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PHOTOCHEMISTRY OF BENZISOTHIAZOLES IN THE PRESENCE OF DIMETHYL ACETYLENEDICARBOXYLATE

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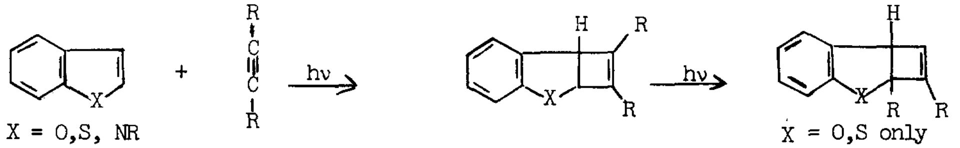
Summary: 1,2-Benzisothiazole gave upon irradiation in the presence of dimethy acetylenedicarboxylate a mixture of cis- and trans- substituted phenylthioalkenes (II) and 7-cyano-2,3-dicarboxybenzothiophene.

Some years ago we reported that photocycloaddition reactions of alkynes and the heterocycles, benzo(b)thiophene, benzo(b)furan[1-4] gave rearranged cyclobutenes (1) as the principle products. Indole and some of its analogs[5-7], gave the same [2+2] π cycloaddition of the triplet state heteroaromatic compounds to the acetylene but there was no following photorearrangement (1). The reaction with indoles was further developed to include a direct one step synthesis of benzazepines in that the fused cyclobutenes were thermally unstable, rearranging to seven- membered analogs via a cyclobutene-butadiene rearrangement.



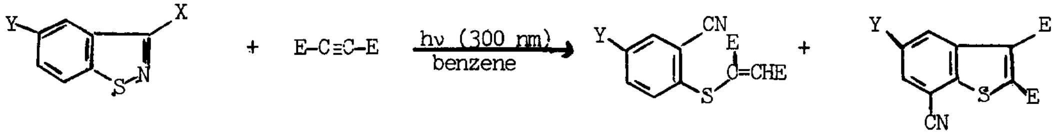
(1)

Our recent studies have aimed at developing photochemical syntheses of unusual heterocyclic compounds using first the photocycloaddition and then the thermal reaction and we have extended the study to fused aromatic systems with two heteroatoms in one ring, such as 1,2-benzisothiazole.

A brief previous report[8] indicated that 1,2-benzisothiazole, upon irradiation, gave 2-cyanophenyl disulfide. The formation of this product suggested to us that a photo-induced cleavage of the S-N bond, leading to a formation of an intermediate diradical, might also give a seven-membered fused heteroaromatic ring system if the biradical could be properly intercepted. To test this postulate we have studied photoreactions of 1,2-benzisothiazole with alkynes.

Irradiation of a mixture of 1,2-benzisothiazole[9] (I) and dimethyl acetylenedicarboxylate in a nitrogen purged benzene solution, at 300 nm (Rayonet) for 24 hrs. gave several products (II, III), (2). Column chromatography on silica gel gave three products in 50% (II trans), 30%

(II) **Cis** , and 15% (III) yield, respectively. Irradiation of 5-chlorobenzisothiazole^{10} gave similar results. The structures of the photoproducts were established by the spectral data, Table I.



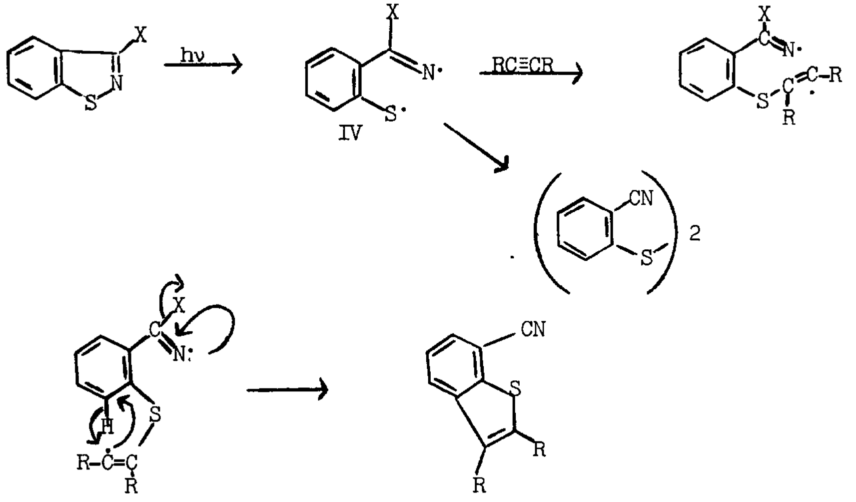
I a) X=H; Y=H
b) X=H; Y=Cl
c) X=Cl; Y=H

E = $COOCH_3$

II a) cis- and trans-
b) cis- and trans-

III a)
b)

Benzisothiazole reacts differently than either benzothiophene or indole. We suggest that on irradiation benzisothiazole suffers an initial homolysis giving the biradical IV which, in the absence of any π-partner produces cyanophenyl disulfide and, in the presence of an unsaturated system, free radical addition (3).^{11} When the adduct biradical closes back on itself the benzothiophenes are formed and this provides a potentially useful route to 5,7-substituted benzothiophenes.



