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Some Reactions of 2H-[1]Benzothieno[3,2-b]pyran-2-ones and Related Compounds

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The conversion of 2*H*-[1]benzothieno[3,2-b]pyran-2-ones into mono- and dithio-derivatives and the preparation of some dibenzothiophenes, sulphines and pyridones are described.

(Keywords: [1]Benzothienopyranones; Thiopyrano[1]benzothiophenones)

Einige Reaktionen von 2H-[1]Benzothieno[3,2-b]pyran-2-onen und verwandten Verbindungen

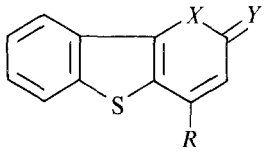
Es wird die Umsetzung von 2*H*-[1]benzothieno[3,2-b]pyran-2-onen zu Mono- und Dithio-Derivaten und die Darstellung einiger Dibenzothiophene, Sulfine, und Pyridone beschrieben.

Introduction

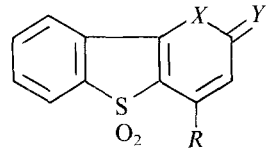
Previously [1] we reported thiation reactions of 4-phenyl-2*H*-[1]benzothieno[3,2-b]pyran-2-one **1a**, the isomeric 1-phenyl-3*H*-[1]benzothieno[3,2-c]pyran-3-one **2** and the corresponding dioxides **3a** and **4**. In continuation of this work we now describe the preparation of thiono-, thiolo- and dithio-derivatives of the 4-methyl (**1b** and **3b**) and 4-unsubstituted (**1c** and **3c**) analogues and report on some *Diels-Alder* and oxidation reactions of members of these series.

Results

The pyrones **1b** and **c**, obtained [2, 3] by the acid-catalysed reaction of *o*-mercaptobenzoic acid and the appropriate 2-pentenedioic acid were oxidised to the dioxides **3b** and **3c**. Compounds **1b**, **1c** and **3b** were converted into the thiono-analogues **5b**, **5c** and **6b** with phosphorus pentasulphide. Treatment of the sulphone **3b** with sodium sulphide in methanol followed by acidification gave, as minor product, the thiolopyrone **7b** and, as major product, an acidic compound which on heating

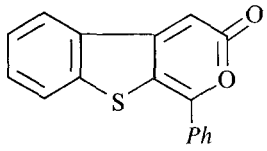


1 $X = Y = O$
5 $X = O$; $Y = S$
10 $X = Y = S$
20 $X = O$; $Y = NNHPh$



3 $X = Y = O$
6 $X = O$; $Y = S$
7 $X = S$; $Y = O$
9 $X = Y = S$
18 $X = S$; $Y = SO$
19 $X = NMe$; $Y = O$

a R = *Ph*; **b** $R = CH_3$; **c** R = H



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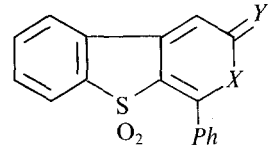
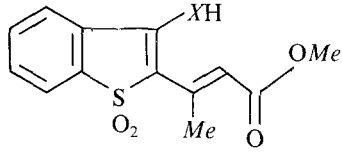


4 $X = Y = O$
15 $X = Y = S$
16 $X = S$; $Y = SO$
17 $X = S$; $Y = O$



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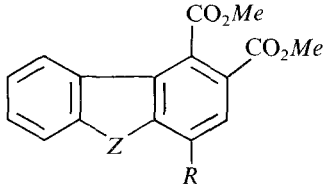
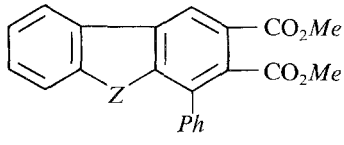
a $X = S$
b $X = O$



11 $Z = S$
12 $Z = SO_2$



13 $Z = S$
14 $Z = SO_2$

a R = *Ph*; **b** $R = CH_3$

was converted into the thiolopyrone **7b**. This acidic compound is presumed to be the δ-mercapto-ester **8a** since on recrystallisation it afforded a compound, $C_{13}H_{12}O_5S$, assigned as the δ-keto tautomer of compound **8b** on the basis of spectroscopic data. The thiolopyrone was converted into the dithiopyrone **9b**. The reaction with sodium sulphide was not carried out on the unsubstituted pyrone **3c** but it was observed that treatment either with phosphorus pentasulphide or *Laweson*'s Reagent [4] in xylene converts the pyrone **3c** into the dithiopyrone **9c**; after the initial rapid thiation of the carbonyl group the pyranthione ring opens and thiation and subsequent cyclisation occur. Both thiating agents proved capable of reducing the sulphone group to sulphide. Since reduction can occur before and after thiation a mixture of six main components **1c**, **5c**, **10c**, **3c**, **6c** and **9c** may be obtained on prolonged heating. The distinctive colours and R_f values of the compounds on t.l.c. allowed for easy monitoring of the reaction. Compound **9c** was separated and characterised; **10c** was also isolated but identified only by mass spectroscopy [m/z 234 (M^+, 95%) and 190 ($M^+ - CS$, 100%)]. Prolonged heating of the 4-phenylpyrone **3a** with *Lawesson*'s Reagent also resulted in ring-opening, thiation, reduction and cyclisation and from the mixture of products formed the previously unavailable red dithiopyrone **10a** was isolated and identified by an accurate mass spectrum.

