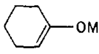
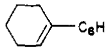
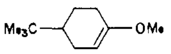
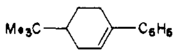
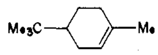
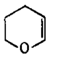
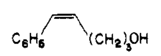
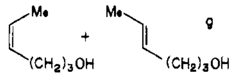
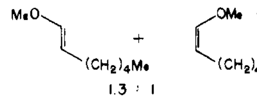
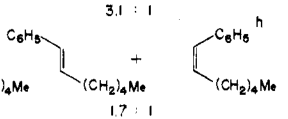
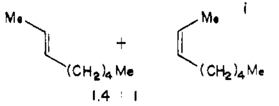
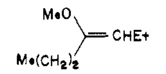
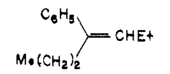
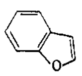
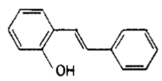
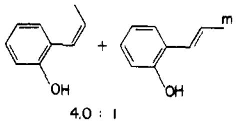
Table I. The Reactions of Enol Ethers with Phenylmagnesium and Methylmagnesium Bromides[a]

Ether	Olefinic Products	% Yield
	 [b]	71
	 [c]	75
	 [d]	59[e]
		64[f]
	 [g]	74[f]
	 [h]	79
	 [i]	66
	 [j]	86
$C_6H_5OCH{=}CH_2$	$C_6H_5CH{=}CH_2$	93[k]
	 [l]	61
	 [m]	75

[a] A benzene solution of ~2 mol of Grignard reagent and 0.1 mol of bis(triphenylphosphine)nickel dichloride/mol of enol ether was refluxed for 15–48 h. Isolated olefin yields are based on the initial enol ether quantity. [b] P. Markov, L. Dimitrova, and C. Ivanov, *Monatsh. Chem.*, **107**, 619 (1976). [c] P. Geneste, J. M. Kamenka, P. Herrmann, and J. Moreau, *Recl. Trav. Chim. Pay-Bas*, **95**, 116 (1976). [d] Y. Kitagawa, S. Hashimoto, S. Iemura, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **98**, 5030 (1976). [e] Reaction time 168 h. [f] 1:2 Grignard reagent–ether. [g] B. Chantegrel and S. Gelin, *Bull. Soc. Chim. Fr.*, 2639 (1975). [h] T. H. Chan and E. Chang, *J. Org. Chem.*, **39**, 3264 (1974). [i] R. B. Bates and W. A. Beavers, *J. Am. Chem. Soc.*, **96**, 5001 (1974). [j] I. I. Lapkin and M. N. Rybakova, *Zh. Obshch. Khim.*, **30**, 1227 (1960). [k] GC yield; GC yield of phenol 62%. [l] W. E. Truce and C.-I. M. Lin, *J. Am. Chem. Soc.*, **95**, 4426 (1973). [m] P. Golborn and F. Scheinmann, *J. Chem. Soc., Perkin Trans. 1*, 2870 (1973).

retention of configuration.[4] The reactions of phenylmagnesium bromide with highly substituted enol ethers, with enolates, and with enamines, as exemplified by 2,6-dimethyl-1-methoxycyclohexene, magnesium 2-methyl-1-propenyl oxide, and 1-(*N*-pyrrolidino)cyclohexene, respectively, do not take place, whereas the reaction with 1-trimethylsilyloxycyclohexene yields the arylation product, albeit in low (35%) yield.

As in the experience of the Felkin reaction with alkylmagnesium halides bearing labile β hydrogens,[1a,c] the reaction of dihydropyran and ethylmagnesium bromide affords alkylation product (*Z*)-4-hepten-1-ol, accompanied by reduction product 4-penten-1-ol (in 1.5:1 ratio and 55% yield). The efficiency of alkylation is enhanced by the use of bis(1,3-diphenylphosphino)propanenickel dichloride as catalyst (5.7:1 ratio, 74% yield).

Although aryl ethers are inert to methylmagnesium bromide, they are attacked by phenylmagnesium bromide in the presence of bis(triphenylphosphine)nickel dichloride. As revealed by Table II, the substitution of methoxy groups is more efficient in the naphthalene nucleus than in the benzene ring. Not only does the reaction take place faster on methoxynaphthalenes than methoxybenzenes, but it even occurs on a vicinal dimethoxynaphthalene in the face of the inertness of *o*-dimethoxybenzene and *o*-cresyl methyl ether. Exposure of β-naphthyl *p*-toluenesulfonate[5] and even magnesium β-naphthoxide to phenylmagnesium bromide in the presence of the nickel catalyst leads to β-phenylnaphthalene in 60 and 16% yield, respectively.

