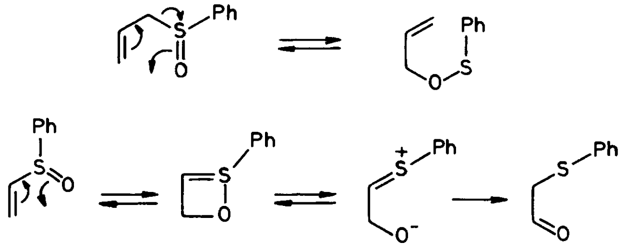
A Novel Rearrangement of Vinyl Sulphoxides

Ottorino De Lucchi,* Gaetano Marchioro, and Giorgio Modena

Centro Studi Meccanismi Reazioni Organiche del C.N.R., Istituto di Chimica Organica, Via Marzolo 1, 35131 Padova, Italy

Acid catalysed isopropenyl acetate treatment of vinyl sulphoxides results in a formal oxygen transposition from sulphur to the β-olefinic carbon *via* a presumed [3,3]-sigmatropic rearrangement of an acetoxysulphonium salt.

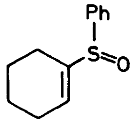
Vinyl sulphoxides are receiving increasing interest in organic synthesis as they are potential dienophiles[1] or Michael acceptors[2] and since they are available in a pure enantiomeric form for asymmetric synthesis.[3] In contrast to the allyl homologues, which undergo the [2,3]-sigmatropic rearrangement outlined in Scheme 1,[4] vinyl sulphoxides are not known to rearrange intramolecularly to the hypothetical molecules of type (**2**) and/or (**3**) that would eventually lead to the more stable carbonyl sulphide (**4**). They do not undergo the Pummerer rearrangement either,[5] as reported by Parham *et al.*[6] who showed that vinyl sulphoxides such as (**5**) and (**6**) remain unchanged even after prolonged heating, when treated with acetic anhydride and acid, *i.e.*, under 'forced Pummerer rearrangement' conditions.



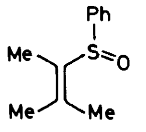
(1) (2) (3) (4)

Scheme 1

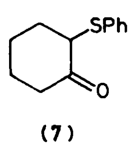
We now report that isopropenyl acetate is able to cause a Pummerer type reaction of the sulphoxides (**1**), (**5**), and (**6**) with the formation of products which would be derived *via* the intramolecular rearrangement shown in Scheme 1. For example, after refluxing (under nitrogen) an acetonitrile solution (*ca.* 5 ml) of the parent sulphoxide (**1**) (5 mmol) with a



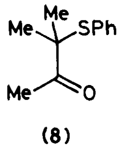
(5)



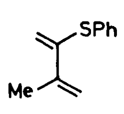
(6)



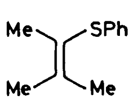
(7)



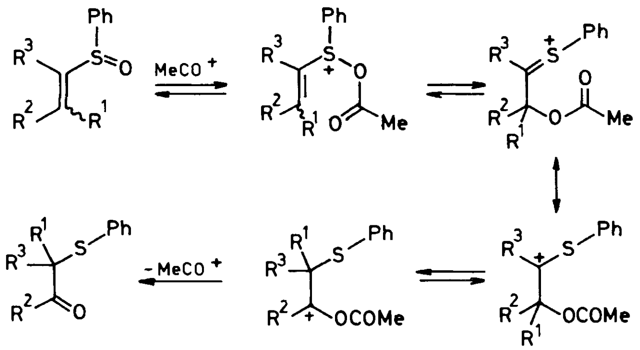
(8)



(9)



(10)



R^1 = H or Me

Scheme 2

catalytic amount of toluene-*p*-sulphonic acid, phenylthioacetaldehyde (**4**) was obtained after standard work-up in about 40% yield. If an equimolar amount of acetic acid was included in the reaction mixture no decomposition of the relatively unstable aldehyde was observed and the transformation of (**1**) into a mixture of (**4**) and its acylal occurred quantitatively.

