Synthesis and Reactions of Cyclohexa-1,4-diene-3-thiones

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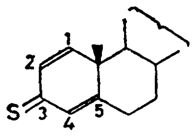
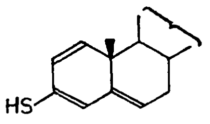
Summary Novel cyclohexa-1,4-diene-3-thiones have been prepared by treating cyclohexa-1,4-dien-3-ones with phosphorus pentasulphide; their chemistry has been investigated.

ALTHOUGH cyclohexa-1,4-dien-3-ones have long been known, especially built into the A ring of steroids, we have found no reference to the corresponding thiones [as in (Ia)]. However, such compounds are easy to prepare, are stable thermally and give correct microanalyses. They are not rapidy oxidised by air nor hydrolysed near pH 7, but they are, as expected, sensitive to light.



(I)



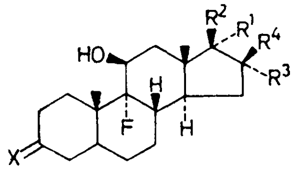
(Ib)

Treatment of dienones [(IIa)—(Va)] with phosphorus pentasulphide in pyridine, toluene, or benzene gave (see Table) the corresponding dienethiones [(IIb)—(Vb)]. The products were all purple-blue crystals with λ_{max} (EtOH) 330—331 (ϵ 18,000—20,000), 565—580 (ϵ 20—25) nm. Since the i.r. spectra indicated the absence of S–H and the n.m.r. the presence of only 3 vinyl signals (τ 3·0—3·3), thioenol tautomer (Ib) formation was discounted.

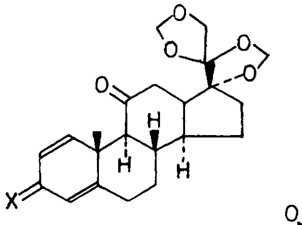
TABLE

	Temperature	Solvent	Yield/%	M.p./°C
(IIb)	90	pyridine	35	212 (decomp.)
(IIIb)	80	pyridine	20	113
	75	toluene	60	
(IVb)	70	toluene	72	184—187
(Vb)	20	benzene	70	163—165
(VIb)	70	toluene	ca. 60	143—144

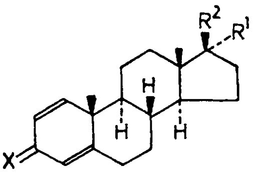
In chemical reactions thiodienones behave like other non-enolised thioketones. Thus, *m*-chloroperbenzoic acid oxidation of the dienethione (IVb) gave the yellow *syn–anti* thione *S*-oxide derivatives (IVc)—(IVd), m.p. 203—204 °C, $[\alpha]_D$ (CH_2Cl_2) + 130°, λ_{max} (EtOH) 358 nm (ϵ 16,000). Although the *syn–anti* isomers were separable by p.l.c. they rapidly interconverted on standing. On irradiation (tungsten lamp) the *S*-oxide (IVc—IVd) in dichloromethane gave 1,4-dien-3-one (IVa).[1]



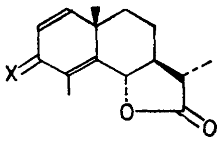
(a) X = O, (b) X = S
(II) R^1=OH, R^2=$COCH_2OH$, R^3=Me, R^4=H, *bis*-methylene dioxy-derivative
(III) R^1 = CO_2Et, R^2= $COCH_2CO_2Et$, R^3=H, R^4= Me



(IV) (a) X = O; (b) X = S; (c) $\overset{O}{\underset{\downarrow}{S}}$, (d) $S{\nwarrow}O$



(a) X = O; (b) X = S (c) X = CPh_2
(V) R^1, R^2 = O



(VI) (a) X = O; (b) X = S

3-(Diphenylmethylene)-androst-1,4-dien-17-one (Vc) was prepared from the dienethione (Vb) and diphenyldiazomethane at room temperature. The intermediate episulphide was not detected.

We have also prepared (see Table) thio-α-santonin (VIb) from α-santonin (VIa) in the same way.

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[1] See: E. Campaigne, 'Chemistry of the Carbonyl Group,' Vol. 1, ed. S. Patai, Wiley, N.Y., 1966, pp. 917—959.