ON THE EFFICIENCY OF INTRAMOLECULAR TRAPPING OF CARBENES AND BIRADICALS BY A
PROXIMATE METHYL GROUP.

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The formation of fulvenallene, (1), from the gas phase pyrolysis of indazole[1,2] poses an
interesting mechanistic dichotomy. Thus, depending upon the seat of migration of the hydrogen
atom from position 1, a "biradical" pathway (a) or a "carbene" pathway (b) may be taken[2,3]
(SCHEME, R = H). Incorporation of a methyl group in the 3-position of N-deuterioindazole led
to the intramolecular trapping of the two intermediates (2) and (3) giving the labelled styrenes.
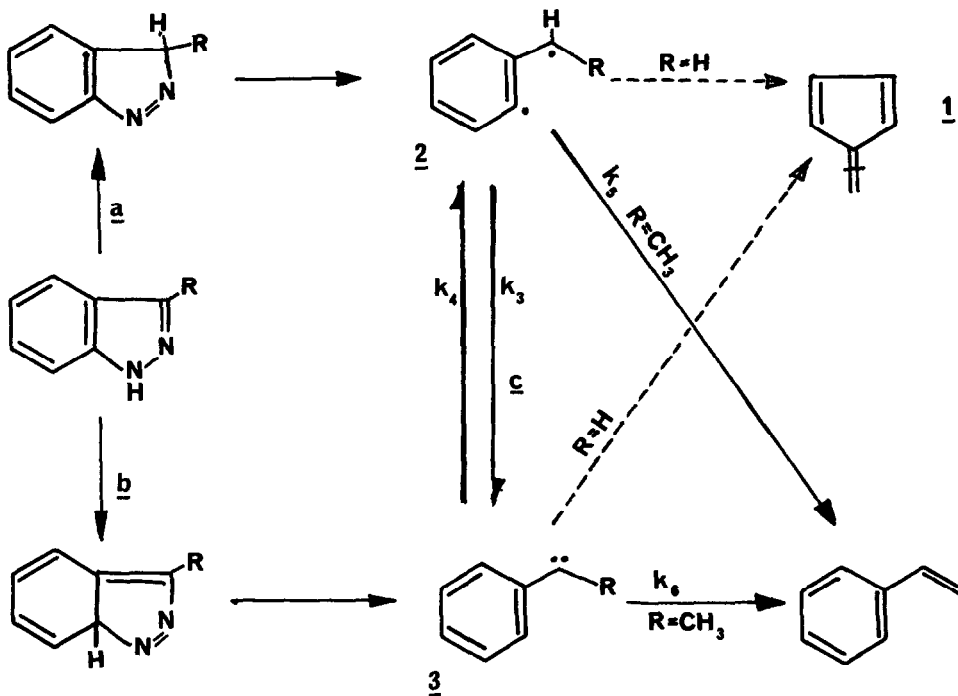
SCHEME   R = H, CH_3; CD_3.

Assay of the deuterium content in the ring and in the exocyclic double bond gave the result that the "biradical" pathway occurred to the extent of 82.5% between 700° and 760°, 0.05 mm. However the correctness of our conclusions depends on the validity of the tacit assumption that little or no interconversion between the biradical (2) and the carbene (3) occurs (pathway (c) of the SCHEME) - in other words, that the methyl group acts as a very efficient trap for carbenes and biradicals. Although there is some qualitative evidence in the literature to support this assumption[4,5] we decided to obtain quantitative evidence concerning this point.

The dry sodium salt of the tosylhydrazone derivative[6] of acetophenone (4) (85% tri-deuteriated at the methyl group[7]) was heated at 95° and the 1-phenyldiazoethane was led directly into the furnace[8] at 630° or 720° at 0.05 mm. Under these conditions the carbene intermediate (3; R = CD_3) is generated. Direct trapping of this carbene by the methyl group would give styrene labelled with deuterium solely at the olefinic sites (5). Leakage to the biradical (2; R = CD_3) and subsequent trapping of this intermediate generates styrene with deuterium incorporated into the ortho position of the aromatic ring (6). Assay of the deuterium content of the
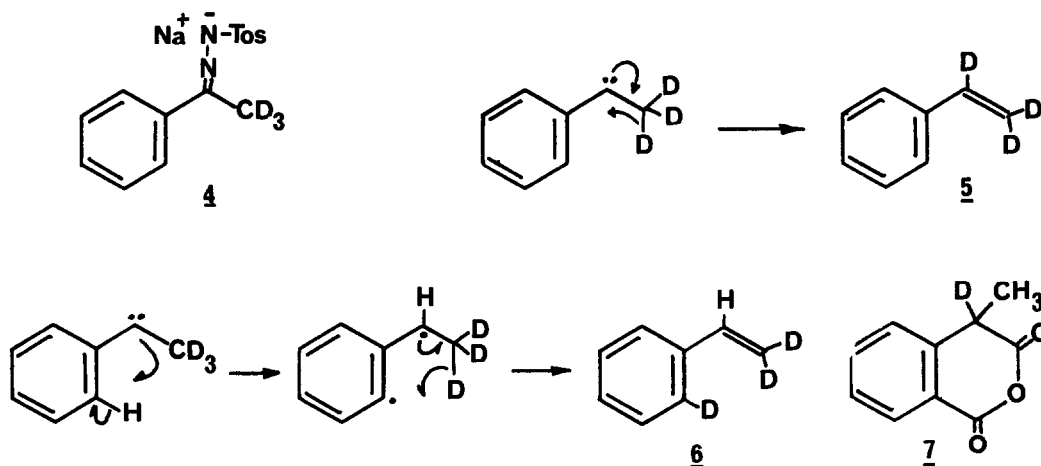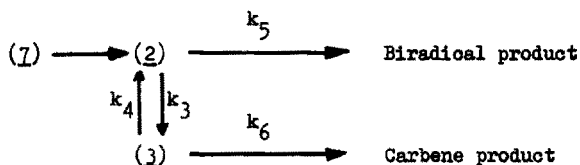

