$[C_{12}H_{16}]^+$ (3.1), 121 $[C_{12}H_{16} - Me]^+$ (5.8), 41, (100). The spectra also display similar hydrocarbon fragmentation patterns with strong peaks that are characteristic of alkyl groups (43, 57, 71, 85), alkenyl groups (41, 55, 69, 83), pinane (77, 79, 93, 121), and α-pinene (79, 81, 95, 119, 121).

A similarity in mass spectra is also apparent between *exo*-2-norborneol (*m/z* (relative intensity) 95 $[M - OH]^+$ (82.4), 93 $[C_7H_9]^+$ (21.1), 67 $[C_5H_7]^+$ (98.9), along with strong alkyl (43, 57, 71, 85) and alkenyl (41, 55, 69, 83) peaks) and the corresponding chloride.[20b]

Radical Quenching Reactions. Five millimoles of trihexylborane was added to 10 mL of pentane or THF in a 50-mL round-bottom flask. The solution was cooled to 0 °C, and a known amount of an internal standard (*n*-undecane) was added, followed by addition of 0.021 g (0.01 eq) or 0.21 g (0.10 equiv) of galvinoxyl (Aldrich). Then, 1.68 mL of *t*-BuOCl and 5.01 mL of 3 N NaOAc were added. The solution was allowed to stir at 0 °C for 6 h, and then it was extracted with ether. The ether layer was washed with water, dried over anhydrous $MgSO_4$, and analyzed by GC.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. This material is based upon work supported by the National Science Foundation. We are grateful to the Department of Chemistry, Oklahoma State University, for allowing usage of their polarimeter and particularly to Dr. Richard Bunce for arranging it.

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(25) CI mass spectral values for *exo*-2-norborneol have been given earlier (*m/z* (relative intensities) $[C_7H_9]^+$ (1.3), 95 $[M - OH]^+$ (83.4); 111 $[M - H]^+$ (2.6)). Jelus, B. L.; Dalrymple, D. L.; Michnowicz, J.; Munson, B. *Org. Mass Spectrom.* **1978**, *13*, 163–6.

Solvent and Temperature Dependence of the Anomeric Effect in 2-[(4-Methoxyphenyl)seleno]-1,3-dithianes. Dominance of the Orbital Interaction Component

B. Mario Pinto,* Blair D. Johnston, and Ruby Nagelkerke

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, V5A 1S6 Canada

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The conformational equilibrium of 2-[(4-methoxyphenyl)seleno]-1,3-dithiane in three solvents at low temperature has been studied by ^{77}Se NMR spectroscopy. The equilibrium of the configurational isomers, *r*-2-[(4-methoxyphenyl)seleno]-*cis*-4,*cis*-6- and -*trans*-4,*trans*-6-dimethyl-1,3-dithiane, in the same solvents at higher temperatures has been studied by acid-catalyzed equilibration experiments. Plots of ln *K* vs $1/T$ using points from both types of experiments are linear, permitting evaluation of the enthalpic and entropic contributions to the S–C–Se anomeric effect in these derivatives. ΔH°_{eq-ax} values of -1.43 ± 0.24, -0.98 ± 0.21, and -1.59 ± 0.16 kcal mol^{-1}, and ΔS°_{eq-ax} values of -3.4 ± 1.0, -2.1 ± 1.0, and -4.8 ± 0.6 cal mol^{-1} K^{-1} in toluene, methylene chloride, and acetone, respectively, are obtained. Uncertainties in the parameters are at the 95% confidence level. The preferential stabilization in enthalpy terms of the axial isomer in acetone vs methylene chloride and its destabilization in entropy terms is interpreted in terms of the dominance of $n_s \rightarrow \sigma^*_{C-Se}$ orbital interactions over dipolar interactions, leading to a polar "double-bond no-bond" structure. Interestingly, the equilibrium in chloroform is almost isoenthalpic, $\Delta H^\circ_{eq-ax} = +0.04$ kcal mol^{-1} and ΔS°_{eq-ax} is positive (+1.5 cal mol^{-1} K^{-1}). The latter results are attributed to specific hydrogen bonding effects, which favor the equatorial isomer enthalpically and the axial isomer entropically.

