Cyclic Sulphones. Part XV.[1] Benzo- and Dibenzo-thiopyran *SS*-Dioxides, 'Active Methylene' Compounds in Substitution and Condensation Reactions

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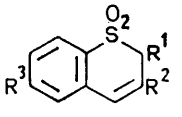
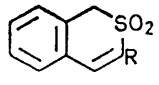
2*H*-Benzo[*b*]thiopyran 1,1-dioxide, 1*H*-benzo[*c*]thiopyran 2,2-dioxide, dibenzo[*b,d*]thiopyran 5,5-dioxide, and thioxanthen 10,10-dioxide are methylated by methyl iodide under mild basic conditions. 2*H*-Benzo[*b*]thiopyran 1,1-dioxide reacts analogously with 2,4-dinitrochlorobenzene. Benzylidene derivatives are obtained by reacting the two benzothiopyran and thioxanthen *SS*-dioxides with *para*-substituted benzaldehydes. This behaviour is discussed and compared with that of other sulphonyl-substituted carbon acids.

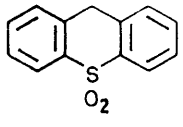
THIOPYRAN *SS*-DIOXIDE systems have been found to display considerable acidity, both kinetically[2] and thermodynamically.[1] Under mildly basic conditions, substrates (1)—(8) should be expected to behave as nucleophiles in nucleophilic substitutions and in condensations with carbonyl compounds.



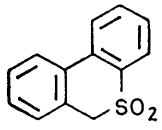
(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = Me$, $R^2 = R^3 = H$
(3) $R^2 = Me$, $R^1 = R^3 = H$
(4) $R^3 = Me$, $R^1 = R^2 = H$



(5) R = H
(6) R = Me



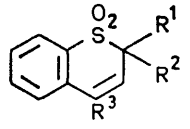
(7)



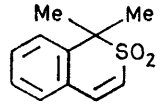
(8)

Substitutions.—Methylation of sulphones (1), (2), (5), (7), and (8) was carried out with methyl iodide in acetone and in the presence of potassium carbonate. Both (1) and (2) gave the same mixture of methylated products, 2,2-dimethyl- (9), 2,2,4-trimethyl- (10), and 2,4-dimethyl-2*H*-benzo[*b*]thiopyran 1,1-dioxide (11), isolated as pure compounds by preparative g.l.c. As the position of one methyl group was already known, structures (9)—(11) were assigned on the basis of ^{1}H n.m.r. spectra.

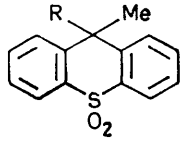
1,1-Dimethyl-1*H*-benzo[*c*]thiopyran 2,2-dioxide (14) was obtained from sulphone (5). Sulphone (7) gave mainly the 9,9-dimethyl 10,10-dioxide (16). Under less forcing conditions the monomethyl derivative (15) could also be obtained. Dibenzo[*b,d*]thiopyran 5,5-dioxide (8) was less reactive: in fact under the above conditions it gave a mixture for which ^{1}H n.m.r. analysis suggested the presence (see Table 2) of the monomethylated product (17), and unchanged starting material in the ratio 1·5 : 1. The dimethylated sulphone (18) could be obtained in quantitative yields from sulphone (8) by



(9) $R^1 = R^2 = Me$, $R^3 = H$
(10) $R^1 = R^2 = R^3 = Me$
(11) $R^1 = H$, $R^2 = R^3 = Me$
(12) $R^1 = H$, $R^2 = R^3 = 2,4\text{-}(NO_2)_2C_6H_3$
(13) $R^1 = H$, $R^2 = Me$, $R^3 = 2,4\text{-}(NO_2)_2C_6H_3$



(14)



(15) R = H
(16) R = Me

(17) R = H
(18) R = Me

treatment with methyl iodide in dimethyl sulphoxide using sodium methoxide as base.

