Tetrahedron Letters, Vol.22, No.23, pp 2221 - 2224, 1981
Printed in Great Britain

0040-4039/81/232221-04$02.00/0

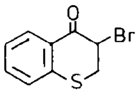
RING CONTRACTION OF 3-BROMOTHIOCHROMAN-4-ONE: FORMATION OF A DIMERIC SPIROTHIOINDOXYL AND VINYLENETHIOINDIGO

Philip J. Cox
School of Pharmacy, Robert Gordon's Institute of Technology,
Schoolhill, Aberdeen AB9 1FR, Scotland

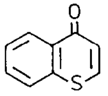
Neil E. MacKenzie and Ronald H. Thomson*
Department of Chemistry, University of Aberdeen, Meston Walk,
Old Aberdeen AB9 2UE, Scotland

Abstract: Contrary to the literature, the reaction of 3-bromothiochroman-4-one with sodium acetate in acetic acid gives a dimeric spirothioindoxyl (whose crystal structure has been determined) which, after bromination and then heating in pyridine yields "vinylenethioindigo".

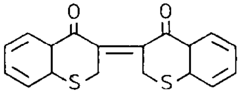
In 1925 Krollpfeiffer et al.[1] reported that heating 3-bromothiochroman-4-one 1 with sodium acetate in boiling ethanol gave thiochromone 2 whereas in boiling acetic acid the product obtained was the diketone 3 (17.5%). The latter formed a dibromide 4 which on heating in pyridine or other high boiling solvent yielded a red vat dye formulated as 5. Clearly the bis-thiochromone 5 is not a red vat dye.



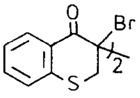
1



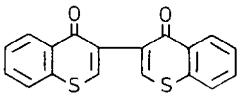
2



3



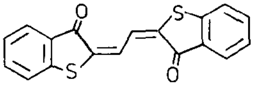
4



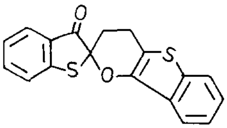
5

This work has now been repeated (in acetic acid both thiochromone and the dimeric compound are formed) and the red vat dye has been identified as "vinylenethioindigo" 6[2] by direct comparison with an authentic sample prepared by condensation of thioindoxyl with glyoxal.[3]

Further investigation showed that structures 3 and 4 are also incorrect.



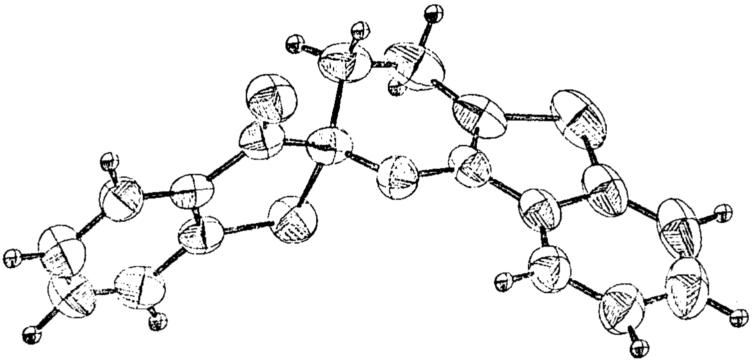
6



7

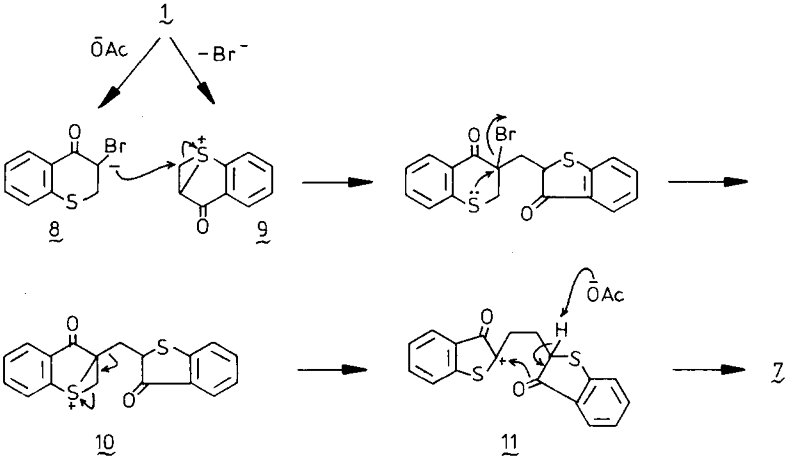
The initial dimeric product showed $\nu_{max.}$(KBr) 1705 cm^{-1}, but UV[4] and ^{1}H NMR[5] spectra not consistent with structure 3 while the ^{13}C NMR[6] spectrum showed clearly that the compound was unsymmetrical with only one carbonyl group. The problem was solved by X-ray crystallographic analysis which led to the spiro structure 7.