Introduction

We have recently reported[1,2] the effects of substitution on the conformational equilibria of 2-[(4-substituted-phenyl)seleno]-1,3-dithianes. The results constituted systematic experimental evidence for stabilizing orbital interactions operating in S–C–Se fragments and for the existence of the S–C–Se anomeric effect. However, our preliminary attempt[2] to evaluate the relative importance of orbital-interaction effects and electrostatic effects by studying the effect of solvent on the conformational free energies was unsuccessful because it yielded anomalous results. For example, an increase in the proportion of the less polar axial conformer was observed in the more polar solvent, acetone, relative to that in methylene chloride. The result was surprising, considering that the more polar medium is predicted[3] to minimize dipolar interactions and to increase the proportion of the more polar equatorial conformer. Two tentative explanations were proposed[2] to account for this behavior: (1) that the conformer with the smaller molar volume (the axial conformer) should increase in the more polar solvent owing to higher internal pressure exerted by the solvent[4] and (2) that the more polar double-bond no-bond structure, resulting from a dominance of orbital interactions in the axial conformer, will be stabilized in the more polar solvent.[5] Although it is tempting to accept the latter explanation, detailed arguments based on conformational free energies and not conformational free enthalpies must be made with caution since it is the latter values that are most readily correlated with electronic effects of this type.[6a] Indeed Booth et al.[6a] in their recent investigation of the enthalpic and entropic contributions to the endo and exo anomeric effect in 2-sub-

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stituted tetrahydropyrans have stressed that it is the $\Delta H°$ values that correlate with steric and polar interactions. We therefore deemed it necessary to perform rigorous studies of this nature on our S–C–Se system especially since the presence of significant anomeric interactions in X–C–Y systems containing second-row and lower row elements,[7] and their origin[8] has been questioned recently.

We present herein a detailed study of the solvent and temperature dependence of the equilibria in 2-[(4-methoxyphenyl)seleno]-1,3-dithianes in order to evaluate the enthalpic and entropic contributions. We show that the less polar axial conformer is stabilized enthalpically in the more polar medium and attribute this result to a dominance of orbital-interaction effects.

Experimental Section

General Information. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. ^1H NMR (400.13 MHz) and ^{77}Se NMR (76.3 MHz) spectra were recorded on a Bruker WM-400 NMR spectrometer. ^{77}Se NMR spectra were measured on 0.11 M solutions in 90:10 mixtures of nondeuteriated–deuteriated solvents. Pulses of 9° with a repetition rate of 0.7 s were used. The spectra were obtained without ^1H decoupling since NOE effects are negligible in these derivatives.[9] The equilibrium constants were obtained by direct integration of the individual conformer resonances. Errors are the standard deviations of several integrations from several spectra. The temperatures were measured as described previously[1,2] and are believed to be accurate to ±2 K.

Analytical TLC was performed on precoated aluminum plates with Merck silica gel 60F-254 as the absorbent. The developed plates were air-dried, exposed to UV light and/or sprayed with 10% H_2SO_4 in ethanol, and heated to 100 °C. Flash column chromatography was performed on Kieselgel 60 (230–400 mesh) according to a published procedure.[10]

Solvents were distilled before use and were dried, as necessary, by literature procedures. Reactions were performed under nitrogen by use of standard Schlenk-tube techniques.

Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

***r*-2-[(4-Methoxyphenyl)seleno]-*cis*-4,*cis*-6-dimethyl-1,3-dithiane (3) and *r*-2-[(4-Methoxyphenyl)seleno]-*trans*-4,-*trans*-6-dimethyl-1,3-dithiane (4).** A solution of (4,4′-dimethoxydiphenyl)diselenide[11] (1.86 g, 5.00 mmol) in dry THF (30 mL) was treated with Na powder (0.243 g, 10.6 mmol) and benzophenone (30 mg) in an ultrasonic bath[12] for 70 min. The almost colorless selenolate suspension was cooled in an ice bath while a benzene solution of 2-chloro-4,6-dimethyl-1,3-dithiane[13] (11.6 mmol) was added. After 30 min at ice-bath temperature and a further 15 min at ambient temperature, the reaction mixture was poured into saturated ammonium chloride solution (75 mL) and extracted with ether. The ether extract was washed with water and saturated NaCl, dried ($MgSO_4$), and concentrated to yield an orange semicrystalline residue. Recrystallization from ether–hexane (1:1, 20 mL) and again from hexane (20 mL) gave 4 (1.27 g, 38%) as colorless needles. The combined mother liquors were concentrated and chromatographed on silica gel [hexane–ethyl acetate (50:1)] to yield pure 4[13] (0.87 g, 26%) and 3 (0.37 g, 11%). Recrystallization of 3 from hexane yielded an analytically pure sample as colorless needles (0.29 g, 9%), mp 84–86 °C. Anal. Calcd for $C_{13}H_{18}OS_2Se$: C, 46.84; H, 5.44. Found: C, 46.70; H, 5.45.

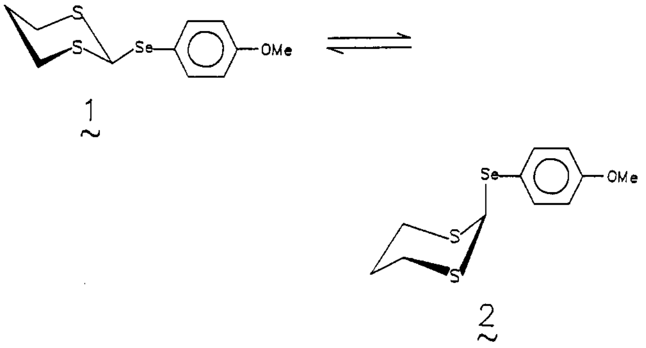
Chemical Equilibration of 3 and 4. A mixture of 3 or 4 (0.010 g) in the chosen dried solvent (3 mL) containing Amberlyst 15 ion-exchange resin (0.010 g)[14] and dried 4A molecular sieves, under nitrogen, was shaken or stirred in the dark in a temperature-controlled bath for the required time. Anhydrous K_2CO_3 was added, the samples were filtered through K_2CO_3, and the solvent was removed to give mixtures of 3 and 4, which were analyzed by ^1H NMR spectroscopy.

Analysis of Results. Thermodynamic parameters and errors were calculated from plots of ln K vs $1/T$ by the use of a weighted, nonlinear least-squares program. The equations for the algorithm underlying the program were obtained from Wolberg.[15] The program weights the equilibrium constants and temperatures in accordance with their estimated errors and specifically treats errors in both temperatures and rate constants. The statistical errors in $\Delta H°$ and $\Delta S°$ results from the uncertainties in K and assumed errors of ±1 and ±2 K in temperature measurement for the equilibration and NMR studies, respectively. The errors are quoted at the 95% confidence level.

Dipole Moment Measurements. The dielectric constants of dilute solutions of 3 and 4 in carbon tetrachloride at 293 K were measured by means of a variable-capacitance dielectric cell by using the heterodyne-beat method.[16] The refractive indices of the solutions were measured with a refractometer. The dipole moments of 3 and 4 were then derived as described by Shoemaker and Garland.[16]

