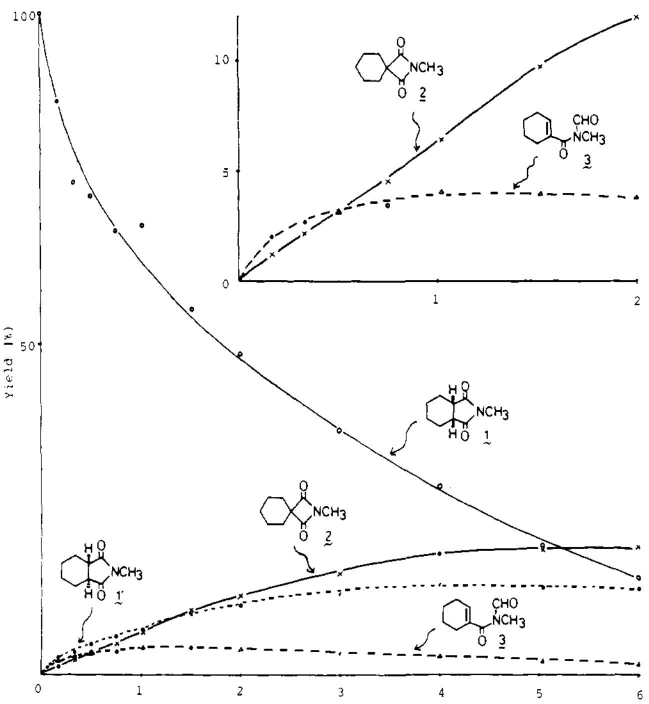

Figure 1. The time dependent variation of products in the reaction followed by LC. An acetonitrile solution (0.06 M) of **1** was irradiated with a 120-W low-pressure Hg lamp at 4 °C.

hypnotic effect.[5a] The previously reported synthetic methods involve sluggish reactions and the yields are generally poor. Since our synthetic approach to azetidine-2,4-diones simply consists of photolysis of the related succinimides which are readily available and the products can be isolated on silica gel column chromatography with ease, this reaction provides a convenient synthetic method of 1,3,3-trialkyl-substituted azetidine-2,4-diones. Further, photolysis of ring-opened imides like **3** or **21** with a low-pressure Hg lamp results in much better yields (Table II). So far the reported photoinduced α-cleavage reactions of acyclic imides[14] and lactams[15] were primarily related to the fission of the C(O)-N bond, and that of the C(O)-C bond was significant in a few exceptional imides.[3] The present example shows the generality and importance of α-cleavage reaction, especially the C(O)-C bond fission of alicyclic imides. Its scope and limitation are being studied.

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(7) **4**, **5**, and **6**, showed reasonable spectral data.

(8) Characterization data follow. **13**: ^{1}H NMR (CCl$_4$) δ 1.26 (t, 3 H, J = 7 Hz), 1.3–1.9 (m, 10 H), 3.24 (q, 2 H, J = 7 Hz); IR (KBr) 1712 (s), 964 cm^{-1}. **14**: ^{1}H NMR (CDCl$_3$) δ 1.8–2.2 (m, 10 H), 2.87 (s, 3 H); IR (KBr) 1840 (w), 1710 (s), 955 cm^{-1}. **15**: ^{1}H NMR (CCl$_4$) δ 0.96 (d, 3 H, J = 6 Hz), 1.1–2.1 (m, 9 H), 2.88 (s, 3 H); IR (KBr) 1720 (s), 950 cm^{-1}. **16**: ^{1}H NMR (CDCl$_3$) δ 2.2–2.5 (m, 4 H), 2.8–3.1 (m, 1 H), 2.95 (s, 3 H), 3.25 (dd, 1 H), 3.72 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 24.8 (q, *N*-CH$_3$), 31.9, 32.1 (t, –CH$_2$–), 42.0, 46.3 (d, >CH–), 52.1, 52.4 (q, *O*-CH$_3$), 69.0 (s, quaternary C), 170.6, 171.7, 172.6, 173.1 (s, >C=O); IR (KBr) 1730 (s), 963 cm^{-1}. **17**: ^{1}H NMR (CDCl$_3$) δ 2.21 (t, 2 H, J = 8 Hz), 2.42 (t, 2 H, J = 8 Hz), 2.74 (s, 3 H), 2.94 (s, 3 H), 3.67 (s, 6 H); IR (CHCl$_3$) 1734 (s), 960 cm^{-1}. **18**: ^{1}H NMR (CCl$_4$) δ 0.98 (t, 3 H, J = 8 Hz), 1.30 (s, 3 H), 1.68 (q, 2 H, J = 8 Hz), 2.86 (s, 3 H); IR 1805 (w), 1720 (s), 945 cm^{-1}.

