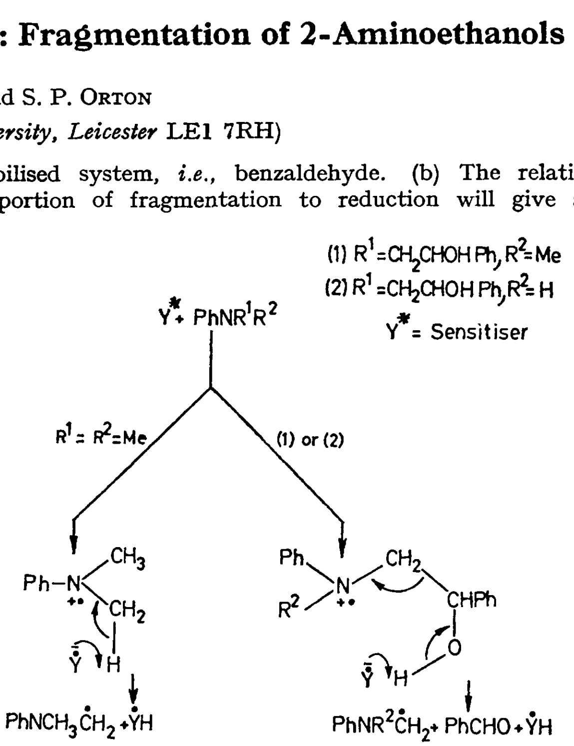
Photo-induced Electron-transfer Reactions: Fragmentation of 2-Aminoethanols

By R. S. DAVIDSON* and S. P. ORTON
(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary U.v. irradiation of carbonyl and heterocyclic compounds and aromatic hydrocarbons in the presence of 2-(*N*-aryl)amino-1-phenylethanols results in fragmentation of the alcohols to *N*-arylamines and benzaldehyde: a mechanism involving electron transfer from the amine to its reaction partner is proposed.

THE reactions of photo-excited carbonyl[1a,b] and heterocyclic compounds[1a,2a–c] and aromatic hydrocarbons[1a,3a–g] with amines and *N*-arylaminoacetic acids have been interpreted as occurring *via* intermediates such as exciplexes and radical ions. Chemical reaction usually occurs *via* these intermediates undergoing a proton transfer reaction, *e.g.*, in the reaction with *NN*-dimethylaniline.

We now report that irradiation of carbonyl and heterocyclic compounds and aromatic hydrocarbons in the presence of the amino-alcohols (**1**) and (**2**) leads to fragmentation of the alcohols into benzaldehyde and *N*-arylamines (see Table). The amino-alcohols (**1**) and (**2**) were chosen for the following reasons. (a) If an exciplex or radical ions are intermediates, fragmentation should be a favoured process because of the formation of a resonance-stabilised system, *i.e.*, benzaldehyde. (b) The relative proportion of fragmentation to reduction will give an



TABLE

Products obtained by irradiation[a] of carbonyl and heterocyclic compounds and aromatic hydrocarbons in the presence of compounds (**1**) and (**2**)

		PhNMeCH$_2$CHOHPh (**1**)				PhNHCH$_2$CHOHPh (**2**)		
	Solvent	Benzaldehyde (%)[c]	*NN*-Dimethylaniline (%)[c]	*N*-Methylaniline[b] (%)[c]	Solvent	Benzaldehyde (%)[c]	*N*-Methyl aniline (%)[c]	Aniline[b] (%)[c]
Anthraquinone ..	Benzene	64	20	4	Benzene	21	4	10
2,3-Diphenylquinoxaline	”	92	58	16	”	85	57	Trace
Acenaphtho[1,2-*b*]-quinoxaline	”	90	38	14	”	47	29	24
Perylene	”	12	7	2	”	2	1	
”	MeCN	48	None	15	MeCN	None	None	None

