Detection of Carbenes by Electron Spin Resonance Spectroscopy: 'Triplet Trapping'

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Summary Triplet carbenes can be converted into relatively long-lived iminoxyl radicals by reaction with nitric oxide and so be detected indirectly by e.s.r. spectroscopy.

Evidence for the transient formation of carbenes in chemical reactions is usually drawn from product studies,[1] reference being made to a known reaction(s) of carbenes and the effect which additives (sensitisers, quenchers) have on the product distribution. Although direct observation of triplet carbenes in solution by e.s.r. is not possible we now show that such species can be detected indirectly by a simple modification of the now well established 'spin trapping' method.[2]

'Spin trapping' involves the conversion of a transient radical into a long-lived one (usually nitroxide) by reaction with a diamagnetic scavenger (usually nitrone or nitroso-compound) [equation (1)]. For the analogous 'triplet trapping' it is necessary to replace the diamagnetic scavenger by a long-lived paramagnetic scavenger, the most convenient for carbene trapping being nitric oxide [equation (2)]. This gives long-lived iminoxyl radicals[3] from whose e.s.r. spectra it is usually possible to obtain structural information about the first-formed carbene.

$$\mathrm{R}\cdot + \mathrm{R'NO} \rightarrow \mathrm{R'N(\dot{O})R} \qquad (1)$$

$$\dot{\mathrm{T}}\cdot + \mathrm{NO} \rightarrow \mathrm{T{=}NO}\cdot \qquad (2)$$

The Table lists some of the carbenes which we have detected in this way. In each case a thoroughly degassed solution of the carbene precursor in a hydrocarbon solvent was saturated with nitric oxide and then irradiated (mercury vapour lamp) in the cavity of the spectrometer. Since some diazo-compounds react with nitric oxide at room temperature[4] it was sometimes necessary to carry out the experiment at a lower temperature when no iminoxyl was detected until irradiation commenced. Significantly, sensitisation of the diazomalonate photolysis with benzophenone, a procedure known[5] to increase the proportion of triplet carbene, greatly increased the concentration of iminoxyl radicals. The spectra of the above iminoxyls were much better resolved, less contaminated by nitroxide signals and more lasting than those obtained by the more usual oxidation of oximes with lead tetra-acetate.[3] Evidence adduced for carbene participation by 'triplet trapping' should of course be treated with the same caution as that recommended[6] for 'spin trapping' results since neither method is quantitative.

We have not been able to find conditions under which triplet nitrenes will react with nitric oxide to give detectable concentrations of diazinoxyls[7] (RN=NO·) and hence are examining other paramagnetic scavengers as 'triplet traps' for such species.

TABLE

Carbenes trapped as iminoxyls[a] with nitric oxide

Carbene	Source and solvent[b]	Temperature/°C
$\mathrm{Me\ddot{C}Me}$	(A)	−40
$\mathrm{Ph\ddot{C}H}$	(A)	22
$\mathrm{Ph\ddot{C}Et}$	(A)	−50
$\mathrm{Ph\ddot{C}C_6H_4OMe}$-*o*	(A)	22
Fluoren-9-ylidene	(A)	22
Tetraphenylcyclopentadienylidene	(B)	22
Cyclohexanylidene	(C)	22
$\mathrm{PhCO\ddot{C}H}$	(A)	10
$\mathrm{EtO_2C\ddot{C}CO_2Et}$	(D)	22
Thioxanthen-10-ylidene *SS*-dioxide	(B)	22

[a] Coupling constants are similar to those previously published; details will be published elsewhere. [b] Irradiated with 100 or 1000 W high-pressure mercury lamp. (A), from diazo-compound in light petroleum; (B) from diazo-compound in light petroleum–benzene; (C), from diazarine in light petroleum; (D) from diazo-compound or diazarine in light petroleum.

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