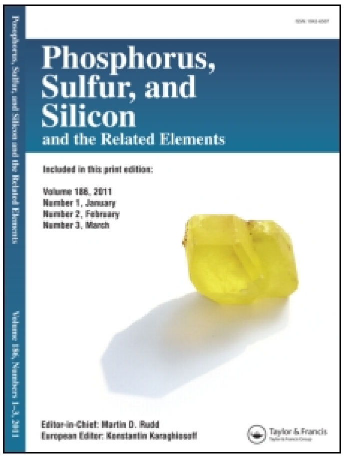

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A 1,5-SHIFT OF THE PHENYLSULFINYL GROUP IN PHENYL PENTADIENYL SULFOXIDES

Yehiel Gaoni[a]
[a] Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

To cite this Article Gaoni, Yehiel(1979) 'A 1,5-SHIFT OF THE PHENYLSULFINYL GROUP IN PHENYL PENTADIENYL SULFOXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 101
To link to this Article: DOI: 10.1080/03086647908080324
URL: http://dx.doi.org/10.1080/03086647908080324

Phosphorus and Sulfur
1979, Vol. 6, p. 101

A 1,5-SHIFT OF THE PHENYLSULFINYL GROUP IN PHENYL PENTADIENYL SULFOXIDES

Yehiel Gaoni

Department of Organic Chemistry, The Weizmann Institute of Science,
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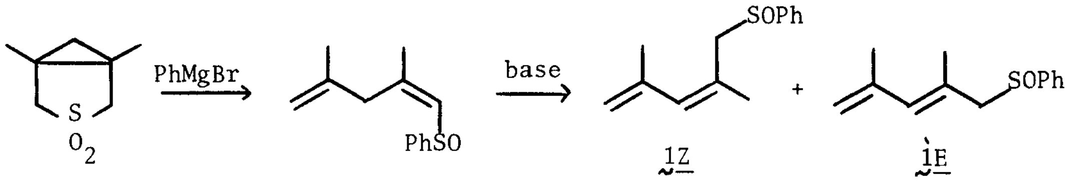
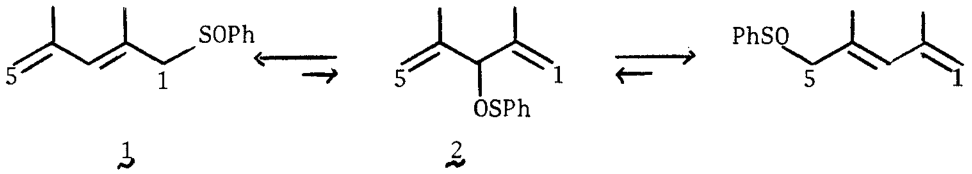
1,4-Pentadienylic sulfoxides, obtained by reaction of 3-thiabicyclo[3,1,0]-hexane-3,3-dioxides with phenyl magnesium bromide[1], undergo a facile rearrangement with base to the conjugated 2,4-pentadienylic sulfoxides, e.g. **1Z** and **1E**.



When separated, each of the two isomers **1** is found to thermally equilibrate to the same 2:1 mixture of **1E** and **1Z**. This is believed to occur through a [2,3]sigmatropic shift[2], with **2** as an intermediate. This intermediate is however, symmetrical and may yield a new sulfoxide by a degenerate



rearrangement to the 5-position. By using deuterated **1Z** it is possible to show that such a process does occur. Also, with sulfoxides giving rise to an unsymmetrical intermediate it is found that the equilibrium shifts in the direction of the thermodynamically more stable isomer.

1. Y. Gaoni, Tetrahedron Letters, 1977, 4521.
2. P. Bickart, F.W. Carson, J. Jacobus, E.G. Miller and K. Mislow, J. Am. Chem. Soc., 90, 4869 (1968).