Ene Reaction Mechanisms. 2. Regioselectivity with N-Aryl-N'-p-tosylsulfur Diimides as Enophiles. Crystal Structure of N-(Pentafluorophenyl)-N'-p-tosylsulfur Diimide[1]

Heribert Münsterer and Günter Kresze*

Organisch-chemisches Institut, Technische Universität München, D-8046 Garching, Germany

Viktor Lamm and Alfred Gieren*

Max-Planck-Institut für Biochemie, Abteilung für Strukturforschung I, D-8033 Martinsried, Germany

The ene reactions of sulfur diimides TosNSNAr (1; Ar = C_6H_5, 4-$O_2NC_6H_4$, and C_6F_5) with 2-methyl-2-butene (2) have been investigated. The products undergo a [2,3] sigmatropic rearrangement. The structures of these rearranged products have been determined. Taking into account the regioselectivities shown by compounds 1 in related cycloadditions, the results suggest that the ArN=S bond is exclusively involved in the ene process. This bond has been proven to be Z configurated for Ar = C_6F_5 by an X-ray structure determination, whereas the TosN=S bond possesses the E configuration. Steric shielding of the (E)-N=S bond by the aromatic system attached to the (Z)-N=S bond is deemed to be important in determining the regioselectivity, especially if the H abstraction is to be executed by the lone electron pair of the nitrogen atom.

In principle, several kinds of regioselectivity are possible for ene reactions. In unsymmetrical alkenes there are two different sites of attack on the carbon atoms of the CC double bond in addition to the different sites of abstraction of the allylic hydrogen. More or less pronounced regioselectivity is usually shown in this respect and many investigations[2] have dealt with such concerns. On the other hand, data on the regioselectivity in the enophilic reagent are lacking as far as we know. This is not surprising because in enophiles of the X=Y type, X and Y either are indistinguishable (e.g., symmetrically substituted alkenes or diazenes) or the atom which acts as an electrophilic center in the ene reaction is predetermined (e.g., carbonyl compounds or thiones). Where cumulenes X=Z=Y act as enophiles, another kind of regioselectivity may be envisaged. Here, either the X=Z or the Y=Z bond may be involved in the ene reaction. However, in the cases investigated up to the present, these bonds have been far too different to observe competition between the bonds in their activity as enophiles; isocyanates[3] and N-sulfinyl compounds are good examples.[4]

Sulfur diimides may be considered as thiocumulenes. As shown earlier,[5] these compounds are very reactive enophiles, their reactivity depending strongly on the electron-attracting power of the N-substituents. Therefore, unsymmetrically substituted sulfur diimides should be uniquely suited for an investigation of the enophilic regioselectivity. As shown in Scheme I, compounds of the type RN=S=NR' (1) should in principle yield two regioisomers, 3 or 4, in their ene reactions with an alkene such as 2-methyl-2-butene (2). Usually, these initial products are converted very rapidly even under mild conditions by a [2,3] sigmatropic rearrangement into the diaminosulfanes 5 and 6. This rearrangement offers a convenient opportunity to prove the structure (or the composition of a product mixture) of the primary products. The ¹H NMR spectra of the Na₂SO₃ degradation products of the rearranged compounds 5 and 6, namely, the 2-alkenylamino derivatives 7 and 8, are plainly distinguishable. In the course of our work on the mechanisms of ene re-

Scheme I
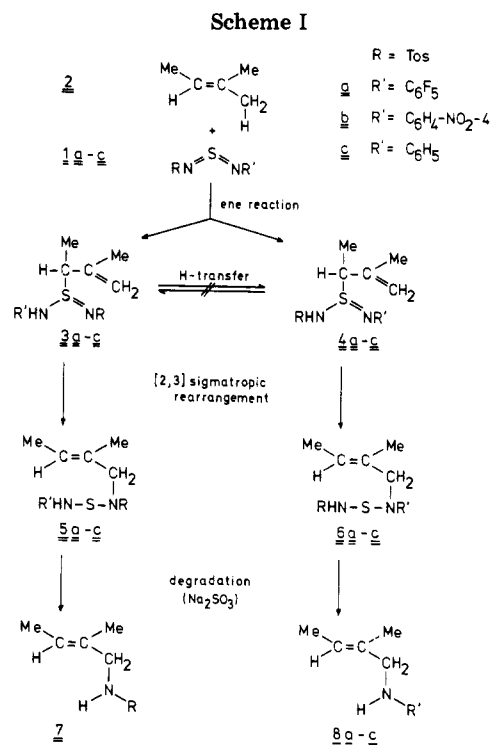
actions, we have investigated the structures of the products of the reactions of the series of enophiles 1 [R = Tos; R' = pentafluorophenyl (1a), R' = 4-nitrophenyl (1b); R' = phenyl (1c)] with the common ene reagent 2. All these reactions proceed in CDCl₃ solution at 20 °C much more slowly than those with the ditosyl derivative (R = R' = Tos, 1d); the latter compound reacts almost quantitatively in less than 1 min, while under identical conditions, the half-reaction time $\tau_{1/2}$ is 24 h for 1a, according to ¹H NMR analysis, and 250 h for 1c in a tenfold greater concentration. At higher temperatures the decomposition of 1a–c becomes predominant.

