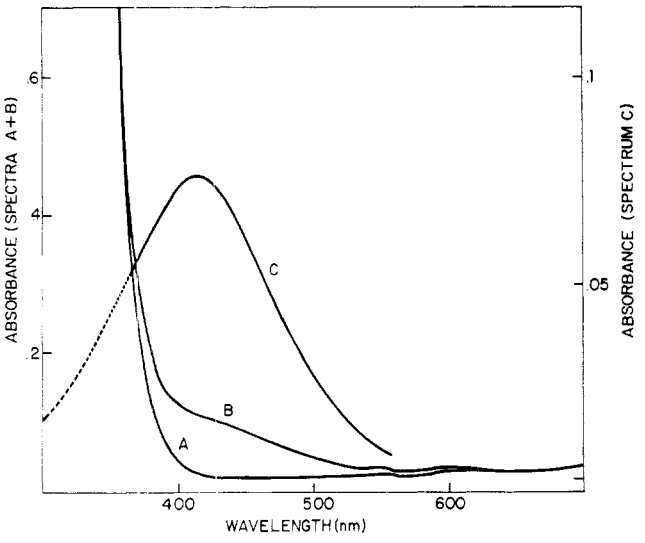
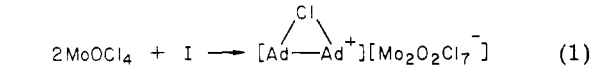


Figure 1. UV-visible spectra in heptane (25 °C) of (A) 0.05 M OsO_4, (B) 0.05 M OsO_4 with 0.05 M I, and (C) difference spectrum (6×).

troduce two chlorine atoms across simple olefins with cis stereochemistry. In contrast to the reactions involving OsO_4, I reacts with these cis-chlorination reagents rapidly, even at −78 °C. Competition studies indicate that $SbCl_5$ reacts ca. 10 times faster with I than with 1-octene. It is noteworthy in this regard that these reagents are ostensibly more sterically congested than OsO_4.[11] The products from this reaction were found to be salts of adamantylideneadamantanechloronium ion (eq 1 and 2) which exhibited remarkable thermal stability.[12] Both salts gave satisfactory analyses (C, H, Cl).



The gold, paramagnetic[13] molybdate from eq 1 (mp 110–111 °C dec) exhibited infrared absorbances due to the terminal oxo ligand at 993 cm^{-1} and due to terminal and bridging chlorides, respectively, at 360 and 308 cm^{-1}. Thus, the $Mo_2O_2Cl_7^-$ anion in this species appears to have the usual[14] triply bridged structure of M_2X_9 dimers, with chloride ligands constituting all three of the bridges. The white, diamagnetic hexachloroantimonate salt exhibited the expected[15] very strong $SbCl_6^-$ absorbance at 340 cm^{-1}. The remaining infrared bands[16] in each case were common to both salts and are assigned to the adamantylideneadamantanechloronium ion. The ^{13}C NMR spectrum[17] of this $SbCl_6^-$ derivative (24 °C, CD_2Cl_2) was virtually identical with that of (thermally unstable) adamantylideneadamantanechloronium chloride (−70 °C, liquid SO_2) reported by Olah.[4] It is also noted that, although discreet compounds[18] containing the $Mo_2O_2Cl_7^-$ anion have not previously been reported, we have been able to prepare several tetraalkylammonium derivatives[19] corresponding to this formulation via eq 3.

$$2MoOCl_4 + NR_4I \rightarrow [NR_4^+][Mo_2O_2Cl_7^-] + ICl \quad (3)$$

Taken as a whole, the observed chemistry of I suggests that its coordination to all of the oxidants in this study occurs readily[20] but that collapse of the resultant complex to organometallic intermediates is considerably more sterically demanding than the initial complexation. For OsO_4, the result is a slow reaction. In the case of $SbCl_5$ and $MoOCl_4$, a less sterically demanding alternative pathway, collapse to an ion pair is available and it is this pathway which predominates. The stability of these salts suggests the possibility of their structural characterization by X-ray crystallography.

