Table I summarizes the data. Attempts were made to fit the kinetics to the integrated second-order rate expression, rate = k_2·[(+)-**5**][DIM], and to the integrated third-order rate expression, rate = k_3[(+)-**5**][DIM]^2, where k_2 is the second-order and k_3 the third-order rate constant. The data points used in each run were the maximum number obtained as the reaction proceeded that would provide a straight line when subjected to a least-squares regression treatment with correlation coefficients greater than 0.98. The average rate constants obtained were $k_2 = 0.0025 \pm 0.001\ M^{-1}$ min^{-1} and $k_3 = 2.3 \pm 2.2\ M^{-2}$ min^{-1}, in which the error is expressed as the standard deviation from the mean. The probable error in k_2 was 32%, and in k_3 was 96%. At the completion of each run, the solution in the polarimeter cell was checked by tlc, and in no case were extraneous products observed. Table II indicates the results of control experiments. The 5–6% racemization observed in the overall reaction was disregarded in the kinetic treatment.

The nonreproducibility of the rate constants of Table I may arise from several sources. Since DIM was only sparingly soluble in benzene, measurements had to be made at low concentrations, and its fluffy character made it difficult to weigh in the drybox. Its extreme hygroscopic properties prohibited handling it outside of a drybox.

Estimate of Rate Constant of (+)-1 with DIM in Benzene. Application of the same polarimetric technique to the reaction of (+)-**1** with DIM in benzene at 25° at approximately the same concentrations as for (+)-**5** and DIM gave $k_2 = 4.68 \pm 1.7 \times 10^{-3}\ M^{-1}$ sec^{-1}. Control experiments similar to those applied to (+)-**5** gave the same results.

Stereochemistry of Sulfur Compounds. VI. Multiple Termolecular Ligand Transfers between Sulfur–Carbon–Carbon, Sulfur–Sulfur–Carbon, or Sulfur–Carbon–Phosphorus Centers[1]

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Abstract: In acetonitrile at 25°, *p*-toluenesulfonyl isocyanate (*p*-tosyl isocyanate) and (+)-(*R*)-methyl *p*-tolyl sulfoxide ((+)-**1**) gave (−)-(*S*)-*N*-*p*-toluenesulfonylmethyl-*p*-tolylsulfimide, (−)-(*S*)-**2**, with net inversion of configuration, but by a mechanism that competitively racemized both starting material and product. All three components were required for the racemization reaction of (−)-**2**. Conversion of **1** to **2** was roughly first order in **1** and second order in isocyanate reagent. Reaction of (+)-(*R*)-**1** with *p*-tosyl isocyanate in acetonitrile in the presence of *tert*-butyl methyl sulfide (**3**) gave (−)-(*S*)-**2** with 80% net inversion (48% yield) and *N*-*tert*-butyl-*N'*-*p*-toluenesulfonylacetamidine (**4**). Reaction of *tert*-butyl methyl sulfoxide (**5**) with *p*-tosyl isocyanate in acetonitrile also gave **4**. In the presence of *N*-*p*-nitrobenzenesulfonyltetramethylenesulfimide (**6**), **1** with *p*-tosyl isocyanate in acetonitrile gave **2**, *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (**7**) and *N*-*p*-toluenesulfonyltetramethylenesulfimide (**8**), as well as recovered **6**. Treatment of **1** with *p*-tosyl isocyanate and diethyl sulfide in acetonitrile gave mainly *N*-*p*-toluenesulfonyldiethylsulfimide (**9**) and methyl *p*-tolyl sulfide (**10**). All three components were required for reaction. By nmr a transient intermediate was detected in the same reaction when dimethyl sulfide was substituted for diethyl sulfide. Reaction of **1** and *p*-tosyl isocyanate in acetonitrile with triphenylphosphine (**11**) produced methyl *p*-tolyl sulfide (**10**) and triphenylphosphine oxide (**12**). All three components were required for reaction, and the *p*-tosyl isocyanate acted only as a catalyst. In acetonitrile, sulfimide **2**, triphenylphosphine (**11**), and *p*-tosyl isocyanate gave triphenylphosphine oxide (**12**), *N*-*p*-toluenesulfonyltriphenylphosphinimide (**13**), recovered **2**, and *p*-toluenesulfonamide (after water treatment). All three components were required for reaction. In acetonitrile, *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (**7**), triphenylphosphine, and *p*-tosyl isocyanate gave **10**, **12**, **13**, *N*-*p*-nitrobenzenesulfonyltriphenylphosphinimide (**14**), *p*-nitrobenzenesulfonamide, and *p*-toluenesulfonamide (after water treatment). General cyclic, termolecular mechanisms are postulated for ligand transfers between sulfur–carbon–carbon, between sulfur–sulfur–carbon, and between sulfur–carbon–phosphorus centers.

Earlier papers reported on the molecularity and stereochemical course of the conversion of methyl *p*-tolyl sulfoxide (**1**) to *N*-*p*-toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide (**2**) with *N*,*N*-bis(*p*-toluenesulfonyl)-sulfur diimide.[3] In pyridine, the reaction was overall termolecular and was interpreted as going through a six-membered ring composed of three sulfur atoms connected by nitrogens and oxygens. The inversion of configuration was explained by an equatorial–equatorial substitution on a trigonal bipyramid at chiral sulfur (see A).[3a] In benzene, the reaction was overall bimolecular and occurred with retention of configuration. The stereochemical course of substitution was explained through an equatorial–axial substitution on a trigonal bipyramid at chiral sulfur (see B).[3b] In methylene dichloride, the substitution went with predominant retention, but both starting material and product were racemized during the conversion. These latter reactions were interpreted as involving multiple ligand exchanges of the equatorial–equatorial variety between three sulfur atoms through intermediates such as C and D.

This paper reports results of a survey of the general

(1) This investigation was supported by U. S. Public Health Service Research Grant No. GM 12640-09 from the Department of Health, Education, and Welfare.

(2) National Institutes of Health Special Research Fellow, 1969–1970.

(3) (a) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970); (b) F. G. Yamagishi, D. R. Rayner, D. C. Garwood, E. T. Zwicker, and D. J. Cram, *ibid.*, **95**, 1916 (1973).

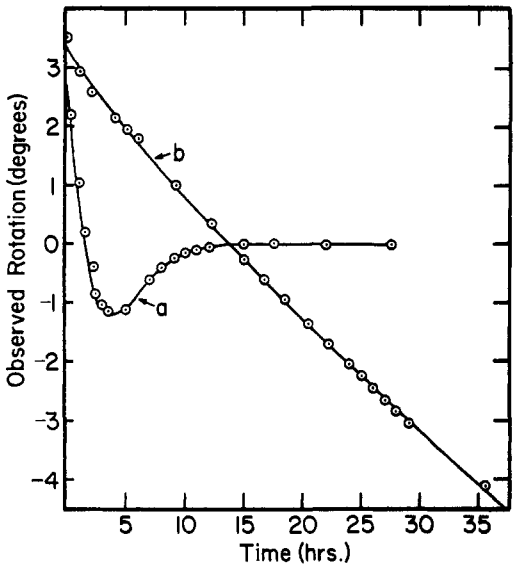
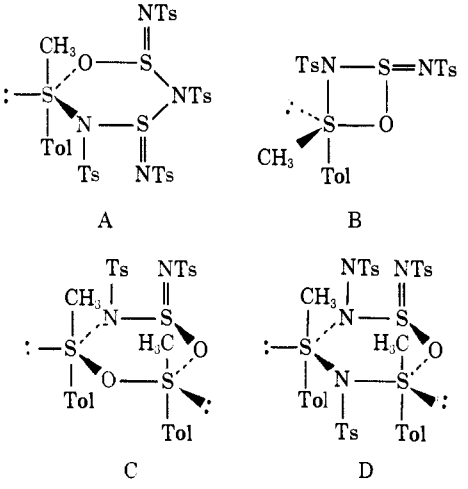


Figure 1. Effect of *tert*-butyl methyl sulfide (**3**) on stereochemical course of reaction of (+)-(*R*)-methyl *p*-tolyl sulfoxide ((+)-**1**) with *p*-tosyl isocyanate in acetonitrile at 25° to give (−)-(*S*)-*N*-*p*-toluenesulfonylmethyl-*p*-tolylsulfimide ((−)-**2**): (a) without added **3**, (b) with added **3**.



mechanisms and stereochemical courses of ligand exchange reactions between *p*-toluenesulfonyl isocyanate (*p*-tosyl isocyanate), sulfoxides, sulfimides, sulfides, and phosphines. Previously, others demonstrated that *p*-tosyl isocyanate[4a,b] or acyl isocyanates[4c] converted sulfoxides to sulfimides.

