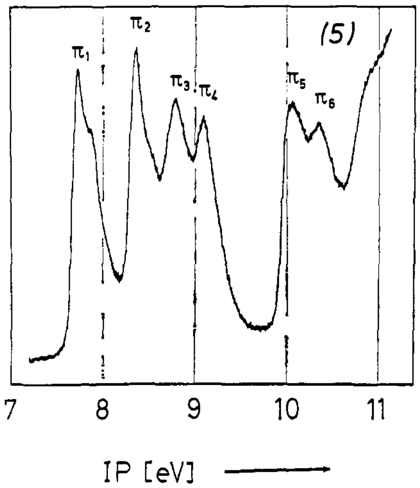
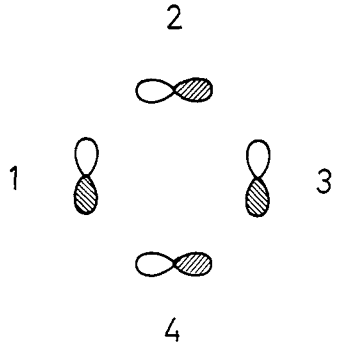


Figure 1. Section of the photoelectron spectrum of 1,1′-spirobiindene (**5**). The He–I (584 Å) photoelectron spectra were measured on a PS-18 spectrometer from Perkin-Elmer Ltd., Beaconsfield (England).

= 0.57; π_3 = 8.80, π_4 = 9.10, splitting = 0.30; π_5 = 10.20, π_6 = 10.48, splitting = 0.28) in the spectrum of the corresponding spiran **5**.

The spiro splitting ΔE (relying on degenerate first-order perturbation theory and considering only interactions (β) between the atomic orbitals (AO's) 1 to 4 next to the tetrahedral atom with coefficients c_1 to c_4 in the unperturbed systems) is given as[2]

$$\Delta E = 2(c_1c_2 - c_1c_4 - c_2c_3 + c_3c_4)\beta \qquad (1)$$



Plotting the measured spiro splittings ΔE in the series of carbon compounds (**1** = 0.30,[4] **5** = 0.57, **3** = 0.73, and spiro[4.4]nonatetraene (**6**) = 1.23 eV[10]) against the values derived from the expression ($c_1c_2 - c_1c_4 - c_2c_3 + c_3c_4$) (**1** = 0.46, **5** = 0.59, **3** = 0.88, and **6** = 1.25)[11] gives a straight line (Figure 2) which passes through the origin. The slope of this line yields β = 0.49 ± 0.05 eV.

With β known eq 1 can now be used to predict spiro splittings. Accordingly the splittings expected for the lower MO's π_2 and π_3 in indene, 0.22 and 0.25 eV, respectively, are in good agreement with the observed ones.

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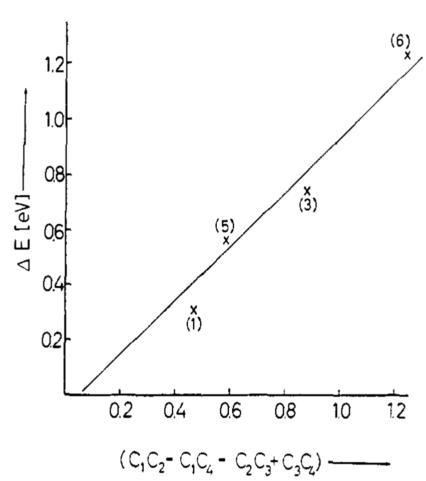

Figure 2. Correlation between the measured spiro splittings ΔE (ordinates) and the values derived from the expression ($c_1c_2 - c_1c_4 - c_2c_3 + c_3c_4$) (abscissa).

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(10) E. Heilbronner, personal communication.

(11) Coefficients obtained by the MINDO/2 method[12] are used throughout.