The reaction carried out on the cyclohexenyl sulphoxide (**5**) gave at low conversion (*ca.* 40%) a high yield (*ca.* 90%) of the expected phenylthiocyclohexanone (**7**). However, yields dropped to low values when the reaction was extended to completion.

The same reaction conducted with (**6**)[7] afforded a more complex mixture of products, 90% of which (excluding *ca.* 40% recovered starting material) accounted for the ketone (**8**)[8] and the two sulphides (**9**)† and (**10**)[7] comprising *ca.* 65, 30, and 5% of the total product mixture respectively.

Even though at this stage of the work we cannot offer a precise interpretation of the mechanism, a likely rationale for these reactions may be as reported in Scheme 2.

While this proposal accounts for the production of (**4**), (**7**), and (**8**), the formation of (**9**) requires a likely double elimination from the transposed intermediate. Finally, the presence of minor amounts of (**10**) shows that other reaction paths are available with polyalkylated substrates. To the best of our knowledge similar [3,3]-sigmatropic rearrangements of acetoxysulphonium salts have not yet been reported.‡ The rearrangement of vinyl sulphoxides herein described may have synthetic interest in view of the well-known utility of β-thiocarbonyl compounds in organic synthesis.[10]

We thank Dr. Moreno Zamai for preliminary experiments on the parent sulphoxide.

Received, 23rd December 1983; Com. 1652

References

1 L. A. Paquette, R. E. Moerck, B. Harirchian, and P. D. Magnus, *J. Am. Chem. Soc.*, 1978, **100**, 1597.

2 *E.g.* G. H. Posner, J. P. Mallamo, K. Miura, and M. Hulce, *Pure Appl. Chem.*, 1981, **53**, 2307.

3 C. Maignan and R. A. Raphael, *Tetrahedron*, 1983, **39**, 3245; T. Koizumi, H. Hirai, and E. Yoshii, *J. Org. Chem.*, 1982, **47**, 4005 and references cited therein.

4 T. Durst in 'Comprehensive Organic Chemistry,' eds. D. Barton and W. D. Ollis, Pergamon Press, 1979, p. 129; D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, 1974, **7**, 147.

5 For a recent report see: H. Sugihara, R. Tanikaga, and A. Kaji, *Synthesis*, 1978, 881.

6 W. E. Parham and L. D. Edwards, *J. Org. Chem.*, 1968, **33**, 4150.

7 For the synthesis of the enol sulphides see: B. M. Trost and A. C. Lavoie, *J. Am. Chem. Soc.*, 1983, **105**, 5075.

8 P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1131.

9 G. A. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, 1966, **31**, 2854; N. Miyamoto, D. Fukuoka, K. Utimoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 1817. For an example of vinylogous Pummerer rearrangement see: S. Yamagiwa, H. Sato, N. Hoshi, H. Kosugi, and H. Uda, *J. Chem. Soc., Perkin Trans. 1*, 1979, 570.

10 B. M. Trost, *Chem. Rev.*, 1978, **78**, 363.

---

† Compound (**9**): pale yellow oil; ^{1}H n.m.r. ($CDCl_3$, Me_4Si) δ 1.98 (3H, Me, m), 5.08 (1H, m), 5.24 (1H, m), 5.54 (1H, m), 5.56 (1H, m), 7.10—7.30 (5H, Ph, m). Characterized as its 4-phenyl-1,2,4-triazoline-3,5-dione adduct: m.p. 167 °C (EtOH), ^{1}H n.m.r. ($CDCl_3$, Me_4Si) δ 2.15 (3H, Me, m), 4.13 (2H, CH_2, m), 4.26 (2H, CH_2, m), 7.20—7.51 (10H, Ph, series of m). Correct elemental composition was obtained by combustion analysis.

‡ To the best of our knowledge similar cases are only encountered in the reaction of vinyl sulphoxides with chlorinating agents such as thionyl chloride and phosphorus pentachloride.[9]