Much of this stabilization would be lost in the anion where the negative charge discourages electron donation by fluorine. Although the importance of such stabilization for ground states has been questioned,[11] it predicts correctly in a qualitative manner the variation in magnitude of ΔpK_{hal} with Y. The relative contribution of III to the resonance hybrid should increase with the ability of Y to form a stable anion; chlorine and nitro being much better leaving groups than carbethoxyl and carbamyl, stabilization of the un-ionized species should be greatest for Y = Cl and NO_2.

Slovetskii and co-workers[3] attribute the lowered acidity of fluorodinitromethane to a positive mesomeric effect of fluorine and consider also the possibility of intramolecular hydrogen bonding to fluorine.

[11] S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964), footnote 23.

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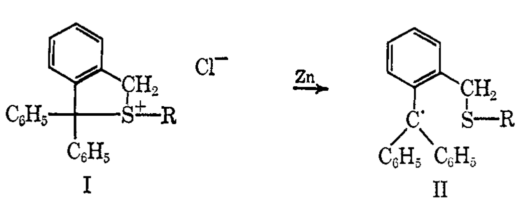
Observation of Conformational Isomers by Electron Nuclear Double Resonance

Sir:

Conformational isomerism and rotation barriers have been extensively studied by nuclear magnetic resonance (nmr) methods,[1] and to a lesser extent by electron paramagnetic resonance (epr) techniques.[2] Epr can be used to investigate much faster processes than nmr, since line separations are typically 10^4 larger, but the technique is somewhat limited by the complexity of epr spectra for large molecules of low symmetry.

Electron nuclear double resonance (endor) of free radicals in solution[3,4] permits the direct observation of hyperfine couplings of much more complicated molecules than can be analyzed by epr. We wish to report an example of the use of endor to detect rapid conformational equilibration in a derivative of the triphenylmethyl radical.



The radical IIa was prepared by treating a 10^{-3} *M* solution of Ia[5] in ethylbenzene with zinc pellets, and the endor spectrum (Figure 1) was examined over the temperature interval −80 to −20°.

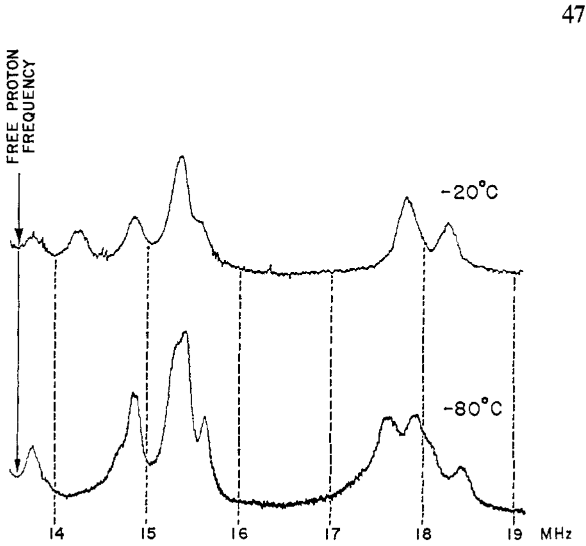


Figure 1. The proton endor spectrum of IIa at −80 and −20°.

For every class of equivalent protons two endor lines are found, one for the local field at the protons from the coupled electron parallel to the applied field and one with these fields antiparallel. Customarily, we begin the scan of the nuclear radio frequency at the free proton frequency and scan to higher frequencies, recording only one line for each class of equivalent protons. About 11 different couplings can be resolved at −80°. The portion of the spectrum between the free proton frequency and 14.7 MHz arises from the methylene and methyl protons of the pendant group. We have not made a detailed assignment of the other lines in the spectrum, but addition of the pendant group to one phenyl ring probably decreases the couplings to the protons on that ring and increases the couplings to the protons on the other two phenyl rings relative to the unsubstituted triphenylmethyl radical. The lines between 17.5 and 18.5 MHz are thus assigned tentatively to the *ortho* and *para* protons of the unsubstituted phenyls.

