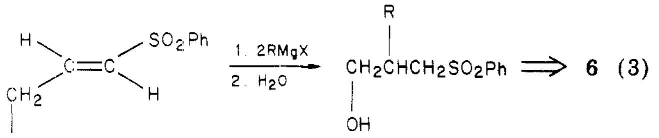


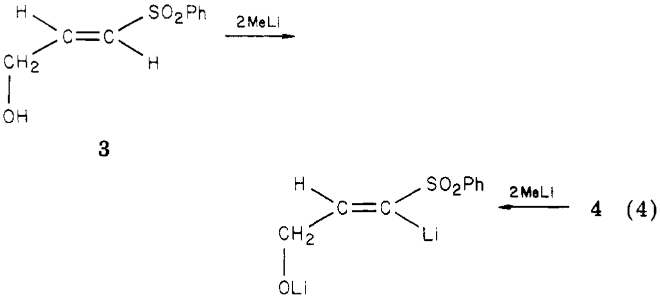
3

8 (70–80%)

R = Et, Ph

is tantamount to an alternative route to 2-substituted-cyclopropyl sulfones (6), since by known methods[6] 8 could be tosylated and cyclized with lithium diisopropylamide.

Finally, by using methyllithium, the metalation of 3 at the vinyl position α to the phenylsulfonyl group[3] could be made to dominate over Michael addition, so that 9 was formed in high yield. Alternatively, 9 resulted directly from 4, if 2 equiv of MeLi were employed. Derivative 9 gives the expected products when treated with D_2O or Me_3SiCl, but alkylation with alkyl iodides does not proceed well. Nevertheless, its multifunctional character seems to warrant a further study of its properties.



3

9

A typical procedure for the preparation of 2-substituted-cyclopropyl phenyl sulfone is as follows. A stirred solution of 7.15 g (27.4 mmol) of 2[8] in 20 mL of anhydrous ether was cooled to 0 °C under nitrogen and then treated dropwise with 15.3 mL of 2.0 M allylmagnesium bromide (30 mmol) in ether. The addition of 20 mL of ether and 20 mL of THF caused the initially gummy mixture to become granular. After 15 min at 20–25 °C the mixture was hydrolyzed with aqueous NH_4Cl solution and the separated ethereal layer was dried over anhydrous $MgSO_4$. After solvent removal the crude product (6.05 g) was chromatographed on silica gel with an ether–hexane eluent. The fractions emerging with 40% ether constituted 4.64 g (76%) of the colorless oil, 2-allylcyclopropyl phenyl sulfone (6a): NMR ($CDCl_3$) δ 7.38–7.95 (m, 5), 4.32–5.87 (m, 3), 1.22–2.44 (m, 5), and 0.73–1.15 (m, 1).

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Registry No. 1, 16212-05-8; *trans*-2, 28187-87-3; *cis*-2, 70941-72-9; 3, 70941-73-0; 4, 70941-74-1; 6a, 70941-75-2; 6b, 70941-76-3; 6c, 70941-77-4; 6d, 21309-15-9; 6e, 70941-78-5; 6 (R = Et), 70941-79-6; 7 (R = Me), 34009-06-8; 7 (R = Et), 70941-80-9; 8 (R = Et), 70941-81-0; 8 (R = Ph), 70941-82-1; 9, 70941-83-2; allyl bromide, 106-95-6; propargyl bromide, 106-96-7; 1-bromo-3-methyl-2-butene, 870-63-3; bromobenzene, 108-86-1; benzyl chloride, 100-44-7.