Registry No. I, 30541-56-1; 1-octene, 111-66-0; OsO_4, 20816-12-0; $SbCl_5$, 7647-18-9; $MoOCl_4$, 13814-75-0.

(9) Nugent, W. A. *Tetrahedron Lett.* **1978**, 3427–3430.
(10) (a) Uemura, S.; Onoe, A.; Okano, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3121–3124. (b) San Filippo, J., Jr.; Sowinski, A. F.; Romano, L. J. *J. Am. Chem. Soc.* **1975**, *97*, 1599–1600.
(11) Molybdenum oxytetrachloride is monomeric in solution with square pyramidal coordination. Barraclough, C. G.; Key, D. J. *Aust. J. Chem.* **1970**, *23*, 2387–2396. Antimony pentachloride in nonpolar solvents is monomeric with trigonal bipyramidal coordination: Carlson, G. L. *Spectrochim. Acta* **1963**, *19*, 1291–1307; Beattie, I. R.; Gilson, T.; Livingston, K.; Fawcett, V.; Ozin, G. A. *J. Chem. Soc. A* **1967**, 712–718.
(12) Adamantylideneadamantanechloronium chloride has been prepared in solution in low temperature studies but such solutions rapidly decompose on warming. See ref 2b and 4.
(13) The magnetic susceptibility of this complex (per Mo atom) was determined by using the Evans technique in CH_2Cl_2 solution, μ_{eff} = 1.51 μ_B. This is close to the spin only value and suggests the absence of a significant Mo–Mo bonding interaction.
(14) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821–3831 and references therein.
(15) Driessen, W. L.; den Heijer, M. *Inorg. Chim. Acta* **1979**, *33*, 261–264 and references therein.
(16) Remaining absorbances for the $SbCl_6^-$ salt (KBr pellet) follow: 2930 (vs), 2920 (vs), 2860 (s), 1451 (vs), 1430 (w), 1371 (w), 1353 (m), 1327 (m), 1305 (w), 1289 (w), 1230 (m), 1208 (w), 1089 (m), 1059 (w), 1027 (w), 1012 (w), 950 (m), 939 (w), 878 (m), 851 (w), 792 (w), 714 (w), 698 (m), 639 (w), 610 (w), 587 (m), 550 (w), 509 (w), 410 (w).
(17) ^{13}C NMR chemical shifts (parts per million vs. internal standard Me_4Si) are as follows, with literature values from ref 4 in parentheses: 27.0 (27.3), 36.4 (36.6), 37.9 (37.6), 39.9 (39.6), 43.6 (43.6), 158.6? (157.7).
(18) See, however: Eliseev, S. S.; Malysheva, L. E.; Vozhdaeva, E. E. *Russ. J. Inorg. Chem.* **1977**, *22*, 728–731.
(19) For instance, the gold tetrabutylammonium derivative, mp 163–164 °C, μ_{eff} = 1.59 μ_B. Anal. ($C_{16}H_{36}NMo_2O_2Cl_7$) C, H, N, Cl. However, this and all $Mo_2O_2Cl_7$ salts prepared in this way had an unaccounted for absorbance in the IR spectrum at 735 cm^{-1}, suggesting that at least some of the anions in this material contained bridging oxo ligands.
(20) In fact, a related complex between SbF_5 and I has been observed at low temperatures (ref 4). The absence of ^{19}F coupling in the ^{13}C NMR spectrum of this adduct suggests coordination to the antimony atom. It is interesting to note that a theoretical study of coordination of SbF_5 to polyunsaturated hydrocarbons favors coordination through the fluorine atom: Kasowski, R. V.; Caruthers, E.; Hsu, W. Y. *Phys. Rev. Lett.* **1980**, *44*, 676–679.

