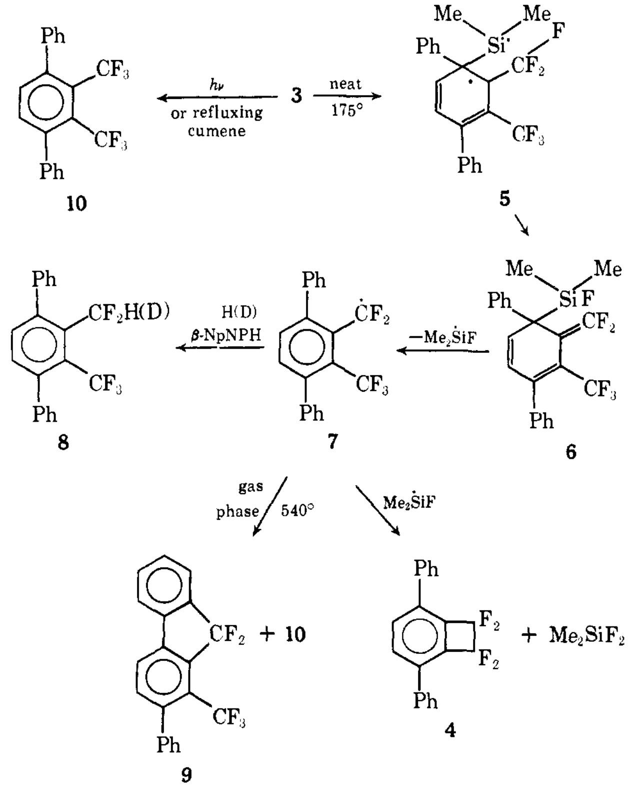
tempting to assume loss of Me_2SiF_2 from **6** to proceed directly to **4**, further experiments make this route unlikely. When the neat pyrolysis of **3** is conducted in the presence of *N*-phenyl-2-naphthylamine, a hydrogen transfer agent,[12] the *p*-terphenyl **8**[5] [49%; mp 113–114°; ^{19}F nmr (*vs.* $FCCl_3$) δ +49.5 (t, J_{FF} = 15 Hz, CF_3), 106.2 and 107.1 ppm (nonoverlapping doublet of quartets, J_{HF} = 50.2 Hz); *m/e* 348.091802, calcd *m/e* 348.09181] is isolated and *no* **4**. Furthermore, when the pyrolysis of **3** is performed in the gas phase at 540° (flow system) an 87% overall yield of a *ca.* equal mixture of **9**[5] [mp 135–136°; ^{19}F nmr (*vs.* $FCCl_3$) $\delta\nu$ +57.7 (t, J_{FF} = 19 Hz, CF_3), +113 ppm (q, J_{FF} = 19 Hz, CF_2)] and **10** can be isolated and separated. Products **8** and **9** would seem to implicate the intermediacy of **7**.

Evidence has recently been accumulating that the bridge elimination of carbenes from norbornadienes occurs through initial homolytic scission of a C–C bond to provide a diradical which may either close to a norcaradiene or aromatize through carbene extrusion.[13] The work reported here makes it quite likely that silylene extrusions from 7-silanorbornadienes generally proceed by this route.[14] It is only because of the favorable location of the trifluoromethyl groups and the great strength of the Si–F bond[16] that we are able to divert the normal reaction and thus be aware of the mode of initial cleavage.

Surprisingly we find that decomposition of **3** brought about either by ultraviolet irradiation or refluxing solvent (cumene) affords the expected thermal product **10**[5,17] [mp 130–132°; ^{19}F nmr (*vs.* $FCCl_3$) δ +51 ppm (s); *m/e* 366.083417, calcd *m/e* 366.084300]. The photochemical reaction provides a 61% yield of **10**, and Me_2Si has been trapped by tolan to give 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene in very low yield.



Acknowledgment. This work has been generously supported by the National Institutes of Health (GM 16689-03). One of us (C. L. M.) also thanks the National Science Foundation (GP 28152X).

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[12] R. F. Bridger, *J. Org. Chem.*, **35**, 1746 (1960).

[13] For a recent review of the evidence for this mechanism see: R. W. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).

[14] The possibility of **3** undergoing a 1,3-sigmatropic migration of silicon (ref 15) to form a silanorcaradiene which could open to **5** (or a similar diradical) is a mechanistic possibility which we tentatively exclude because of the great strain involved in the initial rearrangement.

[15] H. Kwart and J. Slutsky, *J. Amer. Chem. Soc.*, **94**, 2515 (1972).

[16] *D*(SiF) = 193 ± 10 kcal/mol (Me_3SiF): G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, **87**, 5327 (1965).

