

## Photoselection in Carbene Formation by the Use of Polarized Light

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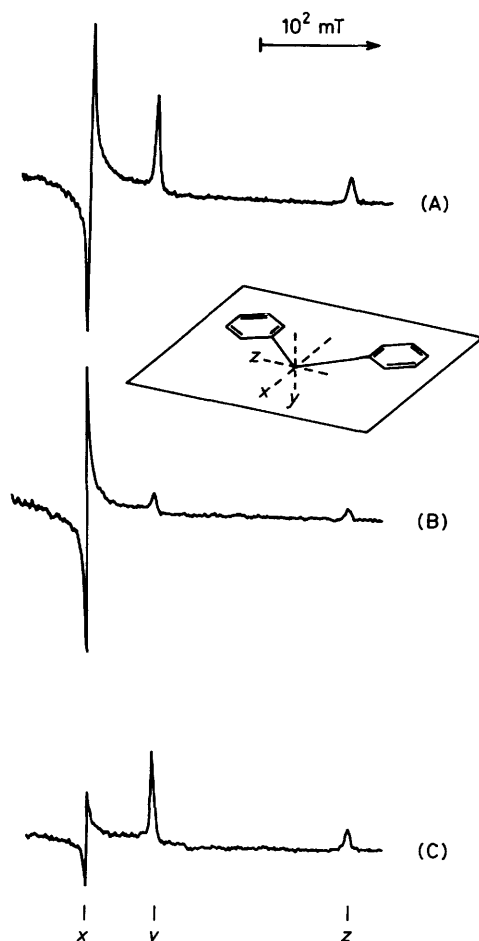
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Photolysis of diaryldiazomethanes in matrices using polarized light is highly selective, so that the e.s.r. spectra of the resulting carbenes show a remarkable degree of polarization.

Little appears to be known about the mode of light absorption by diaryldiazomethanes, even though they are the principal photochemical sources of diarylcarbenes.<sup>1</sup> In this work, we have used plane polarized light to photolyse solid solutions of diaryldiazomethanes. E.s.r. spectra of the resulting carbenes were themselves polarized to a remarkable degree and

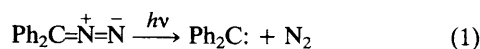
revealed the direction of light absorption by the starting diazo compound.

Direct photolysis of diphenyldiazomethane leads to loss of nitrogen and formation of the singlet carbene,<sup>1</sup> reaction (1). Intersystem crossing to the triplet groundstate<sup>2</sup> takes place within  $10^{-9}$  s. When the diazo compound ( $2 \times 10^{-3}$  M) was



**Figure 1.** (A) E.s.r. spectrum of diphenylcarbene when generated by photolysis with unpolarized light. (B) Spectrum obtained using polarized photolysis (electric vector of light parallel to magnetic field). (C) Spectrum obtained after sample rotation through  $90^\circ$ .

photolysed in a glass of 2-methyltetrahydrofuran at 4 K, the spectrum of the triplet carbene<sup>3-5</sup> was detected by e.s.r. spectroscopy, Figure 1(A). The *x*, *y*, and *z* lines of the spectrum correspond to the molecular directions shown in Figure 1.<sup>4,5</sup>



We repeated the above experiment using polarized light from an argon laser ( $\lambda = 488 \text{ nm}$ ) to photolyse the diazo compound. To ensure a high degree of polarization, the laser output was also passed through a polarizing filter. The axes of the magnetic field and of the laser beam were perpendicular in a horizontal plane while the sample could be rotated about a vertical axis.

The plane of polarization was first arranged so that it was parallel with the magnetic field of the e.s.r. spectrometer. Those molecules of diphenyldiazomethane for which the transition moments for light absorption were approximately

parallel with the electric vector of the light, were preferentially photolysed. The photolysis was stopped and the persistent e.s.r. spectrum of the resulting carbene showed a dramatic enhancement in its *x* line when compared with those for the *y* and *z* directions, Figure 1(B). This meant that the carbenes were preferentially formed with their *x* directions parallel to the magnetic field. Molecules of the parent diazo compound must therefore have absorbed the electric vector of the light in the same molecular direction, *i.e.* along that of the C–N–N bond.<sup>4</sup>

To confirm the assignment, the tube was rotated through  $90^\circ$  about an axis perpendicular to the magnetic field. The *x* direction for the matrix isolated carbenes was then at right angles to the magnetic field. As expected, the intensity of the *x* component of the spectrum was dramatically reduced while those of the *y* and *z* lines were enhanced, Figure 1(C).

The sample was annealed so as to destroy the signal and was rephotolysed at 4 K, but with the plane of polarization arranged so that it was perpendicular to the magnetic field. Diazo molecules with their C–N–N bonds perpendicular to the field were therefore preferentially photolysed. The resulting carbenes had their *x* directions perpendicular to the field and their *y* and *z* directions arranged randomly in the horizontal plane of the field. Accordingly, the *y* and *z* lines were enhanced and rotation about the axis perpendicular to the field produced no significant change in the spectrum.

Similar experiments with dimesityldiazomethane<sup>6</sup> led again to the conclusion that diaryldiazomethanes absorb light in the direction of the C–N–N bond. The most surprising feature of the present experiments was the dramatic polarization achieved in the e.s.r. spectra of the carbenes. Previous i.r. and u.v. experiments, on polarized photolysis of diazocyclopentadiene<sup>7</sup> in matrices of nitrogen and carbon monoxide, revealed some anisotropy in the residual diazo compound. However, that in the resulting carbene was not persistent. The results suggest that the use of more rigid matrices coupled with e.s.r. detection may provide a very effective method for determining the directional properties of light absorption when photolysis gives rise to triplet states.

One of us (I. R. D.) thanks the Carnegie Trust for the Universities of Scotland for the financial support which made this collaboration possible.

Received, 11th November 1985; Com. 1582

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