

phorus compounds. This observation may be accounted for by the stronger interaction between chlorine and $\pi_{C=N}$ than between chlorine and $\pi_{C=P}$ and by the pronounced diffuse character of the $\pi_{C=P}$ bond relative to $\pi_{C=N}$. On the other hand, for both type of compounds the heteroatomic lone pair is not sensitive to chlorination, thus reflecting a counterbalance between the stabilizing inductive effect of chlorine and the destabilizing interaction between the lone pairs of chlorine and of the heteroatom.

Note added in proof: During the course of our investigations, the microwave spectrum of *N*-chloromethanimine, generated from the pyrolysis of *N*-chloroazetidine, has been reported.²⁰

Acknowledgment. We thank Maryse Simon for her efficient technical assistance.

Registry No. 4, 32360-82-0; 5, 34508-68-4; $H_2C=PCl$, 61183-51-5; $NCCH_2NH_2$, 540-61-4; $NCC(CH_3)_2NH_2$, 19355-69-2; *N*-chlorosuccinimide, 128-09-6.

Supplementary Material Available: 300-MHz 1H and 75.47-MHz ^{13}C NMR spectra of *N*-chloromethanimine and 80-MHz 1H and 20.11-MHz ^{13}C NMR spectra of *N*-chloro-2-methylideneamine (6 pages). Ordering information is given on any current masthead page.

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The Use of Precise Structural Information for the Understanding of the Conformational Behavior of *cis*-5-(*tert*-Butylsulfonyl)- and *cis*-5-(*tert*-Butylsulfinyl)-2-*tert*-butyl-1,3-dioxane¹

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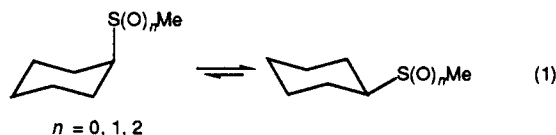
Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, 07000 México, D.F., Mexico, and Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 México, D.F., Mexico

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A single-crystal X-ray structure determination of the title sulfoxide (*cis*-2) was carried out and compared with data previously reported for the corresponding sulfone (*cis*-1). Whereas the latter adopts an eclipsed conformation (one S—C/C—H and two S=O/C—C eclipsed bond pairs), both the *tert*-butyl and the S=O group in the sulfinyl function point outside the ring in a staggered rotamer. A substantial difference in length for the endocyclic C—C bonds in *cis*-2 suggests the effect of through-space $\sigma_{C-C}/\sigma^*_{S-O}$ (attractive) and σ_{C-C}/n_S (repulsive) interactions and/or $\sigma_{C-H} \rightarrow \sigma^*_{C-S}$ stereoelectronic mechanisms. The X-ray diffraction study of the cyclohexane analogue (*cis*-4) shows again a staggered conformation for the *tert*-butylsulfinyl group, but confirms the repulsive steric hindrance between the *gauche* *t*-BuS and endocyclic methylene groups. The contrasting behavior between the sulfone and sulfoxide groups points to the existence of an attractive interaction S=O/C—C, which stabilizes the eclipsed conformer in *cis*-1 and overcomes the torsional strain in the eclipsed bond pair S—C/C—H. The nature of the stabilizing S=O/C—C interaction is proposed in the light of recent theoretical calculations.

Introduction

Several years ago, Eliel and Kandasamy described the conformational free energies (ΔG° values) for the methyl sulfide, methyl sulfoxide, and methyl sulfone groups in the cyclohexane ring.³ The reported values, -1.00, -1.20, and -2.50 kcal/mol, respectively, clearly reflect the steric requirements of the sulfur functions (eq 1).



Eliel et al.⁴ discovered also that the CH_3S group attached at C(5) in a 1,3-dioxane has a stronger preference for the equatorial conformation ($\Delta G^\circ = -1.82$ kcal/mol in solvent cyclohexane) than that measured for (methylthio)cyclo-

Table I

X	ΔG° , kcal/mol
CH_3S	-1.82 ± 0.01
CH_3SO	$+0.82 \pm 0.11$
CH_3SO_2	$+1.19 \pm 0.10$
<i>t</i> -BuS	-1.90 ± 0.11
<i>t</i> -BuSO	$+0.10 \pm 0.01$
<i>t</i> -BuSO ₂	-1.14 ± 0.01

hexane, this being the result of a repulsive interaction of the unshared electrons of sulfur with the unshared electrons of the ring oxygens (the so-called "repulsive *gauche* effect"⁵) (Table I).