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Directed Diastereotopic Lithiation of β-Heterosubstituted Alkyl Sulfones[1]

Summary: The directed, highly diastereoselective lithiation of β-aminoalkyl sulfones by organolithium reagents has been shown capable of producing *either* diastereomeric lithio derivative with greater than 90% selectivity, depending upon the type of amino group.

Sir: The recently reported α-lithiation of phenyl vinylic sulfones represents a highly convenient route to α-(phenylsulfonyl) vinyllithium reagents, which are potentially

(1) Part 3 of the series Sulfone Reagents in Organic Synthesis; for previous parts, cf. *J. Org. Chem.*, 44, 3277, 3279 (1979).

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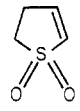
of great value in organic synthesis.[2] In endeavoring to determine the scope of such lithiations, we have observed that certain sulfones, such as phenyl vinyl sulfone (**1a**), 1,3-butadien-1-yl phenyl sulfone (**1b**) and 2-sulfolene (**2**),



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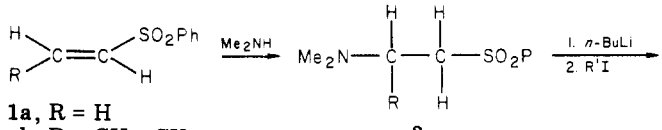
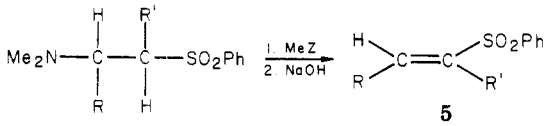
readily undergo competing metalations and Michael-promoted polymerizations when treated with methyllithium in THF solution at −95 °C. We have surmounted this difficulty by the following strategem: (a) the vinylic sulfone is treated with dimethylamine to give the Michael adduct (**3**);[3] (b) the adduct is smoothly lithiated with *n*-butyllithium in THF at −78 °C and then alkylated with an *n*-alkyl iodide (**4**); (c) the product is reconverted to the substituted vinylic sulfone (**5**) by a sequence of quaternization with methyl iodide or methyl *p*-toluenesulfonate and base-promoted elimination. In this manner **1a**, **1b**, and **2** have been indirectly converted into their α-alkylvinylic derivatives in high yield (eq 1).



1a, R = H
b, R = CH_2=CH (1,4-addition of Me_2NH)
c, R = C_6H_5

3

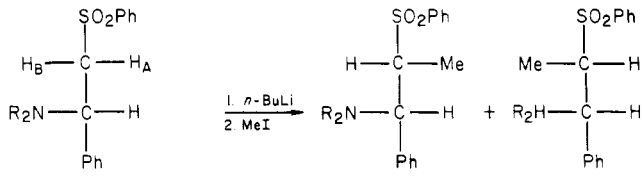


4 **5**

(1)

Although this procedure expands greatly the utility of vinylic sulfones in lithiation processes, what we judge to be truly worthy of communication at this time is the stereochemical course of such lithiations. In cases where the formation of the amine adduct involves a prochiral carbon (**1c**, e.g.), then the amine adduct (**3**, R = C_6H_5) will have a chiral center and the protons α to the sulfone group will be diastereotopic.[4] We now report the directed highly diastereoselective substitution of *either* of these diastereotopic hydrogens by lithium, depending upon what type of amino group is attached at the position β to the sulfone. The factors underlying this directed lithiation should prove of great significance in the stereocontrolled construction of carbon skeletons.

Thus, when phenyl 2-phenylethyl sulfones bearing either a dimethylamino (**6a**) or a morpholino group (**6b**) in the β position were treated with *n*-butyllithium in the THF at −78 °C and then with methyl iodide, the proportions of diastereomeric products (**7**:**8**) isolated in excellent overall yield were 84:16 and 94:6, respectively. When the R_2N group present was NH_2 (**6c**), then the proportion of **7**:**8** isolated (using just *1* mol equiv of *n*-butyllithium) was just the reverse, namely, 13:87. Finally, when the R_2N group was MeHN, then *only* **8** was formed (eq 2; Fischer–Rosanoff representation of relative stereochemistry).

