc}) to the T_2 state and fluorescence (k_f) compete for S_1 deactivation of **1a-c**. The T_2 state then undergoes α-cleavage to $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}{}^3$ ($k_a^{T_2}$) and, concurrently, internal conversion (k_{ic}) to the T_1 state. Formation of $\overline{\mathbf{R}\cdot\cdot\mathbf{R}'}{}^3$ from the T_2 state is in accord with our earlier observation [4] that the 1,3-acyl shift of **1c**

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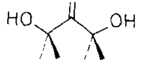
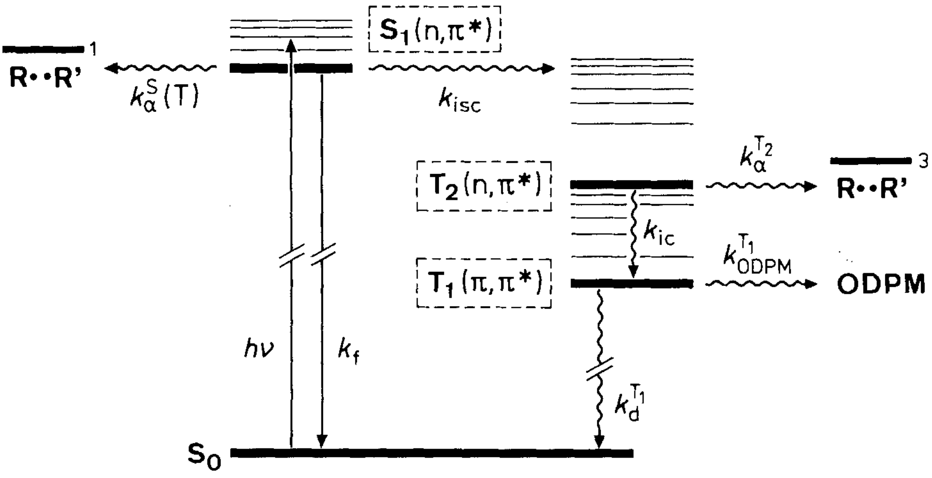
[7]) No major temperature effects were observed with **8** which exhibited triplet photo-CIDNP. at $25° \leq t \leq 80°$ in CD_3CN [17].


8

Scheme 3. *State and reaction diagram of ketones* **1a–c** (ODPM = oxadi-π-methane rearrangement)



can occur from the thermally generated $T_2(n,\pi^*)$ state. In this experiment at 80°, the 1,3-acyl shift from T_2 of **1c** and internal conversion to T_1 occur at similar rates ($k_\alpha^{T_2} \geq k_{ic}$)[3]). A low-temperature range with $k_{isc} \gg k_\alpha^S(t)$ and a high-temperature range with $k_\alpha^S(t) \gg k_{isc}$, which exhibit preferential reactivity from the T_2 and S_1 states respectively, can thus be defined for all three β,γ-unsaturated ketones.

This picture is corroborated by the results of a preliminary fluorescence study [17]. For camphor a temperature-dependent α-cleavage from S_1 is reflected by a substantial temperature dependence of the fluorescence quantum yield [38]. Ketones **1a** and **1c** behave similarly in 3-methylpentane; 30- to 40-fold (**1a**) and 8- to 10-fold (**1c**) increases of the fluorescence quantum yields resulted when the temperature was lowered from 50° to −190°. Furthermore, the fluorescence quantum yield ratio at 25° was $\phi_f(\mathbf{1c})/\phi_f(\mathbf{1a}) = 3.6 \pm 0.4$ in acetonitrile and 3-methylpentane. As the shapes of the UV. spectra of **1a** ($\lambda_{max} = 300$ nm, $\varepsilon_{max} = 175$) and **1c** ($\lambda_{max} = 295$, $\varepsilon_{max} = 119$) are very similar, a ratio $\phi_S(\mathbf{1c})/\phi_S(\mathbf{1a}) \approx 5.3$ follows for the singlet lifetimes τ_S at 25° from equation (1). Both the difference in the

