Tetrahedron Letters No. 22, pp 2235 - 2238, 1972. Pergamon Press. Printed in Great Britain.

GAS PHASE PYROLYSIS OF ANNELATED PYRAZOLES: A DUALITY OF MECHANISM IN AROMATIC RING CONTRACTION

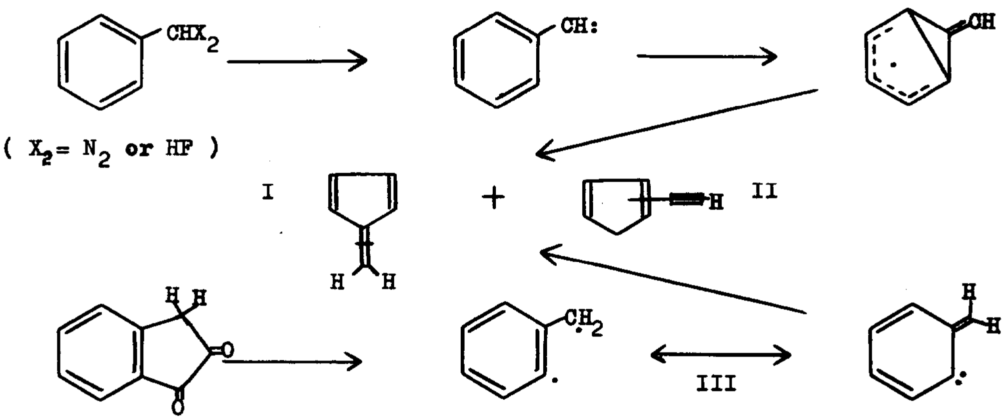
W. D. Crow, A. R. Lea and M. N. Paddon-Row

(Chemistry Department, Australian National University, Canberra, A.C.T.)

(Received in UK 7 April 1972; accepted for publication 27 April 1972)

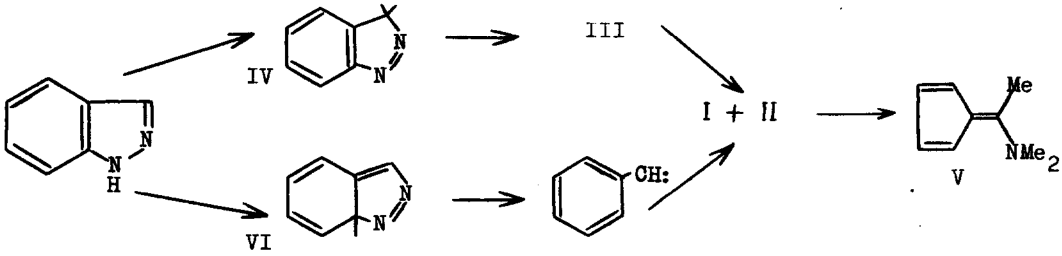
Hedaya and co-workers[1,2] have described the formation of fulvenallene (I) and ethynylcyclopentadiene (II) from the flash vacuum pyrolysis of benzyl fluoride, phenyldiazomethane[3] and indane-1,2-dione. Two distinct mechanisms, involving phenylcarbene and the biradical III respectively, were proposed for generation of I and II from the different precursors (CHART 1.). An analogous duality of mechanism had also been proposed for the corresponding case of formation of 1-cyanocyclopentadiene from phenyl azide[4] and 1(H)-benzotriazole[5]. The distinction between the mechanisms is one of H-shifts, either in the precursors or in the intermediates themselves.

CHART 1.



Our previous work with benzotriazole[5] (a tautomeric system) suggested the obvious extension to indazole as a potential source of the biradical III; all that is required is the necessary H-shift to IV prior to loss of nitrogen.