Compounds **1a** and **b** on treatment with dimethyl acetylene dicarboxylate in refluxing xylene yielded in each case the dimethyl dibenzothiophene 1,2-dicarboxylate **11a** and **b** oxidation of which gave the sulphones **12a** and **b**. The pyrone **2** also reacted with dimethyl acetylene dicarboxylate affording the 2,3-dibenzothiophene dicarboxylate **13** which was oxidised to the sulphone **14**. Attempts to carry out the *Diels-Alder* reactions under milder conditions were unsuccessful. In similar reactions in refluxing xylene the deactivated sulphonyl derivative **4** gave the dibenzothiophene dioxide **14** in low yield while the dithiopyranone **10a** yielded the dibenzothiophene **11** in 27% yield.

Zwanenburg and his group [5] have carried out oxidation of dithioesters and thiaxanthione with 1, 2, and 3 equivalents of peracid and have isolated sulphines, sulphinyl sulphines and sulphonyl sulphines.

In the present work we examined the peracid oxidation of the dithiolactones **9a** and **15**. On reaction with 1, 2 or 3 equivalents of *m*-chloroperbenzoic acid the dithiolactone **15** formed only a dark brown compound, $C_{17}H_{10}O_3S_2$, assigned as the sulphine **16**; the mass spectrum showed the molecular ion at m/z 358, the base peak at m/z 342, indicating loss of one oxygen, and the remaining fragmentation pattern identical with that of the dithiopyrone **15**. The i.r. spectrum showed sulphonyl absorptions at ν 1310 and 1160 cm^{-1} and two peaks at ν 1010 and 1070 cm^{-1} respectively which may be attributed to the C = S = O system [5] and which are absent in the spectrum of the dithiopyrone **15**. When the reaction was carried out at room temperature the 2-oxo-derivative **17** was obtained. Sim-

ilarly oxidation of the dithiopyrone **9a** with peracid at 0° afforded the sulphine **18** and at room temperature the pyrone **7a**. In contrast, oxidation of the thionopyrone **6a** with peracid at 0° gave the pyrone **3a**, the initially formed coloured product, presumably the sulphine, having decomposed during work-up.

The tendency for the sulphonyl derivatives to ring-open was shown by the reaction of compounds **3a** and **b** with methylamine to yield pyridones **19a** and **b**. The pyridones showed i.r. carbonyl absorptions at 1660 cm^{-1} and loss of the fragment m/z 28 (CO) in the mass spectrum. The thione **5a** reacted with phenylhydrazine yielding the phenylhydrazone **20**.

Mass spectroscopic data for the new compounds prepared are given in Table 1.

Experimental

N.m.r. spectra were recorded on a Perkin-Elmer R12B spectrometer at 60 MHz, in deuterochloroform with tetramethyl silane as internal standard. I.r. spectra were recorded on a Perkin-Elmer 337 spectrometer (KBr discs). Merck-silica gel $PF_{254+366}$ was used for preparative layer chromatography.

Analytical and physical data for new compounds are given in Table 2.

Oxidation of Compounds **1b, 1c, 11a, 11b,** *and* **13**

A mixture of the sulphide (100 mg), hydrogen peroxide (28% 1.5 ml), acetic anhydride (2 ml) and acetic acid (2 ml) was heated cautiously to boiling and then

