

CYCLOPROPANES FROM SILYL/SULFUR-STABILIZED CARBANIONS AND OXIRANES -
 THE INTERPLAY OF TWO REACTION PATHWAYS

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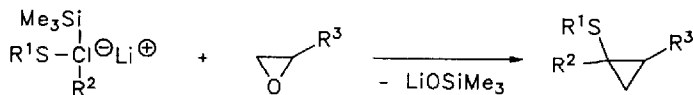
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Summary - Depending on the sulfur substituent, carbanions **1** react with oxiranes **2** giving either cyclopropanes via a Homo-Peterson reaction or isomers with a shifted phenylthio residue.

The Homo-Wittig reaction offers a well-established route to cyclopropanes.² In contrast, the reaction of the tris(trimethylsilyl)methyl anion with phenyloxirane appears at present to be the only example of a successful Homo-Peterson reaction.³ Obviously, a delicate balance of carbanion stabilization, nucleophilicity, and leaving-group ability is required to make cyclopropane formation feasible by cycloelimination of a silanolate. We now report an extension of this approach in which sulfide substituents are present in the attacking carbanion. Moreover, we found that silyl substitution of the oxirane component allows some additional diversity with the actual outcome of the reaction depending on the presence of alkylthio or phenylthio groups in the carbanion. The reactions are summarized in Schemes I-III and Table I.

Scheme I



- | | | |
|--|---|--|
| 1g , R ¹ = Ph, R ² = SiMe ₃ | 2g , R ³ = Ph | 3g , R ¹ = R ³ = Ph, R ² = SiMe ₃ |
| b , R ¹ = Me, R ² = SMe | b , R ³ = SiMe ₃ | b , R ¹ = Ph, R ² = R ³ = SiMe ₃ |
| c , R ¹ + R ² = (CH ₂) ₃ S | | c , R ¹ = Me, R ² = SMe, R ³ = SiMe ₃ |
| d , R ¹ = Ph, R ² = SPh | | d , R ¹ + R ² = (CH ₂) ₃ S, R ³ = SiMe ₃ |

On addition of carbanions **1a-c** to the oxiranes **2a,b** smooth formation of cyclopropanes **3a-d** is observed providing new examples of the Homo-Peterson reaction. However, the phenylthio-substituted organolithium species **1d** and **2b**

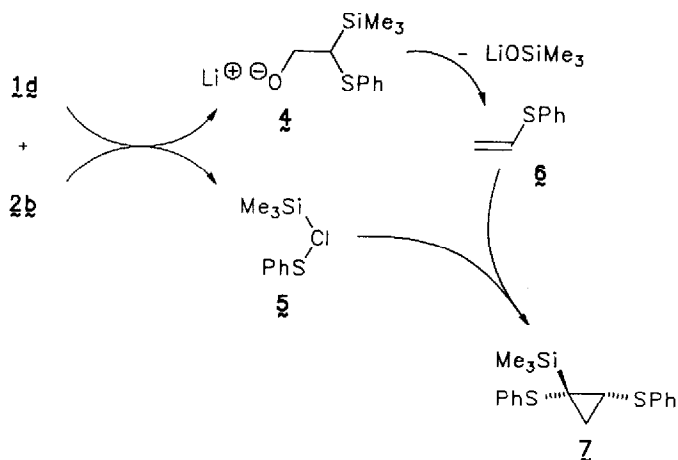
Table I. Yields, Physical Properties and Characteristic ¹H NMR Spectral Data (in CDCl₃) of Products **3**, **7**, **10**

Reac- tants	Pro- duct	Yield [%]	E/Z ratio	mp[°C]/bp [°C/Torr]	NMR (cyclopropane-H)	
					δ _{CH}	δ _{CH₂} ^a
1a+2a	3a	47	1:1	E: 145-147/0.15	2.86	1.45; 1.65
				Z: 56-57	2.53	1.57; 1.70
1a+2b	3b^b	56	1:3	E: 89-91/0.003	1.23	0.46; 0.97
				Z: 86-87/0.001	1.55	0.06; 1.06
1b+2b	3c^c	76	-	40/0.01	1.28	0.36; 0.92
1c+2b	3d^c	75	-	65-67/0.01	1.33	0.39; 1.05
1d+2a+6	7^b	85	d, e	163-165/0.002	2.68	1.16; 1.67
1d+2a+9a	10a	55	d	oil	1.30	0.74; 1.20
1d+2a+9b	3a	80	d	<i>vide supra</i>		
1d+2a+9c	10b	68	d	oil	3.36	1.12; 1.31
1d+2a+9d	3b^b	31	d	<i>vide supra</i>		
1d+2b	7^b	95	d	<i>vide supra</i>		