Both sulphones (1) and (2) reacted with 2,4-dinitrochlorobenzene in the presence of sodium carbonate to

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[1] Part XIV, G. Gaviraghi and G. Pagani, *J.C.S. Perkin II*, 1973, 50.

[2] S. Bradamante, S. Maiorana, A. Mangia, and G. Pagani, *J. Chem. Soc.* (*B*), 1971, 74.

TABLE 1

Analytical and physical data of substitution derivatives

Compound	Method	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(9)	A	63	104·5 [a]	63·7	5·9		$C_{11}H_{12}O_2S$	63·4	5·8	
(10)	A	21	127·5 [a]	65·0	6·2		$C_{12}H_{14}O_2S$	64·8	6·3	
(11)	A	16	120 [a]	63·2	5·9		$C_{11}H_{12}O_2S$	63·4	5·8	
(12)	A	70	165 [b]	41·8	1·9	8·8	$C_{22}H_{13}Cl_3N_4O$	41·9	2·0	8·9
(13)	A [c]	75	167—168 [d]	53·0	3·3	7·7	$C_{16}H_{12}N_2O_6S$	53·3	3·3	7·7
(14)	A [c]	57	96 [e]	63·5	5·5		$C_{11}H_{12}O_2S$	63·4	5·8	
(15)	A	45	239 [f,g]							
(16)	B	50	167 [f,h]							
(18)	C	80	158 [f]	69·6	5·2		$C_{15}H_{14}O_2S$	69·7	5·4	

[a] From preparative g.l.c. [b] From chloroform; crystallizes as adduct with one molecule of solvent, sint. at 142°. [c] At room temperature. [d] From dil AcOH. [e] From benzene–hexane. [f] By fractional crystallization from AcOH. [g] Lit., m.p. 241—242° (A. C. Turney, jun., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, 1969, **34**, 940). [h] Lit., m.p. 164—167° (ref. as note *g*). From absolute EtOH.

TABLE 2

^{1}H N.m.r. data (τ values [a]) of substitution derivatives

Compound	Aromatic	2-H	3-H	4-H	Me	|J|/Hz
(9)	1·95—3 (m) [b]		4·00 (d)	3·46 (d)	8·48 (s)	$J_{3,4}$ 10·2
(10)	1·90—2·85 (m) [b]		4·16 (m)		7·84 (d)	$J_{H(3),Me(4)}$ 1·3
					8·51 (s)	
(11)	1·90—2·75 (m) [b]	6·18 (m)	4·12 (dq)		7·82 (t)	$J_{H(2),Me(2)}$ 7; $J_{2,3}$ 4·5;
					8·48 (d)	$J_{H(3),Me(4)}$ 1·5; $J_{H(2),Me(4)}$ 1·7
(12)	0·80—3·20 (m) [c]	3·65 (d)	3·45 (d)			$J_{2,3}$ 5
(13)	1·00—3·40 (m) [d]	6·02 (m)	3·96 (m)		8·40 (d)	$J_{H(2),Me}$ 7
(14)	2·40—2·70 (m)		3·46 (d)	2·80 (d)	8·27 (s)	$J_{3,4}$ 10·2
(17)	1·82—2·80 (m)	5·92 [q (H-6)]			8·44 (d)	$J_{H(6),Me}$ 7
(18)	1·80—2·80 (m)				8·31 (s)	

[a] In $CDCl_3$ relative to tetramethylsilane. [b] 8-H is present as a multiplet at τ 1·9—2·1. [c] 5-H is present at τ 3·1, the protons of the dinitrophenyl all have different chemical shifts. [d] 5-H is present at τ 3·22.

