Optically Active Solvents for Nuclear Magnetic Resonance. X. Enantiomeric Nonequivalence of Sulfinamides, Sulfinates, Sulfites, Thiosulfinates, Phosphine Oxides, and Amine Oxides

Sir:

Because of the ready accessibility of resolved 2,2,2-trifluorophenylethanol (**1**)[1] and demonstrations of its use in optical purity determinations and absolute configuration correlations of partially resolved amines,[2] sulfoxides,[3] and α-amino esters,[4] we wish to report preliminary findings on the use of chiral fluoro alcohols in promoting nmr enantiomeric spectral nonequivalence in several other types of solutes.

Table I. Enantiomeric Chemical Shift Differences for Type **3** Sulfinamides, Sulfinates, Sulfites, and Thiosulfinates, (−)-**1**[a]

R_1	X	R_2	Δδ, Hz[b] R_1[c]	R_2
$(CH_3)_\alpha CH_\gamma (CH_3)_\beta$	N	$(CH_3)_2$	4.6, 1.3, 3.3	2.4
$(CH_3)_\alpha CH_\gamma (CH_3)_\beta$	O	CH_3	0.0, 0.0, 0.7	0.5
CH_3O	O	CH_3	0.55	
$(CH_3)_\alpha CH_\beta H_\gamma O$	O	CH_2CH_3	0.5, 0.7, 0.0	
$(CH_3)_3C$	S	$C(CH_3)_3$	1.7	2.2

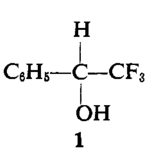
[a] Samples were composed of 2:1:~3 mole ratios of carbinol-solute-$CFCl_3$, respectively. [b] Measured at 100 MHz and 29°. [c] Values are for the α, β, . . . protons, respectively.

Table II. Enantiomer Chemical Shift Differences for Type **4** Phosphine Oxides and Amine Oxides in Chiral Alcohols[a]

X	R	Δδ, Hz[b] CH_3	R
P	$CH_2C_6H_5$	1.4	
P	$CH_2CH_2CH_3$	1.9	
P	$C(CH_3)_3$	3.2	
N	$(CH_2)_\alpha (CH_3)_\beta$	3.5[c]	3.4, 5.5[c]

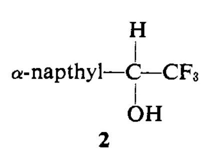
[a] Samples were composed of a 2:1:~3 mole ratios of carbinol **1**-solute-CCl_4, respectively, unless otherwise specified. [b] Measured at 100 MHz and 29°. [c] In (−)-**2** of 79% optical purity.

Based upon differences of their enantiomeric nmr spectra in (−)-**1**, direct optical purity determinations are now possible for type **3** sulfinamides, sulfinates, sulfites, thiosulfinates, and type **4** phosphine oxides. Moreover, the use of optically active 2,2,2-trifluoro-α-naphthylethanol (**2**) as an nmr solvent causes en-



$$C_6H_5-\overset{H}{\underset{OH}{C}}-CF_3$$

1



$$\alpha\text{-napthyl}-\overset{H}{\underset{OH}{C}}-CF_3$$

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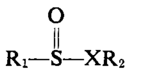
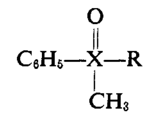
antiomeric spectral dissimilarities for type **4** amine oxides. Tables I and II give the enantiomeric (or enantiotopic) chemical shift differences (Δδ) observed for several of the compounds studied and serves to illustrate the apparent generality of this phenomenon.

We feel that, when applicable, the use of optically active nmr solvents is the method of choice in deter-



$$R_1-\overset{O}{\overset{\|}{S}}-XR_2$$

3, X = N, O, S



$$C_6H_5-\overset{O}{\overset{\|}{\underset{CH_3}{X}}}-R$$

4, X = P, N

mining optical purities of these oxides since it is absolute and convenient and requires no further chemical transformation. The generality of this technique and its application in the determination of absolute configurations will be the subject of a later report.

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(5) National Institutes of Health Predoctoral Fellow.

(6) National Science Foundation Predoctoral Fellow.

Synthesis of Pentaphenylborole, a Potentially Antiaromatic System

Sir:

Studies in carbocyclic antiaromatic systems, such as the substituted cyclopropenyl anion[1] and the cyclopentadienyl cation,[2] have provided support for the converse proposition of the Hückel rule, namely, that monocyclic conjugated sets of sp^2-hybridized atoms having $4n$ π electrons will be especially unstable.[3] That the pentaphenylcyclopentadienyl cation has a thermally populated, low-lying triplet state has been demonstrated by esr spectroscopic detection of half-field transitions. Thus, the gain in stabilization by ensconcing the four π electrons by pairs in bonding orbitals is not large.