In the temperature interval between −80 and −20°, several pronounced changes in the character of the spectrum are observed. Lines at 17.9 and 17.7 MHz collapse to a single line at 17.8 MHz; lines at 18.4 and 18.2 MHz collapse to a line at 18.3 MHz; a line at 14.7 MHz evident as a shoulder has disappeared; and a new line is found at 14.25 MHz.

The endor spectrum of the deuterated compound IIb also was studied between −80 and −20°. The nuclear precession frequency of the deuteron differs so substantially from that of the proton that the deuterated sites are eliminated from the proton endor display. At −20° the endor spectrum of IIb is essentially identical with that of IIa except that the line below 14 MHz is missing. The methyl hyperfine coupling is thus 325 kHz.

The next weakest coupling is with the methylene group, producing the line at 14.25 MHz at −20°; at −80° this has split symmetrically into lines at 13.8 and 14.7 MHz. While in principle this simply shows that there are two equally populated methylene proton environments, there can be little doubt that what has been resolved here is the interconversion of left-hand and right-hand propeller conformations of the radical II. In any one of these the two protons of a methylene

(1) *Cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965, Chapter 9; C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965).

(2) *Cf.* T. M. McKinney and D. H. Geske, *J. Chem. Phys.*, **44**, 2277 (1966).

(3) J. S. Hyde and A. H. Maki, *ibid.*, **40**, 3117 (1964); J. S. Hyde, *ibid.*, **43**, 1806 (1965).

(4) J. S. Hyde, to be published.

(5) Unpublished work of R. Breslow, L. Kaplan, and D. LaFollette.

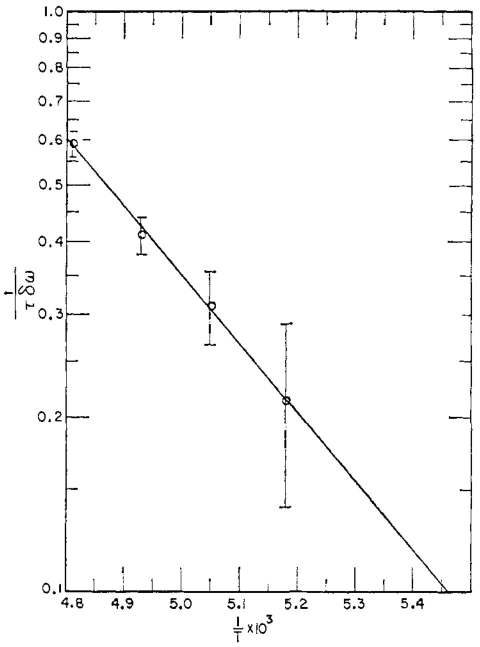


Figure 2. Temperature dependence of the reorientation rate of the methylene protons of II.

group are nonequivalent; models show that with a reasonable orientation of the side chain one C–H bond is more nearly perpendicular to the aromatic ring, and thus should couple more strongly (the two endor lines represent a factor of four difference in coupling). Rotation to the mirror image conformation interconverts these proton environments. Furthermore, such a change has also been seen[6] in 2,2′-bis(methylenethiomethyl)-4′′-dimethylaminotriphenylmethyl cation, a carbonium ion related to II, in which the room-temperature methylene nmr singlet goes to an AB quartet at low temperature. In such a process for II, two different pairs of *ortho* protons also interchange environments, accounting for the other endor changes.