TABLE 3

Analytical and physical data of benzylidene derivatives

Compound	Method	Reaction time (h)	Yield (%)	M.p. (°C) (solvent)	Found (%) C	H	N	Formula	Required (%) C	H	N
(19)	A	24 [a]	50	122·5 (EtOH)	71·4	4·5		$C_{16}H_{12}O_2S$	71·6	4·5	
(20)	A	6 [a]	50	144 (AcOH–H_2O) 147—148 [b]	63·4	3·6		$C_{16}H_{11}ClO_2S$	63·5	3·7	
(21)	A	2 [a]	45	185 (MeOH)	61·2	3·5	4·3	$C_{16}H_{11}NO_4S$	61·35	3·5	4·5
	D	3 Years [c]	80								
(22)	B	16 [c]	*ca.* 30	163 (EtOH)	69·2	5·35	4·3	$C_{18}H_{17}NO_2S$	69·4	5·5	4·5
(23)	A	144 [c]	57	198—200 (AcOH–H_2O)	64·1	4·2		$C_{17}H_{13}ClO_2S$	64·4	4·1	
(24)	A	14 [a]	50	175 (EtOH)	64·5	4·2		$C_{17}H_{13}ClO_2S$	64·4	4·1	
(25)	A	72 [a]	30	190—191 (EtOH)	64·2	4·2		$C_{17}H_{13}ClO_2S$	64·4	4·1	
	B	3 [a]	33								
(26)	B	1 [a]	40	200—201 (Dioxan)	62·1	4·0	4·3	$C_{17}H_{13}NO_4S$	62·4	4·0	4·3
(27)	B	12 [a]	45	209—210 (MeOH)	61·3	3·5	4·5	$C_{16}H_{11}NO_4S$	61·35	3·5	4·5
(28)	B	80 [a]	20	202—203 (MeOH)	62·2	4·0	4·2	$C_{17}H_{13}NO_4S$	62·4	4·0	4·3
(29)	B	24 [a]	50	195 (DMF–H_2O)	67·7	3·6		$C_{20}H_{13}ClO_2S$	68·1	3·7	
(30)	C	40 [d]	60	225—227 (DMF)	72·8	5·3	3·6	$C_{22}H_{19}NO_2S$	73·1	5·3	3·9

[a] At reflux. [b] After sublimation. [c] At room temperature. [d] At 75°.

TABLE 4

^{1}H N.m.r. data (τ values [a]) of benzylidene derivatives

Compound	Solvent	Aromatics	Heterocyclic 3-H	4-H	=CH	Me	|J|/Hz
(19)	$CDCl_3$	1·8—2·8 (m)	3·04 (d)	3·23 (d)	2·15br (s)		$J_{3,4}$ 11·2
(20)	$CDCl_3$	1·8—2·8 (m)	3·07 (d)	3·19 (d)	2·23br (s)		$J_{3,4}$ 11·2
(21)	DMSO	1·6—2·5 (m)	2·92		2·03br (s)		
(22)	$CDCl_3$	1·8—3·5 (m)	2·94 (d)	3·33 (d)	2·28br (s)	6·95 (s)	$J_{3,4}$ 11·2
(22)	CF_3CO_2H [b]	1·9—2·8 (m)	3·4		2·66br (s)	6·75br (s)	
(23)	$CDCl_3$	2·0—3·0 (m)		3·5br (m)	2·31br (s)	8·08 (d)	$J_{H(3),Me} \sim 1$
(24)	$CDCl_3$	1·9—2·8 (m)	3·10 (d)	3·27 (d)	2·24br (s)	7·57 (s)	$J_{3,4}$ 11·2
(25)	DMSO	1·7—2·6 (m)	2·78 (m)		2·04br (s)	7·73 (d)	$J_{H(3),Me}$ 1·5
(26)	DMSO	1·6—2·4 (m)	2·78 (m)		1·92br (s)	7·73 (d)	$J_{H(4),Me}$ 1·5
(27)	$CDCl_3$	1·7—2·9 (m)	3·14 (d)	2·88 (d)	2·1br (s)		$J_{3,4}$ 11
(29)	DMSO	1·7—2·8 (m)			1·95br (s)		
(30)	DMSO	1·7—3·5 (m)			*c*	7·06 (s)	
(30)	CF_3CO_2H [b]	1·7—3·0 (m)			*c*	6·78br (s)	

[a] From tetramethylsilane. [b] From tetramethylsilane as external reference. [c] Covered by aromatic protons.

