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NUCLEOPHILIC SUBSTITUTION REACTIONS OF 1-SULFONYL SUBSTITUTED CYCLOPROPENES WITH ALKYL LITHIUM REAGENTS

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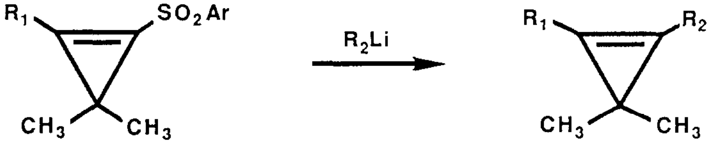
Abstract: Sulfonyl substituted cyclopropenes react with a variety of alkyl lithium reagents to give disubstituted cyclopropenes in good yield.

The stabilization of carbanionic centers by adjacent sulfur groups is the basis of many valuable transformations in organic synthesis.[1-5] Vinyl sulfones undergo conjugate addition with various reagents and the resulting α-sulfonyl anions may be protonated or trapped by an assortment of electrophiles.[6,7] During the course of our research dealing with 1-sulfonyl substituted cyclopropenes,[8] we examined their behavior toward several organometallic reagents. In so doing, we were quite surprised to discover that the reaction of **1** with alkyl lithium reagents afforded alkyl substituted cyclopropenes **2** in good to excellent yield.



1a; R_1= Me_3Si
1b; R_1= Ph

2a; R_1= Me_3Si
2b; R_1= Ph

A typical procedure is as follows: A stirred solution containing 2.0 mmoles of cyclopropene **1** in 15 ml of anhydrous tetrahydrofuran was cooled to -78°C under nitrogen and then treated with 4.0 mmoles of the alkyllithium reagent in hexane. Stirring was continued at -78°C for 1 hr and at 0°C for 3 hr. The mixture was hydrolysed with aqueous ammonium chloride and the separated organic layer was dried over magnesium sulfate. After solvent removal the crude product was chromatographed on silica gel with an ether-hexane eluent. Table I presents the results of the reaction with a variety of alkyllithiums.

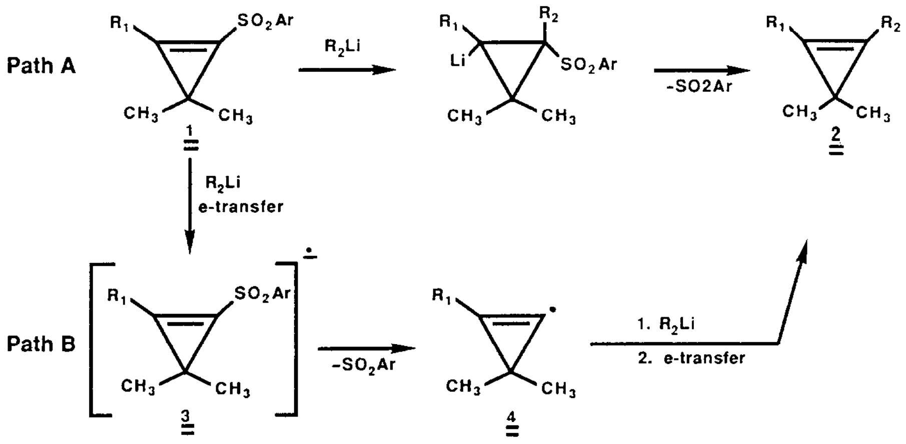
TABLE I Reaction of Sulfonyl Substituted Cyclopropenes (1) with Alkyllithium Reagents

R_1	Lithium Reagent	% Yield of Product
Me_3Si	CH_3	85
Me_3Si	n-C_4H_9	90
Me_3Si	t-C_4H_9	98
Me_3Si	C_6H_5	85
Me_3Si	-CH=CHPh	85
C_6H_5	CH_3	50
C_6H_5	n-C_4H_9	85
C_6H_5	t-C_4H_9	40
C_6H_5	vinyl	35
C_6H_5	allyl	35

As the Table indicates, the reactions derived from the trimethylsilyl substituted cyclopropene **1a** proceed in better yield than those derived from the phenyl substituted compound (i.e. **1b**). In experiments where TMEDA or HMPA were present, the yield of product was significantly lower. Addition of m-dinitrobenzene also caused a significant diminution in product formation.