The molecules crystallise in the monoclinic space group $P2_1/c$ with cell dimensions a = 9.722(4), b = 12.982(16), c = 11.991(6) Å, β = 99.40(4)° and Z = 4. The X-ray intensities were measured with Mo - Kα radiation on a computer-controlled four-circle diffractometer. The crystal structure was solved by direct phasing methods and the atomic parameters were adjusted by least-squares calculations. Final R is 0.050 for 1695 reflexions. A perspective drawing is shown below. As can be seen one methylene group falls partly within

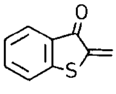


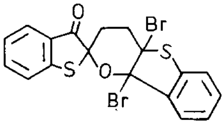
the shielding cone of the carbonyl group which accounts for the ^{1}H NMR signals around δ 3.

The formation of 7 from 1 can be reasonably explained by an intermolecular reaction and two ring contractions as shown below. In the first the thiiranium cation 9 reacts with 8, the anion of 1, while in the second the thiiranium cation 10 undergoes a 1,2-shift to form the tertiary carbonium ion 11 which cyclises to 7. Since this work was carried out a



compound which appears to be 7[7] has been obtained[8] by heating 3-diazothiochroman-4-one with silver oxide in boiling methanol. It was suggested[8] that 7 is a Diels-Alder dimer of 12 derived from the initial carbene. When the preparation of 7 was repeated under our


12


13

conditions but in the presence of a large excess of maleic anhydride or N-phenylmaleiimide the formation of the spiro ketone was not suppressed and no malei-adduct could be detected. A minor product in the reaction of 3-bromothiochroman-4-one with sodium acetate is "vinylene thioindigo" 6 which could arise from 11 by loss of a proton followed by oxidation.

The spiroketone 7 readily forms a yellow insoluble dibromide which darkens on the surface on exposure to light owing to the formation of "vinylenethioindigo". It is converted quantitatively into "vinylenethioindigo" 6 on heating in high-boiling solvents. The structure of the dibromide appears to be 13 as the F.T. ^{1}H NMR spectrum (in very dilute carbon tetrachloride) shows, besides ArH signals, two methylene multiplets (8 lines each) centred at δ 1.77 and 2.41. Several routes from 13 to 6 are possible, and the reaction may be self-catalysed by the hydrogen bromide released.

In the original paper[1] several substituted 3-bromothiochroman-4-ones were converted into analogues of 3 and 5. These must now be regarded as derivatives of 7 and 6, respectively.

References and Notes

[1] F. Krollpfeiffer, H. Schultze, E. Schumbohm, and E. Sommermeyer, *Ber.*, 1925, *58*, 1654.

[2] Assumed to be *trans*.

[3] P. Freidländer and F. Risse, *Ber.*, 1914, *47*, 1919.

[4] $\lambda_{max.}$(EtOH) 237, 264, 296, 304, 381 nm (log ε 4.52, 4.08, 3.80, 3.82, 3.38, 3.36).

[5] ^{1}H δ ($CDCl_3$) 8.0-7.2 (8H, m, ArH), 3.14, 2.70, and 2.22 (total 4H, m in ratio 3:2:2, CH_2CH_2).

[6] ^{13}C δ ($CDCl_3$) 196.66(s), 150.25(s), 143.48(s), 136.88(d), 135.88(s), 131.31(s), 128.30(s), 127.84(d), 125.35(d), 124.75(d), 124.36(d), 123.99(d), 122.36(d), 120.05(d), 112.64(s), 93.75(s), 30.35(t), 20.39(t).

[7] The physical constants agree with those for our compound except for the ^{1}H NMR spectrum which shows a 4H multiplet between δ 2.0 and 2.3 ($CDCl_3$).

[8] Y. Tamura, H. Ikeda, C. Mukai, S.H.M. Bayomi, and M. Ikeda, *Chem. Pharm. Bull.*, 1980, *28*, 3430.

(Received in UK 16 March 1981)