HCl, 37437-09-5; **14,** 37437-00-6; **15,** 37437-01-7; **15** 2HBr, 37437-02-8; **15** 2HCl, 37437-03-9; **16,** 37437-04-0; **16** HBr, 37439-95-5.

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An Empirical Correlation of Proton Magnetic Resonance Chemical Shifts for α Hydrogen to Lone-Pair Electrons

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We[1] earlier proposed an empirical rule to explain the upfield pmr shift of α H in neopentyl ethers and neopentylamines on the basis of (1) a restricted conformation at the C–X bond and (2) an empirical postulate that the α H was shifted downfield by 1.7 ppm when skew to an unshared electron pair on O or N, but was unshifted when trans. We now wish to report how remarkably well this latter simple postulate correlates the pmr chemical shifts for H α to unshared electron pairs in the first-, second-, and third-period elements in examples where conformation is not a complication, the methyl compounds.

The experimental values are listed in Table I, together with values calculated on the basis of the simple postulate made earlier.[1] The only adjustment made in calculating the parenthetical values was to alter the Δ = 1.7 ppm per skew unshared pair for first-period elements to Δ = 1.5 ppm per skew unshared pair for the second-period elements and to Δ = 1.25 ppm for the third-period elements.

TABLE I

PMR CHEMICAL SHIFTS FOR METHYL GROUPS ON SELECTED FIRST-, SECOND-, AND THIRD-PERIOD ELEMENTS, δ

IV	V	VI	VII
Me_3CCH_3	Me_2NCH_3	$MeOCH_3$	FCH_3
0.94	2.12 (2.07)[a]	3.24 (3.21)[b]	4.25 (4.34)[c]
Me_3SiCH_3	Me_2PCH_3	$MeSCH_3$	$ClCH_3$
0.00	0.94 (1.0)[a]	2.08 (2.0)[b]	3.05 (3.0)[c]
Me_3GeCH_3	Me_2AsCH_3	$MeSeCH_3$	$BrCH_3$
0.13[d]	0.88[e] (0.96)[a]	1.95[f] (1.80)[b]	2.68 (2.63)[c]

[a] The calculated value in parentheses is $\delta_{IV} + 2\Delta/3$; for first-period elements, Δ = 1.7 ppm; for second, Δ = 1.5 ppm; for third, Δ = 1.25 ppm. [b] The calculated value is $\delta_{IV} + 4\Delta/3$. [c] The calculated value is $\delta_{IV} + 2\Delta$. [d] H. Schmidbaur, *Chem. Ber.*, **97,** 1639 (1964). [e] C. R. Russ, Ph.D. Dissertation, Department of Chemistry, University of Pennsylvania, 1965. [f] G. Klose, *Ann. Phys.*, **8,** 220 (1961).

For methyl fluoride (or chloride or bromide), each H must be flanked by two skew unshared pairs so the downfield shift will be 2Δ. Therefore the calculated $\delta_{CH_3F} = \delta_{Me_4C} + 2\Delta = 4.34$. For dimethyl ether (or sulfide or selenide) one hydrogen will be flanked by two skew unshared pairs, the other two by one each. The average downfield shift will then be 4Δ/3. Similarly for trimethylamine (or phosphine or arsine), two H will be flanked by a single skew unshared pair, the third by none, so the average downfield shift will be 2Δ/3.

Inspection of Table I reveals that all the calculated shifts, based on our empirical rule, agree with experiment within less than 0.1 ppm (except for Me_2Se, where the difference is 0.15 ppm). Since all these literature data are not in the same solvent, this may be one factor in the small discrepancies between experimental and calculated values for δ.

Since the form of the relationships in Table I is a simple linear correlation, these data could, of course, be fit to other factors, *e.g.*, the number of methyl groups attached to the heteroatom. There have, of course, been extensive efforts to correlate the chemical shifts with electronegativity.[2] The marked upfield shifts in neopentyl ether and amines[1] and other steric factors influencing the chemical shifts[2b] indicates that electronegativity is at least not the only factor affecting chemical shifts.

The complication of preferred conformation for primary alkyl groups, RCH_2, on O or N was discussed earlier.[1] An examination of ethyl halides suggests yet another possible factor which may influence the NMR shift of α H in primary and secondary alkyl groups. The normal downfield shift on substituting an H by CH_3 is about 0.3 ppm (see Table II). In ethyl fluoride and alcohol, the actual downfield shift is somewhat less; for chlorine and especially bromine and OCOR it is appreciably more. In the secondary alkyl derivatives, the enhanced downfield shift compared to calculated (see Table II) is much more marked, again increasing with the size of the group X. Simple scale molecular models, using standard bond angles, bond radii, and van der Waals radii, show that the van der Waals radii of β-H and F or O interpenetrate less than 0.2 Å, whereas the interpenetration is 0.45 Å for Cl and 0.5 Å for Br. A significant repulsive effect at the latter degree of interpenetration could be relieved by bending the C–C–X angle slightly outward.[3] A consequence of this would be to bring the α H closer

TABLE II

PMR CHEMICAL SHIFTS FOR METHYL, ETHYL, AND ISOPROPYL COMPOUNDS, δ

X	CH_3X	RCH_2X	R_2CHX
CH_3	0.9	1.2	1.5
OH	3.4	3.55 (3.70)[a]	3.85 (4.0)
OCOR	3.65	4.10 (3.95)	5.0 (4.25)
F	4.25	4.35 (4.55)	(4.85)
Cl	3.05	3.4 (3.35)	4.0 (3.65)
Br	2.7	3.3 (3.0)	4.1 (3.3)

[a] The parenthetical values are those calculated assuming that the downfield shift for introducing R in place of H in CH_3X would be the same as for X = CH_3.