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S_1 vs. T_2 Photoreactivity of β,γ-Unsaturated Ketones. Temperature Dependent Photo-CIDNP of 2-Cyclopentenyl Methyl Ketones[1]

Sir:

Among the diverse facets of the photochemistry of β,γ-unsaturated ketones (β,γ-UK),[2] the mechanism of the allylic 1,3-acyl shift (AS), most commonly observed on direct irradiation only, has persisted as a prominent matter of debate. On the basis of earlier results, the AS was assumed to occur from the singlet n,π^* state (S_1) via a concerted process.[2] Only for β,γ-unsaturated phenyl ketones has the AS been shown to proceed via a radical-pair mechanism, predominantly from the n,π^* triplet, which is the lowest lying excited state of these compounds.[3] Subsequently, AS from a short-lived T_2 state of prevalent n,π^* character has also been taken into consideration for β,γ-UK's with a lowest lying triplet π,π^* state.[2b,c,4,5] While results of fluorescence studies remained inconclusive on this point,[4,5] it has been unequivocally shown recently that the AS can indeed occur from the T_2(n,π^*) state of a β,γ-UK, **1c**.[6] CIDNP effects have been taken as evidence for all three of the current views on the AS mechanism.[2c,3,7,8]

We now report results on the β,γ-UK's **1a–c** which allow the assembly of a more coherent, mechanistic picture of the S_1 vs. T_2 reactivity of these ketones. Photo-CIDNP effects from **1a–c** exhibited a remarkable temperature dependence in the range of −60 to 140 °C. *They are interpreted in terms of an AS via radical pairs that originate from both the S_1 and T_2 states depending on the reaction temperature.*

When a 0.1 M solution of **1a**[9,10a] in CD$_3$OD was irradiated at 45 °C in the modified ^{1}H probe of an FT NMR spectrometer,[11] CIDNP effects of the starting ketone (**1a**) and acetaldehyde (**2**) were observed (Figure 1B).[13] Additional enhanced resonances were assigned to 1,2-dimethyl-3-methylenecyclopentene, R$_{-H}$, on the basis of previous evidence.[3] Both CIDNP and product structures are in accord with the reactions summarized in Scheme I. At 45 °C, these reactions of **1a** occur predominantly from S_1: all polarizations are readily rationalized in terms of reactions from a singlet radical pair, $\overline{R \cdot \cdot R'}^{1}$ when Kaptein's rules[14] are applied using the respective radical parameters.[15]

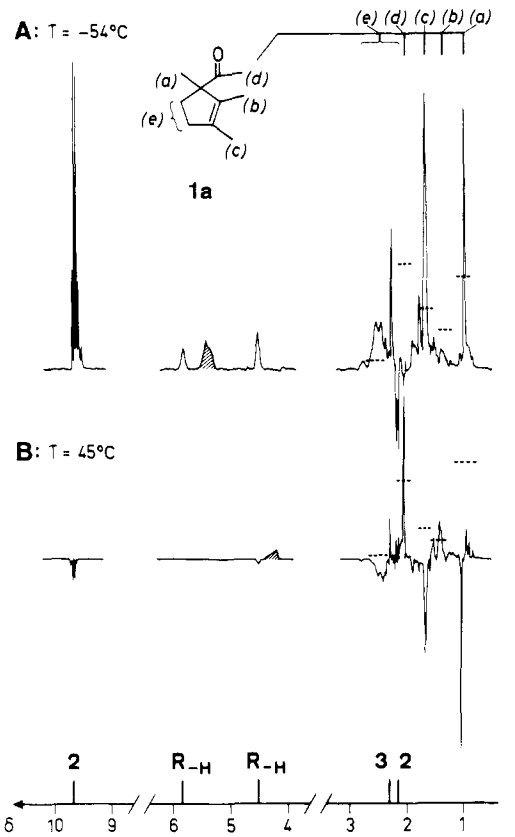


Figure 1. Photo-CIDNP effects of **1a**, **2**, **3**, and R_{-H} at −54 °C (A) and 45 °C (B) in CD_3OD. Dotted lines denote spin-equilibrated NMR intensities after irradiation, shaded areas solvent signals.

