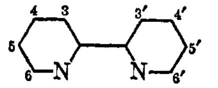
Table I. Isotropic Shifts[a] for $Co(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$



Compound	$\Delta\nu_{6,6'}$	$\Delta\nu_{5,5'}$	$\Delta\nu_{4,4'}$	$\Delta\nu_{3,3'}$
$Ni(bipy)_3Cl_2 \cdot 2H_2O$	...	−2227	−363	−3151
$Co(bipy)_3Cl_2 \cdot H_2O$	−4855	−2313	−365	−4471

[a] Relative to the diamagnetic complex $Fe(bipy)_3Cl_2 \cdot 2H_2O$.

For ease in presentation we shall start by making an assumption we intend to prove wrong; namely, that the mechanisms are identical in the cobalt(II) and nickel(II) complexes. By showing that this leads to an untenable result in our otherwise rigorous calculation, we will have disproved this assumption. If the mechanisms are identical, it follows that for any 2 nonequivalent protons, say i and j, $(\Delta\nu_i)_{Ni}/(\Delta\nu_j)_{Ni} = (\Delta\nu_i)_{Co}/(\Delta\nu_j)_{Co}$, where $\Delta\nu_i$ is the *contact* shift for proton i. For $Co(bipy)_3^{2+}$, $\Delta\nu_i = \overline{\Delta\nu_i} - X_i$, where $\overline{\Delta\nu_i}$ is the *observed isotropic* shift and X_i is the pseudocontact shift. Equation 1 results.

$$(\Delta\nu_i)_{Ni}/(\Delta\nu_j)_{Ni} = (\overline{\Delta\nu_i} - X_i)_{Co}/(\overline{\Delta\nu_j} - X_j)_{Co} \quad (1)$$

For octahedrally coordinated complexes having axial symmetry, the pseudocontact shift is given by[7]

$$\left(\frac{\Delta\nu}{\nu}\right)_i = \frac{-\beta^2 S(S+1)(g_{\|} - g_{\perp})F(g_{\|},g_{\perp})}{3kT}\left[\frac{3\cos^2\theta_i - 1}{r_i^3}\right]$$

The term $(3\cos^2\theta_i - 1)/r_i^3$ is often called the geometric factor which is denoted by G_i. F is a simple linear function of $g_{\|}$ and $g_{\perp}$, the value of which depends upon the symmetry of the complex and the magnitudes of T_{1e} and τ_c. The geometric factors, G_i and G_j, are then calculated from a knowledge of the geometries of the cobalt(II) complexes. Since $G_i/G_j = X_i/X_j$, one can solve for X_i in terms of X_j, substitute this into eq 1, and then solve for X_j. The same calculation is repeated using the data for protons j and k and again solving for X_j. The two values of X_j, which are calculated independently, are then compared for consistency. If they are close in magnitude, one may say that the mechanisms are identical in $Co(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$, but if, however, the two calculated pseudocontact shifts for X_j are radically different, this implies that the spin delocalization mechanisms are different and that $(\Delta\nu_i)_{Ni}/(\Delta\nu_j)_{Ni} \neq (\Delta\nu_i)_{Co}/(\Delta\nu_j)_{Co}$.

For the calculation of the geometric factors for $Co(bipy)_3^{2+}$, a cobalt–nitrogen bond length of 2.04 Å was used along with an NCoN angle of 86.8°. Bond lengths and bond angles for the ligand were selected from the X-ray structural determination of the structure[8] of $[Cu(bipy)_2I]I$, and any differences in bond lengths in this and our complexes are insignificant in this calculation. The geometric factors, G, at the various protons, for $Co(bipy)_3^{2+}$ are as follows: $G_{6,6'} = 2.56 \times 10^{-2}$, $G_{5,5'} = 3.37 \times 10^{-3}$, $G_{4,4'} = 1.68 \times 10^{-3}$, and $G_{3,3'} = 7.85 \times 10^{-3}$.

