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# ON THE MECHANISM OF THE FORMATION OF FULVENALLENE FROM THE GAS PHASE PYROLYSIS OF INDAZOLE. THE GAS PHASE PYROLYSIS OF N-DEUTERIO-3-METHYLINDAZOLE.

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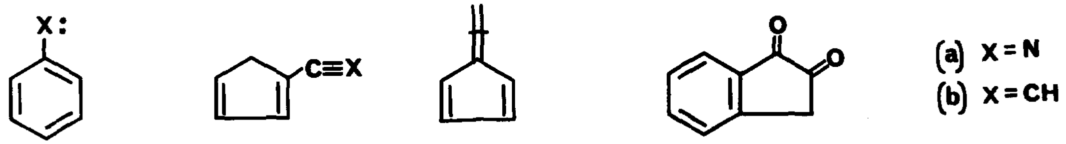
A significant property of phenylnitrene and phenylcarbene generated in the gas phase at temperatures $\geq 700^{\circ}$ is their ability to undergo ring contraction to give cyanocyclopentadiene[1,2] (2a) and fulvenallene[6] (3) plus ethynylcyclopentadiene (2b) respectively. However it




1 2 3 4

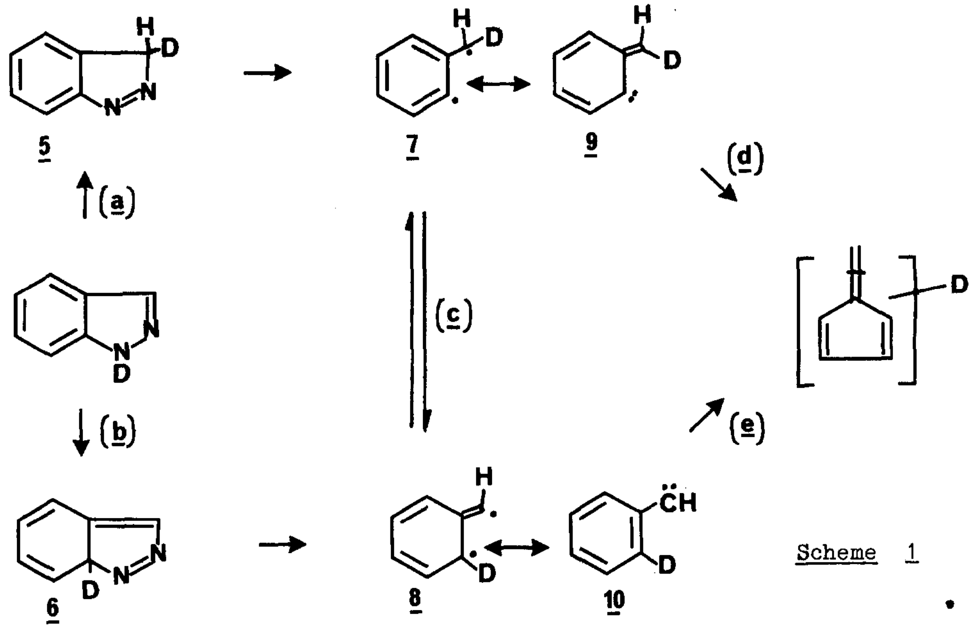
was discovered subsequently that the gas phase pyrolysis of benzotriazole[7] yielded (2a) and that indazole[8] and 1,2-indanedione[9] (4) both gave (3) in good yields. The mechanisms of these reactions are similar and may be discussed in terms of the decomposition of indazole, the more likely pathways being outlined below in Scheme 1.

Pathway (a)-(d) ("biradical" pathway) proceeds *via* 3H-indazole (5) with loss of nitrogen to give an intermediate biradical (7) which may be identified with a particular electronic state of the carbene (9). Formation of fulvenallene from this intermediate may be rationalized in terms of a Wolff rearrangement[7].

Pathway (b)-(e) ("carbene" pathway) involves an H-shift to give 8H-indazole (6) with subsequent loss of nitrogen to give (8) which may be identified with a particular electronic state of phenylcarbene (10).

Finally both pathways may be interrelated *via* the operation of a "leakage" mechanism (c).