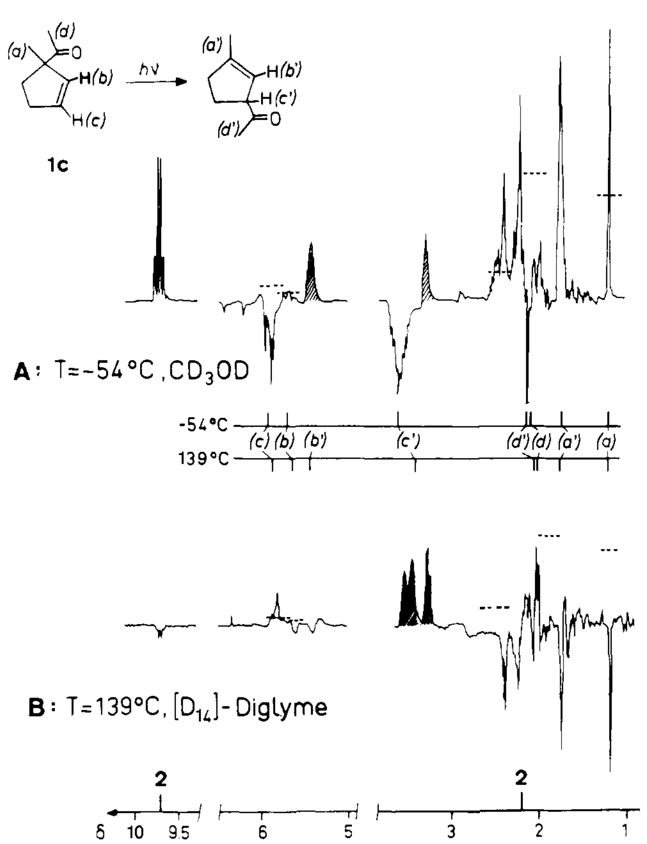
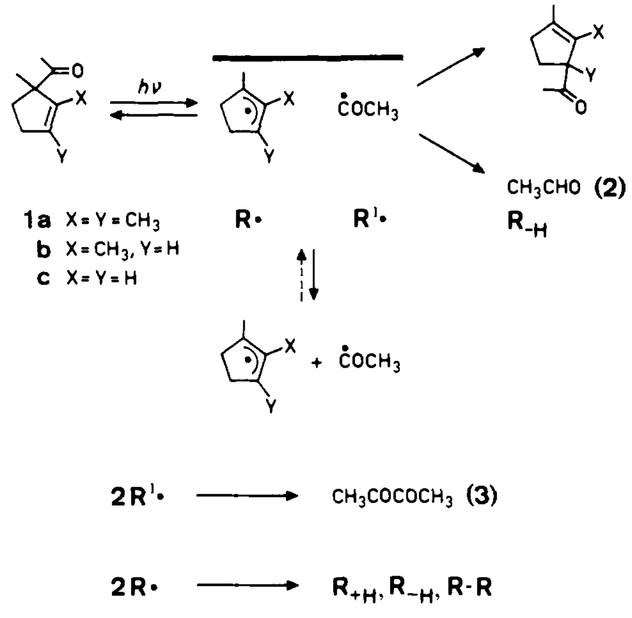


Figure 2. Photo-CIDNP effects of **1c**, the AS isomer, **2**, and **3** at −54 °C in CD_3OD (A) and 139 °C in $[D_{14}]$-diglyme (B). Dotted lines denote spin-equilibrated NMR intensities after irradiation, shaded areas solvent signals.