The usual nmr approaches[1,7] to the study of chemical rate processes make the assumption that radiofrequency power saturation is not occurring—an invalid assumption for the endor experiment. We have, nevertheless, attempted to use the method of Gutowsky and Holm[7] to obtain an activation energy E_a and a frequency factor ν_0. One may rewrite the Arrhenius equation as

$$\log 1/\tau\delta\omega = \log 2\nu_0/\delta\omega - E_a/(2.3RT)$$

where $\delta\omega$ is the separation of the lines in the limit of slow exchange and τ is the lifetime of a proton in a particular site. If $1/T_2 < \delta\omega$, where T_2 determines the observed line width, then values for τ as a function of temperature may be determined from the equation

$$1/\tau\delta\omega = 2^{-1/2}[1 - (\delta\omega_e/\delta\omega)^2]^{1/2}$$

where $\delta\omega_e$ is the experimentally observed separation. For IIb, the value of $\delta\omega$ at −85° was assumed to be at the limit 890 kHz. The data are plotted in Figure 2. The slope yields an activation energy of 5.5 kcal/mole, and the frequency factor determined from the intercept is about 10^{11} cps.

The original interest in radical II was the possibility that the sulfur might solvate the radical appreciably. Kinetic evidence for solvation of radicals is well known,[8] and cations related to II (*e.g.*, I) show strong interaction.[5] However, the relatively low spin density at the methyl of II (which is, however, 40% of that at the methylene) and the high spin density in the aromatic rings suggest no major coordination of the sulfur with the methine carbon.

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[6] D. LaFollette, unpublished observations. The rate of equilibration is ~10^5 slower in this cation than in II. Since in the nmr experiment the nonequivalent protons are seen to be coupled, other types of conformational isomerism are excluded. A somewhat different equilibration in some trityl cations has been studied by Kurland, *et al.*, *J. Am. Chem. Soc.*, **87**, 2278, 2279 (1965).

[7] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[8] A particularly relevant study is that by W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

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Steroids. CCCIII.[1] Angular Methylation and a "Wittig" Reaction with a Zinc–Methylene Iodide Reagent

Sir:

We wish to report an unusual example of methylenation with a modified Simmons–Smith reagent.[2] Reaction of 17β-acetoxy-11β-hydroxyestr-5(10)-en-3-one (I) with a reagent obtained by refluxing a large excess of zinc–copper couple[3] with methylene iodide for 4–6 hr in ether solution affords the product of replacement of the 3-ketone function by methylene [II, mp 146–148°; infrared (Nujol) 3475, 3070, 1727, 1653, and 877 cm^{-1}; nmr (60 Mcps) 63 (18-H), 122 (OAc), 160 (4-H), 259 (11α-H), ~280 (17α-H), and 283 (methylene) cps. *Anal.* Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.36; H, 9.09].[4] In addition, the noncrystalline 3-spirocyclopropane [IIIa, infrared 3500, 3080, and 1735 cm^{-1}; nmr 16 (cyclopropyl-H), 64 (18-H), 121 (OAc), 259 (11α-H), and 280 (17α-H) cps; characterized after base hydrolysis as the 17-carbinol, IIIb, mp 74–78°; infrared (KBr) 3450, 3075 cm^{-1}; nmr 16 (cyclopropyl-H), 61 (18-H), 218 (17α-H), and 260 (11α-H) cps. *Anal.* Calcd for $C_{20}H_{30}O_2 \cdot 0.5H_2O$: C, 77.12; H, 10.03. Found: C, 77.24; H, 9.92] was obtained in experiments where the preparation of the reagent had been interrupted after 2–3 hr reflux. The observation of a Wittig reaction with a zinc reagent is unprecedented.[5] The importance of the 11β-hydroxy group is suggested by the lack of reaction of either saturated 3- or 17-keto steroids or the 11-desoxy analog of I.

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[1] Steroids. CCCII: P. Hodge, J. A. Edwards, and J. H. Fried, *Tetrahedron Letters* (publication pending).

[2] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); **81**, 4256 (1959); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964); G. Wittig and F. Wengler, *Chem. Ber.*, **97**, 2146 (1964).

[3] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[4] In a typical experiment, 2 ml of methylene iodide, 2.5 g of zinc–copper couple, and 8 ml of ether were refluxed under nitrogen for 4 hr. After adding 200 mg of I, reflux was continued an additional hour followed by standard work-up.

[5] *Cf.* S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).