Under the reaction conditions employed, all ene products rearrange spontaneously to the diaminosulfanes 5/6; only one isomer is produced in each case according to the ¹H NMR. These products are reduced by treatment with Na₂SO₃ to give allylamine derivatives. In all three cases only N-[(E)-2-methyl-2-butenyl]-4-toluenesulfonamide (7a) was isolated as the degradation product in 50–70% yield. This means that the reaction of the enophiles 1a–c with

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(4) (a) Kresze, G.; Bussas, R. *Liebigs Ann. Chem.* **1980**, 843. (b) Bussas, R.; Kresze, G. *Ibid.* **1982**, 545.

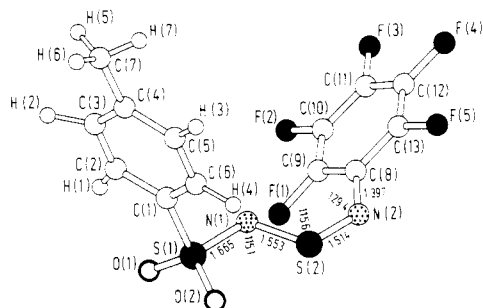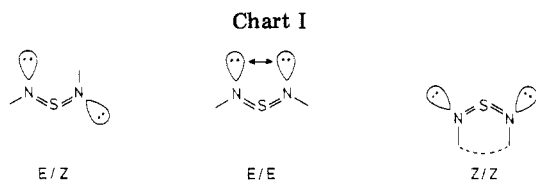(5) Bussas, R.; Kresze, G. *Liebigs Ann. Chem.* **1980**, 629 and literature cited therein.

Figure 1. Molecular structure of N-(pentafluorophenyl)-N'-p-tosylsulfur diimide (1a). Given bond lengths are in angstroms and angles in degrees.

Chart I

2 proceeds with high regioselectivity, the only detectable products being the diaminosulfanes **5a-c.** This conclusion was confirmed by an X-ray analysis of **5b.**[6]

Full knowledge of the structure of the starting material is an essential requirement for any discussion of these results. Previous investigations of open-chain, symmetrically substituted sulfur diimides with R = R' = Me, 4-MeC$_6$H$_4$, 4-PhC$_6$H$_4$, or Tos[7–10] have proven that these reagents possess the *E,Z* configuration in the crystalline or gaseous state. Compounds with an RS group bonded to both nitrogens form an exception: here, the *Z,Z* configuration is realized in the crystal[11,12] probably because of S⋯S interactions similar to those which are known for S$_4$N$_4$.[13] However, no data exist for simple, open-chain, unsymmetrically substituted sulfur diimides; full knowledge of the configuration of such a derivative seemed important not only in connection with the investigation of the ene reaction but also for a more general understanding of the principles governing the structural features of NSN compounds. Therefore, the crystal structure of the pentafluorophenyl compound **1a** was determined.

Stereochemistry of
N-(Pentafluorophenyl)-N'-p-tosylsulfur Diimide
(1a)

The molecular structure of **1a** is represented in Figure 1. As in the case of the sulfur diimides mentioned above,[7–10] an *E/Z* configuration with respect to the S–N double bonds of the sulfur diimide unit also is found in the asymmetrically substituted **1a**. Until now, in crystal structures of open-chain compounds only the *E/Z* configuration and in cyclic ones only the *Z/Z* configuration

Chart II
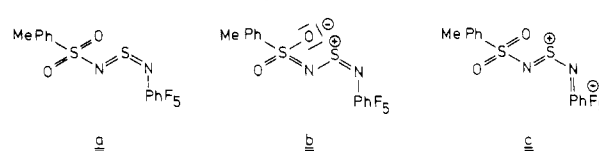
have been observed. An *E/E* configuration has never been identified in any crystal structure. The preference of the *E/Z* to the *E/E* configuration for open-chain sulfur diimides might be attributed to the repulsion of the lone pairs at the nitrogen atoms in the case of the *E/E* configuration, as shown in Chart I.