Multiple Ligand Exchange Reactions

Stereochemical Course of Reaction between *p*-Tosyl Isocyanate and (+)-(*R*)-Methyl *p*-Tolyl Sulfoxide ((+)-1) in Acetonitrile. Although the reaction between 1 *M* *p*-tosyl isocyanate and 1 *M* **1** in acetonitrile at 25° was only 62% complete in 48 hr, the reaction to give carbon dioxide and *N*-*p*-toluenesulfonylmethyl-*p*-tolylsulfimide (**2**) was free of side products (thin layer and isolation criteria). No reaction occurred in pyridine as solvent. When the rotational change of a 0.2 *M* solution of optically pure (+)-**1** in acetonitrile–0.64 *M* in *p*-tosyl isocyanate was followed at 25°, the initial rotation of α_{obsd} 4.8° (l = 1 dm, λ 546 nm) smoothly decreased to a minimum of −0.7° at 180 min, and then gradually approached 0° (*e.g.*, −0.01° after 480 min) (see Figure 1). This reaction was conducted preparatively, and aliquots were quenched when the rotation first became 0° and also when the negative minimum was reached. Starting sulfoxide and product sulfimide were isolated by chromatography on silica gel without fractionation of antipode and racemate, and their optical purities were determined. After 90 min (α_{obsd} 0), an 80% yield of 19% optically pure (+)-**1** and an 8% yield of 27% optically pure (−)-**2** were produced. After 180 min (α_{obsd} −0.7°), a 60% yield of 4% optically pure (+)-**1** and a 20% yield of 7% optically pure (−)-**2** were obtained.

Control experiments demonstrated the following. (1) Reagent *p*-tosyl isocyanate did not react with acetonitrile at 25°. (2) Sulfoxide (+)-**1** and sulfimide (−)-**2** in acetonitrile at 25° (no *p*-tosyl isocyanate) did not react either with solvent or with each other. (3) Sulfimide (−)-**2** and *p*-tosyl isocyanate in acetonitrile at 25° underwent no visible reaction. (4) Racemic sulfoxide **1** and *p*-tosyl isocyanate in acetonitrile at 25° caused sulfimide (−)-**2** to racemize. (5) Racemic methyl phenyl sulfoxide and *p*-tosyl isocyanate in acetonitrile at 25° caused sulfimide (−)-**2** to lose optical activity. (6) The plot of optical rotation *vs.* time of the reaction mixture of (+)-**1** and *p*-tosyl isocyanate in acetonitrile at 25° was not changed by saturation of the acetonitrile solution with carbon dioxide.

These results demonstrate that sulfoxide (+)-**1** gives sulfimide (−)-**2**, which racemizes in subsequent reactions, but only in the presence of both sulfoxide and *p*-tosyl isocyanate. Sulfoxide (+)-**1** itself racemizes in a competing reaction which depends on the presence of tosyl isocyanate. The absolute configurations of (+)-**1** and (−)-**2** have been established[5] (X-ray method), and the reaction occurs with predominating inversion of configuration.

Kinetics of Imidation by *p*-Tosyl Isocyanate of Methyl *p*-Tolyl Sulfoxide (1) to Give *N*-*p*-Toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide (2). The rate of conversion of **1** to **2** was followed in acetonitrile at 25.0° by both an nmr and a titrimetric technique. The nmr method involved integration of the relative CH_3–S peak areas for **1** (τ 7.37) and **2** (7.29) in acetonitrile at appropriate times. The actual concentrations of **1** and **2** at various times were checked to obtain a mass balance by comparison of CH_3–S peak areas with the ^{13}C satellite peak of the solvent at τ 6.94.

The titrimetric method involved conversion of unreacted *p*-tosyl isocyanate in a measured aliquot of reaction mixture to *O*-methyl-*N*-*p*-toluenesulfonyl carbamate by reaction with absolute methanol, which also served to quench the reaction. The acidic proton on nitrogen of the *N*-sulfonyl carbamate was titrated in one-to-twenty methanol to acetonitrile solution with sodium methoxide in methanol to a thymol-blue end point. Neither **1** nor **2** interfered with the titration. The reaction of *p*-tosyl isocyanate with methanol was rapid and quantitative. The carbon dioxide evolved in the reaction of **1** and *p*-tosyl isocyanate was removed by boiling the methanol–acetonitrile solution prior to titration, which was conducted in an argon atmosphere.

(4) (a) C. King, *J. Org. Chem.*, **25**, 325 (1960); (b) R. Appel and H. Ritterslacher, *Chem. Ber.*, **97**, 852 (1964); (c) R. Neidlein and W. Hausmann, *Angew. Chem., Int. Ed. Engl.*, **3**, 446 (1964).

(5) (a) H. Hope, U. de la Camp, G. D. Homer, H. W. Messing, and L. H. Sommer, *Angew. Chem., Int. Ed. Engl.*, **8**, 612 (1969); (b) H. Hope and N. Kim, private communication.

Table I. Rate Constants for Reaction of Methyl *p*-Tolyl Sulfoxide (**1**) with *p*-Tosyl Isocyanate in Acetonitrile at 25.0 ± 0.1°

Run no.	Initial concn, *M*		No. of points	% reaction followed	Rate constants[a] × 10^5	
	Sulfoxide	Isocyanate			k_2, M^{-1} sec^{-1}	k_3, M^{-2} sec^{-1}
1[b]	1.874	0.377	7	83	0.44 ± 0.02	3.20 ± 0.61
2[b]	1.869	0.806	17	48	1.10 ± 0.04	2.10 ± 0.12
3[b]	0.163	0.784	7	85	1.60 ± 0.12	2.30 ± 0.22
4[b]	0.412	1.521	16	61	2.10 ± 0.11	1.50 ± 0.09
5[c]	1.869	0.801	13	76	0.80 ± 0.07	2.20 ± 0.21
6[c]	0.163	0.784	6	80	1.90 ± 0.24	2.80 ± 0.39
7[c]	0.401	1.554	9	89	2.0 ± 0.20	1.50 ± 0.18

[a] Error associated with the rate constant is two standard deviations. [b] Reaction followed by nmr. [c] Reaction followed titrimetrically.

Table I records both second-order (first order in each reactant) and third-order (first order in sulfoxide and second order in *p*-tosyl isocyanate) rate constants. To obtain convenient rates at 25°, the concentrations of reactants had to be quite high (ranged between 0.163 and 1.874 *M*) and the medium changed as the concentration of reactants changed. Also the nmr and titrimetric techniques used to follow the reaction were of limited precision. Nevertheless, over the range of concentrations reported (sulfoxide and isocyanate were varied by factors of 10 and 4, respectively), the kinetics are better represented by a third-order process. Thus, k_3 = 2.2 ± 0.45 M^{-2} sec^{-1} and the average deviation is about 20%, whereas k_2 = 1.42 ± 0.55 M^{-1} sec^{-1} and the average deviation is about 40%.

