Direct Measurement of Chemical Shielding Anisotropies. Fluoranil

Sir:

Although the nuclear magnetic shielding coefficient $\boldsymbol{\sigma}$ is a tensor quantity, nearly all measurements of it have been confined to the mean shielding $\sigma = {}^1/_3\,\mathrm{Tr}(\boldsymbol{\sigma})$, since all spectral information about its anisotropy is erased by rapid isotropic molecular tumbling in the usual liquid nmr sample. In solids, all information about $\boldsymbol{\sigma}$ is typically obscured by static dipolar broadening, although in a few favorable cases measurements of limited accuracy have been possible.[1-10] In recent years several rather precise measurements have been made on molecules aligned in liquid-crystal solvents.[11-15] These are complicated in the sense of requiring a rather elaborate analysis of dipolar and J-coupling effects and the manner in which they are averaged over an anisotropic molecular motion. And in general they yield only a linear combination of the three principal elements of $\boldsymbol{\sigma}$ rather than full knowledge of the tensor.

One of the principal promises of the multiple-pulse nmr coherent averaging technique[16-18] has been the full measurement of shielding anisotropies without the dipolar obscuration which beset direct measurements in solids and without the loss of information, due to motional averaging, which is inherent in the liquid crystal technique.

In this communication we illustrate the first experimental realization of this promise. Figure 1 shows the ^{19}F powder spectrum of solid fluoranil, $C_6F_4O_2$, obtained at room temperature using a spectrometer[19] operating in the four-pulse mode[16] at 54.0 MHz. The spectrum remains unchanged down at least to −90°, indicating that no motional averaging is present. The pattern obtained is typical of that expected for a chemical shift tensor all of whose principal values are different. These values, referred to an external reference of neat liquid C_6F_6, are

$$\sigma_{11} = -101 \pm 6 \text{ ppm}$$

$$\sigma_{22} = -62 \pm 6 \text{ ppm}$$

$$\sigma_{33} = 86 \pm 6 \text{ ppm}$$

defined in order of increasing magnitude.

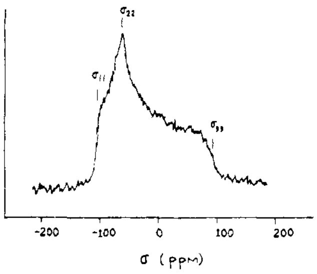

Figure 1. ^{19}F spectrum of powdered fluoranil at room temperature, obtained by the four-pulse dipolar narrowing technique. The zero of the horizontal scale refers to the resonance of an external liquid C_6F_6 sample, also recorded using the four-pulse method.

We have made preliminary measurements of a similar sort in a number of other ^{19}F compounds. After completion and refinement they will be reported at length elsewhere, in conjunction with a discussion of the problem of referring $\boldsymbol{\sigma}$ to molecule-fixed axes x, y, z, the implications of the results in valence theory, their use to obtain new information about molecular geometry and molecular motion, and some possible large discrepancies with earlier results obtained by less direct means.

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Electron Spin Resonance Evidence for the Pyramidal Structure of the Radical-Center Carbon Atom of 7-Oxabicyclo[2.2.1]hept-2-yl Radicals

Sir:

The structure around the radical-center carbon atom of free radicals of the 2-norbornyl type has been assumed essentially planar,[1,2] and the preference of free radicals of the 2-norbornyl type for reacting in atom-transfer reactions at the exo rather than the endo position has been explained as an effect of basically steric origin.[1,2] On the basis of extended Hückel calculations, Fujimoto and Fukui[3] proposed an idea that the radical-center carbon of 2-norbornyl radical may have a shallow pyramidal structure with the C_2–H bond bent to the endo direction and that the stereoselectivity of this radical in transfer reactions is basically controlled by the frontier orbital.