This interpretation is supported also by the crystal structure of the N,N'-di-*tert*-butyl-N-methylsulfur diimidium tetrafluoroborate.[14] There the blocking of a lone pair at an N atom by a methyl group leads to an *E/E* form of the di-*tert*-butylsulfur diimide moiety. A further source of support for this interpretation is the crystal structure of the tungsten(0) tetracarbonyl complex of di-*tert*-butylsulfur diimide.[15] In this compound the sulfur diimide unit is coordinated to the tungsten via both lone pairs at the N atoms. The participation of the lone pairs in coordinative bonds also allows an *E/E* configuration at the S–N bonds in this case.

The important question with respect to the stereochemistry of the ene reaction of sulfur diimides, i.e., which substituent occupies the *E* and *Z* configuration, respectively, can now be resolved in that the Tos—N=S bond has the *E* configuration and the C$_6$F$_5$—N=S bond the *Z*.

As in other sulfur diimides which may be open-chain or cyclic,[16] in **1a** the atoms bound to nitrogen [S(1) and C(8)] are also within the plane of the sulfur diimide unit.[16] The torsion angles around the S^{IV}–N bonds deviate only insignificantly from the ideal values of 180° and 0°, respectively. As in open-chain, symmetrically substituted sulfur diimides, the bond angle at the nitrogen atom N(1) of the *E*-configurated S–N double bond (115.1°) is remarkably smaller than the bond angle at the nitrogen atom N(2) of the *Z*-configurated one (129.4°). The bond angle at the S^{IV} sulfur, S(2) (115.6°), differs only slightly from those in **1d** (114.7°)[10] and di-*p*-tolylsulfur diimide (117.2°).[8] The asymmetric structure of the heterocumulene system is manifested in differing S^{IV}–N bond lengths. The *Z*-configurated S–N bond with a length of 1.514 Å is remarkably shorter than the *E*-configurated bond with 1.553 Å. The average of both bond lengths corresponds to the mean value found in sulfur diimides having no significant π interaction with substituents.[16] A comparison with corresponding values in **1d** indicates that the elongation of the *E*-configurated S^{IV}–N bond (**1a**, 1.553 Å; **1d**, 1.524 Å) is correlated with a shortening of the S^{VI}–N bond (**1a**, 1.665 Å; **1d**, 1.686 Å). A quantitative relation between these S–N distances recently was derived for systems of the type RSO$_2$N=S=.[17,18] Because the correlation mentioned is independent of the coordination number of the tetravalent sulfur (two or three) it is not surprising that an almost equivalent pair of bond distances for the S^{IV}–N and the S^{VI}–N bond with values of 1.55 and 1.65 Å is established in the structure of 2,5-di-*tert*-butyl-1-[(*p*-tolylsulfonyl)imino]-1λ^4,2,5-thiadiazolidine-3,4-dione,[18]

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though here the tetravalent sulfur is tricoordinate.

For steric reasons, the pentafluorophenyl residue does not lie in the plane of the NSN system. There is a torsion angle around the N(2)–C(8) bond of about 42° in relation to the NSN system (torsion angles: S(2)–N(2)–C(8)–C(9), -44°; S(2)–N(2)–C(8)–C(13), 141°). This degree of torsion is forced by the intramolecular repulsion F(1) ↔ N(1), which, in turn, is to be correlated with the relatively short contact distance of 2.762 (7) Å. The F(1)–N(1) contact distance contributes also to the stretched angle at N(2) and to the deformation of the exterior angles of the phenyl ring at C(8), so that the angle N(2)–C(8)–C(9) within the all-cis system N(1) → F(1) of 126.3° is larger than the neighboring angle N(2)–C(8)–C(13) by about 9°. Despite the torsion around the N(2)–C(8) bond, there exists a π interaction, albeit very small, between the sulfur diimide system and the pentafluorophenyl residue demonstrated by a shortening of this formal single bond to a value of 1.397 Å.

In accordance with the molecular geometry discussed above the bonding relationships in **1a** can be described by the resonance formulas a–c (Chart II). The main contribution arises from a. Of the remaining forms c contributes much less than b.