As heterocyclic rings of boron interest us as potential aromatic[4] and antiaromatic analogs of carbocycles, we

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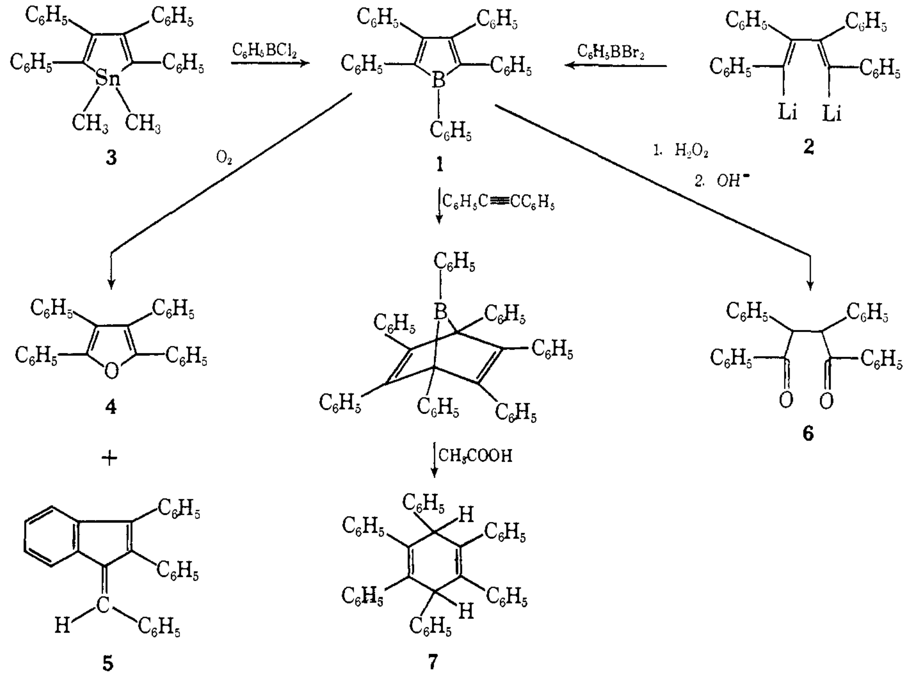
(1) R. Breslow and M. Douek, *J. Am. Chem. Soc.*, **90**, 2698 (1968).

(2) R. Breslow and H. W. Chang, *ibid.*, **83**, 3728 (1961); **85**, 2033 (1963).

(3) R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967).

(4) *Cf.* J. J. Eisch and L. J. Gonsior, *J. Organometal. Chem.* (Amsterdam), **8**, 53 (1967).

Chart I



were surprised by the report that pentaphenylborole was a colorless solid, inert to amines and stable both to air and to ethanol.[5] Extension of the Hückel theory would suggest a high reactivity for this boron counterpart of the pentaphenylcyclopentadienyl cation. Our reinvestigation has now shown that pentaphenylborole is actually a highly reactive green solid which forms a stable 1:1 complex with pyridine. Since current research reports and monographs[6] place explicit reliance upon the previous report,[5] we wish to publish our findings now.

Pentaphenylborole (**1**) was prepared in two ways: (a) modification of the previous report[5] whereby 1,4-dilithiotetraphenylbutadiene (**2**) was now added to a solution of phenylboron dibromide in ether at 0°, the solvent removed *in vacuo*, benzene added to precipitate the lithium bromide (90–100%), and the green solution freed of solvent (all operations performed under nitrogen); and (b) the interaction of 1,1-dimethyl-2,3,4,5-tetraphenylstannole[7] (**3**) with phenylboron dichloride in CCl_4 or toluene to yield the borole and dimethyltin dichloride (quantitative by nmr monitoring), treatment with 3 equiv of pyridine to form the borole–pyridine and the $(CH_3)_2SnCl_2$–$2C_5H_5N$ complexes, separation of the insoluble tin complex, and recrystallization of pentaphenylborole–pyridine complex from a benzene–petroleum ether (bp 30–60°) mixture. The yellow solid melted at 180–182° dec. *Anal.* Calcd for $C_{39}H_{30}BN$: C, 89.48; H, 5.73; B, 2.10; N, 2.67. Found: C, 89.44; H, 5.65; B, 2.32; N, 2.58. The mass spectrum (50° inlet, 70 eV) displayed a weak parent ion at m/e 523, the base peak at 444 (P − 79, loss of pyridine), and prominent low mass peaks at 79 and 52 [P of pyridine and P − 27 (loss of HCN)]. The nmr spectrum (CS_2, δ) showed multiplets centered at 6.5 (7 H) and 7.15 (10 H), doublets at 7.70 (1 H) and 8.6 (2 H) (γ- and α-pyridinoid H), and a singlet at 6.81 ppm (10 H). Treatment of the compound with picric acid in benzene caused deposition of pyridine picrate.