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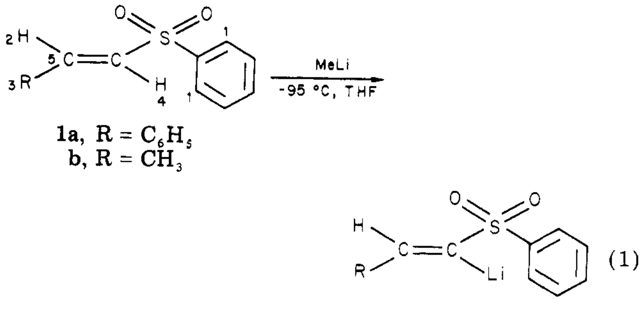
Generation of α-Sulfonylvinyllithium Reagents by the Lithiation of Vinylic Sulfones

Summary: Methyllithium lithiates phenyl vinylic sulfones at −95 °C in THF solution to yield α-(phenylsulfonyl)-vinyllithium reagents.

Sir: Although sulfone derivatives have come to play an expanding and versatile role in organic synthesis,[1] no direct or practical synthesis of 1-(organosulfonyl)vinylmetallic derivatives has yet been reported. In fact, only recently has the generation of 1-(arylsulfinyl)-1-alkenyllithium reagents from vinylic sulfoxides and lithium diisopropylamide been realized.[2–7] Even the α-lithiation of 1-alkenyl aryl sulfides has been achieved only in the last few years.[8–10] In view of this lacuna in the sulfone literature, therefore, we are pleased to report that methyllithium causes the remarkably facile and highly locoselective[11] α-lithiation of phenyl vinylic sulfones at −95 °C in THF solution. Although a vinylic sulfone, such as phenyl (*E*)-1-propenyl sulfone, could conceivably be lithiated also at the *o*-phenyl (1),[12] β-vinyl (2), or γ-allyl (3) site, lithiation occurs only at the α-vinyl position (4) (eq 1). Furthermore, even though such systems are also prone to Michael additions of organometallics (5),[13] no such competing reaction is observed with 1 and methyllithium.



1a, R = C_6H_5
b, R = CH_3

2a, R = C_6H_5
b, R = CH_3

The resulting 1-(phenylsulfonyl)-1-alkenyllithium reagents (2) can be alkylated with methyl or *n*-butyl iodide in high yield (75–90%). In the case of 3a, the stereochemistry shown is supported by obtaining the same product from bromo derivative 4, of known configuration,[14]

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[1] P. D. Magnus, *Tetrahedron*, **33**, 2019 (1977).

[2] G. H. Posner, P.-W. Tang, and J. P. Mallamo, *Tetrahedron Lett.*, 3995 (1978).

[3] For studies of the stabilizing influence of the sulfinyl group on an adjacent carbanion, cf. E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, N.Y., 1978, and ref 4–7.

[4] J. F. Biellmann and J. J. Vicens, *Tetrahedron Lett.*, 467 (1978).

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[6] S. Lavielle, S. Borg, B. Moreau, M. J. Luche, and A. Marquet, *J. Am. Chem. Soc.*, **100**, 1558 (1978).

[7] H. Sugihara, H. Tanikaga, K. Tanaka, and A. Kaji, *Bull. Chem. Soc. Jpn*, **51**, 655 (1978).

[8] K. Oshima, K. Shimoji, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **95**, 2694 (1973).

[9] I. Vlattas, L. D. Vecchia and A. O. Lee, *J. Am. Chem. Soc.*, **98**, 2008 (1976).

[10] R. H. Everhardus, H. G. Euwhorst, and L. Brandsma, *J. Chem. Soc., Chem. Commun.*, 801 (1977).

[11] Term designating that site (L, *locus*), out of several possibilities, where chemical reaction occurs (J. J. Eisch and K. R. Im, *Adv. Chem. Ser.*, **No. 173**, 195 (1979); in substrate **1b**, out of four conceivable sites, only the α-vinyl proton is removed (locoselectively).

[12] W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

[13] G. H. Posner and D. J. Brunnelle, *J. Org. Chem.*, **38**, 2747 (1973).

