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

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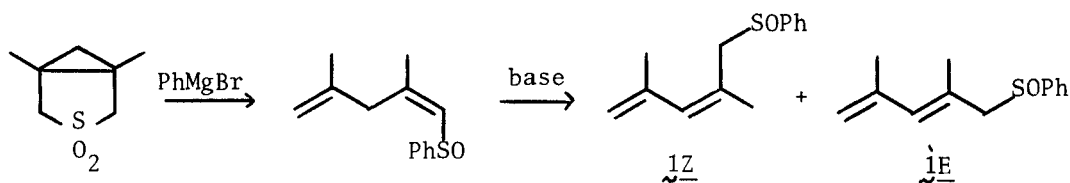
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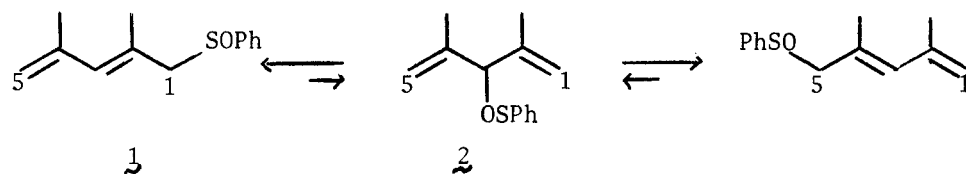
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1,4-Pentadienylic sulfoxides, obtained by reaction of 3-thiabicyclo[3,1,0]-hexane-3,3-dioxides with phenyl magnesium bromide¹, undergo a facile rearrangement with base to the conjugated 2,4-pentadienylic sulfoxides, e.g. 1Z and 1E.



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 shift², 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).