TABLE III
CORRELATION OF COUPLING CONSTANTS WITH CHEMICAL SHIFTS[a]
$J = a\delta_1 + b\delta_2 + c\delta_4 + d$

J	a	b	c	d	R^b	Error[c]
1,2	−0.700	1.221	0.289	7.990	0.937	0.271
1,4	−0.751	0.891	0.284	5.074	0.939	0.273
2,3	0.662	1.095	−1.321	8.251	0.887	0.299
2,4	−0.917	−4.363	3.746	−2.185	0.824	0.582
2,5	0.304	−0.186	1.128	5.353	0.963	0.190
4,5	0.786	0.135	−0.676	8.653	0.895	0.366

[a] δ_1 is the chemical shift for the α proton, δ_2 is the shift for the β proton trans to the substituent, and δ_4 is the shift for the β proton cis to the substituent. [b] Correlation coefficient. [c] Standard error.

Experimental Section

Materials.—Cyclopropylamine, cyclopropyl bromide, cyclopropylcarbinol, cyclopropanecarboxylic acid, cyclopropyl cyanide, cyclopropyl methyl ketone, cyclopropyl phenyl ketone, cyclopropyl 4-fluorophenyl ketone, cyclopropyl 4-methoxyphenyl ketone, 1,1-dicyclopropylethylene, and dicyclopropyl ketone were commercial samples (Aldrich). Cyclopropyl acetate,[21] cyclopropanol,[22] cyclopropyl methyl ether,[23] 2-cyclopropylethanol,[24] cyclopropyl chloride,[25] cyclopropyl iodide,[26] cyclopropanecarboxaldehyde,[27] nitrocyclopropane,[28] and phenylcyclopropane[29] were prepared using previously reported methods. All samples were purified by preparative scale vpc using a 20-ft 20% Carbowax 20M column.

Samples of 2-cyclopropylethanol and 2-cyclopropylethyl bromide were supplied by Dr. Elliot Barber. A sample of nitrocyclopropane was provided by Dr. Gary Lampman, and a sample of cyclopropylcarbinyl acetate was provided by Dr. Gunther Szeimies.

Spectra.—All spectra were taken using a Varian HA-100 nmr spectrometer in the frequency sweep mode. The peak positions were determined by stopping the frequency sweep at the peak maximum and counting the difference in frequency between the observing and locking oscillators. The compounds were examined as 0.5 M solutions in carbon tetrachloride and were degassed using three freeze–thaw cycles. Tetramethylsilane was generally used as the internal standard. In those cases for which this overlapped the cyclopropyl protons, the reference and locking signals were obtained using concentric capillaries containing either benzene or methylene chloride.

The analysis of the spectra were performed using LAOCN3.[30] The coupling constants which are obtained are not unique since the calculated spectra are not affected by interchanging the cis-β-β' coupling constants. All of the calculated and observed spectra are reproduced in the Ph.D. thesis of D.E. Barth.

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[21] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

[22] C. H. DePuy, L. R. Mahoney, and K. L. Eilers, *J. Org. Chem.*, **26**, 3616 (1961).

[23] W. T. Olson, *et al.*, *J. Amer. Chem. Soc.*, **69**, 2451 (1947).

[24] H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).

[25] J. D. Roberts and P. H. Dirstine, *ibid.*, **67**, 1281 (1945).

[26] M. Hanack and H. Eggensperger, *Tetrahedron Lett.*, 1975 (1963).

[27] D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, **27**, 51 (1962).

[28] G. L. Lampman, D. A. Horne, and G. D. Hager, *J. Chem. Eng. Data*, **14**, 396 (1969).

[29] D. Davidson and J. Feldman, *J. Amer. Chem. Soc.*, **66**, 488 (1944).

[30] A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin Inc., New York, N. Y., 1968, Chapter 3.

Dipolar Nature of Lanthanide-Induced Shifts. Detection of the Angular Dependency Factor

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The contribution of the angular dependency factor can be clearly seen in the improvement of the pseudocontact shift correlations with the $Eu(dpm)_3$, $Eu(fod)_3$, and $Pr(fod)_3$ induced shifts in the symmetrical and rigid ethers, 1,4-dihydronaphthalene 1,4-oxide (**1**), 1,2,3,4-tetrahydronaphthalene 1,4-oxide (**2**), and benzonorbornadiene *exo*-oxide (**3**). The lanthanide positions in the complexes were determined through a least-squares fit. These improvements upon inclusion of this geometric factor support the contention that the lanthanide-induced shifts are largely dipolar in origin.