Comparison of the structure of **1a** with that of **1d** shows that the conformation of the Tos—N=S=N fragment in **1a** is almost identical with that of the (E)-Tos—N=S=N moiety in **1d**. Apart from different S–N bond distances, all the other bond lengths and bond angles are nearly identical. The largest difference among the bond angles is 1.7°, with the torsion angles also differing only slightly. Noteworthy is the fact that even the relatively small angle deviations from 120° within the phenyl rings of these groups are replicated in both compounds. Therefore, one can conclude that the configuration and conformation of these Tos—N=S=N fragments found in the crystalline state are essentially molecular properties and are not significantly influenced by the crystal packing.

Discussion

The secondary products **5** observed undoubtedly arise from the intermediate **3** by sigmatropic rearrangement. For the formation of these intermediates, however, two principal possibilities exist: (a) either compounds **3** are the kinetically controlled products of the ene reaction occurring with participation of the ArN=S double bond (b) or the ene reaction proceeds with participation of the TosNS double bond, yielding products **4**; these, in turn, undergo rapid proton transfer to **3**. This second possibility, at first sight, seems by far the more probable. The intramolecular proton transfer should be very fast, even in comparison to the sigmatropic rearrangement. Furthermore, the "normal" order of reactivity for SN double bonds in RNSO and RNSNR derivatives follows that of the electron acceptor character of the N-substituents R, i.e., R = R′SO₂ > R′O₂C > Ar. On this basis one should expect that the TosNS double bond in compounds like TosNS-NAr is by far more reactive than the ArNS bond. However, one has to be very cautious in extrapolating the behavior of unsymmetrically substituted compounds from that of symmetrically substituted analogues in systems characterized by strong interactions.[19]

One indication that such interactions prevail throughout the whole RN=S=NR′ system, which exhibits strong dependence on the nature of R and R′, may be derived from the ¹³C NMR spectrum of **1c**. For phenyl derivatives

C_6H_5X, the shift of the NMR signal for the paracarbon atom is correlated empirically with the Hammett σ constant. In this way, a σ^+ value of -0.1 has been determined for X = C_6H_5N=S=N[20] while a σ^+ value of 0.6 has been deduced for Tos—N=S=N from the ¹³C NMR spectrum of **1c**. The electronic effect of a sulfur diimide group, then, is not constant but depends on the substituent on the N atom. It can thus be deduced that the bond structure of the C_6H_5N=S bond is strongly influenced by the group attached to the sulfur atom. These circumstances may lead to considerable enhancement of the reactivity, e.g., in ene reactions.

The second indication of a possible enhancement of reactivity of the ArNS bond in compounds like **1c** is found in the X-ray structure data. A general correlation between the SN bond length and reactivity in the ene reaction has been postulated for the related RNSO compounds.[21] Although the shortness of the bond length seems to be a necessary but insufficient condition for high reactivity in ene reaction, the relative bond length of the ArNS (1.514 Å) and TosNS (1.553 Å) in **1a** clearly corresponds to the reactivity order ArNS > TosNS (cf. the TosNS bond lengths in TosN=S=NTos: 1.524 and 1.521 Å).

The third argument is the most direct one. Whatever the detailed mechanism of the ene reaction in the present case may turn out to be, it should be closely related to that of other pericyclic processes of the same educts. Thus [2 + 3][22] and [2 + 4][23] cycloadditions of compounds of type 1 are known, and their regioselectivity has been investigated. In each instance these reactions occur preferentially with participation of the S=N bond with the *less* electronegative substituent on the nitrogen atom, that is to say with compounds of type 1 with participation of the "less reactive" ArNS and *not* the TosNS bond. In these cases, *no* proton transfer is involved and kinetic control of the reactions has to be assumed. This, in our opinion, strengthens the suspicion that in the ene reaction, too, this bond participates as proposed in the above-mentioned mechanism (a). We cannot at the moment disprove the possibility of the TosNS double bond reaction followed by the proton transfer.

However, this would be equivalent to the assumption of reverse regioselectivity in the ene reaction and in cycloadditions of the same compounds. The reasons for such a strange behavior would be somewhat difficult to explain.

On the other hand, the assumption that the ArNS double bond participates in an analogous fashion in all three pericyclic processes leads to more coherent descriptions of the geometry of the corresponding transition states. Generally, the approach of an alkene molecule to the NSN system in an E,Z configuration is sterically less hindered for the Z than for the E moiety of a sulfur diimide. This difference in hindrance is particularly important in **1a** where the pentafluorophenyl ring effectively shields the (E)-S=N—Tos moiety. This shielding reaches a maximum where the H abstraction proceeds with participation of the lone pair of the nitrogen atom, as previously proposed.[24] Thus, electronic as well as steric factors contribute to making the ArNS bond more prone to participation in the ene reaction than the TosNS bond.

