

204. Concerning the Stereochemical Course and Mechanism of the Photochemical 1,3-Acetyl Shift in a β,γ -Unsaturated Ketone

Preliminary communication¹⁾

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Summary

Enantiomerically enriched samples of 1,2-dimethyl-3-(²H₃)methyl-2-cyclopentenyl (**1**) and 1-(²H₃)methyl-2,3-dimethyl-2-cyclopentenyl methyl ketones (**2**) have been irradiated at 313 nm in methanol in the temperature range +50 to –45°. The 1,3-acetyl shift, which interconverts the two isomeric ketones, occurs with a small change in the enantiomeric composition and independently of temperature in the range studied. This change corresponds to an upper limit of approximately 20% reaction with racemization. It is proposed that reaction occurs from both the $S_1(n, \pi^*)$ and $T_2(n, \pi^*)$ excited states with stereospecific reaction from S_1 (rapid primary geminate recombination of a singlet radical pair, with a possible contribution by a concerted 1,3 shift) dominating throughout the temperature range, but with the proportion of reaction from T_2 increasing as the temperature is lowered. The racemization results from secondary geminate recombination of the singlet and triplet radical pairs and the random recombination of free radicals. Viscosity effects are proposed to explain the independence of the racemization on temperature.

The photochemistry of β,γ -unsaturated ketones has been extensively investigated over the past two decades²⁾. In recent years the nature of the 1,3-acetyl shift observed in these systems, and in particular the possibility that the reaction may occur from the $T_2(n, \pi^*)$ as well as the $S_1(n, \pi^*)$ excited state, has aroused much interest [3]. We report now further work on this topic carried out with ketones of type **1** in continuation of our systematic study of this particular β,γ -enone system [3a, d] [4].

Photo-CIDNP. experiments [4c] have shown that the photochemical 1,3-acetyl shift in enones of type **1**³⁾ must, at least in part, be a radical process. Experiments

¹⁾ Presented in part at the 9th IUPAC Symposium on Photochemistry, Pau/France 1982 [1].

²⁾ For a recent review of the photochemistry of β,γ -unsaturated ketones see [2].

³⁾ The deuteriated ketones **1** and **2** give rise to qualitatively the same CIDNP. spectra and demonstrate the same temperature dependence as their non-deuteriated analogue [4c].

with radical trapping agents indicated that this part of the reaction proceeds predominantly *via* a cage radical pair ($\overline{\text{RP}}$) which also gives rise to disproportionation products such as acetaldehyde and diene [4c]. The inversion of the CIDNP polarizations which occurs on changing the temperature, was explained in terms of the radical pair mechanism for CIDNP.⁴⁾ by postulating that $\overline{\text{RP}}$ is formed from a singlet excited state, $S_1(n, \pi^*)$, in the high-temperature region (*e.g.*, $+50^\circ$ for **1** and **2**) and from a triplet state, $T_2(n, \pi^*)$, in the low-temperature region (*e.g.*, -50° for **1** and **2**) [4c]⁵⁾.

In order to generate magnetic nuclear polarization in the cage products, the radical pair mechanism for CIDNP.⁴⁾ requires that the components of the radical pair diffuse far enough apart to render the electron exchange energy small relative to the electron-nuclear hyperfine interactions (typically 6–10 Å, *i.e.*, solvent separated [5b]), and then undergo intersystem crossing (in competition with complete separation of the radical pair) before secondary geminate recombination [6]. For typical organic radicals the intersystem crossing process can take place on a time scale as short as $\approx 10^{-9}$ s [5] [7]⁶⁾. However, rotation of the cyclopentenyl component by 180° about the axis indicated in the *Scheme* is expected to occur on a time scale of $\approx 10^{-12}$ to 10^{-11} s⁷⁾.

In an experiment starting with any one enantiomer, formation of both (+)- and (–)-**1** and (+)- and (–)-**2** has thus to be expected for a reaction *via* $\overline{\text{RP}}$ which leads to polarized products. In contrast, a mechanism in which the acetyl group remains on the same face of the cyclopentenyl group would be enantiospecific, leading to interconversion of either (+)-**1** and (–)-**2** or (–)-**1** and (+)-**2**. Possible examples are a concerted 1,3 shift or a reaction in which recombination of $\overline{\text{RP}}$ is faster than rotation of the cyclopentenyl radical.