(12) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

Concerning the Stereochemistry of Reduction of Cyclohexanones with Complex Metal Hydrides

Sir:

One of the most fundamental reactions in organic chemistry is the reduction of a ketone to an alcohol using $LiAlH_4$ in ether solvent. In spite of the widespread use and fundamental nature of this reaction, little is known about the mechanism. Although there has been speculation[1] concerning the role of lithium in the reaction, it has only recently been demonstrated that a ketone will associate with a lithium cation in tetrahydrofuran.[2] Even if a complex is observed when $LiAlH_4$ is added to a ketone, it would not prove that the reaction is occurring *via* a complex. For example, when 4-*tert*-butylcyclohexanone is allowed to react with $Al(CH_3)_3$ in a 1:1 ratio in benzene, a complex is formed involving an aluminum–oxygen bond yet the product is not formed directly from the complex.[3] When the ratio is 1:2 a second molecule of $Al(CH_3)_3$ attacks the complex giving very different stereochemical results than when the ratio of reactants is 1:1. Eliel[4] and coworkers have reported

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(1) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, Calif., 1972, p 49 ff.

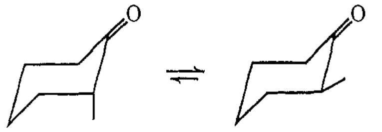
(2) Frank R. Dobbs, Ph.D. Thesis, 1972, Georgia Institute of Technology, Atlanta, Ga.

(3) (a) H. M. Neumann, J. Laemmle, and E. C. Ashby, *J. Amer. Chem. Soc.*, **95**, 2597 (1973); (b) J. Laemmle, E. C. Ashby, and P. V. Roling, *J. Org. Chem.*, **38**, 2526 (1973).

(4) (a) E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970); (b) J. Klein, E. Durkelblum, E. L. Eliel, and Y. Senda, *Tetrahedron Lett.*, 6127 (1968).

that if complexation of the carbonyl group by hydride is a step in the reduction of cyclohexanones by lithium tri-*tert*-butoxyaluminohydride, it is not rate determining. However, they further pointed out that this does not mean that such complexation is not important in determining stereochemistry. We wish to report for the first time stereochemical results that demonstrate that complexation of the carbonyl group by a metal cation does occur in reduction of ketones by complex metal hydrides and that the stereochemical outcome is affected by such complexation.

The increase of apparent equatorial attack on 2-methylcyclohexanone (I) over that observed with 4-*tert*-butylcyclohexanone (II) by $LiAlH_4$ and other reducing agents has been explained by (1) an increase in the steric requirement for axial attack on Ie and (2) axial attack on conformer Ia which produces the same alcohol (cis) as if equatorial attack had taken place on Ie.[5]



Ia Ie

Table I. Cis Alcohol from the Reaction of Complex Metal Hydrides with Cyclohexanones

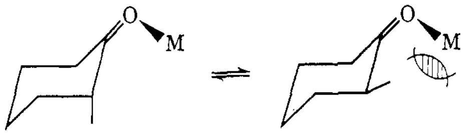
Hydride[a]	I[c]	II[c]	III[d]
$LiAlH_4$[b]	24	10	17
$LiAlH_4$	25	8	17
$ClMgAlH_4$[b]	36	10	21
$ClMgAlH_4$	43	10	21
$Mg(AlH_4)_2$[b]	49	13	27
$Mg(AlH_4)_2$	49	14	27

[a] THF, 0°. [b] Excess hydride. [c] Purified commercial samples. [d] Pure synthetic sample.

Table I shows the extent of apparent equatorial attack on I and II by $LiAlH_4$, $ClMgAlH_4$, and $Mg(AlH_4)_2$. The trend shows an increase in equatorial attack on Ie which is rather surprising since the same hydrides show little variation in their reaction with II. This decrease in axial attack on Ie cannot be explained by an increase in steric hindrance toward axial attack since $ClMgAlH_4$ and $Mg(AlH_4)_2$ give more exo attack on camphor and more axial attack on 3,3,5-trimethylcyclohexanone[6] than $LiAlH_4$.

