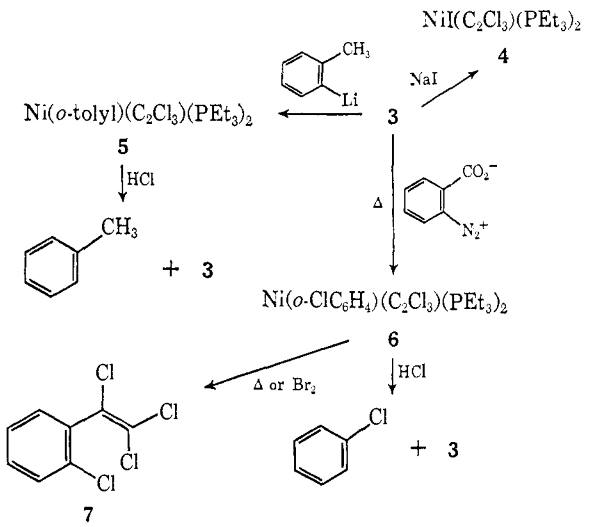

yield of a compound believed to be **6**, mp 155.5–156.5,° which, on thermolysis in tetrachloroethylene or on treatment with bromine in hexane, afforded **7**. Reaction of **6** with HCl in ether afforded small amounts of **3** and chlorobenzene.

The above series of reactions suggests strongly that **3** is chloro(trichlorovinyl)bis(triethylphosphine)nickel(II), presumably derived from oxidative addition of tetrachloroethylene to a nickel(0) species generated in the decomposition of **1**. The compound exists in the *trans* configuration suggested by the low dipole moment of 1.95 D and the general features of the Et_3P proton resonances. In view of the evidence for the generation of benzyne *via* the thermal decomposition of benzenediazonium-2-carboxylate,[13] the formation of **6** possibly results from "insertion" of benzyne into the nickel–chlorine bond of **3**. The formation of *o*-trichlorovinylchlorobenzene from bromination of **6** appears to be an example of a coupling reaction induced by oxidative addition of bromine to **6** and is probably related to the coupling reactions reported by Corey.[14]

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of North Dakota grant-in-aid program for support of this research.

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(13) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(14) E. J. Corey and M. F. Semmelhack, *ibid.*, **89**, 2755 (1967).

(15) NDEA Predoctoral Fellow, 1965–1968.

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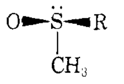
Optically Active Solvents in Nuclear Magnetic Resonance Spectroscopy. VII. Direct Determination of Optical Purities and Correlations of Absolute Configurations of Sulfoxides[1]

Sir:

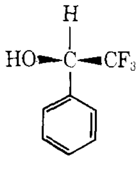
While dissimilarly substituted sulfoxides, asymmetric by virtue of the tetrahedral configuration at sulfur, have not been resolved except through the agency of other functional group "handles,"[2] optically active samples can be readily obtained through the Andersen synthesis[3] or *via* asymmetric oxidation of thioethers.[4] We herein report the first method, to our knowledge, for the direct determination of optical purities of sulfoxides.

In appropriate optically active solvents, the nmr spectra of enantiomeric type **1** sulfoxides are sufficiently different to allow not only direct determinations of enantiomeric purity, but also correlations of absolute configuration.

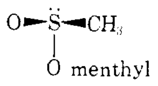


$\underset{\mathrm{CH_3}}{\mathrm{O{-}\ddot{S}{-}R}}$

(*R*)-1, R = alkyl, aryl



(−)-(*R*)-2



$\underset{\mathrm{O\ menthyl}}{\mathrm{O{-}\ddot{S}{-}CH_3}}$

(−)-(*R*)-3

For example, in achiral solvents, the 100-MHz nmr spectrum of partially resolved methyl *t*-butyl sulfoxide, prepared[5] by the action of *t*-butylmagnesium chloride on a 1.78:1.00 mixture[6] of the two diastereomeric (−)-menthyl methanesulfinates (**3**),[7] shows two sharp singlets in a 3:1 ratio. However, in (−)-(*R*)-2,2,2-trifluorophenylethanol[8] (**2**), the methyl and *t*-butyl resonances of the two sulfoxide enantiomers have appreciably different chemical shifts, and the spectrum of the partially resolved sulfoxide consists of two unequally intense *t*-butyl resonances (δ 1.01 and 1.02, relative intensities 1.59:1.00) and two unequally intense methyl resonances (δ 2.09 and 2.07, relative intensities 1.63:1.00). Since by virtue of fast-exchange processes, the optical purity of the solvent affects only the chemical shift differences between the resonances of the enantiomers and not their relative intensities, this nmr method is, to our knowledge, the first method for the direct determination of the enantiomeric purity of a sulfoxide.

