will prove to be the first example of a planar cyclooctatetraene ring.[10]

Acknowledgment. We wish to thank Professor E. Vogel for making the data of ref 9 available to us. The support of the NSF is also gratefully acknowledged.

(10) X-Ray analysis of **5** is being pursued.

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Axial Pseudoasymmetry in Sulfenamides. A Method for Assignment of Configuration to *meso* and *dl* Secondary Amines[1]

Sir:

Molecules containing pseudoasymmetric carbon atoms have been objects of interest to organic stereochemists for many years.[2] Although planar and axial pseudoasymmetries were discussed some time ago,[2d] it has been only recently that examples of planar and axial pseudoasymmetry have been reported.[3,4] Planar pseudoasymmetry has been investigated in the ferrocene[3] and cyclophane[4] systems, and axially pseudoasymmetric biphenyls[4] have been reported. In the present paper we wish to report the first example of axial pseudoasymmetry in the S–N bond in a sulfenamide and to demonstrate the application of sulfenamide pseudoasymmetry in making unambiguous configurational assignments to the *meso* and *dl* diastereomers of secondary amines.

The considerable torsional barrier at the S–N bond in 2,4-dinitrobenzenesulfenamides renders the sulfenamide bond a chiral axis in sulfenamides of the general form $RSNR^1R^2$ ($R = 2,4\text{-}(NO_2)_2C_6H_3$, $R^1 \neq R^2$).[5] In such compounds torsion about the S–N bond effects racemization and rates of degenerate racemization can be measured by D nmr spectroscopy. When one of R^1 and R^2 is chiral, torsional diastereomerism is possible and is manifest in nmr[1,6,7] and ORD–CD spectra.[7] It was of interest to us to examine sulfenamides wherein R^1 and R^2 are identical or enantiomeric chiral substituents. In the latter case the sulfenamide bond is an element of axial pseudoasymmetry while in the former it is neither an asymmetric nor a pseudoasymmetric axis.

The two amines chosen for this study were the *meso* and *dl* isomers of bis-α-phenylethylamine (**1**).[8] Conversion to the 2,4-dinitrobenzenesulfenamides (**2**) was accomplished by reaction with 2,4-dinitrobenzenesulfenyl chloride.[9]

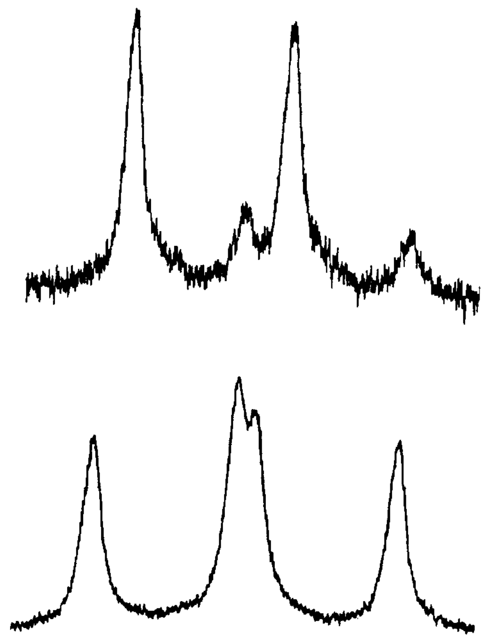


Figure 1. Portions of the nmr spectra of **2** (in $CDCl_3$ at 50°) featuring resonances due to the *C*-methyl groups: upper curve, *meso*-**2**; lower curve, *dl*-**2**.

The sulfenamide axis is a unit of pseudoasymmetry in *meso*-**2**, and torsion about the S–N bond converts one *meso* diastereomer into another. The presence of pseudoasymmetry is readily apparent in the nmr spectrum of *meso*-**2** (Figure 1). Two *C*-methyl doublets are present in a ratio of 4.5:1, the equilibrium constant for interconversion of the *R* and *S meso* isomers.[10] Each *meso* isomer gives rise to only one *C*-methyl doublet since the two methyl groups in each isomer lie on opposite sides of the σ plane and are enantiotopic. The nmr spectrum of *dl*-**2** also features two *C*-methyl doublets with identical integrated intensities.[10] There is only one diastereomer present, since rotation about the S–N bond does not generate a new isomer. However, *dl*-**2** possesses no symmetry elements and the two *C*-methyl groups are diastereotopic.