In strong contrast, similarly placed methylsulfinyl (CH_3SO) and methylsulfonyl (CH_3SO_2) groups prefer the axial conformation.⁴ (Table I). This unusual behavior was

(1) Conformational Analysis of 5-Substituted 1,3-Dioxanes. 4. Part 3: Gordillo, B.; Juaristi, E.; Rubio, M. F. *J. Org. Chem.* Submitted.
 (2) (a) Instituto Politécnico Nacional. (b) Universidad Nacional Autónoma de México.
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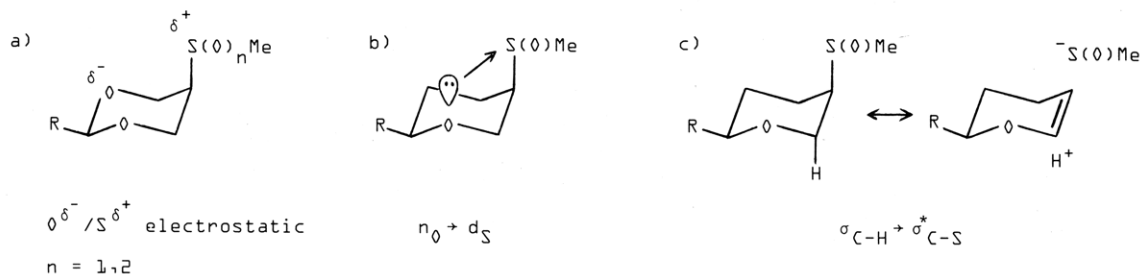


Figure 1. Models proposed to explain the axial preference of the methylsulfinyl and methylsulfonyl groups at C(5) or C(3) in oxygen-containing heterocycles.

rationalized in terms of an attractive, electrostatic interaction between the (negative) endocyclic oxygens and the (positive) sulfinyl or sulfonyl sulfur (Figure 1a).⁴ Nevertheless, the axial predominance of a methylsulfinyl group in analogous oxane rings has been explained in terms of (1) a donor-acceptor ($n_O \rightarrow d_S$) stabilizing interaction (Figure 1b)^{6,7} and (2) a stereoelectronic orbital interaction between the axial, occupied σ_{C-H} bonds at C(2) and the antiperiplanar, empty σ^*_{C-S} orbital⁸ (Figure 1c).

In this context, the positions of equilibrium between diastereomeric *cis*- and *trans*-5-(*tert*-butylthio)-, -5-(*tert*-butylsulfinyl)-, and -5-(*tert*-butylsulfonyl)-2-isopropyl-1,3-dioxanes were reported recently⁹ (Table I). Although ΔG° values for the sulfides are very similar, the difference in conformational behavior for the sulfoxides is significant, and the effect of changing from methyl to *tert*-butyl in the sulfones is quite dramatic: the large preference for the methyl analogue for the axial position (1.19 kcal/mol; Table I) is reversed in the *tert*-butyl derivative, where the equatorial isomer is more stable by 1.14 kcal/mol.

A crystallographic X-ray diffraction study of *cis*-2-*tert*-butyl-5-(*tert*-butylsulfonyl)-1,3-dioxane (**1**) was also undertaken in order to gain definitive evidence for its stereostructure.⁹ The heterocyclic six-membered ring exists in a chair conformation with the substituent at C(5) being axial. The sulfonyl *tert*-butyl group is outside the ring, suggesting that the steric congestion that would be present if the alkyl group was inside the ring is more severe than the electrostatic repulsion between the (negative) oxygens, $S^+-O^-/O_{1,3}$. This repulsion (which is reflected in the $\Delta G^\circ = -1.14$ kcal/mol value) is nonetheless manifested as some bending of the C(5)-S bond away from the ring [C(4)-C(5)-S = 112°, C(6)-C(5)-S = 112.7°] and by an unusually large torsional angle in the O-C-C-S segments of ca. 78°. Also, the C(5)-S bond length (1.829 (9) Å) is longer than normal (1.80 Å).¹⁰

The most interesting feature of the crystallographic data was, however, that they correspond to a conformation with eclipsed S-O/C-C and C-*t*-Bu/C-H bonds.⁹ Indeed, the average torsional angles O-S-C are $8.25 \pm 2.35^\circ$, indicating the nearly eclipsed nature of the crystal structure. The eclipsing of bonds in *cis*-1 could be necessary to mitigate *gauche* *t*-Bu/CH₂ steric interactions present in staggered rotamers.^{1,9} In addition, the eclipsed conformer may lead to significant stabilizing attraction between the

