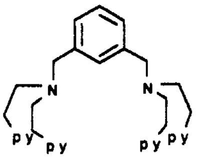
Table III. Products Obtained in the Epoxidation of Olefins by OIPh Catalyzed by Al(TPP)X (X = Cl, OH)[a]

catalyst	olefin (concn, mmol)	product(s) detected	yield, mmol	yield,[b] %	turnover[c]
Al(TPP)Cl	*cis*-stilbene (5)	IPh	0.29		
		cis-stilbene oxide	0.18	62	9.3
		trans-stilbene oxide	0.005		
		benzaldehyde	0.0008		
Al(TPP)Cl	*cis*-stilbene (1)	IPh	0.18		
		cis-stilbene oxide	0.037	22	2.0
		trans-stilbene oxide	0.003		
		benzaldehyde	0.001		
Al(TPP)Cl	*trans*-stilbene (1)	IPh	0.14		
		cis-stilbene oxide	0.003		
		trans-stilbene oxide	0.006	6.4	0.5
		benzaldehyde	0.002		
Al(TPP)Cl	cyclohexene (5)	IPh	0.20		
		cyclohexene oxide	0.016	8	0.8
Al(TPP)OH[d]	cyclohexene (5)	IPh	0.22		
		cyclohexene oxide	0.054	25	5

[a] For the experiments using Al(TPP)Cl, 0.4 mmol of iodosylbenzene was added all at once to a solution of olefin and Al(TPP)Cl (0.02 mmol) in 2 mL of toluene under an inert atmosphere. The reaction mixture was stirred at room temperature for 1 day, after which time 100 μL of the solution was removed and diluted with 1 mL of acetonitrile. The resulting solution was filtered through a 0.45-μm filter and analyzed by HPLC and GC/MS. [b] Percent yield of epoxide based on IPh formed. [c] (Millimoles of epoxide)/(millimoles of metal complex). [d] In this experiment, 0.22 mmol of iodosylbenzene was added to a solution of olefin, Al(TPP)OH (0.011 mmol), and $Li(CF_3SO_3)$ (0.044 mmol) in 2 mL of acetonitrile. Other conditions were the same as in the previous experiments.

Chart I



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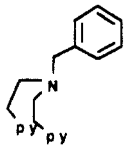

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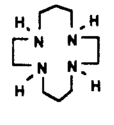
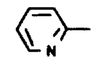


3

(py = )

OH) as catalysts for such reactions. As can be seen from the results in Table III, Al(TPP)X is also a competent catalyst for epoxidation reactions of iodosylbenzene.[12,13] Moreover, the reactivity pattern observed for *cis*- and *trans*-stilbenes is similar to that observed in the case of Fe^{III}(TPP)Cl-catalyzed reactions, i.e., *cis*-stilbene is significantly more reactive than *trans*-stilbene and the product in the case of the former is predominantly *cis*-stilbene oxide,[14] although the Al(TPP)X-catalyzed reactions are significantly slower than those catalyzed by Fe(TPP)Cl.[14]

On the basis of the studies described above, we conclude that metal complexes can catalyze olefin epoxidation by pathways that do not involve high-valent metal oxo intermediates and that ^{18}O incorporation from $H_2{}^{18}O$ cannot be used as evidence to support such intermediates. In other work, we have obtained results suggesting that the alternative reaction pathway may involve metal complexes containing the elements of OIPh and that the first step of the reaction mechanism may best be described as electrophilic attack of I^{III} on the olefin.[9,15] On the basis of our results, we believe that the assumption that metal complex catalyzed reactions of iodosylbenzene invariably involve high-valent metal oxo intermediates should be reconsidered for porphyrin and nonporphyrin systems alike.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

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(12) We submitted our Al(TPP)Cl catalyst for analysis by atomic absorption and ascertained that it contained 62 ppm Fe, >1 ppm Mn, and 7.6 ppm Cr, insufficient amounts to attribute the observed catalytic activity to transition-metal contaminants.