TABLE 5

U.v. and visible data [a] [λ/nm (log $\varepsilon_{max.}$)]

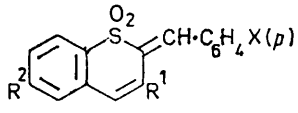
Compd.	Sulphonyl derivatives								Benzofulvene analogues [f]		
(12) [b]	608(3·69)	*518*(3·48)		*360*(3·18)	*304*(3·68)		244(4·22)				
(12) [b]	607(4·36)	520(4·18)		359(3·86)			246(4·47)				
(12) [d]					296(4·13)		246(4·58)				
(13) [e]				*325*(3·15)	*305*(3·48)		249(3·94)				
					296(3·58)						
(13) [f]			387(3·56)			278(3·83)					
(19) [b]				346(4·30)	291(4·04)		240(4·16)		340(4·30)	282(4·30)	240(4·27)
(20) [b]				349(4·33)	293(4·05)	270(3·95)	242(4·25)	377(3·20)	345(4·32)	286(4·29)	241(4·12)
(21) [b]				360(4·25)	298(4·19)		244(4·17)	400(3·25)	360(4·30)	285(4·13)	248(4·17)
(22) [g]			451(4·54)	328(3·62)		270(4·03)	240(4·22)	400(4·60)			253(4·37)
(22) [h]				353(4·23)		275(4·16)	244(4·16)				
(23) [b]				340(4·06)	292(4·18)		237(4·29)				
(24) [b]				348(4·29)	292(4·07)	273(4·06)	245(4·20)				
(25) [b]				327(4·27)			245(3·93)				
(26) [b]				340(4·31)			248(4·07)				
(27) [b]				333(3·99)	285(3·89)		247(4·12)				
(29) [b]				329(4·19)	285(3·86)	*277*(3·80)			330(4·24)	259(4·53)	228(4·67)
(30) [g]			410(4·18)		*293*(3·83)	261(4·16)				295(4·38)	243(4·68)
(30) [h]				321(4·17)	282(3·96)						

[a] Figures in italics refer to inflections. [b] In MeOH. [c] In MeOH–0·1N-NaOH (2 : 3). [d] In MeOH–0·1N-HCl (2 : 3). [e] In MeOH–H_2O (2 : 3). [f] In MeOH–0·066N-NaOH (2 : 3). [g] In MeOH–H_2O (1 : 1). [h] In MeOH–2N-HCl (1 : 1). [i] See ref. 14.

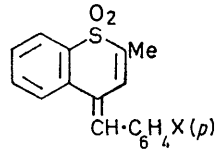
give products (12) and (13) respectively. In this case the bulky dinitrophenyl group is prevented from giving 2,2-disubstituted products. It appears relevant that in the ^{1}H n.m.r. spectra of both (12) and (13) 5-H is appreciably shielded by the ring current diamagnetic effect of the dinitrophenyl ring. As expected, compound (13) is extremely acidic. While it gives pale yellow solutions in chloroform or benzene, solutions in methanol or acetone are deep blue denoting the presence of the conjugate anion; also, when adsorbed on silica gel or alumina with chloroform, compound (13) gives brown-blue colours.

Condensation with Aldehydes.—2-Methyl-2*H*-benzo[*b*]-thiopyran 1,1-dioxide (2) condensed with *p*-chloro- and *p*-nitro-benzaldehyde, either in acetic acid in the presence of sodium acetate or in methanol in the presence of sodium methoxide, to give the corresponding benzylidene derivatives. Condensation must have occurred at C-4 and the 4-benzylidene structures (25) and (26) are unambiguously proved by ^{1}H n.m.r. data (Table 4). Also the 2-unsubstituted 2*H*-benzo[*b*]thiopyran 1,1-dioxides (1), (3), and (4) condensed with *p*-chloro-, *p*-nitro-, and unsubstituted benzaldehyde to give the benzylidene derivatives (19)—(21), (23), and (24) either in acetic acid in the presence of sodium acetate or in pyridine–piperidine. Sodium methoxide in methanol when used as condensation promoter gave only high-melting products which were not characterized. It has been subsequently verified that compounds (19)—(21), (23), and (24) are unstable to sodium methoxide thus giving rise to the high-melting materials.