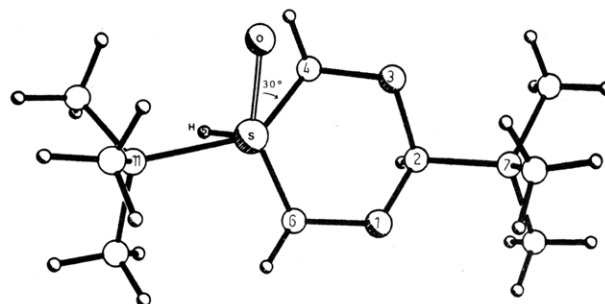
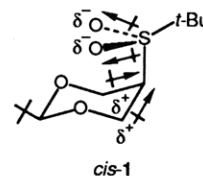


Figure 2. Structure and solid-state conformation in *cis*-2.

negatively charged sulfone oxygens and the positively charged methylenes.^{1,9} Finally, dipole-induced dipole interactions might also be important in lowering the energy of the eclipsed sulfone.^{1,9,11}



As a consequence of these and related arguments, the question arose as to whether the analogous sulfoxide (*cis*-2) adopts also an eclipsed conformation. We also asked ourselves whether the analysis of precise structural data on these systems could help in the interpretation of the factors responsible for the stability in the axial sulfoxide and sulfone groups.

Results and Discussion

A. X-ray Diffraction Study of 2-*tert*-Butyl-5-(*tert*-butylsulfinyl)-1,3-dioxane (*cis*-2). The crystal structure of *cis*-2 was solved by direct methods.¹² Refinement of atomic parameters converged to $R = 0.069$ over 875 reflections. A view of the solid-state conformation is provided in Figure 2. The 1,3-dioxane ring has a chair conformation with the *tert*-butylsulfinyl group at C(5) oriented axially. The sulfinyl *tert*-butyl group is outside the ring, and the same is true for the S=O function, which, in contrast with *cis*-1, is not eclipsed to an endocyclic C-C bond but rather presents a torsional angle O=S-C(5)-C(4) = 30.4°. [The deviation from an ideally staggered conformer, $\tau = 60^\circ$, is the result of steric hindrance between the *t*-BuS group and the *gauche* methylene at C(6); see section B.]

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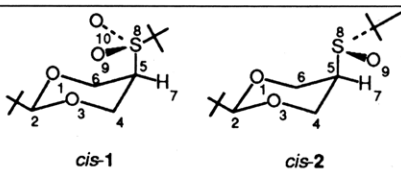
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(11) Consider Wiberg's arguments on eclipsed *n*-alkyl ketones: Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* 1985, 107, 5035-5041. Wiberg, K. B. *Ibid.* 1986, 108, 5817-5822.

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Table II. Selected Interatomic Distances and Angles in *cis*-1 and *cis*-2^a


	<i>cis</i> -1		<i>cis</i> -2	
Bond Lengths (Å)				
C(4)–C(5)	1.485 (13)		1.493 (12)	
C(5)–C(6)	1.526 (13)		1.571 (10)	
C(5)–S(8)	1.829 (9)		1.844 (8)	
O(1)–C(6)	1.418 (10)		1.437 (9)	
O(3)–C(4)	1.440 (11)		1.427 (9)	
S(8)–O(9)	1.446 (7)		1.498 (7)	
Bond Angles (deg)				
C(4)–C(5)–S(8)	112.7 (7)	108.7 (5)		
C(6)–C(5)–S(8)	112.0 (7)	107.5 (5)		
C(5)–S(8)–O(9)	107.9 (4)	106.4 (4)		
Torsional Angles (deg)				
C(4)–C(5)–S(8)–O(9)	10.6 (8)	30.4 (6)		
C(6)–C(5)–S(8)–O(10)	5.9 (7)			
O(1)–C(6)–C(5)–S(8)	79.1 (8)	69.2 (7)		
O(3)–C(4)–C(5)–S(8)	77.1 (9)	67.7 (7)		

^aStandard deviations are in parentheses.

Selected bond lengths and angles for *cis*-2, together with corresponding values for *cis*-1, are in Table II. No manifestation of a repulsion between the axial substituent and the heterocyclic ring is apparent; indeed, there is no bending of the sulfinyl group away from the ring [C(4)–C(5)–S = 108.7°, C(6)–C(5)–S = 107.5°], and the torsional angle in the O–C–C–S segments, ca. 68°, is also close to normal.

