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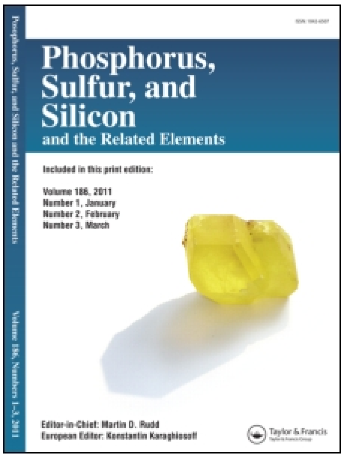

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Structures and Reactivities of Cyclopropyl α-Sulfonyl Carbanions

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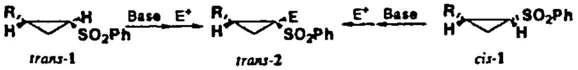
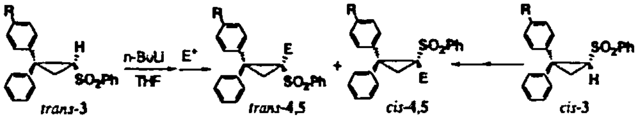
In order to clarify the relationship between structures and reactivities of sulfur-stabilized carbanions the diastereomeric isomers of phenylsulfonylcyclopropanes **1**, **3** and **6** were synthesized.

The carbanions generated from *trans*-**1** underwent deuteration, alkylations, acylations and aldol-type reactions to give the products *trans*-**2** in high yields, but no diastereoisomeric *cis*-**2** were obtained. On the other hand, the α-sulfonyl carbanions produced from *cis*-**1** instantly led to the complete inversion of their configurations to provide selectively the same products *trans*-**2**.



E = D, alkyl, R'CO, R'CH(OH)

The configurationally defined cyclopropyl α-sulfonyl carbanions generated from *trans*-**3** and *cis*-**3** using n-BuLi were similarly found to undergo the rapid isomerization to attain the equilibrium, and the subsequent reaction in THF at 0 °C or in THF containing HMPA at -80 °C resulted in the formation of both isomers *trans*-**4** and *cis*-**4** in 50:50 ratio. However, upon treatment of *trans*-**3** and *cis*-**3** with n-BuLi in THF at -80 °C, followed by deuteration, *trans*-**4** and *cis*-**4** were obtained in 40:60, while methylation afforded *trans*-**5** and *cis*-**5** in 56:44 ratio.

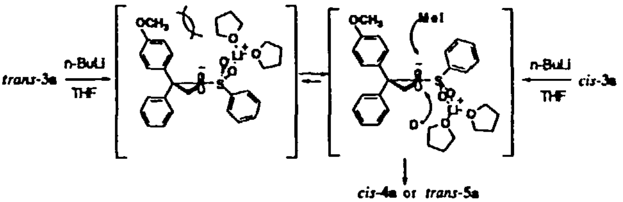


The stereochemistry of the products was deduced by a combination of COSY and NOESY NMR spectra. Some of these results are shown Table 1.

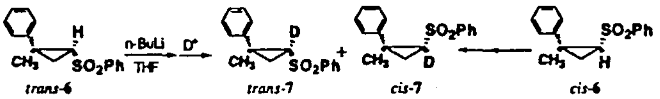
Table 1. Reactions of carbanions generated from *trans*-3 or *cis*-3

	R	4 (E=D)		5 (E=Me)	
		yield (%)	*trans*/*cis*	yield (%)	*trans*/*cis*
trans-3a	CH_3O	99	40 / 60	92	56/44
cis-3a	CH_3O	98	40 / 60	90	55/45
trans-3b	i-C_3H_7	99	43 / 57	94	56/44
cis-3b	i-C_3H_7	97	42 / 58	93	55/45
trans-3c	Cl	90	49 / 51	94	43/57
cis-3c	Cl	95	47 / 53	98	44/56

These findings mean that the interconversion between two intermediary diastereoisomeric carbanions might be influenced by the steric requirement between a remote *para*-substituent and a bulky carbanion aggerigation in which a sulfonyl group, a lithium cation and THF molecules are held by chelation.



Treatment of the carbanions from *trans*-6 and *cis*-6 with C_2H_5OD gave two isomeric products *trans*-7 and *cis*-7 in 35:65, and these results may also be explained by the above-mentioned hypothesis.



-80 °C: *trans*/*cis* = 35 / 65 (98% yield)
0 °C: = 41 / 59 (97% yield)