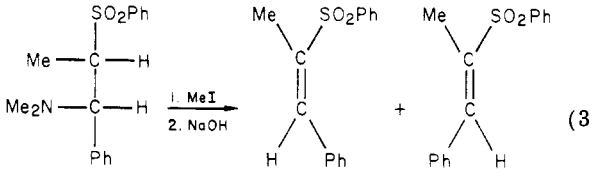


6a, R = Me, Me
b, R = $O(CH_2CH_2)_2$
c, R = H, H
d, R = Me, H

7 **8**

(2)

For proof of structure, the resulting methyl diastereomers (**7** and **8**) were separated from each other. Individual degradation of the separated and pure dimethylamino diastereomers (e.g., **8a**) by the Hofmann method (quaternization with methyl iodide or methyl *p*-toluenesulfonate and base-promoted elimination) gave, as the major product in each case (60–95%), the olefin expected to be formed from anti elimination (eq 3).



8a **9** major **10** minor

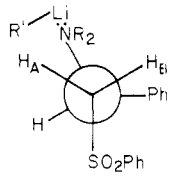
(3)

For the lithiation–methylation sequence of **6c** and **6d**, where R_2N = H_2N or MeHN, the methyl reaction products were reductively methylated with formaldehyde and formic acid (Eschweiler–Clarke reaction)[5] to convert the H_2N and MeHN groups into Me_2N. These products were then identified as already described.

Of the two steps possibly responsible for the diastereoselective alkylations of these sulfones, namely, lithiation or methylation, we have reasons to conclude that lithiation is the configuration-determining step. Support for the conclusion that the configurations and proportions of such methyl derivatives accurately reflect the proportions of their lithio precursors comes from the following considerations: (1) sp^3 carbanions adjacent to the sulfone group are known to be formed with retention of configuration under various conditions;[6] (2) the proportion of methyl isomers obtained from **6a** is sensitive to the time and temperature allowed for the lithiation step but not very sensitive to the conditions used for the methyl iodide quench; (3) that the product ratios reported here are kinetically controlled is evident from the observation that treating a mixture of isomers of **7** and **8** (**a** and **b**) with *n*-butyllithium at 0 °C eventually leads to a 55:45 mixture of **7** and **8**; (4) from other studies of the quenching of organolithium compounds with methyl iodide, there is abundant evidence that methylation proceeds with retention of configuration.[2,7]

A rationalization of these opposite diastereoselectivities can be formulated in terms of coordination complexes and their preferred transition states for lithiation. For **6a** or **6b** complexed with RLi, the Newman projection for the transition state leading to abstraction of proton A (**9**) indicates lessened gauche repulsion than that leading to abstraction of proton B (**10**).

(2) J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 44, 3279 (1979).
(3) In the case of **1b**, addition of dimethylamine occurs in a 1,4 manner and yields Me_2NCH_2CH=$CHCH_2SO_2Ph$.
(4) In the NMR spectrum of **6d** in trifluoroacetic acid, for example, the protons of the CH_2 group α to the sulfonyl display individually the expected doublet-of-doublet pattern: one centered at δ 3.70 (J_{gem} = 14, J_{vic} = 4 Hz), the other centered at δ 4.25 (J_{gem} = 14, J_{vic} = 8 Hz).
(5) M. L. Moore, *Org. React.*, 5, 301 (1949).
(6) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, p 105.
(7) J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, 98, 4646 (1976).