ring may be achieved through conversion of the styrene to benzoic acid.[9] As we have shown previously[1] that essentially all of the deuterium label in the ring is located at the ortho position it was only necessary then to estimate the total deuterium content of the styrene and the benzoic acid by low voltage mass spectrometry. The results are presented in the Table. For the biradical generator we chose the D-labelled methylhomophthalic anhydride (7) since Spangler and Kim have shown that, on gas phase pyrolysis, homophthalic anhydride is converted into

<div align="center">Table</div>

Compound	Temp.	% D in styrene	% D in benzoic acid[10]	% biradical pathway	% carbene pathway
(2)	630°	85.4	1.8	2.1	97.9
(2)	720°	84	4.4	5.2	94.8
(3)	720°	26.7	2.2	91.8	8.2

fulvenallene.[11] Pyrolysis of this compound[12] at 720°, 0.05 mm gave the expected styrene and the results are given in the Table.

We define the efficiency of the methyl group in trapping the biradical (2) and the carbene (3) in terms of the ratios $k_5/(k_3 + k_5)$ and $k_6/(k_4 + k_6)$ respectively (see SCHEME). We make the assumption that equilibrium conditions prevail in the furnace which implies that, at constant temperature and pressure, the energies of the biradical (2) and the carbene (3) are independent of the chemical nature of their generators. Thus the relevant rate constants remain unaltered for the generators (4) and (7) and the kinetic scheme for the direct generation of the biradical (2) may be represented by:

$$(7) \longrightarrow (2) \xrightarrow{k_5} \text{Biradical product}$$

$$k_4 \Big\uparrow \Big\downarrow k_3$$

$$(3) \xrightarrow{k_6} \text{Carbene product}$$

and a similar scheme may be written for the carbene generator. From these two schemes, and using the steady state approximation, two equations may be derived:

Biradical Generator $\quad \dfrac{\text{% biradical product}}{\text{% carbene product}} = \dfrac{k_5}{k_3}\left[1 + \dfrac{k_4}{k_6}\right]$

Carbene Generator $\quad \dfrac{\text{% Carbene product}}{\text{% Biradical product}} = \dfrac{k_6}{k_4}\left[1 + \dfrac{k_3}{k_5}\right]$

from which the trapping efficiencies may be readily obtained. We find that, at 720° (0.05 mm), the methyl group traps the biradical (2) with 91% efficiency and that the carbene (3) is trapped with 94% efficiency. We conclude, therefore, that the methyl group does indeed trap carbenes and biradicals efficiently.

Finally, the possibility that a significant proportion of the ring label was derived from scrambling in styrene from the double bond into the aromatic nucleus was eliminated by

subjecting α-D-styrene to the same pyrolysis conditions. At 720°, only 0.6% scrambling into the aromatic ring was observed with no overall loss of deuterium. However at 800°, an overall loss of 13% deuterium resulted with scrambling into the aromatic ring occurring to the extent of 15%.

References and Footnotes

1.   J.D. Crow, A.R. Lea and M.N. Paddon-Row, Tetrahedron Letters, 2235 (1972).

2.   W.D. Crow and M.N. Paddon-Row, Aust. J. Chem., 1973, in press.

3.   J.D. Crow and M.N. Paddon-Row, Tetrahedron Letters, 3207 (1972).

4.   G.L. Closs, L.R. Kaplan and V.I. Bendall, J. Amer. Chem. Soc., 89, 3376 (1967).

5.   J.J. Baron, M. Jones, Jr. and P. Gasper, ibid., 92, 4739 (1970); E. Hedaya and M.E. Kent, ibid., 93, 3283 (1971); G.G. Vander Stouw, A.R. Kraska and H. Shechter, ibid., 94, 1655 (1972).

6.   G.M. Kaufman, J.A. Smith, G.G. Vander Stouw and H. Shechter, J. Amer. Chem. Soc., 87, 935 (1965).

7.   Prepared by refluxing acetophenone with D_2O and K_2CO_3.

8.   W.D. Crow and R.K. Solly, Aust. J. Chem., 19, 2119 (1966).

9.   By oxidation of the styrene with $H_2SO_4/KMnO_4$.

10.   Corrected for natural abundance.

11.   R.J. Spangler and J.H. Kim, Tetrahedron Letters, 1249 (1972).

12.   The dimethyl   ester of homophthalic acid was methylated ($NaNH_2$/liq.NH_3/MeI) and subsequently deuteriated (NaOMe/MeOD) and hydrolyzed to the diacid. Conversion to (3) was effected by dicyclohexylcarbodiimide.