CIDNP from a 1,4-Biradical in the Norrish Type II Photoreaction of Valerophenone

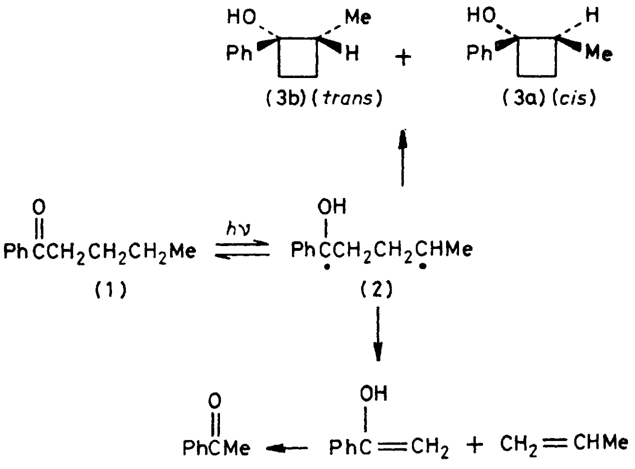
By ROBERT KAPTEIN,*[a] FRANS J. J. DE KANTER[a] and GÜNTHER H. RIST[b]

([a]*Department of Physical Chemistry, University of Groningen, Groningen, The Netherlands*, and [b]*Ciba-Geigy Ltd., Basle, Switzerland*)

Summary Biradical CIDNP observed in the title reaction indicates that two intersystem-crossing mechanisms are operative in the intermediate 1,4-biradical, one involving hyperfine coupling of the odd electrons with protons and the other, which is product selective, involving spin–orbit coupling.

THERE is little doubt that the 1,4-biradical (**2**) is an intermediate in the Norrish type II photoreactions of valerophenone (**1**).[1–5] For aromatic ketones the reaction occurs exclusively from the triplet state.[1] The biradical can be trapped by thiols, hydrogen bromide, and selenoketones.[1,4,5] Recently it has been directly observed in a laser flash-photolysis experiment.[3] In the absence of scavengers the lifetime of the triplet biradical (**2**) in benzene is about 100 ns and is likely to be determined by intersystem-crossing processes. However, it is not known whether intersystem-crossing involves hyperfine coupling (h.f.c.) with nuclear spins or spin–orbit coupling (s.o.c.), or both. Also, either a singlet biradical may be formed as a distinct intermediate or intersystem-crossing may lead directly to the singlet product energy surfaces. We report here the observation of chemically induced dynamic nuclear polarization (CIDNP) originating from biradical (**2**), from which information bearing on these questions can be obtained. CIDNP from small biradicals has previously been observed for a 1,5-biradical derived from camphor[6] and for the 1,3-biradical, cyclopentane-1,3-diyl.[7]

The Figure shows the 100 MHz ^{1}H n.m.r. spectra obtained before and during light irradiation of a 0·12 M solution of valerophenone in [$^2H_6$]benzene. Pronounced polarizations are observed for acetophenone [δ 2·1, emission (E)], and propene [absorption–emission (AE) multiplet effect with net absorption (A) for the CH proton (δ 5·8) and net E for the CH_2 (δ 5·0) and CH_3 (δ 1·52) moieties]. The cyclobutanols (**3**) show weaker polarizations: AE for the *cis*-compound (**3a**) at δ 0·59 and probably also AE for the *trans*-compound (**3b**) at δ 1·07, although this is less certain due to overlap. Valerophenone shows a decreased intensity for its α-CH_2 group at δ 2·58 and close inspection reveals that its CH_3 group acquires EA polarization during irradiation.†



It is first necessary to establish the origin of the polarization effects. The time-evolution of the effects indicates that the acetophenone emission is due to secondary photoreactions. At very short irradiation times it is weaker than that of propene, whereas during prolonged irradiation it

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† This was confirmed with a 100 MHz photo-CIDNP difference experiment carried out at the University of Groningen, in which light and dark spectra were taken alternately. Although the signal to noise ratio was less than that of the Figure, the resulting difference spectrum clearly showed an EA multiplet effect for the valerophenone CH_3 group.