Gloux, Guglielmi, and LeMaire[4] reported an esr study on 2-hydroxybicyclo[2.2.1]hept-2-yl radical. Their results show that the radical-center carbon of

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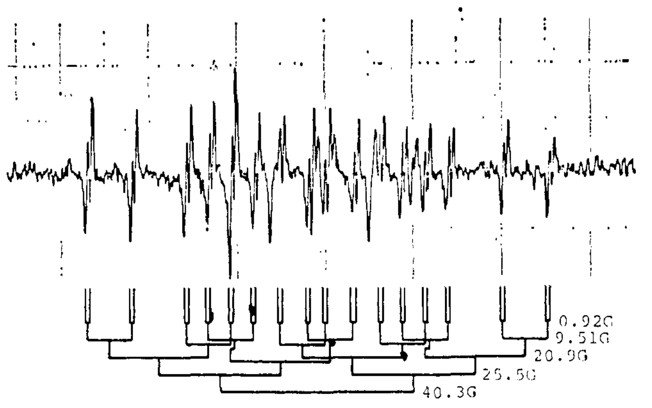

Figure 1. Esr spectrum of radical **1**.

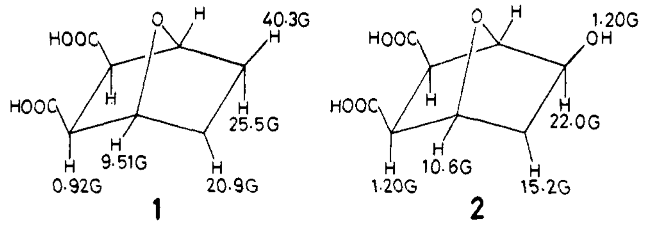

Figure 2. Assignments of the proton hyperfine coupling constants of **1** and **2**.

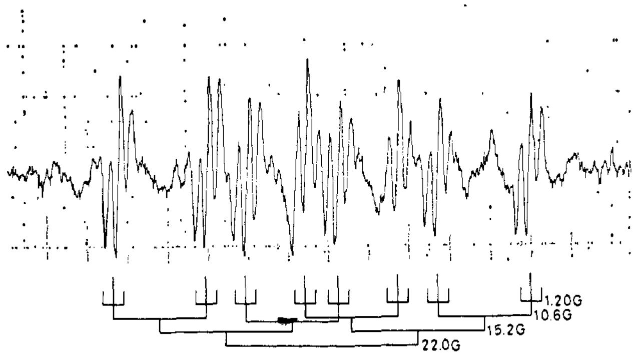

Figure 3. Esr spectrum of radical **2**.

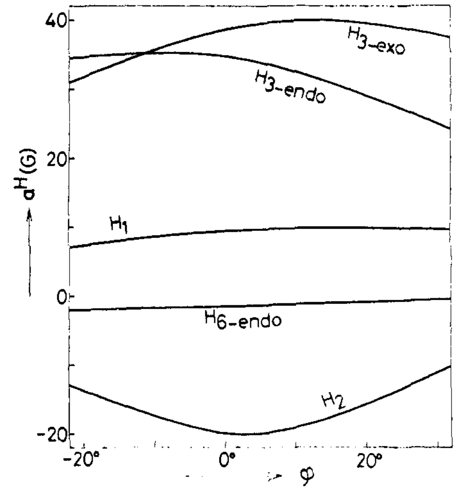

Figure 4. Relation between calculated hyperfine coupling constants of the 7-oxabicyclo[2.2.1]hept-2-yl radical and the angle φ.

this radical is pyramidal. Norman and his coworkers[5] showed that a trivalent radical-center carbon atom with π-electron releasing substituents, such as the hydroxy group, is more pyramidal than the corresponding carbon atom without such substituents. Thus we thought it desirable to study the structure around the radical-center carbon atom without a substituent of radicals of the 2-norbornyl type and examine esr spectra of radicals in the title, using a rapid-flow technique.[6]

When H_2O_2 and $TiCl_3$ were allowed to react with *exo-cis*-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, the esr spectrum shown in Figure 1 was observed. This spectrum consists of five doublets (40.3, 25.5, 20.9, 9.51, and 0.92 G). The radical was identified as *exo-cis*-5,6-dicarboxy-7-oxabicyclo[2.2.1]hept-2-yl radical (**1**) and the proton hyperfine coupling constants were assigned as shown in Figure 2 in reference to unrestricted SCF–MO calculations (*vide infra*). The *g* factor of this radical is 2.0027, which shows that the carboxy substituent is not attached to the radical-center carbon atom, otherwise the *g* factor would be in the range of 2.0030–2.0032.[7] Dixon, Norman, and Buley[8] reported that in acidic media the hydroxy radical (or complex of it) formed from the H_2O_2–$TiCl_3$ system preferentially abstracts the hydrogen atom attached to the carbon furthest from the carboxyl group, which also supports the present identification of the radical.