We have carried out experiments with enantiomerically enriched **1** and **2**⁸⁾ which were designed to determine the stereochemical course of the 1,3-acetyl

⁴⁾ For an introduction to the radical pair mechanism see [5].

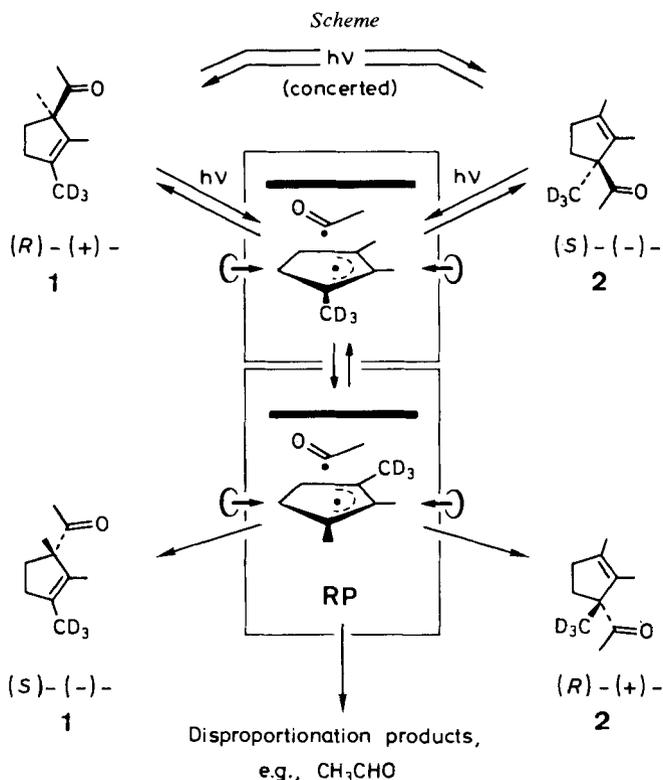
⁵⁾ See [3d] for the configurational assignments of the T_1 and T_2 states which undergo the oxa-di- π -methane rearrangement and the 1,3 shift, respectively.

⁶⁾ For the CIDNP. experiments, which are conducted in a high field (*e.g.*, $H = 21140$ G), intersystem crossing ($S \leftrightarrow T_0$) in $\overline{\text{RP}}$ due to Δg (≈ 0.0021 [4c]) occurs on a time scale of the order of 8×10^{-9} s (see p. 371 in [7b]); this figure will be modulated by the different electron-nuclear hyperfine interactions in each $\overline{\text{RP}}$. In the low-field extreme (*e.g.*, earth's magnetic field) intersystem crossing ($S \leftrightarrow T_-, T_0, T_+$) will be occasioned solely by the hyperfine interactions. Estimates of the magnitude of these interactions [8] allow an upper limit of $\approx 2 \times 10^{-9}$ s for the time scale of this process (see p. 371 in [7b]).

Under the irradiation conditions for **1** and **2**¹¹⁾, *i.e.*, a weak magnetic field due to the stirrer, the rate of intersystem crossing should be less than in either of the two extreme cases (see [7] for an explanation and some of the possible applications of this effect).

⁷⁾ Measurements of the rates of rotational diffusion of cyclohexane, cyclohexene and benzene in solution show that these molecules undergo a 180° tumbling motion about a C_2 axis on a time scale of the order of 10^{-12} to 10^{-11} s at viscosities corresponding to those in methanol between $+50^\circ$ (0.4 cP) and -50° (2.2 cP) [9].

⁸⁾ The resolution of racemic **1** and **2** was accomplished by column chromatographic separation of the diastereoisomeric acetals formed with (–)-butane-2,3-diol. The irradiations were carried out with *ca.* (15:85)-mixtures of the enantiomers in order to have optimum signal ratios in the NMR. for integration.



shift⁹⁾, and thus to provide more information on the $\overline{\text{RP}}$ pathway. With the aid of an optishift reagent the $^1\text{H-NMR}$. signals of the quaternary methyl groups of (+)-**1** and of (-)-**1** can be separated¹⁰⁾. This allowed the determination of the change in the ratio of enantiomers resulting from photolytic α -cleavage and back reaction ($\mathbf{1} \rightleftharpoons \overline{\text{RP}}$) and the 1,3-acetyl shift ($\mathbf{2} \rightarrow \mathbf{1}$).

