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spiro[1,3-Benzodioxole-2,4'(4H-3,1)-benzothiazines] and their Cleavage with Amines and Hydrazines. A New Series of Spiranes.

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Previously we have reported on a new synthesis of 1:3-benzodioxoles by the action of tetrahalo-o-benzoquinones on thiones (1).

In the present work, it is found that tetrachloro-o-benzoquinone reacts with the benzothiazine-4-thiones (Ia-c) in boiling toluene to give the hitherto unknown spiranes, 2-aryl-4,5,6,7-tetrachloro-spiro[1,3-benzodioxole-2,4'-(4H-3,1)-benzothiazines] (IIa-c). Tetrabromo-o-benzoquinone reacts similarly with Ia affording IId. The spiranes are colourless; their i.r. spectra lack $\nu_{C=O}$ and $\nu_{C=S}$ and exhibit $\nu_{C=N}$ at 1560 cm^{-1} (cf. 2). They are cleaved by HCl in dioxane affording Id-f together with tetrahalocatechol (1). II undergo unusual cleavage with amines and hydrazines affording the quinazoline-4-thiones III and tetrahalocatechol. Thus, IIIa-e are obtained by the action of the corresponding anilines and phenylhydrazine on IIa. Similarly IIIf-i are produced by the action of aniline and phenylhydrazine on IIb and IIc, respectively. IIIa-c,e,h, and i have been previously described (3), whereas structure of IIId,f, and g is supported by oxidation to the corresponding quinazoline-4-ones. Apparently, cleavage proceeds through the initial attack of the nucleophile on the spiro-2,4'-carbon and formation of IV through ring opening and recyclization (3). Subsequent cleavage of the dioxole ring affords III and the catechol (cf. V).

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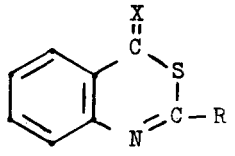
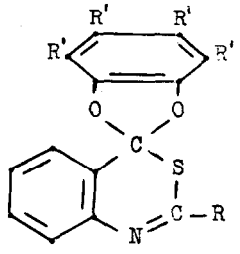
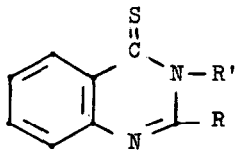


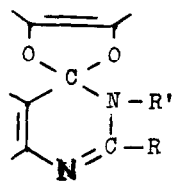
Ia, R=C_6H_5; X=S
b, R=p-$CH_3C_6H_4$; X=S
c, R=p-$CH_3OC_6H_4$; X=S
d, R=C_6H_5; X=O
e, R=p-$CH_3C_6H_4$; X=O
f, R=p-$CH_3OC_6H_4$; X=O



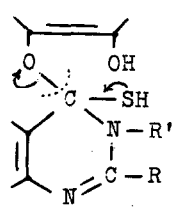
			m.p.°C.	yield %
IIa, R=C_6H_5;	R'=Cl		247	49
b, R=p-$CH_3C_6H_4$;	R'=Cl		253-4	38
c, R=p-$CH_3OC_6H_4$;	R'=Cl		250-1	48
d, R=C_6H_5;	R'=Br		263-4	41.5



		m.p.°C.	yield %
IIIa, R=R'=C_6H_5		208	77
b, R=C_6H_5;	R'=p-$CH_3C_6H_4$	227-8	76
c, R=C_6H_5;	R'=p-$CH_3OC_6H_4$	215	78
d, R=C_6H_5;	R'=p-ClC_6H_4	230-1	64
e, R=C_6H_5;	R'=NHC_6H_5	138	85
f, R=p-$CH_3C_6H_4$;	R'=C_6H_5	238-9	67
g, R=p-$CH_3C_6H_4$;	R'=NHC_6H_5	162	76
h, R=p-$CH_3OC_6H_4$;	R'=C_6H_5	231-2	74
i, R=p-$CH_3OC_6H_4$;	R'=NHC_6H_5	143	73



IV



V