(13) Lithium triflate was required in order for Al(TPP)OH to be reactive, suggesting that the triflate anion plays a role either in solubilizing OIPh or in generating the active oxidant. Similar anion effects were observed previously.[8]

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Quantitative Detection of Remotely Disposed Chiral Centers Using Selenium-77 Nuclear Magnetic Resonance Spectroscopy

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The application of ^{77}Se NMR spectroscopy, via selone **1**,[1] to the detection of enantiomeric excesses at remote chiral centers is described.[2] There exists a plethora of methods for both determination of enantiomeric excesses and, to a lesser extent, absolute configurational assignment.[3] Current NMR spectroscopic methods take advantage of either the formation of contact solution

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† Permanent address: University of California, Los Alamos National Laboratory.

(1) A U.S. Patent application has been filed to cover the use of **1** for the detection of enantiomeric excesses and absolute configurational assignment at chiral centers.

(2) For an application of ^{77}Se NMR for the determination of enantiomeric purity of alcohols, see: Michelsen, P.; Annby, U.; Gronowitz, S. *Chem. Scr.* **1984**, *24*, 251.

(3) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983–1985. Sullivan, G. R. *Topics in Sterochemistry*; Eliel, E. L.; Allinger, N. L.; Wilen, S. H., Eds.; Wiley-Interscience: New York, 1978; p 263. *Methods in Stereochemical Analysis*; Marchand, A. P., Ed.; VCH Publishers, Inc.: New York, 1986; Vols. 1–9. For chromatographic separations, see: Francotte, E.; Lohmann, D. *Helv. Chim. Acta* **1987**, *70*, 1569. Maibaun, J. *J. Chromatogr.* **1988**, *436*, 269. *Chromatographic Chiral Separations. Chromatographic Science Series 40*; Zief, M., Crane, L. J., Eds.; Marcel Dekker: New York and Basel, 1988. For chiral NMR shift reagents, see: Pirkle, W. H.; Hoover, D. J. In *Topics in Sterochemistry*; Eliel, E. L., Allinger, N. L., Wilen, S. H., Eds.; Wiley-Interscience: New York, 1982; p 287. *Methods in Stereochemical Analysis*; Morrill, T. C., Ed.; VCH Publishers, Inc.: New York, 1986; Vol. 5. For direct chirality determination of secondary alcohols, see: Kato, K. *J. Am. Chem. Soc.* **1990**, *112*, 254.

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diastereomers (shift reagents) or derivatization with chiral reagents giving diastereomers.[4] These methods are limited by either the sensitivity of the NMR active nucleus or the incompatibility of the reagent with the functional groups on the enantiomers. Our objective was to broaden the utility of the detection species by designing a chiral reagent which would both complement currently existing reagents and make use of a more sensitive NMR active nucleus.

The NMR properties of ^{77}Se have been exploited in the study of various inorganic, organic, and biochemical systems. The sensitivity of the selenium-77 nucleus (6.93×10^{-3} with respect to ^{1}H and 2.98 compared to ^{13}C), its natural abundance (7.5%), and spin ($I = 1/2$) make it an excellent NMR reporter group.[5] Selenium has the special feature of possessing a large chemical shift range (~3400 ppm), and it is *extremely* sensitive to its electronic environment.[6] In particular, comparisons of ^{77}Se and ^{31}P chemical shifts reveal that the sensitivity of the selenium shielding to changes in electronic structure is several times greater than that of phosphorus.[7] In designing a selenium-containing chiral auxiliary, we wanted to take advantage of several features reported for compounds containing the selenocarbonyl group (C=Se): (1) The range of ^{77}Se chemical shifts for selenocarbonyl groups (~2600 ppm) is larger than that for any other type of selenium moiety and spans more than 80% of the current limits of the ^{77}Se NMR chemical shift range.[8] (2) The T_1's (spin lattice relaxation times) of ^{77}Se selenocarbonyls are relatively short (1–8 s), while those for dialkyl selenides, and especially the diaryl and dibenzyl diselenides, are relatively long (27.0 s).[9] (3) Selenocarbonyl groups display enhanced sensitivity toward small changes in the electronic structure of the selenium atom and its directly bonded carbon atom as compared to selenides and diselenides.[10] Our strategy, then, was to place the C=Se moiety in a rigid chiral environment, as in selone **1**, and evaluate the potential use of ^{77}Se NMR for the detection of the status of remote chiral centers.