^aThe signals are observed as doublets of doublets with $J_{gem} = 4.8-8.4$ Hz, $J_{cis} = 3.6-6.4$ Hz, $J_{trans} = 6.4-10.8$ Hz. ^bRef. 8. ^cRef. 7. ^dOnly the Z isomer is detected. ^eAssignment of stereochemistry is based on the X-ray structural investigation of the bis-sulfone.⁹

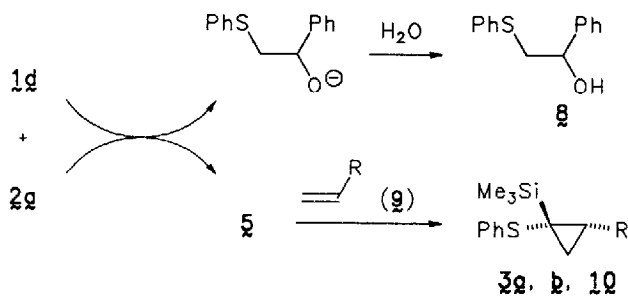
do not afford a cyclopropane **3**, but the isomeric product **7** resulting from a formal 1,2-shift of the sulfur residue. To account for this mechanistic dichotomy, we have to take into consideration the improved leaving-group ability of phenylthio as in **1d** vs. alkylthio groups⁴ as in **1a-c** and the change in regiochemistry of ring-opening as imparted by the silyl substituent in **2b**. Thus, lithio compound **1d** may be looked upon as a carbenoid species which may be in equilibrium with carbene **5** and thiophenolate. This equilibrium may be essentially on the carbanion side. However, on addition of oxirane **2b**, thiophenolate is trapped with formation of alkoxide **4**. Species **4** corresponds to the intermediate of a Peterson olefination of formaldehyde and, consequently, leads to alkene **6**. This provides a reaction partner for the liberated carbene **5** giving Z-**7** in a stereospecific [2+1] cycloaddition.

Scheme II



If **2b** allows scavenging of thiophenolate from **1d**, other oxiranes such as **2a** should give the same reaction; the liberated carbene **5** would then be available for other cycloaddition partners. In fact, the three-component reaction of anion **1d**, oxirane **2a**, and an olefin **9** gives good yields of cyclopropanes **3a,b,10a,b** (Table I); at the same time, addition of thiophenolate to **2a** provides alcohol **8**⁵ in 60 to 80% yield. In accord with the suggested mechanism for the formation of **7** from **1d** and **2b** via **6**, this cyclopropane is also formed if **6** is used as C=C component (Table I). In conclusion, depending on the nature of the organosulfur group in **1** and the oxirane employed, two efficient routes to highly functionalized and synthetically useful⁶ cyclopropanes are available.

Scheme III



9: **g**, R = *n*Bu; **4**, R = Ph; **g**, R = OEt; **4**, R = SiMe₃
10: **g**, R = *n*Bu; **4**, R = OEt

General Procedure for the Reaction of Carbanions 1 with Oxiranes 2. Under nitrogen and with rigorous exclusion of moisture, butyllithium in hexane (17.24 mL, 27.5 mmol) is added dropwise to protonated **1** (25 mmol) in THF (75 mL) at -78°C over 10 min. The mixture is allowed to warm to 0°C over 1 h and stirred for an additional 30 min. Then **2** (26 mmol) and - in the three-component modification (cf. Table I) **9** (50 mmol), are injected into the well-stirred solution. When the exothermic reaction has subsided, the mixture is allowed to warm to room temperature. After being stirred for an additional 4 h, the mixture is poured into ether (200 mL) and extracted with water (4 x 100 mL). The organic layer is dried (Na_2SO_4), evaporated, and the product purified by distillation or column chromatography.

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