

oxy)prop-2-enyl]-2-enyl]cyclopent-1-ene-1-carboxaldehyde, 86902-47-8; 5-(1,1-dimethylethyl)-2-(α -methoxy- β -oxopropyl)-cyclohex-1-ene-1-carboxaldehyde, 86902-48-9; 5-(1,1-dimethylethyl)-2-(α -ethoxy- β -oxopropyl)cyclohex-1-ene-1-carboxaldehyde, 86902-49-0; 5-(1,1-dimethylethyl)-2-[α -(methoxymethoxy)- β -oxopropyl]cyclohex-1-ene-1-carboxaldehyde, 86902-50-3; 3-methyl-2-(α -ethoxy- β -oxopropyl)cyclohex-1-ene-1-carboxaldehyde, 86902-51-4; 2-(α -ethoxy- β -oxopropyl)cyclohept-1-ene-1-carboxaldehyde, 86902-52-5; 2-(α -ethoxy- β -oxopropyl)cyclododec-1-ene-1-carboxaldehyde, 86902-53-6; 3,4-dihydro-1-(α -ethoxy- β -oxopropyl)naphthalene-2-carboxaldehyde, 86902-54-7; 3,4-dihydro-1-[α -(methoxymethoxy)- β -oxopropyl]naphthalene-2-carboxaldehyde, 86902-55-8; 3,4-dihydro-6-methoxy-1-(α -methoxy- β -oxopropyl)naphthalene-2-carboxaldehyde, 86902-56-9; 2-[α -(methoxymethoxy)- β -oxopropyl]cyclopent-1-ene-1-carboxaldehyde, 86902-57-0; 5,6,7,8-tetrahydro-6-(1,1-dimethylethyl)-1-methoxynaphthalen-2-ol, 86902-58-1; 5,6,7,8-tetrahydro-6-(1,1-dimethylethyl)-1-ethoxynaphthalen-2-ol, 86902-59-2; 5,6,7,8-tetrahydro-6-(1,1-dimethylethyl)-1-(methoxymethoxy)naphthalen-2-ol, 86902-60-5; 5,6,7,8-tetrahydro-8-methyl-1-methoxynaphthalen-2-ol, 86902-61-6; 5,6,7,8,9-pentahydro-1-ethoxybenzocyclohepten-2-ol, 86902-62-7; 5,6,7,8,9,10,11,12,13,14-decahydro-1-ethoxybenzocyclododecen-2-ol, 86902-63-8; 9,10-dihydro-4-ethoxyphenanthren-3-ol, 86902-64-9; 9,10-dihydro-4-methoxymethoxyphenanthren-3-ol, 86902-65-0; 9,10-dihydro-4,7-dimethoxyphenanthren-3-ol, 86902-66-1; 2,3-dihydro-4-methoxymethoxy-1(*H*)-inden-5-ol, 86902-67-2; 4-(1,1-dimethylethyl)-2-[[trimethylsilyloxy]methylene]-1-(α -methoxyprop-2-enyl)cyclohexan-1-ol, 86902-68-3; 4-(1,1-dimethylethyl)-2-[[trimethylsilyloxy]methylene]-1-(α -ethoxyprop-2-enyl)cyclohexan-1-ol, 86902-69-4; 4-(1,1-dimethylethyl)-2-[[trimethylsilyloxy]methylene]-1-[α -methoxymethoxy]prop-2-enyl]cyclohexan-1-ol, 86902-70-7; 6-methyl-2-[[trimethylsilyloxy]methylene]-1-[α -(methoxymethoxy)prop-2-enyl]cyclohexan-1-ol, 86902-71-8; 2-[[trimethylsilyloxy]methylene]-1-(α -ethoxyprop-2-enyl)cycloheptan-1-ol, 86902-72-9; 2-[[trimethylsilyloxy]methylene]-1-(α -ethoxyprop-2-enyl)cyclododecan-1-ol, 86902-73-0; 1,2,3,4-tetrahydro-2-[[trimethylsilyloxy]methylene]-1-(α -ethoxyprop-2-enyl)naphthalen-1-ol, 86902-74-1; 1,2,3,4-tetrahydro-2-[[trimethylsilyloxy]methylene]-1-[α -(methoxymethoxy)prop-2-enyl]naphthalen-1-ol, 86902-75-2; 1,2,3,4-tetrahydro-6-methoxy-2-[[trimethylsilyloxy]methylene]-1-(α -methoxyprop-2-enyl)naphthalen-1-ol, 86902-76-3; 2-[[trimethylsilyloxy]methylene]-1-[α -(methoxymethoxy)prop-2-enyl]cyclopentan-1-ol, 86902-77-4; 4-(1,1-dimethylethyl)-2-(hydroxymethylene)cyclohexanone, 22252-96-6; 6-methyl-2-(hydroxymethylene)cyclohexanone, 15409-53-7; 2-(hydroxymethylene)cycloheptanone, 934-20-3; 2-(hydroxymethylene)cyclododecanone, 949-07-5; 1,2,3,4-tetrahydro-2-(hydroxymethylene)naphthalene-1-one, 40685-04-9; 1,2,3,4-tetrahydro-6-methoxy-2-(hydroxymethylene)naphthalen-1-one, 16252-53-2; 2-(hydroxymethylene)cyclopentanone, 930-91-6; allyl methyl ether, 627-40-7; allyl ethyl ether, 557-31-3; allyl methoxymethyl ether, 62322-45-6.