Results

The conformational equilibrium in 2-[(4-methoxyphenyl)seleno]-1,3-dithiane was examined directly at the slow-exchange limit by ^{77}Se NMR spectroscopy. However, owing to restrictions placed upon the experiments by the freezing points of the solvents, the solubilities of the compounds, and the limited temperature range available for sampling at the slow-exchange limit, the conformational equilibrium 1 ⇄ 2 was assessed at only two temperatures (180 and 185 K) in methylene chloride, toluene, and acetone. In order to obtain information at higher temperatures, we initially considered the use of an approximate method of analysis that has recently been used[17] to evaluate the solvent effects on conformational equilibria of 2-substituted 1,3-dithianes. The method is based on the premise that chemical-shift differences between axial and equatorial protons ($\Delta\delta_{ax/eq}$) at C-4,6 in time-averaged spectra increase with increasing population of the axial conformers. The successful application of this method is not general, however, and rests upon the assumption that the corresponding chemical-shift differences in the extreme conformations, that is, at the slow exchange limit, remain



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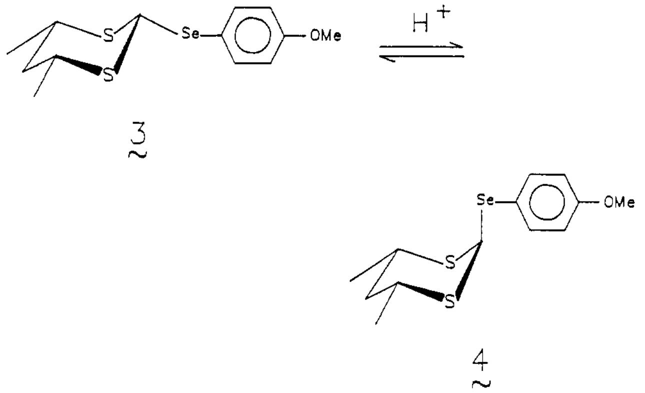
the same upon changes in solvent (or substituent, if such correlations are being sought). A general mathematical proof is given.[18] We have shown this assumption not to be valid for some of the 2-(arylseleno)-1,3-dithianes by examination of their low-temperature ^{1}H NMR spectra in $CFCl_3/CD_2Cl_2$ (80:20) and $CFCl_3/(CD_3)_2CO$ solvent mixtures. An extreme violation is also observed in the conformationally averaged spectra of these compounds in toluene in which specific solvent interactions lead to a marked shielding of H-4,6eq. Thus $\Delta\delta_{ax/eq}$ is not necessarily a sensitive probe of $\Delta G°$, and the method should be used with caution.

We turned, therefore, to the chemical equilibration of the configurational isomers, namely the 4,6-dimethyl derivatives **3** and **4**, to furnish reliable information at higher temperatures. This reasoning presumes that the configurational equilibrium **3** ⇄ **4** would serve as a good model for the conformational equilibrium **1** ⇄ **2** and that the results would be directly comparable. Indeed, this turned out to be the case (vide infra).



3

4

The configurational equilibrium **3** ⇄ **4** was assessed at 273 and 300 K in methylene chloride, toluene, acetone, and chloroform. Chemical equilibration of **3** and **4** was performed according to the procedure of Abraham et al.[14] with an acidic ion-exchange resin as catalyst. Chemical equilibrium was approached from both sides and was established in about 7 days at 300 K and about 14 days at 273 K. Equilibrations at lower temperatures were inconveniently slow, and attempts were frustrated by the decomposition of the substrates owing to the prolonged reaction times. Equilibrations at higher temperatures also resulted in significant decomposition. Equilibrium constants were readily obtained from the integration of the H-2 signals of the two isomers in the ^{1}H NMR spectra.[13] Experiments were repeated several times, and the errors reported are derived from the standard deviations of all measurements. The results are presented in Table I. The K values obtained from the equilibration experiments at 273 K are of similar magnitude to those obtained[2] in $CFCl_3/CD_2Cl_2$ (80:20) at 270 K by use of an approximate method of analysis. This observation supports the contention that the configurational isomers **3** and **4** are good models for **1** and **2**, respectively, and that comparison of data for both the conformational and configurational equilibria is meaningful. Indeed, plots of ln K vs $1/T$ (Figure 1) using data from both types of experiments are linear. Thermodynamic parameters, derived from these plots by use of a weighted nonlinear least-squares program, are listed in Table II.