A most interesting finding is the substantial difference in bond lengths between the two endocyclic C–C bonds; while C(4)–C(5), which is *syn* to the S=O group, seems shorter than normal (1.493 Å), C(5)–C(6), which is *syn* to the sulfur lone pair (n_S), is unusually long (1.571 Å). A theoretical model¹³ that explains this structural effect is the following: the through-space $\sigma_{C-C}/\sigma^*_{S-O}$ interaction is stabilizing¹⁴ and leads to a shortening in the C(4)–C(5) σ bond, but the through-space σ_{C-C}/n_S interaction is destabilizing and causes a length increase in the σ bond. It should be noted, however, that according to this interpretation the S–O bond length was expected to be longer than normal (because of electron transfer into the antibonding σ^*_{S-O} orbital¹⁴); in the event, the sulfinyl S=O bond length was found to be normal (1.498 Å).¹⁵

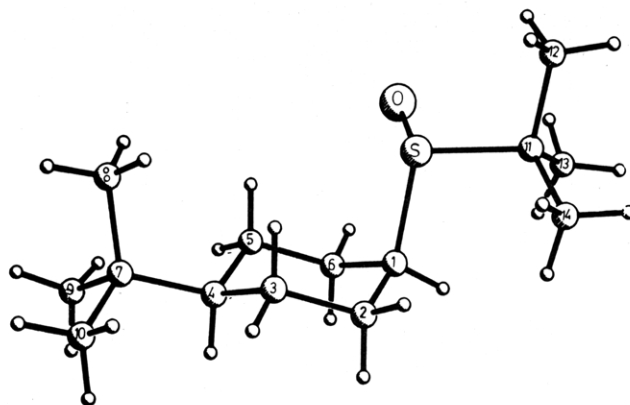
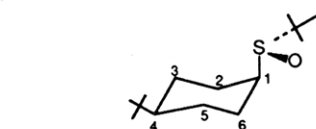
In this context, the short C(4)–C(5) bond, together with the finding (Table II) of a longer than normal C(5)–S bond (1.844 Å),¹⁵ could be accounted for in terms of a hyperconjugative interaction between the (antiperiplanar) axial C(4)–H bond and the C(5)–S antibonding orbital, $\sigma_{C-H} \rightarrow \sigma^*_{C-S}$. Such a stereoelectronic effect has been proposed by Alcudia et al.⁸ to operate in axial 3-(methylsulfinyl)-oxanes (Figure 1c). It should be mentioned, however, that

(13) We are grateful to Professor D. Seebach, ETH-Zürich, for this suggestion.

(14) For a pioneering study concerning the availability of the σ^*_{S-O} orbital in two-electron stabilizing interactions, see: Wolfe, S. Sulfur-Containing Carbanions and Related Species. In *Organic Sulfur Chemistry*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Chapter 3.

(15) A list of C–S and S=O bond lengths as found in the Cambridge Structural Database (CSD) gave 40 entries for sulfoxides with two alkyl groups next to sulfur (structure analyses of very poor quality were excluded). The mean values are as follows: C–S = 1.80 ± 0.07 Å and S–O = 1.496 ± 0.015 Å.¹⁶

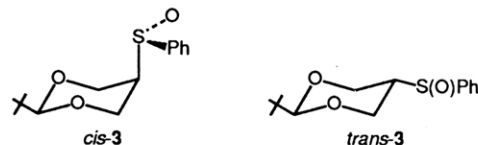
(16) We are indebted to Bernd Lamatsch and Prof. Dieter Seebach, ETH-Zürich, for providing us with this list.

**Figure 3. Structure and solid-state conformation in *cis*-4.****Table III. Selected Interatomic Distances and Angles in *cis*-4^a**

Bond Lengths (Å)	
C(1)–C(2)	1.522 (4)
C(1)–C(6)	1.531 (4)
C(1)–S(1)	1.844 (3)
S(1)–O(1)	1.493 (2)
Bond Angles (deg)	
C(2)–C(1)–S(1)	108.6 (2)
C(6)–C(1)–S(1)	109.6 (2)
C(1)–S(1)–O(1)	108.2 (1)
Torsional Angles (deg)	
C(6)–C(1)–S(1)–O(1)	27.6 (2)

^aStandard deviations are in parentheses.

the ¹³C NMR data for the analogous sulfoxides *cis*- and *trans*-3 have been measured,¹⁷ with special attention to the



aromatic signals: C(ortho) and C(para) were found to be slightly *downfield* (125.47 and 131.71 ppm, respectively) in the axial (*cis*) isomer relative to those in the equatorial sulfoxide (124.04 and 131.36 ppm, respectively). Because electron transfer interactions of this sort are expected to produce an opposite trend,^{18,19} the spectroscopic observation is hard to reconcile with the electron transfer argument.

