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Conformational Analysis of the Favorskii Rearrangement Using 3(a)-Chloro-3(e)-phenyl-*trans*-2-decalone and 3(e)-Chloro-3(a)-phenyl-*trans*-2-decalone[1a]

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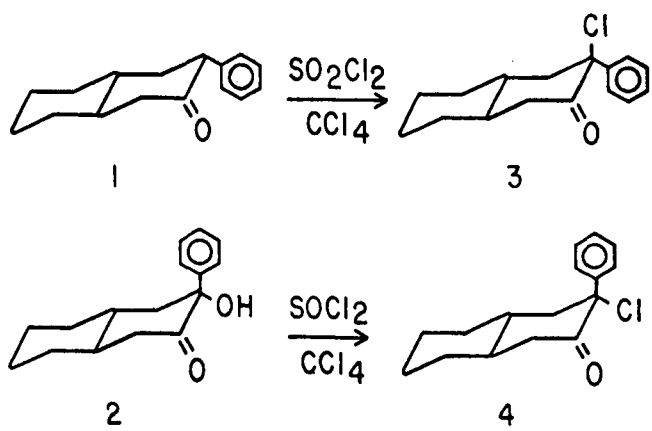
Received July 26, 1974

The starting material for the synthesis of the isomeric chloro ketones (3 and 4) was *trans*-2-decalone, which was converted to 3(e)-phenyl-*trans*-2-decalone (1) and 3(e)-hydroxy-3(a)-phenyl-*trans*-2-decalone (2). Compound 1 was chlorinated by sulfuryl chloride in carbon tetrachloride to yield the axial chloro ketone 3, while compound 2 was chlorinated by thionyl chloride in carbon tetrachloride to yield the equatorial chloro ketone 4. Potassium *tert*-butoxide was used to effect the rearrangement both in ethanol (E) and 1,2-dimethoxyethane (D). The product from 3 when the rearrangement was performed in D included 2-phenylhexahydroindan-2-carboxylic acid [isolated as the methyl ester (5)] and 2-phenacyl-1-cyclohexaneacetic acid [isolated as the methyl ester (6)]. Rearrangement of 3 in E yielded 5, 6, and 1-ethoxy-3-phenyl-*trans*-2-decalone (7). Favorskii products were not evident when 4 was subjected to rearrangement conditions. It can be concluded that the axial conformation of the chlorine atom is more favorable for the Favorskii rearrangement. Compound 7 was apparently produced either from a cyclopropanone intermediate or an enol allylic chloride.

An attempt was made by Smissman et al.[2] to determine whether a cyclopropanone intermediate or a dipolar ion was operative in the Favorskii rearrangement of a pair of conformers, viz., 3(a)-bromo-*trans*-2-decalone (8) and 3(e)-bromo-*trans*-2-decalone (9). Since the axial compound gave no rearrangement product in either polar or nonpolar solvents whereas the equatorial compound rearranged in both solvent types, it was concluded that the results of this study disputed the role of the dipolar ion as an active participant in the Favorskii rearrangement. If this conclusion were valid, if not on a general basis, then at least for rigid systems such as the *trans*-decalones, it could be predicted that of the two conformers used in the present study, viz., 3(a)-chloro-3(e)-phenyl-*trans*-2-decalone and 3(e)-chloro-3(a)-phenyl-*trans*-2-decalone, the equatorial isomer would give the Favorskii product.

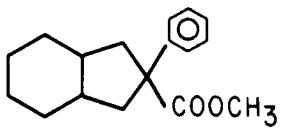
Results

The two chloro ketones 3 and 4 were synthesized by the chlorination of 3(e)-phenyl-*trans*-2-decalone (1) and 3(e)-hydroxy-3(a)-phenyl-*trans*-2-decalone (2). Compounds 1 and 2 were synthesized by published methods.[3] Potassium *tert*-butoxide was used to effect the rearrangement both in the polar solvent ethanol and in the nonpolar solvent 1,2-dimethoxyethane. The products of the rearrangement were hydrolyzed and separated into an acidic fraction and a neutral fraction. The former was subjected to Fischer–Spier esterification prior to column chromatography on alumina. The components of the neutral fraction were separated by column chromatography on silica gel.