Table II. The Reactions of Aryl Ethers with Phenylmagnesium Bromide[a]

ether	products	% yield
1-methoxynaphthalene	1-phenylnaphthalene	70
2-methoxynaphthalene	2-phenylnaphthalene	77[b]
2,3-dimethoxynaphthalene	2,3-diphenylnaphthalene[c]	45
m-dimethoxybenzene	*m*-methoxybiphenyl	23 (79)
p-dimethoxybenzene	*p*-methoxybiphenyl,	33 (37)
	p-terphenyl	24 (27)
p-methoxybiphenyl	*p*-terphenyl	30 (55)
m-cresyl methyl ether	*m*-methylbiphenyl	16 (74)
p-cresyl methyl ether	*p*-methylbiphenyl	20 (60)

[a] A benzene solution of 2–4 mol of Grignard reagent and 0.1 mol of bis(triphenylphosphine)nickel dichloride/mol of aryl ether was refluxed for 72 h. Isolated product yields are based on the initial ether quantity, whereas those listed in parentheses take into account recovered ether. [b] Reaction time 24 h. [c] H. M. Crawford, *J. Am. Chem. Soc.*, **61**, 608 (1939).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

(1) (a) H. Felkin and G. Swierczewski, *Tetrahedron*, **31**, 2735 (1975); (b) C. Chuit, H. Felkin, C. Frajerman, G. Roussi, and G. Swierczewski, *J. Organomet. Chem.*, **127**, 371 (1977); (c) H. Felkin, E. Jampel-Costa, and G. Swierczewski, *ibid.*, **134**, 265 (1977); (d) B. L. Buckwalter, I. R. Burfitt, H. Felkin, M. Joly-Goudket, K. Naemura, M. F. Salomon, E. Wenkert, and P. M. Wovkulich, *J. Am. Chem. Soc.*, **100**, 6445 (1978).

(2) For related reactions, see R. Noyori, "Transition Metal Organometallics in Organic Synthesis", Vol. 1, H. Alper, Ed., Academic Press, New York, 1976, pp 83–187; R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5535 (1968); L. Blaszczak, J. Winkler, and S. O'Kuhn, *Tetrahedron Lett.*, 4405 (1976); I. Arai and G. D. Daves, Jr., *J. Am. Chem. Soc.*, **100**, 287 (1978).

(3) New compounds gave satisfactory elemental and spectral analyses.

(4) Whereas the product of the ring opening of benzofuran is one of inversion of configuration, it may be the outgrowth of the isomerization of an initially formed *cis*-stilbene under the reaction conditions.

(5) The isolation of *p*-methylbiphenyl indicates the attack of the Grignard reagent to occur also at the site of the aryl–sulfur bond.

Ernest Wenkert,* Enrique L. Michelotti
Charles S. Swindell
Department of Chemistry, Rice University
Houston, Texas 77001

Received November 20, 1978

Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 4. Chiral Silylcyclopentadienes: New Evidence for a 1,2 (1,5) Metallotropic Shift

Sir:

Over the course of the past 20 years, the fluxional nature of *monohapto*cyclopentadienyl derivatives of a range of both transition and nontransition metals has been clearly established through application of variable-temperature NMR techniques.[1] While such dynamic behavior has been thoroughly characterized as metallotropic[2] and intramolecular,[3,4] the mechanism of the degenerate rearrangement has remained

0002-7863/79/1501-2247$01.00/0

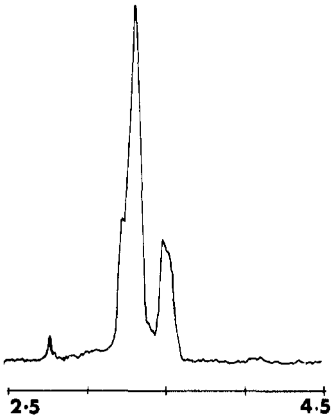


Figure 1. ^1H NMR spectrum, τ 2.5-4.5, of compound II at −60 °C recorded at 90 MHz.