The free borole, melting about 120° dec, gave a nmr spectrum very similar to its pyridine complex, excepting the amine's resonances (CCl_4, δ: multiplets between 6.8 and 7.3 ppm, with prominent peaks at 6.95, 7.15, 7.18, and 7.25 ppm). The compound is most labile: (a) refluxing in benzene destroys the ring system (green color replaced by brown), and hence recrystallization to a sharp melting point has been unsuccessful; (b) exposure to dry air promptly discharges the green color and column chromatographic work-up (*cf.* ref 5) yields tetraphenylfuran (**4**) and 3-benzylidene-1,2-diphenylindene (**5**); (c) treatment with 30% H_2O_2 followed by aqueous NaOH yields principally 1,2,3,4-tetraphenyl-1,4-butanedione (**6**) (inverse order yields mainly *cis*-2,3,4-triphenyl-3-butenophenone, presumably by B–C bond hydrolysis); and (d) treatment with diphenylacetylene in refluxing benzene, followed by acetolysis of the product with glacial acetic acid, gave a mixture of hexaphenylbenzene, *cis,cis*-1,2,3,4-tetraphenylbutadiene, and, as principal product, hexaphenyl-1,4-dihydrobenzene (**7**). The structure of this last product we assign as the unknown *cis* isomer, based upon the following evidence: (a) mp 188°, whereas the known,[8] presumably *trans*, isomer melts at 226°; (b) treatment with bromine and pyridine afforded an 80% yield of hexaphenylbenzene; (c) analysis (*Anal.* Calcd for $C_{42}H_{32}$: C, 93.99; H, 6.01. Found: C, 94.04; H, 6.01); and (d) nmr (CCl_4, δ): singlets at 4.67 (2 H), 6.92 (20 H), and 7.15 ppm (10 H). The reactions and their interpretation are summarized in Chart I.

Samples of the uncomplexed borole prepared according to the stannole procedure do display a prominent

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(5) E. H. Braye, W. Hübel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).

(6) *Inter alia:* (a) R. E. Dessy, and R. L. Pohl, *ibid.*, **90**, 1995 (1968); (b) G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, Methuen, London, 1968, p 230.

(7) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *J. Am. Chem. Soc.*, **82**, 5099 (1960).

(8) R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963), report that their hexaphenyl-1,4-dihydrobenzene results when 1,2,3-triphenylcyclopropene is treated with potassium amide. Since they suggest protonation of the cyclohexadienyl anion, possibly a *trans* structure might be favored. Their reported nmr spectrum has a 30-proton multiplet at 7.0 ppm and a 2-proton singlet at 4.67 ppm.

esr signal in toluene, but no half-field transitions have as yet been detected. Conceivably any $(CH_3)_2SnCl_2$ present may cause the borole to form a radical cation, as has been observed for many aromatic compounds in contact with Lewis acids.[9]

In conclusion, pentaphenylborole is a highly reactive nucleus, undergoing readily oxidation, partial protolysis, and the Diels–Alder reaction with a dienophile of low reactivity. Although a low-lying triplet has not been established, this borole seems to deserve further consideration as a potential antiaromatic system. In any event, previous claims about the inertness of this nucleus must be rectified.[10]

Acknowledgments. Support by the Army Research Office, Durham, under Grant DA-AROD-31-124-G879 made this investigation possible, and assistance by Dr. Henry Fales of the National Institutes of Health in obtaining the mass spectral data made this report feasible. Dr. E. C. Braye was most cooperative in aiding this reinvestigation by providing a sample of the previously reported products[10] and by expressing reservations concerning the nature of the reported borole.

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(9) *Cf.* I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965), and references cited therein.