Rearrangement of the axial chloro ketone 3 in ethanol gave, after esterification, the methyl ester of 2-phenylhexahydroindan-2-carboxylic acid (5, 2% yield) and 2-phenacyl-1-cyclohexaneacetic acid (6, 2% yield). The neutral components included compounds 1-ethoxy-3-phenyl-*trans*-2-decalone (7, 2% yield) and 3(e)-hydroxy-3(a)-phenyl-*trans*-2-decalone (2, 42% yield). A polymeric material was also isolated.

The yield of 5 was similar (2%) when the rearrangement of 3 was performed in dimethoxyethane. Compound 6 was also isolated (<1% yield). Sublimation of the crude acid fraction prior to Fischer–Spier esterification yielded benzoic acid. The neutral components included polymeric material.



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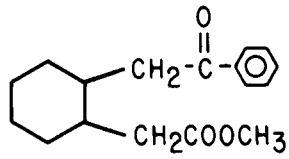

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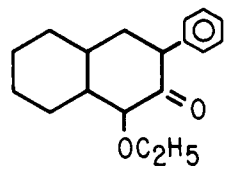

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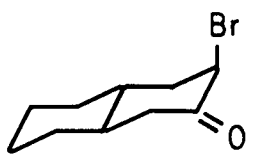
Base treatment of the equatorial chloro isomer 4 when dissolved in ethanol yielded the ester 6 (7% yield) and some unknown material. The neutral products contained polymeric material.

Acidic products from the rearrangement of 4 in a nonpolar solvent included benzoic acid. Compound 6 was isolated after esterification (<1% yield). Again polymeric material was present in the neutral fraction.

Discussion

Previous results[2] using the bromo compounds 8 and 9 had indicated that the dipolar ion is not a necessary inter-



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mediate in the Favorskii rearrangement. It was suggested by Bordwell[4a] and House[4b] that the axial bromo compound 8 undergoes side reactions faster that it undergoes the Favorskii rearrangement. To provide further evidence concerning the steric requirements of the Favorskii rearrangement, compounds 3 and 4 were synthesized. The infrared analysis of these compounds supported the assigned stereochemistry, since the carbonyl stretching frequency observed in 4 was increased by about 20 cm^{-1} relative to 3.[5] Only the axial isomer 3 gave the Favorskii compound 5 and the neutral compound 7 even though larger amounts of 4 were used in the study. Both isomers gave compound 6 and both produced polymeric compounds as the major products.

Many references to the Favorskii rearrangement may be found in the papers by Bordwell, who has provided additional evidence that ionization of the carbon–halogen bond facilitates the formation of the Favorskii product, and that a dipolar ion is probably in equilibrium with a cyclopropanone[6-8] (Figure 1).

The results obtained from this study of 3 and 4 indicate that the conformation of the chlorine atom does influence the yield of compound 5. That 7 could have arisen from 1-chloro-3-phenyl-*trans*-2-decalone, which might have been present as an impurity in compound 3, was discounted. Analysis by NMR did not reveal the presence of such an impurity, and yet compound 7 could be obtained in enhanced yield (10–15%) when 3 was treated with sodium ethoxide in ethanol. Further, there was no difference in the physical properties of 3 when it was prepared from 1 or from 13. A cyclopropanone intermediate might be involved

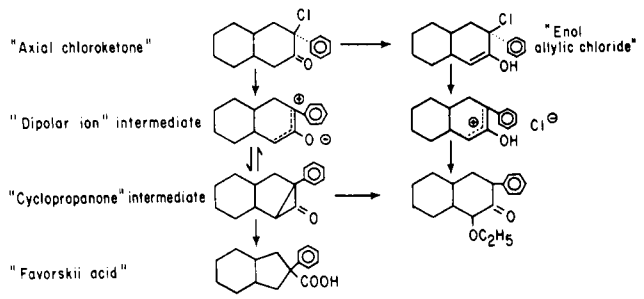
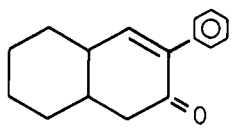


Figure 1. Intermediates involved in the formation of the Favorskii acid 5 and compound 7.