If steric hindrance is the governing factor, then reduction of *cis*-2-methyl-4-*tert*-butylcyclohexanone (III) by the same hydrides should result in decreased axial attack as the steric requirement of the hydride increases. The results of our study show the steric requirement of each hydride to be nearly the same. We conclude from these results that more of conformation Ia is involved in the reduction of I by $Mg(AlH_4)_2$ and $ClMgAlH_4$ than by $LiAlH_4$.

It has been shown that lithium and magnesium salts or protic solvents[7] catalyze borohydride reduction of ketones and esters. A mechanism suggested[1] for ketone reduction by $LiAlH_4$ involves prior or concurrent association of the carbonyl oxygen with Li^+ as the hydride is transferred. Such a mechanism is supported by the results reported here. If complexation of the carbonyl group occurs during reduction, then the concentration of IaC (and its transition state corresponding to axial attack) should increase relative to Ia because the equatorial methyl group sterically interacts with the complexing agent and the energy difference between IaC and IeC is less than that between Ia and Ie. Therefore, since there is no reason to expect a slower rate of axial attack on IaC than IeC, it is not surprising that more reaction proceeds through IaC (Ia) with bulkier complexing agents, $-MgCl^+$ and $-MgAlH_4^+$, than with a smaller complexing agent, Li^+.



IaC IeC

In the case of III the methyl group is fixed in an equatorial position, and, because a change in conformation cannot easily occur, the stereochemical outcome is nearly the same with all three hydrides. The results do not vary as with I where the conformation of the 2-methyl group can change from equatorial to axial positions.

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[6] E. C. Ashby and J. R. Boone, unpublished results.

[7] (a) H. C. Brown, E. J. Mead, and B. C. S. Rao, *J. Amer. Chem. Soc.*, 77, 6209 (1955); (b) H. C. Brown and K. Ichikawa, *ibid.*, 83, 4372 (1961); (c) P. T. Lansbury, R. E. MacLeay, and J. O. Peterson, *Tetrahedron Lett.*, 311 (1964); (d) P. T. Lansbury and R. E. MacLeay, *J. Amer. Chem. Soc.*, 87, 831 (1965).

Thermolysis of Aryloxypyridinium Salts. Possible Generation of Aryloxenium Ions

Sir:

There has been much activity recently in connection with the intermediacy of phenoxenium[1] ions (the names phenoxonium and phenoxylium have also been used), particularly in biosynthetic-type oxidative coupling reactions.[2] In view of this and of our interest in the isoelectronic nitrene and carbene reactive intermediates, we have sought an unambiguous method of generating such species and of observing their reactions. Since, by analogy with phenylnitrene, it was expected[3a] that the phenoxenium ion PhO^+ itself might not be electrophilic enough to attack an aromatic nucleus, it was

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[1] The oxenium ion nomenclature is in accord with current usage with the isoelectronic species: nitrenium and carbenium ions.

[2] (a) D. H. R. Barton, *Chem. Brit.*, 3, 330 (1967); (b) A. Ronlán and V. D. Parker, *J. Chem. Soc. C*, 3214 (1971); (c) K. Dimroth, W. Umbach, and H. Thomas, *Chem. Ber.*, 100, 132 (1967); (d) M. Chauhan, F. M. Dean, K. Hindley, and M. Robinson, *Chem. Commun.*, 1141 (1971); (e) W. A. Waters, *J. Chem. Soc. B*, 2026 (1971); (f) D. G. Hewitt, *J. Chem. Soc. C*, 1750 (1971); (g) M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *J. Amer. Chem. Soc.*, 95, 612 (1973).

[3] (a) R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Org. Chem.*, 37, 2705 (1972); (b) R. A. Abramovitch, S. Kato, and G. M. Singer, *J. Amer. Chem. Soc.*, 93, 3074 (1971).