It is well known that sulfoxides associate with alcohols,[9] and it seems reasonable to assume that the spectral nonequivalence observed for enantiomers of unsymmetrical sulfoxides in optically active alcohol **2**

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(1) For part VI, see W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *Tetrahedron Lett.*, in press.

(2) One possible exception is the resolution of ethyl *p*-tolyl sulfoxide with platinum complexes containing optically active α-methylbenzylamine: A. C. Cope and E. A. Caress, *J. Amer. Chem. Soc.*, **88**, 1711 (1966).

(3) K. K. Andersen, *Tetrahedron Lett.*, 93 (1962).

(4) U. Folli, D. Iarossi, F. Montanari, and G. Torre, *J. Chem. Soc.*, *C*, 1317 (1968), and references cited therein.

(5) M. Axelrod, P. Bickart, M. L. Goldstein, M. M. Green, A. Kjaer, and K. Mislow, *Tetrahedron Lett.*, 3249 (1968).

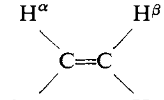
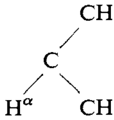
(6) Andersen has previously noted[7] a 0.02-ppm chemical shift difference between the methanesulfinyl resonances for the diastereomeric sulfinates (in chloroform) at 60 MHz, although the diastereomeric purity was presumably too low to be determined on the basis of relative peak heights. We have found that, at 100 MHz and 28°, the methanesulfinyl chemical shift difference ($\Delta\delta_{\mathrm{SOCH_3}}$) is increased to 3.4 Hz in (−)-alcohol **2**, greatly facilitating the ratio measurement. When racemic **2** is used as solvent the chemical shift difference is 1.7 Hz, while in (+)-**2** it is diminished to the extent that it is not observable.

(7) (a) K. K. Andersen, *J. Org. Chem.*, **29**, 1953 (1964). (b) For a modification of Andersen's procedure yielding ester **3** of higher diastereomeric purity, see J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967).

(8) (a) For the absolute configuration of **2**, see H. M. Peters, D. M. Feigl, and H. S. Mosher, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April, 1967, No. O-67. (b) For the resolution of **2**, see D. M. Feigl, Ph.D. Thesis, Stanford University, 1966. A more convenient resolution of **2** will be reported shortly (W. H. Pirkle, S. D. Beare, and T. G. Burlingame, submitted for publication).

(9) C. P. Rader, *J. Amer. Chem. Soc.*, **88**, 1713 (1966), and references cited therein.

Table I. Correlation of Nmr Sense of Nonequivalence with Absolute Configuration for Some Partially Resolved Type **1** Sulfoxides[a,b]

R	Δδ, Hz[c] R	Δδ, Hz[c] CH$_3$	Nonequivalence sense R[d]	Nonequivalence sense CH$_3$	% optical purity[e]
CD$_3$[f]		1.7		Low	28
CH$^{\alpha}_2$CH$^{\beta}_3$	2.4, 2.5	2.5	High	Low	29
	0.8, 1.3, 1.8	1.9	High	Low	30
	2.6, 1.1, 3.0	3.1	High	Low	37
C(CH$_3$)$_3$	1.2	2.6	High	Low	24
CH$_2$C$_6$H$_5$		2.5		Low	31
C$_6$H$_5$		1.2		Low	28
p-CH$_3$C$_6$H$_4$		1.4		Low	30
p-CH$_3{}^{\alpha}$O-C$_6$H$^{\beta}_4$	0.8, 2.5[g]	1.8	High	Low	29
α-Napthyl		1.3		Low	31

[a] The sulfoxides were prepared[7b] from a single batch of (−)-(*R*)-menthyl methanesulfinate of 28% diastereomeric purity,[7b] in each case using *ca.* 1 mol excess of the appropriate Grignard reagent except for dimethyl-1,1,1-d_3 sulfoxide, where a 20% excess of methyl-d_3-magnesium iodide was employed. The sulfoxides have physical and spectral properties consistent with their assigned structures. [b] Nmr spectra were measured on a Varian HA-100 spectrometer at 28° using samples composed of 2:1:*ca.* 3 mol ratios of alcohol:sulfoxide:carbon tetrachloride or fluorotrichloromethane, respectively. [c] Chemical shift differences (±0.1 Hz) are for the α, β, ... protons, respectively. Proton resonances for which no Δδ is reported were either obscured by other resonances or exhibited unresolvable chemical shift differences. [d] In each case where more than one proton in the alkyl (or aryl) group exhibits a chemical shift difference, the sense of nonequivalence is the same as that for other protons within the group. [e] Optical purities (±1%) calculated from the relative peak heights of the enantiomeric methanesulfinyl resonances. [f] Dimethyl-1,1,1-d_3 sulfoxide, previously unreported, was characterized by its elemental analysis, its infrared spectrum, and its proton and deuterium nmr spectra. Based on its observed optical rotation, enantiomerically pure material would have an $[\alpha]^{25}\text{D}$ −3.8° (neat). This sample was shown by vpc to contain less than 0.05% menthol, menthone, or menthyl methanesulfinate, and to contain less than 0.1% of any impurity other than water. [g] Observed for the high-field portion of the AA′BB′ aromatic multiplet.

