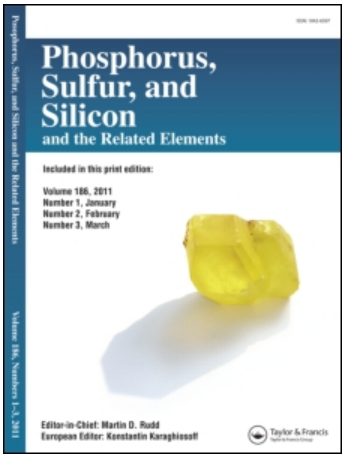

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND PROPERTIES OF AN OPTICALLY ACTIVE SPIROSULFURANE

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To cite this Article Kapovits, István , Huszthy, Péter , Kucsman, Árpád and Radics, Lajos(1979) 'SYNTHESIS AND PROPERTIES OF AN OPTICALLY ACTIVE SPIROSULFURANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 155
To link to this Article: DOI: 10.1080/03086647908080351
URL: http://dx.doi.org/10.1080/03086647908080351

Phosphorus and Sulfur
1979, Vol. 6, p. 155

SYNTHESIS AND PROPERTIES OF AN OPTICALLY ACTIVE SPIROSULFURANE

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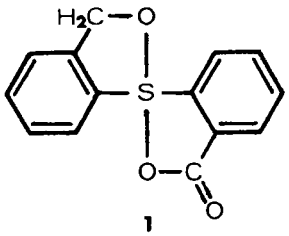
The (+) and (-) enantiomers of spirosulfurane (1) were prepared from the optically active precursor sulfoxides (2) with acetyl chloride in the presence of triethylamine at -78° (enantiomeric purity>95%). The mixed anhydride (3) was isolated as a possible intermediate of acyloxysulfurane formation. The enantiomers of (1) proved to be surprisingly stable against heating and hydrolysis. The oxidation of (+)-or (-)-(1) with ozone or acetyl nitrate afforded optically inactive spirosulfurane oxide (4). Contrary to the behaviour of (1) and (2), the ^1H n.m.r. spectrum of (4) showed a sharp singlet resonance at δ 5.37 ppm for CH_2 protons at 25°. On lowering the temperature, this resonance undergoes changes characteristic of exchanging AB spin systeme (the coalescence occurred at -49°). The substantial decrease of the configurational stability of (4) with respect to that of (1) is readily understood in terms of assumptions of Nyholm-Gillespie theory. The mechanism for the formation of spirocyclic diaryldiacyloxysulfuranes will also be discussed.



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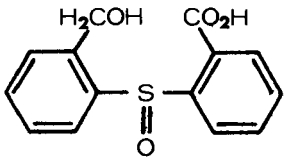

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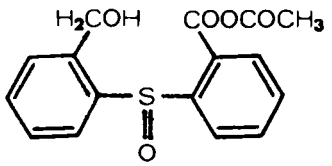

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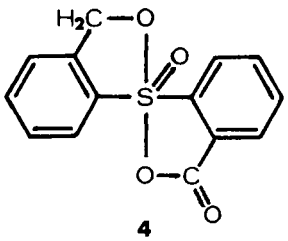

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