The pseudocontact nature of the lanthanide-induced paramagnetic shifts in the pmr spectra of a large number of organic compounds is generally accepted although it has not been rigorously established. The observed shift is a weighted average reflecting the rapid equilibration of a lanthanide shift reagent, $Ln(Y)_3$, and the organic substrate, RX:. The size of the induced

$$Ln(Y)_3 + RX: \rightleftharpoons RX{:}Ln(Y)_3$$

shift obviously depends on these relative concentrations as well as the value of the equilibrium or binding constant, which in turn is related to the basicity of the coordination site in the organic molecule.

The magnitude of a lanthanide-induced pseudocontact shift within a given molecule can be expressed as[1]

$$\Delta\delta_i = \delta_i[\mathrm{Ln}{\neq}0] - \delta_i[\mathrm{Ln}{=}0] = k(3\cos^2\theta_i - 1)(1/R_i^3)$$

where δ_i is the chemical shift of the ith proton, k represents[2] a collection of constants, R_i is the proton–lanthanide distance, and θ is the angle between the crystal field axis of the complex and the radius vector from the lanthanide ion to the ith proton. A vast amount of evidence already suggests a reasonable correlation of the paramagnetic shift with $1/R_i^3$, a correlation that tends to substantiate the importance of the pseudocontact contribution to these induced shifts.[3] Small discrepancies from the $1/R_i^3$ dependency possibly reflect contact contributions[4] or the failure to consider

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[1] B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3281 (1971).

[2] (a) H. J. Keller and K. E. Schwartzhaus, *Angew. Chem., Int. Ed. Engl.*, **9**, 196 (1970); (b) G. N. La Mar, *J. Chem. Phys.*, **43**, 1085 (1965); (c) H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).

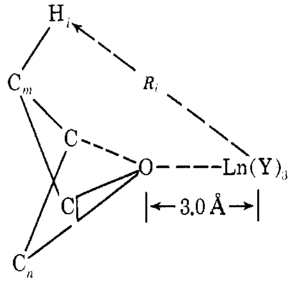
[3] For example see (a) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); (b) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971); (c) K. J. Liska, A. F. Fentiman, and R. L. Foltz, *Tetrahedron Lett.*, 4657 (1970); (d) O. Achmatowicz, A. Ejchart, J. Jurczak, L. Kozerski, and J. St. Pyrek, *Chem. Commun.*, 98 (1971); (e) F. I. Carroll and J. T. Blackwell, *Tetrahedron Lett.*, 4173 (1970).

[4] For example see (a) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734, 5737 (1970); (b) A. F. Cockerill and D. M. Rackham, *Tetrahedron Lett.*, 5149, 5153 (1970); (c) A. J. Rafalski, J. Barciszewski, and M. Weiwiorowski, *ibid.*, 2829 (1971).

the angular dependency portion of the pseudocontact relationship. This geometric factor, which often does not vary greatly from proton to proton, has been more difficult to evaluate, owing largely to uncertainties in vector distances and angles in nonrigid molecules with flexible coordination sites. Nevertheless, certain results have clearly shown that this dependency can be detected and it has been used to account for anomalous shifts.[1,5] An improvement in the correlation of the tris(dipivalomethanato)prasoedymium(III), Pr(dpm)$_3$, induced shifts in borneol by inclusion of the angular dependency factor has been reported.[6,7]

We hoped to circumvent some of the uncertainties associated with a flexible coordination site by examining the rigid bicyclic ethers **1**, **2**, and **3**. In all these ethers the coordination site is locked in the skeletal system. These ethers seem to be ideally suited for an investigation of this type for several other reasons. First of all, the ether coordination site should lead to adequate isotropic shifts. Secondly, the ethers **1**, **2**, and **3** have a variety of spectrally distinct hydrogens at varying distances from the coordination site. Furthermore, the ethers, possessing a plane of symmetry, provide relatively simple spectra with minimal coupling and the shifted spectra are amenable to a first-order analysis with no ambiguity in the assignment of chemical shifts and hence $\Delta\delta_i$ values.