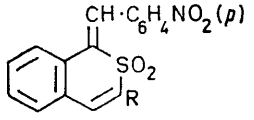
A strong base such as sodium methoxide in methanol was necessary to condense (1) with *p*-dimethylaminobenzaldehyde to give the adduct (22). The products arising from 2-unsubstituted 2*H*-benzo[*b*]thiopyran 1,1-dioxides have been assigned the 2-benzylidene structures (19)—(24) on the basis of u.v. (Table 5) and ^{1}H n.m.r. data (Table 4). In fact the maxima for the *p*-chlorobenzylidene derivatives (20), (23), and (24) are nearly constant along the series and are bathochromically



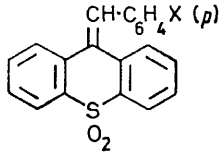
(19) $R^1 = R^2 = H$; X = H
(20) $R^1 = R^2 = H$; X = Cl
(21) $R^1 = R^2 = H$; X = NO_2
(22) $R^1 = R^2 = H$; X = NMe_2
(23) R^1 = Me; R^2 = H; X = Cl
(24) R^1 = H; R^2 = Me; X = Cl



(25) X = Cl
(26) X = NO_2



(27) R = H
(28) R = Me



(29) X = Cl
(30) X = NMe_2

shifted (*ca.* 20 nm) with respect to the maxima for compound (25). An analogous result is found for the two *p*-nitrobenzylidene derivatives (21) and (26). The more extended conjugation of chromophores within the 2-benzylidene derivatives is probably responsible for the observed red shift, relative to the 4-benzylidene derivatives. The longest wavelength absorption of compound (22) is considerably bathochromically shifted (*ca.* 100 nm) relative to the unsubstituted derivative (19), whose spectrum is analogous instead to that of the 'onium salt of (22). This is clear evidence for considerable charge transfer character of the band in the neutral molecule (22). In the electronic ground state of compound (22) sulphonyl stretching vibrations are not apparently affected by the possible mesomeric participation of the nitrogen lone pair. Their position (ν_{as} 1290, ν_{sym} 1125 cm^{-1}) is similar to standard values.[3]

[3] P. M. G. Bavin, G. W. Gray, and A. Stephenson, *Spectrochimica Acta*, 1960, **16**, 1312; L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 1957, 863; O. Exner, *Coll. Czech. Chem. Comm.*, 1963, **28**, 935; D. Barnard, Y. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 1949, 2442.

1*H*-Benzo[*c*]thiopyran 2,2-dioxides (5) and (6) condensed with *p*-nitrobenzaldehyde in acetic acid and in the presence of sodium acetate to give the corresponding benzylidene derivatives (27) and (28). In this case also high-melting products were obtained when the condensation was carried out in methanol using sodium methoxide as base.

Sodium acetate in acetic acid did not promote condensation of thioxanthen 10,10-dioxide (7) and dibenzo-[*b*,*d*]thiopyran 5,5-dioxide (8) with aromatic aldehydes, the starting materials being recovered unchanged. Sodium methoxide in methanol or potassium t-butoxide in t-butanol did promote condensation of compound (7) with *p*-chloro- and *p*-dimethylamino-benzaldehyde to the benzylidene derivatives (29) and (30) respectively. In the case of dibenzo[*b*,*d*]thiopyran 5,5-dioxide (8) alkali metal alkoxides as condensation promoters gave either the starting sulphone or ill defined, uncharacterized, high-melting materials.