Supplementary Material Available: NMR, IR, and MS data for the products of Table I (3 pages). Ordering information is given on any current masthead page.

Relative Stabilization of an Iminium Ion by the Charge-Transfer Interaction of Arylthio Groups

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The evidence for an intramolecular charge-transfer (CT) interaction between a sulfide sulfur atom and a neighboring iminium ion has been reviewed for the thiaspirane class of alkaloids and their analogues.¹ The same review

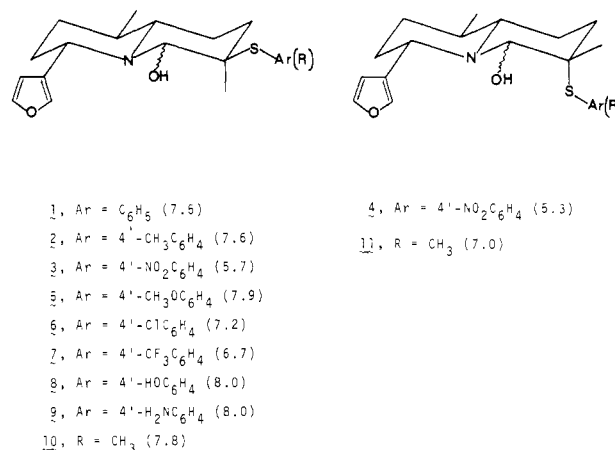
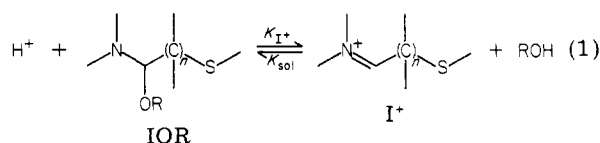


Figure 1. α -Thio hemiaminal derivatives of deoxynupharidine whose K'_{1+} values have been determined. K'_{1+} values are given in parentheses.

points out the usefulness of CT-circular dichroism (CD) in measuring the extent to which iminium ions are stabilized against solvolysis by the CT interaction with sulfur. Thus a reflection of this stabilization is $\log K'_{1+}$ whose meaning follows from its derivation from the equilibrium reaction in eq 1 and expression 2. Arguments were given



$$K'_{1+} = \frac{[\text{HOR}][\text{I}^+]}{[\text{IOR}][\text{H}^+]} \quad (2)$$