The dipole moments of **3** and **4** were determined to be 3.23 ± 0.1 D and 2.13 ± 0.03 D, respectively. The relative

Table I. Equilibrium Data for Conformational Equilibrium 1 ⇄ 2 and Configurational Equilibrium 3 ⇄ 4

	K (error)			
solvent (ε)[a]	180[b] K	185[b] K	273[c] K	300[c] K
C_7H_8 (2.4)	9.9 (0.2)	9.1 (0.2)	2.42 (0.09)	2.10 (0.08)
$CHCl_3$ (4.7)			1.94 (0.02)	1.97 (0.09)
CH_2Cl_2 (8.9)	5.4 (0.1)	4.8 (0.2)	2.01 (0.07)	1.87 (0.08)
$(CH_3)_2CO$ (20.5)	8.1 (0.2)	6.8 (0.1)	1.68 (0.04)	1.34 (0.03)

[a] Values at 298 K; Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29. [b] For the conformational equilibrium **1** ⇄ **2**. [c] For the configurational equilibrium **3** ⇄ **4**.

Table II. Thermodynamic Parameters Derived from Data for Conformational Equilibrium 1 ⇄ 2 and Configurational Equilibrium 3 ⇄ 4

solvent (ε)[a]	ΔH° (error), kcal mol^{-1}	ΔS° (error), cal mol^{-1} K^{-1}
C_7H_8 (2.4)	-1.43 (0.24)	-3.4 (1.0)
$CHCl_3$ (4.7)	+0.04	+1.5
CH_2Cl_2 (8.9)	-0.98 (0.21)	-2.1 (1.0)
$(CH_3)_2CO$ (20.5)	-1.59 (0.16)	-4.8 (0.6)

[a] Values at 298 K; Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

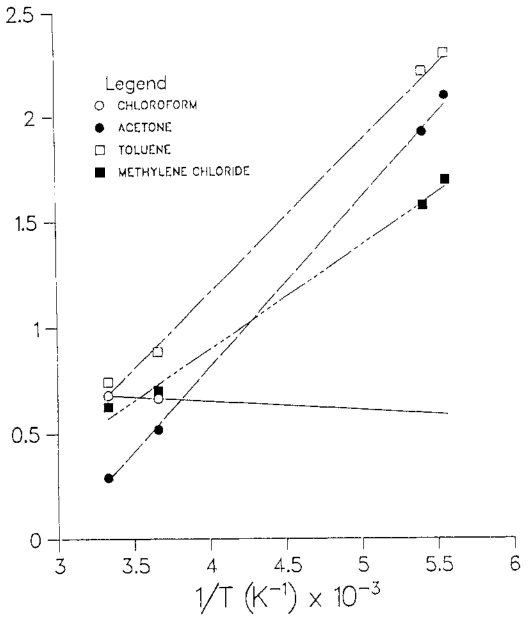


Figure 1. Plots of ln K vs $1/T$ using data from the conformational equilibrium **1** ⇄ **2** and the configurational equilibrium **3** ⇄ **4** in various solvents; data in $CHCl_3$ are only from equilibration studies of **3** and **4**. The plots show experimental points and the calculated lines.

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[18] Let A, E be δ of axial and equatorial protons of conformer X; a, e be δ of axial and equatorial protons of conformer Y.

$$\delta_1 = \text{average chemical shift of Ae}$$

$$\delta_2 = \text{average chemical shift of Ea}$$

$$\delta_1 = \delta_A([X]/[X] + [Y]) + \delta_e([Y]/[X] + [Y])$$

$$\delta_2 = \delta_E([X]/[X] + [Y]) + \delta_a([Y]/[X] + [Y])$$

$$\Delta\delta_1\delta_2 = \delta_1 - \delta_2 = \delta_A - \delta_E([X]/[X] + [Y]) + \delta_e - \delta_a([Y]/[X] + [Y])$$