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Experimental Section

All reactions except degradations of **5a–c** were carried out under dry nitrogen. Solvents were dried according to standard methods, distilled, and stored over molecular sieves (400 pm). Melting points are uncorrected. IR spectra were taken with a Perkin-Elmer 257 spectrometer. ¹H NMR spectra were recorded on a Varian A 60 and ¹³C NMR spectra on a JEOL JNM-FX 60 (15.0 MHz) spectrometer for CDCl₃ solutions with Me₄Si as an internal standard.

Materials. 2-Methyl-2-butene (**2**) was purchased from Aldrich and 2,3,4,5,6-pentafluoroaniline from Fluka. Ditosylsulfur diimide (**1d**) was obtained by a one-step procedure recently published.[5]

N-(Pentafluorophenyl)-N'-p-tosylsulfur Diimide (1a). A solution of 2,3,4,5,6-pentafluoroaniline (6.6 g, 36 mmol) in 40 mL of benzene was slowly added to a chilled suspension of ditosylsulfur diimide (13.1 g, 35 mmol) in 55 mL of benzene. After the mixture was stirred 16 h at 20 °C, tosylamide was filtered off and the solvent distilled from the filtrate. The remaining solid was recrystallized from ethyl acetate to afford orange, moisture-sensitive prisms: yield 11.3 g (84%); mp 145–146 °C; ¹H NMR δ 2.48 (s, 3, CH₃-Ar), 7.45 ("d", 2, J = 8.5 Hz, H3 of 4-MeC₆H₄), 7.93 ("d", 2, J = 8.5 Hz, H2 of 4-MeC₆H₄); ¹³C NMR δ 21.7, 128.1, 130.8, 136.7, 146.5 (only C₆H₄CH₃, other signals split due to C–F coupling). Anal. Calcd for C₁₃H₇F₅N₂O₂S₂: C, 40.84; H, 1.85; N, 7.33. Found: C, 40.98; H, 1.97; N, 7.25.

N-(4-Nitrophenyl)-N'-p-tosylsulfur Diimide (1b). The compound was prepared by transimidation according to a procedure already described for the corresponding benzenesulfonyl species:[25] orange-red crystals; yield 82%; mp 135–137 °C (ethyl acetate); ¹H NMR δ 2.45 (s, 3, CH₃-Ar), 7.42 ("d", 2, J = 8.5 Hz, H3 of 4-MeC₆H₄), 7.93 ("d", 2, J = 8.5 Hz, H2 of 4-MeC₆H₄), 8.08 ("d", 2, J = 9 Hz, H2 of 4-NO₂C₆H₄). 8.33 ("d", 2, J = 9 Hz, H3 of 4-NO₂C₆H₄); ¹³C NMR δ 21.7, 125.5, 128.0, 130.8, 137.4, 146.0, 149.0, 176.2. Anal. Calcd for C₁₃H₁₁N₃O₄S₂: C, 46.28; H, 3.29; N, 12.46. Found: C 46.49; H, 3.38; N, 12.32.

N-Phenyl-N'-tosylsulfur Diimide (1c). See **1b**: yellow needles; yield 67%; mp 114–116 °C (ethyl acetate); ¹H NMR δ 2.41 (s, 3, CH₃-Ar), 7.2–7.7 (m, 5, C₆H₅), 7.9–8.3 (m, 4, C₆H₄Me); ¹³C NMR δ 21.6, 127.5, 128.3, 130.0, 130.6, 132.3, 138.2, 145.3, 145.6. Anal. Calcd for C₁₃H₁₂N₂O₂S₂: C, 53.41; H, 4.14; N, 9.58. Found: C, 53.64; H 3.79; N, 9.45.

