Skeletal Rearrangement Processes of Aromatic Azoxy-compounds on Electron Impact

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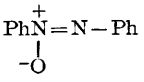
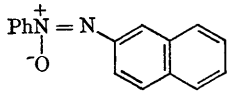
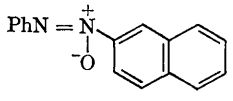
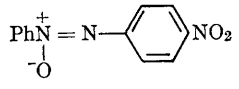
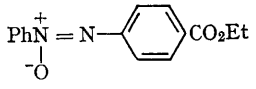
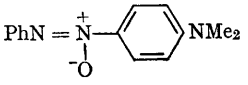
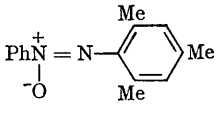
AROMATIC azoxy-compounds have been found to exhibit prominent skeletal rearrangement ions in their mass spectra. Seven examples are summarised in the Table. An asterisk denotes the presence of a metastable ion for the process indicated, and the compositions of all ions have been established by exact mass measurements.

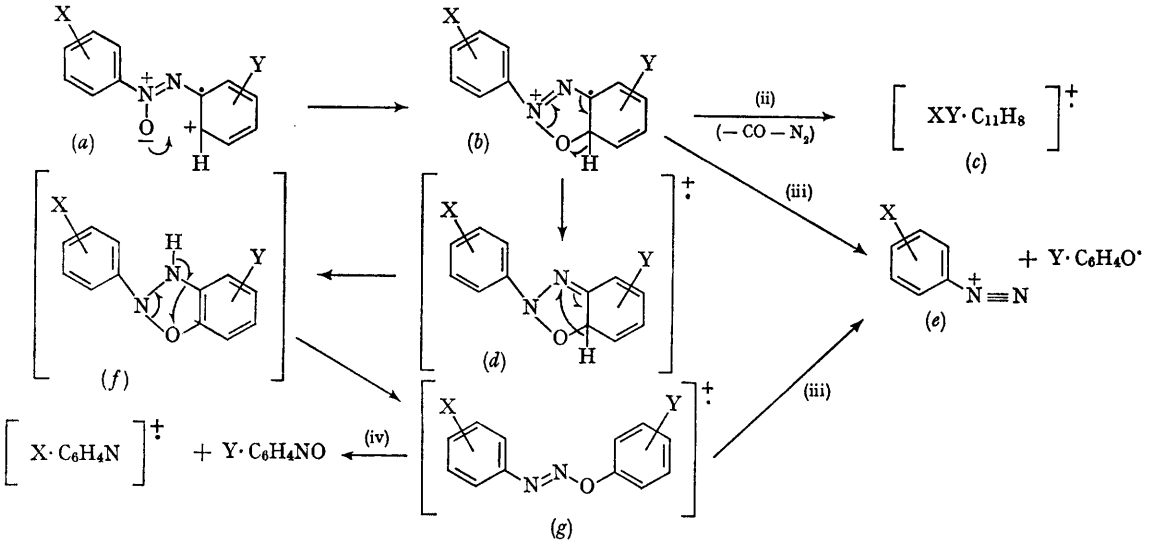
The rearrangement modes may be divided into four processes:

(i) M^+–N_2O. This is a process of the general type[1], ABC → AC + B, in which diaryl radical ions are formed. Such ions, when observed, are of low intensity;

TABLE 1

Skeletal rearrangement ions in the spectra of azoxy-compounds

Compound	Process	Final ion	Relative abundance of final ion (%)
	$M-N_2O-H_2$	152	4
	$M-\overset{*}{CO}-\overset{*}{N_2}-H\cdot$ $M-\overset{*}{(CO+N_2)}-\overset{*}{H}\cdot$	141	16
	$M-\overset{*}{CO}-\overset{*}{H}\cdot-\overset{*}{N_2}$	191	9
	$M-\overset{*}{C_{10}H_7N}\cdot$	105	13
	$M-\overset{*}{C_{10}H_7NO}$	91	28
	$M-\overset{*}{CO}-\overset{*}{H}\cdot-\overset{*}{N_2}$	191	9
	$M-\overset{*}{C_6H_5O}\cdot$	155	4
	$M-\overset{*}{C_6H_5NO}$	141	26
	$M-\overset{*}{C_6H_4NO_3}$	105	36
	$M-\overset{*}{EtO}-\overset{*}{CO}-\overset{*}{CO}-N_2$	141	10
	$M-\overset{*}{CO}-\overset{*}{N_2}-\overset{*}{H}\cdot$	213	2
	$M-\overset{*}{CO}-\overset{*}{N_2}-\overset{*}{H}\cdot$ $M-\overset{*}{(CO+N_2)}-\overset{*}{H}\cdot$	184	4
	$M-C_6H_5O\cdot$	148	12
	$M-\overset{*}{C_6H_5NO}$	134	92
	$M-\overset{*}{Me}-CO-N_2$	169	3



(ii) M^+–CO–N_2 or M^+–(CO + N_2). This process which may occur in either successive steps or in a concerted manner is observed in most spectra. The process is modified by the presence of substituents on either aromatic ring (see the Table);

(iii) M^+–Y·C_6H_4O· (see *a*). This process is not observed in all spectra;

(iv) M^+–Y·C_6H_4·NO· (see *a*). This process likewise is not observed in all spectra.

The above scheme is postulated to explain the rearrangement processes. It should be noted that the *o*-hydroxyazobenzene radical ion is not the intermediate in the rearrangement process of azoxybenzene, as its rearrangement process[2] is M^+–N_2–CO–H· (not M^+–CO–N_2–H· as in the case of azoxybenzene). The oxygen migration to form the cyclised intermediate *b*, is similar to the behaviour of aryl sulphones on electron impact,[1] and the mechanism suggested for the formation of *g* is very similar to that suggested to explain the photochemical rearrangement of azoxybenzenes.[3]

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[1] J. H. Bowie, D. H. Williams, S. O.Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, 1966, **22**, 3515 and references therein.
[2] J. H. Bowie, R. G. Cooks, and G. E. Lewis, *J. Chem. Soc.* (*B*), in the press.
[3] G. E. Lewis and J. A. Reiss, *Austral. J. Chem.*, 1966, **19**, 1887.