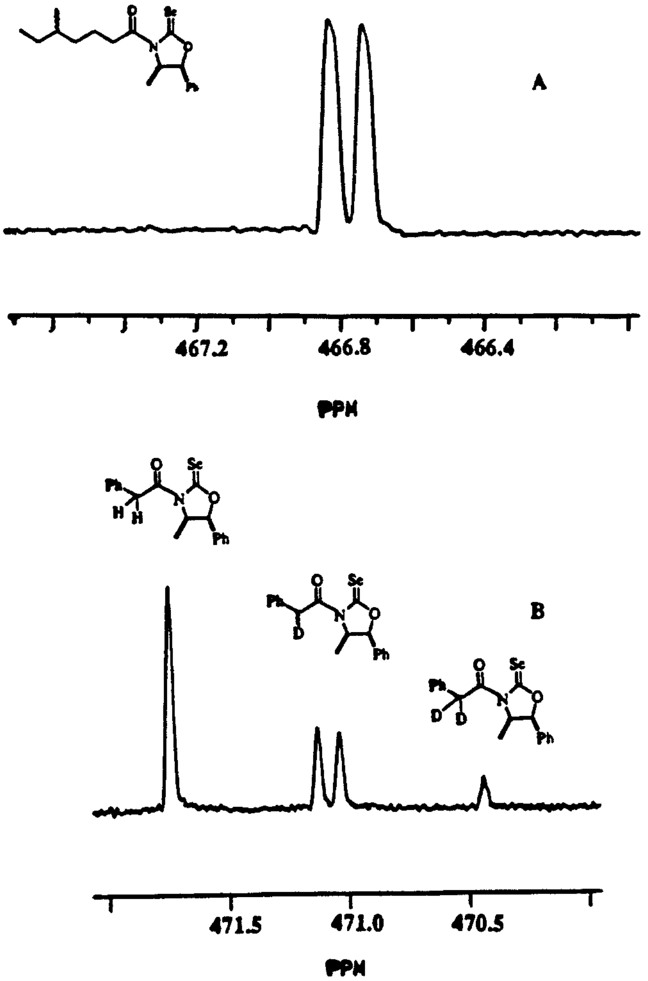

Figure 1. A. Selenium-77 spectrum of **3** was obtained at 7.05 T. Measurements were made by using a 5-mm NMR tube with $CDCl_3$ as an internal lock solvent. A 0.3 M solution was used, with 4439 scans were acquired by using a pulse angle of 89° and a recycle time of 7.2 s. Digitization (Hz/pt) of 0.14 Hz was obtained by using a 64 K data table and a sweep width of 80 ppm. B. Selenium-77 spectrum of a mixture of isotopomers **5**. Measurements were obtained at 7.05 T by using a 5-mm NMR tube with $CDCl_3$ as an internal lock solvent. A 0.2 M solution was used, and 15 360 scans were acquired by using a pulse angle of 30° and a recycle time of 2.8 s. Digitization (Hz/pt) of 0.35 Hz was obtained by using a 32 K data table and a sweep width of 100 ppm.

The coupling of the selone **1** to racemic carboxylic acids **2** and **4**[11] with dicycyclohexylcarbodiimide (DCC) in CH_2Cl_2 with (dimethylamino)pyridine (DMAP)[12] at 0 °C for 0.5–1.0 h afforded the acylated derivatives in 90–95% yields (Scheme I).[13]