[17] This compound was synthesized for comparison from the Diels–Alder reaction between 1,4-diphenylbutadiene and perfluoro-2-butyne followed by dehydrogenation with sulfur. Compound **8** was found to be thermally stable when heated neat at 170–180° and in the gas phase (flow system) at 540°, thus excluding that route to **4**.

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Reliability of Coupling Constants Obtained from Tris(dipivalomethanato)europium Shifted Proton Magnetic Resonance Spectra

Sir:

Pseudocontact nuclear magnetic resonance shift reagents have received considerable attention in molecular structure studies due to their ability to provide first-order spectra from which chemical shifts and coupling constants can be directly obtained.[1–3]

Chemical shifts are usually dealt with by comparing the experimentally found isotropic shift with that calculated from the pseudocontact shift equation.[4] Certain precautions regarding this approach have been recorded.[5–9]

Coupling constants obtained from shifted spectra have not received careful attention regarding their validity. However, claims have been made that coupling constants from shifted spectra of both σ[10] and π[11] systems are unaffected by the shift reagent.

We now wish to report a case where a shift reagent does affect the values of coupling constants. Tris(dipivalomethanato)europium, $Eu(dpm)_3$,[12] shifted spectra from benzocyclopenten-2-ol[13] (**1**) and benzocyclobuten-1-ol[14] (**2**) were obtained at 60 MHz[15] on 20% solutions of the solute in carbon tetrachloride at

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

[2] J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

[3] W. DeW. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

[4] M. R. Willcott, III, R. E. Lenkinskc, and R. E. Davis, *ibid.*, **94**, 1743 (1972).

[5] B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *ibid.*, **93**, 3281 (1971).

[6] S. B. Tjan and F. R. Visser, *Tetrahedron Lett.*, 2833 (1971).

[7] I. Fleming, S. W. Hanson, and J. K. M. Sanders, *ibid.*, 3733 (1971).

[8] I. Armitage and L. D. Hall, *Can. J. Chem.*, **49**, 2770 (1971).

[9] J. Goodisman and R. S. Matthews, *Chem. Commun.*, 127 (1972).

[10] I. Armitage and L. D. Hall, *Chem. Ind. (London)*, 1537 (1970).

[11] A. F. Bramwell, G. Riezebos, and R. D. Wells, *Tetrahedron Lett.*, 2488 (1971).

[12] Obtained from Alfa Inorganics, Inc., Beverly, Mass.; mp 189–191.5°.

[13] W. F. Whitmore and A. I. Gebhart, *J. Amer. Chem. Soc.*, **64**, 912 (1942); mp 66.5–68°.

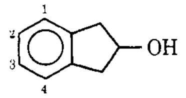
[14] H. H. Wasserman and J. Solodar, *ibid.*, **87**, 4002 (1965); mp 60–61°.

[15] A Varian Model T-60 spectrometer was used. The probe temperature was 35°.

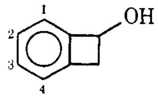
Eu(dpm)$_3$-solute mole ratios of 0.4:0.7. Pmr spectra were also obtained on 10% solutions of **1** and **2** in carbon tetrachloride at 220[16] and 300 MHz,[16] respectively.

The aromatic protons of both **1** and **2** appear as singlets at 60 MHz in the absence of Eu(dpm)$_3$, thus making it impossible to determine the aromatic coupling constants. In the presence of Eu(dpm)$_3$, the aromatic protons of **1** appear as an AA'XX' pattern and the aromatic protons of **2** appear as an AMXY pattern. Under high-field strength conditions, the aromatic protons of **1** show an AA'BB' pattern and the aromatic protons of **2** show an ABCD pattern. All spectra were analyzed by best fit iteratative computer analysis using the LAOCN3 program.[17] Eu(dpm)$_3$-shifted spectra gave good computer fits but were not perfect due to slightly broadened and asymmetric peaks. The coupling constants did not vary more than ±0.05 Hz for the Eu(dpm)$_3$-solute mole ratios used. Spectra obtained at 220 (**1**) and 300 MHz (**2**) gave very good computer fits. Coupling constants obtained from the Eu(dpm)$_3$-shifted spectra are good to at least ±0.5 Hz while those obtained from the 220- and 300-MHz spectra are good to at least ±0.1 Hz.[18] The results are shown in Table I.