Since [Y] = 1 − [X]

$$\delta_1 - \delta_2 = \{\delta_A - \delta_E[X] + \delta_e - \delta_a(1 - [X])\}/[X] + [Y]$$

$$= \delta_A - \delta_E[X] + (\delta_e - \delta_a) - (\delta_e - \delta_a)[X]$$

Therefore:

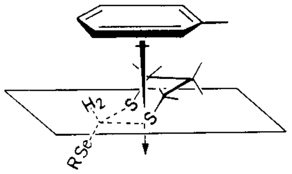
$$\Delta\delta_1\delta_2 = (\delta_A + \delta_a - \delta_E - \delta_e)[X] + (\delta_e - \delta_a)$$

as [X] varies from 0 → 1. If $\Delta\delta_1\delta_2$ is directly related to [X], then $\delta_e - \delta_a$ must be constant and therefore $\delta_A - \delta_E$ must also be constant.

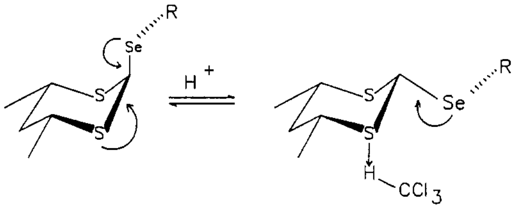
magnitudes are in accord with expectations based on the interaction of the ring dipole of the 1,3-dithiane ring[19] with the dipole associated with the C–Se bond (see below).

Discussion

The equilibrium data presented in Table I indicate that although no apparent correlation with the dielectric constant of the medium exists at low temperatures, the expected behavior is certainly manifested at higher temperatures. Thus, as the dielectric constant of the medium increases in the order toluene < methylene chloride < acetone, so does the proportion of the more polar equatorial isomer for the equilibrium at 273 and 300 K. (The result in chloroform appears anomalous and this will be discussed later.) The results are consistent with the presence of diminished intramolecular dipolar interactions and enhanced solvation as the medium becomes increasingly polar.[3] The reason for the discrepancy in the behavior at low temperature and at higher temperature now becomes clear. Not surprisingly, it is the balance of enthalpic and entropic contributions that dictates the overall conformational behavior (Table II and Figure 1). Hence, the axial form is favored more in acetone than in methylene chloride, in enthalpy terms, but exactly the opposite is true in terms of entropy. The behavior in toluene, both in enthalpic and entropic terms, is intermediate between those in the former two solvents, and it is likely that there are specific solvation effects operating here. For instance, previous workers[14,20] have noted anomalous behavior for equilibria involving polar molecules in solvents such as benzene and toluene, in particular, a preferential stabilization of the more polar isomers. It is likely that the solvent–solute interaction derives from a collision complex involving the ring dipole and the π-aromatic system, as proposed[21] for the complexes with 1,3-dioxanes (see below). According to this model, protons at C-4, C-5, and C-6 that lie above the reference plane will be shielded, protons below the plane will be deshielded, and those in or near the plane will experience small shielding or deshielding effects.[21] The marked shielding of $\text{H-4}_{eq},6_{eq}$ in 2-(arylseleno)-1,3-dithianes[2] in the spectra measured in toluene as compared to those in nonaromatic solvents certainly supports this hypothesis. The thermodynamic parameters $\Delta H°(C_7H_8) < \Delta H°(CH_2Cl_2)$ suggest that the complexation with toluene stabilizes the axial form enthalpically relative to methylene chloride. More favorable complexation in the case of the axial isomer should give a more ordered structure, and, indeed, $\Delta S°(C_7H_8) < \Delta S°(CH_2Cl_2)$.