The foregoing results show that in mild basic media incipient sulphonyl anions derived from benzo- and dibenzo-thiopyran *SS*-dioxides (1)—(7) are formed and are capable of nucleophilic attack on either saturated or unsaturated carbon. Under mild basic conditions dibenzo[*b*,*d*]thiopyran 5,5-dioxide is relatively inert as a nucleophile and strongly basic conditions are required to force the reaction. Since the α-benzylidenesulphones so far isolated are unstable under those conditions, the formation of high melting materials in the attempted condensation of compound (8) with benzaldehydes can be explained by assuming the intermediacy of the corresponding benzylidene derivatives.

Thiopyran dioxides can be regarded as ' active methylene ' compounds notwithstanding the weaker reactivity of dibenzo[*b*,*d*]thiopyran 5,5-dioxide. Such behaviour, expected on the basis of kinetic [2] and thermodynamic acidity,[1] is analogous to that of very activated, highly acidic substrates such as β-keto-sulphones,[4] β-sulphonyl-carboxylic acids,[5] and β-disulphones.[6] The incipient anion of 2,5-dihydrothiophen dioxide has been reported[7] to condense with carbonyl compounds. However, a completely different situation is involved with thiopyran dioxides as shown by the relative stability of their conjugate anions to that of 2,5-dihydrothiophen dioxide. The former are long-lived, stable, observable species,[8] while the latter is not, undergoing instantaneous ring opening to buta-1,3-dienesulphinic acid anion.[9] The nucleophilic behaviour of thiopyran dioxide anions is not opposed to their considerable thermodynamic stability, since highly stabilized aromatic anions such as indenyl and fluorenyl are known to undergo methylation,[10] cyanomethylation,[11] carbonation,[12] and aldol and crotonic condensations,[13] giving rise to benzo- and dibenzo-phenylfulvenes. It seems relevant that the electronic absorptions of these benzofulvenes [14] (Table 5) are very similar to those of the benzylidene derivatives described here and that therefore there are analogies [14] between the two systems.

EXPERIMENTAL

Methylation and Arylation of Sulphones (1)—(6).—*Method A.* Methyl iodide (12 ml) and anhydrous finely powdered potassium carbonate (20 g) were added to a solution of the sulphone (20 mmol) in dry acetone (120 ml) under nitrogen. The mixture was stirred at room temperature for 10 h and then heated under reflux for 1 h after the addition of more methyl iodide (10 ml). The solution was filtered and evaporated to dryness and the residue was taken up with dilute hydrochloric acid and chloroform. The organic layer was dried and evaporated to dryness to give a residue which, after chromatography (SiO_2–$CHCl_3$) was crystallized.

Method B. A mixture as in A was heated under reflux for 12 h, then more methyl iodide (10 ml) was added and heating continued for another 12 h. Work-up was as above.

Method C. A mixture of the sulphone (20 mmol), dry sodium methoxide (20 mmol), and methyl iodide (10 ml) in anhydrous dimethyl sulphoxide (10 ml) was heated under nitrogen at 60—70° for 12 h. The mixture was filtered from sodium iodide and then evaporated to dryness. Work-up was as Method A.

Condensation of Sulphones (1)—(6) *with Benzaldehydes.*—*Method A.* A mixture of the sulphone (5 mmol), anhydrous sodium acetate (5 g) in acetic acid (10 ml), and the benzaldehyde (5 mmol) was heated under reflux. The mixture was added to water and then extracted with chloroform which was washed with water, dried, and evaporated to give the crude benzylidene derivative.

Method B. A mixture of the sulphone (5 mmol) and the benzaldehyde (5 mmol) in methanol (15—30 ml) was added under nitrogen to sodium methoxide in methanol (5 ml). After a few h, the base was neutralized with diluted hydrochloric acid and the solid was filtered off, washed with methanol, and crystallized.

Method C. As method B, but t-butyl alcohol and potassium butoxide were used.

Method D. The sulphone (5 mmol) and the benzaldehyde (5 mmol) in pyridine (10 ml) containing a few drops of piperidine were set aside under nitrogen for a long period. Crystals were collected and recrystallized.

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