B. X-ray Diffraction Study of *cis*-4-*tert*-Butyl-1-(*tert*-butylsulfinyl)cyclohexane (*cis*-4). The crystal structure of *cis*-4 was solved¹² in order to gain information concerning the influence of the oxygen atoms in the conformational behavior of the heterocyclic analogue *cis*-2. Refinement of atomic parameters converged to $R = 0.0437$ over 1907 reflections. A view of the solid-state confor-

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(18) Juaristi, E.; Valle, L.; Valenzuela, B. A.; Aguilar, M. A. *J. Am. Chem. Soc.* 1986, 108, 2000–2005. Juaristi, E.; López-Núñez, N. A.; Valenzuela, B. A.; Valle, L.; Toscano, R. A.; Soriano-García, M. *J. Org. Chem.* 1987, 52, 5185–5189.

(19) See also: Pinto, B. M.; Johnston, B. D.; Sandoval-Ramírez, J.; Sharma, R. D. *J. Org. Chem.* 1988, 53, 3766–3771.

mation is provided in Figure 3. The cyclohexane ring adopts a chair conformation with the *tert*-butylsulfinyl group at C(1) oriented axially. As in the case of *cis*-2, both the sulfinyl *tert*-butyl group and the sulfinyl S=O function point outside the ring, the latter presenting a torsional angle O=S—C(1)—C(6) = 27.6°. This partial eclipsing seems to be necessary to mitigate *t*-Bu/CH₂ steric interactions present in the staggered conformers.

Selected bond lengths and angles for *cis*-4 are in Table III. In contrast to the heterocyclic analogue (*cis*-2; see above), C(1)—C(2) and C(1)—C(6), the C—C bonds adjacent to the C—S bond, show no difference in bond lengths, which are normal (ca. 1.53 Å). This result may argue against the through-space $\sigma_{C-C}/\sigma^*_{S-O}$ and σ_{C-C}/n_S model discussed in section A, but would be in line with the $\sigma_{C-H} \rightarrow \sigma^*_{C-S}$ hyperconjugation effect suggested for *cis*-2, when according to the arguments of Alcudia et al.⁸ such interaction is turned on in the dioxane because of the significant acidity of the antiperiplanar C—H bond involved (raising the energy of the donor σ_{C-H} orbital), but turned off in the cyclohexane ring with little acidity of the corresponding C—H bonds.²⁰

C. Nature of the Eclipsing in *cis*-1. Perhaps the most remarkable result from the present study is that the *tert*-butylsulfonyl group at C(5) in the 1,3-dioxane adopts an eclipsed conformation (two S=O/C—C pairs and one S—C/C—H pair of eclipsing bonds), whereas the *tert*-butylsulfinyl group adopts a staggered conformation, even when only two pairs of bonds would become eclipsed in such a case. We feel that this result points to the existence of a stabilizing interaction in the eclipsed S=O/C—C pair, so that in the sulfone derivative two stabilizing interactions of this kind are able to overcome the unfavorable S—C/C—H eclipsing, while only one stabilizing interaction in the sulfoxide is unable to overcome the simultaneous S—C/C—H repulsive eclipsing of σ bonds.

Theoretical calculations on these and related compounds were interpreted¹ as an indication that the stabilizing nature of the S=O/C—C eclipsing is due to (1) electrostatic, attractive interactions between the negative end of the S⁺—O⁻ bonds and the partial positive character of the methylene groups at C(4,6) in the dioxane and/or (2) a dipole-induced dipole mechanism similar to that proposed by Wiberg et al.¹¹ to explain the lower energy of eclipsed *n*-alkyl ketones.