Although the equilibrium in chloroform could only be examined at higher temperatures, the limited data (Table I) indicate that the equilibrium is almost isoenthalpic and that, unlike for the other solvents, $\Delta S°$ is positive. The result is reminiscent of that obtained[6,22] for the equilibrium of 2-methoxytetrahydropyran in $CDCl_3$ or $CFCl_3/CDCl_3$ (85:15) as solvent. Lemieux and Praly[22] have attributed the unusual stabilization of the equatorial conformer in the latter compound ($\Delta H° \approx 0$) to a specific hydrogen-bonding interaction between chloroform (acting as a donor) and the ring oxygen (acting as an acceptor); the preferential interaction in the equatorial conformer is attributed to the greater exo-anomeric effect relative to that in the axial conformer, which places greater negative charge on the ring oxygen atom.[22] A similar rationale would account for the results obtained in the present work. Thus, preferential hydrogen-bonding to the ring sulfur atom in the equatorial isomer owing to greater $n_{Se} \rightarrow \sigma^*_{C-S}$ exo-anomeric interactions[2] (see below) would favor this isomer enthalpically and would offset the stabilization due to the $n_S \rightarrow \sigma^*_{C-Se}$ endo-anomeric effect[2] in the axial isomer. Conversely, the axial isomer would be favored entropically ($\Delta S° > 0$).



Several explanations have been advanced to account for the anomeric effect.[23] However, those formulated in terms of electrostatic or dipolar interactions[24] and in terms of stabilizing orbital interactions[25–27] have been most widely accepted. According to the former proposal, the more polar equatorial isomer should be stabilized to a greater extent in more polar media, in the absence of specific solvation effects. Comparison of the data (Table II) for the 2-[(4-methoxyphenyl)seleno]-1,3-dithianes 1–4 in acetone and methylene chloride indicates that the less polar axial isomer is favored enthalpically in the more polar solvent, acetone. It would appear, therefore, that dipolar interactions are not dominant in these compounds. The preferential stabilization of the axial isomer in the more polar solvent suggests that this isomer might, in fact, be more polar in this solvent than expected on the basis of the dipolar moments of 3 and 4, measured in CCl_4 solution. Fuchs et al.[5] have suggested that when the molecular dipoles of the axial and equatorial isomers are of similar magnitudes, the more polar double-bond no-bond structure,[25] resulting from stabilizing orbital interactions in the axial isomer (endo-anomeric interactions), will be stabilized in the more polar solvent. We propose a similar expla-

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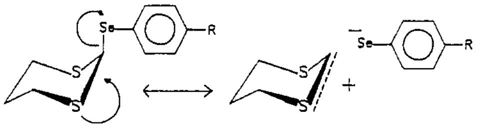
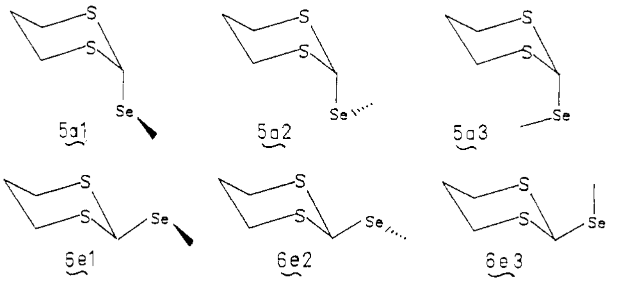
nation to account for the solvent dependence of the equilibria in **1**-**4**. We have already provided[2] evidence for the existence of significant $n_S \rightarrow \sigma^*_{C-Se}$ endo-anomeric interactions [and double-bond no-bond structures (see below)] in the axial conformers of 2-(arylseleno)-1,3-dithianes.



Such polar structures would be more stabilized in acetone than in methylene chloride, resulting in a greater anomeric effect in the former solvent. One also predicts a more negative entropy difference in acetone relative to methylene chloride, owing to imposed order, and this indeed is found to be the case. The results constitute evidence for the dominance of orbital interactions over dipolar interactions in controlling the conformations of 2-(arylseleno)-1,3-dithianes.

