Chemically Induced Dynamic Nuclear Polarization in the Photo-reactions of 4-Diazocyclohexa-2,5-dienones

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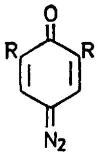
Summary Photolysis of 4-diazocyclohexa-2,5-dienones gives rise to CIDNP spectra indicating that cyclohexadienone carbene reacts in a singlet state, whereas its di-t-butyl derivative reacts as a triplet.

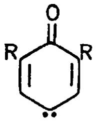
4-Diazocyclohexa-2,5-dienone (1a) and its 2,6-di-t-butyl derivative (1b),[1,2] when photolysed in solution, give rise to chemically induced dynamic nuclear polarization. The CIDNP technique can be applied to derive the spin multiplicity (μ) of carbenes involved in abstraction–recombination reactions,[3,4] if the e.s.r. parameters of the intermediates radicals are known.[5] Surprisingly, though both cyclohexadienone carbenes are ground-state triplets,[6] they appeared to react in different spin states: (2a) in a singlet state, (2b) as a triplet.

During the photolysis of (1b) in cyclohexane and tetrachloromethane we observed CIDNP signals due to the olefinic protons of (5b) (doublet, enhanced absorption) and

(6b) (singlet, emission), respectively. Both (5b) and (6b) are obviously coupling products. As for Δg, we assume that (3b) has a larger g value ($\Delta g > 0$) than that of the cyclohexyl radical (2·0027) and (4b) has a smaller g value ($\Delta g < 0$) than the trichloromethyl radical (2·0091). The sign of the hyperfine coupling constant (a) of the polarized nuclei in the radical precursors was determined by an additional CIDNP experiment.



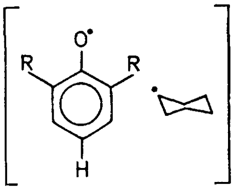
(1)



(2)

a; R = H b; R = Bu^t

We observed polarized (6b) in the photoreaction of (1b) with deuteriochloroform; in the reaction of (1b) with $CHCl_3$ (6b) was isolated in 8% yield. The olefinic hydrogens showed an emission signal. In $CDCl_3$, product (6b) can only be formed from radicals that are not generated in pairs, and whose coupling gives the same polarization as coupling of geminate triplet pairs.[7] Therefore, μ is known and Kaptein's rule indicates that the *meta*-hydrogens of phenoxy-radical (4b) have positive hyperfine coupling constants ($a > 0$). Assuming that chlorine substitution does not grossly change the spin density distribution in a phenoxy-radical, we also assign positive a values to the *meta*-hydrogens of (3b).



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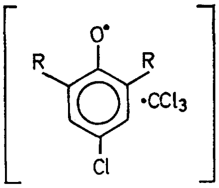

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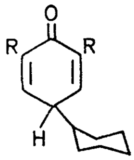

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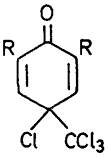

(6)

a; R = H b; R = Bu^t

With parameters as discussed above, the signal direction of (5b) and (6b) indicate that the *triplet* state of carbene (2b) is involved in abstraction reactions from both C–H and C–Cl bonds.

Photolysis of (1a) in CCl_4 gives rise to a CIDNP spectrum (Figure) which features *inter alia* a four-line (AB) spectrum (^3J *ca.* 10 Hz) in the olefinic region. The intensities and directions of these signals reflect the a-values of (4a) (a_{ortho} $-6{\cdot}6$ Gauss; a_{meta} $+1{\cdot}9$ Gauss)[8]. Therefore, we assign these signals to spin-polarized (6a), and a *singlet* state to the carbene (2a) involved in its formation.

Do the observed CIDNP signals represent major fractions of products (5) and (6)? For the reactions with CCl_4 this must be the case, since there appears to be no alternative one-step mechanism. For the reaction with cyclohexane, we cannot rule out the possibility that a fraction of (5b) is formed by one-step insertion of singlet-(2b). However, the enhancement of (5b) is comparable in magnitude with that of (6b) so that the observed CIDNP spectrum must represent more than an insignificant fraction of (5b).

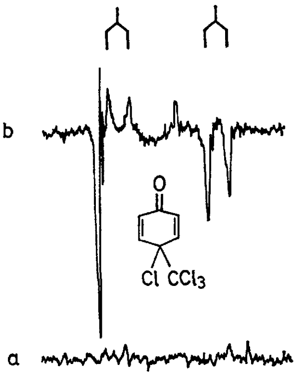

FIGURE. *N.m.r. spectra (olefinic region) of a solution of* (1a) *in* CCl_4 *before* (a) *and during* (b) *u.v. irradiation in a specially modified Jeolco* C-60 HL *probe.*

The contrasting behaviour of (2a) and (2b) is consistent with a delicate balance between the rates of reaction and of intersystem crossing of the carbenes (2) or of their photoexcited precursors (1). Since the presence of heavy atoms does not affect (2a) and (2b) in the same manner [(2a) and other ground-state triplet carbenes react with CCl_4 in their singlet states],[4] we conclude that a faster rate of reaction differentiates (2a) from (2b).

A scheme in which reaction rates determine the reacting spin state of (2) would also accommodate the apparent involvement of singlet-(2b) in the addition to *cis*- and *trans*-butene.[9] For various singlet carbenes rates of addition are faster than rates of insertion. Therefore, it is possible that for singlet-(2b) addition competes favourably with intersystem crossing, whereas insertion competes less effectively.

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