An inspection of Scheme 1 reveals that in the pyrolysis of N-deuterioindazole a distinction between the various pathways is maintained up to and including the formation of (7-9) and (8-10). An analysis of the deuterium distribution in the resulting fulvenallene would be useless

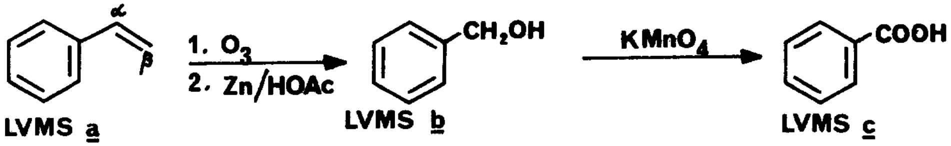



Scheme 1

because we would expect extensive deuterium scrambling in fulvenallene itself (e.g. via (2b)); moreover our labelling studies on phenylnitrene[10a] and phenylcarbene[10b] have demonstrated the occurrence of extensive hydrogen shifts prior to the ring contraction of (10).

A satisfactory way out of this difficulty may readily be attained by the judicious introduction of a substituent in the 3-position of N-deuterioindazole which would trap intramolecularly (7) and (8) as soon as they are formed. Accordingly we have studied the gas phase pyrolysis of N-deuterio-3-methylindazole, since the methyl group is known to trap efficiently both 1,3-biradicals[11a] (7a) and carbenes[11b] (8a) giving styrenes. Thus the biradical pathway leads to α-deuteriostyrene (11a) whereas the carbene pathway produces 2-deuteriostyrene (11b).


Pyrolysis of N-deuterio-3-methylindazole (92% D by p.m.r.) at 0.05-0.08 mm between 630° and 800° gave styrene[12] in good yields (ca 80%). The deuterium content was analysed according to the plan below, using low voltage mass spectrometry (LVMS), and the results are summarized in the Table.

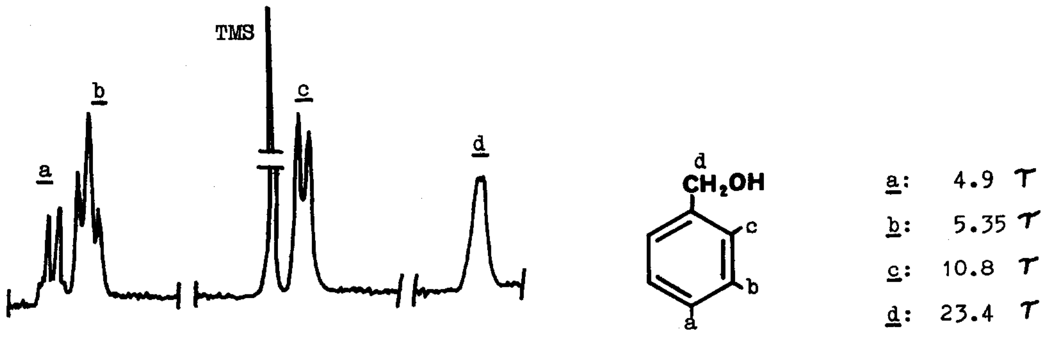



| Temp. | Styrene % D (a) | $\phi CH_2OH$ % D (b) | % D at β:(a)-(b) | % D in aromatic (c) | % D at α:(b)-(c) | "biradical" % | "carbene" % |
|---|---|---|---|---|---|---|---|
| 630 | 93 | 93 | 0 | 15.5 | 77.5 | 83.3 | 16.7 |
| 700 | 93 | 93 | 0 | 16.3 | 76.7 | 82.5 | 17.5 |
| 760 | 91 | 82.1 | 8.9 | 15.6 | 66.5 | 82.8 | 17.2 |
| 800 | 87 | 76 | 11 | 18.5 | 57.5 | 78.6 | 21.4 |

It is observed that at 760° and 800° deuterium is found at the β-position of styrene and that there is a decrease in the overall deuterium content. However, styrene labelled at the α-position behaves analogously[13] when subjected to these conditions and accordingly the contribution of the biradical pathway was computed on the basis of the total deuterium content at both α- and β-positions of styrene.

The distribution of deuterium over the aromatic ring was determined by examination of the $^1H$ nmr spectra (Figure) of the benzyl alcohols (40 mg) in the presence of the paramagnetic shift reagent $Pr(fod)_3$[14] (200 mg) in $CDCl_3$ (0.4 ml). Repeated integration of the signals revealed that ~ 95% deuterium was located at the ortho positions[15] as predicted.

Figure: 60 MHz $^1H$ nmr spectrum of benzyl alcohol (760° pyrolysis) in $CDCl_3$ with $Pr(fod)_3$



We conclude that, over the temperature range studied, there exists a duality of mechanism operating for the gas phase decomposition of 3-methylindazole and that the major pathway (d2%) proceeds via the "biradical" (7-9). The minor pathway may be rationalized in terms of the intermediacy of the "carbene" (8-10) which may be formed from either paths (b) or (c).

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