The esr spectrum given in Figure 3 is obtained by treatment with H_2O_2 and $TiCl_3$ of *exo-cis*-7-oxabicyclo-[2.2.1]hept-2-ene-5,6-dicarboxylic acid. The spectrum consists of three doublets (22.0, 15.2, and 10.6 G) split into a triplet (1.20 G). This radical has the *g* factor of 2.0024. Berson and Swidler[9] and Berson[10] reported that homolytic bromination of *exo-cis*-7-oxabicyclo-[2.2.1]hept-2-ene-5,6-dicarboxylic acid anhydride gives mainly the *exo-cis*-dibromide. Studies of radical additions to norbornene and related systems point to the fact that a radical adds to these systems preferentially from the exo direction.[2] On the basis of these results and also by the comparison of the observed parameters of this radical with those of **1**, this radical is identified as the hydroxy radical adduct, *exo*-3-hydroxy-*exo-cis*-5,6-dicarboxy-7-oxabicyclo[2.2.1]hept-2-yl radical (**2**). The observed hyperfine coupling constants are assigned as shown in Figure 2 by comparing with the calculated results (*vide infra*).

If the radical **1** has a planar radical-center carbon, a triplet splitting of about 40 G due to two β protons is expected, while only one proton with a coupling constant of this magnitude (40.3 G assigned to the 3-exo proton) is observed for **1**. Radical **2** does not show this splitting. These results qualitatively show that these species have a pyramidal radical-center carbon with the C_2–H bond bent to the endo direction.

Unrestricted SCF–MO calculations with the indo approximations[11] are performed to assign the proton hyperfine coupling constants and to estimate the angle,

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φ, between the C_2–H bond and the C_1–C_2–C_3 plane. (A positive value of φ corresponds to bending of the C_2–H bond in the endo direction.) Calculated results are shown in Figure 4. The comparison between the observed hyperfine coupling constants and the calculated results shows that the angle φ of **1** is about +20°, that is the C_2–H bond is bent out of the C_1–C_2–C_3 plane about 20° to the endo direction, and that the angle of **2** is about 10° larger than φ of **1**.

The pyramidal structure of the radical-center carbon of the present radicals should be, at least, one of the dominant factors which controls the stereoselectivity of these radicals in transfer reactions, and the present results support the proposal of Fujimoto and Fukui.[3]

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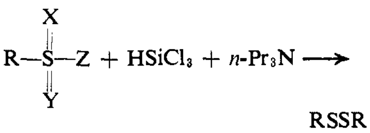
Reductive Formation of Disulfides from Sulfenyl, Sulfinyl, and Sulfonyl Derivatives Using Tri-*n*-propylamine and Trichlorosilane

Sir:

Disulfides are generally prepared by the oxidative coupling of thiols.[1] Recently however, nucleophilic substitution of sulfenylthiocyanates,[2] thiolsulfonates,[3] sulfenylhydrazo compounds,[4] and sulfenimides[5] with thiols have also been reported as general routes to disulfides. In the course of our studies on the deoxygenation of sulfur compounds,[6] we have found that the sulfur–sulfur linkage is not cleaved by trichlorosilane.[7] This leads to the possibility that disulfides may be prepared reductively from sulfur compounds of higher oxidation state.