Finally, we comment on the entropy differences in the equilibria **1** $\rightleftarrows$ **2** and **3** $\rightleftarrows$ **4**. The rotamers for axial and equatorial 2-(arylseleno)-1,3-dithianes are shown below. Knowledge of the preferred rotamers about the exocyclic bond in acetals and related structures, derived from consideration of the exo-anomeric effect and steric effects,[6a,23,28] leads to the prediction that whereas only $\mathbf{5a}_1$ and $\mathbf{5a}_2$ in the axial isomer will be appreciably populated, all three rotamers in the equatorial isomer might be populated.[29] It is expected, however, that $\mathbf{6e}_1$ and $\mathbf{6e}_2$ will dominate over $\mathbf{6e}_3$. Hence, the equatorial isomer will be favored entropically by a maximum factor of $R \ln {}^3/_2$ (0.81 kcal mol^{-1}) owing to the entropy of mixing. The entropy differences observed for the equilibria in toluene, acetone, and methylene chloride are in excess of this value.



Conclusions

The conformational equilibria of 2-[(4-methoxyphenyl)seleno]-1,3-dithiane and the configurational equilibria of the corresponding 4,6-dimethyl-1,3-dithianes in various solvents have been examined. Plots of ln K vs $1/T$ using data from both types of experiments are linear and yield values for the enthalpy and entropy differences. The equilibrium data in toluene and chloroform are attributed to specific solvation effects. The preferential stabilization, in enthalpy terms, of the axial isomer in acetone vs methylene chloride, and its destabilization, in entropy terms, is interpreted in terms of the dominance of $n_S \rightarrow \sigma^*_{C-Se}$ orbital interactions over dipolar interactions, leading to a polar double-bond no-bond structure.

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[28] Fuchs, B.; Schleifer, L.; Tartakovsky, E. *Nouv. J. Chim.* 1984, *8*, 275.

[29] The $n_{Se} \rightarrow \sigma^*_{C-S}$ exo-anomeric interactions in 2-(arylseleno)-1,3-dithianes have been discussed previously.[2]

1,4-Dioxene in Organic Synthesis. 6.[1] Substituted 2-Vinyl-1,4-dioxenes: Useful Intermediates for the Synthesis of Highly Functionalized Compounds

Marcel Fêtizon,* Pierre Goulaouic, and Issam Hanna

Laboratoire de Synthèse Organique DCSO, Ecole Polytechnique 91128 Palaiseau Cedex, France

Thierry Prangê

LURE, Universitê de Paris-Sud, Bâtiment 209D, 91405 Orsay Cedex, France

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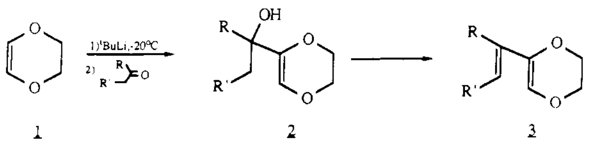
Substituted 2-vinyl-1,4-dioxenes **3**, prepared by dehydration of allylic alcohols **2** with MsCl-Et$_3$N or SOCl$_2$-Py, undergo a [4 + 2] cycloaddition reaction with various dienophiles. Exposure of **4**, obtained by Diels-Alder reaction with dimethyl acetylenedicarboxylate to DBU followed by acidic hydrolysis affords highly functionalized compounds.

As part of our general interest in synthetic applications of 2,3-dihydro-1,4-dioxin (1,4-dioxene) **1**, we have examined the use of this electron-rich olefin in the formation of carbon-carbon bonds with simultaneous introduction of useful functional groups. Thus, allylic alcohols **2**, easily obtained from 2-lithio-5,6-dihydro-1,4-dioxin and ketones or aldehydes, undergo various transformations leading to α-hydroxymethyl ketones,[2] α,α'-dihydroxy ketones[3] and

Scheme I



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[1] For part 5, see: Bernasseau, J. M.; Bouillot, A.; Fêtizon, M.; Hanna, I.; Rose Maia, E.; Prangê, T. *J. Org. Chem.* 1987, *52*, 1993.

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