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[1] C. C. Price, *Tetrahedron Lett.*, 4527 (1971).

[2] (a) B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, **77,** 3977 (1955); (b) H. Spresecke and W. G. Schneider, *J. Chem. Phys.*, **35,** 722 (1961); (c) J. C. Muller, *Bull. Soc. Chim. Fr.*, 2022 (1964).

[3] Values reported for the C–C–X bond angles in ethyl halides are 109.5, 110.5, 110.5, and 112° for F, Cl, Br, and I, respectively (see "Tables of Interatomic Distances," L. E. Sutton, Ed., The Chemical Society, London, 1958 and 1965).

to the lone pair on X, which would then shift it further downfield. This steric hindrance in an isopropyl (or other secondary) compound would be much greater and would therefore produce the enhanced increment in downfield shift. An effect of the lone pair H distance on δ is also reflected in the decreasing value for Δ for the first, second, and third period elements, corresponding to an increasing C–X bond length and thus increasing α H to X distance.

The rather remarkable success of the empirical postulate of a constant chemical shift for α H by an adjacent skew unshared electron pair for cases where conformational changes are not a factor lends strong support to the utility of this postulate as one useful empirical means of estimating conformational relationships for such hydrogens.

Ionic Addition Mechanism Investigation. Determination of Deuterated Nortricyclyl Alcohol Stereochemistry

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Ionic additions to norbornadiene[1] and related solvolyses[2] have historically been scrutinized by stereochemical investigation of the olefinic product; this represented incomplete investigation of the various attendant ionic processes in that nortricyclyl (nonolefinic) product often was the *major* product. Complete analysis of labeled nortricyclyl derivatives in previous studies has been omitted because the nmr spectrum is such a complicated band of absorptions that even 220 MHz plus 100-MHz nmr spectra combined with spin-decoupling analyses have not permitted complete proton assignments.[3] This paper describes the successful application of shift reagents,[4] combined (in part) with spin-decoupling techniques, to the precise determination of the position of deuterium in so-labeled nortricyclyl alcohol samples. Thus the stereochemistry of the processes described above can be determined whenever significant amounts of nortricyclyl derivatives are obtained that can be converted into nortricyclyl alcohol without skeletal rearrangements.

The addition of acetic acid-O-d_1, using 0.018 M sulfuric acid catalyst, to norbornadiene (**1**) was carried out to afford the labeled products shown in Scheme I; nomenclature, analysis, and structure determination of the **2a**/**2b** (55:45 in this work) and the **2**/**3** (20:80 in this work) ratios have been described before.[1d-g] The **3a**/**3b** ratio is the focus of much of the remaining discussion. Mass spectroscopic analysis[1g] of the total deuterium content in the product **2a** plus **2b** acetates (77%) indicated that 77% of the sample was deuterated; this agreed within experimental error (*ca.* ±1%) with the deuterium content of the **3a**–**3b** sample measured mass spectroscopically, and both figures corresponded well to the total deuterium content in the product nortricyclyl acetate as determined by nmr (79%, see below). The data in Scheme I represent the spread of isomers within the *labeled* samples only (see below).

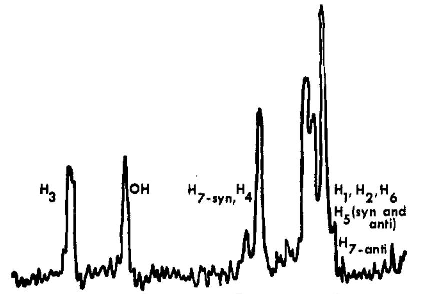
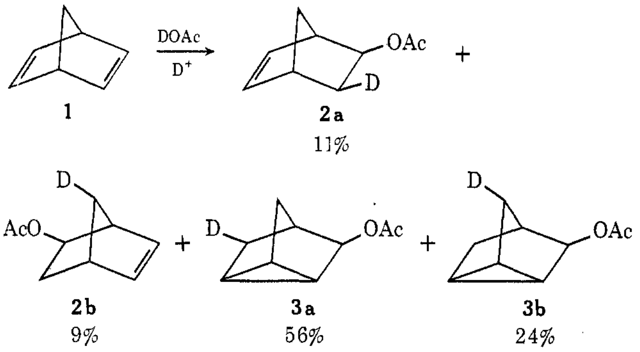


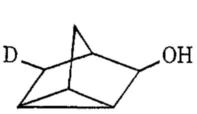
Figure 1.—60-MHz nmr spectrum of **4** in 0.5 ml of CCl_4.

SCHEME I

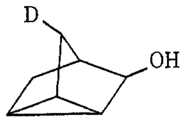


OAc = acetoxy

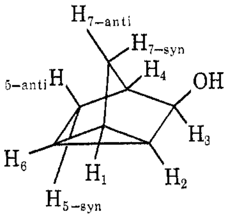
In view of the fact that alcohols respond more to shift reagents' effects than do acetates,[5] the **3a**/**3b** mixture was converted (Na/CH_3OH) into the corresponding **4a**/**4b** mixture. The nmr spectrum of Figure 1 allows assignment of only H_3 (α to OH[6]) and the $H_4/H_{7\text{-syn}}$ pair (β to OH[6]). The signal for H_2 is expected to be further upfield since it is a cyclopropyl proton[7] and is least proximate to the OH group of the three β protons. The remaining protons are assigned



4a



4b



4

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