HETEROCYCLES, Vol. 24, No. 10, 1986

PHOTOCYCLOADDITION of DIETHYL ACETYLENEDICARBOXYLATE to 2-PHENYL-4H-1,3-BENZOTHIAZINE DERIVATIVES

Marija Sindler-Kulyk*[1], Alojz Dumbović[1], Dunja Srzić[2], Biserka Metelko[2], and Lajosz Fodor[3]

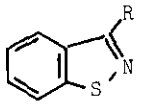
[1] Department of Organic Chemistry, Faculty of Technology, Marulićev trg 20, 41000 Zagreb, Yugoslavia

[2] Rugjer Bošković Institute, Zagreb, Yugoslavia

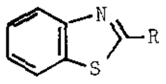
[3] Department of Laboratory Medicine, County Hospital, Gyula, Hungary

Abstract - Upon irradiation in the presence of diethyl acetylenedicarboxylate 6,7-dimethoxy-2-phenyl-4H-1,3-benzothiazine gives two main products: benzonitrile (X) and 2,3-carbethoxy-4,5-dimethoxy-7-methylbenzothiophene (XI). We report herein the first photochemical reaction of a 4H-1,3-benzothiazine derivative.

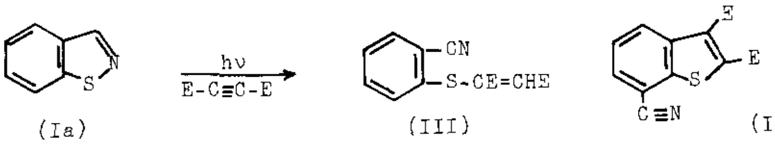
Photochemical cycloaddition reactions of alkynes and fused ring heteroaromatic compounds containing sulfur and nitrogen (I) and (II) have been under extensive investigation[1-6] in view of the potential of this as a synthetic route to pharmacologically active benzothiazepine derivatives.



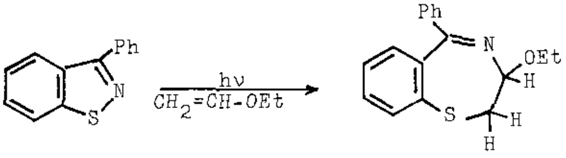
(I)



(II)



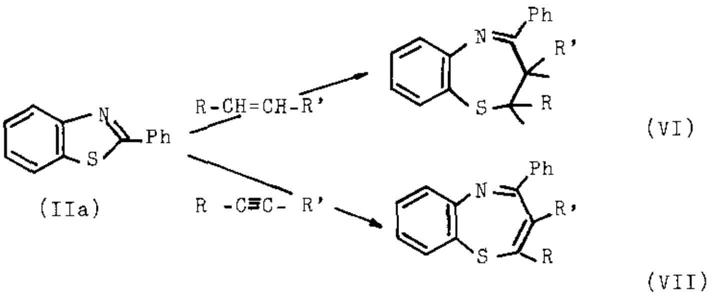
(Ia) (III) (IV)



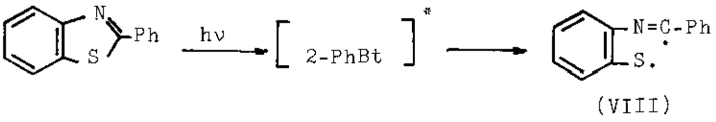
(Ib) (V)

As we have previously reported[1,2] photocycloaddition of benzisothiazoles (I) to alkynes, such as dimethyl acetylenedicarboxylate, or to alkenes such as ethyl vinyl ether results in the formation of the photoproducts (III), (IV) and (V) by trapping the intermediate biradical obtained after homolytic cleavage of the benzisothiazole sulfur-nitrogen bond[4,6].

Photocycloaddition reactions of 2-phenylbenzothiazole (IIa) with alkenes[3] or electron-rich alkynes[5] gave 1,5-benzothiazepines (VI) and (VII).



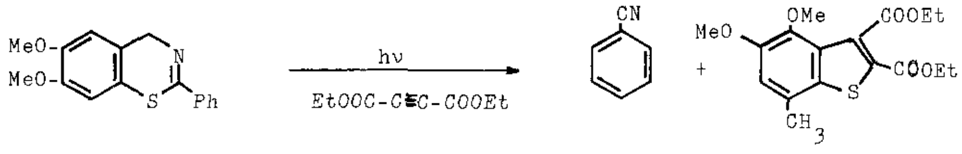
One of the mechanisms had to explain the formation of 1,5-benzothiazepines via this route was that in which the trapping of the intermediate biradical (VIII) obtained after homolytic cleavage of the sulfur-carbon bond is required.



As part of continuing study, we have now investigated the comparable reactions of 2-phenyl-4H-1,3-benzothiazine which might provide a route to the cephalosphorine-like structures.

We report herein preliminary results on the photocycloaddition of diethyl acetylenedicarboxylate (DEAD) to 6,7-dimethoxy-2-phenyl-4H-1,3-benzothiazine (IX)[7].

