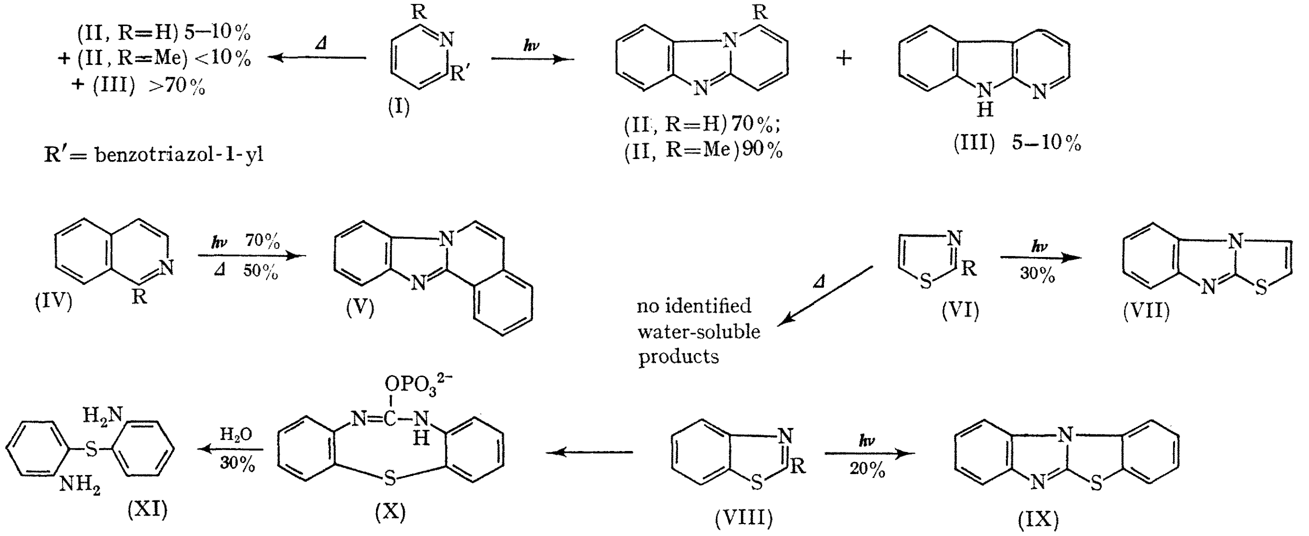
A Comparison of the Thermolysis and Photochemistry of Benzotriazoles

By A. J. HUBERT*

(*Union Carbide European Research Associates, s.a.,* 95, *rue Gatti de Gamond, Brussels* 18, *Belgium*)

A RECENT publication[1] on the photosynthesis of carbazole from phenylbenzotriazole prompts us to report on the photolysis of benzotriazoles substituted in the position 1 by a heterocyclic component containing a nitrogen atom vicinal to the benzotriazolyl group.



1-(2-Pyridyl)benzotriazole (I; R = H) gives 9*H*-pyrido-[2,3-*b*]indole (III) when heated with an acid or a salt such as $ZnCl_2$.[2] Irradiation of (I; R = H) gave pyrido[1,2-*a*]-benzimidazole (II; R = H) (>70%: quartz lamp, filter; unfiltered light gave only tars). Although a small amount of (III) (*ca.* 5—10%) was detected (t.l.c.). A small amount of (II; R = H) is formed in the acid-catalysed decomposition of (I; R = H); this had not been reported previously. It appears therefore that the photodecomposition of benzotriazoles proceeds in a completely different way from the thermal decomposition. In two cases, however, the only isolable compounds were the same as those obtained from the thermal decomposition; [see (IV) → (V) and (I; R = Me) → (II; R = Me)]. In other cases [(VI) and (VIII)] no cyclic compounds were obtained by the acid-catalysed decomposition and water-soluble compounds were formed. Di-*o*-aminophenyl sulphide (XI) was identified as the exclusive product of the reaction of (VIII).

Two different mechanisms are probably involved in these reactions. The photolysis takes place under neutral conditions and is inhibited in acid solutions. The pyrolysis, however, is catalysed by acids. In the photolysis, cyclization takes place on the nitrogen atom whereas in the pyrolysis the nitrogen is not involved in the new ring {except when the other position is blocked by a substituent [(IV) and (I; R = Me)]}. The formation of (XI) may be explained by an initial ring-closure of the product of the pyrolysis of (VIII), between the phenyl group of the benzotriazole and the sulphur of benzothiazole. In the presence of polyphosphoric acid, the intermediate (X) may result, which is easily hydrolysed to the end product (XI). The structure of (XI) was proved by comparing its i.r. spectrum with that of a sample of di-*o*-aminophenyl sulphide prepared according to the reported procedure.[3]

Comparison of the products of the photolysis with those of the thermolysis of benzotriazoles

		Photolysis		Thermolysis	
Substrate	Product of decomposition	Yield (%)	M.p.	Yield (%)	M.p.
(I)	(II)[a]	70	179°	5-10	*
	(III)	5—10	*	70	210°
(IV)	(V)[b]	70	130	50	130
(VI)	(VII)	90	118—122	<10	122
(VIII)	(IX)[c]	30	140	0	—
(X)	(XI)	20	145	0	—
	(XIII)[d]	0	—	30	87

[a] G. Morgan and J. Stewart, *J. Chem. Soc.*, 1938, 1292; [b] H. Reimbinger and J. Vandewalle, personal communication; [c] A. E. Alper and A. Taurins, *Canad. J. Chem.*, 1967, **45**, 2903; [d] ref. 3.

(*Received, January* 20*th*, 1969; *Com.* 072.)

---

[1] E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, 1968, **90**, 1923.

[2] B. W. Ashton and H. Suschitzky, *J. Chem. Soc.*, 1957, 4559; W. H. Perkin, *ibid.*, 1924, 626.

[3] R. Nietzki and H. Bothof, *Ber.*, 1896, **29**, 2774.