Table I. Precoalescence Proton-Decoupled ^{13}C NMR Data[a] for Cyclopentadienylsilanes, $R(Cl)(H)SiC_5H_5$

R	T, K	chemical shifts, ppm[b] C (olefinic)	chemical shifts, ppm[b] C (aliphatic)
Me[c]	223	133.7 (91)[d] 132.8 (100) 132.1 (78) 130.5 (77)	51.2 (62)
n-Bu[e]	218	133.7 (51) 132.6 (100) 129.9 (45)	50.6 (42)
Me_3SiCH_2[f]	223	133.5 (94) 132.7 (100) 132.3 (89) 130.9 (87)	52.2 (78)

[a] $CDCl_3$ was used as solvent and internal reference throughout. [b] High frequency relative to δ 77.2 ppm for $CDCl_3$ (central component of triplet); high frequency corresponds to low field and vice versa. [c] $\delta(^{13}C(Me))$ at −0.8 ppm. [d] Numbers in parentheses indicate relative peak heights (pulse interval 1.36 s, pulse width 8 μs). [e] $\delta(^{13}C(n\text{-}Bu))$ at 25.6, 23.9, 20.0, and 14.0 ppm. [f] $\delta(^{13}C(Me_3SiCH_2))$ at 2.2 (CH_2) and 0.7 (CH_3) ppm.

uncertain; unsymmetrical collapse of olefinic NMR signals (either ^1H or ^{13}C) during coalescence rules out a random migration but assignment to a 1,2 (rather than 1,3)[5] shift rests rather uneasily on a variety of circumstantial evidence.[1,6] Most recently within this latter category we have proposed[4] that the effect on ^{13}C resonant frequencies of increasing chlorine substitution at silicon in the cyclopentadienylsilanes $(C_5H_5)SiH_{3-x}Cl_x$ (x = 0-2) provides a basis for distinguishing between the two types of olefinic ring carbon atoms, a differentiation which is crucial[1] in identifying the rearrangement mechanism. In exploring the NMR properties of some chiral analogues, $C_5H_5Si^*XYZ$, we have encountered further evidence which we believe to be extremely significant in the context of this problem.

Reaction at −45 °C between the alkyldichlorosilanes[7] $RSiHCl_2$ (R = Me, n-Bu, or Me_3SiCH_2) and a molar equivalent of potassium cyclopentadienide using conditions described earlier[4] afforded the alkylchlorosilylcyclopentadienes I-III in up to 65% yield. The colorless, liquid products were purified by trap to trap condensation in vacuo and were completely characterized by IR and mass spectroscopic data as well as by the NMR measurements. Variable-temperature ^1H and ^{13}C NMR spectra were recorded as detailed elsewhere.[4]

Chirality at the silicon center in compounds I-III renders the pairs of chemically equivalent C_5-ring nuclei (either ^1H or ^{13}C) anisochronous. The low-field region of the slow-limiting ^1H NMR spectrum of the n-butyl compound II recorded at −60 °C is shown in Figure 1. This appears to consist of two

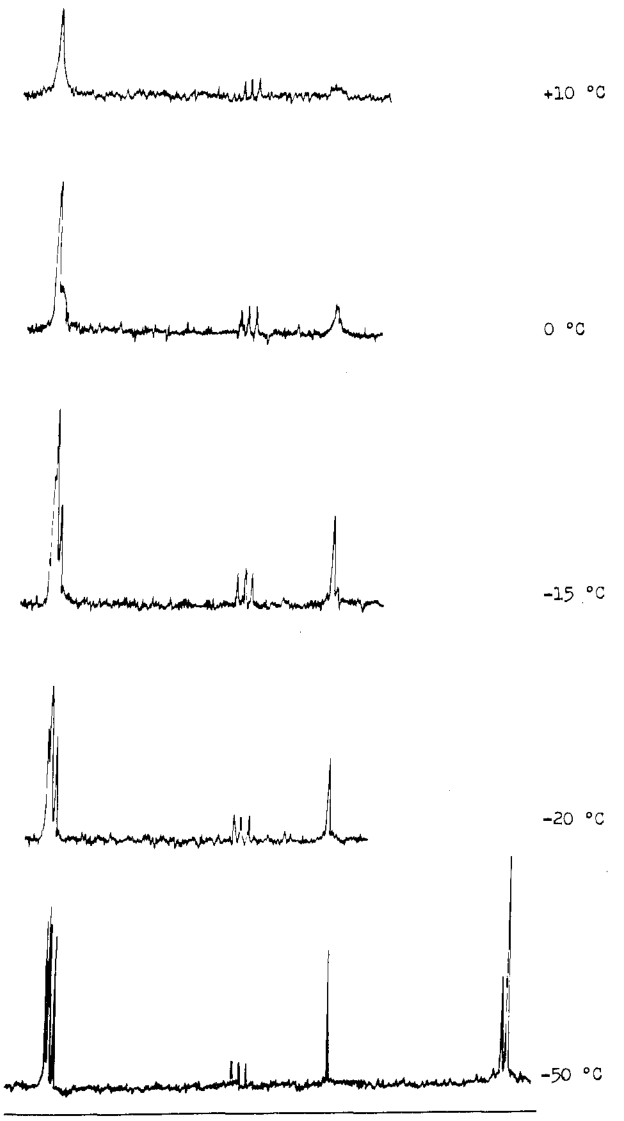
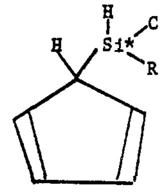