Scheme I



The CIDNP intensities decreased continuously on lowering the reaction temperature from 60 to 10 °C. At ~8 °C, the phases of all polarizations were inverted and the intensities again increased strongly with further decreases in temperature (Figure 1A).[18] This unique temperature effect indicates that, at lower temperatures, formation of acyl-allyl radical pairs, $\overline{R\cdot\cdot R'}$, from the triplet and/or free radicals competes with and ultimately overrides the corresponding reaction from S_1.[20] In principle, the observed CIDNP effects do not directly discriminate between reaction within $\overline{R\cdot\cdot R'}^3$ and reaction of free radicals diffused from $\overline{R\cdot\cdot R'}$.[1] However, any major contribution to CIDNP by $\overline{R\cdot\cdot R'}^1$-born free radicals would depend on temperature and viscosity changes opposite to those observed.[21] The temperature trend of the CIDNP must therefore definitely arise from an increase of $\overline{R\cdot\cdot R'}^3$ formation with decreasing temperature. Accordingly, a CIDNP enhancement factor of 5400 was determined at −54 °C for $CH_3C\mathit{H}O$,[22] which corresponds in magnitude to factors measured for well-established triplet reactions of radical pairs with similar *g*-value difference and hyperfine splitting constants.[12]

Photo-CIDNP of **1b**[10a] and **1c**[6] at ambient and lower temperatures (for **1c** see Figure 2A) had the characteristics of $\overline{R\cdot\cdot R'}^3$ and/or free-radical origin.[20,23] In the presence of tri-*n*-butylstannane as a free-radical scavenger (0.05–0.25 M in C_6D_{12}, room temperature), these effects were somewhat reduced but remained qualitatively unchanged. The effects persisted up to ~100 °C where they also inverted, indicating preferential formation of $\overline{R\cdot\cdot R'}^1$ at higher temperatures (for **1c** see Figure 2B). Over the whole temperature range, the AS products and the corresponding starting ketones (**1b,c**) exhibited polarizations with similar CIDNP intensities. This is evidence that the AS involves, at least in part, radical-pair formation as the primary step, leading to AS products and starting ketones with similar probabilities.

The results are readily explained if we assume that S_1 deactivation in **1a**–**c** occurs by both *temperature-activated α* cleavage to $\overline{R\cdot\cdot R'}^1$ (rate constant, $k_\alpha^1(T)$) and intersystem crossing to T_2 (k_{isc}). Substantial formation of $\overline{R\cdot\cdot R'}^3$ from T_2 is in accord with our earlier observation[6] that at 80 °C α cleavage from T_2 of **1c** and internal conversion to T_1 occur at similar rates ($k_\alpha^3 \geq k_{ic}$). A "low-temperature range" with $k_{isc} \gg k_\alpha^1(T)$ and a "high-temperature range" with $k_\alpha^1(T) \gg k_{isc}$, which exhibit preferential reactivity from T_2 and S_1, respectively, can thus be defined for all three β,γ-UK's. It should be stressed that the attribution of the AS reaction to $T_2(n,\pi^*)$ rather than $T_1(\pi,\pi^*)$ cannot be made by way of CIDNP alone: it is based on both the CIDNP evidence for an AS via $\overline{R\cdot\cdot R'}$[3] and the earlier result that T_1 of **1a–c** undergoes the oxadi-π-methane rearrangement[6,10a] *but not the AS.*

This reaction scheme is corroborated by fluorescence data. At 25 °C, in 3-methylpentane, the fluorescence quantum yield of **1a** is 3.6 times lower than that of **1c** ($\Phi_f = (9 \pm 3) \times 10^{-4}$), from which one may expect a similar ratio in singlet lifetimes for these ketones.[24] This significant difference in singlet lifetimes at 25 °C is in accord with the observed singlet CIDNP for **1a** and triplet CIDNP for **1c** at this temperature.

Our results unveil a novel aspect of β,γ-UK photochemistry and may provide a key to the understanding of the AS reaction. Studies on the temperature dependence of fluorescence[25] and product quantum yields are in progress to further quantify the present picture, and to rationalize the differences between **1a** and **1b,c**.

Acknowledgments. We thank Miss I. Gerlach and Dr. K. Hildenbrand for technical advice on the NMR spectrometer and Drs. Marlies and Manfred Mirbach for stimulating discussions.

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(13) CIDNP effects at 45 °C (*A* = enhanced absorption, *E* = net emission;[14] see Figure 1): **1a,** *A* for signals a, c, and e, *E* for b and d; **2**, *E* for CH_3, *A* for CHO. Similar effects were observed in CD_3CN and C_6D_{12} in the range 0–60 °C.