N-[(E)-2-Methyl-2-butenyl]-N-[[(pentafluorophenyl)-amino]thio]-p-tosylamide (5a). 2-Methyl-2-butene (0.7 g, 10 mmol) was added to a suspension of **1a** (2.0 g, 5.2 mmol) in 8 mL of CHCl₃. The mixture was stirred for 5 days at room temperature, and **5a** was then precipitated by addition of pentane. Dissolving the product in CHCl₃/pentane (1:4) at 20 °C and cooling to –20 °C afforded colorless plates: yield 1.8 g (77% with respect to **1a**); mp 105–106 °C; IR (KBr) 3300 (NH), 1340, 1160 (OSO) cm⁻¹; ¹H NMR δ 1.46 ("s", 3, CH₃C=), 1.52 (d, 3, J = 7 Hz, CH₃CH), 2.46 (s, 3, CH₃-Ar), 3.97 (s, 2, CH₂), 5.1–5.6 (m, 1, CH=), 5.9 (br s, 1, NH), 7.35 ("d", 2, J = 8.5 Hz, H3 of 4-MeC₆H₄), 7.82 ("d", 2, J = 8.5 Hz, H2 of 4-MeC₆H₄). Anal. Calcd for C₁₈H₁₇F₅N₂O₂S₂: C, 47.78; H, 3.39; N, 6.19. Found: C, 47.95; H, 3.89; N, 6.28.

N-[(E)-2-Methyl-2-butenyl]-N-[[(4-nitrophenyl)amino]-thio]-p-tosylamide (5b). A solution of **1b** (1.6 g, 4.7 mmol) and **2** (0.5 g, 7.1 mmol) in 8 mL of CHCl₃ was stirred for 10 days at room temperature. Thereafter, the solvent and excess **2** were removed in vacuo, and the residue was dissolved in a minimum of CH₂Cl₂. By addition of pentane and cooling to 0 °C the product was obtained as a solid, which was recrystallized several times from CH₂Cl₂/pentane (1:5) according to the method described for **5a** to give pale yellow prisms: yield 1.1 g (58% with respect to **1b**); mp 122–123 °C; IR (KBr) 3330 (NH); 1510, 1330 (ONO), 1330, 1165 (OSO) cm⁻¹; ¹H NMR δ 1.37 ("s", 3, CH₃C=), 1.57 (d, 3, J = 7 Hz, CH₃CH), 2.44 (s, 3, CH₃-Ar), 4.01 ("s", 2, CH₂), 5.2–5.7 (m, 1, CH=) 6.7 (br s, 1, NH), 7.16 ("d", 2, J = 9 Hz, H2 of 4-NO₂C₆H₄), 7.35 ("d", 2, J = 8.5 Hz, H3 of 4-MeC₆H₄), 7.83 ("d", 2, J = 8.5 Hz, H2 of 4-MeC₆H₄), 8.17 ("d", 2, J = 8.5 Hz, H3 of 4-NO₂C₆H₄). Anal. Calcd for C₁₈H₂₁N₃O₄S₂: C, 53.05; H, 5.19; N, 10.31. Found: C, 53.01; H, 5.18; N, 10.35.

N-[(E)-2-Methyl-2-butenyl]-N-[(phenylamino)thio]-p-tosylamide (5c). Compound **1c** (2.0 g, 6.8 mmol) and **2** (0.8 g,

11 mmol) were stirred in a CHCl₃ solution (8 mL) for 30 days at room temperature. Subsequent addition of pentane and cooling to –20 °C precipitated the product from which solvent was drawn off, and the residue was purified by recrystallization from CCl₄/pentane (1:5) as described for **5a** to afford colorless needles: yield 0.9 g (37% with respect to **1c**); mp 64–65 °C; IR (KBr) 3340 (NH), 1340, 1160 (OSO) cm⁻¹; ¹H NMR δ 1.32 ("s", 3, CH₃C=), 1.53 (d, 3, J = 7 Hz, CH₃CH), 2.43 (s, 3, CH₃-Ar), 3.93 (s, 2, CH₂), 5.0–5.5 (m, 1, CH=), 6.2 (br s, 1, NH), 6.9–7.5 (m, 7, C₆H₅ and H3 of 4-MeC₆H₄), 7.83 ("d", 2, J = 8.5 Hz, H2 of 4-MeC₆H₄). Anal. Calcd for C₁₈H₂₂N₂O₂S₂: C, 59.64; H, 6.12; N, 7.73. Found: C, 59.43; H, 6.22; N, 7.61.