Figure 2. Temperature dependence of the ^{13}C NMR spectrum of compound III. The appearance of the signals at 2.2 and 0.7 ppm due to the trimethylsilylmethyl carbon atoms was unchanged throughout; the triplet at 77.2 ppm is due to $CDCl_3$, solvent and reference. Chemical-shift data are listed in Table I.



(I) R = Me

(II) R = n-Bu

(III) R = Me_3SiCH_2

equal components separated by ~0.2 ppm and overlapped by a single resonance having twice the relative intensity. We suggest that the protons nearest to the center of asymmetry ($H_{a,a'}$) are diastereotopically shifted by 0.2 ppm, with no detectable inequivalence between the more distant pair[8] ($H_{b,b'}$). When the temperature is raised, the signals thus distinguished as belonging to the $H_{a,a'}$ nuclei are those which broaden first accompanying collapse of the high-field (H_X) resonance. This observation verifies a 1,2 shift as the rearrangement mechanism.

The tentative conclusion put forward above is supported overwhelmingly by examination of the temperature dependence of proton-decoupled ^{13}C NMR spectra for I-III. Observed frequencies at the slow limit of rearrangement are listed in Table I. In the olefinic region the *n*-butyl compound II shows two resonances, which we assign to $C^{2,5}$ diastereotopically shifted from one another by 3.8 ppm, flanking an unsplit $C^{3,4}$ resonance at 132.6 ppm. For I and III both pairs of carbon atoms are anisochronous: the $C^{2,5}$ resonances remain ~3 ppm apart, but a separation which is much smaller (0.7, I; 0.4 ppm, III) is also found between C^3 and C^4. The temperature dependence of these spectra is typified by that shown in Figure 2 for the trimethylsilylmethyl compound III. With increasing temperature and in spite of the substantially larger chemical-shift difference between them, the outer pair of lines (attributed to $C^{2,5}$) begin to broaden and lose intensity more rapidly than the central signals. Exactly similar changes occur in the spectra of I and II: for the latter the resonance due to the carbon atoms showing no resolvable diastereotopic effect ($C^{3,4}$) collapses more slowly than those for the anisochronous pair.

By providing a new approach to the assignment of resonances due to the cyclopentadienyl ring nuclei these observations constitute a more convincing substantiation of the 1,2 (equivalent to 1,5) migration pathway than those put forward hitherto.

Acknowledgment. We thank the National Research Council (Canada) and the University of Victoria for financial support.

References and Notes

(1) This subject has recently been critically reviewed by F. A. Cotton, In "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, 1975, Chapter 10.
(2) A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970).
(3) C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, 3282 (1971); P. C. Angus and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 2374 (1973); R. J. Goodfellow and S. R. Stobart, *J. Magn. Reson.*, **27**, 143 (1977).
(4) A. Bonny, S. R. Stobart, and P. C. Angus, *J. Chem. Soc., Dalton Trans.*, 938 (1978).
(5) Nomenclature and numbering of ring positions for compounds of the type described in this communication have been discussed in ref 4.
(6) D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organomet. Chem.*, **42**, 159 (1972); C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, 1318 (1970); F. A. Cotton and T. J. Marks, *Inorg. Chem.*, **9**, 2802 (1970). Evidence for a 1,2 shift as the mechanism for the nondegenerate rearrangement of corresponding indenyls is also reviewed in ref 1.
(7) Methyldichlorosilane is commercially available; the *n*-butyl and trimethylsilylmethyl compounds were obtained through alkylation of trichlorosilane with the appropriate organolithium reagent.
(8) While there exists the possibility that this interpretation could be reversed, we feel it is extremely unlikely that the 3,4 nuclei would be more strongly influenced by the presence of the asymmetric center than those in the 2,5 positions. A related argument was advanced in explaining the behavior of the ^1H NMR spectrum of $(C_5H_5)_3MoNO$ below −52 °C, where it was proposed that configurational rigidity led to restricted rotation about the bond between a *monohapto*cyclopentadienyl group and the molybdenum atom: F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, **90**, 6232 (1968).

