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1,3- AND 1,4-DIENYLIC SULFOXIDES BY REACTION OF SULFOLENES AND BICYCLIC SULFONES WITH GRIGNARD REAGENTS

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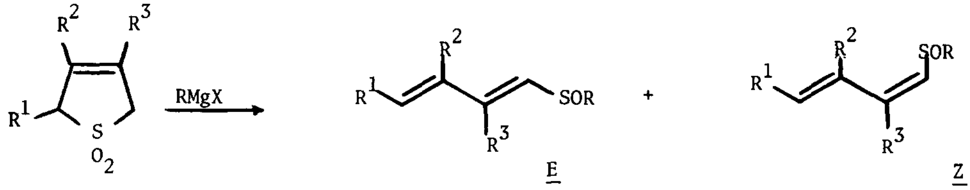
The reaction of 2,5-dihydrothiophene-1,1-dioxides (sulfolenes) with Grignard reagents has been studied by Krug[1], who could isolate halomagnesium sulfinate salts when using one mole of the magnesium reagent but no definite products when higher proportions of the same reagent were being used. It has now been found that the reaction of two moles of alkyl- or arylmagnesium halides with the sulfolenes **1** produces 1,3-dienylic sulfoxides (**2**), as distillable liquids, in 20 to 66% yields[2]. (UV-spectra of compounds **2** are given in Table 1)

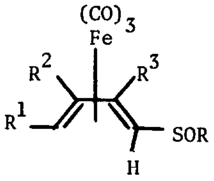


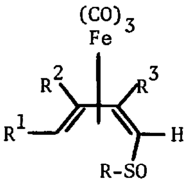
1a, $R^1=R^2=R^3=H$
b, $R^1=R^2=H$, $R^3=CH_3$
c, $R^1=H$, $R^2=R^3=CH_3$
d, $R^1=R^3=CH_3$, $R^2=H$

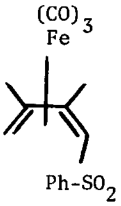
2a, $R^1=R^2=R^3=H$ (R=Ph, 37%)
b, $R^1=R^3=H$, $R^2=CH_3$
c, $R^1=R^2=H$, $R^3=CH_3$ } ($R=CH_3$, 20%; R=Ph, 50%)
d, $R^1=H$, $R^2=R^3=CH_3$ ($R=CH_3$, 26%; $R=C_2H_5$, 32%; R=Ph, 58%)
e, $R^1=R^3=CH_3$, $R^2=H$ (R=Ph, 66%).

The **2**-*Z* isomers were preponderately or exclusively formed in all cases, the largest proportion of *E*/*Z* (=1/4) being observed for **2a**. The unsymmetrical sulfolene **1b** produced mainly **2c**, containing about 5% of **2b**. Only one isomer, **2e**, was isolated from reaction of the unsymmetrical **2d**.

The *E* or *Z* geometries of compounds **2** were determined through their iron tricarbonyl complexes, prepared by reaction with iron pentacarbonyl and trimethylamine oxide in benzene[3].







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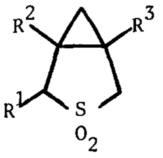
4a, $R^1=R^2=R^3=H$ (R=Ph)
b, $R^1=H$, $R^2=R^3=CH_3$ (R=Ph)

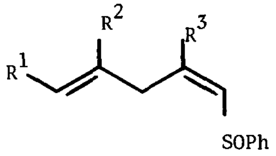
5a, $R^1=R^2=R^3=H$ (R=Ph)
b, $R^1=H$, $R^2=R^3=CH_3$ (R=CH_3; Ph)
c, $R^1=R^2=H$, $R^3=CH_3$ (R=CH_3; Ph)
d, $R^1=R^3=CH_3$, $R^2=H$ (R=Ph)

The complexes, either **4** or **5**, obtained from any diene, consisted each of a mixture of two diastereomers, representing two different spatial relationships of the iron nucleus and the directed sulfinyl group. These solid, stable diastereomers, greatly differing in polarity[4], could be separated by chromatography and were used to characterize the dienes. Observation of the NMR chemical shift of the α-vinylic protons of any of them readily distinguished the more highly shielded *anti*-protons of the *E*-isomers **4** (δ 1.4-1.8) from the relatively deshielded *syn*-protons of the *Z*-isomers **5** (δ ∿3.5 ppm). That no isomerization had occured during complexation was shown by re-oxidation of **4b** and of **5b** (R=Ph), each to its own starting material. The diastereomeric relationship was shown by oxidation of the two isomeric **5b** (R=Ph), with *m*-chloroperbenzoic acid, to the same sulfone-complex **6**.