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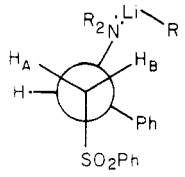

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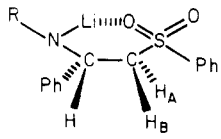

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The *opposite* diastereoselectivity observed in the lithiation of the amino derivatives of **6** (R_2N = H_2N or MeHN) suggests that initially the amino proton is replaced by lithium and a rigid chelate involving coordination of the lithium center by both the RN^- and SO_2 groups, may be a reasonable intermediate for proton abstraction (**11**). An external base (RLi) or a base coordinated at nitrogen should be able to abstract H_B with a lower $\Delta G^{\ddagger}$ than that required for H_A because approach to the flank phenyl group is avoided (cf. footnote 8 for further mechanistic implications).

A typical procedure for preparing **6a** and then lithiating such a phenyl 2-amino-2-phenylethyl sulfone is as follows. A warm solution of phenyl (*E*)-β-styryl sulfone (**1c**, 12.2 g, 50 mmol) in 30 mL of 95% alcohol was sealed in a Hoke tube together with 16.87 g (0.15 mol) of a 40% aqueous dimethylamine solution. The tube was heated for 48 h on a steam bath, cooled, emptied, and rinsed with chloroform. The solvents were removed in vacuo and the residue was recrystallized from 95% ethanol to give 10.54 g (73%) of **6a**, mp 132–134 °C. In $CDCl_3$ the NMR spectrum showed δ 7.82 (m, 2), 7.53 (m, 3), 7.25 (m, 5) 4.28–3.28 (m, 3), and 2.0 (s, 6). In $CDCl_3$–CF_3CO_2H the NMR spectrum showed δ 7.60–6.83 (m, 10), 4.87 (m, 1), 4.17 (m, 2), 2.88 (d, 3, J = 4 Hz), and 2.70 (d, 3, J = 4 Hz). The addition of 5.5 mmol (3.44 mL of a 1.6 M solution in hexane) of *n*-butyllithium to a solution of 1.45 g (5.0 mmol) of **6a** in 40 mL of anhydrous THF cooled in a CO_2/acetone bath was followed after 15 min by the addition of 6.0 mmol of CH_3I. After 15 min more at −78 °C, the reaction was quenched with aqueous NH_4Cl. After the solution was warmed to 25 °C, usual workup gave 1.51 g (99%) of a colorless solid. The NMR spectrum indicated this product to be a 84:16 mixture of **7a** and **8a**. When this mixture was retreated with *n*-butyllithium in THF as above, stirred for 1 h in an ice bath, and quenched, workup as before showed a 55:45 mixture of **7a** and **8a**. Isomer **8a**, mp 158–60 °C, could be obtained by several recrystallizations of such mixtures from 95% EtOH. In $CDCl_3$ the NMR spectrum of **8a** showed δ 7.8–6.9 (m, 10), 4.1–3.68 (m, 2), 2.03 (s, 6), and 1.68 (imperfect t, 3, J = 7 Hz). In $CDCl_3/CF_3CO_2H$ the NMR spectrum of **8a** showed δ 7.70–7.05 (m, 10), 4.68–3.97 (m, 2), 3.10 (d, 3, J = 4 Hz), 2.74 (d, 3, J = 4 Hz), and 1.30 (d, 3, J = 6 Hz). Further processing of the above mother liquors gave **7a**, mp 112–114 °C (hexane). Isomer **7a** showed the following NMR spectrum: ($CDCl_3/CF_3CO_2H$) δ 8.0–7.0 (m, 10), 4.86 (d, 1, J = 11 Hz), 4.42–3.63 (m, 1), 2.97 (d, 3, J = 4 Hz), 2.85 (d, 3, J = 4 Hz), and 0.95 (d, 3, J = 6 Hz).

