Mechanism of the Rearrangement of 2-Thioacylmethylene-1,3-dithioles to 1,6,6a-Trithiapentalenes (6a-Thiathiophthens)

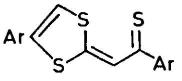
By S. DAVIDSON and D. LEAVER*

(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary The rearrangement of 2-thioacylmethylene-1,3-dithioles to 1,6,6a-trithiapentalenes is catalysed by sulphur and a mechanism involving the formation and decomposition of a spiro compound is proposed; the rearrangement, and an alternative source of the spiran from a thioacylcarbene are considered to be responsible for the formation of trithiapentalenes from 1,2-dithiole-3-thiones and arylacetylenes.

VIALLE and his co-workers[1] have reported that the rearrangements of 2-thioacylmethylene-1,3-dithioles (**1**) to 1,6,6a-trithiapentalenes (**2**) do not occur thermally but require the presence of phosphorus pentasulphide[1] or a 1,2-dithiole-3-thione[2] as a catalyst.

We have confirmed that dithiolethiones accelerate the rearrangements but have found that elemental sulphur is a much more effective catalyst; in boiling xylene, the 1,3-dithiole (**1**; Ar = Ph) remains little changed during 70 h in the absence of additives but is 40% rearranged during 60 h in the presence of 5-phenyl-1,2-dithiole-3-thione (1 mol. equiv.) and >95% rearranged during 21 h in the presence of sulphur (1 mol. equiv.). Rearrangement of the dithioles (**1**) occurs rapidly at 200 °C in the absence of a solvent but this could be due to catalysis by traces of sulphur formed by thermal decomposition.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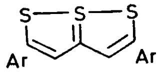
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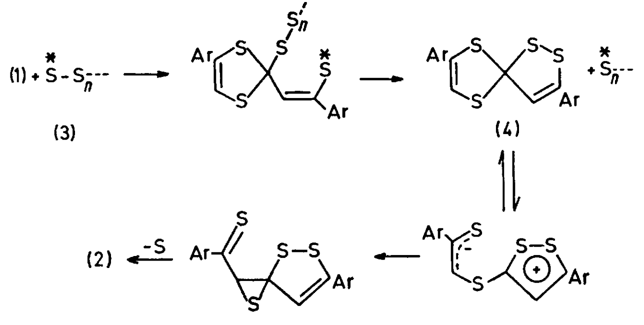
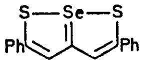


SCHEME 1

A mechanism which accounts for the catalytic effect of sulphur is shown in Scheme 1. We envisage the participation of a reactive polysulphur species (**3**), formed by homolytic[3] or by heterolytic[4] ring-fission in S_8, which initiates the rearrangement by conjugate addition to the enethione grouping of the dithiole (**1**). The new reactive site may then effect a displacement at the first atom of the polysulphur chain, leading to the spiran (**4**) which is envisaged as existing in equilibrium with the zwitterion (**5**). The remaining stages, of episulphide formation and sulphur extrusion,[5] are analogous to the reactions involved in the base-induced conversion[6] of 3-phenacylthio-1,2-dithiolylium salts into 3-phenacylidene-1,2-dithioles.

Two further observations support the proposed mechanism: (i) heating the 1,3-dithiole (**1**; Ar = Ph) with selenium, in boiling 1,2,4-trichlorobenzene, gave the 6a-selena-1,6-dithiapentalene (**6**) in addition to the trithiapentalene (**2**; Ar = Ph), and (ii) the rate of the sulphur-catalysed reaction was further increased by addition of vulcanisation accelerators (*e.g.* zinc dibenzyldithiocarbamate, 2-mercaptobenzothiazole, tetramethylthiuram disulphide). Metal-free accelerators required the presence of zinc oxide for maximum catalytic effect (>95% rearrangement during 3 h in boiling xylene) but zinc oxide alone had little effect on the sulphur-catalysed reaction.

The suggestion[7] that the effect of accelerators in rubber vulcanisation depends on their reaction with sulphur to form polysulphur anions, $R-S_n-S^-$ (usually in the form of zinc salts), accords well with our proposed mechanism for the rearrangement. Furthermore, the "sulphur-rich" complex (**7**; Ar = p-MeC$_6$H$_4$), representative of those obtained by Fackler and his co-workers[8] from the reactions of transition metal dithiocarboxylates with sulphur, is highly effective as a catalyst for the rearrangement, even in the absence of added sulphur.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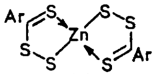
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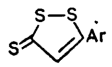
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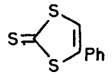
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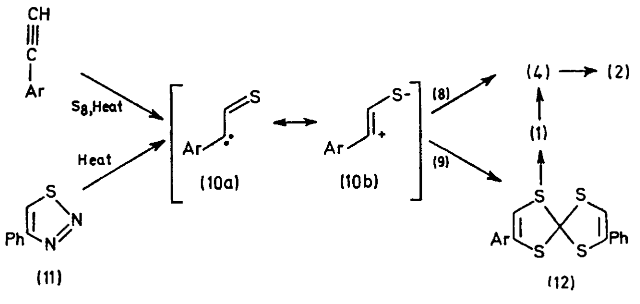

SCHEME 2

In several instances,[1,9] 1,2-dithiole-3-thiones have been observed to react with acetylenes to give trithiapentalenes (**2**) in place of, or together with, the normal adducts (**1**). It now seems likely that these "abnormal" additions are caused by the presence of sulphur as a contaminant; in all cases that we have investigated, adducts of type (**1**) are the major products from the reactions of pure 5-aryl-1,2-

dithiole-3-thiones (**8**)† with arylacetylenes but trithiapentalenes usually become dominant when a trace of sulphur is present. Part of the trithiapentalene is no doubt formed from the "normal" adduct (**1**) but the rate of rearrangement of the latter appears to be insufficient to account for the total amount of trithiapentalene formed during the time taken for the reaction. We suggest, therefore, that there is an alternative route to trithiapentalenes involving the formation, from the acetylene and sulphur, of a thioacylcarbene (**10a**) $\leftrightarrow$ (**10b**) which then yields the spiran (**4**) by 1,3-dipolar cycloaddition to the thiocarbonyl bond of the dithiolethione (**8**) (Scheme 2).

In support of this hypothesis we have shown (Scheme 2) that 2,5-diaryltrithiapentalenes (**2**) are formed in the following ways; (i) by heating 5-phenyl-1,2-dithiole-3-thione (**8**; Ar = Ph) with 4-phenyl-1,2,3-thiadiazole (**11**) [a likely[10] alternative source of the intermediate (**10**)] at 200 °C, (ii) by heating 4-phenyl-1,3-dithiole-2-thione (**9**) with 4-phenyl-1,2,3-thiadiazole, a reaction that probably proceeds by sulphur extrusion (analogous to Scheme 1) from an initial spirobis-(1,3-dithiole) (**12**) and, thereafter, by rearrangement of the resulting 2-thio-acylmethylene-1,3-dithiole (**1**), (iii) from the 1,3-dithiole-2-thione (**9**), which does not react with arylacetylenes alone, by reaction with *p*-methoxyphenylacetylene in the presence of sulphur.

We are grateful to the S.R.C. for a maintenance grant (to S.D.) and to Dr. J. D. R. Vass for helpful discussions.

(*Received, 9th December* 1971; *Com.* 2097.)

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† Apparently this statement cannot be generalised to include alkyl-1,2-dithiole-3-thiones since these yield trithiapentalenes much more readily than the aryl compounds.

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