The rate of conversion of **1** to **2** was several times slower than the racemization of the components of the reaction mixture. In 8 hr, both optically active sulfoxide and sulfimide were essentially completely racemized, whereas in run 3 of Table I, after 50 hr, conversion of **1** to **2** was only 85% complete. Data quoted in the last section indicated that (+)-**1** was 96% racemized at the time when **1** was only 20% converted to **2**.

Effect of *tert*-Butyl Methyl Sulfide (3) on the Stereospecificity of Conversion of (+)-(*R*)-Methyl *p*-Tolyl Sulfoxide ((+)-1) to (−)-(*S*)-*N*-*p*-Toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide ((−)-2). Introduction of *tert*-butyl methyl sulfide (**3**) at 0.4 *M* into a reaction mixture of 0.13 *M* sulfoxide (+)-**1** and 0.51 *M* *p*-tosyl isocyanate in acetonitrile at 25° led to 80% optically pure sulfimide (−)-**2** (48%) of inverted configuration. The effect of added sulfide on the stereochemical course of the reaction between (+)-**1** and tosyl isocyanate is illustrated by Figure 1, in which rotation is plotted against time both in the presence and absence of added sulfide. The rate of production of (−)-**2** in the presence of hindered sulfide **3** as measured by the polarimetric curve was comparable to the reaction rate measured by nmr in the absence of sulfide **3**. Besides (−)-**2**, the reaction carried out in the presence of sulfide **3** produced *N*-*tert*-butyl-*N'*-*p*-toluenesulfonylacetamidine (**4**). The structure of **4** was deduced from its elemental analysis, nmr, ir, and mass spectra (see Experimental Section). The structure of **4** was confirmed by its independent synthesis by a known method[6] by reaction of *N*-*tert*-butylacetamide with *p*-tosyl isocyanate. The substance was also produced (63%) from *tert*-butyl methyl sulfoxide[7] (**5**) and *p*-tosyl isocyanate in acetonitrile at 25°.

(6) W. Logemann, D. Artini, and G. Tosolini, *Chem. Ber.*, **91**, 2566 (1958).

(7) H. Henbest, J. A. W. Reid, and C. J. M. Stirling, *J. Chem. Soc.*, 1220 (1964).

In an additional run, sulfoxide **1**, sulfide **3**, and *p*-tosyl isocyanate in acetonitrile at 25° gave sulfimide **2** (44%), acetamidine **4** (29%), and methyl *p*-tolyl sulfide (**10**, 29%). Control experiments demonstrated that sulfide **3** did not react with *p*-tosyl isocyanate in acetonitrile in the absence of sulfoxide **1** at either 25° or reflux temperature. Sulfoxide **1** did not react with sulfide **3** in acetonitrile at 25° (10 days). To test the possibility that *N*-*p*-toluenesulfonyl-*tert*-butylmethylsulfimide might be a precursor of amidine **4**, the sulfimide was prepared and was heated at 65° in acetonitrile (24 hr). The sulfimide was recovered essentially quantitatively.

These experiments demonstrate the following facts. (1) Sulfide **3** inhibited the reactions of racemization of sulfoxide (+)-**1** and of sulfimide (−)-**2** in acetonitrile at 25°, and (−)-**2** was produced from (+)-**1** with 80% net inversion of configuration. (2) To produce amidine **4**, the three reagents (*p*-tosyl isocyanate, sulfoxide **1**, and sulfide **3**) had to be present at the same time in acetonitrile. (3) The same amounts of amidine **4** and methyl *p*-tolyl sulfide (**10**) were produced. (4) Had *tert*-butyl methyl sulfoxide (**5**) been produced, it would have been converted to amidine **4** under the reaction conditions. (5) The substance *N*-*p*-toluenesulfonyl-*tert*-butylmethylsulfimide was not a reaction intermediate.

Imide and Oxygen Ligand Transfers between Sulfimide, Sulfoxide, and *p*-Tosyl Isocyanate. The racemization of sulfimide (−)-**2** by sulfoxide (±)-**1** and *p*-tosyl isocyanate suggested that racemization probably occurred by imide and oxygen ligand transfers to and from chiral sulfur. Accordingly, a cross-breeding experiment was conducted in which *N*-*p*-nitrobenzenesulfonyltetramethylenesulfimide (**6**), sulfoxide **1**, and *p*-tosyl isocyanate were heated for 3 hr in acetonitrile at 80°. This temperature was required to dissolve enough **6** to give a 0.2 *M* solution (**1** and *p*-tosyl isocyanate were both 0.4 *M*). All four possible sulfimide products were obtained: **6** (25%), **2** (44%), *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide or **7** (13% based on **1**), and *N*-*p*-toluenesulfonyltetramethylenesulfimide or **8** (17% based on **6**). A similar reaction was conducted at 25° (0.05 *M* in the three components in acetonitrile) for 163 hr to give 1% of cross-bred product, **7**. Control experiments demonstrated the chemical stability in acetonitrile at 80° in the absence of *p*-tosyl isocyanate of sulfimide **6** to the presence of sulfoxide **1**, and sulfimide **6** to the presence of sulfimide **2**. At 80° in acetonitrile, sulfimide **6** was stable to *p*-tosyl isocyanate in the absence of sulfoxide **1**. Thus all three components, sulfimide, sulfoxide, and *p*-tosyl isocyanate, are required before imide and oxygen ligand transfers occur. In-

deed, transfer of one ligand seems dependent on transfer of the other.

Imide and Oxygen Ligand Transfers between *p*-Tosyl Isocyanate, Sulfoxide, and Sulfide. An acetonitrile solution, 0.01 *M* in each of racemic sulfoxide **1**, *p*-tosyl isocyanate, and diethyl sulfide, at 25° for 26 hr gave (besides carbon dioxide) 82% *N*-*p*-toluenesulfonyldiethylsulfimide **(9)**, 75% methyl *p*-tolyl sulfide **(10)**, 2% of sulfimide **2**, and 5% recovered **1**. Diethyl sulfide did not react with *p*-tosyl isocyanate in acetonitrile at 25° in the absence of sulfoxide **1**, and diethyl sulfide did not react with **1** in acetonitrile in the absence of *p*-tosyl isocyanate.

The progress of a similar reaction with dimethyl sulfide (1.1 *M*), **1** (1.0 *M*), and *p*-tosyl isocyanate (1.0 *M*) in acetonitrile was followed in an nmr tube. The disappearance of starting materials and appearance of products were followed making use of the CH_3S proton chemical shifts, which in acetonitrile (tetramethylsilane as internal standard) were as follows (τ): dimethyl sulfide, 7.93; methyl *p*-tolyl sulfide **(10)**, 7.73; *N*-*p*-toluenesulfonyldimethylsulfimide, 7.41; methyl *p*-tolyl sulfoxide **(1)**, 7.37; *N*-*p*-toluenesulfonylmethyl-*p*-tolylsulfimide **(2)**, 7.29. As time passed, the intensities of the dimethyl sulfide and sulfoxide **1** bands decreased, and those of sulfide **10** and *N*-*p*-toluenesulfonyldimethylsulfimide increased, but no band due to sulfimide **2** was observed. During the first 30 min, a new band at τ 7.49 of a reaction intermediate developed and then slowly disappeared during 5 hr, after which time the reaction mixture was quenched with methanol to give a 78% yield of the *N*-*p*-toluenesulfonyldimethylsulfimide product. Control experiments demonstrated that all three components were required for reaction, and for appearance of the reaction intermediate band at τ 7.49.

The rotation of a reaction mixture of (+)-**1** (0.2 *M*), *p*-tosyl isocyanate (0.93 *M*), and dimethyl sulfide (1.29 *M*) in acetonitrile decreased monotonically to zero. Evidently added dimethyl sulfide diverted *p*-tosyl isocyanate and sulfoxide **1** from their normal course to give a new transient intermediate which decomposed to products in which dimethyl sulfide had been imidated by *p*-tosyl isocyanate, and sulfoxide had oxidized the isocyanate to produce carbon dioxide.