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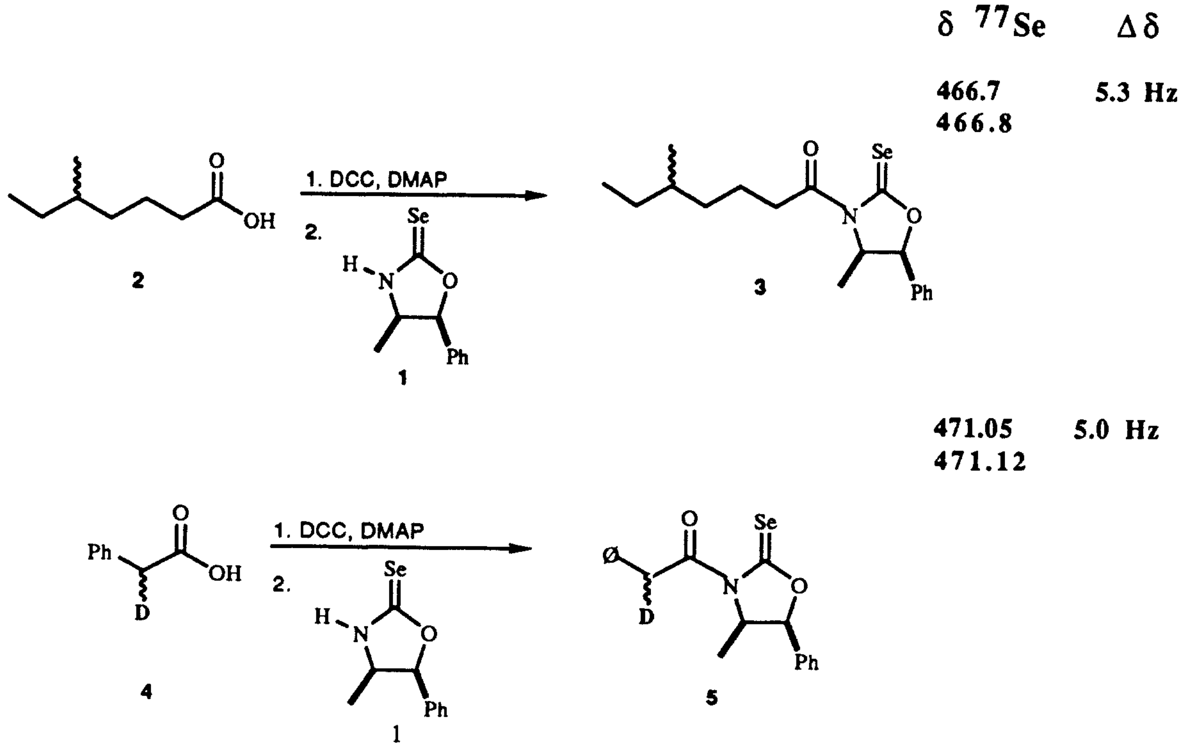
(12) Acid chlorides with triethylamine give similar results.

(13) A referee has expressed his concern that the yields of the coupling reaction are not quantitative. We have performed experiments similar to the ones which Johnson, C. R. et al. included in his initial report. We have taken known enantiomeric ratios of 2-methylbutyric acid, coupled them to **1**, and have quantified the resonance areas. The areas of the resonances closely matched the known enantiomeric excesses. These results will be reported elsewhere. Complete spectroscopic data are provided as supplementary material.

Scheme I



A ^{77}Se–^{13}C coupling constant of 239 Hz in **3** indicates N-acylation, which is indicative of selenium bonds which possess π-character.[14] The most compelling evidence for N-acylation is the fact that only one ^{77}Se–^{13}C coupling is observed in the ^{13}C NMR spectrum of both acylated derivatives.[15]

The ^{77}Se NMR of **3** illustrates that a distance of eight atoms gives rise to two clearly resolved peaks which possess a $\Delta\delta = 5.3$ Hz (Figure 1A).[16] In an attempt to examine the limits of this method the deuterated acylated selone **5** was constructed (Scheme I). The ^{77}Se NMR spectrum exhibited four resonances (Figure 1B). The largest peak has been assigned to the fully protonated species which has a chemical shift at $\delta = 471.7$ ppm.[17] The diastereomeric monodeuterated species exhibited observable $\Delta\delta$ differences of 5 Hz. The most shielded peak has been assigned to the bis-deuterated species which resonates at $\delta = 470.4$ ppm. *Not only is it remarkable that the selenium nucleus has the special ability to distinguish between a hydrogen and a deuterium five atoms removed, but also it can discern the presence of four different species (with a $\Delta\delta$ range of 1.3 ppm) which differ only by the number of deuteriums present.* Clearly, from these results we readily determined that deuterium incorporation was fortuitously incomplete even though the integration of the parent carboxylic acid ^{1}H spectrum indicated 95% deuterium incorporation.[18]