$$\frac{\tau_S(\mathbf{1c})}{\tau_S(\mathbf{1a})} = \frac{\phi_f(\mathbf{1c})}{\phi_f(\mathbf{1a})} \cdot \frac{k_f(\mathbf{1a})}{k_f(\mathbf{1c})} \approx \frac{\phi_f(\mathbf{1c})}{\phi_f(\mathbf{1a})} \cdot \frac{\varepsilon_{max}(\mathbf{1a})}{\varepsilon_{max}(\mathbf{1c})} \qquad (1)$$

temperature-dependent fluorescence of **1a** and **1c** and the increased singlet lifetime of **1c** over **1a** strongly support the general excited-state reaction scheme given for these β,γ-unsaturated ketones *(Scheme 3).*

It should be pointed out that the current semiquantitative CIDNP. theory (*e.g.* [25]) gives a merely qualitative picture of the temperature dependence of the relative rates $k_\alpha^S(t)$ *vs.* k_{isc}. In particular, no quantitative interpretation of the CIDNP. inversion temperature in terms of a definitive $k_\alpha^S(t)/k_{isc}$ ratio (or: ratio of S *vs.* T pair formation rates) can be given.

The qualitative description of the photochemistry of **1a–c** in terms of excited-state reactions rates (see *Scheme 3*) can now be extended by including the oxadi-π-

methane rearrangement (ODPM) ($k^{T_1}_{ODPM}$) from T_1 and the radiationless decay of this state to the ground state ($k^{T_1}_d$). The temperature dependence of the product ratio (1,3-acyl shift)/(oxadi-π-methane rearrangement) from **1b** and **1c** *(Table 6)* appears to reflect either or both of the following factors: (i) $k^{T_2}_a$ might possess a higher activation energy than k_{ic}, which would favour the population of the T_1 state from T_2 at low temperatures; (ii) the efficiency of 1,3-acyl shift product formation from $\overline{\mathbf{R}\cdot\,\cdot\mathbf{R}'}^3$ might be reduced at low temperature owing to an increase of the disproportionation/combination ratio of the radical pair, as is commonly observed for other termination reactions [39] [40]. Some support for (ii) may be seen in the increase of the acetaldehyde (**4**) yield and CIDNP. effects upon lowering of the temperature. However, this aspect has not yet been investigated in detail.

Our observations for **1a–c** together with a critical evaluation of literature data, leads us to the conclusion that α-cleavage from the S_1 state of ketones is dependent on structural factors, although as yet too little is known about this for a proper evaluation. Several claims for S_1 α-cleavage which had been made on the basis of quenching experiments [41], could not be substantiated by photo-CIDNP. [21] [33] except in CCl_4 where exciplex mechanisms have been proposed [42]. From the lack of temperature-dependent fluorescence [38] [43] of several aliphatic ketones with long S_1 lifetimes *Turro et al.* [38] recently concluded that S_1 α-cleavage either proceeds with zero activation energy *or* does not occur in the temperature range $-5° \leq t \leq 80°$. In fact, most of the experimental evidence cited in the literature in favour of S_1 α-cleavage, appears to us just as compatible with reaction from a vibrationally excited triplet state.

Ring strain, such as in camphor derivatives [38], and β-unsaturation as in **1a–c**, their phenyl ketone analogues [10], and possibly in other β,γ-unsaturated ketones are at present the only structural factors which have been unequivocally recognized to render $k^S_a(t)$ competitive with k_{isc}. The substantially greater S_1 contribution to α-cleavage at RT. in **1a** than in **1b** and **1c** is the subject of continued studies. The stabilization of the incipient allylic radical of **R**· by the terminal methyl substitution [44] (**1a**: two methyl groups, $Y = CH_3$; **1b, c**: one methyl, $Y = H$) can be expected as one factor which determines this difference.

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