The Photochemical and Mass Spectral Properties of 5-Phenoxy-1-phenyl-1*H*-tetrazole

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Summary The formation of a benzimidazole (III) or pseudourea derivative (IV) when the starting tetrazole (I) is irradiated in different solvents is attributed to an azomethine biradical or nitrene intermediate and the mass spectral properties of (I) and (III) indicate a novel 1,3-$O \rightarrow N$ phenyl migration.

WE report here the unusual photochemical and mass spectral properties† of 5-phenoxy-1-phenyl-1*H*-tetrazole (I).

Irradiation‡ of (I) (0·05M) in acetonitrile (15 hr.) with RPR 2537 Å lamps caused evolution of N_2 and afforded photo-product (III) (25%) m.p. 224—226°; λ_{max} 276 (ϵ 8190, MeCN) and 282 nm (ϵ 7968); ν_{max} (KBr) centred at 2850 (broad NH) and 1160 cm.$^{-1}$ (strong O–C stretch); *M* (mass spectrometric) 210. Loss of CO and CONH in the mass spectrum of (III) appeared to indicate structure (V), however, the u.v. and i.r. spectra of (III) were identical with those of authentic (III) prepared by a known method.[1] A 1,3-$O \rightarrow N$ phenyl migration has been invoked to explain this anomaly in the mass spectrum of (III). The mechanism outlined in Scheme 1 for the conversion of (I) into (III) is analogous to an earlier suggestion.[2]

Unexpectedly, photoproduct (IV) (30%) m.p. 140—141°; λ_{max} (Pr^iOH) 225 nm. (ϵ 15,900); ν_{max} (KBr) 1670 cm.$^{-1}$

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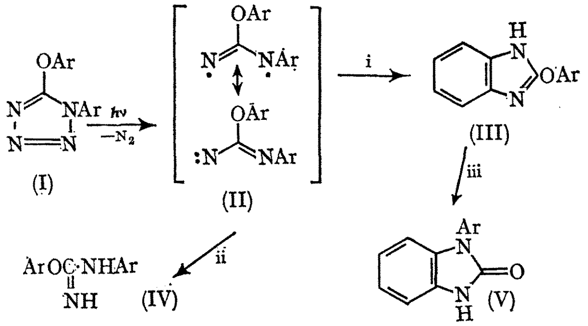
† Mass spectra were measured using an Associated Electrical Industries, Ltd., mass spectrometer Model MS-9 at 70 ev ionizing voltage. Accurate mass assignments of all ions in the spectra discussed were done at resolution 10,000.

‡ No photodecomposition occurred when a solution of (I) in acetonitrile was irradiated with RPR 3500 Å lamps in the presence of acetophenone using a Pyrex glass vessel; quartz vessels were used in all other photolyses.

(strong C–NH stretch); *M* (mass spectrometric) 212; was obtained when a solution of (I) (0·05M) in propan-2-ol was irradiated (RPR 2537 Å lamps) for *ca.* 15 hr. An authentic sample of (IV) prepared by a known procedure[3] was identical with photo-product (IV). Intermediate (II), which can explain the formation of (III) and (IV), is tentatively described as an azomethine nitrene or biradical. The multiplicity of (II) is under study using various photochemical techniques.



SCHEME 1. (i) MeCN, 2537 Å; (ii) Propan-2-ol, 2537 Å; (iii) Electron impact; Ar = Ph.

A 1,3-*O* → *N* phenyl migration, similar to the one described above for (III), was found in the mass spectrum of (I), since the composition of ions 182, 181, and 168 shows loss of CO with retention of both phenyl rings (Scheme 2). Absence of a $C_{12}H_{10}$ ion at *m/e* 154 indicates *O* → *N* phenyl migration.

$$\begin{tikzcd}
\begin{array}{c}C_{13}H_{10}N_4O\\ \text{(I) }238(35\%)\end{array} \arrow[r, "-N_2"] & \begin{array}{c}C_{13}H_{10}N_2O\\ 210(12\%)\end{array} \arrow[r, "-H\cdot", "*"'] \arrow[d, "-\dot{C}O"] \arrow[dl, "*-CO\dot{N}"'] & \begin{array}{c}C_{13}H_9N_2O\\ 209(85\%)\end{array} \arrow[d, "-CO", "*"'] \\
\begin{array}{c}C_{12}H_{10}\dot{N}\\ 168(13\%)\end{array} & \begin{array}{c}C_{12}H_{10}N_2\\ 182(21\%)\end{array} \arrow[r, "-H\cdot", "*"'] & \begin{array}{c}C_{12}H_9\dot{N}_2\\ 181(35\%)\end{array}
\end{tikzcd}$$

SCHEME 2. Numbers in parentheses are ^{13}C, ^{15}N corrected abundances relative to the base peak at 77 (C_6H_5); metastables indicated by asterisk.

Whether the H atom is lost from the $M - N_2$ (*m/e* 210) ion prior to phenyl migration in (I) is not clear from the existing data.

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