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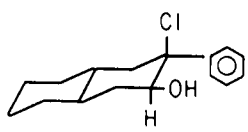

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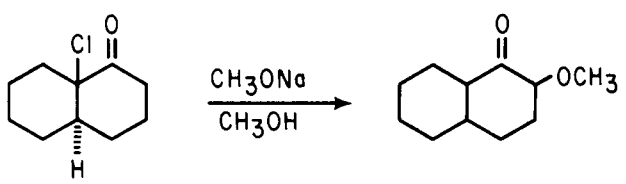
in the formation of 7. A similar explanation was advanced by House and Frank,[9] who demonstrated that the *trans*-decalone derivative 14 under Favorskii rearrangement conditions will produce side product 15, analogous to com-

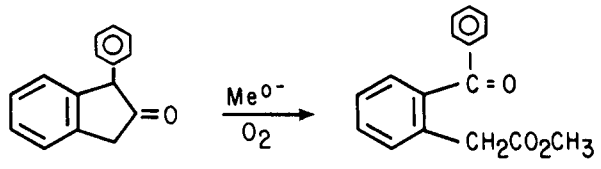


14 15

pound 7. Alternatively, as envisioned by Bordwell and Carlson,[7] the enolate anion may form an equilibrium with an enol allylic chloride and its corresponding ion pair. The latter could then react with ethanol to produce compound 7.

It is unlikely that hydroxy ketone 2 was produced by an SN1 type reaction during the course of the reaction, since it was demonstrated that hydroxy ketone formation during the course of the Favorskii reaction is not subject to a salt effect.[4a] Therefore, compound 2 probably arose from the corresponding alkoxy oxirane during work-up.

Compound 6 was produced by ring opening but the reaction mechanism was not elucidated. A similar acidic product was observed when the bromo compounds 8 and 9 were exposed to Favorskii conditions.[2] Bordwell[10] has demonstrated that compound 10 is converted to compound 11 by reaction with oxygen in the presence of methanolic sodium hydroxide, which suggests that compound 6 is formed by a similar mechanism. Apparently, the benzoic acid found in the present investigation was generated from acid 6. The



10 11

formation of polymers under Favorskii conditions might be a consequence of alkylation by the enolate anion,[11] although the possibility that an enone such as **12** might be produced and then polymerize should be considered.

If we invoke a dipolar ion intermediate, then the sequence of events illustrated in Figure 1 will explain why it was the axial chloro and not the equatorial isomer that gave the desired Favorskii acid. However, the results obtained in this study are in contrast to those obtained by Smissman et al.[2] in the closely related system described above. Presumably, the axial bromo ketone **8** and the equatorial chloro ketone **4** undergo side reactions faster than they can undergo the Favorskii rearrangement.

Although an interesting example of a Favorskii-like reaction has been reported where an internal SN2 displacement of the halide ion probably occurs,[12] it appears that in the Favorskii rearrangement of α-halo ketones such a displacement is unlikely.

Experimental Section

3(a)-Chloro-3(e)-phenyl-*trans*-2-decalone (3). A. Sulfuryl chloride (650 mg) was added to a solution of 3(e)-phenyl-*trans*-2-decalone (1.1 g) in CCl_4 (25 ml). After 6 hr at room temperature, the mixture was poured onto ice water. The CCl_4 layer was separated, dried ($MgSO_4$) and evaporated to yield a solid, mp 115° (recrystallized from acetone in 72% yield). Anal. Calcd for $C_{16}H_{19}ClO$: C, 73.10; H, 7.25; Cl, 13.5. Found: C, 73.23; H, 7.40; Cl, 13.20. Infrared ($CHCl_3$) 3.43, 3.5, 5.85, 6.26, 6.92 μ.

B. A solution of 2(e)-phenyl-*trans*-decalin 2,3-oxide[3] (300 mg) in $CHCl_3$ (30 ml) was stirred with concentrated HCl (5 ml) for 45 min. The $CHCl_3$ layer was separated, dried, and evaporated to yield an oil, 3(a)-chloro-3(e)-phenyl-*trans*-2-decalol (**13**): trifluoroacetate derivative mp 65–66° (recrystallized from isopropyl alcohol). Anal. Calcd for $C_{18}H_{20}ClF_3O_2$: C, 60.84; H, 5.53; Cl, 9.8. Found: C, 60.84; H, 5.53; Cl, 9.8. Compound **13** (250 mg) was dissolved in a solution of DMSO (4 ml) and acetic anhydride (4 ml)[13] and the mixture was then stirred for 24 hr at room temperature. Addition of water precipitated an oil which then crystallized, mp 115° (acetone).

