A New Synthesis of Thioindigo; Acyl Migration and Ring Contraction in Thiochromone Derivatives

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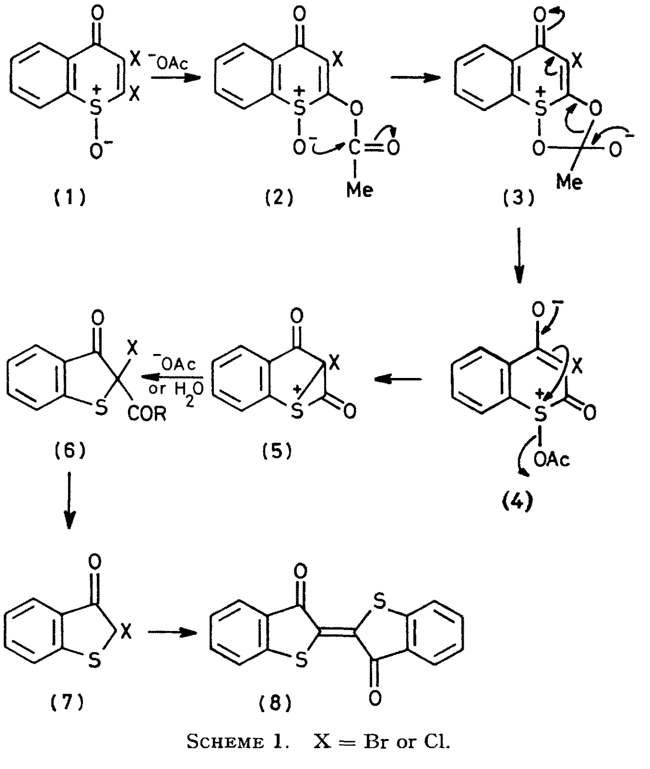
Summary Reaction of 2,3-dihalogenothiochromone *S*-oxide with sodium acetate in refluxing acetic acid gives thioindigo in 80% yield.

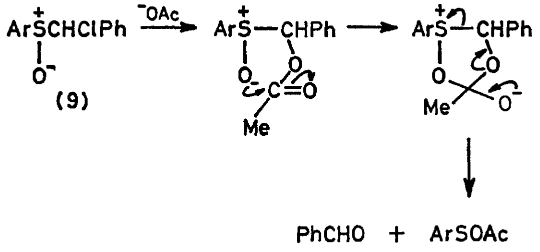
In previous work[1] we have observed the formation of thioindigo (**8**) in minor amounts in various reactions of thiochromone and thiochromanone derivatives. We now report that when 2,3-dibromo(or chloro)thiochromone *S*-oxide (**1**) is heated with sodium acetate (2 mol. equiv.) in refluxing acetic acid for 15 min thioindigo is obtained in 80% yield. However no thioindigo is formed if a 2,3-dihalogenothiochromone is used as starting material. The reaction with the sulphoxide (**1**) also proceeds slowly at room temperature in dry acetonitrile using silver acetate (1 or 2 mol. equiv.) to give (**8**) in 29 and 54% yield, respectively; with sodium benzoate (2 mol. equiv.) the yield is 52%. In the room-temperature reactions trace amounts of colourless products could be detected by t.l.c. but attempts to isolate these invariably led to thioindigo, and we were unable to stop the reaction at any intermediate stage.



Scheme 1. X = Br or Cl.

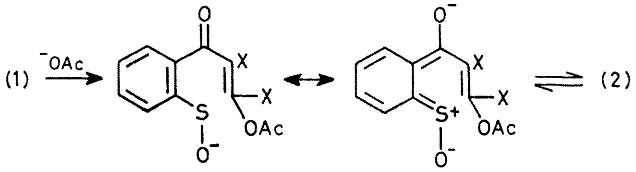
Scheme 1 is consistent with these observations. Nucleophilic displacement[1] of the halogen at C-2 leads to the acetate (**2**) which then rearranges by way of (**3**) to the *S*-acetate (**4**). The acetate function is now displaced from sulphur by intramolecular attack of the enolate (**4**) to give the thiiranium ion (**5**) which will react rapidly with any available nucleophile. Under preparative conditions in acetic acid this may well be water giving the thioindoxyl

(**6**, R = OH) which will promptly decarboxylate to the thioindoxyl (**7**) which is a known[2] precursor of thioindigo The evolution of carbon dioxide during the reaction was confirmed In dry acetonitrile acetate ion would attack (**5**) to form the mixed anhydride (**6**, R = OAc), and this on reaction with a second molecule of acetate would collapse to give the enolate of (**7**) and diacetyl carbonate (or acetic anhydride and carbon dioxide)



SCHEME 2 Ar = p-$O_2NC_6H_4$

The *O*-acetyl migration (**2**) → (**4**) is similar to 1,2-glycol monoester rearrangements, and a closer analogy involving a sulphoxide is shown in Scheme 2 Heating the chlorosulphoxide (**9**) with potassium acetate in acetic acid gave benzaldehyde in 72% yield The sulphenyl carboxylate, only stable at −20 °C,[3] did not survive



(10)

An interesting feature of the thioindigo reaction at room temperature is the appearance, after *ca* 5 min, of a blue colour (λ_{max} 600 nm) which persists for *ca* 10 min This is attributed to the formation of the sulphenate anion (**10**) The colour is transient as (**10**) is in equilibrium with (**2**) which is consumed as thioindigo formation proceeds Comparison with *o*-nitrobenzenesulphenate ions (λ_{max} 588 nm, ϵ *ca* 5 × 10^3)[4] indicates that 5—10% of (**1**) is present as (**10**) at the peak of the blue phase

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