Alan Bonny, Stephen R. Stobart*
Department of Chemistry, University of Victoria
Victoria, British Columbia, Canada, V8W 2Y2

Received December 26, 1978

Hemiorthothiolate Ester Anions—RC(OR′)$_2$S$^-$ $^+$Na. A Novel Class of Thermally Stable Tetrahedral Intermediates[1]

Sir:

Tetrahedral intermediates play a pivotal role in a whole host of enzymatic and nonenzymatic carbonyl reactions.[2] Our knowledge of the chemistry of three-heteroatom tetrahedral intermediates[3] is derived from numerous kinetic,[4] spectroscopic,[5] and theoretical studies.[6] Deslongchamps' elegant investigations[7] have furthered our understanding of stereoelectronic effects in the generation and breakdown of short-lived tetrahedral species of the type $RC(OR)(OH)_2$, $RC(OR)_2(OH)$, and $RC(OR)(NR_2)(OH)$; stereoelectronic effects have also been noted in the breakdown of hemiorthothioamide intermediates—$RC(OR)(NR_2)(SH)$.[8] While a variety of neutral intermediates (T^0) have been isolated,[9] only three stable anionic three-heteroatom intermediates (T^-) are known.[10] We report on the isolation and characterization of a novel class of thermally stable anionic tetrahedral intermediates—$RC(OR')_2S^-$ ^+Na—formed during the intramolecular transesterification of thionobenzoate and thionoacetate esters.

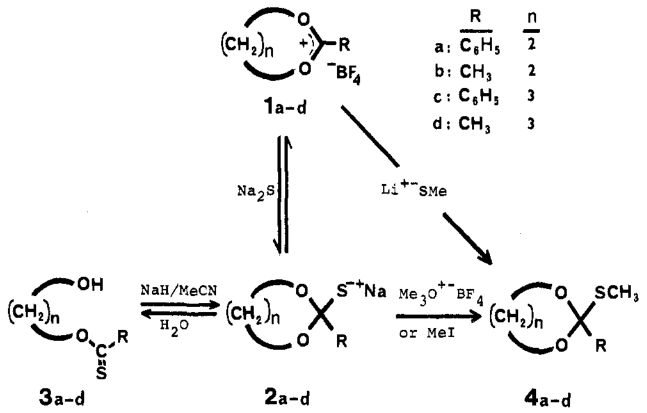


Figure 1. Synthesis and trapping of tetrahedral intermediates **2a–d**.

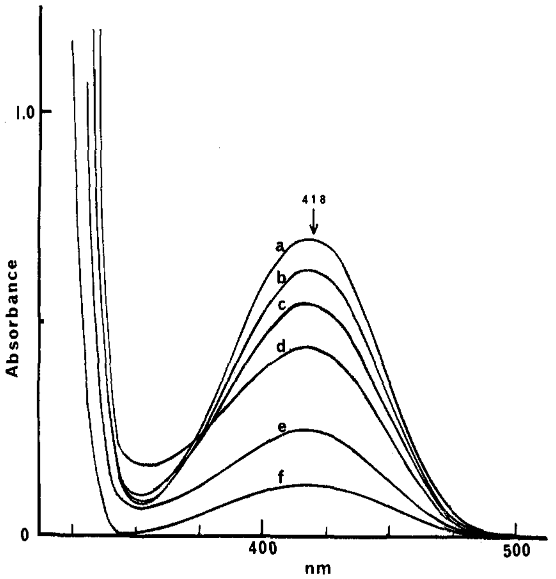


Figure 2. Visible spectra of the **3a** → **2a** transformation: a, 6.09 × 10^{-3} M solution of **3a** (hexane); b–f, after addition of 1.0, 1.5, 2.5, 4.0, and 6.0 mg of NaH to 3.0 mL of a.

We recently reported that the sulfhydrolysis of various acyclic and cyclic dialkoxycarbonium ions may be carried out through a two-step addition–protonation sequence to give good yields of thionobenzoates and monothionoesters of 1,2- and 1,3-diols.[11] In the course of these experiments, it was observed that the reaction of 2-phenyl-1,3-dioxolan-2-ylium fluoroborate (**1a**) with an equivalent amount of anhydrous sodium sulfide in acetonitrile gave a crude white solid which, after thorough washing with dry acetonitrile under nitrogen, could be hydrolyzed to give a yellow oil, **3a**, in 27% yield. Treatment of the crude solid above with 1.5 equiv of Me_3O^+ $^-BF_4$/

0002-7863/79/1501-2249$01.00/0