The mechanism by which these sulfonyl substituted cyclopropenes undergo reaction with alkyllithium reagents is of considerable interest. Two fundamentally different paths seem possible and these are presented in Scheme I. Path A is somewhat unique in that it involves addition of the lithium reagent to the "wrong" end of the pi-bond. It should be pointed out, however, that various nucleophilic reagents are known to add to unactivated cyclopropenes presumably as a consequence of relief of strain.[9] In this case, the bulky trimethylsilyl substituent may actually block attack of the reagent at the β-position as well as stabilize the resulting carbanion. Chelation of the incoming alkyllithium with the oxygen atoms of the sulfonyl group

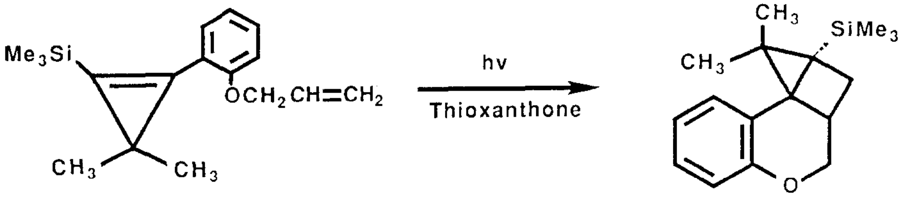
Scheme I



may also be a factor in promoting Path A. Recently, Russell has shown that phenyl vinyl sulfones react with alkyl mercury reagents by an addition-elimination sequence.[10] The mechanism suggested for that process may also be applicable to the cyclopropenyl systems.

The alternate path (B) involves a $S_{RN}1$ type radical anion chain mechanism.[11-13] The ability of alkyl lithiums to serve as a one electron donor toward other organic substrates has been established by Ashby.[14] The propagation cycle for the reaction is sketched in Scheme I. According to this mechanism, the alkyllithium reagent initiates the process by transferring an electron to the cyclopropenyl sulfone. The resulting radical anion 3 undergoes loss of the sulfinate group to give cyclopropenyl radical 4. Further reaction of this species with more alkyllithium produces the radical anion of the product which, in turn, transfers an electron to starting material (i.e. 1). At the current time, the available data do not distinguish between the two possibilities.

In connection with our program dealing with the photochemistry of small ring compounds, we have taken advantage of the above process to synthesize a variety of substrates suitable for excited state studies. For example, cyclopropene 5 was prepared in 79% by treating 1a with o-allyloxyphenyllithium. The triplet-sensitized irradiation of 5 afforded the novel intramolecular cycloadduct 6 in 85% yield.



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Further studies on the scope and mechanism of these displacement reactions are in progress and will be reported in due course.

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References and Notes

(1) Posner, G. H.; Brunelle, D. J. **J. Org. Chem., 1973,** 38, 2747.
(2) Conrad, P. C.; Fuchs, P. L. **J. Am. Chem. Soc., 1978,** 100, 346; Hutchinson, D. K.; Fuchs, P. L. **J. Am. Chem. Soc., 1985,** 107, 6137; **Tet. Lett., 1986,** 1429.
(3) Eisch, J. J.; Galle, J. E. **J. Org. Chem., 1980,** 45, 4534.
(4) Taber, D. F.; Saleh, S. A. **J. Org. Chem., 1981,** 46, 4817.
(5) Ford-More, A. H.; Peters, R. A.; Wakelin, R. W. **J. Chem. Soc., 1949,** 1754.
(6) Block, E. "Reactions of Organosulfur Compounds", Academic Press, New York, N. Y. 1978.
(7) Magnus, P. D. **Tetrahedron, 1977,** 33, 2019.
(8) Padwa, A.; Wannamaker, M. W. **Tetrahedron Lett., 1986,** 2555.
(9) Hauck, G.; Durr, H. **J. Chem. Res., 1981,** 180.
(10) Russell, G. A.; Ngoviwatchai, P. **Tetrahedron Lett., 1986,** 3479.
(11) Kornblum, N. **Angew. Chem. Int. Ed. Engl., 1975,** 14, 734.
(12) Russell, G. A.; Mudryk, B.; Jawdosink, M. **J. Am. Chem. Soc., 1981,** 103, 4610.
(13) Bunnett, J. F. **Acc. Chem. Res., 1978,** 11 413.
(14) Ashby, E. C.; Pham, T. N.; Park, B. **Tetrahedron Lett., 1985,** 4691.

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