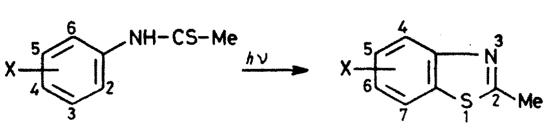
Photochemical Synthesis of 2-Methylbenzothiazoles

By RANGASAMY PARAMASIVAM, RANGASAMY PALANIAPPAN, and VAYALAKKAVOOR T. RAMAKRISHNAN*
(*Department of Chemistry, University of Madras, Post-Graduate Centre, Coimbatore* 641 041, *India*)

Summary The photochemical synthesis of 2-methylbenzothiazoles from *ortho*-halogenothioacetanilides is reported.

IN continuation of our work[1] on the photo-Fries reaction,[2] we have studied *ortho*-halogenothioacetanilides. Irradiation of a 0·02—0·03 M methanolic solution of the thioacetanilides (**1**) in a quartz vessel in a Rayonet RPR-208 reactor furnished, after chromatography, the 2-methylbenzothiazoles (**2**) as the major products. They were characterized by n.m.r. data and their m.p.s. (**1a**) gave (**2a**) (64%), m.p. 43 °C (lit.[3b] 38—39 °C), δ ($CDCl_3$–CCl_4) 2·82 (s, 3H) and 7·2—8·0 (m, 3H); (**1b**) gave (**2b**) (69%), m.p. 86 °C (lit.[3a] 84—86 °C), δ ($CDCl_3$–CCl_4) 2·77 (s, 3H), 7·3 (dd, 5-H, *J* 8 and 2 Hz), and 7·75—7·9 (overlapping peaks, 4-H and 7-H); (**1c**) and (**1d**) gave (**2c**) 94 and 66%, respectively, m.p. 109—110 °C (lit.[3a] 105—107 °C), δ ($CDCl_3$–CCl_4) 2·83 (s, 3H) and 7·4 and 7·63 (2d, 2H, *J* 2 Hz).



(**1a**); X = 2,3-dichloro
(**1b**); X = 2,4-dichloro
(**1c**); X = 2,3,6-trichloro
(**1d**); X = 6-bromo-2,4-dichloro

(**2a**); X = 7-chloro
(**2b**); X = 6-chloro
(**2c**); X = 4,6-dichloro

These photo-induced cyclizations involving dehydrohalogenation occurred smoothly in high yields. Further, when there was competition between Br and Cl in the dehydrohalogenation, as in the reaction of (**1d**), only dehydrobromination took place to yield (**2c**), instead of 4-bromo-6-chloro-2-methylbenzothiazole, which would have been formed by dehydrochlorination.

In the present study, photo-Fries rearrangement products were not observed although *ortho*-chloroaryl esters are known to give Fries-products with migration to either the free or the substituted *ortho*-position with displacement of chlorine, under photochemical conditions.[4]

Formation of 2-phenylbenzothiazole by the photochemical oxidative cyclization of thiobenzanilide has been reported.[5] The benzothiazoles (**2**) have been reported to be formed by treatment of (**1**) with sodium hydride,[3] by the cyclization of *o*-(methylthio)anilides with 2,2,4,4,6,6-hexachlorocyclo[triphosph(v)azene] or from *o*-aminothiophenol with aliphatic selenoesters.

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