3(e)-Chloro-3(a)-phenyl-*trans*-2-decalone (4). Thionyl chloride (12 ml) was added to a solution of 3(e)-hydroxy-3(a)-phenyl-*trans*-2-decalone (2 g) in CCl_4 (4 ml). The solution was stirred for 18 hrs and then ice-cold water was added dropwise until the thionyl chloride was destroyed. The CCl_4 layer was separated, dried over $MgSO_4$, and evaporated to yield an initial oily product which was recrystallized from Skelly B (mp 136–137°) in 55% yield. Anal. Calcd for $C_{16}H_{19}ClO$: C, 73.10; H, 7.25; Cl, 13.5. Found: C, 73.14; H, 7.39; Cl, 13.32. Infrared ($CHCl_3$) 3.42, 3.5, 5.78, 6.22, 6.89 μ.

Favorskii Rearrangement of Compounds 3 and 4. To study the reaction under polar conditions a solution of compound **3** (1.6 g) and potassium *tert*-butoxide (2 g) or **4** (3.7 g) and potassium *tert*-butoxide (4.6 g) in absolute ethanol (125 ml) was stirred at room temperature for 10 hr. Reactions using nonpolar conditions involved stirring a solution of compound **3** (7.8 g) and potassium *tert*-butoxide (9.6 g) or compound **4** (11.3 g) and potassium *tert*-butoxide (12.8 g) in dimethoxyethane (250 ml). The solvent was then removed by evaporation and water (30–100 ml) was added. The mixture was refluxed for 8 hr, cooled, and extracted with ether (4 × 15 ml or 4 × 50 ml) to remove neutral fraction A. Acidification of the mother liquor with 10% HCl, followed by extraction with ether (4 × 15 ml or 4 × 50 ml), gave an acidic fraction B.

Analysis of Fractions A and B Obtained from 3 Using Potassium *tert*-Butoxide in Ethanol. Fraction B was dissolved in methanol which had been saturated with dry HCl gas, and te solution was then refluxed for 24 hr. Dry column chromatography using $CHCl_3$ and neutral alumina resulted in the isolation of the Favorskii methyl ester **5** (33 mg): 2.2% yield; ir (liquid film) 5.78 (s), 6.24, 6.9 μ; NMR ($CDCl_3$) δ 7.2 (5 H, aromatic), 3.62 (3 H, methyl ester), 0.8–3.1 (14 H, aliphatic envelope). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.02; H, 8.50. Found: C, 79.48; H, 7.60.

A sample of the Favorskii methyl ester **5** was refluxed with 20% KOH (aqueous) solution for 6 hr. Upon cooling the solution was extracted with ether. The aqueous phase was separated, acidified with 10% HCl, and extracted with ether. The ether solution was separated, washed with water, dried, and evaporated to yield an oil which crystallized (mp 111–112° from aqueous ethanol): ir (liquid film) 2.7–4.2, 5.85, 6.24 μ; NMR ($CDCl_3$) δ 10.87 (1 H, broad acidic), 7.3 (5 H, aromatic), 0.2–2.8 (14 H, aliphatic envelope). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.6; H, 8.25. Found: C, 78.94; H, 8.71.

The second component of the acidic fraction was the methyl ester **6** (28 mg, 1.7% yield): ir (liquid film) 5.76, 5.92, 6.25, and 6.9 μ; NMR ($CDCl_3$) δ 7.9 (aromatic ortho protons), 7.3 (aromatic meta protons), 3.6 (3 H, methyl ester), 0.7–3.1 (14 H, aliphatic). The ester was converted to its 2,4-dinitrophenylhydrazone derivative, mp 165° (from aqueous ethanol). Anal. Calcd for $C_{23}H_{26}N_4O_6$: C, 60.51; H, 6.18. Found: C, 60.64; H, 5.79. A 2,4-DNP derivative (mp 126–129°) was also prepared of the free acid of **6**. Anal. Calcd for $C_{22}H_{24}N_4O_6$: N, 12.7. Found: N, 12.6.

Ether extract A was chromatographed on a silica gel column using $CHCl_3$–CCl_4 (1:1) as the eluent. The first fractions contained **7** (24 mg, 1.4%): mp 63° (isopropyl alcohol–water). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.4; H, 8.8. Found: C, 79.63; H, 9.1. NMR ($CDCl_3$) δ 7.2 (5 H, aromatic), 4.25 (1 H, methine), 3.5 (3 H, methine and methylene superimposed), 0.5–2.5 (aliphatic envelope). Successive fractions contained the hydroxy ketone **2** in 42% yield (379 mg) and finally an unknown polymeric material (240 mg).