arises by the formation of short-lived, hydrogen-bonded diastereomeric solvates.[10] When (−)-(*S*)-α-methylbenzylcarbinol (**4**), less acidic than **2**,[11] is used as a solvent for methyl *t*-butyl sulfoxide, the magnitude of nonequivalence is reduced by a factor of *ca.* 1.5, consistent with weaker solvent–solute association, although other factors may also be involved.

The nonequivalence of the nmr spectra of the enantiomers of type **1** sulfoxides in optically active **2** is quite general, as shown by Table I. The power of the method is strikingly demonstrated by the direct determination of the optical purity of a partially resolved sample of dimethyl-1,1,1-d_3 sulfoxide, a compound which is asymmetric only by virtue of isotopic substitution.[12]

An inspection of Table I suggests that the degree of spectral nonequivalence depends upon the extent of association and upon relative population levels of various conformers.[13] For example, the alkyl aryl sulfoxides generally show a smaller Δδ for the methanesulfinyl group than do the more basic dialkyl sulfoxides, while among the substituted methyl phenyl sulfoxides studied, an increasing $\Delta\delta_{\text{SOCH}_3}$ is observed in the order of increasing basicity.[14]

Since the partially resolved sulfoxides in Table I were prepared by the action of an excess of the appropriate Grignard reagent upon portions of a single batch of a 1.78:1.00 mixture of the diastereomeric (*R* configuration at sulfur in excess)[15] (−)-menthyl methanesulfinates (**3**), all of the major enantiomers should have the same absolute configuration (*i.e.*, *R*),[15] although they need not necessarily have identical optical purities.[16]

Further inspection of Table I reveals that in (−)-**2** the partially resolved methyl-substituted sulfoxides all exhibit low-field senses of nonequivalence for the methanesulfinyl resonances and high-field senses of nonequivalence for the resonances of the remaining alkyl or aryl substituents.[17] Contrasting senses of nonequivalence have been previously observed and rationalized[1,18] for other solutes in optically active solvents. In the present instances, the reliability of the correlation between the senses of nmr nonequivalence and sulfoxide absolute configuration suggests that the method may be safely extended and used to assign absolute configurations to methyl sulfoxides of unknown stereochemistry similar to those in Table I. The effect which added functional groups in the sulfoxides will have upon nonequivalence sense has not yet been ascertained.

Acknowledgments. This work was supported by Grant No. GM 14518 from the U. S. Public Health Service. We wish to thank Dr. R. W. Woody for obtaining the ORD spectrum of dimethyl-1,1,1-d_3 sulfoxide.

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(10) A similar explanation has been recently proposed [F. A. L. Anet, L. M. Sweeting, T. A. Whitney, and D. J. Cram, *Tetrahedron Lett.*, 2617 (1968)] to account for the nmr spectral nonequivalence of enantiomeric alkylarylcarbinols in suitable optically active sulfoxides.

(11) The pK_a of **2** is 11.9 [R. Stewart and R. Van der Linden, *Can. J. Chem.*, **38**, 399 (1960)].

(12) Isotopic exchange of dimethyl-1,1,1-d_3 sulfoxide with alcohol **2** is negligible, since no change in optical purity (by nmr) was observed for the partially resolved sulfoxide in (−)-**2** over a period of several weeks.

(13) The magnitudes of the enantiomeric chemical shift differences may be enhanced by lowering the temperature or by increasing the alcohol concentration.

(14) K. K. Andersen, W. H. Edmonds, J. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966), have determined the apparent pK_a values for several substituted methyl phenyl sulfoxides, obtaining values of −0.488, 0.014, and 0.55 for phenyl, *p*-tolyl, and *p*-anisyl methyl sulfoxides, respectively. The pK_a for dimethyl sulfoxide is 0.911.

(15) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, 90, 4835 (1968).

(16) In view of the recent work of Mislow and coworkers[15] demonstrating the nearly complete stereospecificity of the Andersen synthesis, it would appear that kinetic resolution is responsible for any significant deviations of optical purities of the sulfoxides in Table I from the 28% diastereomeric purity of sulfinate ester **3**.

(17) Significantly, these same senses of nonequivalence are also observed in (−)-**4**, which is known to have the same stereochemistry as does (−)-**2**.[18]

(18) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **89**, 5485 (1967), and references cited therein.

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The Photochemistry of 2,7-Cyclooctadienone

Sir:

Cross-conjugated cyclohexadienones have received great attention as photochemical substrates in both