# Communications to the Editor

## The Relationship between 1,3- and 1,5-Sigmatropic Rearrangements of Sulfonium Ylides

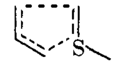
*Sir:*

Recently we[1] and others[2] have recognized and explored a rather general 1,5 rearrangement of sulfonium ylides, **1** to **2**. This process, involving the cyclic participation of six electrons, has many of the characteristics of a concerted reaction and may be viewed as an intramolecular SN2′ reaction in which the suprafacial relationship[3] between breaking and forming bonds is readily achieved in the cyclic array **3**. However, the four-electron 1,3 rearrangement, **4** to **5**, commonly known as the Stevens rearrangement of sulfonium salts,[4] presents a problem of mechanism since a concerted SN2-like displacement at R by the ylide electrons would involve an inversion of R and of necessity be difficult to achieve geometrically. In the analogous nitrogen (Stevens) and oxygen (Wittig) reactions[4b-d] many workers have in fact postulated ionic dissociation–recombination mechanisms for these processes. In spite of the fact that the original claim of Stevens[4a] has since been shown to involve a 1,5 rearrangement,[5] there is evidence in the literature that the sulfur 1,3 rearrangement does proceed,[6] and we here report our results on this problem.

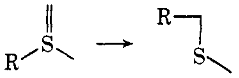
Careful quantitative analysis (glpc) of the rearrangement of **6** (R = Me or Et), produced by the action of base on the salt,[1a] at 60° gave the products **7**, **8**, and **9** in the proportions 95:3:2. The *trans*-vinyl sulfide ($J_{trans}$ = 15.0 Hz)[7] resulted from a Cope rearrangement of **7** under the conditions of the glpc analysis (190°) and was shown by suitable blanks to be absent (<0.5%) in the reaction product. The possibility that the Stevens product **8** originates from a 1,5 rearrangement of the ylide of rearranged salt **10**, derived from the facile salt rearrangement which we have previously described,[1c] was eliminated by nmr analysis of salt **6** before base treatment, at the temperature of the reaction. By adding known amounts of the prepared salt **10** (R = Me) we were able to calibrate our method and could conclude that there is less than 0.5% **10** in the sulfonium salt **6**. Since it seems reasonable that the rates of conversion of both salts to sulfide are similar, we feel that this militates against the origination of the Stevens product **8** from the salt **10** by way of a 1,5 rearrangement of the corresponding ylide. In summary, therefore, in this system at 60° there is a small but reproducible amount of Stevens rearrangement product (**8**) which competes with the 1,5 rearrangement product **7** and originates from the ylide.

Others in this area have published observations[2b,f] which are pertinent to our results. Thus ylide **11**, produced by action of benzyne on the sulfide, was reported[2b] to yield three products, **7**, **8**, and **9** (R = Ph),

