Photochemistry of Aromatic Compounds. Fragmentation Reactions originating in a Photo-induced Electron Transfer in Solution

By J. Nasielski,* A. Kirsch-Demesmaeker, P. Kirsch, and R. Nasielski-Hinkens

(*Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles,* 50 *Av. F. D. Roosevelt,* 1050 *Bruxelles, Belgium*)

Summary Diethylamine accelerates the photolysis of 5-bromopyrimidines and of oxindole through a photo-induced electron transfer.

The photolysis of 5-bromo-2-methoxypyrimidine (I) in methanol with a Hanau NK6 low-pressure mercury arc leads to at least five products (II—VI) with a poor overall yield. Slightly different proportions are obtained with the Hanovia medium-pressure 450w lamp, probably because of further decompositions induced by the longer-wavelength components of the light source. The photo-induced alkylation and hydroxyalkylation of hetereocycles is a well-known process.[1]

When the photolysis is run in the presence of diethylamine, the dehalogenated pyrimidine (II) is formed much faster, the other products appearing only as minor components. The influence of the amine increases with its concentration (Table), but no product containing a diethylamino-group could be isolated.

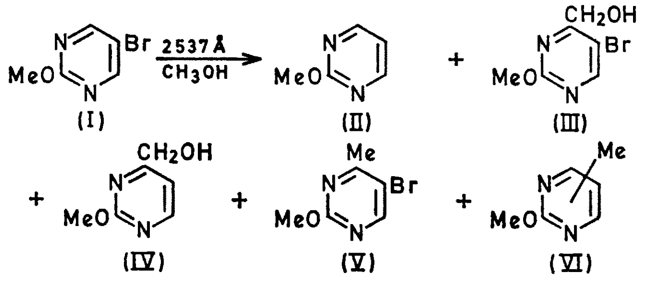
Influence of diethylamine on the photolysis of 5-bromo-2-methoxypyrimidine in methanol (low-pressure mercury arc).

Initial concentrations (I)	Initial concentrations Et_2NH	Duration of photolysis	(I)%	(II)%	(III)%	(IV)%
0·01	—	40 min	74·2	2·2		
0·01	0·10	40 min	49·6	15·9		
0·01	0·40	40 min	30·0	34·2		
0·02	0·38	3 hr	6·6	5·6	12·2	3·9

Similar results were found with 2-dimethylamino- and 2-phenyl-5-bromopyrimidine.

A simple way to rationalise the results is to assume that Et_2NH acts as an electron donor towards the excited state of the pyrimidine, yielding two radical-ions:

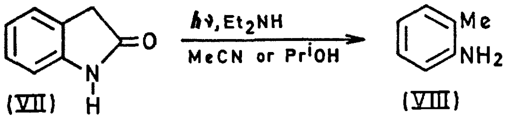
$$(I^*) + Et_2NH \rightarrow (I)\cdot^- + Et_2NH\cdot^+$$



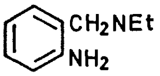
The pyrimidine radical-anion then undergoes a classical dehalogenation as in typical Birch reductions.[2] The fact that fairly high concentrations of amines are required to effect the reaction suggests that the amine is intercepting a very short-lived species, with a lifetime of the order of 10^{-9} sec, in agreement with the lifetime expected for the lowest excited singlet state of the bromopyrimidine. This mechanism bears some resemblance to the one suggested for the photo-dehalogenation of halogenobenzenes with dimethylaniline,[3] but with reversed roles: in our case it is the electron acceptor which is photoexcited. The efficiency of the process is due to the fact that electron transfers are diffusion-controlled in polar solvents[4] if they are exothermic.

In other experiments, it was found that oxindole (VII) is fairly photostable[5] when irradiated with the medium-pressure lamp in solvents such as methanol, acetonitrile, cyclohexane, or benzene. Some decomposition occurs, and very small amounts (less than 1%) of *o*-toluidine are formed. When the photolysis is run in the presence of $0{\cdot}13$M-diethylamine, most of the starting material has disappeared after the same irradiation time and larger amounts (*ca.* 10%) of *o*-toluidine (VIII) are formed, together with a diethylamine adduct (IX) and, in the case of isopropyl alcohol, a solvent adduct (X). Here again, an electron transfer from diethylamine to excited oxindole offers an attractive mechanistic pathway, the radical-anion of oxindole undergoing typical fragmentations leading to a decarbonylated intermediate.

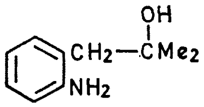
The photo-induced electron transfers, which have been extensively examined in the photochemistry of ketones,[6] seem thus to offer promising openings in the synthetic and mechanistic photochemistry of a wider range of substrates.



(VII) (VIII)



(IX)



(X)

We thank Professor R. H. Martin for his interest and Professor E. Vander Donckt for very stimulating and fruitful discussions. We also thank the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture for fellowships (to A.K.-D. and P.K.) and the Fonds de la Recherche Fondamentale Collective for support to the laboratory.

(*Received, January* 1*st*, 1970; *Com.* 002.)

---

[1] M. Ochiai, E. Mizuta, Y. Azahi, and K. Morita, *Tetrahedron*, 1968, **24**, 5861; H. Steinmaus, I. Rosenthal, and D. Elad, *J. Amer. Chem. Soc.*, 1969, **91**, 4921.

[2] H. Smith, "Organic Reactions in Liquid Ammonia—Chemistry in Nonaqueous Ionising Solvents," Interscience, New York, 1963; J. de Lannoy, A. Gysen, and R. Nasielski-Hinkens, to be published.

[3] T. Tosa, C. Pac, and H. Sakurai, *Tetrahedron Letters*, 1969, 3635.

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

[5] M. Fischer and F. Wagner, *Chem. Ber.*, 1969, **102**, 3486; M. Fischer, *ibid.*, p. 3495.

[6] R. A. Caldwell, *Tetrahedron Letters*, 1969, 2121 and references cited therein; J. B. Guttenplan and S. G. Cohen, *ibid.*, p. 2125, and references cited therein.