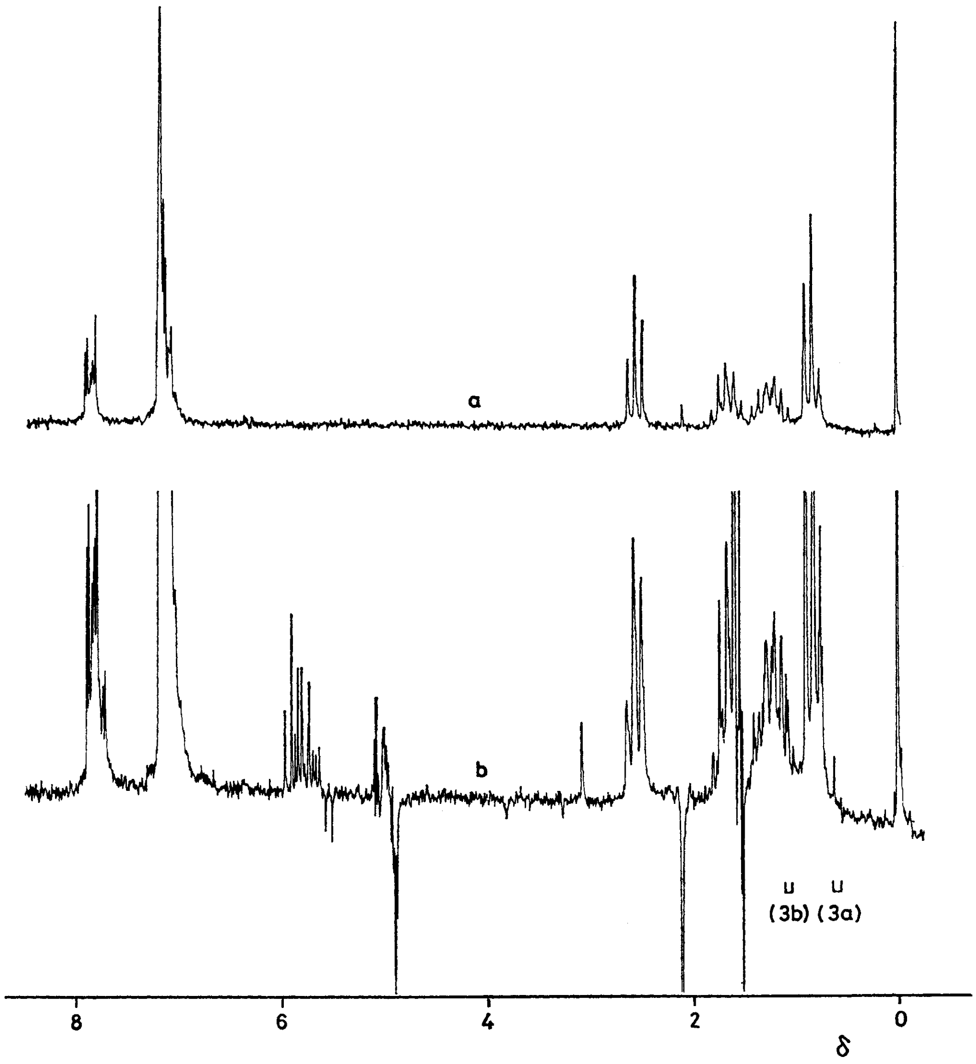

FIGURE. 100 MHz ^1H N.m.r. spectrum of 0·1 M valerophenone in [$^2H_6$]benzene (a) before and (b) during u.v. irradiation. The light from a 1000 W Philips high-pressure mercury arc was filtered with a $NiSO_4$–$CoSO_4$ solution. The light spectrum is the sum of five spectra of fresh valerophenone solutions each representing ten free induction decays (4 s repetition time, 22° flip angle).

becomes much stronger. Furthermore, the addition of small amounts of acetophenone (0·05—0·10 M) to the valerophenone solution gives rise to strong emission at δ 2·1 even at short irradiation times. It is likely that the emission of the α-CH_2 group of (**1**) is also due to a radical-pair, owing to the competing photoreduction reaction. However, the CIDNP effects for propene, the cyclobutanols, and the CH_3 group of (**1**) can only originate from the biradical (**2**). The polarization is purely of the T_0-S type as is usually observed for radical-pair reactions but only rarely[8,9] for biradicals, where the T_-—S mechanism is more common.[10] The T_0–S mechanism, being a spin-sorting mechanism in which no net nuclear polarization is generated, requires a nuclear-spin independent reaction path equivalent to cage escape in the case of radical pairs. As was first suggested by Closs,[8] this escape route is most likely provided by a spin–orbit coupling mechanism, which then must act specifically to generate certain products. According to the CIDNP rules[11] the CIDNP spectrum in our case would indicate that propene and the cyclobutanols (**3a** and **b**), which carry recombination-type polarization, are formed after h.f.c.-induced intersystem-crossing to a singlet-state biradical. Of course, this route is also open to the back reaction to valerophenone, but in addition must also involve an s.o.c.-induced surface crossing from specific triplet biradical conformations to the singlet product. This would provide the 'escape' route and yield the opposite multiplet effect.

A further requirement for the observation of T_0–S polarization is that the biradical spends sufficient time (of the order of, say, 1—10 ns) in conformations in which the singlet–triplet splitting (or exchange interaction, J) is very small. The absence of $T_\pm$-S-derived net polarizations suggests that in other conformations J is much larger than the Zeeman interaction, $g\beta B$, so that h.f.c intersystem-crossing is then ineffective. Although the same photoproducts are formed, either zero or very weak polarization effects were observed in MeOD and C_6D_{12}. It seems, therefore, that the conformational properties of the biradical depends on interactions with the solvent, which affect both intersystem-crossing and product yields.[1]

We were not able to detect biradical CIDNP during irradiation of γ-chlorobutyrophenone and γ-methoxybutyrophenone, although the Norrish type II products were formed in high yield. In these cases only the photoreductions gave rise to radical-pair polarization in the α-CH_2 group of the parent ketones. The absence of biradical polarization is possibly due to enhanced s.o.c. in the respective 1,4-biradicals and this seems to indicate that a delicate balance between h.f.s. and s.o.c. mechanisms is a prerequisite for CIDNP generation in biradical products.

The present data do not allow a more quantitative description at this stage. However, as will be reported elsewhere,[12] the underlying ideas are fully supported by a simulation of magnetic-field-dependent CIDNP curves for biradicals derived from cyclic ketones. This has been done by means of a modified theory for biradical CIDNP[10] in which the effects of spin–orbit coupling have been incorporated.[12]

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