Analysis of Fractions A and B Obtained from 3 Using Potassium *tert*-Butoxide in 1,2-Dimethoxyethane. Benzoic acid was sublimed by heating fraction B in a sublimation flask at 120° (oil bath). Identification was achieved by mixture melting point, ir, and NMR analysis.

Fraction B was subjected to Fischer–Spier esterification. The methanolic solution was separated from an insoluble material (2.1 g) and then evaporated to yield an oil (750 mg) which was then chromatographed on neutral alumina (dry column) by eluting with chloroform. The first fraction contained the methyl ester **5** (193 mg, 2.6%) whereas the second fraction contained the methyl ester **6** (27 mg), <1% yield.

Ether extract A after evaporation left a polymeric residue (mp 215–220°, mol wt 660).

Analysis of Fractions A and B Obtained from 4 Using Potassium *tert*-Butoxide in Ethanol. Ether extract B was evaporated and esterified (methanolic HCl). After removal of the solvent an oil was obtained which was purified by dry column chromatography (alumina and $CHCl_3$). The first fraction was an unknown (18 mg), ir 5.76 μ, NMR ($CDCl_3$) δ 7.3, 3.65, 3.55, 0.8–3.05, whereas the major fraction was the methyl ester **6** (260 mg, 7% yield).

Analysis of ether extract A by column chromatography (silica gel and $CHCl_3$–CCl_4) revealed the presence of an unknown polymeric material.

Analysis of Fractions A and B Obtained from 4 Using Potassium *tert*-Butoxide in Dimethoxyethane. After evaporation of the ether, the acidic fraction B was heated at 120° in a sublimation apparatus. Benzoic acid was sublimed. A Fischer–Spier esterification was then performed on the residue. The esterified products were chromatographed on alumina (Woelm), eluting with chloroform. The first fraction (50 mg) was not identified. Its infrared spectrum was devoid of aromatic and carbonyl absorption bands. A second fraction was also unknown (176 mg). The third fraction was identified as the methyl ester of **6** (38 mg, 1% yield).

Analysis of the residue obtained from ether extract A by column chromatography (silica gel and $CHCl_3$–CCl_4) revealed the presence of an unknown polymeric material.

Registry No.—**1**, 19297-03-1; **2**, 33201-01-3; **3**, 53993-55-8; **4**, 53993-56-9; **5**, 53993-57-0; **5** free acid, 53993-58-1; **6**, 53993-59-2; **6** 2,4-DNP, 53993-60-5; **6** free acid 2,4-DNP, 53993-61-6; **7**, 53993-62-7; **13**, 53993-63-8; **13** trifluoroacetate, 53993-64-9; 2(e)-phenyl-*trans*-decalin 2,3-oxide, 54053-46-2.

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Stereochemistry in Trivalent Nitrogen Compounds. XXV. Solvent and Medium Effects on Degenerate Racemization in Aminosulfenyl Chlorides[1]

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Received August 12, 1974

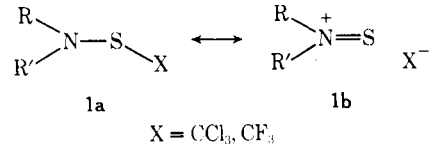
The barriers to degenerate racemization in a series of *N*-benzyl-*N*-methylsulfenamides, $RSN(CH_3)CH_2C_6H_5$, have been determined by observing the coalescence of the nmr signals of diastereotopic benzyl methylene protons which is associated with degenerate racemization. In each of these compounds the ligand, R, at sulfur has a heteroatom (Cl, O, N, or S) attached to sulfenyl sulfur. The barrier of the chlorosulfenamide (R = Cl) in contrast to the other members of the series, showed a dramatic decrease (4.2 kcal/mol) when the solvent was changed from toluene-d_8 to chloroform-*d*. Addition of tetramethylammonium chloride or tetraethylammonium perchlorate also results in a substantial increase in the rate of degenerate racemization. These changes provide evidence for a pathway for degenerate racemization in addition to torsion about the N–S bond. Heterolysis of the S–N bond and SN2 displacement by chloride ion at sulfur were considered as possible racemization mechanisms.