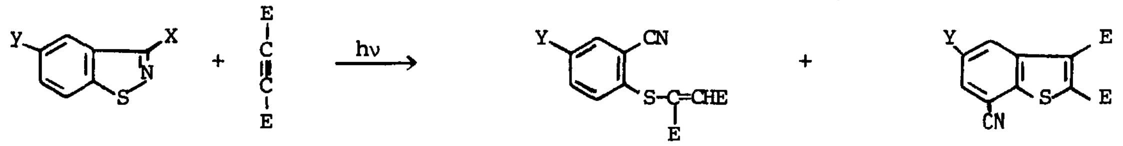
II

(3)

The formation of products II and III is solvent dependent. Irradiation in methanol or acetonitrile gives mainly cyanophenylthioalkenes (II) while in carbon tetrachloride about 70 percent of the benzothiophenes (III) were isolated. 3-chloro-1,2-benzisothiasole^{12} gives in benzene as well as in CCl_4, only the benzothiophene (III).

That the benzothiophenes (III) were formed as primary products and not by prolonged irradiation from already formed cyanophenylthioalkenes (II), was demonstrated by extended irradiation of II. Only cis-trans isomerization was observed and no benzothiophene was formed.

Table I
Photocycloaddition Products of Benzisothiazoles and Acetylenes



I a) X=H; Y=H
b) X=H; Y=Cl
c) X=Cl; Y=H

E = $COOCH_3$

II a) cis-; trans-
b) cis-; trans-

III a)
b)

comp.	m.p. [°C]	IR [cm^{-1}]	NMR, δ ($CDCl_3$)	UV [nm, ε]	m/e	cal. found	Anal [%] C	H	N	S
II a) trans-	76-77	2220 (C≡N) 1740 (C=O) 1720	6.72 (S, $H_{CH=}$) 3.82, 3.47 (2S, $2COOCH_3$) 7-7.8 (m, 4H)	210 (12000) 225 (11150) 265 (5700) 302 (5900)	277 (M^+, 95%) 246 ($M-OCH_3$, 48%) 218 ($M-COOCH_3$, 100%)		56.32 56.66	4.00 4.00	5.05 5.05	11.56 11.45
II a) cis-	73-74	2220 (C≡N) 1740 (C=O) 1720	5.84 (S, $H_{CH=}$) 3.70, 3.66 (2S, $2COOCH_3$) 7.74-8.05 (m, 44)	220 (11700) 237 (12400) 278 (10300)			56.31 56.40	4.00 4.02	5.05 4.99	11.56 ---
II b) trans-	81-82		6.78 (S, $H_{CH=}$) 3.82, 3.55 (2S, $2COOCH_3$) 7.48-7.66 (3H)				50.08 50.08	3.23 3.17	4.49 4.50	10.29 10.22
II b) cis-	63-64		5.92 (S, $H_{CH=}$) 3.72, 3.68 (2S, $2COOCH_3$) 7.60-7.76 (3H)				50.08 50.25	3.23 3.23	4.49 4.48	10.29 10.21
III a)	147-148	2220 (C≡N) 1740 (C=O) 1730	4.03 (2S, $2COOCH_3$) 3.98 8.19 (H_6; dd, J=2Hz, 10Hz) 7.86 (H_4; dd, J=2Hz, 9Hz) 7.66 (H_5; dd, J=9Hz, 10Hz)	260 (12800) 281 (9500) 290 (9800) 314 (4400) 326 (3800)	275 (M^+, 39%) 244 ($M-OCH_3$, 100%)		56.72 56.66	3.30 3.26	5.09 5.24	11.65 ---
III b)	160-161		4.03 (2S, $2COOCH_3$) 3.99 8.24 (H_6; d, J=2Hz) 7.81 (H_4; d, J=2Hz				50.41 50.30	2.60 2.55	4.52 4.57	10.35 10.25

Cis and *trans* (IIa) were identical with authentic samples prepared in a thermal free radical addition reaction of o-mercaptobenzonitrile[13] and dimethyl acetylenedicarboxylate. The structure of IIIa was confirmed by preparing it by irradiating 2-cyanophenyl disulfide in the presence of DMAD. The product III is formed as a result of addition of the 2-cyanophenyl sulfide radical (RS) to the triple bond. Thus, it is not excluded that o-mercaptobenzonitrile could possibly be an intermediate in the photoaddition of benzisothiazole to DMAD though no evidence favoring this has accumulated.

It is reasonable to conclude that the irradiation of substituted 1,2-benzisothiazoles whose substituent in the position 3 cannot be homolytically eliminated would more likely give cyclic products. This is the subject of the following paper.

Acknowledgement

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10. Prepared as 1,2-benzisothiazole (ref 9)
11. We have shown the biradical IV adding to the acetylene first at sulfur. There is no evidence for this nor is there any for the formation of IV. In view of the observed products, however, and the evidence in the subsequent communication, IV seems reasonable.
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