We have evaluated the feasibility of performing quantitation intensity measurements for ^{77}Se NMR spectra under nonideal and ideal conditions and have found that "integration" of the peak areas is reproducible to ±0.5% if adequate digitization and signal-to-noise ratios are obtained.[19]

This rapid and very sensitive method provides for the detection of the status of a chiral center up to eight atoms from the selenium reporter group and has been demonstrated to be sensitive enough to distinguish between a hydrogen and deuterium atom six atoms away. We are in the process of evaluating the scope and limitation of this novel method for the detection of enantiomeric excesses at remote chiral centers by using ^{77}Se NMR spectroscopy.[20]

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(14) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055. Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Chem. Soc. Perkin Trans. II* **1982**, 473.

(15) Reaction of bromoethyl acetate with **1** results in alkylation at the selenium atom.

(16) Typically, the selenium-77 NMR spectra were obtained in the Fourier transform mode on a Bruker AM-300 superconducting spectrometer at 7.05 T. Chemical shifts were measured with respect to 60% $(CH_3)_2Se$ in $CDCl_3$.[21] Positive chemical shifts denote resonances deshielded with respect to the reference. Measurements were typically made at, or near, ambient probe temperature in 5-mm NMR tubes by using $CDCl_3$ as an internal lock solvent. All spectra were acquired in the proton-decoupled mode; generally; 0.15–0.30 M solutions were used, and 128–1024 scans were acquired by using a pulse angle of 30° and a recycle time of 2.2 s. A resolution of 0.1 ppm was obtained by using a 32 K data table and a sweep width of 100 ppm. Use of a higher field NMR instrument (500 MHz) resulted in increased peak broadening.

(17) The chemical shift is identical with the chemical shift of the fully protonated species which was constructed independently.

(18) The deuterated phenylacetic acid was constructed as follows. To a −78 °C solution of phenylacetic acid was added 2.2 equiv of *n*-butyllithium (in hexanes). The reaction was stirred for 1 h and then slowly allowed to rise to 0 °C. The reaction was quenched by the rapid addition of deuterium oxide. Acidification with 5% HCl and extraction with diethyl ether followed by drying ($MgSO_4$), filtration, and concentration afforded the crude acid. The acid was purified by column chromatography (230–400 mesh SiO_2). ^{1}H NMR spectroscopy was performed on a EM-390 Varian instrument. We are evaluating the possibility that deuterium incorporation may have been complete but reversed during coupling to **1**.

(19) In calculating the integrals from the parameters of the best fit curves, a mild Gaussian weighting function (GB = 0.1) was applied to the FID prior to Fourier transformation. The resulting frequency domain spectra have an rms (root mean square) signal-to-noise ratio of ca. 60:1. By using curve fitting routines in Bruker's DISNMR program, each resonance was fit by a Gaussian line shape.[22] Iteration was performed automatically until the convergence limit of 1×10^{-8} was achieved (5–9 iterations depending upon the quality of the data). Residual standard deviations were on the order of 0.1–0.3. The ^{77}Se T_1 values for many selones have been determined, and they range from 2–10 s.[23] In order to measure the areas of the two resonances of interest under rigorously quantitative conditions, an upper limit on T_1 was determined from the optimum tip angle α by using $\cos \alpha = \exp(-t/T_1)$, where t is the pulse spacing. T_1 was found to be less than 9 s for both resonances, and spectra were acquired with and without NOE suppression with relaxation delays of 93 s. Acquisition times were chosen to be longer than 5 times T_2, ensuring accurate determination of peak line shapes, and data were zero-filled to improve digital representation of the line shape. Spectra with S/N of 60:1 can typically be obtained with 2 h of signal-to-noise averaging.