The experiments with (+)-enriched **1** (*Table*) in methanol show that the starting material does not noticeably racemize in the temperature range -45 to 50° ¹¹⁾. For

⁹⁾ For previous investigations of 1,3-acyl shifts in optically active β,γ -enones see [4a] [10].

¹⁰⁾ Typically, the addition of 50-80 mg of praseodymium tris(*D*-3-heptafluorobutyrylcamphorate) [$\text{Pr}(\text{hfc})_3$; Lancaster Synthesis, Ltd.] was required to separate the quaternary methyl signals of (+)- and (-)-**1** (ca. 10 mg in ca. 0.6 ml CDCl_3) and to determine their relative amounts by planimetry. Spectral separation and resolution were best between 30 and 50° . The separated signals were assigned to the appropriate enantiomers by comparison with the optical rotation [4a] [11].

¹¹⁾ Argon-purged solutions of 0.06-0.08M ketone in MeOH (with *m*-xylene as an internal GC. standard) were irradiated at 313 nm in an electronically integrating actinometer [12] using a variable-temperature cuvette and magnetic stirring. Products **1** and **2** (not separable by GC.) and the oxa-di- π -methane rearrangement product [4a, b] in the irradiated solutions were determined by GC. (65 m OV 101 glass capillary column). For $^1\text{H-NMR}$. (80 MHz) measurements the mixtures of **1**+**2** were isolated (ca. 10 mg) by preparative GC. and then dissolved in ca. 0.6 ml CDCl_3 . The absolute amounts of **1** and **2** were calculated from the ratio **1**/**2**, obtained from integration of the quaternary and acetyl methyl signals, in conjunction with the analytical GC. data. Addition of optishift reagent then allowed the ratio of the enantiomers of **1** to be determined¹⁰⁾.

Table. Enantiomeric composition of **1** resulting from the irradiation of mixtures of **1** and **2** enriched in the (R)-(+)-enantiomer^{a)}

Temperature of irradiated solution [°C]	Irradiation of 84.3% (R)-(+)- 1 , 15.7% (S)-(-)- 1 ^{b)}		Irradiation of 86.0% (R)-(+)- 2 , 14.0% (S)-(-)- 2 ^{b)}	
	Conversion 1 → 2 [%]	(S)-(-)- 1 after irradiation [%] ^{b)c)}	Conversion 2 → 1 [%]	(R)-(+)- 1 formed by irradiation [%] ^{b)c)}
		[15.7 ± 2.0 ^{d)}]		[14.0 ± 2.0 (S)-(-)- 2 ^{d)}]
50	18.7	17.7	11.6	18.9
50	22.7	15.0	–	–
20	13.1	18.9	11.9	16.5
20	22.6	19.1	23.2	18.5
–10	10.0	17.1	10.3	18.6
–10	25.2	15.6	22.0	20.8
–45	11.4	16.4	11.0	16.6
–45	26.8	16.1	14.6	17.1

^{a)} For experimental details see footnote 11. ^{b)} Determined for **1** by ¹H-NMR, with Pr(hfc)₃, and for **2** by GC. (70 m PPG glass capillary column) of the mixture of diastereoisomeric acetals before hydrolysis to the ketone. Using **1**, the two methods gave the same result within ±2%. ^{c)} Percentage of the total of the two enantiomers. ^{d)} Before irradiation; value given for comparison with the values after irradiation.

the purposes of comparison it can be calculated that, for a reaction solely *via* a long-lived **RP**, an enantiomeric composition of 24.3% (–)-**1** and 75.7% (+)-**1** would result on 20% conversion to the 1,3-shift product. Since **1** is the starting material, however, even a fairly sizeable loss of optical purity in **1** regenerated from **RP** would not be detectable. This limitation does not apply to the formation of **1** on irradiation of **2**. The results obtained with (+)-enriched **2** do indeed show a small change in the enantiomeric composition of the 1,3-shift product (**1**) as compared with the starting material, independent of the temperature in the range studied, although this change is on the border of our experimental accuracy. Only an upper limit of approximately 20% reaction with racemization, *i.e.*, a maximum of about 20% reaction through an **RP** which yields polarized products, can be calculated from the results in the *Table*.