Imide and Oxygen Ligand Transfers between Sulfoxide, Phosphine, and *p*-Tosyl Isocyanate, and between Sulfimide, Phosphine, and *p*-Tosyl Isocyanate. At 45°, an acetonitrile solution 1.0 *M* in sulfoxide **1** and in triphenylphosphine **(11)** and 0.5 *M* in *p*-tosyl isocyanate (24 hr) gave 79% methyl *p*-tolyl sulfide **(10)**, 83% triphenylphosphine oxide **(12)**, and 89% *p*-tosyl isocyanate (isolated as its hydrolysis product, *p*-toluenesulfonamide), but no sulfimide **2**, the product of sulfoxide **1** and *p*-tosyl isocyanate in the absence of a third component. Control experiments demonstrated that phosphine **11** and sulfoxide **1** do not react in the absence of *p*-tosyl isocyanate, and that **11** and *p*-tosyl isocyanate do not react in the absence of sulfoxide **1**. Thus, all three components are necessary for oxygen-ligand transfer from sulfur to phosphorus, and *p*-tosyl isocyanate catalyzes this reaction.

At 45° an acetonitrile solution 0.2 *M* in triphenylphosphine **(11)**, 0.2 *M* in *N*-*p*-toluenesulfonylmethyl-*p*-tolylsulfimide **(2)**, and 0.2 *M* in *p*-tosyl isocyanate gave after 96 hr 70% methyl *p*-tolyl sulfide **(10)**, 30% triphenylphosphine oxide **(12)**, 2% *N*-*p*-toluenesulfonyltriphenylphosphinimide **(13)**, 75% *p*-tosyl isocyanate (recovered as *p*-toluenesulfonamide), and 7% recovered **2**. Control experiments demonstrated that **11** did not react directly with **2** in the absence of *p*-tosyl isocyanate, and that **11** did not react directly with *p*-tosyl isocyanate in the absence of sulfimide **2**. That phosphinimide **13** was not hydrolyzed to phosphine oxide **(12)** during isolation was also demonstrated.

At 45° after 120 hr, an acetonitrile solution 0.40 *M* in *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide **(7)** and in triphenylphosphine **(11)**, and 0.5 *M* in *p*-tosyl isocyanate gave 40% methyl *p*-tolyl sulfide **(10)**, 26% *N*-*p*-toluenesulfonyltriphenylphosphinimide **(13)**, 18% *N*-*p*-nitrobenzenesulfonyltriphenylphosphinimide **(14)**, 11% recovered sulfimide **7**, 44% triphenylphosphine oxide **(12)**, 40% *p*-toluenesulfonamide, and 5% *p*-nitrobenzenesulfonamide. The last two compounds were undoubtedly formed as hydrolysis products during isolation.

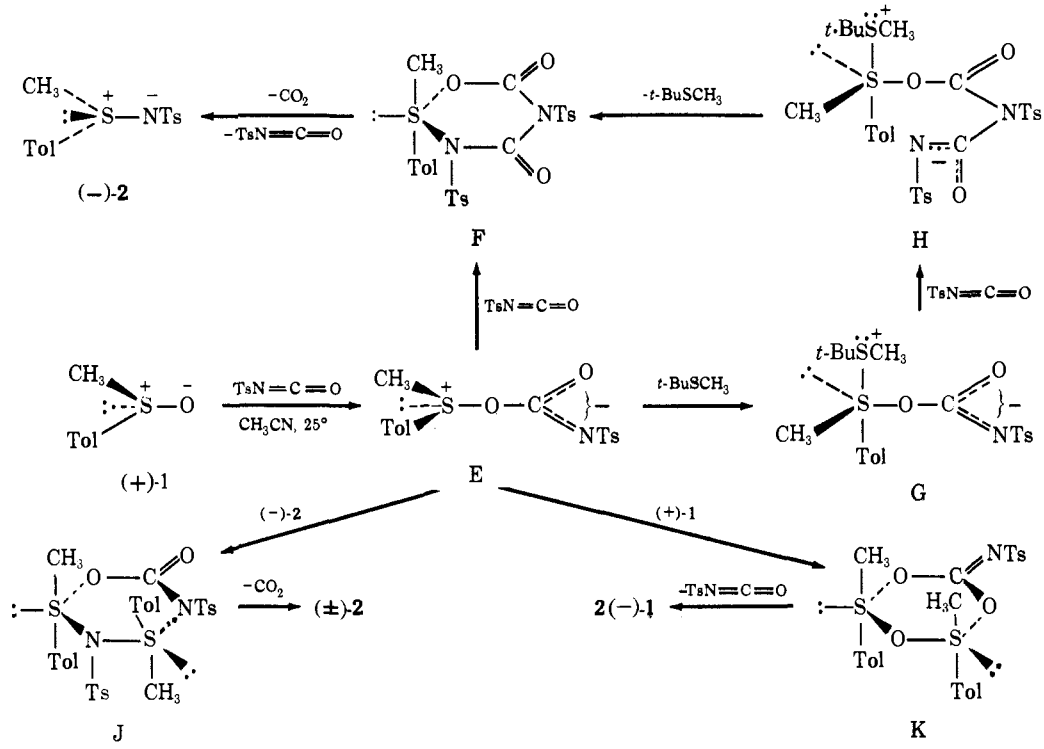
Discussion

The above reactions have many common features. (1) All transformations involve *p*-tosyl isocyanate as reactant or catalyst in acetonitrile solvent and occur at 25–50° at comparable rates. (2) All the reactions involve three components except the conversion of sulfoxide **1** to sulfimide **2** in the presence of only *p*-tosyl isocyanate. Even this reaction approaches termolecularity, and involves 2 mol of *p*-tosyl isocyanate. (3) If *p*-tosyl isocyanate is regarded as the first component, the second component is either a sulfoxide or sulfimide. The third component is either a second molecule of *p*-tosyl isocyanate, a sulfoxide, a sulfimide, a sulfide, or a phosphine. Common to all components is the mechanistic availability of two bonding sites, one for an electrophile and the other for a nucleophile. (4) The reactions consist of multiple *transfers of oxygen and/or imide ligands* between sulfur–carbon–carbon, between sulfur–sulfur–carbon, or between carbon–sulfur–phosphorus.

Most of these reactions appear to be termolecular. The products can be explained most simply in terms of three important general steps. (1) Two components add (possibly reversibly) to give either a 1,4- or a 1,3-dipole. (2) The new dipole undergoes a dipolar addition reaction with a third component to form either a five- or six-membered ring. (3) The ring undergoes stepwise fragmentation to three components, at least two of which are different from the starting materials.

Mechanism of Conversion of (+)-(*R*)-Methyl *p*-Tolyl Sulfoxide ((+)-1) to (−)-(*S*)-*N*-*p*-Toluenesulfonylmethylsulfimide ((−)-2). When mixed with *p*-tosyl isocyanate, in competing reactions (+)-**1** gives (−)-**2** with net inversion, (+)-**1** gives (±)-**1**, and (−)-**2** gives (±)-**2**. Since the racemization of (+)-**1** is faster than the production of (−)-**2**, and since (−)-**2** racemizes at a rate comparable to its production, the stereospecificity of (+)-**1** → (−)-**2** could not be determined. Addition of *tert*-butyl methyl sulfide **(3)** to the medium inhibited (or diverted) the racemizations of (+)-**1** and (−)-**2**, and 90% of the **2** produced was of inverted and 10% was of retained configuration. The production

Chart I



of **2** from **1** in the absence of added sulfide **3** approached third-order kinetics, the reaction being roughly first order in **1** and second order in *p*-tosyl isocyanate. Chart I provides general mechanistic explanations for the three competing reactions that occur in the absence of added sulfide **3**, as well as an explanation for the fact that the racemization reactions are absent in the presence of sulfide **3**. In Chart I (and the others as well), the probable two component intermediates produced by opening of the ring compounds (three components) are omitted for sake of simplicity.