Commercial grade indazole was therefore pyrolysed at 0.01-0.05 mm over the temperature range 600-950°. Between 700° and 800° yields of I+II between 55% and 68% were obtained (Yields by NMR using C_6H_{12} as calibrant, and by trapping with Me_2NH[6]); the reaction seems to constitute a better route to enamines such as V than that currently in vogue[7]. It will be appreciated that, in the C_7H_6 system, evidence for the alternative H-shifts (to IV or VI) cannot be obtained



by D-labelling, due to the high mobility of H in compounds such as I and II. We have, however, extended the reaction further to the C_6H_5N system for comparison with other generators of phenylnitrene and pyridylcarbenes[8], and in this case evidence for the duality of mechanism can be observed in the products.

Pyrazolo[3,4-b]pyridine (VII)[9] was pyrolysed in the gas phase at 650-850°/ 0.03 mm. , collecting the volatile products in liquid N_2 traps. Analyses were made by NMR/IR/MS on the freshly thawed condensates, and structures were assigned for known compounds by comparison with authentic specimens. Between 700° and 760° a yield of ca. 65% 1-cyanocyclopentadiene (XI) was obtained, with a mixture of three highly reactive compounds which have so far resisted all attempts at separation. Separation by GLC was unsuccessful, due to reaction on the column, and treatment with Me_2NH gave only black tars even under conditions where fulvenallene reacted smoothly to give the enamine V (-30° under N_2). This fraction became a minor component of the mixture at higher pyrolysis temperatures, but represented some 45% of the total pyrolysate at 650°, the rest being largely XI. Under these conditions, the NMR/IR/MS data are consistent with the structural assignments as the azafulvenallenes XII and XIII and an ethynylpyrrole XIV:

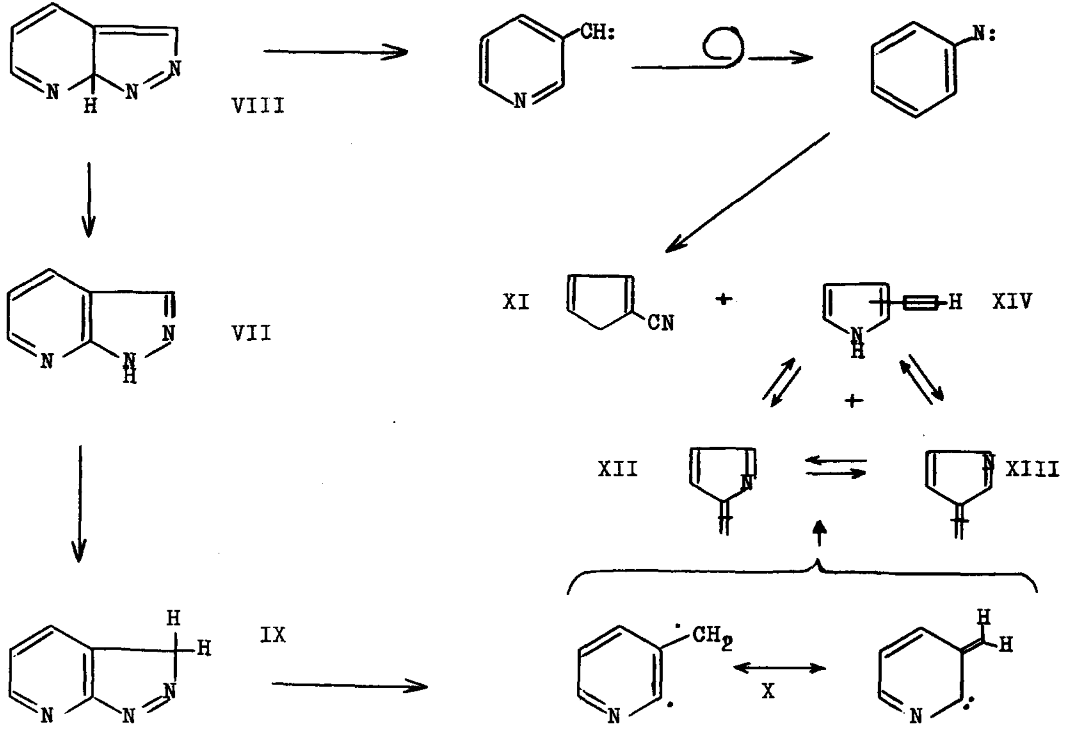
NMR (τ, CCl_4): 6.97s, C:C.H; 4.92s/4.80s, :C:CH_2; 3.03m, 3.33m (partly obscured by signals for XI), 3.53m, 3.85m, ring H.