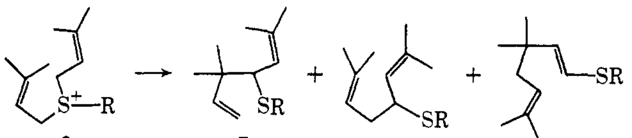
**1** **2**



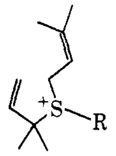
**3**



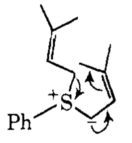
**4** **5**



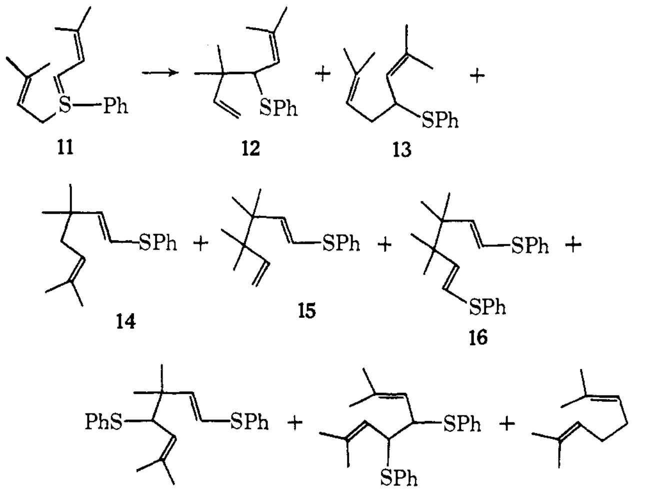
**6** **7** **8** **9**



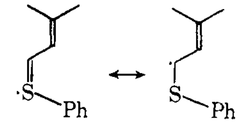
**10**



**20**



**21**



**22**

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[1] (a) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 537, 538, 1083 (1968); (b) J. E. Baldwin and D. P. Kelly, *ibid.*, 899 (1968); (c) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *J. Am. Chem. Soc.*, **90**, 4758 (1968).

[2] (a) R. B. Bates and D. Feld, *Tetrahedron Letters*, 417 (1968); (b) G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith, and I. O. Sutherland, *Chem. Commun.*, 186 (1968); (c) B. M. Trost and R. LaRochelle, *Tetrahedron Letters*, 3327 (1968); (d) W. Kirmse and M. Kapps, *Chem. Ber.*, **101**, 994, 1004 (1968); (e) G. M. Blackburn and W. D. Ollis, *Chem. Commun.*, 1261 (1968); (f) G. M. Blackburn, W. D. Ollis, C. Smith, and I. O. Sutherland, *ibid.*, 99 (1969).

[3] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965), and references cited therein.

[4] (a) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932); (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 224; (c) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 342; (d) H. E. Zimmerman in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 345.

[5] (a) E. B. Ruiz, *Acta Salmenticensi Ser. Cience*, **2**, 64 (1958); *Chem. Abstr.*, **54**, 7623 (1960); (b) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **33**, 70 (1968).

[6] H. Hellmann and D. Eberle, *Ann.*, **662**, 188 (1963).

[7] M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Am. Chem. Soc.*, **88**, 5747 (1966).

in the proportions 7:2:1, respectively. Because of its relevance to our work and also because of the abnormally high level of Stevens product (**8**, R = Ph) we have reexamined this report. To avoid the ambiguities inherent in glpc analysis (*vide supra*) of these 1,5-dienes we separated products by adsorption chromatography over silica gel. The products[8] **12–19** (Table I) were stable to the reaction conditions and to the separation procedure.[9] Furthermore, those compounds **14–17** containing the vinyl sulfide residue all have the *trans* configuration ($J$ = 14.5–16 Hz),[7] and also we have shown that *cis*- and *trans*-vinyl sulfides do not interconvert under the reaction and work-up conditions. Thus the suggestion[2b] that **14** arises from an electrocyclic reaction (**20**) is excluded since this mechanism demands the formation of a *cis*-vinyl sulfide only. In order to demonstrate beyond any doubt that unusual products **13–19** originated from the ylide **11** we prepared the parent salt **6** (R = Ph)[10] and studied its base-catalyzed decomposition. At 65° in tetrahydrofuran, the same conditions of temperature and solvent as the benzyne reaction, **6** (R = Ph) was transformed by potassium *t*-butoxide in the same product mixture as was obtained in the benzyne run. The product distribution (Table I) was almost identical, in accord with the view that the ylide **11** is the common precursor in both reactions. However at −45° it was converted almost quantitatively into the 1,5-rearrangement product (**11**). A reasonable interpretation of these results is that, along with the 1,5 process, there is a competing homolytic dissociation of the ylide which is of higher activation energy and yields the recombination products of the radical pair **21** and **22**.[11] Apparently the S-phenyl group assists this process since, as we observed, in the S-alkyl series the unusual products are much less favored under similar reaction conditions. Spin delocalization into the phenyl moiety is probably the source of this effect. In summary, therefore, vinylsulfonium ylides rearrange preferentially by the 1,5 pathway, but there is also a competing mechanism, whose importance is a function of the molecular environment and temperature and which is most simply viewed as a homolytic dissociation–recombination reaction.[12]

**Table I.** Product Composition (wt %)

| Method | Temp, °C | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|---|
| Benzyne[2b,c] | 65 | 69 | 12 | 6 | 6 | 2 | 3 | 2 | 0.2 |
| Salt + KO-*t*-Bu | 65 | 74 | 11 | 5 | 4 | 2 | 3 | 1 | 0.2 |
| | −45 | 99 | 0.3 | 0.3 | 0.3 | | | | |

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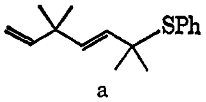
[8] All new compounds have correct (±0.3%) elemental analyses and spectral properties. The dimer **18** occurs as an approximately equal mixture of two diastereoisomers. An excellent materials balance has been achieved in these reactions.