The stereospecific portion of the conversion of sulfoxide to sulfimide is visualized by the sequence (+)-**1** → E → F → (−)-**2**. The competing racemization of sulfoxide involves

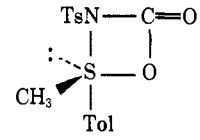
$$(+)\text{-}\mathbf{1} \longrightarrow \mathrm{E} \xrightarrow{(+)\text{-}\mathbf{1}} \mathrm{K} \longrightarrow 2(-)\text{-}\mathbf{1}\text{'s}$$

This mechanism is bimolecular in (+)-**1**, and since K possesses a plane of symmetry, it should decompose both in the direction it was formed as well as to inverted product. The enantiomer of E, although a required intermediate (principle of microscopic reversibility), is omitted from the scheme for reasons of simplicity. The competing racemization of sulfimide involves the sequence

$$(+)\text{-}\mathbf{1} \longrightarrow \mathrm{E} \xrightarrow{(-)\text{-}\mathbf{2}} \mathrm{J} \longrightarrow (\pm)\text{-}\mathbf{2}$$

In this scheme, the role played by the highly nucleophilic sulfide **3** when present is to intercept E to give G, which lasts long enough to add a second mole of *p*-tosyl isocyanate to give H → F → (−)-**2**. This sequence dominates over those that provide racemization because of the better nucleophilicity of sulfide **3** as compared to sulfoxide **1** or sulfimide **2**. The control exerted by sulfide **3** over the stereochemical direction of the reaction resembles that exerted by pyridine when *N,N'*-bis(*p*-toluenesulfonyl)sulfur diimide reacts with sulfoxide **1** to give sulfimide **2** with high inversion[3a] of configuration. The competing racemization processes of Chart I resemble the racemization processes found with the same sulfur diimide reagent in its conversion of sulfoxide **1** to sulfimide **2** in dichloromethane as solvent.[3b]

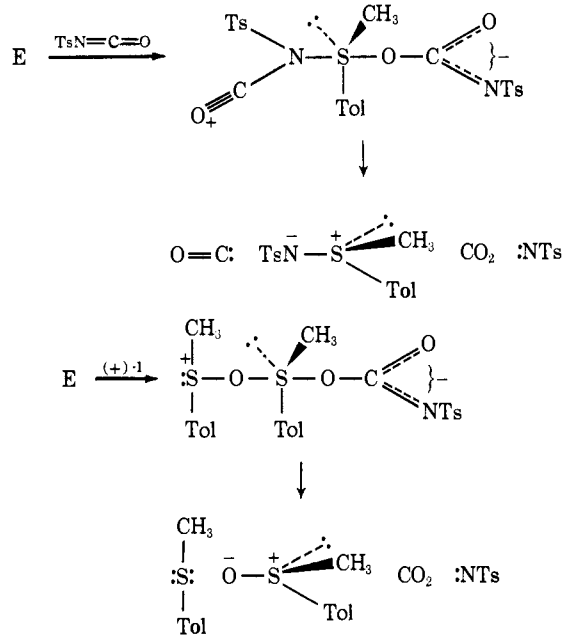
The 10% of sulfimide produced with retention of configuration ((+)-(*R*)-**2**) in the presence of hindered sulfide **3** is explained by a competing bimolecular reaction between sulfoxide (+)-(*R*)-**1** and *p*-tosyl isocyanate. This slower reaction involves first E, then a four-membered ring as intermediate, in which an equatorial, axial substitution on chiral sulfur occurs. This intermediate resembles **B**, in which sulfur diimide reagent in benzene or dichloromethane was used in place of *p*-tosyl isocyanate in acetonitrile.



In the inversion mechanism, nucleophilic substitution processes on sulfur are all formulated as passing through trigonal bipyramids as intermediates. The leaving and entering groups are placed in equatorial positions. The character of the products indicates the entering and leaving groups must be part of the same ring system which is not more than six-membered. Only axial–axial and equatorial–equatorial substitutions give inversion. The ring system is not large enough to accommodate axial–axial substitution (three ring atoms colinear). Thus, the equatorial–equatorial route seems mandatory. Nonring axial–axial mechanisms lead to high energy products. Two examples that lead to nitrenes are formulated and are highly improbable (Scheme I).

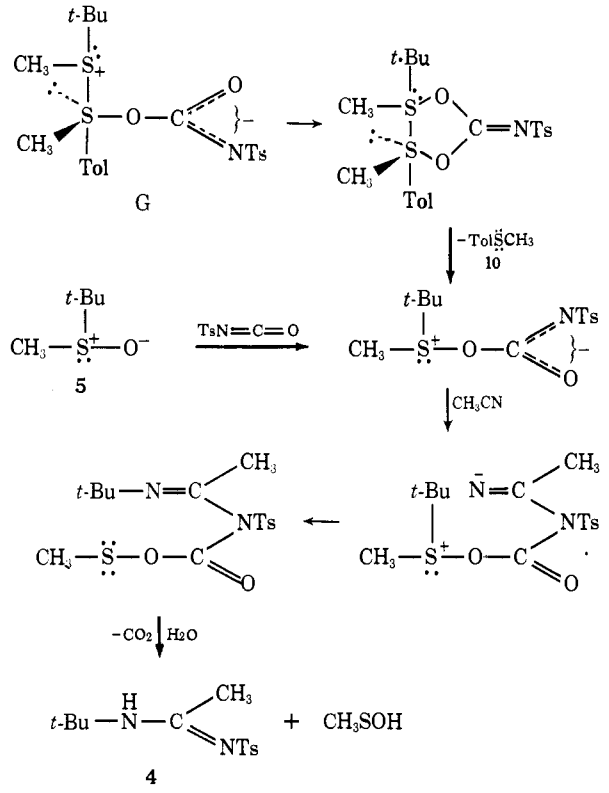
When sulfide **3** was present in the medium, amidine

Scheme I



4 and methyl *p*-tolyl sulfide (**10**) were produced in about equal amounts. Also, *tert*-butyl methyl sulfoxide (**5**) was converted to amidine **4** under the same conditions. Chart II provides the most likely of a number of

Chart II



possible schemes that rationalize these facts. Intermediate G is common to processes leading to both sulfimide (−)-**2** in Chart I, and amidine **4** and sulfide **10** in Chart II.

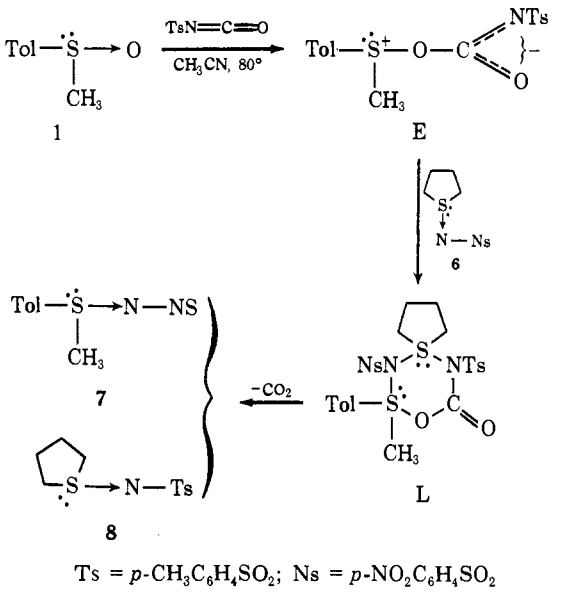
Several other possible open-chain and six-membered ring intermediates that involve the elements of sulfoxide **1**, sulfimide **2**, and *p*-tosyl isocyanate can be imagined which probably contribute to the products. The schemes of Charts I and II represent only the more probable examples that illustrate the possibilities.