When the temperature is increased so that torsion about the S–N bond becomes rapid on the nmr time scale, coalescence is observed.[11] The free energies of

(1) Stereochemistry in Trivalent Nitrogen Compounds. XVII. Part XVI: M. Raban, E. H. Carlson, S. K. Lauderback, J. M. Moldowan, and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, in press.

(2) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 28; (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, p 91; (c) H. Hirschmann and K. R. Hanson, *J. Org. Chem.*, **36**, 3293 (1971); (d) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem.*, 78, 413 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

(3) S. J. Goldberg and W. D. Bailey, *J. Amer. Chem Soc.*, **93**, 1046 (1971).

(4) G. Helmchen, quoted in V. Prelog, *Chem. Brit.*, **4**, 382 (1968); 21st Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, 1969, Abstracts, pp 82–84.

(5) (a) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969). (b) M. Raban and F. B. Jones, Jr., *ibid.*, **93**, 2692 (1971).

(6) M. Raban, G. W. J. Kenney, Jr., J. M. Moldowan, and F. B. Jones, Jr., *ibid.*, **90**, 2985 (1968).

(7) M. Raban and S. K. Lauderback, *ibid.*, **93**, 2781 (1971).

(8) The two isomers were isolated from their commercially available mixture (Aldrich) by fractional crystallization of the benzoate salts from isopropyl alcohol: *meso*-**1** benzoate, mp 104–106°; *dl*-**1** benzoate, mp 135–136°. The commercial mixture was found by nmr to be composed of 65% of the *dl* isomer in which the *C*-methyl doublet resonates at higher field and 35% of the *meso* isomer. The configurational assignments were made on the basis of the nmr spectra of the 2,4-dinitrobenzenesulfenamides, *vide infra*.

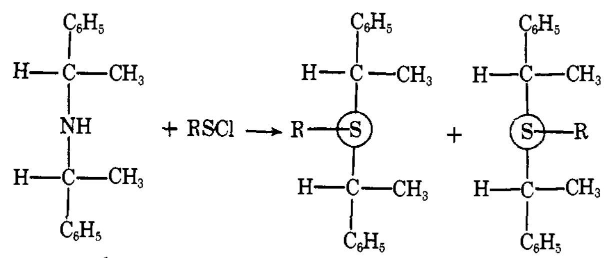
(9) All new compounds had satisfactory elemental analyses and spectral data were in accord with assigned structures: *meso*-**2**, mp 187–188°; *dl*-**2**, mp 133–134°.

(10) The two *meso*-**2** doublets were centered at δ 1.53 (J_{vic} = 6.7 Hz) (major isomer) and 1.45 (J_{vic} = 7.0 Hz) (minor isomer); the two *dl*-**2** doublets were centered at δ 1.40 (J_{vic} = 6.6 Hz) and 1.49 (J_{vic} = 6.6 Hz).

(11) Although the type of conformational change, torsion about the S–N bond, and the consequences in the nmr spectra are the same for both *dl*-**2** and *meso*-**2**, the stereochemical descriptions of the events associated with coalescence are distinct. Coalescence in the spectrum of *meso*-**2** is associated with the rapid reversible interconversion of two diastereomers and the coalescing peaks correspond to methyl groups in different molecules. On the other hand, the coalescence in *dl*-**2** is a topomerization[12] and the coalescing peaks derive from methyl groups in the same molecule.

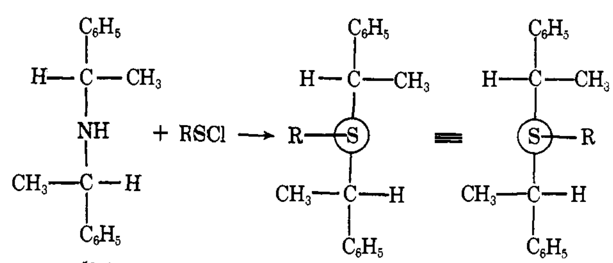
activation at the coalescence point, which can be accurately determined using approximate equations or calibration curves,[13] were comparable in the two compounds. The barrier in *dl*-**2** was found to be intermediate between the free energies of activation for the forward and reverse interconversions of the two diastereomers of *meso*-**2**: *dl*-**2**, $\Delta\nu$ = 5.6 Hz, T_c = 91°, $\Delta G^{\ddagger}$ = 19.6 kcal/mol; *meso*-**2**, $\Delta\nu$ = 4.6 Hz, T_c = 86°, $\Delta G^{\ddagger}$(forward) = 19.5 kcal/mol, $\Delta G^{\ddagger}$(reverse) = 20.5 kcal/mol.