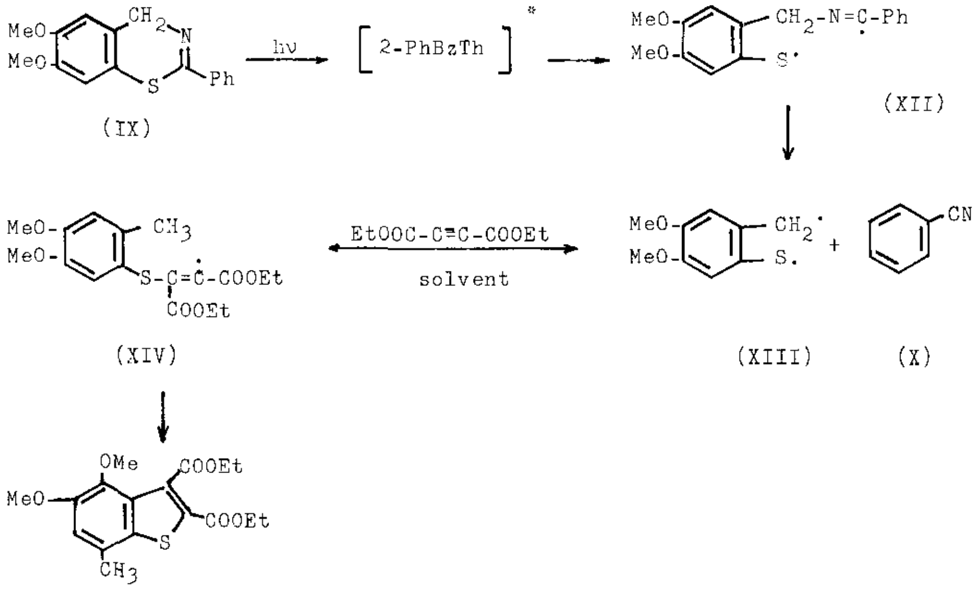
Benzothiazine (IX)[8] was irradiated with an excess of DEAD in benzene solution (10^{-3}M) purged with nitrogen, in Pyrex glass tube and in Rayonet reactor at 300 nm for 40 h. After evaporation of solvent the photomixture was chromatographed on silica gel eluting with petroleum-ether solution. Among other high-molecular materials, two products, (X) and (XI), were isolated in 30% yield. Benzonitrile



(IX) (X) (XI)

(X) was identified by its strong IR absorption band near 2210 cm^{-1} and by comparison with authentic material. The structure of 2,3-carbethoxy-4,5-dimethoxy-7-methylbenzothiophene (XI) was determined spectroscopically[9].

The mechanism of this reaction is not yet completely investigated but we propose first the sulfur-carbon cleavage from the excited state of benzothiazine (IX) to the biradical (XII)[10] which rearranges by the elimination of benzonitrile to the



(XI)

more stable biradical (XIII). Biradical (XIII) in the presence of DEAD gives adduct (XIV) which closes on itself to form the benzothiophene derivative (XI) as a main product.

More experiments are in progress.

ACKNOWLEDGMENT

We thank Professor D.C.Neckers for helpful discussions.

REFERENCES

1. M.Sindler-Kulyk and D.C.Neckers, *Tetrahedron Lett.*, 1981, 525.
2. M.Sindler-Kulyk and D.C.Neckers, *Tetrahedron Lett.*, 1981, 529.
3. M.Sindler-Kulyk and D.C.Neckers, *Tetrahedron Lett.*, 1981, 2081.
4. M.Sindler-Kulyk, D.C.Neckers, and J.R.Blount, *Tetrahedron*, 1981, **37**, 3377.
5. M.Sindler-Kulyk and D.C.Neckers, *J.Org.Chem.*, 1982, **47**, 4914.
6. M.Sindler-Kulyk and D.C.Neckers, *J.Org.Chem.*, 1983, **48**, 1275.
7. J.Szabo, L.Fodor, I.Varga, T.E.Vinkler, and P.Sohar, *Acta Chim. Budapest*, 1977, 93, 403.
8. The synthesis was made by L.Fodor.
9. Spectroscopical data for the (XI), mp 136-138°C: m/e 352 (M^+); ^{1}H NMR ($CDCl_3$, TMS): δ 7.01 (1H, q, J=0.73 Hz), δ4.47 (2H, q, J=7.16 Hz), δ 4.38 (2H, q, J=7.16 Hz), δ 3.92 (3H, s), δ 3.88 (3H, s), δ2.49 (3H, d, J=0.73 Hz), δ 1,43 (3H, t, J=7.16 Hz), δ 1.38 (3H, t, J=7.16 Hz); IR (in KBr): ν_{co} 1715, 1735 cm^{-1}; UV (λ_{max}, EtOH): 208 (24470), 245 (19980), 296 (13605), 356 (3278).

10. D.W.Young et al. have proposed the similar biradical formation in case of the photolysis of 1,3-thiazines: *J.Chem.Soc.,Chem.Commun.*, 1981, 608; *ibid.*, 1982, 1418; *ibid.*, 1983, 199.

Received, 30th May, 1986