We wish to report that good to excellent yields of symmetrical disulfides can be obtained from the reduction of the corresponding sulfenyl, sulfinyl, and sulfonyl chlorides as well as sulfenate and sulfinate esters with the tri-*n*-propylamine–trichlorosilane system (n-Pr_3N–$HSiCl_3$)[8] (Table I). Thus to a mixture of

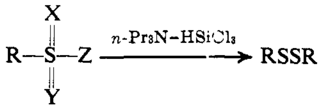


$$R\text{—}\overset{\overset{\textstyle X}{\|}}{\underset{\underset{\textstyle Y}{\|}}{S}}\text{—}Z + HSiCl_3 + n\text{-}Pr_3N \longrightarrow$$

$$RSSR + n\text{-}Pr_3\overset{+}{N}HCl^- + (SiCl_2O)_n$$

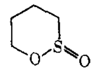
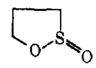
X = Y = O, electron pair
Z = Cl, OR′ (see Table I, footnote *a*)

Table I. Reduction of Various Sulfur Compounds with n-Pr_3N–$HSiCl_3$



$$R\text{—}\overset{\overset{\textstyle X}{\|}}{\underset{\underset{\textstyle Y}{\|}}{S}}\text{—}Z \xrightarrow{n\text{-}Pr_3N\text{–}HSiCl_3} RSSR$$

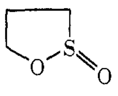
X = Y = O, electron pair
Z = Cl, OR′ [a]

Compound	Time, hr (T, °C)[b]	Product	% yield
C_6H_5S–Cl	4 (20)	$C_6H_5SSC_6H_5$	53
C_6H_5S–OCH_3	4 (20)	$C_6H_5SSC_6H_5$	88
p-$CH_3C_6H_4SO$–Cl	5 (20)	p-$CH_3C_6H_4SSC_6H_4CH_3$-p	91
C_6H_5SO–OCH_3	4 (20)	$C_6H_5SSC_6H_5$	85
	4 (20)	$HO(CH_2)_4SS(CH_2)_4OH$	60
	4 (20)	$HO(CH_2)_3SS(CH_2)_3OH$	80
$C_6H_5SO_2Cl$	20 (20)	$C_6H_5SSC_6H_5$	67
	6 (80)		85
$C_6H_5SO_2OCH_3$	15 (20)		*a*, *c*
	70 (80)		

[a] Sulfonate esters (X = Y = O; Z = OR′) do not react. [b] All reactions were carried out in benzene solution. [c] Starting material recovered.

methyl benzenesulfinate (0.04 mol) and trichlorosilane (0.06 mol) in 70 ml of benzene at 20°, tri-*n*-propylamine (0.042 mol) in 50 ml of benzene was added dropwise. After a stirring period of 4 hr, the mixture was hydrolyzed with water (20 ml) and extracted, affording an 85% yield of diphenyl disulfide. Similarly, disulfides were obtained from sulfonyl chlorides (RSO_2Cl), sulfinyl chlorides (RSOCl), sulfenyl chlorides (RSCl), and sulfenates (RSOR′) in high yield (Table I).

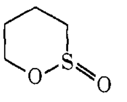
The generality and utility of this method of disulfide preparation is illustrated by the reaction of two cyclic sulfinate esters (1,2-oxathiolane 2-oxide (I) and 1,2-oxathiane 2-oxide (II))[9] with n-Pr_3N–$HSiCl_3$. In both cases, rupture of the heterocycle occurred along with reduction of the sulfinyl oxygen to give the symmetrical hydroxy disulfides III and IV in 80 and 60% yield, respectively. The identity of structures III and IV was established by correct elemental analysis, spectral properties, and synthesis by an independent route according to Scheme I.



I

$\longrightarrow$ $HOCH_2CH_2CH_2SSCH_2CH_2CH_2OH$

III

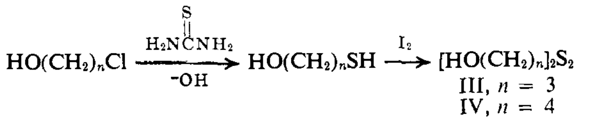


II

$\longrightarrow$ $HOCH_2CH_2CH_2CH_2SSCH_2CH_2CH_2CH_2OH$

IV

Scheme I



$$HO(CH_2)_nCl \xrightarrow[{}^-OH]{H_2N\overset{\overset{\textstyle S}{\|}}{C}NH_2} HO(CH_2)_nSH \xrightarrow{I_2} [HO(CH_2)_n]_2S_2$$

III, n = 3
IV, n = 4

The mechanistic details of the reduction of organic functional groups with trichlorosilane are far from

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