$$\log K'_{1+} = \text{pH}_{1/2} \quad (3)$$

for reducing expression 2 to 3 wherein $\text{pH}_{1/2}$ represents the pH at which one-half of the original hemiaminal (IOR) was converted to iminium ion (I^+). Furthermore, it was demonstrated that a plot of the molecular ellipticity, $[\theta]$, against pH yielded S-shaped curves from which the value of $\text{pH}_{1/2}$ (or $\log K'_{1+}$) could be determined.¹ This paper concerns the extension of these measurements to several α -(arylthio)hemiaminal derivatives, 1-9 (Figure 1), of deoxynupharidine. Their preparation was reported earlier.² The study was undertaken to ascertain if additional stabilization to solvolysis would result from attaching electron-donating aryl substituents to sulfur. Possibly such substitution would enhance the electron availability at the interacting sulfur atom. The values of $\log K'_{1+}$ are compared by way of a Hammett $\rho\sigma$ analysis³ in order to assess the relative stabilization of the various aryl groups attached to the sulfur atom. Additional comparisons are made to the $\log K'_{1+}$ values previously reported¹ for the methylthio derivatives 10 and 11.

A plot of the $\log K'_{1+}$ values against σ_p^4 for eight α -(arylthio) hemiaminal derivatives of deoxynupharidine is shown in Figure 2. Least-squares analysis of all the points gives a slope (ρ) of -1.56 with a correlation coefficient (r) of 0.9467. Two points, that for the *p*-NH₂ and that for the *p*-NO₂ substituents, appear to be responsible for the low value of r . The variance of the former point can be at-

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(2) LaLonde, R. T.; Eckert, T. S. *Can. J. Chem.* 1981, 59, 2298.

(3) Hammett, L. P. "Physical Organic Chemistry", 1st ed.; McGraw Hill: New York, 1941; pp 184-207.

(4) Values of σ_p were taken from the following: Ritchie, C. D.; Sager, W. F. In "Progress in Physical Organic Chemistry"; Cohen, S. C., Streitwieser, A., Taft, R. W., Eds.; Interscience: New York, 1964; Vol. 2, p 323.

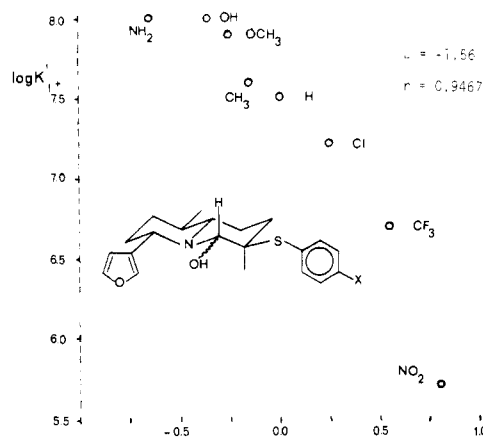


Figure 2. A plot of $\log K'_{1+}$ against σ_p (○) and σ_p^- (□) for para-substituted α -(arylthio) hemiaminal derivatives (1-9) in 70% methanol-water solution at 25 °C. Points are designated according to the para substituent (X) of the arylthio group.

tributed to too low a σ_p value, one which fails to account for the protonation of the NH_2 group in acidic solution. The variance of the point for the p - NO_2 derivative (3) can be attributed to the delocalization of electrons from the sulfur atom toward the nitro group. If σ_p for the p -nitro group is replaced by σ_p^- , proposed for reactions in which electron withdrawal of the substituent is greater than that of the usual resonance interaction,⁵ and the point for the p - NH_2 compound is omitted, a much better linear correlation results for seven points; $\rho = -1.42$ and $r = 0.9976$ are obtained.

Clearly the sign of ρ indicates stabilization of the CT iminium ion resulting from para electron-donating aryl groups attached to the sulfur atom. The magnitude of ρ indicates an involvement of sulfur similar to this element's stabilization of cationic intermediates produced during the solvolysis of various β -chloroethyl sulfides. By way of comparison, ρ values of -1.671 ,⁶ -1.398 ,⁷ and -1.431 ⁷ have been determined from the solvolysis rates of β -chloroethyl, *trans*-2-chlorocyclopentyl, and *trans*-2-chlorocyclohexyl aryl sulfides, respectively. Also instructive is the comparison of the $\log K'_{1+}$ value for the methylthio, 10, with the $\log K'_{1+}$ values for the arylthio groups (2, 5, 8, 9) that are capable of strong electron release by way of resonance. All are nearly the same. A final noteworthy comparison is the larger $\log K'_{1+}$ value for the β -thio diastereomer, 3 (β used in the usual stereochemical sense), compared to its α counterpart, 4. The result is in agreement with an earlier finding¹ regarding $\log K'_{1+}$ values for 10 and 11, a finding that was rationalized in terms of greater resistance to solvolysis from the α surface of the iminium ion than the less hindered β surface.