Table I. Coupling Constant Values Obtained for **1** and **2**



1



2

	1		**2**	
J_{12}	7.29	7.88	6.56	7.45
J_{13}	1.08	1.26	1.28	0.80
J_{14}	0.04	0.11	−0.39	1.87
J_{23}	7.22	7.68	8.35	7.56
J_{24}	1.08	1.26	0.60	0.37
J_{34}	7.29	7.88	7.01	7.59
Rms	0.13	0.05	0.17	0.05
Method	Eu(dpm)$_3$	220 MHz	Eu(dpm)$_3$	300 MHz

Statistical analysis of the data reported in Table I using the "t" test method[19] allows several statements concerning comparisons of coupling constants obtained from the Eu(dpm)$_3$-shifted spectra with coupling constants obtained from the spectra determined at 220 and 300 MHz. The confidence in our results is greater than 99%. In both unstrained[20] **1** and strained[20] **2** the ortho (J_{12}, J_{23}, J_{34}) and para (J_{14} in **2**) coupling constants are *not* within experimental error. Thus, coupling constants obtained from Eu(dpm)$_3$-shifted spectra can be affected by the shift reagent and erroneous results obtained.[21,23] We therefore suggest that conclusions about aromatic electronic structure based on coupling constants obtained from Eu(dpm)$_3$-shifted spectra may not be reliable in some cases. A pertinent example for the present work is the study by Cooper and Mannatt[20] who have found that J_{14} increases substantially in benzocycloalkenes on going from large to small cyclic fused rings. This is not observed in the Eu(dpm)$_3$-shifted spectra.

Acknowledgment. Financial support from the Research Corporation and the Office of Research and Projects, Southern Illinois University, is greatly appreciated.[23a]

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(16) These spectra were recorded by the Varian NMR applications laboratory, Palo Alto, Calif. The probe temperature was 35°.

(17) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(18) The error is obtained by multiplying the parameter set error[17] by 5 as suggested by S. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Lett.*, 5205 (1967). M. A. Cooper and S. L. Mannatt (*J. Amer. Chem. Soc.*, **91**, 6325 (1969)) have shown that the error may be better than that obtained by multiplying the parameter set error by 5. Our statistically determined confidence level (99%) would be increased if the multiplication were omitted.

(19) W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951, p 24.

(20) M. A. Cooper and S. L. Mannatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970).

(21) The J values obtained for **1** at 220 MHz and **2** at 300 MHz are considered to be correct due to their near identity with the J values reported for benzocyclopentene and benzocyclobutene.[20] Our slightly higher J (ortho) values are consistent with the electronegative influence of the –OH group as reported by S. Castellano and C. Sun, *ibid.*, **88**, 4741 (1966). The invariance of J with respect to the field strength is well established,[22] thus making comparisons of coupling constants obtained at 60 MHz with coupling constants obtained at high-field strengths valid.

(22) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, Chapter 3, and references cited therein.

(23) Proof that the coupling constant differences observed in the present work are not due to the fact that observations were carried out on different instruments (as suggested by the referees) comes from two sources. (a) The aliphatic ring coupling constants could be extracted directly from the spectra of **1** and **2** in the absence of shift reagent on all spectrometers used. These J values were exactly the same regardless of the spectrometer used. (b) L. F. Johnson (*Anal. Chem.*, **43**, 28A (1971)) has shown that coupling constants do not change for acrylonitrile using different spectrometers operating at 60, 100, and 220 MHz.

(23a) NOTE ADDED IN PROOF. B. L. Shapiro, M. D. Johnston, Jr., and R. L. R. Towns (*J. Amer. Chem. Soc.*, **94**, 4381 (1972)) have recently noted lanthanide-induced changes of coupling constants in some ketones.

(24) Research submitted for the degree of Master of Science.

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Proton-Enhanced Nuclear Induction Spectroscopy. Silicon-29 Chemical Shielding Anisotropy in Some Organosilicon Compounds

Sir:

Nmr spectroscopy of ^{29}Si is made relatively difficult both by relatively low isotopic abundance (4.7%) and by the long spin–lattice relaxation times T_1 characteristic of this species. Both of these difficulties are largely circumvented by a double resonance technique[1] in which the rare spins derive an enhanced and rapidly repeatable polarization from abundant spins (protons) by a rotating-frame cross-relaxation process. The experiment is performed in the solid state and therefore affords the possibility of observing anisotropies in the interactions of the rare spins. In many cases the anisotropy of interest is that of the chemical shift; the dipolar broadening by the abundant spins which would otherwise obscure this is then removed by spin decoupling.[1,2]

Table I gives the principle elements of the ^{29}Si chemical shielding tensor obtained by the cross-polarization procedure in polycrystalline samples of a number of organosilicon compounds at −186°. The static

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(1) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **56**, 1776 (1972).

(2) L. R. Sarles and R. M. Cotts, *Phys. Rev.*, **111**, 853 (1958).