One must still place the lanthanide ion at some given position around the oxygen atom. For our initial work we placed the lanthanide ion in a plane defined by the oxygen and the two adjacent carbons. We made the oxygen–lanthanide distance 3.0 Å, and, although this value cannot be determined exactly, this appears to be a reasonable selection.[8] Furthermore, small changes in this distance are relatively unimportant in comparison to the larger R_i distances. The distance and angle parameters are then defined as indicated. We desired to see, then, if inclusion of the 3 cos^2 θ_i − 1 factor, as defined in this model, would improve the induced chemical shift correlations. It must be assumed in this model that at least the average structure simulates axial symmetry along the O–Ln bond.[9]



Our preliminary results have shown in fact that one can detect an improvement by inclusion of the angular term with the tris(dipivalomethanato)europium(III), Eu(dpm)$_3$, induced shifts in the rigid bicyclic ethers **1**, **2**, and **3**.[10] It seemed reasonable to test the validity of this correlation by comparing the induced shifts with the more soluble, and hence often more useful, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III), Eu(fod)$_3$, shift reagent and especially with the praseodymium(III) analog, Pr(fod)$_3$, which typically induces larger shifts in the upfield direction. Successful correlations of this type, in the process of showing the significance of the geometric factor, certainly aid in confirming the pseudocontact (dipole) nature of these induced shifts, justify the assumption of axial symmetry in solution, and will hopefully permit a better estimate of the oxygen–lanthanide distance in the complex.

Although the 60-MHz nmr spectra for the ethers **1**, **2**, and **3** are straightforward, a striking improvement can be made with the addition of shift reagents. For example, upon addition of 0.2 equiv of Eu(fod)$_3$ to **2**, magnetically equivalent aromatic hydrogens, δ 431 Hz, are resolvable as an A$_2$B$_2$ pattern where $\Delta\delta_A$ = 206 Hz and $\Delta\delta_B$ = 160 Hz and a first-order analysis yields J_{ortho} and J_{meta}. The A protons are, of course, closer to the coordination site and hence shifted further downfield. With 0.2 equiv of Pr(fod)$_3$, complementary upfield shifts are observed for the aromatic hydrogens with $\Delta\delta_A$ = 231 Hz and $\Delta\delta_B$ = 144 Hz. The value of using these complementary reagents is often in making unequivocal spectral assignments. Thus in the A$_2$B$_2$ pattern of the aromatic portion of ether **1**, δ_A = 434 Hz and δ_B = 416 Hz. This small separation increases upon incremental addition[11] of Eu(fod)$_3$. This A$_2$B$_2$ assignment is further confirmed by the incremental addition of Pr(fod)$_3$, whereby the A$_2$ portion, which must still be affected more strongly, moves through the B$_2$ portion leading to an inverted B$_2$A$_2$ pattern. Similar considerations can be made for the other protons in **1**, **2**, and **3**.

It has been suggested that the shifts will be pseudocontact in nature except for protons extremely close to the coordination site where a contact contribution might be anticipated.[3a,b] In fact we have observed, with the ethers **1**, **2**, and **3** with the shift reagents Eu(dpm)$_3$, Eu(fod)$_3$, and Pr(fod)$_3$, that the hydrogens on the carbons bearing oxygen (H$_1$ and H$_4$ in **1** and **2**, and H$_2$ and H$_3$ in **3**) sometimes exhibited a deviation that probably could be attributed to a contact contribution. To remove this doubt, these hydrogens were deleted from the correlation plots.[11] The results are shown in Tables I–III. A comparison of the standard deviations of the plots of the induced shifts, $\Delta\delta_i$, *vs.* R_i^{-3} shows a significant improvement in every instance upon inclusion of the geometric, 3 cos^2 θ_i − 1, factor. The results are most striking for the ethers **1** and **2** and this suggests that steric considerations can probably influence the lanthanide position in **3**.

A statistical refinement of data of this type can be used to test the initial assumption regarding the lanthanide–substrate geometry.[6,7,12] This has been accomplished more recently by Willcott and Davis[13] by utilizing the statistical agreement factor *R*.

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(5) (a) M. R. Willcott, J. F. M. Oth, J. Thio, G. Plincke, and G. Schroder, *Tetrahedron Lett.*, 1579 (1971); (b) P. H. Mazzocchi, H. J. Tamburin, and G. R. Miller, *ibid.*, 1819 (1971); (c) S. Farid, A. Atega, and M. Maggio, *Chem. Commun.*, 1285 (1971); (d) C. Beaute, Z. W. Wolkowski, J. P. Merda, and M. D. Lelandais, *Tetrahedron Lett.*, 2473 (1971); (e) S. B. Tjan and F. R. Visser, *ibid.*, 2833 (1971).

(6) J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970).

(7) J. Briggs, F. A. Hart, and E. W. Randall, *ibid.*, 364 (1971).