[a] Irradiations carried out in a Rayonet Photochemical Reactor fitted with lamps having maximum emission at 350 nm. All solutions were thoroughly purged with nitrogen. Solutions were 1 × 10^{-1}M in the amino-alcohol and 1 × 10^{-2}M in the reactant. Products and yields were determined by v.p.c. (Pye 104 gas chromatograph). [b] The occurrence of demethylation in the photoreactions of amines has been previously discusssed.[4b] [c] Yields are based on the amount of amino-alcohol. Multiplication of these figures by ten gives yield based on the amount of the reactant.

indication of the efficiency of the hydroxy-group as a proton donor compared with the N–H bonds of the amino-group and the C–H bonds α to the nitrogen atom.

Inspection of the Table shows that in many cases more fragmentation took place than could be accounted for by a mechanism which required 1 mol of the excited species to be consumed by 1 mol of the amino-alcohol. This observation can be readily explained by the radicals formed in the fragmentation process undergoing a hydrogen atom exchange reaction and so regenerating the sensitiser.[4a,b]

The influence of the N–H group shows up particularly strongly when aromatic hydrocarbons are used as sensitisers. Thus, no fragmentation was observed with (**2**) whereas it takes place with (**1**) in both benzene and acetonitrile solution. The lack of fragmentation with (**2**) may be ascribed to reaction occurring preferentially at the N–H bond. It has been previously noted that in the reactions of aromatic hydrocarbons with pyrrole[3a,f] and other secondary amines,[2b,3a] proton transfer from the amino-group occurs. However, in the case of *N*-arylaminoacetic acids, the N–H group is not sufficiently acidic to divert reaction from the carboxy-group.[5]

The described reactions emphasise the point that the direction of photochemical reactions involving exciplexes and radical ions is determined by the location and acidity of protons within the reactant molecules. They also illustrate the similarity in reactivity of excited carbonyl and heterocyclic compounds and aromatic hydrocarbons with amines and related compounds.

We thank Dr. D. R. G. Brimage for carrying out some preliminary experiments.

(*Received*, 11*th December* 1973; *Com.* 1680.)

---

[1] (a) A. Lablache-Combier, *Bull. Soc. chim. France*, 1972, 4791; A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, 1971, **93**, 6998; (b) S. G. Cohen, G. A. Davis, and W. D. K. Clark, *ibid.*, 1972, **94**, 869; J. B. Guttenplan and S. G. Cohen, *Tetrahedron Letters*, 1972, 2163; R. S. Davidson and M. Santhanam, *J.C.S. Perkin II*, 1972, 2355; R. S. Davidson and P. R. Steiner, *ibid.*, p. 1357.

[2] (a) G. A. Davis and S. G. Cohen, *Chem. Comm.*, 1971, 675; G. A. Davis, *Tetrahedron Letters*, 1971, 3045; (b) P. Grandclaudon, A. Lablache-Combier, and C. Párkányi, *Tetrahedron*, 1973, **29**, 651; (c) D. R. G. Brimage, R. S. Davidson, and P. R. Steiner, *J.C.S. Perkin I*, 1973, 526.

[3] (a) M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 263, 862; (b) R. S. Davidson, *ibid.*, 1969, 1450; (c) C. Pac and H. Sakurai, *Tetrahedron Letters*, 1969, 3829; (d) D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916; (e) J. A. Barltrop and R. J. Owers, *Chem. Comm.*, 1970, 1462; V. R. Rao and V. Ramakrishnan, *ibid.*, 1971, 971; (f) J. J. McCullough, W. S. Wu, and C. W. Huang, *J.C.S. Perkin II*, 1972, 370; (g) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, 1973, **95**, 5783.

[4] (a) for examples see R. S. Davidson, P. F. Lambeth, and M. Santhanam, *J.C.S. Perkin II*, 1972, 2351; (b) R. S. Davidson and P. R. Steiner, *J. Chem. Soc.* (*C*), 1971, 1682.

[5] D. R. G. Brimage and R. S. Davidson, *J.C.S. Perkin I*, 1973, 496.