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PHOTOCYCLIZATION OF METHYL 2-ARYLTHIOACETOACETATES A FACILE SYNTHESIS OF BENZOTHIOPHENES

Tadashi Sasaki* and Kenji Hayakawa

Institute of Applied Organic Chemistry, Faculty of Engineering
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Summary: A series of methyl 2-arylthioacetoacetates was irradiated in a benzene-methanol solution to give benzothiophenes in satisfactory yields.

Photocyclization of S-aryl vinyl sulfides is a useful new method for preparing five-membered sulfur heterocycles.[1-3] The reaction is known to occur from the triplet excited state[4] *via* the thiocarbonyl ylide intermediates.[3] We wish to report in this letter a facile synthesis of 2-methoxycarbonylbenzothiophenes by photocyclization of methyl 2-arylthioacetoacetates which were conveniently prepared in high yields by the reaction of methyl 2-chloroacetoacetate with appropriate arylmercaptanes in the presence of equimolar triethylamine. Thus obtained compounds (1) exist predominantly in the enolic form (IR,NMR). Irradiation of 1a (Ar = phenyl) in a benzene-methanol (1:1) solution under argon with a high pressure mercury lamp through a Pyrex filter followed by purification gave 2a (X = H) in 66% yield. The similar cyclodehydration occurred on irradiation of the related compounds to give the corresponding benzothiophenes in fair yields (Table 1). In a case of 1h, a regiospecific cyclization was observed and only naphth[2,1-b]thiophene 4 was formed. The structure was supported by a characteristic downfield shift of methyl signal (δ 3.24 ppm) owing to the deshielding effect of a proximate aromatic ring. Compound 1j was inactive on

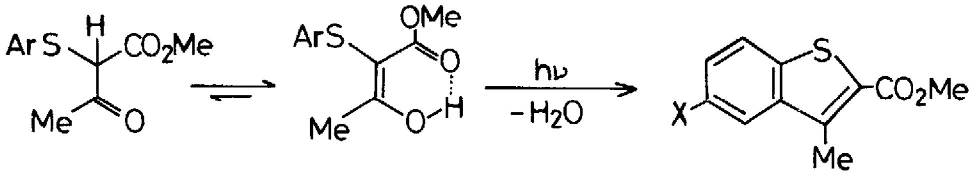

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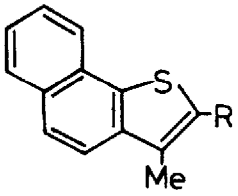
Table 1. Photocyclization of Methyl 2-Arythioacetoacetates [a,b]

Starting Materials (Ar =)	Products (Yields)[c]		mp	NMR (δ, CDCl$_3$)	
				COOMe	Me
1a (C$_6$H$_5$-)	2a (X = H)	(66%)	104-105° d	3.91	2.77
1b (p-Me-C$_6$H$_4$-)	2b (X = Me)	(61%)	89-90°	3.92	2.75
1c (p-MeO-C$_6$H$_4$-)	2c (X = OMe)	(57%)	93-95°	3.90	2.72
1d (p-F-C$_6$H$_4$-)	2d (X = F)	(56%)	131-132°	3.92	2.71
1e (p-Cl-C$_6$H$_4$-)	2e (X =Cl)	(51%)	146-147°	3.93	2.73
1f (p-Br-C$_6$H$_4$-)	2f (X = Br)	(55%)	160-161°	3.90	2.70
1g (1-naphthyl)	3	(64%)	159-161°	3.90	2.74
1h (2-naphthyl)	4	(56%)	127-128.5°	3.93	3.24
1i (2-pyridyl)	5	(50%)	122-124°	3.95	2.76
1j (4-pyridyl)	no				
1k (8-quinolyl)	6	(53%)	138-139°	3.96	2.72

a. All photolyses were carried out in a benzene-methanol (1:1) solution.

b. Satisfactory elemental analyses were obtained for all new compounds.

c. Isolated yields. d. Lit.[6] mp. 102.5-103°.



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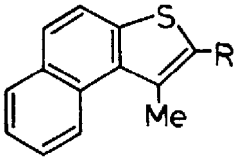

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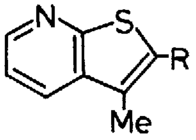
R = CO$_2$Me



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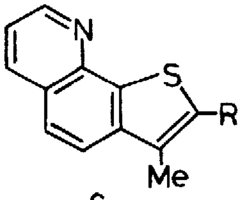

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the similar irradiation and only slow polymer formation was observed. The photocyclization most probably occurs from the enolic form of 1 *via* the ylide intermediates. The similar photocyclization reaction of N-analogs was reported.[5] Further studies of other enolizable systems are in progress.

References

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