The Thio-Claisen and Thiopropynyl Rearrangements of Prop-2-ynyl and Allenyl Phenyl Sulphides

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Summary A preliminary thiopropynylic rearrangement (by analogy with the thioallylic shift in allyl phenyl sulphides) occurs in prop-2-ynyl phenyl sulphides; both the starting substances and the allenyl phenyl sulphides which result from this thermal reorganization reaction must be separately capable of subsequent thio-Claisen rearrangement to account for the cyclic products (benzo[b]thiophens and 2H-thiachromenes) observed.

THE course of the oxy-Claisen rearrangement of prop-2-ynyl phenyl ethers has been the subject of several investigations.^{1,2} However, there exist no reports of the successful thio-Claisen rearrangement³⁻⁵ of prop-2-ynyl phenyl sulphides, although a recent communication ^{6,8} has reported the transformation of prop-2-ynyl 4-quinolyl sulphide, into a single product, 2-methylthieno[3,2-c]quinoline. We now present several examples of such rearrangements and some unusual observations indicating the occurrence of two other (hitherto unknown) types of rearrangement reactions.

Thermolysis of prop-2-ynyl phenyl sulphide (1) in (15%) quinoline solution at 200° yielded mainly two rearrangement products, 2-methylbenzo[b]thiophen (2) and phenyl allenyl sulphide (4); (see Table). The latter was first

Product composition	(%)ª	in	thermoly	sis	of(A)	prop-2-ynyl	phenyl
		su	lphidec ((1)	• • • •		

Reaction	condition
5 hr	0.5 hr
200°	250°
71.0	47.5
	39.5
$24 \cdot 5$	
4.5	13.0
	Reaction 5 hr 200° 71.0 24.5 4.5

(B) But-2-ynyl phenyl sulphide^c (7)

		24 hr 200°	4 hr 270°
2-Ethylbenzo[b]thiophen	(9)	35.0	46 ·0
2,3 Dimethylbenzo[b]thiophen	(10)	17.5	15.0
4-Methyl-2H-thiachromen	(11)	0.5	5.0
But-2-ynyl phenyl sulphide	`(7)	4 ·0	$2 \cdot 0$
Minor unknowns ^b (total)	()	42	32

^a The usual yield of distillable product was about 30% except when cyclopentadiene was present to trap the intermediate allenyl phenyl sulphide and prevent its conversion into polymer. Under these circumstances the yield of distillables was almost quantitative.

^b Components of less than 5% of the total distillables.

^c All products and reactants were fully characterized as to (100%) purity and identity by means of g.l.c., i.r., n.m.r., and high-resolution mass-spectral criteria.

identified by conversion into 1-phenylthiopropan-2-one (3) under the hydrolytic conditions of working-up the reaction mixture and separating the quinoline by acid extraction. This component (4) of the product was also trapped as a reaction intermediate by addition of an equivalent of cyclopentadiene to the quinoline solution and isolating the Diels-Alder adduct (5) after 1 hr. of heating at 200°. The structure of (5) was established by mass-spectral, n.m.r., and i.r. criteria. At higher temperatures or longer periods of heating (4) is completely consumed and a second major component of the product, 2H-thiachromene, (6), can be isolated and characterized.



These data can be accommodated best by the assumption of a prior thiopropynylic rearrangement establishing the equilibrium:

$$PhS \cdot CH_2 \cdot C \equiv CH \Rightarrow PhS \cdot CH : C : CH_2$$

(1)

(4)

Subsequently *both* (1) and (4) experience thio-Claisen rearrangement in the same medium; this accounts for the multiplicity of products observed in contrast to the oxy-Claisen rearrangement of prop-2-ynyl aryl ethers where only a single rearrangement product is found)^{1,2} (Scheme 1).



SCHEME 1. Routes of rearrangement of prop-2-ynyl phenyl sulphide (1).

The possibility that (4) was formed from (1) by a prototropic shift is diminished by the occurrence of rearrangement in the instance of a substrate which cannot undergo such reaction except through migration of sulphur. Thus, the rearrangement of but-2-ynyl phenyl sulphide (7) (under the same conditions) is slower and leads to a more complex product mixture, which is reminiscent of the homologous thio-Claisen rearrangement of crotyl phenyl sulphide⁵ (see Table). However, the predominant components of the product, once again, can only be reconciled with the assumption of a prior thiopropynylic equilibrium ($7 \Rightarrow 8$) and a subsequent competition of thio-Claisen rearrangement mechanisms originating, respectively, with the interconvertible allenyl and prop-2-ynyl phenyl sulphide partners as starting materials. The flow of reactants and products encompassing the course of these several rearrangements is shown in Scheme 2.

The butynyl phenyl sulphide (7) can form both the dimethylbenzo[b]thiophen (10) and the 2*H*-thiachromen (11), presumably because of the competition of 1,5-sigmatropic rearrangement and thiol radical or anion addition to the neighbouring allene centre.⁶ On the other hand, we have found that the oxygen analogue of (7) does not form



SCHEME 2. Routes of rearrangement of butynyl phenyl sulphide (7).

the dimethylbenzo[b]furan (via an analogous reaction pathway) and only 4-methyl-2*H*-chromen is obtained. This is consistent with the formation of an o-allenylphenol via the oxy-Claisen rearrangement mechanism suggested by Zsindely and Schmid.² The observation that (7a) can produce the benzothiophen (10) implies that an identical route in the rearrangement of (1a) leading to the formation of (2) may also be taking place to some extent (as indicated by an appropriate arrow in Scheme 1).

Thiopropynylic and thioallylic⁷ rearrangements apparently proceed with considerable ease and have no parallel occurrence with corresponding oxy-substrates. Thus the course of the reaction,⁸ \cdot



suggests that the thio-Claisen rearrangement of this heterocyclic prop-2-ynyl sulphide proceeds entirely through an intermediate allenyl sulphide arising from thiopropynylic isomerization. The Japanese workers,⁸ who observed this reaction, neither noticed nor suspected an allenic sulphide intermediate similar to (4) or (8). On the other hand, it is pertinent that a prop-2-ynyl-allenyl isomerization of the nature identified here for sulphur migration has very recently also been observed⁹ for Group IVB elements like Sn, $[viz; (RC_6H_4)_3 SnCH_2 \cdot C \equiv CH]$.

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