The presence of pseudoasymmetry in *meso*-**2** provides a convenient and unequivocal means for the assignment of configuration to *meso*-**1**. Such a method complements that of Hill and Chan[14] which permits unequivocal assignment of configuration to the *dl* isomer. In the present instance, the *N*-benzyl derivative of *dl*-**1** (prepared by reduction of the benzamide) features an AB quartet for the *N*-benzylmethylene protons: $\Delta\nu_{AB}$ = 0.45 ppm, J_{AB} = 15 Hz. The present method offers a useful alternative or supplement to the method of Hill and Chan when both isomers are not available or in instances when the latter method is not successful.[15]



meso-**1** (*R*)-**2** (*S*)-**2**

meso-**2**



dl-**1** *dl*-**2**

R = 2,4-dinitrophenyl

(12) G. Binsch, E. L. Eliel, and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 10, 570 (1971).
(13) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).
(14) R. K. Hill and T.-H. Chan, *Tetrahedron*, **21**, 2015 (1965).
(15) We thank the National Science Foundation for support of this work.

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Primary Amine Catalysis of the Cleavage of Mesityl Oxide to Acetone

Sir:

In the course of a previous investigation[1] of primary amine catalysis of the dealdolization of diacetone alcohol, we found that mesityl oxide (an impurity in commercial diacetone alcohol) reacts rapidly in moderately basic solution with *n*-propylamine. Although this reaction had previously been observed[2] with ethylamine, neither characterization of the product nor investigation of the reaction mechanism was attempted. We now wish to report that this reaction is the primary amine catalysis of the cleavage of mesityl oxide to acetone, and furthermore, that the mechanism does *not* involve the intermediate formation of diacetone alcohol.

On adding mesityl oxide to a solution of *n*-propylamine in water, a biphasic reaction may be observed,[3] consisting of an initial, rapid first-order decay of mesityl oxide, followed by a slower first-order decay until no detectable mesityl oxide is left. The rate constants for both reactions increase with increasing concentration of amine. In addition, the pseudoequilibrium reached at the end of the first decay is proportional to the concentration of the amine. It is important to note that the kinetics require one molecule of amine as a reactant for the first step and a second molecule of amine as a catalyst for the second step. This type of kinetic behavior may be analyzed in terms of eq 1. Values of the

$$\text{mesityl oxide} + \text{amine} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{intermediate} \xrightarrow{k_2[\text{amine}]} \text{acetone} + \text{amine} \quad (1)$$

pseudoequilibrium constant K (= [intermediate]/[mesityl oxide][amine]) calculated from initial and infinity absorbances for the first decay were found to vary little over a wide pH range (Table I). The fact that these values are essentially invariant over a pH range of more than 1 pH unit on each side of the pK_a of *n*-propylamine (pK_a = 10.9)[1] indicates that not only does the intermediate have the elements of the amine in it but that it has a pK_a very similar to *n*-propylamine itself.

Table I. Variation with pH of Observed Equilibrium Constants for Formation of the Michael Adduct from Mesityl Oxide and *n*-Propylamine[a]

pH	K
9.59	11.4 ± 1.5
10.00	11.4 ± 1.0
10.42	15.4 ± 0.3
10.80	19.0 ± 1.1
11.36	19.4 ± 2.8
11.76	21.2 ± 2.6
12.42	23.1 ± 2.0

[a] Equilibrium constants were calculated using the *total* amine concentration.

The intermediate was identified as the Michael adduct of *n*-propylamine and mesityl oxide by a consideration of the following changes in the nmr spectrum as the reaction proceeds. Mesityl oxide shows a spectrum consisting of four singlets at δ 6.1 (1 H), 2.1 (3 H), 2.0

(1) R. M. Pollack and S. Ritterstein, *J. Amer. Chem. Soc.*, in press.
(2) R. W. Hay and K. R. Tate, *Aust. J. Chem.*, **19**, 1651 (1966).
(3) The reaction was monitored spectrophotometrically by following the loss of mesityl oxide at 243 nm. The concentration of mesityl oxide was approximately 2 × 10^{-4} *M*. The pH was maintained by using *n*-propylamine and its hydrochloride as a buffer at the lower pH values and by addition of KOH at higher pH. The temperature was kept at 25.0 ± 0.2° and potassium chloride was added where necessary to maintain an ionic strength of 0.2.