Cross-Breeding Ligand Exchange Reaction Mechanism. The racemization mechanism for sulfimide of Chart I involves

$$(+)\text{-}\mathbf{1} \xrightarrow{TsN=C=O} E \xrightarrow{(-)\text{-}2} J \xrightarrow{-CO_2} (\pm)\text{-}\mathbf{2}$$

This sequence predicts that if a sulfimide with different carbon and imide ligands is substituted for (−)-**2**, it might intercept E and generate cross products as well as those predicted from the reaction of sulfoxide **1** with *p*-tosyl isocyanate. Chart III outlines the cross

Chart III



products observed and a possible mechanism for their production, when *N*-*p*-nitrobenzenesulfonyltetramethylenesulfimide (**6**) was added to a reacting mixture of **1** and *p*-tosyl isocyanate. The scheme

$$E \xrightarrow{6} L \longrightarrow 7 + 8$$

predicts equal amounts of cross-bred sulfimide products, **7** and **8**. The substances were isolated in 13 and 17% yields, respectively. These results support the general mechanisms based on E as a central intermediate that undergoes 1,4-dipolar addition reactions (Chart I).

Mechanism of Imide and Oxygen Ligand Transfers between *p*-Tosyl Isocyanate, Sulfoxide, and Sulfide. Sulfides less hindered than *tert*-butyl methyl sulfide (**3**) appear to divert the dipolar intermediate E into a simpler ligand exchange reaction path. With the more hindered sulfide, the products suggested that the 1,4 cycloaddition to the sulfide involved S^+ and O^- of dipole E. With the less hindered dimethyl sulfide or diethyl sulfide, the products indicate that the 1,4 cycloaddition involved S^+ and the more hindered N^- of E. Possibly the new S–CH_3 proton resonance that appeared and then decayed in the nmr spectrum of a reacting mixture of **1**, *p*-tosyl isocyanate and dimethyl sulfide was due to intermediate M, whose decay accounts for the observed products (Chart IV).

Mechanism of Imide and Oxygen Ligand Transfers between *p*-Tosyl Isocyanate, Sulfoxide, and Phosphine. Chart V provides a scheme that explains the products of oxygen ligand exchange between sulfoxide **1** and

Chart IV

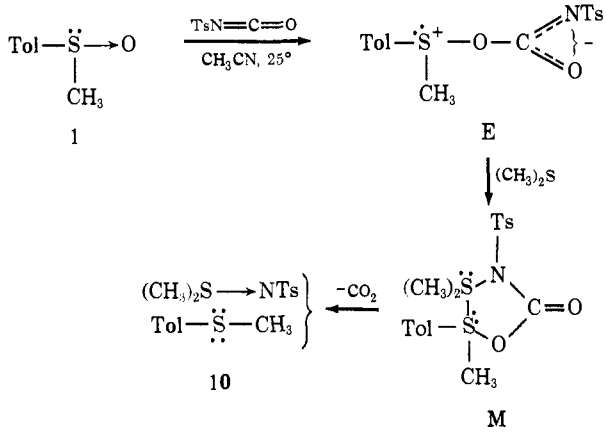
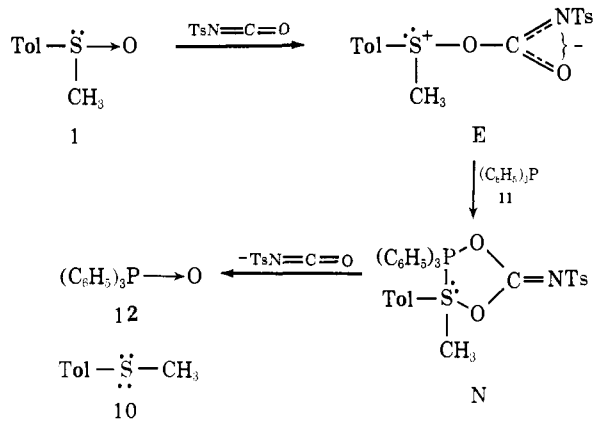


Chart V



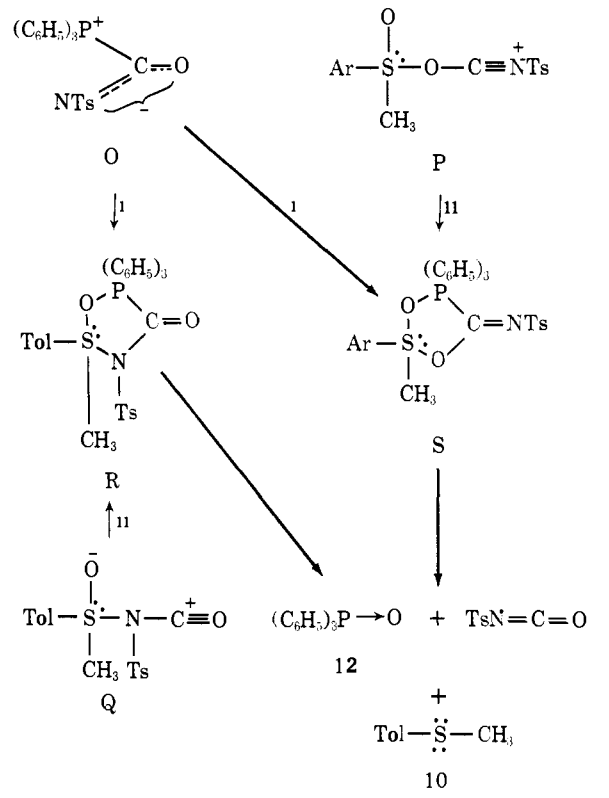
triphenylphosphine (**11**). Again, 1,4-dipolarophile intermediate E is intercepted by a strong nucleophile (**11**) to give a cycloaddition product (N) much as sulfide intercepts E in Chart IV. An interesting difference between sulfide and phosphine is that sulfide adds to the sulfur and nitrogen ends of dipole E (Chart IV), whereas the phosphine adds to the sulfur and oxygen ends of E. Another expression of the bias that sulfur shows toward sulfonimide over oxygen is shown in the ready formation of *N,N'*-bis(*p*-toluenesulfonyl)-sulfur diimide from *N*-sulfinyl-*p*-toluenesulfonamide in pyridine.[8]

Equally probable and possibly competing schemes involve two component adducts **O**, P and Q, which converge on cycles R and S, and which provide the same products as N on decomposition (Scheme II). Adducts of these general types are required to explain the products of multiple ligand exchange between the *p*-nitro-labeled sulfimide **7**, triphenylphosphine (**11**) and *p*-tosyl isocyanate. Triphenylphosphine accepted O, NTs, and NNs in competing reactions, the carbon of *p*-tosyl isocyanate exchanged NTs for NNs, and sulfimide **7** exchanged an electron pair for NNs.

Chart VI provides a mechanistic scheme that accounts for these products and is based on initial adducts T, W, and X between sulfimide **7** and *p*-tosyl isocyanate. Adduct T resembles E (sulfoxide **1** and *p*-tosyl isocyanate) and in principle can add triphenylphosphine in two ways, one to give U and the other V. Cycle U on decomposition provided triphenylphosphine oxide (**12**), *p*-tolyl methyl sulfide (**10**), and NsN=C=NTs, which on water treatment probably hydro-

(8) W. Wucherpfennig and G. Kresze, *Tetrahedron Lett.*, 1671 (1966).