General Procedure for the Degradation of 5a–c into N-[(E)-2-Methyl-2-butenyl]-p-tosylamide (7). About 4 g (20 mmol) of Na₂SO₃·7H₂O and catalytic amounts of benzyltributylammonium bromide were added to a solution of **5** (2 mmol) in 40 mL of ether. The resulting suspension was stirred for 7 days at room temperature. Thereupon undissolved material was filtered off and washed with ether, and the solvent was removed in vacuo. The residue was extracted with cyclohexane (100 mL) at 70 °C. After evaporation of the cyclohexane the product was obtained as an oil, which was brought to crystallization by adding about 30 mL of CHCl₃/pentane (1:10) and subsequent cooling to –20 °C: yield 50–70%; mp 43–44 °C; IR (KBr) 3270 (NH), 1325, 1165 (OSO) cm⁻¹; ¹H NMR δ 1.50 (d, 3, J = 7 Hz, CH₃CH), 1.53 (s, 3, CH₃C=), 2.40 (s, 3, CH₃-Ar), 3.43 (d, 2, J = 6 Hz, CH₂), 5.03 (t, 1, J = 6 Hz, NH), 5.1–5.6 (m, 1, CH=), 7.30 ("d", 2, J = 8.5 Hz, H3 of 4-MeC₆H₄), 7.78 ("d", 2, J = 8.5 Hz, H2 of 4-MeC₆H₄). Anal. Calcd for C₁₂H₁₇NO₂S: C, 60.22; H, 7.16; N, 5.85. Found: C, 60.07; H, 7.25; N, 5.94.

X-ray Structure Analysis of 1a. Compound **1a** crystallizes in the monoclinic, face-centered noncentrosymmetric space group Cc (No. 9). The crystal selected for X-ray measurements was sealed under Ar as the protecting gas in a Debye–Scherrer capillary tube. Approximate cell dimensions and the space group were determined by precession and Weissenberg photographs. The space groups Cc or C2/c were derived by Laue diffraction symmetry and systematic extinctions. From symmetry considerations the centrosymmetric space group C2/c could be excluded. Because the unit cell contains four molecules, these should occupy special positions in this space group either on a symmetry center or a twofold axis. But, assuming a nondisordered structure, the known chemical constitution of **1a** fulfills none of these symmetry elements.

The precise cell dimensions were determined by a Nonius CAD4 diffractometer: a = 9.768 (4) Å, b = 13.028 (5) Å, c = 13.359 (5) Å, β = 119.52 (3)°, V = 1479.3 Å³, Z = 4, d = 1.714 Mg m⁻³. The reflection intensities were measured on a computer-controlled Siemens AED-I diffractometer using Mo Kα radiation (Nb filter). By the five-point measurement procedure[26] 1270 independent reflections with I > 2σ_I were collected in the θ/2θ scan mode (θ_max = 26°) by using the diffractometer program HERCULES.[27] Lorentz–polarization corrections were applied to the intensities in the usual way. An absorption correction (μ Mo Kα = 0.365 mm⁻¹) was omitted.

The E-value statistics confirmed the noncentrosymmetric space group. The structure was solved by direct methods by using 184 reflections with E > 1.3 for phase determination. For computer calculations mainly the SHELX 76 program[28] was used on a VAX-11/780 computer. The atomic scattering factors of C, N, O, F, and S[29] as well as of H[30] were those implied in this program. An E Fourier synthesis calculated with the best phase set according to the R_α criterion unequivocally showed both sulfur positions. By subsequent Fourier syntheses all nonhydrogen atoms could be localized. In this process, the symmetry of the space group C2/c had to be overcome in the beginning because the nearly equal y coordinates of the sulfur atoms imply approximately a special

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Table I. Fractional Atomic Coordinates of the
Non-Hydrogen Atoms of 1a with Standard
Deviations in Parentheses[a]