(8) R. R. Fraser and Y. Y. Wigfield, *ibid.*, 1471 (1970).

(9) W. DeW. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971), and references cited therein.

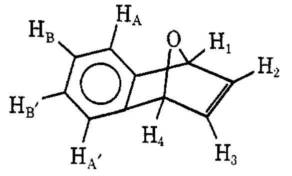
(10) R. Caple and S. C. Kuo, *Tetrahedron Lett.*, 4416 (1971).

(11) In every instance the shift reagents were added in increments to yield unambiguous chemical shift assignments.

(12) S. Farid, A. Ateya, and M. Maggio, *Chem. Commun.*, 1285 (1971).

(13) M. R. Willcott, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742, 1744 (1972).

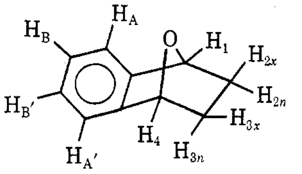
TABLE I
SHIFT CORRELATIONS FOR 1,4-DIHYDRONAPHTHALENE 1,4-OXIDE (**1**)[a]



Shift reagent[b]	$1/R_i^3$		$\frac{3\cos^2\theta_i - 1}{R_i^3}$	
	Std dev	Slope	Std dev	Slope
Eu(dpm)$_3$[c]	0.36	12.89	0.03	7.29
Eu(fod)$_3$	0.27	9.36	0.03	5.31
Pr(fod)$_3$	0.48	15.82	0.06	8.99

[a] Spectra obtained with CDCl$_3$ solutions on a Varian A-60D. [b] Ln(Y)$_3$ about 0.2 equiv. [c] Refinement of Eu(dpm)$_3$ shifts in ref 10.

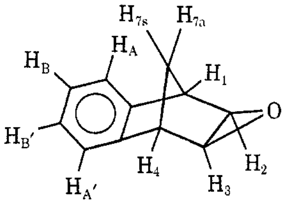
TABLE II
SHIFT CORRELATIONS FOR 1,2,3,4-TETRAHYDRONAPHTHALENE 1,4-OXIDE (**2**)[a]



Shift reagent[b]	$1/R_i^3$		$\frac{3\cos^2\theta_i - 1}{R_i^3}$	
	Std dev	Slope	Std dev	Slope
Eu(dpm)$_3$[c]	0.52	8.15	0.07	6.40
Eu(fod)$_3$	0.39	8.60	0.14	6.51
Pr(fod)$_3$	0.81	13.13	0.17	10.25

[a] Spectra obtained with CDCl$_3$ solutions on a Varian A-60D. [b] Ln(Y)$_3$ about 0.2 equiv. [c] Refinement of Eu(dpm)$_3$ shifts in ref 10.

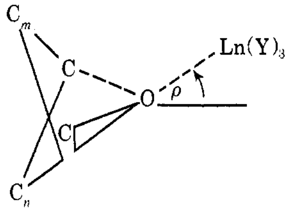
TABLE III
SHIFT CORRELATIONS FOR BENZONORBORNADIENE *exo*-OXIDE (**3**)[a]



Shift reagent[b]	$1/R_i^3$		$\frac{3\cos^2\theta_i - 1}{R_i^3}$	
	Std dev	Slope	Std dev	Slope
Eu(dpm)$_3$[c]	0.30	7.46	0.11	7.63
Eu(fod)$_3$	0.22	7.24	0.07	7.40
Pr(fod)$_3$	0.23	8.90	0.16	9.07

[a] Spectra obtained with CDCl$_3$ solutions on a Varian A-60D. [b] Ln(Y)$_3$ about 0.2 equiv. [c] Refinement of Eu(dpm)$_3$ shifts in ref 10.

This type of least-squares fit to a model is easy to apply to ethers **1**, **2**, and **3** owing to the plane of symmetry. Thus the lanthanide, Ln, need only be moved in a plane rather than over the surface of a sphere. For a lanthanide–oxygen distance of 3.0 Å, one therefore needs only to find the angle ρ that provides the best fit to the observed shifts. The angle ρ = 0° corresponds to the positioning of Ln in the plane defined by the oxygen and the two adjacent carbons as was done in the initial assumption.



These results are listed in Table IV. The ρ values listed are all positive, which corresponds to an angle to the right of 0° as the structures are written for the ethers **1**, **2**, and **3**. The small deviation from 0° for the ethers **1** and **2** is consistent with the similarity in steric requirements on either side of oxygen. It is difficult to say whether the small observed differences for the three shift reagents is real, but the general agreement is very satisfactory.