Experimental Section

The preparation of *cis*-1 and *cis*-2 is described in ref 9. Sulfoxide *cis*-4 was prepared from *trans*-4-*tert*-butylcyclohexanol²¹ according to the sequence *trans*-alcohol → *trans*-mesylate → *cis*-sulfide → *cis*-sulfoxide.²²

The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

***trans*-4-*tert*-Butylcyclohexyl Mesylate.**²³ *trans*-4-*tert*-Butylcyclohexanol (8.0 g, 51 mmol) in 130 mL of freshly distilled pyridine was cooled to 0 °C and treated dropwise with 5.12 mL (66 mmol) of mesyl chloride. The reaction mixture was left in the refrigerator for 24 h and then poured over ice-water with stirring. The precipitates were recrystallized from *n*-hexane to afford 11.7 g (97.5% yield) of the product as white crystals: mp 70–71 °C; ¹H NMR (CDCl₃, 60 MHz) δ 0.83 (s, 9 H), 1.0–2.47 (m, 9 H), 3.03 (s, 3 H), 4.63 (m, 1 H); ¹³C NMR (CDCl₃, 22.49 MHz) δ 25.53, 27.52, 32.20, 33.20, 38.75, 46.55, 82.22; IR (KBr) 2940, 2870,

1350, 1330, 1170, 935, 920 cm⁻¹; MS, *m/z* 177 (M⁺ - 57), 139, 79, 57, 41.

Anal. Calcd for C₁₁H₂₂SO₃: C, 56.38; H, 9.46. Found: C, 56.42; H, 9.42.

***cis*-4-*tert*-Butyl-1-(*tert*-butylthio)cyclohexane.**²⁴ Sodium hydride (0.63 g, 53 mmol) was suspended in 75 mL of dimethylformamide under nitrogen and treated with a solution of 2.54 mL (24 mmol) of 2-methyl-2-propanethiol in 15 mL of DMF. *trans*-4-*tert*-Butylcyclohexyl mesylate (5 g, 21 mmol) was then added, and the reaction mixture was stirred for 2 h at room temperature. Excess hydride was then destroyed by the careful addition of water, the organic materials were extracted with ether, and the combined extracts were washed with brine and water, filtered, and concentrated. Final purification of the product was accomplished by flash chromatography [*n*-hexane-ethyl acetate (95:5)], which furnished 2.0 g (45.7% yield) of the desired product: mp 52–53 °C; ¹H NMR (CDCl₃, 60 MHz) δ 0.89 (s, 9 H), 1.33 (s, 9 H), 0.98–2.03 (m, 9 H), 3.15 (m, 1 H); ¹³C NMR (CDCl₃, 22.49 MHz) δ 22.74, 27.42, 31.28, 32.45, 34.83, 39.47, 42.68, 47.91; IR (KBr) 2922, 2859, 1390, 1365, 600 cm⁻¹; MS, *m/z* 228 (M⁺), 171, 138, 81, 57.

Anal. Calcd for C₁₄H₂₈S: C, 73.61; H, 12.35. Found: C, 73.96; H, 12.14.

***cis*-4-*tert*-Butyl-1-(*tert*-butylsulfinyl)cyclohexane (*cis*-4).**²⁵ *cis*-4-*tert*-Butyl-1-(*tert*-butylthio)cyclohexane (0.46 g, 2 mmol) was dissolved in 7 mL of CH₂Cl₂ and 21 mL of CH₃OH and cooled to 0 °C. To this was added a solution of 0.47 g (2.2 mmol) of NaIO₄ in 5 mL of H₂O slowly with vigorous stirring. The reaction mixture was stirred at 0 °C for 8 h and left standing in a refrigerator for 24 h. The mixture was then filtered, and the filtrate was concentrated almost to dryness. The product was extracted with CH₂Cl₂, dried (Na₂SO₄), and concentrated to give a solid, which was recrystallized²⁶ from petroleum ether to yield 0.37 g (82%) of white crystals, mp 117–119 °C, suitable for X-ray diffraction analysis: ¹H NMR (CDCl₃, 60 MHz) δ 0.85 (s, 9 H), 1.23 (s, 9 H), 1.0–2.07 (m, 8 H), 2.37 (m, 1 H), 3.0 (m, 1 H); ¹³C NMR (CDCl₃, 22.49 MHz) δ 22.98, 22.91, 23.47, 25.29, 29.31, 27.42, 32.54, 47.21, 49.22, 54.19; IR (KBr) 2960, 2860, 1395, 1365, 1020 cm⁻¹; MS, *m/z* 244 (M⁺), 139, 105, 57, 41.