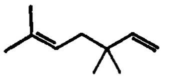
[9] Blank experiments showed that sulfide **11**, on prolonged contact with silica gel, was isomerized to a small extent to compound a.



a

[10] This salt was obtained by the reaction of phenyl 3-methyl-2-butenyl sulfide and 3-methyl-2-butenyl chloride with silver fluoroborate at −45° in tetrahydrofuran.

[11] We could not find hydrocarbon b, but since its isomer was the least abundant product it could have escaped our separation procedure. In the original benzyne work[6] there is a brief note that a dimeric type material was obtained in small amount from dibenzyl sulfide, which is in keeping with our present results.



b

[12] It is significant that a similar radical dissociation–recombination mechanism has been suggested for certain Wittig reactions (*cf.* P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Am. Chem. Soc.*, **88**, 78 (1966)), and more recently direct physical evidence from the same pathway in a Stevens nitrogen reagent has been reported (A. R. Lepley, *ibid.*, **91**, 1237 (1969).

[13] National Science Foundation Predoctoral Fellow, 1968–1969.

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## Nuclear Polarization in a Thermal 1,3-Sigmatropic Rearrangement. Evidence for a Radical Pathway

*Sir:*

In principle a concerted 1,3 shift of a carbon–carbon bond in an allyl system, *i.e.*, **1** to **2**, may proceed with conservation of orbital symmetry by two geometrical pathways, either as a suprafacial migration with inversion in R or as an antarafacial migration with retention in R.[1,2] An alternative, stepwise process could be a radical dissociation–recombination mechanism, proceeding through an intermediate radical pair such as **3**. Since the recombination of a radical pair would, under conditions of favorable electron and nuclear spin relaxation, lead to a nuclear polarized product,[3] we have examined a suitable system in the hope of observing such an effect.

The thermal conversion of the *exo*-methylenecyclohexadienamine (**4**) to the aromatic isomer **5** was discovered and studied by Hauser and Van Eenam,[4] who showed that the reaction was unimolecular and proceeded readily under homogeneous conditions at rates which were compatible with our experimental facilities.[5] A gas–liquid partition chromatographic analysis of the products of this thermolysis, in the temperature range 140–170°, showed that under these conditions **4**

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[1] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965), and references cited there. Reviewed by (a) R. B. Woodward in "Aromaticity," Special Publication No. 21, The Chemical Society, London; (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); G. B. Gill, *Quart. Rev.* (London), 22, 338 (1968).

[2] Concerted 1,3- and 1,5-sigmatropic rearrangements have been extensively studied by J. A. Berson, who has reviewed the area in *Accounts Chem. Res.*, **1**, 152 (1968).

[3] H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967); (b) R. G. Lawler, *ibid.*, **89**, 5519 (1967); (c) J. Bargon, H. Fischer, and H. Johnson, *Z. Naturforsch.*, **22a**, 1551, 1556 (1967); (d) A. R. Lepley, *J. Am. Chem. Soc.*, **90**, 2710 (1968); (e) H. R. Ward, R. G. Lawler, and H. Y. Loken, *ibid.*, **90**, 7359 (1968); (f) R. Kaptein, *Chem. Phys. Letters*, **2**, 261 (1968); (g) A. R. Lepley, *Chem. Commun.*, 64 (1969); (h) H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Am. Chem. Soc.*, **91**, 747 (1969); (j) A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969); (j) A. R. Lepley, *ibid.*, **91**, 749, 1237 (1969).

[4] C. R. Hauser and D. N. Van Eenam, *ibid.*, **79**, 5512, 5520, 6274, 6277 (1957).

[5] These studies were carried out on a Varian A-60 instrument with a variable-temperature probe.