TABLE IV
STATISTICAL EVALUATION OF ANGLE ρ

Compd	Shift reagent	ρ, deg	Minimum agreement factor *R*
1	Eu(dpm)$_3$	9	0.005
	Eu(fod)$_3$	13	0.014
	Pr(fod)$_3$	7	0.008
2	Eu(dpm)$_3$	27	0.011
	Eu(fod)$_3$	6	0.048
	Pr(fod)$_3$	16	0.008
3	Eu(dpm)$_3$	42	0.018
	Eu(fod)$_3$	42	0.034
	Pr(fod)$_3$	42	0.014

With benzonorbornadiene *exo*-oxide (**3**) a definite tipping away from the methylene bridge is noted. The agreement with the three reagents is unexpectedly good and the results suggest that considerable steric interaction must arise as ρ approaches 0° in the oxide. This is again stereochemically agreeable.

The agreement observed with these ideal systems certainly supports the contention that the induced shifts are very likely dipolar in nature. The results again illustrate the improvement in shift correlations that can be observed by inclusion of the angular dependency factor and also the type of refinement that can be obtained by a statistical fit such as with the agreement factor *R*.

Experimental Section

Analytical.—Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were obtained on a Varian A-60D spectrometer with tetramethylsilane as an internal standard.

Reagents.—1,2,3,4-tetrahydronaphthalene (**2**) and 1,4-dihydronaphthalene 1,4-oxide (**1**) were made according to reported procedures.[14,15] Nmr for **1**: H$_1$ and H$_4$, s,[16] 340 Hz, H$_2$ and H$_3$, s,[16] 420 Hz, and A$_2$B$_2$ pattern centered at 425 Hz. Nmr for **2**: H$_1$ and H$_4$, q,[17] 323 Hz, H$_{2x}$ and H$_{3x}$, m, 123 Hz, H$_{2n}$, and H$_{3n}$ m, 81.5 Hz, aromatic s, δ 431 Hz.

Benzonorbornadiene *exo*-oxide (**3**) was made by the epoxidation of benzonorbornadiene with *m*-chloroperbenzoic acid in the usual

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[14] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

[15] L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965).

[16] *J* values less than 0.5 Hz.

[17] Small, *ca.* 1.5 Hz virtual coupling observed in addition to bridgehead exo coupling of 3.0 Hz.

manner.[18] Only **3** could be detected in the nmr spectrum of crude product, which was obtained in a near quantitative yield.

Recrystallization from cyclohexane-benzene gave an analytical sample, mp 93°.

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.05; H, 5.05.

Analytical Procedure.—The nmr samples were made by dissolving *ca.* 70 mg of the ether in 1.0 ml of $CDCl_3$ and adding the shift reagent (Norell Chemical Co., stored over P_2O_5) in quantities up to 0.2 equiv. Dreiding models were used to estimate distances and angles. Angles were both measured directly and checked by appropriate geometric relationships.

Statistical Correlations.—A calculation of an agreement factor R was accomplished in a manner similar to the procedure employed by Willcott and Davis.[13] As mentioned in the Discussion, the lanthanide was moved in a plane bisecting the ethers **1**, **2**, and **3** at a distance of 3.0 Å from the coordination site. At each position of Ln, the variable term $\Delta H_i = \alpha(3\cos^2\theta_i - 1)/R_i^3$ was evaluated for all the ith protons to yield a set of calculated $(\Delta H/H)_{ci}$ values (α is a constant). A minimum value of R was then obtained by the best least-squares fit for

$$R = \left\{\frac{\sum_i\left[\left(\frac{\Delta H}{H}\right)_{oi} - \left(\frac{\Delta H}{H}\right)_{ci}\right]^2}{\sum_i\left(\frac{\Delta H}{H}\right)_{oi}^2}\right\}^{1/2}$$

where $(\Delta H/H)_{oi}$ are observed shifts.

Registry No.—**1**, 573-57-9; **2**, 35185-96-7; **3**, 13137-34-3; Eu(dpm)$_3$, 15522-71-1; Eu(fod)$_3$, 17631-68-4; Pr(fod)$_3$, 17978-77-7.

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

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[18] L. F. Fieser and M. Fieser, "Organic Reagents," Vol. 1, Wiley, New York, N. Y., 1967, p 135.