Butadienylic sulfoxides have recently found interesting synthetic applications[5], and various methods for the preparation of these sulfoxides or of the corresponding sulfides have been described[5-8]. In this respect our method seems to have the serious drawback of producing mainly 2-Z, too hindered for cycloadditions. It has, however, been found that 2a-Z (and perhaps also other 2-Z compounds) can be almost totally converted into 2a-E by irradiation of its solutions, in the presence of iodine, with an incadescent lamp or in direct sunlight. From these irradiation 2a-E is recovered chromatographically pure in 75%, and the total overall yield of 2a-E from 1a is of 25-30%. Considering the simplicity of the operations and the availability of the commercial, or otherwise readily prepared, starting materials, this should be the method of choice for the preparation of 2a-E.

The above reaction of the sulfolenes with Grignard reagents was extended also to the bicyclic sulfones 7, obtainable in good yields by reduction with lithium tetrahydroaluminate in THF of the dichlorocarbene adducts of the sulfolenes 1[9]. The interaction of 7 with two moles of phenylmagnesium bromide produced the 1,4-dienylic sulfoxides 8, in varying yields[2]. Approximately equal amounts of 8a and 8b were obtained from 7a, while only 8c was obtained from 7b.



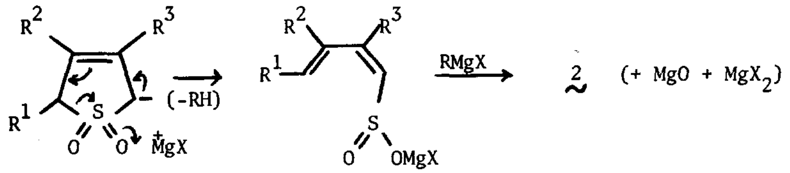


7a, $R^1=R^2=H$, $R^3=CH_3$
b, $R^1=R^3=CH_3$, $R^2=H$
c, $R^1=H$, $R^2=R^3=CH_3$

8a, $R^1=R^3=H$, $R^2=CH_3$	31%
b, $R^1=R^2=H$, $R^3=CH_3$	
c, $R^1=R^3=CH_3$, $R^2=H$	36%
d, $R^1=H$, $R^2=R^3=CH_3$	58%

The sulfoxides 8 are interesting in regard to the formation and reactions of the pentadienyl anions which are generated from them with base. Results of this work will be described separately.

The production of the dienylic sulfoxides is assumed to proceed in two steps, the first being the formation of a sulfinate salt[1] through ring opening of an incipient anion, and the second



involving an exchange with another RMgX molecule to produce the sulfoxide, in a reaction which is similar to that of sulfinate esters. The bicyclic sulfones would undergo a similar ring cleavage through participation of the cyclopropyl ring.

Table 1. UV-spectra of conjugated dienylic sulfoxides **2** in isooctane

	R=CH_3		R=C_6H_5	
	λmax nm	ε	λmax nm	ε
2a-*E*	-	-	240	20500
2a-*Z*	-	-	242	22000
2c-*Z*	228	20500	248	19900
2d-*Z*	216	9400	223	15200
2d-*Z*[a]	219	8250	-	-
2e-*Z*	-	-	250	26400

a. R=C_2H_5

References and Notes

1. R.C. Krug, J.A. Rigney and G.R. Tichelaar, J. Org. Chem., 27, 1305-1309 (1962).
2. In practice, the sulfone (1 equiv.) in benzene is introduced into an ether solution of the Grignard reagent, prepared from 2.3 equiv. of magnesium and 2.4 equiv. of the halide. Inverse addition sometimes gives better yields.
3. Y. Shvo and E. Hazum, J.C.S., Chem. Comm., 1975, 829-830.
4. See: N.A. Clinton and C.P. Lillya, J. Am. Chem. Soc., 92, 3058-3064 (1970).
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