(20) Use of **1** with other functional groups is currently under investigation and will be reported in due course. Construction of **1** will be reported elsewhere. A one-step synthesis of 2-oxazolidineselones employing carbon diselenide and mercuric chloride with 1,2-amino alcohols has recently appeared. Yields ranged from 31–57%. See: Skrydstrup, T.; Kjaer, A. *Heterocycles* **1989**, *28*, 269.

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Acknowledgment. We gratefully acknowledge financial support from the University of South Carolina Venture Fund and Institutional Biomedical Research Support Grant NIH (08-S7RR07160K14). Support of high field NMR spectrometer purchases at the University of South Carolina by the NSF (CHE 84-11172) and the NIH (1-S10-RR02425) is acknowledged. We thank Dr. Ron Garber for his support and advice. We would especially like to thank Dr. Dave Deaton for the suggestion that we construct and evaluate **5**.

Supplementary Material Available: Full spectroscopic data for compounds **3** and **5** (17 pages). Ordering information is given on any current masthead page.

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Novel Silicon-Directed Alkylative Cyclization

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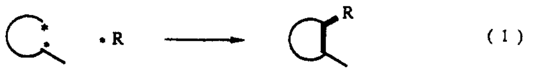
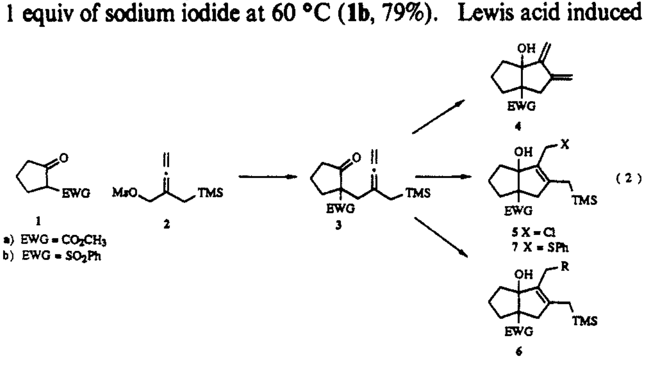
In conversion of simple building blocks to complex molecular arrays, enhanced efficiency results from synthetic methods that form more than one carbon–carbon bond in a single step (either concertedly or nonconcertedly). Cycloadditions represent examples of such reactions in which ring formation occurs as a result of more than one bond being formed between the two reacting partners. An alternative multibond ring-forming strategy involves a sequence of an intra- followed by an intermolecular bond formation as shown in q 1.[1] We record an example of such a process in which a silicon substituent plays a key role in promoting alkyl transfer without desilylation.

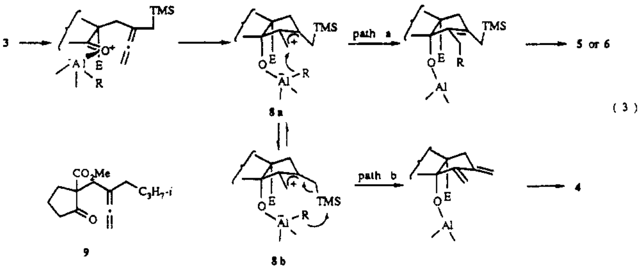


The allenyl silane **3**[2] (eq 2) readily forms by alkylation of the sodium salt of the appropriate precursor, the β-keto ester **1a** or β-keto sulfone **1b**, with the bifunctional conjunctive reagent **2** in THF at room temperature (**1a**, 82%) or DMF in the presence of 1 equiv of sodium iodide at 60 °C (**1b**, 79%). Lewis acid induced cyclization of **3** showed a remarkable dependence on the choice of acid. Exposing **3a** to 1.1 equiv of ethylaluminum dichloride in methylene chloride at −78 to 0 °C provides the desilylative cyclization product **4a** in 82% yield. TBAF in refluxing THF provides the same product in 75% yield, but the reaction is less clean. The sulfone **3b** cyclizes under these latter conditions to give a 78% yield of **4b**. The high reactivity of dienes such as **4** in Diels–Alder reactions makes such a simple annulation protocol for their direct formation valuable for polycyclic construction.