Table 1. *Spectroscopic data*

No.	m/z (relative intensity)	$\nu_{C=O}$ cm^{-1}
1b	216 (M^+, 100%), 188 (M^+-28, 92%), 187 (M^+-29, 60%)	1720
1c	202 (M^+, 100%), 174 (M^+-28, 84%)	1740
3b	248 (M^+, 100%), 220 (M^+-28, 88%), 136 (M^+-112, 30%)	1720
3c	234 (M^+, 100%), 206 (M^+-28, 45%), 136 (M^+-98, 25%)	1750
5b	232 (M^+, 100%), 203 (M^+-29, 7%), 188 (M^+-44, 55%)	
5c	218 (M^+, 100%), 190 (M^+-28, 5%), 174 (M^+-44, 78%)	
6b	264 (M^+, 100%), 236 (M^+-28, 15%), 220 (M^+-44, 10%)	
7b	264 (M^+, 100%), 236 (M^+-28, 100%), 136 (M^+-128, 70%)	1620
8b	280 (M^+, 3%), 248 (M^+-32, 100%), 220 (M^+-60, 98%)	1700, 1730
9b	280 (M^+, 100%), 236 (M^+-44, 65%), 136 (M^+-144, 32%)	
9c	266 (M^+, 100%), 222 (M^+-44, 52%), 136 (M^+-130, 38%)	
10a	310 (M^+, 100%), 277 (M^+-33, 15%), 266 (M^+-44, 98%)	
11a	376 (M^+, 100%), 345 (M^+-31, 70%)	1720
11b	314 (M^+, 95%), 283 (M^+-31, 100%)	1720, 1740
12a	408 (M^+, 100%), 377 (M^+-31, 99%)	1730
12b	346 (M^+, 58%), 315 (M^+-31, 100%)	1720, 1735
13	376 (M^+, 100%), 345 (M^+-31, 88%), 258 (M^+-118, 30%)	1720, 1730
14	408 (M^+, 70%), 377 (M^+-31, 100%), 346 (M^+-53, 23%)	1740
16	358 (M^+, 15%), 342 (M^+-16, 100%), 298 (M^+-60, 70%)	
18a	358 (M^+, 100%), 342 (M^+-16, 35%), 298 (M^+-60, 38%)	
19a	323 (M^+, 100%), 295 (M^+-28, 28%), 136 (M^+-187, 10%)	1660
19b	261 (M^+, 100%), 233 (M^+-28, 26%), 136 (M^+-125, 25%)	1660
20a	368 (M^+, 100%), 276 (M^+-92, 33%)	

Table 2. *Analytical and physical data*

No.	M.p. (0 °C)	Solvent of crystallisation	Yield	Found C	Found H	Found S	Molecular formula	Required C	Required H	Required S
3b	226–227	*Et*OH	68	57.8	3.0	13.1	$C_{12}H_8O_4S$	58.1	3.2	13.0
3c	244–245	*Et*OH	59				$C_{11}H_6O_4S$[a]			
5b	201–202	$CHCl_3$/*Me*OH	90	61.7	3.8	27.1	$C_{18}H_8OS_2$	62.0	3.5	27.6
5c	158–159	$CHCl_3$/*Me*OH	90	60.35	3.1	29.1	$C_{11}H_6OS_2$	60.5	2.8	29.4
6b	225–227	$CHCl_3$/*Me*OH	48	54.8	2.85	24.1	$C_{12}H_8O_3S_2$	54.5	3.05	24.3
7b	223–224	*Et*OH	68[b]	54.1	3.1	23.8	$C_{12}H_8O_3S_2$	54.5	3.05	24.3
8b	110–112[d]	C_6H_6/*DIE*[c]	62	55.95	4.2	11.1	$C_{13}H_{12}O_5S$	55.7	4.3	11.4
9b	268–271[d]	$CHCl_3$/*Me*OH	59	51.4	2.7	34.8	$C_{12}H_8O_2S_2$	51.4	2.9	34.3
9c	232–233	$CHCl_3$/*Me*OH	53	49.4	2.7	36.2	$C_{11}H_6O_2S_2$	49.6	2.3	36.1
10a	212–213	*Me*OH	29				$C_{17}H_{10}S_3$[e]			
11a	111–112	$CHCl_3/C_6H_{12}$	52	70.3	4.5	8.6	$C_{22}H_{16}O_4S$	70.2	4.3	8.5
11b	162–163	C_6H_{12}	58	64.7	4.4	10.2	$C_{17}H_{14}O_4S$	64.95	4.5	10.2
12a	191–192	*Et*OH	86	64.5	3.8	8.0	$C_{22}H_{16}O_6S$	64.7	3.95	7.85
12b	214–215	*Et*OH	79	58.8	3.95	9.6	$C_{17}H_{14}O_6S$	58.95	4.1	9.3
13	130–131	$CHCl_3/C_6H_{12}$	88	69.8	4.3	9.0	$C_{22}H_{16}O_4S$	70.2	4.3	8.5
14	232–233	*Et*OH	91	64.2	4.15	8.3	$C_{22}H_{16}O_6S$	64.7	3.95	7.85
16	196 [d]	*Et*OH	85	57.0	3.0		$C_{17}H_{10}O_3S_3$	57.0	2.8	
18a	200 [d]	*Et*OH	79	57.1	2.5		$C_{17}H_{10}O_3S_3$	57.0	2.8	
19a	243–245	*Et*OH	92	66.6	3.8	9.8	$C_{18}H_{13}NO_3S$[f]	66.85	4.05	9.9
19b	249–252	*Et*OH	71	59.9	4.2	12.5	$C_{13}H_{11}NO_3S$[g]	59.75	4.2	12.3
20a	171–172	C_6H_6/*Me*OH	94	75.4	4.4	8.4	$C_{23}H_{16}N_2OS$[h]	75.0	4.3	8.7