	x	y	z	B_{eq}
S(1)	0.4127 (2)	0.5606 (1)	0.4075 (2)	4.4 (1)
S(2)	0.7137 (2)	0.5423 (1)	0.4502 (2)	5.1 (1)
F(1)	0.8165 (6)	0.4892 (4)	0.7074 (5)	6.0 (2)
F(2)	0.9427 (9)	0.3443 (6)	0.8689 (5)	7.7 (3)
F(3)	1.1288 (8)	0.1989 (5)	0.8566 (6)	7.2 (3)
F(4)	1.1825 (7)	0.1937 (5)	0.6764 (7)	7.7 (2)
F(5)	1.0537 (8)	0.3362 (6)	0.5118 (6)	8.3 (3)
O(1)	0.3660 (7)	0.5867 (5)	0.4904 (6)	6.4 (3)
O(2)	0.4176 (7)	0.6401 (4)	0.3365 (6)	5.7 (2)
N(1)	0.5870 (6)	0.5030 (4)	0.4790 (5)	4.4 (2)
N(2)	0.8727 (7)	0.4905 (6)	0.5145 (6)	5.2 (2)
C(1)	0.2930 (7)	0.4603 (5)	0.3200 (6)	3.8 (2)
C(2)	0.1969 (8)	0.4091 (5)	0.3533 (6)	4.5 (3)
C(3)	0.1036 (9)	0.3310 (5)	0.2855 (7)	4.9 (3)
C(4)	0.1050 (8)	0.3028 (5)	0.1844 (6)	4.4 (3)
C(5)	0.2008 (9)	0.3561 (6)	0.1541 (6)	5.0 (3)
C(6)	0.2936 (9)	0.4355 (6)	0.2203 (7)	4.8 (3)
C(7)	−0.0007 (11)	0.2172 (7)	0.1104 (8)	5.9 (4)
C(8)	0.9248 (7)	0.4156 (5)	0.6004 (6)	4.1 (2)
C(9)	0.8996 (8)	0.4146 (6)	0.6946 (6)	4.6 (2)
C(10)	0.9679 (9)	0.3431 (7)	0.7794 (7)	5.2 (3)
C(11)	1.0642 (9)	0.2678 (6)	0.7736 (6)	5.2 (3)
C(12)	1.0908 (8)	0.2657 (6)	0.6813 (8)	5.1 (3)
C(13)	1.0221 (8)	0.3381 (6)	0.5970 (7)	5.3 (3)

[a] The given isotropic temperature parameters (B_{eq}) are one-third of the trace of the orthogonalized anisotropic B_{ij} tensor.

position for the S–S arrangement on a twofold axis. The structure was refined by least-squares methods first with isotropic and then with anisotropic temperature parameters. After some steps of refinement, only the two atoms H(1) and H(4) positioned next

to the molecular center of mass could be clearly recognized in a difference Fourier synthesis. The remaining H positions were calculated to be in accord with expectation. Only the H atoms found in the difference Fourier synthesis and H(2) of the phenyl residue could be refined in the normal way with isotropic temperature parameters. The refinement of the remaining H atoms was carried out under constraints with fixed bond distances (1 Å) and temperature parameters (10 Å²) and by taking the hydrogens of the methyl as a rigid group. The refinement was done in two strongly overlapping blocks. It converged to $R_w = 0.072$ ($R_w = \sum_w{}^{0.5}|F_c| - |F_c|/\sum_w{}^{0.5}|F_0|$). The following weighting scheme was applied: $w = k/[\sigma^2|F_0| + 0.001|F_0|^2]$. The final positional and isotropic temperature parameters of the nonhydrogen atoms are given in Table I.

Binding Profiles for Oligoethylene Glycols and Oligoethylene Glycol Monomethyl Ethers and an Assessment of Their Abilities To Catalyze Phase-Transfer Reactions

George W. Gokel,* Deepa M. Goli, and Rose Ann Schultz

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Received March 16, 1983

The equilibrium binding or stability constants (K_s) between Na$^+$ and oligoethylene glycols [HO(CH$_2$CH$_2$O)$_n$H], monomethyl ethers [HO(CH$_2$CH$_2$O)$_n$CH$_3$], and dimethyl ethers [CH$_3$O(CH$_2$CH$_2$O)$_n$CH$_3$] have been determined in anhydrous methanol solution. The ranges of compounds involved are as follows: diols, n = 3–312; monoethers, n = 6–15; diethers, n = 3–21. Although the slopes vary some from species to species, the plot of log K_s vs. log molecular weight is an essentially straight line. There is no peak in binding observed when a particular number of oxygens might be present to provide, for example, an octahedron of donor groups or a quasi-crown coil. The molecular weight is not crucial to the binding since equal weights of different glycols afford the same net sodium binding. This similarity does not extend to reactivity in the liquid–liquid phase-transfer catalytic system in which it appears that one molecule of polyethylene glycol derivative effects one reaction at a time. Thus equal weights of shorter chains are much more effective than longer chain lengths of similar species.

Ever since Pedersen's discovery of crown ethers and their cation-binding properties,[1] there has been considerable general interest in the corresponding oligoethylene glycols as less expensive analogues. In the same year the crowns were reported, Smid and his co-workers reported the first results of their efforts to assess cation binding by the related open-chained materials.[2–4] Cram and his co-

workers have compared the efficacy of open-chained equivalents of their crown host systems in binding a variety of cationic guests.[5]

The interest in these molecules has increased considerably in recent years. Efforts have been made to quantify

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