Cyanocyclopentadienes by Pyrolysis of Isatins and 1*H*-Benzotriazoles

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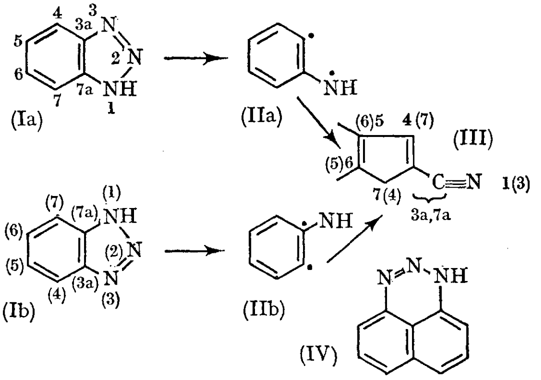
DURING studies on the mechanisms of high-energy reactions, we have examined the gas-phase pyrolysis of aromatic azides,[1] which results in generation of singlet nitrene, with subsequent ring contraction to 1-cyanocyclopentadienes. The initial experiments showed that triazoloarenes gave similar products, and this reaction has been shown to be of general application,[†] proceeding (Scheme 1) in high yield (80—100%) at 500—800°. The experimental procedure has been described.[2] Thus methyl- and fluoro-substituted benzotriazoles (I) yield the corresponding compound (III).[‡] It was found necessary to use only a low degree of conversion in investigating the mechanism (pyrolysis at 500°/0·01 mm.), since at higher temperatures H- and CN-shifts occur.[3] This tendency is decreased by the presence of additional fused aromatic rings; thus the isomers naphtho[1,2-*d*]triazole and naphtho[2,3-*d*]triazole give, at 500°, 1- and 2-cyanoindene respectively. At 800° these interconvert, and at 1000° the CN-group migrates evenly to all positions on the π-surface. While an isopolar transition state is probably involved at the lower temperatures, at 1000° the intermediate could consist of a gas-phase ion pair. The third member of this series, naphtho[1,8-*de*]triazine (IV) is structurally unsuited for ring contraction, and loses N_2 to give only 1-naphthylamine. Phenanthro[9,10-*d*]triazole loses N_2 at 600° to give a quantitative yield of 9-cyanofluorene, which at 1000° rearranges further to 1-cyanofluorene; similar migrations have been observed in other benzylic cyanides, *viz.* phenylacetonitrile and



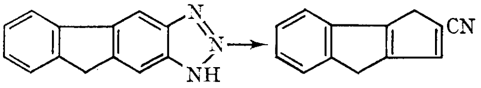
SCHEME 1

[†] Presented at the 40th ANZAAS Congress, Christchurch, New Zealand, in January, 1968.

[‡] The tautomerism in (I) must be taken into account, and is illustrated in Scheme 1 by dual numbering. Experiments using ^{14}C and ^{15}N are in progress to determine the exact origin of C(1)–C $\equiv$ N of (III).

[§] The spectral data is fully consistent with this structure. N.m.r.: τ 2·30 (m, 4H) 3·72 (m, H–3), 6·85 (m, 2H), and 7·35 (m, 2H). Mass spectrum: M^+ 197 (40%), $M-1$ (43%), $M-2$ (100%), $M-26$ (13%) $[M-2]-26$ (12%), and $[M-2]^{2+}$ (13·5%). The u.v. spectrum in cyclohexane shows peaks at 244, 261, 270, 280, 316, 328, 342, and 352 mμ.

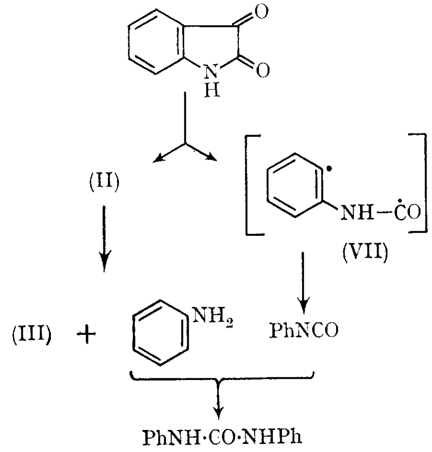
diphenylacetonitrile at 1000°. Triazolo[4,5-*b*]fluorene (V) at 600° gives rise to a product which is apparently§ the 2-cyano-1,4-dihydrobenzo[*a*]-pentalene (VI).



(V) (VI)

Evidence for the intermediacy of the diradical (II) is provided by the isolation, in low yield, from simple benzotriazoles of the anilines which correspond to (IIa) and (IIb). It is assumed, from the principle of spin conservation, that at least the first-generated species is the singlet.

That N_2 is only one example of a suitable leaving group is shown by the pyrolysis of isatin, which at 500—900° gives comparable yields of (III) and aniline by loss of 2CO (Scheme 2). The yield of (III) increases, and that of aniline decreases, with rising temperature, probably due to collisional excitation of the intermediate. The loss of CO is also observed, giving the intermediate (VII), which should rearrange to phenyl isocyanate. The latter is not isolated, however, due to interaction with aniline to give diphenylurea (isolated in 1% yield). Under conditions of low conversion (500°/0·005 mm.) one other product, nitrobenzene, is formed in low yield by what must be regarded as an obscure mechanism.



Scheme 2

The mass spectra of isatin and the simple benzotriazoles have been measured, and are characterised by stepwise loss of 2CO or N_2, followed by HCN loss.

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[1] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, 1967, 4379.
[2] W. D. Crow and R. K. Solly, *Austral. J. Chem.*, 1966, **18**, 2119.
[3] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, to be published.