[a] Accurate mass agreed to 0.9 mmu with $C_{11}O_6O_4S$
[b] Total yield after pyrolysis of compound (**7b**)
[c] Diisopropyl ether
[d] With decomposition
[e] Accurate mass agreed to 1.3 mmu with $C_{17}H_{10}S_3$
[f] Found: N, 4.3. $C_{18}H_{13}NO_3S$ requires N, 4.3%
[g] Found: N, 5.47. $C_{13}H_{11}NO_3S$ requires N, 5.6%
[h] Found: N, 7.5. $C_{23}H_{16}N_2OS$ requires N, 7.6%

allowed to cool. After some hours the solution deposited colourless crystals which were recrystallised from ethanol.

Thiation of Compounds **1b**, **1c**, **3b**, *and* **7b**

Treatment with tetraphosphorus decasulphide (1.2 g) of the pyrones **1b** and **1c** (400 mg) for 6 h in refluxing toluene (40 ml) and of the pyrones **3b** and **7b** (400 mg) for 8 h in refluxing xylene (40 ml) afforded the corresponding thioxo pyrans.

4-Methyl-2H-thioyprano[3,2-b]benzothiophen-2-one (**7b**)

A mixture of sodium sulphide (400 mg) and the pyrone **3b** (200 mg) in methanol (15 ml) was refluxed for 1 h. The mixture was concentrated, treated with water, acidified and extracted into choloroform. The extracts were washed with water, dried and concentrated. The product on separation on p.l.c. with chloroform as eluant gave the thiopyran **7b** (25 mg, 12%) and a yellow compound (134 mg) at lower R_f value. The latter on purification gave a compound assigned structure **8b**. The experiment was repeated and the crude product was pyrolysed at 250–270° for 10 minutes yielding the thiopyran **7b** (140 mg, 68%).

2H-Thiopyrano[3,2-b]benzothiophen-2-thione (**10c**)

Lawesson's Reagent (172 mg) was added to a solution of pyrone **3c** (200 mg) in dry xylene (20 ml) and the reaction mixture was heated under reflux for 5 h. Evaporation of the solvent *in vacuo* and p.l.c. in the dark of the residual oil with chloroform as eluant afforded as one major product, the dithiopyrone **10c**.

4-Phenyl-2H-thiopyrano[3,2-b]benzothiophen-2-thione (**10a**)

Lawesson's Reagent (561 mg) was added to a mixture of the pyrone **3a** (430 mg) and xylene (20 ml) and the whole refluxed for 7 h. The mixture was worked up as before yielding the thiopyrone **10a** as red needles.

Dimethyl dibenzothiophene dicarboxylates **11a**, **11b**, *and* **13**

A mixture of dimethyl acetylene dicarboxylate (2.5 ml) and pyrone (**1a**, **1b** or **2**) (300 mg) in xylene (15 ml) was refluxed for 18 h. The xylene was evaporated *in vacuo* and p.l.c. of the residual oil with chloroform as eluant afforded the dibenzothiophene.

Oxidation of Dithiopyrones **9a** *and* **15**

A solution of *m*-chloroperbenzoic acid (75 mg) in ether (10 ml) was added dropwise to a solution of the dithiopyrone (40 mg) in chloroform (10 ml) at 0 °C and the mixture stirred for 30 min. The red colour of the dithiopyrone was discharged rapidly and a dark brown solid separated. Collection of the dark solid followed by crystallisation gave sulphine **18a**; in the case of sulphine **16** work-up was by p.l.c. (chloroform as eluant) followed by crystallisation.

1-Methyl-2H-[1]benzothieno[3,2-b]pyrid-2-one 5,5-dioxides (**19a** *and* **19b**)

A solution of the pyrone **3a** (100 mg) and methylamine (25%, 1 ml) in methanol (9 ml) was refluxed for 30 min. The reaction mixture was treated with ice and extracted with chloroform. The extracts were washed with water, dried and concentrated and the residue recrystallised yielding compound **19a**. A similar experiment in which the pyrone **3b** was heated for 1 h gave the pyridone **19b**.

4-Phenyl-2H-[1]benzothieno[3,2-b]pyran-2-thione phenylhydrazone (**20 a**)

A solution of the pyran-2-thione **5 a** and phenylhydrazine (0.5 g) in a mixture of benzene (7 ml) and methanol (7 ml) was refluxed for 12 h. Removal of the solvent and crystallisation of the residual solid gave the phenylhydrazone as red needles.

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