Anal. Calcd for C₁₄H₂₈SO: C, 68.79; H, 11.34. Found: C, 68.91; H, 11.37.

Structural X-ray Analysis of *cis*-2. A crystal measuring approximately 0.20 × 0.42 × 0.08 mm was used to collect intensity data on a Nicolet R3m four-circle diffractometer within the angular range 3° < 2 θ < 110°, using Ni-filtered Cu K α radiation and the $2\theta/\theta$ mode. Least-squares refinement of the setting angles of 25 reflections with a good distribution throughout reciprocal space provided the unit cell dimensions: monoclinic, *a* = 22.639 (9) Å, *b* = 5.896 (2) Å, *c* = 10.815 (6) Å; β = 98.08 (4)°; *V* = 1429.28 Å³; *F*₀₀₀ = 544; μ (Cu K α) = 19.12 cm⁻¹; *Z* = 4; *D*_{calcd} = 1.15 g cm⁻³. Possible space groups from systematic absences were *C*₂ or *C*_{2h}; successful structure solution and refinement confirms the former as correct. Of 923 independent reflections measured, corrected for Lorentz and polarization effects, 48 had intensities less than 3 σ (*F*_o) and were flagged as unobserved. The remaining 875 reflections were used to solve and refine the structure.

Positions of all non-hydrogen atoms were located by using the direct-methods program available as part of the SHELXTL package.¹² Idealized hydrogen positions were calculated and tied to the associated non-hydrogen positions through a riding model. Final refinement of 16 non-hydrogen atoms using anisotropic thermal parameters and 24 hydrogen atoms using fixed isotropic thermal parameters, *U* = 0.06 Å², gave residual values of *R*₁ = 0.069 and *R*₂ = 0.0712, where *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$ and *R*₂ = $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where *w* = $(\sigma^2 F_o + g F_o^2)^{-1}$ and *g* = 0.004.

Structural X-ray Analysis of *cis*-4. A crystal measuring approximately 0.12 × 0.12 × 0.38 mm was used to collect intensity data on a Nicolet R3m four-circle diffractometer within the an-

(20) We note, however, that the (axial) C(1)—S bond length in *cis*-4 is again (cf. structural data for *cis*-2) longer than normal: 1.844 vs 1.80 Å.¹⁵

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(24) The displacement conditions described recently by Luly et al. were employed: Luly, J. R.; Dellaria, J. F.; Pattner, J. J.; Soderquist, J. L.; Yi, N. *J. Org. Chem.* 1987, 52, 1487–1492.

(25) Cf.: Juaristi, E.; Cruz-Sánchez, J. S. *J. Org. Chem.* 1988, 53, 3334–3338.

(26) Cf.: Jones, P. G. *Chem. Br.* 1981, 17, 222–225.

gular range $3.0^\circ < 2\theta < 110^\circ$, using Ni-filtered Cu K α radiation and the $2\theta/\theta$ mode. Least-squares refinement of the setting angles of 25 reflections with a good distribution throughout reciprocal space provided the unit cell dimensions: monoclinic, $a = 6.064$ (1) Å, $b = 10.427$ (2) Å, $c = 23.916$ (5) Å; $\beta = 91.10$ (1) $^\circ$; $V = 1511.90$ Å 3 ; $F_{000} = 544$; $\mu(\text{Cu K}\alpha) = 16.97$ cm $^{-1}$; $Z = 4$; $D_{\text{calcd}} = 1.07$ g cm $^{-3}$. Systematic absences indicated the monoclinic space group $P_{21/c}$. Of 1907 independent reflections measured and corrected for Lorentz and polarization effects, 329 had intensities less than $3\sigma(F_o)$ and were not used in the refinement. The remaining 1578 reflections were used to solve and refine the structure.

Positions of all non-hydrogen atoms were located by using the direct-methods program available as part of the SHELXTL package.¹² Idealized hydrogen positions were calculated and tied to the associated non-hydrogen positions through a riding model. Final refinement of 16 non-hydrogen atoms using anisotropic thermal parameters and 28 hydrogen atoms using fixed isotropic thermal parameters, $U = 0.06$ Å 2 , gave residual values of $R_1 = 0.0437$ and $R_2 = 0.0529$, where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where $w = (\sigma^2 F_o + g F_o^2)^{-1}$ and $g = 0.002$.