By using the isotropic shifts for the 4,4′ and 5,5′ protons, the equation $G_i/G_j = X_i/X_j$, and the proper geometric factors, $X_{4,4'}$ is calculated to be 19 cps. By using the contact shifts for the 4,4′ and 3,3′ protons and the proper geometric factors, $X_{4,4'}$ is calculated to be −320 cps. If the g tensor is isotropic for the nickel(II) complex, the above inconsistency proves that the spin delocalization mechanisms in $Co(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$ are different and *a priori* assumption of an equivalent mechanism for spin delocalization in cobalt(II) and nickel(II) cannot be made. If there is anisotropy in the g tensor in the nickel(II) complex, the factoring procedure we are attacking is obviously invalid.

Acknowledgment. We wish to acknowledge the support by the National Science Foundation through Grant No. GP 5498.

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Received January 8, 1968

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[7] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

[8] G. A. Barclay, B. W. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 5691 (1963).

The Stereochemistry of Hydride Attack in the Reduction of 1-*t*-Butyl-3-phenylallyl Alcohol

Sir:

The well-known reaction of propargylic alcohols with lithium aluminum hydride (LAH) to produce *trans*-allylic alcohols has recently received attention because of the synthetic utility of the organoaluminum intermediate formed.[1] Moreover, with certain substrates it has been found possible, by varying the nature of the hydride reagent used, to direct initial hydride attack to either the 2 or the 3 position.[1]

A key point in the elucidation of the mechanisms of these interesting reactions is the establishment of the role of the oxygen in activating proximate multiple bonds to attack.[2] Undoubtedly the first step in these reactions is the formation of an O–Al bond, as evidenced by the immediate liberation of hydrogen on mixing an alcohol with LAH. The question, then, is whether the function of the aluminum bound to the oxygen is to donate a hydride to the multiple bond or to facilitate intermolecular hydride attack from another aluminum.

This question is not easily answered in a propargylic system; either mechanism could explain the observed *trans* stereochemistry. Therefore, we turned our attention to an allylic system designed to provide an unequivocal stereochemical answer to the problem of whether hydride attack is intra- or intermolecular.[3]

Previous results with the rearrangement of the xanthate of *trans*-1,3-di-*t*-butylallyl alcohol exclusively to the *trans* dithiocarbonate suggested that this system existed in only one conformation.[4] However, attempts to reduce the allylic alcohol in refluxing tetrahydrofuran (THF) with a variety of hydride reagents led almost entirely to recovered starting material. This

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[1] E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 4245 (1967).

[2] Alkynes and conjugated alkenes also are reduced by LAH, but much severer conditions are required: E. F. Magoon and L H. Slaugh, *Tetrahedron*, **23**, 4509 (1967).

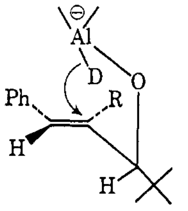
[3] A study of the relative stereochemistry of the two hydrogens added to the double bond in the LAH reduction of the cinnamyl system has recently been carried out by E. I. Snyder, *J. Org. Chem.*, **32**, 3531 (1967).

[4] W. T. Borden and E. J. Corey, unpublished results.

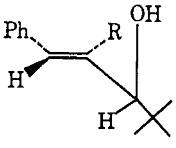
is not surprising in view of the fact that allyl alcohol is only partially reduced after heating for several hours with LAH in di-*n*-butyl ether at 100°.[5]

So that the mildest possible conditions might be used for the reduction, the *t*-butyl group in the 3 position was replaced with a phenyl, which serves to activate the double bond to hydride attack. Models show that this substitution should not affect the conformational preference of the system. *trans*-1-*t*-Butyl-3-phenylallyl alcohol (**1**)[6] was obtained as an oil in 98% yield by LAH reduction in refluxing THF of the propargylic alcohol produced by the reaction of lithium phenylacetylide with pivaldehyde.[7] The ir (neat) showed conjugated C=C at 6.08 μ and *trans* CH at 10.80 μ; nmr ($CDCl_3$) δ 0.95 (s, 9), 1.95 (s, 1), 3.85 (d, 1, J = 7 cps), 6.20 (q, 1, J = 7 and 15 cps), 6.58 (d, 1, J = 15 cps), and 7.3 (m, 5).