IR (cm^{-1}, CCl_4): XIV - 3460 NH, 3300 C:C.H, 2110 C:C; XII-XIII - 1940/1970

C:C:C.

These assignments must be considered tentative at this stage, although it is difficult to propose alternatives; more definite evidence will depend on the isolation of these sensitive compounds. The appearance of XI is quite consistent with our earlier observations[10] on the isomerisation of the pyridylcarbenes to phenylnitrene, and leads to the logical conclusion that this product was formed from 3-pyridylcarbene by way of the intermediate species VIII. as shown in CHART 2. It will be noted that no fraction corresponding to XII-XIV resulted from generation of 3-pyridylcarbene by other routes[10], suggesting that these compounds are most probably generated from another precursor. The alternative pyrazolo[3,4-b]pyridine tautomer IX would appear to constitute the obvious choice, leading as it does to the biradical X which is analogous to III and the iminocarbene formed from the pyrolysis of 1(H)-benzotriazole[5]. Wolff rearrangement of X would lead to the azafulvenallene XII, and a ring-walk of the C_2H_2 chain would equilibrate this with its other isomer XIII. The ethynylpyrrole

CHART 2.



components are, of course, tautomeric with these and require no special explanation.

The details of the mechanism of ring contraction operating in phenylcarbene and phenylnitrene are matters for conjecture, and likely to remain so for some time. We have recently shown[11] that complete randomisation of C_7 occurs in phenylcarbene as a process preceding ring contraction; it follows that isotopic labelling is unlikely to produce any definite conclusions as to atom movements. In the related case of phenylnitrene, our evidence[12] is not quite so conclusive, but the same process of H-shifts and atom-scrambling is strongly indicated. In both cases we believe that the randomisation process is a consequence of the energy carried by the carbene or nitrene, rather than an intrinsic property of the species. In the case of the biradical mechanisms discussed, it remains to be seen whether a similar randomisation process precedes ring contraction, and experiments towards this end are now in progress.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of this project by the Australian Research Grants Committee. One of us (A.R.L.) is indebted to the Australian National University for the award of a Research Assistantship.

REFERENCES

1. P.Schissel, M.E.Kent, D.J.McAdoo and E.Hedaya, J.Amer.Chem.Soc., 92, 2147 (1970)
2. E.Hedaya and M.E.Kent, J.Amer.Chem.Soc., 92, 2149 (1970)
3. s.a. C.Wentrup and K.Wilczek, Helv.Chim.Acta, 53, 1459 (1970)
4. W.D.Crow and C.Wentrup, Tetrahedron Letters, 4379 (1967)
5. W.D.Crow and C.Wentrup, Chem.Comm., 1026 (1968); Tetrahedron, 26, 3965 (1970)
6. Yields quoted are based on the amount of indazole pyrolysed.
7. K.Haffner, K.H.Vöpel, G.Ploss and C.König, Annalen, 661, 52 (1963)
8. W.D.Crow, M.N.Paddon-Row and D.S.Sutherland - preceding communication
9. T.L.P.Hatt and J.D.R.Vass, Chem.Comm., 293 (1966)
10. W.D.Crow and C.Wentrup, Tetrahedron Letters, 6149 (1968) and ref. 8
11. W.D.Crow and M.N.Paddon-Row, J.Amer.Chem.Soc., 94, in press (1972)
12. W.D.Crow and M.N.Paddon-Row, Tetrahedron Letters, preceding communication.