Scheme II



lyzed to either the observed products, $NsNH_2$ and $TsNH_2$, or more likely to the urea derivative (lost during chromatography). Cycle V decayed to tosyl-labeled phosphinimide **13**, **10**, and *p*-nitrobenzenesulfonyl isocyanate, which on water treatment gave the observed $NsNH_2$. Neither of these processes explain formation of *p*-nitrobenzenesulfonyl-labeled phosphinimide, **14**. This imide can be accounted for by formation of either cycles Y or Z, which lead to the same products, **14**, **10**, and *p*-tosyl isocyanate. Cycles Y and Z can be formed from either adduct dipoles W and X (respectively), or by the addition of dipolar adduct O (from triphenylphosphine and *p*-tosyl isocyanate) to *p*-nitro-labeled sulfimide **7**. For lack of reasonable alternatives, mechanisms **7** → T → U → **12** + **10**, and **7** → T → V → **13** + **10** seem required to explain the observed products without resort to high energy (*e.g.*, nitrene) intermediates. Although not experimentally differentiated, one or more of the following four mechanisms are also required.

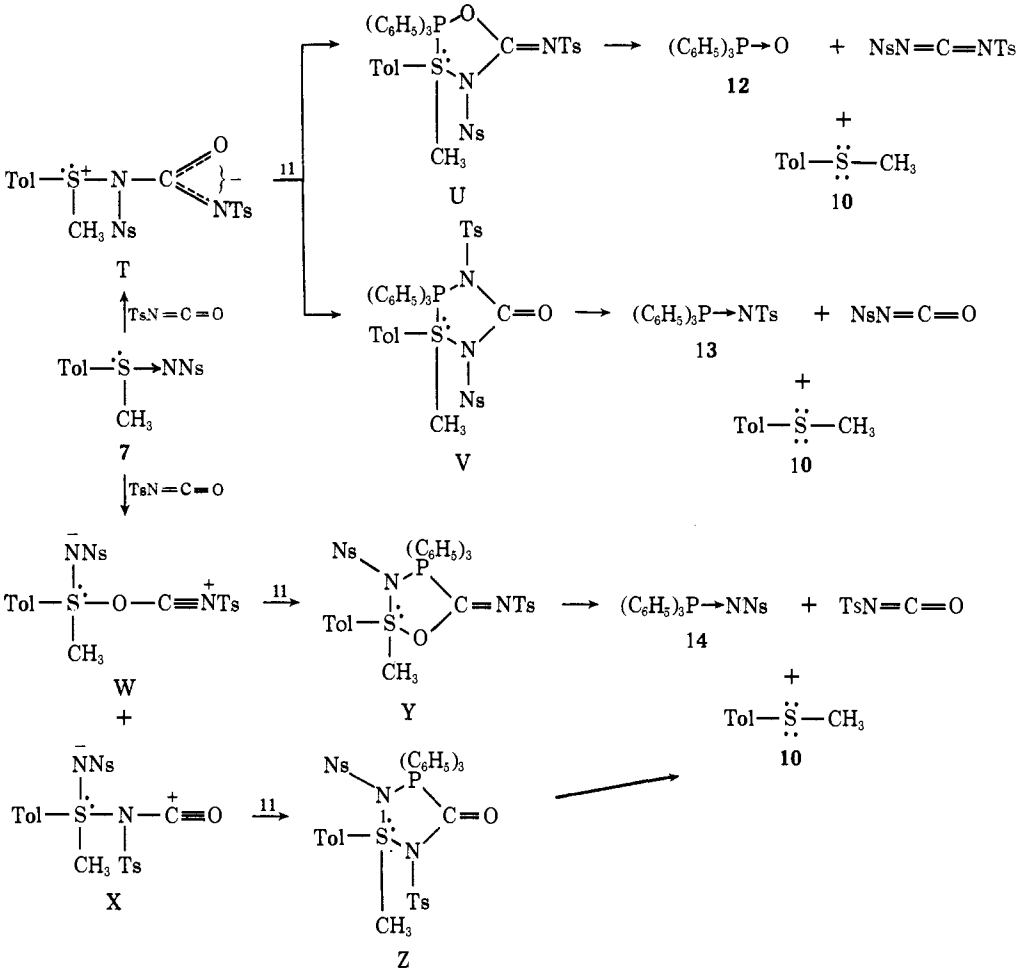
7 → W → Y → **14** + **10**; **7** → X → Z → **14** + **10**

11 → O $\xrightarrow{7}$ Y → **14** + **10**; **11** → O $\xrightarrow{7}$ Z → **14** + **10**

The first two of these mechanisms involve 1,4-dipolar cycloaddition of tricoordinate phosphorus, whereas the latter two involve 1,3-dipolar addition of a 1,2-dipole. In all four mechanisms, the same three entities are involved, and are only assembled in different orders and ways.

Multiple Termolecular Ligand Transfers. This paper has provided examples of what appear to be polar termolecular ligand transfers between sulfur–carbon–carbon, between sulfur–sulfur–carbon, and between sulfur–carbon–phosphorus. Earlier work with *N,N'*-bis(*p*-toluenesulfonyl)sulfur diimide[3] and *N*-sulfinyl-*p*-toluenesulfonamide provided examples of ligand

Chart VI



transfers between sulfur–sulfur–sulfur. Common to these multiple ligand transfers are the following components: a heterocumulene, a sulfoxide or sulfimide, a molecule centered around an element capable of mechanistically expanding its number of ligands by two (*e.g.*, a sulfide or phosphine), or a highly polarized or polarizable double or triple bond (a sulfoxide, a sulfimide, or a second heterocumulene). When chiral centers are involved, and the products and starting materials can be prevented from racemizing, the three component reactions go with inversion of configuration. Many new examples of reactions of these general types will undoubtedly be discovered in the future.

Experimental Section

General. Racemic methyl *p*-tolyl sulfoxide (**1**) and methyl phenyl sulfoxide were prepared by sodium metaperiodate oxidation of the corresponding methyl aryl sulfides.[9] Optically pure (+)-(*R*)-methyl *p*-tolyl sulfoxide, $[\alpha]^{25}_{546}$ +169.1° (*c* 1.7, acetonitrile), $[\alpha]^{25}_{546}$ +180° (*c* 1.4, acetone), and (−)-(*S*)-*N*-*p*-toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide ((−)-**2**), $[\alpha]^{25}_{546}$ −360.5° (*c* 1.21, acetonitrile), $[\alpha]^{25}_{546}$ −326° (*c* 1.36, acetone), were available from previous studies.[5a] Racemic **2** was prepared as before,[10] as was *N*-*p*-toluenesulfonyltetramethylenesulfimide.[11] The reagent *p*-tosyl isocyanate was prepared[12] and fractionally distilled through a 30-in. Nester–Faust gold spinning-band column, bp 71° at 0.25 Torr. Reagent grade acetonitrile was distilled from phosphorus pentoxide through a 10 × 0.25 in. (diameter) column packed with glass helices. Reagent grade sulfides were distilled from molecular sieves 3A. Optical rotations were measured with a Perkin-Elmer 141 polarimeter and a 1-dm water-jacketed cell. Nuclear magnetic resonance spectra were obtained on a Varian A-60D spectrometer for dilute solutions (10–20%) in chloroform-d_3, acetonitrile-d_3, or acetonitrile with tetramethylsilane as internal standard. Infrared spectra were obtained on a Beckman IR-5 spectrophotometer. Melting points are uncorrected, and all temperatures are in degrees Celsius.