The following mechanism may explain these results: the 1,3 shift proceeds at least in part *via* **RP**, and α -cleavage does occur from both the $S_1(n, \pi^*)$ and $T_2(n, \pi^*)$ excited states, with the proportion of T_2 reaction indeed increasing with decreasing temperature *but* with reaction from S_1 , either concerted or *via* **RP**, dominating throughout the temperature range studied.

At 50°, where the effect of T_2 reaction is assumed to be negligible, ¹**RP**, formed from S_1 , can undergo rapid primary geminate recombination (10^{-13} – 10^{-11} s) [6] to yield unpolarized (no CIDNP.) disproportionation and recombination products [5], in competition with separation of the radicals by diffusion. Recombination may even be faster than rotation of the cyclopentenyl radical about its in-plane axis (see *Scheme*; molecular tumbling is estimated to proceed at 10^{-12} – 10^{-11} s⁷⁾, allowing for highly enantioselective interconversions (+)-**1** \rightleftharpoons (–)-**2** and (–)-**1** \rightleftharpoons (+)-**2**. A concerted contribution would similarly proceed enantiospecifically and give rise

to no CIDNP. effect. Radicals which have diffused apart can still react with each other (secondary geminate recombination) [6]. The observed singlet CIDNP. is due to the small proportion of radicals reacting by this mechanism on the time scale of $\approx 10^{-9}$ – 10^{-7} s. The racemization (for **2**→**1**) at 50° is the result of both secondary geminate recombinations and random reaction of free radicals (*i.e.*, uncorrelated pairs)¹²).

Since $^3\overline{\text{RP}}$ has to undergo intersystem crossing prior to reaction, most $^3\overline{\text{RP}}$ will live long enough to be able to contribute to CIDNP. A small proportion of T_2 reaction will therefore suffice to cause a polarization intensity equal to or greater than the singlet CIDNP.¹³).

As the temperature is lowered from 50° (where the effect of T_2 reaction is postulated to be negligible), the proportion of T_2 reaction increases: at *ca.* –5°, it produces a triplet polarization of sufficient intensity to cancel out the singlet contribution, and at –45° it leads to a pronounced triplet CIDNP. spectrum although the proportion of T_2 reaction is still small¹⁴), reaction from S_1 dominating.

The independence of the racemization of **1** on temperature (Table) may be caused by a decrease of racemization from $^1\overline{\text{RP}}$ on lowering the temperature, and thus increasing the viscosity, compensating a concomitant increase due to $^3\overline{\text{RP}}$. Thus, when the viscosity was increased by changing the solvent [(D₄)MeOH, (D₆)EtOH, (D₈)*i*-PrOH] the ratio of triplet/singlet CIDNP. signals increased at any given temperature¹⁵). An increase in viscosity will decrease the rates of rotational and translational diffusion and thus increase both the amount of primary geminate recombination of $^1\overline{\text{RP}}$ and the extent to which the latter can compete with rotation. A lower singlet CIDNP. intensity and less racemization from $^1\overline{\text{RP}}$ should result.

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- ¹²) The products resulting from reaction of uncorrelated pairs will be polarized (F pair polarization) in the opposite sense to those formed by secondary geminate recombination of $^1\overline{\text{RP}}$. Since the specific polarization arising from the former is expected to be weaker than that due to the latter, no quantitative conclusions can be drawn about the relative importance of the two pathways.
¹³) The specific polarization generated by triplet radical pairs is higher than that generated by singlet radical pairs (see [5c], p. 101). This effect will have to be borne in mind in studies where photo-CIDNP. is used to decide whether a singlet of a triplet excited state is reactive.
¹⁴) Preliminary results of CIDNP. experiments show that the proportion of T_2 reaction continues to increase as the temperature is lowered still further. The observed triplet polarizations [$(I_p/I_0)(t/T_1)$] for acetaldehyde and **1** (formed on irradiation of **2**) increase markedly on going from –40 to –80°.
¹⁵) This change was much smaller than that observed in (D₄)MeOH on lowering the temperature to cause the same variation in viscosity.

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