Mechanism of the Formation of Semiquinone Radicals by Ultra-violet Irradiation of Six-membered Aromatic Aza-compounds in Neutral Methanol, and of Radical Cations by Ultra-Violet Irradiation of Six-membered Aromatic Diaza-compounds in Methanol acidified with Hydrochloric Acid

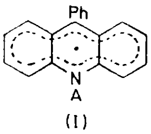
By Azélio Castellano, Jean-Pierre Catteau, and Alain Lablache-Combier*

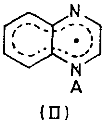
(*Laboratoire de Chimie Organique Physique, Université des Sciences et Techniques de Lille, B.P.* 36—59650 *Villeneuve d'Ascq, France*)

Summary 9-Phenylacridine and quinoxaline react with methanol but do not directly abstract a hydrogen radical from the solvent; in methanol–HCl, pyrazine, quinoxaline, and phenazine give radical cations.

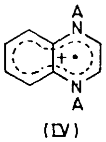
Many photoexcited six-membered aromatic aza-compounds react with neutral alcohols to give NH and semiquinone radicals.[1] It has been proposed that the reaction involves a $n\pi^*$ excited state of the aromatic aza-compound, the C=N group abstracting a solvent hydrogen as does the C=O chromophore of aromatic ketones.[1]

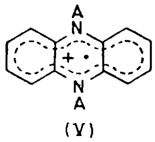
We have evidence that the formation of (I)H and (II)H, by irradiation of 9-phenylacridine and quinoxaline respectively in neutral methanol, does not proceed by this mechanism.


(I)


(II)

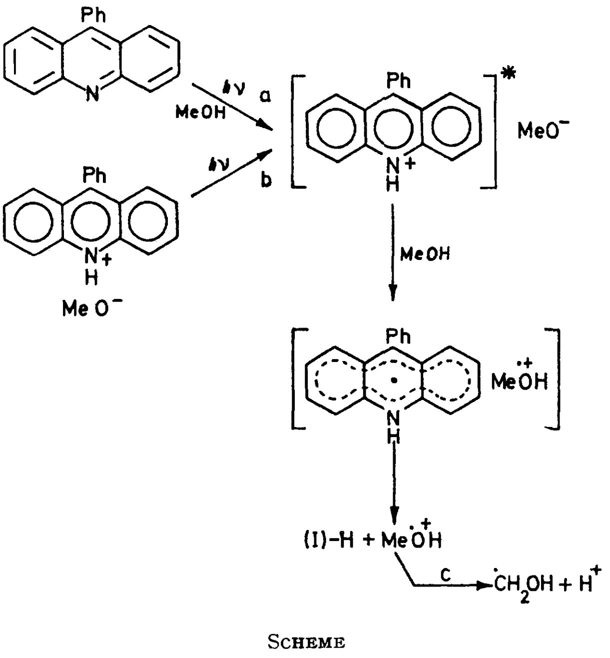

(III)


(IV)


(V)

A = H or D

Methanolic solutions of 9-phenylacridine (0·2M) and quinoxaline (0·4M) were irradiated in the cavity of an e.s.r. spectrometer at 233 K (liquid phase) and 133 K (glassy matrix) respectively. The structure of the radicals formed have been studied previously.[2] It is clear from the Table that the radicals observed are not the ones which would be expected had the reactions proceeded by direct H• abstraction by the aromatic aza-compound. An exchange between the N–H hydrogen atom and the acidic hydrogen atom of methanol is unlikely. In both cases the e.s.r. signals of the radicals are strong after 15 s of irradiation and their structure remains the same after further irradiation.



Scheme

The scheme shows the postulated mechanism. The first step is protonation of the aromatic aza-compound (path a

TABLE

Compound	Temperature (K)	Solvent	Radical seen by e.s.r.	Radical which would be formed by H· abstraction
9-Phenylacridine	233	CH_3OH	(I)H	(I)H
		CH_3OD	(I)D	(I)H
		CD_3OH	(I)H	(I)D
		CD_3OD	(I)D	(I)D
		$CH_3OH(50)$–$CH_3OD(50)$	(I)H(50), (I)D(50)	(I)H
		$CH_3OH(80)$–$CH_3OD(20)$	(I)H(80), (I)D(20)	(I)H
Quinoxaline	133	CH_3OH	(II)H	(II)H
		CH_3OD	(II)D	(II)H
Pyrazine	293	CH_3OH–HCl	(III)H	
		CD_3OD–DCl	(III)D	
Quinoxaline	293	CH_3OH–HCl	(IV)H	
		CD_3OD–DCl	(IV)D	
Phenazine	293	CH_3OH–HCl	(V)H	
		CD_3OD–DCl	(V)D	

is more probable than path b, aromatic monoaza-compounds being roughly 10^6 times more basic in the first singlet excited state than in the ground state.[3] It is followed by the formation of an exciplex which ionizes in the polar solvent.[4] The products result from combination of semiquinone radicals with $\dot{C}H_2OH$. $\dot{C}H_2OH$ is formed from $CH_3\overset{\cdot+}{O}H$ (path c).

Photoreaction of pyrazine (0·6M), quinoxaline (0·4M), and phenazine (0·25M) in methanol acidified with HCl proceeds in a similar way. Radical cations are formed, the structures of which have been previously determined.[5] Exciplex formation probably occurs by interaction between the photoexcited diprotonated aromatic diaza-compound and the methanol. Such a mechanism is more probable than one previously proposed[6] for the formation of the phenazine radical cation, by irradiation of phenazine in strongly acidified methanol.

Radicals (III)—(V) (H or D) are formed by daylight in comparison to radical (II) (H or D) which is only produced by u.v. irradiation. This supports the proposed mechanism. It is certainly easier to form an exciplex from the photoexcited diprotonated aromatic diaza-ion than from the photoexcited monoprotonated one.

(*Received*, 26*th July* 1972; *Com.* 1295.)

---

[1] For a review see A. Lablache-Combier in 'Elements de Photochimie avancée,' ed. P. Courtot, Hermann, Paris, 1972, p. 289.

[2] A. Castellano, J. P. Catteau, A. Lablache-Combier, B. Planckaert, and G. Allan, *Tetrahedron*, 1972, **28**, 3511, and unpublished results (for 9-phenylacridine).

[3] E. Vander Donckt in 'Progress in Reaction Kinetics,' ed. G. Porter, Pergamon Press, Oxford, 1970, vol. 5, p. 273.

[4] A. Weller, *Pure Appl. Chem.*, 1968, **16**, 115.

[5] B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **41**, 1455.

[6] D. N. Bailey, D. K. Roe, and D. M. Hercules, *J. Amer. Chem. Soc.*, 1968, **90**, 6291.