(8) This mechanistic proposal requires that the thermodynamic acidity of the CH_2SO_2 protons be greater than that of the RNH protons but that the kinetic acidity of the RNH protons be greater than that of the CH_2SO_2 protons. Both requirements can find support in previous work: (1) the pK_a values of $CH_3SO_2CH_3$ and $(CH_3CH_2)_2NH$ are 23 and 36, respectively; (2) cyclohexylamine and piperidine (or their lithium salts) are widely used kinetic bases for promoting the deprotonation of carbon acids. Cf. D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, pp 15–16, 20–31; R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(9) All new compounds exhibited spectral and analytical properties in accord with the assigned structures.

Registry No. **1c**, 16212-06-9; **6a**, 65885-20-3; **6b**, 75032-53-0; **6c**, 75032-54-1; **6d**, 75032-55-2; **7a**, 75032-56-3; **7b**, 75032-57-4; **7c**, 75032-58-5; **8a**, 75032-59-6; **8b**, 75032-60-9; **8c**, 75032-61-0; **8d**, 75032-62-1; **9**, 72568-90-2.

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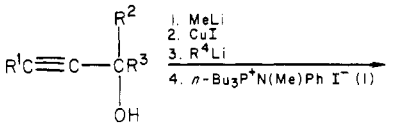
Organocuprate-Induced Coupling of Propargyl or Enyne Alcohols Using (Methylphenylamino)tributylphosphonium Iodide. Regiocontrolled Synthesis of Allenes and Conjugated Enynes

Summary: Regioselective synthesis of allenes is directly achieved via organocuprate-mediated γ-coupling of propargyl alcohols by using the title reagent (**1**). Alternatively, the coupling between 1,4-enyn-3-ols and alkyllithium affords the conjugated *Z* enynes regio- and stereoselectively.

Sir: Recently, interest in allenic chemistry has been noted from both mechanistic[1] and synthetic aspects,[2] and a number of synthetic methods for allenes have been hitherto published.[3] 1,3-Coupling (S_N2' reaction) between propargyl units and alkyl groups in diorganocuprates appears to be one of the most valuable methods for synthesis of allenes. However, besides requiring an excess of alkyl groups in the cuprate reagents, the previous processes require propargyl derivatives such as an ether,[3a] acetate,[3b] tosylate,[3c] halide,[3d] sulfinate,[3e] and carbamate,[3f] which are not always accessible.

We now communicate a highly regiocontrolled alkylation of propargyl or enyne alcohols via organocopper intermediates by using the reagent **1**,[4] which affords an efficient method for synthesis of allenes (eq 1) or conjugated enynes (eq 2).



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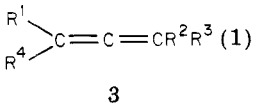

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The full scope of the allene synthesis is summarized in Table I. This new synthetic method for allenes has proven to be valuable in the following aspects. (1) The reaction

(1) Claesson, A.; Olsson, L. I. *J. Am. Chem. Soc.* **1979**, *101*, 7302 and references cited therein.

(2) (a) Crabbé, P.; Carpio, H. *J. Chem. Soc., Chem. Commun.* **1972**, 904. (b) Crabbé, P.; Andre, D.; Fillion, H. *Tetrahedron Lett.* **1979**, 893. (c) Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423. For a review article concerning the enallene system, see: (d) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845.

(3) (a) Olsson, L. I.; Claesson, A. *Acta Chem. Scand., Ser. B* **1979**, 679. (b) Rona, P.; Crabbé, P. *J. Am. Chem. Soc.* **1969**, *91*, 3289. (c) Vermeer, P.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 112. (d) Pasto, D. J.; Shults, R. H.; McGrath, J. A.; Waterhouse, A. *J. Org. Chem.* **1978**, *43*, 1389. (e) Kleijn, H.; Elsevier, C. J.; Westmijze, H.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1979**, 3101. (f) Pirkle, W. H.; Boeder, C. W. *J. Org. Chem.* **1978**, *43*, 1950.

(4) Tanigawa, Y.; Ohta, H.; Sonoda, A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1978**, *100*, 4610.

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