

CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION (CIDNP) IN
THE CORRELATED RADICAL PAIR PRODUCT OF THE REACTION
OF ETHOXYNITRENE WITH TRANS-DECALIN

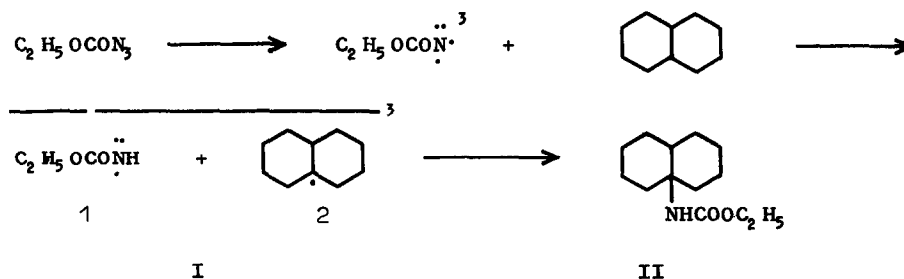
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Chemically induced dynamic nuclear polarization has been used to study triplet^{1,2} and singlet³ carbene reactions proceeding via radical mechanisms. Nitrenes have been shown in general to behave in a similar fashion to carbenes.⁴

We would like to report the first example of polarization in the NMR spectrum of the correlated radical pair product arising from the insertion of triplet ethoxynitrene into the tertiary C-H bond of trans-decalin. Thermolysis of ethyl azidoformate in trans-decalin at 135^o C in the NMR probe produces II via collapse of the triplet radical pair I.



It has been previously postulated⁴ that this reaction proceeds via the triplet radical pair involving the tertiary decalin radical 2, and our results are consistent with this contention.

The NMR signal of the proton attached to the nitrogen in II is observed as emission, (see Figure).



Figure : Polarised N-H resonance of (II) at 135°

Although the typical nitrogen-14 quadrupole broadening is evident, direct nitrogen-hydrogen coupling is observed ($J_{14N-1H} = 4.0$ Hz). Observation of a broad triplet ($I_N = 1$) is consistent with reduced quadrupole broadening at higher temperatures due to an increase in intramolecular motions.

Application of CIDNP⁶ theory reveals that since the electron g-factor of radical 2 is less than that of 1, the isotropic hyperfine interaction constant A_H (for the hydrogen on the nitrogen) is negative. Since CIDNP experiments have shown the unexpected result that singlet carbenes can also produce radical pairs³ and therefore polarized correlated products, further work is necessary to evaluate the relative role of singlet nitrenes in radical reactions.

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