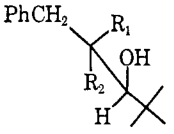
Reduction of this allylic alcohol by stirring with 2 moles of LAH in ether followed by hydrolysis of the intermediate, filtration of the alumina precipitate, and evaporation of the solvent gave a 98% yield of the saturated alcohol **3**, a clear oil; nmr ($CDCl_3$) δ 0.88 (s, 9), 1.5–2.0 (m, 3), 2.3–3.0 (m, 2), 3.2 (q, 1, J = 3 and 10 cps), and 7.24 (s, 5). The ABB′ splitting of the methine proton by the adjacent methylene can be dissected using the preferred conformation of **3**, shown below with that for **1**. From the relationship of Karplus for the dependence of J on dihedral angle,[8] the 10-cps coupling is assigned to H_1 and the 3-cps coupling to H_2.



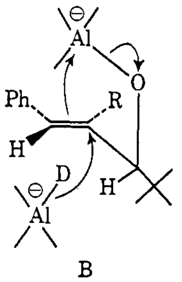
A



1, R = H
2, R = D



3, $R_1 = R_2 = H$
4, $R_1 = D; R_2 = H$
5, $R_1 = H; R_2 = D$



B

Now, if the hydride donation is intramolecular and LAD is substituted for LAH, then compound **4** will be produced from **1** *via* transition state A. However, if it is intermolecular, **5** will be obtained *via* a transition state which might resemble B. When the experiment was carried out, the nmr spectrum of the product showed the 10-cps coupling to have collapsed, demonstrating that **4** had been produced and that hydride attack is intramolecular. The other diastereomer, **5**, has also been obtained. When **2**, synthesized by the LAD reduction of 1-*t*-butyl-3-phenylpropargyl alcohol,[7] was allowed to react with LAH in ether, the nmr of the product showed the expected doublet at δ 3.2, split by 10 cps with no trace of **4** detectable.

Work on the mechanism of the analogous reduction of propargylic alcohols is in progress, as is further application of the conformational preference of allylic systems such as **1** to other stereochemical problems.

Acknowledgment. The author wishes to thank John A. Katzenellenbogen and Professor E. J. Corey for stimulating discussions.

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[5] F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, 70, 3484 (1948).

[6] All compounds gave satisfactory analytical data and a molecular ion whose exact mass was in agreement with the calculated value.

[7] E. E. Smissman, R. H. Johnson, A. W. Carlson, and B. F. Aycock, *J. Am. Chem. Soc.*, 78, 3395 (1956).

[8] M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

[9] National Science Foundation Predoctoral Fellow, 1965–1968.

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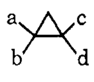
Received January 13, 1968

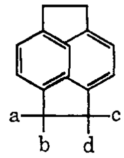
Carbanion–Carbonium Ion Pairs as Intermediates in Racemization, Solvolyses, and Ring-Expansion Reactions[1]

Sir:

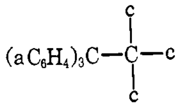
Since ion pairs that involve carbonium ions[2] and carbanions[3] are known to play prominent roles in isomerization and solvolytic reactions, it seemed probable that a system could be designed which upon heating in an appropriate solvent would produce a carbanion–carbonium ion pair from a covalent bond. The structural features envisioned as favoring such a transformation are as follows. (1) The covalent bond to be cleaved should be highly strained to provide a driving force for cleavage. (2) Carbanion-stabilizing substituents should be attached to one of the carbon atoms and carbonium ion stabilizing substituents to the second carbon atom involved in the cleavage. For example, systems I, II, and III all contain highly strained covalent carbon–carbon bonds which upon cleavage to an ion pair would release strain. Should substituents a and b be anion stabilizing, and c and d cation stabilizing, the covalent bond might undergo heterolysis when the systems are heated in polar solvents. These expectations have been realized in system IV.



I



II



III

The substance was prepared in optically active form as follows. Metalation with *n*-butyllithium in ether of

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[1] This investigation was supported in part by Public Health Service Research Grant No. GM 12640-02 from the Department of Health, Education, and Welfare.

[2] A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.