Experimental Section

The pH of a solution of the α -(thioaryl) hemiaminal, 0.10–0.21 mg/mL in 70% methanol-water, was adjusted with solid NaOAc or KOH to its highest level, as determined with a pH meter, and the CD was determined from 250 to 400 nm with a Jasco Model 5 spectropolarimeter. The pH was adjusted downward in increments with HOAc, and the pH and CD were determined after each increment. For each set of CDs, a CT peak was chosen that was furthest removed from the aryl absorptions observed at the highest pH. The $[\theta]$ values were calculated for this peak at each pH. Plots of pH vs. $[\theta]$ were made, and the value of $\text{pH}_{1/2}$ was

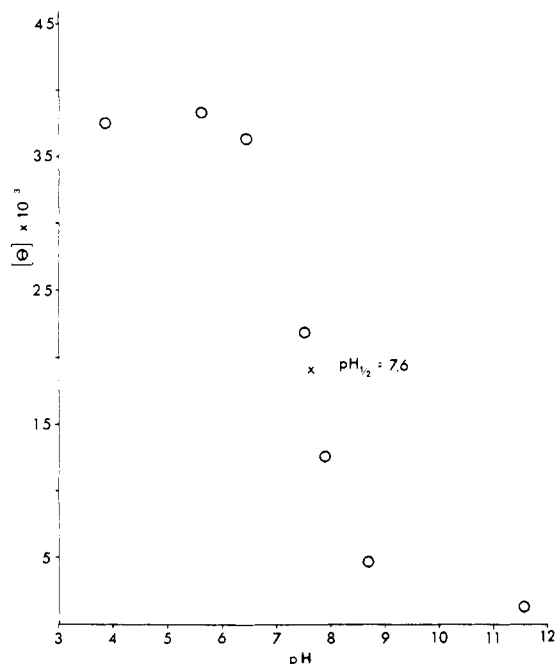


Figure 3. A plot of the charge-transfer molecular ellipticity, $[\theta]$, $\times 10^{-3}$ in degree/mole for the 300-nm band vs. pH for (*R*)-6-[(4-methylphenyl)thio]deoxynupharidin-6-ol, 2, in 70% methanol-water solution at 25 °C.

taken from the resulting S-shaped curve as half the difference of the maximum $[\theta]$ at the lowest pH and the minimum $[\theta]$ at the highest pH. An example of such a plot is shown in Figure 3.

Registry No. 1, 57897-34-4; 1 iminium ion, 57897-40-2; 2, 59187-39-2; 2 iminium ion, 86994-05-0; 3, 86994-00-5; 3 iminium ion, 87011-62-9; 4 iminium ion, 87011-63-0; 5, 86994-01-6; 5 iminium ion, 87011-64-1; 6, 86994-02-7; 6 iminium ion, 86994-06-1; 7, 86994-03-8; 7 iminium ion, 86994-07-2; 8, 87011-61-8; 8 iminium ion, 86994-08-3; 9, 86994-04-9; 9 iminium ion, 86994-09-4.

2-Mercapto-1,3-benzoxazole: A Useful Reagent for the Preparation of Symmetrical and Unsymmetrical Sulfides

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One of the most commonly used methods for the preparation of mixed sulfides is the alkylation of thiols.¹ This approach is straightforward if the thiol starting materials are readily available. However, when the thiols must be prepared by synthesis, the procedure becomes less satisfactory, owing to the wide variations in thiol yields and the unpleasant odors accompanying these preparations.

We report a novel, convenient, and odorless procedure for the synthesis of sulfides which takes advantage of the base lability of 2-(alkylthio)-1,3-benzoxazole derivatives (1, BoxSR, Scheme I). In the presence of sodium hydroxide and a halide (RX), 1 functions as a sulfur-transferring agent to provide sulfides 2 and 4 in good yields.²

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