

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

Sir:

Because of the ready accessibility of resolved 2,2,2-trifluorophenylethanol (**1**)<sup>1</sup> and demonstrations of its use in optical purity determinations and absolute configuration correlations of partially resolved amines,<sup>2</sup>

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



mining optical purities of these oxides since it is absolute and convenient and requires no further chemical

**Table I.** Enantiomeric Chemical Shift Differences for Type 3 Sulfinamides, Sulfinates, Sulfites, and Thiosulfinates, (-)-**1**<sup>a</sup>

R <sub>1</sub>	X	R <sub>2</sub>	Δδ, Hz <sup>b</sup>	
			R <sub>1</sub> <sup>c</sup>	R <sub>2</sub>
(CH <sub>3</sub> ) <sub>α</sub> CH <sub>γ</sub> (CH <sub>3</sub> ) <sub>β</sub>	N	(CH <sub>3</sub> ) <sub>2</sub>	4.6, 1.3, 3.3	2.4
(CH <sub>3</sub> ) <sub>α</sub> CH <sub>γ</sub> (CH <sub>3</sub> ) <sub>β</sub>	O	CH <sub>3</sub>	0.0, 0.0, 0.7	0.5
CH <sub>3</sub> O	O	CH <sub>3</sub>	0.55	
(CH <sub>3</sub> ) <sub>α</sub> CH <sub>β</sub> H <sub>γ</sub> O	O	CH <sub>2</sub> CH <sub>3</sub>	0.5, 0.7, 0.0	
(CH <sub>3</sub> ) <sub>3</sub> C	S	C(CH <sub>3</sub> ) <sub>3</sub>	1.7	2.2

<sup>a</sup> Samples were composed of 2:1:~3 mole ratios of carbinol-solute-CFCl<sub>3</sub>, respectively. <sup>b</sup> Measured at 100 MHz and 29°. <sup>c</sup> Values are for the α, β, ... protons, respectively.

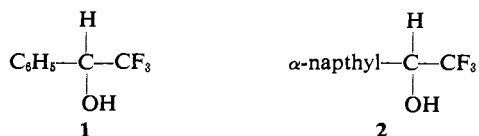
**Table II.** Enantiomer Chemical Shift Differences for Type 4 Phosphine Oxides and Amine Oxides in Chiral Alcohols<sup>a</sup>

X	R	Δδ, Hz <sup>b</sup>	
		CH <sub>3</sub>	R
P	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1.4	
P	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1.9	
P	C(CH <sub>3</sub> ) <sub>3</sub>	3.2	
N	(CH <sub>2</sub> ) <sub>α</sub> (CH <sub>3</sub> ) <sub>β</sub>	3.5 <sup>c</sup>	3.4, 5.5 <sup>c</sup>

<sup>a</sup> Samples were composed of a 2:1:~3 mole ratios of carbinol 1-solute-CCl<sub>4</sub>, respectively, unless otherwise specified. <sup>b</sup> Measured at 100 MHz and 29°. <sup>c</sup> In (-)-**2** of 79% optical purity.

sulfoxides,<sup>3</sup> and α-amino esters,<sup>4</sup> 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.

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-



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.

(1) W. H. Pirkle, S. D. Beare, and T. G. Burlingame, *J. Org. Chem.*, **34**, 470 (1969).

(2) W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *Tetrahedron Lett.*, 5849 (1968).

(3) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **90**, 6250 (1968).

(4) W. H. Pirkle and S. D. Beare, *ibid.*, in press.

transformation. The generality of this technique and its application in the determination of absolute configurations will be the subject of a later report.

**Acknowledgment.** The authors wish to thank the U. S. Public Health Service (Grant No. GM 14518) for supporting this work. We are also grateful to Dr. K. Mislow and Dr. M. J. Sabacky for phosphine oxide samples.

(5) National Institutes of Health Predoctoral Fellow.  
(6) National Science Foundation Predoctoral Fellow.

William H. Pirkle, Steven D. Beare,<sup>5</sup> Ronald L. Muntz<sup>6</sup>

Department of Chemistry and Chemical Engineering  
University of Illinois, Urbana, Illinois 61801

Received May 26, 1969

**Synthesis of Pentaphenylborole, a Potentially Antiaromatic System**

Sir:

Studies in carbocyclic antiaromatic systems, such as the substituted cyclopropenyl anion<sup>1</sup> and the cyclopentadienyl cation,<sup>2</sup> have provided support for the converse proposition of the Hückel rule, namely, that monocyclic conjugated sets of sp<sup>2</sup>-hybridized atoms having 4n π electrons will be especially unstable.<sup>3</sup> 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<sup>4</sup> and antiaromatic analogs of carbocycles, we

(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).