

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

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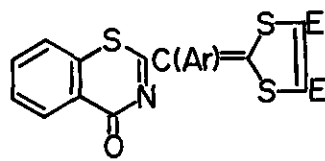
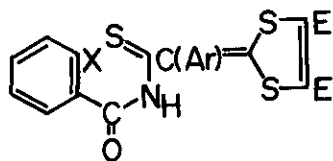
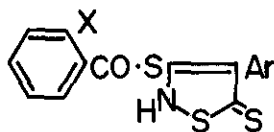
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Abstract- The photo-cyclisation of N-o-iodobenzoylthioamides
has been found to provide a novel and efficient synthesis of
4H-1,3-benzothiazin-4-ones.

Approaches to the synthesis of 4H-1,3-benzothiazines so far reported utilise
appropriately substituted o-mercapto-benzoic acids and benzamides,¹ N-(phenylthio-
methyl)benzamides,² and 1,2-benzoisothiazoles.³ We now report a new and efficient
synthetic method of this ring system which involves the photo-cyclisation⁴ of
N-o-iodobenzoylthioamides (6)-(10), prepared from 4-aryl-3-o-iodobenzoylthio-3-iso-
thiazoline-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 N₂ 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). C₂₂H₁₅NO₅S₃ requires
C, 56.27; H, 3.22; N, 2.98%; M⁺, 469]. Its structure was assigned from spectral
data [ν_{\max} . (nujol) 1645, 1725, and 1740 cm⁻¹ (C=O); λ_{\max} . (CHCl₃) 332 (log ϵ
3.74) and 433 nm (4.59); δ_{H} (CF₃CO₂D) 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 ob-
tained 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

(5) Ar=Ph, X=Cl, E=CO₂Me

(11) Ar=Ph, E=CO₂Me

(2) Ar=Ph, X=I

(6) Ar=Ph, X=I, E=CO₂Me

(12) Ar=p-MeC₆H₄, E=CO₂Me

(3) Ar=p-MeC₆H₄, X=I

(7) Ar=p-MeC₆H₄, X=I, E=CO₂Me

(13) Ar=p-ClC₆H₄, E=CO₂Me

(4) Ar=p-ClC₆H₄, X=I

(8) Ar=p-ClC₆H₄, X=I, E=CO₂Me

(14) Ar=Ph, E=CO₂Et

(9) Ar=Ph, X=I, E=CO₂Et

(15) Ar=p-MeC₆H₄, E=CO₂Et

(10) Ar=p-MeC₆H₄, X=I, E=CO₂Et

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 availability⁶ of simple N-benzoylthioamides, and studies of relevance are now in progress.

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