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(22) Determined with $t_1(CH_3C\mathit{H}O) = 2.1$ s, using a small flip angle, $\alpha \sim 20°$. See Schäublin, S.; Höhener, A.; Ernst, R. R. *J. Magn. Reson.* **1974,** *13,* 196–216.

(23) CIDNP effects at −54 °C (for denotations see footnote 13 and Figure 2): **1c** and AS isomer, *A* for a, a′, b, and $(CH_2)_2$ (δ 2.1–2.6), *E* for c, c′, d, and d′. Effects with the same phase were observed in CD_3OD, CD_3CN, and C_6D_{12} at temperatures ≲50 °C.

(24) This is a lower limit. Correction for the absorption coefficients of **1a** (λ_{max} 300 nm (ϵ_{max} 175)) and **1c** (λ_{max} 295 nm (ϵ_{max} 119)) increases the ratio of singlet lifetimes (τ_s) to

$$\frac{\tau_S(\mathbf{1c})}{\tau_S(\mathbf{1a})} = \left(\frac{\Phi_f(\mathbf{1c})}{\Phi_f(1\mathrm{a})}\right)\left(\frac{k_f(\mathbf{1a})}{k_f(\mathbf{1c})}\right) \approx \left(\frac{\Phi_f(\mathbf{1c})}{\Phi_f(\mathbf{1a})}\right)\left(\frac{\epsilon(\mathbf{1a})}{\epsilon(\mathbf{1c})}\right) \approx 5$$

(25) Preliminary results on the temperature-dependent luminescence of **1a** and **1c** strongly corroborate the present picture: Henne, A.; Hildenbrand, K.; Siew, N. P. Y.; Schaffner, K., unpublished work.

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Valence Electrons in Open-Shell Molecules: Experimental Studies Using Polarized Neutron Scattering

Sir:

Valence electron densities in crystals are being defined with increasing precision, very largely through the use of accurate X-ray diffraction measurements coupled to the neutron diffraction definition of nuclear positional and vibrational parameters (the X-N technique).[1] This method, although valuable, has limitations; for example, significantly accurate ($\sigma(\rho) \simeq 0.01$-0.02 e Å^{-3}) electron densities of the valence shells of transition metal complexes will remain difficult because of high local electron densities. An improvement in accuracy and interpretation can be achieved if the elastic scattering process could be referred exclusively to a relatively small number of the total electrons in the unit cell; this can be achieved via polarized neutron scattering experiments.

The electronic spin system of a paramagnetic single crystal can be ordered by the application of an external magnetic field (typically 1.5-5 *T* at 4.2 K) along the direction of polarization of the incident neutrons. For magnetic neutron scattering, only those magnetization components perpendicular to the scattering vector are effective. Therefore, only a limited three-dimensional set of magnetic structure factors is obtainable from any particular alignment of the crystal with respect to the applied magnetic field. Given $N(hkl)$ and $M(hkl)$ are the nuclear and magnetic structure factors, respectively; the observed Bragg intensities, $[N(hkl) \pm M(hkl)]^2$, result from coupling of the nuclear and magnetic scattering vectors. Precise magnetic structure factors can be obtained from "spin-flip" ratios,[2] $[N(hkl) + M(hkl)]^2/[N(hkl) - M(hkl)]^2$, of a large number of Bragg reflections whose nuclear structure factors have been determined from conventional diffraction experiments. Fourier inversion of the magnetic structure factors gives the magnetization density throughout the crystallographic unit cell, and maps of such densities have been described for simple ferro- and ferrimagnetic structures.[3] In the absence of independent orbital angular momentum in the ground state of an ion, spin density may be directly related to magnetization density. We now outline the power of the method for transition metal compounds of chemical interest and complexity.

The five complexes to which we have access to extensive sets of magnetic structure factors are manganese- and cobalt-phthalocyanine, the hexafluorochromium(III) anion,[4] the tetrachlorocobalt(II) anion, and aquabis(bipyridyl)di-μ-hydroxo-sulfatodicopper(II).

The magnetic structure factors may be analyzed quantitatively to provide local (atomic) spin densities and overlap charges in at least two ways. Firstly, the formulae for the

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