Hydrogenolysis of Acetals and Ketals by Alkoxyalanes and Alkoxychloroalanes[1]

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The hydrogenolysis of acetals, ketals, and 1,3-dioxolanes was examined using alkoxy-substituted alanes. Alkoxychloroalanes are moderately reactive and show potential as stereoselective reducing reagents. Alkoxyalanes were less reactive and dialkoxyalanes too unreactive for hydrogenolysis.

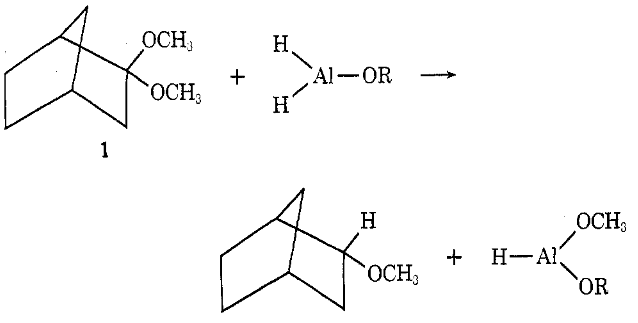
Cyclic and acyclic acetals and ketals can be hydrogenolyzed to the corresponding ethers by alane, chloroalane, and dichloroalane.[2] Having previously examined what structural features in the ketals affect the hydrogenolysis reaction,[3,4] we turned our attention to what structural modifications in the hydrogenolyzing reagent might affect the course of the reaction. Chloro groups are known to increase the reactivity of alanes.[5] Since oxygen and chlorine have similar electronegativities, we have investigated the use of alkoxyalanes, dialkoxyalanes, and alkoxychloroalanes for hydrogenolyzing acetals and ketals.

Isopropoxyalane and diisopropoxyalane have been prepared from the proper ratios of alane and triisopropoxyalane.[6] Ethoxyalane and diethoxyalane were prepared in a similar manner.[7] Many of the simpler alkoxyalanes and dialkoxyalanes have been prepared by the addition of 1 or 2 molar equiv of the corresponding alcohols to alane in THF.[8] The alkoxyalanes and dialkoxyalanes have been characterized by elemental analyses, molecular weight determinations, nmr and ir spectra,[6,8] and X-ray diffraction patterns.[7]

Early work showed dialkoxyalanes to be selective reagents which will reduce aldehydes, ketones, and acid chlorides, but not esters, nitriles, amides, nitrates, or aryl halides.[9] The use of alkoxyalanes has been extended to the reduction of epoxides.[10] The lone acetal reaction reported is the hydrogenolysis of 2-methyl-1,3-dioxolane by chloroethoxyalane.[11]

Results and Discussion

The hydrogenolysis of norcamphor dimethyl ketal (**1**) to 2-*endo*-norbornyl methyl ether (**2**) was examined



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2

using various alkoxyalanes and solvents to find the best conditions for the hydrogenolysis of acetals and ketals. These exploratory results are listed in Table I. First it can be seen that the dialkoxyalanes are less reactive than the alkoxyalanes. Secondly, Table I shows that none of the alkoxyalanes are as reactive as the parent compound, alane. Thirdly, the results show that both ether and benzene are better solvents than is THF.

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[1] Taken from the Ph.D. Thesis of K. J. B., Villanova University, 1972.

[2] M. N. Rerick, "Reduction," R. L. Agustine, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, pp 46–50.

[3] W. W. Zajac, Jr., and K. J. Byrne, *J. Org. Chem.*, **37**, 521 (1972).

[4] W. W. Zajac, Jr., and K. J. Byrne, *ibid.*, **35**, 3375 (1970).

[5] (a) U. E. Diner, H. A. Davis, and R. K. Brown, *Can. J. Chem.*, **45**, 207 (1967); (b) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 48.

[6] E. E. Flagg and D. L. Schmidt, *J. Inorg. Nucl. Chem.*, **31**, 2329 (1969).

[7] N. E. Matzek and W. H. Crawford, U. S. Patent 3,524,870 (1970); *Chem. Abstr.*, **73**, 98379k (1970).

[8] H. Noth and H. Suchy, *Z. Anorg. Allg. Chem.*, **358**, 44 (1968).

[9] M. W. Hunt, U. S. Patent 3,281,443 (1966); presented at Midwest Regional Meeting of the American Chemical Society, Lincoln, Nebr., Oct 1970.

[10] B. Cooke, E. C. Ashby, and J. Lott, *J. Org. Chem.*, **33**, 1132 (1968).

[11] H. A. Davis and R. K. Brown, *Can. J. Chem.*, **49**, 2166 (1971).