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 2*H*-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 rearrangement[3-5] 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 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, 2*H*-thiachromene, (**6**), can be isolated and characterized.

Product composition (%)[a] *in thermolysis of* (A) *prop-2-ynyl phenyl sulphide*[c] (**1**)

		Reaction conditions	
Products[c]		5 hr 200°	0·5 hr 250°
2-Methylbenzo[*b*]thiophen	(**2**)	71·0	47·5
Prop-2-ynyl phenyl sulphide	(**1**)	—	—
2*H*-Thiachromen	(**6**)	—	39·5
2-Phenylthiopropan-2-one	(**3**)	24·5	—
Minor unknowns[b] (total)		4·5	13·0

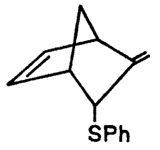
(B) *But-2-ynyl phenyl sulphide*[c] (**7**)

		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-2*H*-thiachromen	(**11**)	0·5	5·0
But-2-ynyl phenyl sulphide	(**7**)	4·0	2·0
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.

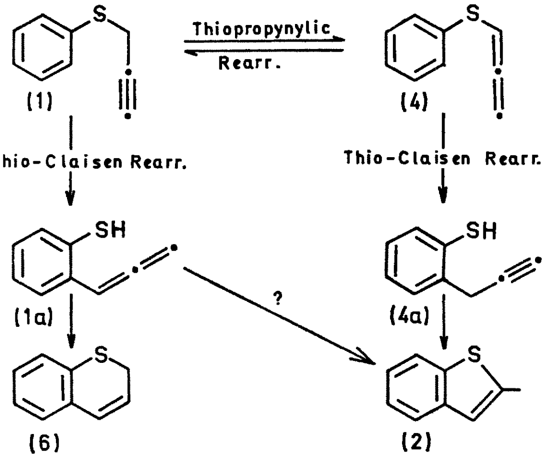


(**5**)

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

$$\underset{(\mathbf{1})}{\mathrm{PhS{\cdot}CH_2{\cdot}C{\equiv}CH}} \rightleftharpoons \underset{(\mathbf{4})}{\mathrm{PhS{\cdot}CH:C:CH_2}}$$

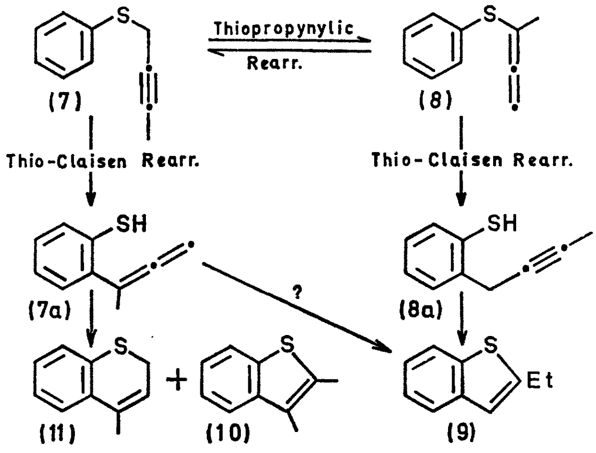
Subsequently *both* (**1**) and (**4**) experience thio-Claisen rearrangement in the same medium; this accounts for the multiplicity of products observed in contrast to the oxy-Claisen rearrangement of prop-2-ynyl aryl ethers where only a single rearrangement product is found)[1,2] (Scheme 1).



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

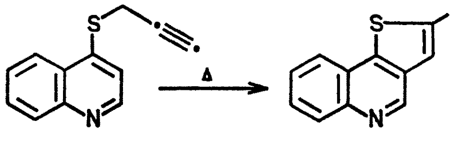
The possibility that (**4**) was formed from (**1**) by a prototropic shift is diminished by the occurrence of rearrangement in the instance of a substrate which cannot undergo such reaction except through migration of sulphur. Thus, the rearrangement of but-2-ynyl phenyl sulphide (**7**) (under the same conditions) is slower and leads to a more complex product mixture, which is reminiscent of the homologous thio-Claisen rearrangement of crotyl phenyl sulphide[5] (see Table). However, the predominant components of the product, once again, can only be reconciled with the assumption of a prior thiopropynylic equilibrium (**7** $\rightleftharpoons$ **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 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).



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

Thiopropynylic and thioallylic[7] rearrangements apparently proceed with considerable ease and have no parallel occurrence with corresponding oxy-substrates. Thus the course of the reaction,[8] 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 observed[9] for Group IVB elements like Sn, [*viz*; $(RC_6H_4)_3\ SnCH_2{\cdot}C \equiv CH$].



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[1] I. Iwai and I. Ide, *Chem. and Pharm. Bull.* (*Japan*), 1962, **10**, 926; 1963, **11**, 1042; B. S. Thyagarajan, K. K. Balasubramanian, and R. B. Rao, *Tetrahedron*, 1967, **23**, 1893 and references cited therein.

[2] J. Zsindely and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1510.

[3] H. Kwart and M. C. Hackett, *J. Amer. Chem. Soc.*, 1962, **84**, 1754; H. Kwart and J. L. Schwartz, *Chem. Comm.*, 1969, 44; H. Kwart and M. H. Cohen, *ibid.*, 1968, 1296.

[4] H. Kwart and E. R. Evans, *J. Org. Chem.*, 1966, **31**, 413.

[5] H. Kwart and M. H. Cohen, *J. Org. Chem.*, 1967, **32**, 3135; *Chem. Comm.*, 1967, 319.

[6] The possibility of a free-radical pathway for ring closure in the *o*-allylthiophenol product of thio-Claisen rearrangement has been previously discussed.[4] This appears to have been recently confirmed by Y. Makisumi and A. Murabayashi, *Tetrahedron Letters*, 1969, 2453. The analogous free-radical addition to allenic double bonds may be the result of both attack at the central and terminal carbons; see T. L. Jacobs and G. E. Illingworth, jun., *J. Org. Chem.*, 1963, **28**, 2692.

[7] H. Kwart and N. Johnson, unpublished results from these laboratories.

[8] Y. Makisumi and A. Murabayashi, *Tetrahedron Letters*, 1969, 1971.

[9] M. Lequan, G. Guillerm, and A. Jean, *Compt. rend.*, 1969, **268**, **C**, 17.