The substantial barriers to rotation about the N–S formal single bond in sulfenamides renders this moiety a unit of axial chirality in suitably substituted compounds.[3] This axial chirality can be made manifest by the observation of chemical shift nonequivalence of diastereotopic benzyl methylene protons in the low-temperature nmr spectra of *N*-benzylsulfenamides. The coalescence of signals for diastereotopic benzyl methylene protons which is observed at higher temperatures is associated with a topomerization in which a chiral sulfenamide molecule is reversibly interconverted with its mirror image, *i.e.*, a degenerate racemization.

It has been shown that the electronic nature of the substituent at the sulfenyl sulfur atom has a major effect on the chemical properties of the sulfenamide group.[4] Similarly the conformational properties of sulfenamides are strongly related to the electron-withdrawing power of the ligand at sulfenyl sulfur. Electron-withdrawing substituents in the para position of benzenesulfenamides dramatically increase the barrier to torsion about the nitrogen–sulfur bond.[5] Thus, the barrier to rotation about the N–S bond in *N*-benzenesulfonyl-*N*-isopropyl-2,4-dinitrobenzenesulfenamide is nearly 4 kcal/mol higher than that in the corresponding benzenesulfenamide. The rate data obtained for a series of para-substituted *N*-benzenesulfonyl-*N*-isopropylbenzenesulfenamides afforded a Hammett reaction constant (ρ) of −2.1 for torsion about the sulfenyl S–N bond as a function of the para substituent on the sulfenyl phenyl ring. Analysis of the linear free energy relationships for compounds in this and related series implicated p–d π bonding between nitrogen and sulfur as a major contributor to the enhanced barriers in these compounds.[5]

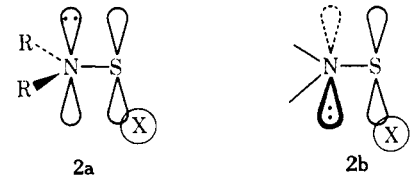
By contrast, differences in p–d π bonding did not seem to have an appreciable effect on the nitrogen inversion barriers in *N*-(arenesulfenyl)aziridines.[6] The dependence of the nitrogen inversion barriers upon the electron-withdrawing capability of the para substituent in the sulfenyl phenyl ring was negligible and the Hammett constant obtained, −0.16 ± 0.1, was not significantly outside of experimental error. On the other hand, the presence of a trihalomethyl group at sulfenyl sulfur results in a fairly substantial lowering of the nitrogen inversion barrier. The inversion barriers in 1-trichloromethanesulfenyl and 1-trifluoromethanesulfenyl-2,2-dimethylaziridine are 2–2.5 kcal/mol less than the barriers which would be estimated on the basis of steric factors alone.[7] This rate acceleration was attributed to σ–π conjugation (negative hyperconjugation) as expressed in canonical structures **1a** and **1b**. A similiar explanation had been used by Bystrov and coworkers to account for the anomalously low nitrogen inversion barriers in methylenealkoxyaziridines.[8] They referred to overlap between the nitrogen lone-pair orbital and C–O antibonding σ^* orbital. This explanation in a molecular orbital framework is equivalent to that expressed in a resonance framework using canonical structures **1a** and **1b**. The observed dependence of the nitrogen inversion barriers in sulfenylaziridines upon the electronic nature of substituents at sulfenyl sulfur also implies that the nearly planar geometry at nitrogen found in the solid state for an *N*-trichloromethanesulfenylsulfonamide derives from σ–π conjugation rather than p–d π bonding as originally suggested.[3c]

Since σ–π conjugation has been implicated as the origin for reduced nitrogen inversion barriers in sulfenylaziridines as well as decreased ground-state pyramidality in an acyclic sulfenylsulfonamide, it might also play a role in determining the magnitude of S–N torsional barriers in acyclic sulfenamides. Thus, overlap between the nitrogen lone-pair orbital and the sulfur atomic orbital used in bonding to X can be important only in the ground state **2a** where the



1a **1b**

X = CCl_3, CF_3



2a **2b**

XSN plane bisects the RNR′ angle and must be negligible in the transition state for torsion where the S–X bond axis lies in or near the nodal surface of the nitrogen lone-pair orbital. The effect of significant σ–π conjugation in the ground state would be to increase the torsional barrier