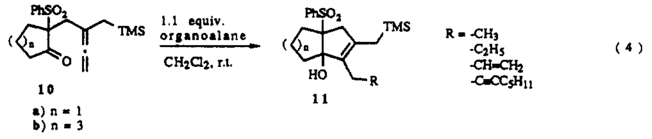


Switching to 1.1 equiv of dimethylaluminum chloride (4:1 methylene chloride–ether, room temperature) effected cyclization in 95% yield to form a 20:1 mixture of the very sensitive chloride **5b** and the diene **4b** in which the latter was the very minor constituent. Subjecting the crude cyclization reaction mixture to sodium benzenethiolate produced the stable sulfide **7b**, which was isolated in 79% overall yield from **3b**. Remarkably, chloride transfer superceded desilylation. An organoaluminum lacking any halide still promotes cyclization but with alkyl transfer rather than desilylation. Thus, exposing **3a** or **3b** to 1.1 equiv of trimethylaluminum (CH_2Cl_2, room temperature) produced the methylated cyclization product **6a** (R = CH_3, 81%) or **6b** (R = CH_3, 95%).

Equation 3 provides a rationale for the observation. It invokes the intermediacy of a silyl-stabilized allyl cation which may collapse by group transfer from aluminum to carbon (path a)[3] or by desilylation (path b).[4] If the complexed aluminum moiety is sufficiently nucleophilic, as it is with the dialkyl- or trialkylaluminums, two factors may favor group transfer from aluminum rather than the normally highly favored desilylation: (1) the steric bias for silicon to be on the less hindered face as in **8a**, which precludes the silylophile from approaching it and (2) the favorability of a six-center process (path a) over an eight-center one (path b). The importance of silicon stabilization of the allyl cation for this process is indicated by the failure of the allene **9** to be reactive under these conditions.



The reaction proves to be reasonably general both with respect to the alkyl group to be transferred and the annulation substrate. For example, the cycloheptanone produces the alkylative cyclization product **11b** (R = CH_3)[2] in 53% yield. Higher saturated alkylaluminums frequently engage in hydride transfer to carbocations, but in alkyl transfer in this system [eq. 4, $(C_2H_5)_3Al$, 80% (**11a**)[2]]. Depending upon the group to be transferred, some tuning of the organoalane is necessary. Whereas vinyl- and 1-heptynyldimethylalanes do not effectively participate, divinyl- and di-1-heptynylmethylalanes do [eq 4, $CH_3Al(CH{=}CH_2)_2$, 60% (**11a**); $CH_3Al(C{\equiv}CC_5H_{11}\text{-}n)_2$, 84–100% (**11a**), 52–78% (**11b**)],[2] with the group that can best stabilize anionic character exclusively transferring. On the other hand, organoboranes, such as triethylborane, do not effect alkylative cyclization.



We have previously shown that compounds like **11** ($n > 3$) can undergo Lewis acid catalyzed pinacol-like rearrangements in which the sulfone functions as a leaving group.[5] Telescoping the alkylative cyclization with cyclorearrangements produces the al-

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[1] For some examples involving transition-metal cascades, see: Negishi, E.; Tour, J. M. *Tetrahedron Lett.* **1986**, *27*, 4869; *J. Am. Chem. Soc.* **1985**, *107*, 8289. Fournet, G.; Balme, G.; Gore, J. *Tetrahedron Lett.* **1989**, *30*, 69. Semmelhack, M. F.; Kim, C. R.; Dobler, W.; Meker, M. *Tetrahedron Lett.* **1989**, *30*, 4925. For an example in radical cyclizations, see: Barton, D. H. R.; deSilva, E.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1988**, 285.

[2] All new compounds have been fully characterized spectrally.

[3] For overviews, see: Maruoka, K.; Yamamoto, H. *Tetrahedron* **1988**, *44*, 5001; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 668. Negishi, E. *Organometallics in Organic Synthesis*; John Wiley & Sons: New York, 1980; pp 363–368.

[4] For recent reviews, see: Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. Schinzer, D. *Synthesis* **1988**, 263.

[5] Trost, B. M.; Adams, B. *J. Am. Chem. Soc.* **1983**, *105*, 4849.

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