[14] (a) J. C. Phillips, M. Aregullin, M. Oku, and A. Sierra, *Tetrahedron Lett.*, 4157 (1974). (b) The retention of configuration in transforming **1b** to **2b** to **3b** is also assured, since both **3b** and its *Z* isomer have previously been prepared and their configurations have been determined: cf. I. Sataty and C. Y. Meyers, *Tetrahedron Lett.*, 4161 (1974).

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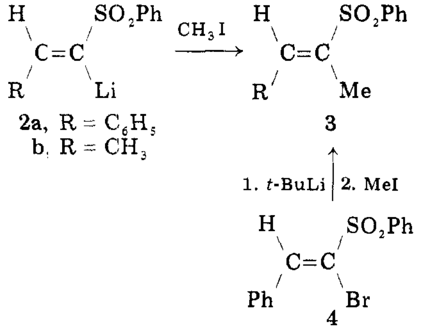
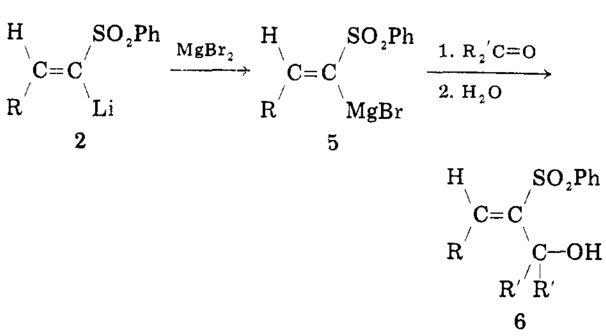
by a sequence of bromine–lithium exchange at −95 °C and methylation (eq 2).



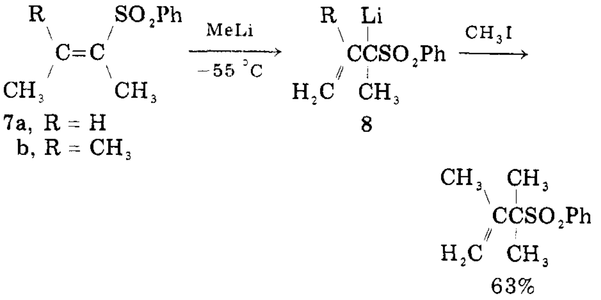
(2)

Such vinyllithium reagents react readily with other electrophiles as well (Me_3SiCl, D_2O or $R_2C{=}O$), but with enolizable carbonyl substrates (e.g., cyclohexanone) only poor yields of adducts are isolated. By the stratagem of transforming the lithium reagent **2** into the vinylmagnesium reagent **5** (by adding $MgBr_2$), however, excellent yields of the desired adducts (**6**) are obtained (eq 3).



(3)

Finally, in the absence of an α-vinylic hydrogen, such as with **7b** (R = CH_3), at −55 °C methyllithium abstracts the γ-allylic hydrogen readily to give an allylic lithium reagent **8** that alkylates exclusively next to sulfur (eq 4).



(4)

Since **7a** does not react with methyllithium under these conditions and only slowly reacts at −10 °C, the kinetically more acidic methyl group in **7b** must be that syn with respect to the sulfonyl group. The slow reaction of **7a** at −10 °C involves loss of the *anti*-γ-methyl proton, rather than the β-vinyl proton.[15] Therefore, the kinetic acidity of the protons in vinylic sulfones toward MeLi can be ordered thus: α-vinyl > γ-methyl syn to $PhSO_2$ > γ-methyl anti to $PhSO_2$ ≫ β-vinyl or *o*-phenyl.