(10) The procedure previously described in ref 5 was repeated faithfully, but the pale yellow solids isolated were air stable and unreactive to pyridine or to alkynes and had molecular weights >800 (mass spectroscopy). Such solids were identical by mass spectral, infrared, and tlc criteria with a sample generously provided by Dr. Braye.

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Stabilities of Trivalent Carbon Species. I. Aromatic and Antiaromatic Species Related to Triphenylmethyl

Sir:

The striking success of the Hückel approximation in the prediction of stabilities of nonalternant trivalent carbon species is generally recognized.[1] However, comparisons of various systems have been made using widely different experimental techniques, as illustrated by 9-phenylfluorenyl and triphenylmethyl species. Thus, the relative stabilities of the cations were first derived from conductivity measurements in liquid SO_2,[2] the anions from hydrocarbon acidity measurements,[3] and the free radicals from dimer dissociation equilibria[4] which were subsequently reinvestigated by thermochemical[5] and kinetic techniques.[6] The triphenylcyclopropenyl species have likewise been studied by a variety of methods.[7,8] We present here results for several systems which are structurally related to triphenylmethyl, for which relative stabilities of the various trivalent species are measured under identical conditions and may be referred to a single standard.

The stabilities of a large number of triarylcarbonium ions have been established by means of the H_R acidity function[9] and confirmed by potentiometric measurements.[10] The free energy of a triarylcarbonium ion (R^+) relative to triphenylcarbonium (R_0^+) is given by ΔF for reaction 1, which is readily obtained from pK_{R^+} values.

$$ROH + R_0^+ \rightleftharpoons R_0OH + R^+ \qquad (1)$$

The stabilities of the corresponding free radicals and anions, relative to the cation, may be determined from potentiometric measurements[11,12] (reactions 2 and 3). Thus, the series of trivalent carbon

$$R^+ + e \rightleftharpoons R\cdot \qquad (2)$$

$$R\cdot + e \rightleftharpoons R^- \qquad (3)$$

species may be related to the triphenylcarbinol ionization.

We have measured the reduction peak potentials of a group of cations which are structurally related to triphenylmethyl, and consequently should have nearly equal solvation energies, using triangular wave cyclic voltammetry. The cations were generated from the corresponding alcohols in aqueous sulfuric acid, and the reductions were carried out in this medium. Voltammograms were recorded with a Chemtrix SSP-2 instrument which was modified to permit the scan rate to vary from 1 to 200 V/sec. A three-electrode cell was used, with a dropping mercury working electrode, a platinum wire counter electrode, and a reference electrode of $Hg|Hg_2SO_4$–17 *M* H_2SO_4.[13] With the exception of triphenylcyclopropenium, the cations are reduced in successive one-electron steps, corresponding to reversible formation of the radical (eq 2) and irreversible reduction to the hydrocarbon (eq 4). For

$$R\cdot + e + H^+ \longrightarrow RH \qquad (4)$$

the series of structurally related radicals, we assume the potential obtained for reaction 4 measures *approximately* the free energy difference between the carbanion and radical.

The reversibility of the first reduction is demonstrated at fast scan rates, where oxidation of the radical is faster than its dimerization.[14] The peak potential for this reduction is very sensitive to the composition of the solvent and shifts dramatically to more negative potentials with increasing acidity. At high acid concentrations, the first wave merges with the second, which is generally insensitive to solvent composition, and a two-electron wave is observed. Two-electron reduction of triphenylcarbonium ion has previously been noted in direct current polarography in 97% H_2SO_4[15] and methanesulfonic acid.[16] We shall present detailed results of the solvent effect on the reduction of these and other cations in a subsequent paper.

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(7) A. W. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

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(9) N. C. Deno, J. Jaruzelski, and A. Schriescheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

(10) R. W. Taft, *et al.*, *ibid.*, **86**, 116 (1964); **87**, 2489 (1965); **88**, 4747 (1966).

(11) J. B. Conant, *et al.*, *ibid.*, **47**, 1959 (1925); **55**, 3752 (1933).

(12) H. E. Bent and N. B. Keevil, *ibid.*, **58**, 1228 (1936).

(13) The potential of this electrode is +0.256 V *vs.* sce; *cf.* A. A. Vlček, *Collection Czech. Chem. Commun.*, **16**, 373 (1951).

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(16) S. Wawzonek, R. Berkey, and D. Thomson, *J. Electrochem. Soc.*, **103**, 513 (1956). Two one-electron waves are observed if water is added to the solvent.