A New and Efficient Approach to a 4H-1,3-Benzothiazine Ring that Utilises the Photo-cyclisation of N-o-Iodobenzoylthioamides: the Ring Transformation of Isothiazoles

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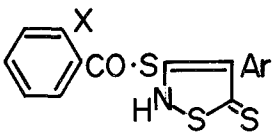
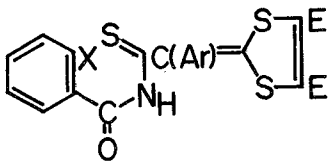
Abstract- The photo-cyclisation of N-o-iodobenzoylthioamides has been found to provide a novel and efficient synthesis of 4H-1,3-benzothiazin-4-ones.

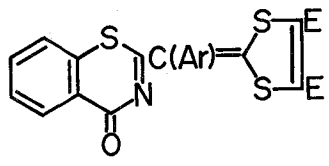
Approaches to the synthesis of 4H-1,3-benzothiazines so far reported utilise appropriately substituted o-mercapto-benzoic acids and benzamides,[1] N-(phenylthiomethyl)benzamides,[2] and 1,2-benzoisothiazoles.[3] We now report a new and efficient synthetic method of this ring system which involves the photo-cyclisation[4] of N-o-iodobenzoylthioamides (6)-(10), prepared from 4-aryl-3-o-iodobenzoylthio-3-isothiazoline-5-thiones (2)-(4) as described earlier.[5]

A solution of the N-o-iodobenzoylthioamide (6) (0.10 g) in dry THF (580 ml) was irradiated with a high pressure mercury lamp (100 W) for 10 h; the solution was deaerated by a stream of N_2 before and during photolysis. Evaporation to dryness and silica gel chromatography of the residue with benzene followed by chloroform gave the benzothiazin-4-one (11) in 93% yield [m.p.>300°C, yellow needles (from MeCN). Found: C, 56.10; H, 2.98; N, 2.96; M^+, 469 (FD Ms). $C_{22}H_{15}NO_5S_3$ requires C, 56.27; H, 3.22; N, 2.98%; M^+, 469]. Its structure was assigned from spectral data [$\nu_{max.}$ (nujol) 1645, 1725, and 1740 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 332 (log ε 3.74) and 433 nm (4.59); δ_H (CF_3CO_2D) 4.10 (s, 6H), 7.33-7.53 (m, 3H), 7.70-8.03 (m, 5H), and 8.60 (d, J 8 Hz, 1H)]. This cyclisation proceeds more inefficiently when the corresponding chloro-derivative is used; thus the compound (11) was obtained in 26% yield after 50 h of irradiation of (5) [prepared from (1)].

Similarly, the N-o-iodobenzoylthioamides (7)-(10) afforded the following benzothiazin-4-ones (12) [m.p. >300°C, 80% yield], (13) [m.p. >300°C, 83% yield], (14) [m.p. 222-223°C (decomp.), 86% yield], and (15) [m.p. 239-240°C (decomp.), 84%







(1) Ar=Ph, X=Cl
(2) Ar=Ph, X=I
(3) Ar=p-MeC_6H_4, X=I
(4) Ar=p-ClC_6H_4, X=I

(5) Ar=Ph, X=Cl, E=CO_2Me
(6) Ar=Ph, X=I, E=CO_2Me
(7) Ar=p-MeC_6H_4, X=I, E=CO_2Me
(8) Ar=p-ClC_6H_4, X=I, E=CO_2Me
(9) Ar=Ph, X=I, E=CO_2Et
(10) Ar=p-MeC_6H_4, X=I, E=CO_2Et

(11) Ar=Ph, E=CO_2Me
(12) Ar=p-MeC_6H_4, E=CO_2Me
(13) Ar=p-ClC_6H_4, E=CO_2Me
(14) Ar=Ph, E=CO_2Et
(15) Ar=p-MeC_6H_4, E=CO_2Et

yield], for which satisfactory microanalytical and spectral data have been obtained. Synthetical value of the above-mentioned photochemical heterocyclisation of the N-o-iodobenzoylthioamides is further obvious from the fact that their thermal cyclisation, unlike that of N-chloroacetylthioamides,[5b] is very slow and unprofitable. For instance, heating of 9 in THF for 24 h gave the benzothiazinone (14) in only 7% yield, together with other products.

Although the present study was carried out from our continued interest in the ring transformation reactions of isothiazoles,[5b] the reactions given herein appear promising as a synthetic method of 4H-1,3-benzothiazin-4-ones in the light of ready availability[6] of simple N-benzoylthioamides, and studies of relevance are now in progress.

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