A typical procedure for preparing an α-sulfonylvinyllithium reagent and forming derivatives is as follows. To a stirred solution of 4.88 g (20 mmol) of phenyl β-styryl sulfone in 40 mL of THF cooled with a −95 °C (acetone/liquid N_2) bath was added over 3 min a solution of methyllithium–lithium bromide complex (12.0 mL of a 2.0 M solution in ether). The bath was allowed to warm to −60 °C over 0.5 h during which time methane evolution was completed. Methyl iodide (2.18 mL, 35 mmol) was added, and after 5 min the cooling bath was removed. After 0.5 h at room temperature a water/ether workup gave the crude product as a solid. Recrystallization from CH_2Cl_2/EtOH or hexane gave 4.03 g (78.7%) of phenyl (*E*)-1-phenyl-1-propen-2-yl sulfone, mp 93–95 °C. Alternatively, the solution prepared from the methyllithium and sulfone, as above, was recooled to −80 °C and 24 mL of a 1 M solution of magnesium bromide etherate in 25% benzene/ether (prepared by allowing ethylene dibromide to react with a small excess of magnesium) was added. The cooling bath was allowed to warm to −45 °C over 0.5 h and 2.48 mL (24 mmol) of cyclohexanone was added. After 1 h at room temperature an ether/aqueous NH_4Cl workup gave the product. Recrystallization from ether–hexane gave 5.20 g of 1-[(*E*)-2-phenyl-1-(phenylsulfonyl)-1-ethenyl]cyclohexanol (76%), mp 122–124 °C.[16]

Available methods for the reductive conversion of vinylic sulfones to sulfur-free olefins[17] give these conversions (eq 2–4) relevance for the synthesis of di- and trisubstituted ethylenes. In this regard, it is noteworthy that 1-alkenyl phenyl sulfones can be readily obtained in high yield from terminal olefins by copper chloride catalyzed addition of benzenesulfonyl chloride and the dehydrochlorination of the adduct with triethylamine.[18] Furthermore, since diisobutylaluminum hydride cleanly reduces sulfones to sulfides,[19] these sulfone transformations may be coordinated with the numerous synthetic schemes based upon sulfide or sulfoxide chemistry.[2,3,8–10]

Acknowledgment. The authors wish to thank the Department of Energy for support of this work under Grant EF-77-G-01-2739.

Registry No. 1a, 16212-06-9; **1b**, 28691-72-7; **2a**, 70982-64-8; **2b**, 70941-84-3; **3a**, 30246-74-3; **4**, 65210-94-8; **6** (R′ = R′ = $-(CH_2)_5-$; R = Ph), 70941-85-4; **7a**, 37418-36-3; **7a** methylated dimer, 70941-86-5; **7b**, 70941-87-6; **8a**, 70941-88-7; **8b**, 70941-89-8; 2,3-dimethyl-3-(phenylsulfonyl)-1-butene, 70941-90-1; methyllithium, 917-54-4; methyl iodide, 74-88-4; cyclohexanone, 108-94-1; 2-bromo-1-methyl-2-phenylsulfonylethene, 54897-43-7.

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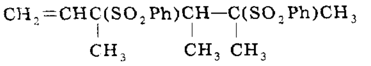
[15] Sulfone **7a** is slowly transformed into **8a** at −10 °C; subsequently **8a** adds to remaining **7a** in a Michael fashion. When the reaction mixture is quenched with MeI, ~70% of the methylated dimer of **7a** is isolated.



$$CH_2{=}CH\underset{CH_3}{C}(SO_2Ph)\underset{CH_3}{C}H{-}\underset{CH_3}{C}(SO_2Ph)CH_3$$

NMR δ 7.4–7.9 (m, 10 H), 5.75–6.2 (d of d, CH=), 4.9–5.3 (m, CH_2=), 1.7 (m, 1 H), 1.41 (s, 6 H), 1.23 (s, 3 H), and 1.08 (d, 3 H).

[16] All compounds reported here gave analytical and spectral data consistent with the proposed structures.

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[18] (a) M. Asscher and D. Vofsi,, *J. Chem. Soc.*, 4962 (1964); (b) J. Sinnreich and M. Asscher, *J. Chem. Soc. Perkin Trans. 1*, 1543 (1972).

[19] J. N. Gardner, S. Kaiser, A. Krubiner, and H. Lucas, *Can. J. Chem.*, 51, 1419 (1973).