Monatshefte für Chemie 118, 1197—1199 (1987)

Monatshefte für Chemie
Chemical Monthly

Peracid Oxidation of Benzothiopyranthiones and Benzopyranthiones

Short Communication

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(Received 10 June 1987. Accepted 17 June 1987)

Benzothiopyran-2 and 4-thiones and benzopyran-2-thiones undergo oxidation to sulphines which on further oxidation give the carbonyl derivatives or polymeric products.

(Keywords: 2H-[1]Benzopyran-2-thiones; 2-H and 4H-[1]Benzothiopyranthiones; Sulphines)

Persäure-Oxidation von Benzothiopyranthionen und Benzopyranthionen (Kurze Mitteilung)

Benzothiopyran-2 und 4-thione und Benzopyran-2-thione werden mit Persäuren zu Sulfinen oxidiert, die ihrerseits bei weiterer Oxidation die Carbonylderivate oder polymere Produkte ergeben.

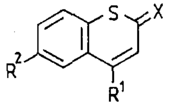
Controlled peracid oxidation of dithiocarboxylic esters has been investigated by *Zwanenburg* and his group [1]. They achieved stepwise addition of three oxygen atoms to phenyl dithiobenzoate isolating the sulphine (thione-S-oxide) sulphinyl sulphine and sulphonyl sulphine. While oxidation of 2*H*-[1]benzothiopyran-2-thiones to benzothiopyran-2-ones has been described [2], controlled oxidation to the sulphine has not been carried out on these compounds. We report here on the formation of sulphines from benzothiopyran-2-thiones (**1 a–d**) and benzopyran-2-thiones (**2 a–f**).

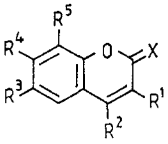
Treatment of solutions of the compounds **1 a–d** in chloroform with one equivalent of *m*-chloroperbenzoic acid in ether at 0 °C yielded the orange sulphines **3 a–d** which were purified by p.l.c. (chloroform as eluant). When two equivalents of peracid were added to dilute solutions of the thiones **1 a–d** the corresponding carbonyl compounds were isolated but addition of the peracid to concentrated solutions resulted in formation

Table 1. *M.p.s and selected spectroscopic data for the sulphines*

Compound	m.p.[a] °C	^{1}H (ppm)[b] vinylic protons	^{13}C (ppm)[c] C=S=O	Relative Abundance %		
				M$^+$	M$^+$-O	M$^+$-SO
3 a	89.5– 90.5	7.05 (d, H-3), 7–12 (d, H-4), *J* 10 Hz	185.17	87	4	100
3 b	82 – 86	6.94 (q, H-3, *J* 1 Hz)	186.18	100	26	85
3 c	154 –157	6.73 (d, H-3), 6.77 (d, H-4), *J* 10 Hz		100	56	90
3 d	116 –121	6.91 (q, H-3, *J* 1 Hz)		100	38	94
4 a	130 –137	6.64 (d, H-3), 6.9 h (d, H-4), *J* 10 Hz		100	11	38
4 b	141 –148	6.65 (d, H-3), 7.01 (d, H-4), *J* 10 Hz		100	15	22
4 c	105 –114	6.43 (q, H-3, *J* 1 Hz)				
4 d	119 –127	6.50 (q, H-3, *J* 1 Hz)				
4 e	114 –120	6.52 (q, H-3, *J* 1 Hz)				
5	91 – 97	7.30–8.05 (H-3, H-5, *Ar*H)	180.98	59	100	–
6	132 –134	6.63 (q, H-3, *J* 1 Hz), 9.92–10.12 (m, H-5)	177.23	48	32	14

[a] Thermally unstable
[b] Perkin-Elmer R 12 spectrometer operating at 60 MHz
[c] Joel PFT 100 spectrometer



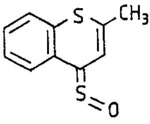


1 X=S
3 X=SO

2 X=S
4 X=SO

a $R^1=R^2=H$
b $R^1=Me;\ R^2=H$
c $R^1=H;\ R_2=Me$
d $R^1=R^2=Me$

a $R^1=R^2=R^4=R^5=H;\ R^3=Me$
b $R^1=R^2=R^5=H;\ R^3=R^4=Me$
c $R^1=R^3=R^5=H;\ R^2=R^4=Me$
d $R^1=R^5=H;\ R^2=R^3=R^4=Me$
e $R^1=R^4=H;\ R^2=R^3=R^5=Me$
f $R^3=R^4=R^5=H;\ R^1, R^2= -CH=CH-CH=CH-$



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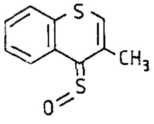

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of polymeric products. The conversion of the benzopyran-2-thiones **2 a–f** into sulphines **4 a–f** required slow addition of about 0.5 equivalents of peracid as use of more oxidant caused formation of the carbonyl compounds and dark products. In each of the experiments only one of the two possible isomers, *E* and *Z*, was isolated (derived from ^{1}H NMR).

Earlier it was reported [1] that stepwise oxidation of thiaxanthione proceeded to the sulphonyl sulphine while, in contrast, 2-phenyl-4*H*-[1]benzothiopyran-4-thione was found [3] to yield the sulphine and then the ketone. In the present work we prepared the sulphines **5** and **6** and also found that further oxidation gave the corresponding ketones.

Correct microanalytical data were obtained for the sulphines **3 a–d**, **5** and **6** but the less stable sulphines **4 a–e** were identified by mass and/or ^{1}H NMR (Table 1) and UV spectroscopy. Desulphurisation of the sulphines **4 a–f** to the carbonyl analogues, could be followed by repetitively scanning the UV-vis spectrum at constant time intervals and observing the diminution of the characteristic 410–413 nm absorption. The decomposition time depended upon the structure and ranged from 40 min (**4 f**) to 10 h (**4 a**).

References

[1] *Zwanenburg B* (1982) Recl Trav Chim Pays-Bas 101: 1 and references therein
[2] *Charlton JL, Loosmore SM, McKinnon DM* (1974) Can J Chem 52: 3021
[3] *Bognar R, Balint J, Rakosi M* (1977) Liebigs Ann Chem: 1529