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Registry No. *cis*-2, 109181-88-6; *cis*-4, 123185-95-5; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; mesyl chloride, 124-63-0; *trans*-4-*tert*-butylcyclohexyl mesylate, 18508-90-2; 2-methyl-2-propanethiol, 75-66-1; *cis*-4-*tert*-butyl-1-(*tert*-butylthio)cyclohexane, 123185-94-4.

Supplementary Material Available: Listings of anisotropic thermal parameters for all non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms, bond distances, bond angles, torsional angles, and the fractional coordinates for *cis*-2 and *cis*-4 (12 pages). Ordering information is given on any current masthead page.

Nucleophile and Nucleofuge Effects, Catalysis, and Stereochemistry in Vinylic Substitution of Electrophilic Nitro Olefins¹⁻³

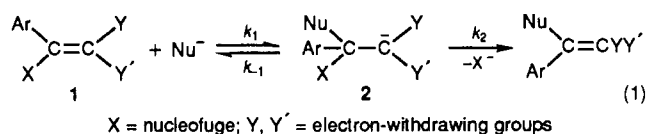
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The substitution of (*E*)- and (*Z*)- β -iodo- α -nitrostilbenes (**E-3-I** and **Z-3-I**) and of the (*E*)- β -chloro (**E-3-Cl**) and of (*E*)- β -nitro (**E-3-NO₂**) analogues with several nucleophiles were studied in MeCN and EtOH. Amine catalysis in the substitution with morpholine and piperidine was observed in the reactions of **E-3-NO₂** in EtOH but not in MeCN. The reaction with N_3^- gave 3,4-diphenylfuroxan. The reactions of **E**- and **Z-3-I** with *p*-TolS $^-$ in EtOH and NCS $^-$, piperidine, and morpholine in MeCN gave a single geometric isomer (presumably *E*) of the product, i.e., they show complete stereoconvergence. The precursor vinyl iodides were not isomerized during the substitution. $k_{\text{E-3-Cl}}/k_{\text{E-3-I}}$ values were 0.67–5.2 with the anionic nucleophiles and 20.1–23.7 with the amines. $k_{\text{E-3-NO}_2}/k_{\text{E-3-Cl}}$ were 2.8–9.8, and $k_{\text{E-3-I}}/k_{\text{Z-3-I}}$ were 1.86–2.86 (*p*-TolS $^-$, NCS $^-$) and 0.08–0.13 (piperidine, morpholine). $k_{\text{Pip}}/k_{\text{Morp}}$ ratios were 3.0–9.5. The relative nucleophilicity toward **E-3-Cl** changes by 4 orders of magnitude between the most reactive *p*-TolS $^-$ and the least reactive morpholine. The reaction is discussed in terms of a multistep substitution involving the intermediacy of zwitterions or carbanions. The lifetime of the carbanions is sufficiently long to enable a faster rotation around the $\text{C}_\alpha\text{-C}_\beta$ bond than nucleofuge expulsion. The lifetimes of the zwitterions derives from **E-3-NO₂** and amines are sufficiently long for deprotonation to compete with NO_2 expulsion in EtOH, but not in MeCN. The $k_{\text{Cl}}/k_{\text{I}}$ and $k_{\text{NO}_2}/k_{\text{Cl}}$ reactivity ratios are discussed in terms of a complex rate constant and contribution to the ratios from the individual rate constants. The $k_{\text{E-3-I}}/k_{\text{Z-3-I}}$ ratios were ascribed to different steric effects in the neutral precursors. Nucleophilicity scales toward electrophilic alkenes are discussed and the nitro group compared to other electron-withdrawing activators in vinylic substitution. The possibility of the intervention of other reaction routes is considered.

Our recent studies on nucleophilic vinylic reactions dealt mainly with substitution of highly activated electrophilic olefins (1) in a search for evidence that the substitution is a multistep process proceeding via the intermediacy of carbanions (2) or zwitterions (eq 1, shown for a negatively



charged nucleophile).⁴ The problem is that with good nucleofuges, e.g., Cl, Br, or OSO_2R , the lifetime of 2 is so short that nucleofuge expulsion is mostly faster than other reactions of 2, making difficult its detection. For example, when X is a good nucleofuge, protonation of 2 is apparently slower than nucleofuge expulsion since Michael type adducts are not formed under the substitution conditions. Likewise, substitution is faster than *E* = *Z* isomerization of the precursor alkene, except for a few systems.⁵ On the other hand, the mild amine catalysis observed in the substitution of few ArC(X)=C(CN)_2 , X = Cl, Br with

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