***N*-*p*-Toluenesulfonyl-*p*-tolylsulfimide (2) from Methyl Tolyl Sulfoxide (1) and *p*-Tosyl Isocyanate.** A solution of 1.587 g (10.3 mmol) of racemic methyl *p*-tolyl sulfoxide (**1**) and 2.008 g (10.2 mmol) of *p*-tosyl isocyanate in 10.0 ml of dry acetonitrile protected from atmospheric moisture was allowed to stand at 25° for 48 hr. The reaction was quenched by addition of 1.0 ml of absolute methanol which forms *O*-methyl *N*-*p*-toluenesulfonylcarbamate with unreacted *p*-tosyl isocyanate. The solution was reduced to an oil under a slow stream of argon on the steam bath and 2 ml each of ethyl acetate and *n*-pentane were added. Colorless needles of **2** separated from the cooled solution (1.413 g, mp 121–122°). An analytical sample (mp 123.5–124.5°) was obtained by recrystallization from ethyl acetate and then hexane–acetonitrile. The ir and nmr spectra were identical with those of an authentic sample, and a mixture melting point with an authentic sample showed no depression. The filtrate containing the remaining reaction products was chromatographed on 50 g of silica gel packed in *n*-pentane. Elution with *n*-pentane–ethyl acetate mixtures gave in order of elution 0.046 g of methyl *p*-tolyl sulfide (3% yield), 0.927 g of *O*-methyl *N*-*p*-toluenesulfonylcarbamate (40%), 1.952 g of sulfimide **2**, and 0.351 g of sulfoxide **1** (22%). The total yield of sulfimide was 62% after 48 hr of reaction at 25°.

The nmr spectrum of a solution of 2.56 mmol of *p*-tosyl isocyanate and 2.85 mmol of dry acetonitrile remained unchanged over a period of 2 weeks. The nmr spectrum in dry benzene, 2.13 *M* in acetonitrile, and 0.966 *M* in *p*-tosyl isocyanate gave two methyl singlets at 5.20 ppm (aryl CH_3) and 6.03 ppm (CH_3CN) upfield from the benzene absorption. The relative peak areas and positions did not change for 62 hr nor did any new absorptions appear.

(9) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).
(10) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1052 (1922).
(11) D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, **63**, 2939 (1941).
(12) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Org. Chem.*, **31**, 2658 (1966).

Polarimetric Study of Reaction of (+)-Methyl *p*-Tolyl Sulfoxide ((+)-1) with *p*-Tosyl Isocyanate in Acetonitrile at 25°. Sulfoxide (+)-**1** was weighed into an oven-dried, tared volumetric flask and was dissolved in dry acetonitrile. The solution was made up to near final volume at 25° with allowance for *p*-tosyl isocyanate to be added. The solution was weighed, isocyanate was added under dry nitrogen from an oven-dried disposable pipet, and a final weighing was made. The volume was adjusted with dry acetonitrile, and the solution was mixed by several inversions of the volumetric flask. A dry, water-jacketed 1-dm polarimeter cell, thermostated at 25.0°, was filled with the solution with a dry pipet under dry nitrogen. The polarimeter cell was quickly stoppered and transferred to the polarimeter which had been previously set to the calculated initial rotation in those instances in which large initial rotations were expected. The optical rotation of the mixture was recorded at frequent intervals. Figure 1 illustrates typical results obtained. Measurements were made until significant changes in rotation had ceased. The stoppers of the cell were loosened at intervals to relieve pressure due to carbon dioxide evolved by the reaction.

Polarimetric Control Experiments. The following control experiments established that sulfoxide (+)-**1** was optically stable in acetonitrile solution and that sulfimide (−)-**2** was optically stable in the presence of either sulfoxide **1** or *p*-tosyl isocyanate in acetonitrile at 25°. A 0.0927 *M* solution of optically pure (+)-**1** in Spectrograde acetonitrile contained in a 1-dm water-jacketed polarimeter cell thermostated at 25.0° exhibited a constant rotation within ±0.02° (±1%) at a wavelength of 546 nm over a period of 202 hr. Similarly, an acetonitrile solution 0.1621 *M* in optically pure (+)-**1** and 0.1695 *M* in optically pure (−)-**2** maintained at 25° exhibited a constant rotation of −12.61 ± 0.01° over a period of 93 hr. An acetonitrile solution 0.394 *M* in methyl phenyl sulfoxide (instead of methyl *p*-tolyl sulfoxide) and 0.0293 *M* in (−)-**2** had a constant rotation of −3.334° for 70 hr at 25°. However, a 0.353 *M* solution of (−)-**2** in dry dimethyl sulfoxide heated to a temperature of 75° lost optical activity with a half-life of about 62 hr.[13] Finally a dry, acetonitrile solution of 0.0429 *M* in (−)-**2** and 0.123 *M* in *p*-tosyl isocyanate gave a constant rotation of 3.90 ± 0.02° over a period of 101 hr at 25.0°.

Polarimetric Study of Racemization of (−)-*N*-*p*-Toluenesulfonylmethyl-*p*-tolylsulfimide ((−)-2) by *p*-Tosyl Isocyanate and Racemic Methyl *p*-Tolyl Sulfoxide or Racemic Methyl Phenyl Sulfoxide. A dry acetonitrile solution of 0.0234 *M* (−)-**2**, $[\alpha]^{25}_{546}$ −326° (*c* 1.36, acetone), 0.299 *M* in (±)-**1**, and 0.485 *M* in *p*-tosyl isocyanate was placed in a 1-dm polarimeter tube thermostated at 25.1 ± 0.1°. The observed rotation taken at 546 nm decreased steadily from −2.535° after 5 min to −2.270° after 100 min to −1.764° after 240 min to −0.962° after 485 min to −0.444° after 785 min to −0.250° after 1800 min.

A similar experiment was conducted with an acetonitrile solution 0.0195 *M* in (−)-**2**, 1.093 *M* in racemic methyl phenyl sulfoxide, and 1.134 *M* in *p*-tosyl isocyanate. The observed rotation decreased from −2.040° after 1 min to −1.906° after 11 min to −1.596° after 31 min to −1.236° after 51 min to −0.079° after 181 min to −0.009° after 241 min.

Optical Purity of Recovered (+)-Methyl *p*-Tolyl Sulfoxide ((+)-1) and (−)-*N*-*p*-Toluenesulfonylmethyl-*p*-tolylsulfimide ((−)-2) after Partial Reaction. The change in optical rotation at 546 nm was monitored in a 1-dm polarimeter tube thermostated at 25.0 ± 0.1° of a dry solution of acetonitrile which was 0.203 *M* in (+)-**1** and 0.642 *M* in *p*-tosyl isocyanate. Figure 1 records the change with time. Aliquots of 10.00 ml each were removed when the rotation first became zero (after 90 min) and when the (negative) minimum was attained (after 180 min). Each of these two aliquots was pipeted into 0.5 ml of water and then was chromatographed on 100 g of silica gel packed in benzene. Elution was accomplished with the following series of solvents: benzene, 1:1 benzene–ether, ether, 1:1 ether–ethyl acetate, ethyl acetate. Some fractions were rechromatographed on silica gel with elution with ethyl acetate to complete the separation of sulfoxide **1** and sulfimide **2**. The completeness of the separation was checked by nmr. From the first aliquot was obtained 80% of recovered **1** in two portions, $[\alpha]^{25}_{546}$ +34.36° (*c* 0.39, acetonitrile, 20% optically pure) and $[\alpha]^{25}_{546}$ +26.43° (*c* 1.12, acetonitrile, 18% optically pure). Sulfimide **2** isolated in 8% yield from the first aliquot was 27% optically pure, $[\alpha]^{25}_{546}$ −95.8° (*c* 1.87, acetonitrile). Sulfoxide was recovered in 60% yield from the second aliquot, $[\alpha]^{25}_{546}$ +7.1° (*c* 1.56, acetonitrile, 4% optically pure), whereas a 20% yield of sulfimide **2** was obtained which was 7% optically pure.

Kinetics of Reaction of Methyl *p*-Tolyl Sulfoxide (1) with *p*-Tosyl Isocyanate to Give *N*-*p*-Toluenesulfonylmethyl-*p*-tolylsulfimide (2). Nmr Method. Aliquots (0.5 ml) of a reaction mixture were removed from a thermostated (25.1 ± 0.1°) reaction flask (tightly stoppered) and quickly transferred to nmr tubes containing 0.1–0.2 ml of deuterium oxide to quench the reaction. Peak areas were determined from the average of three or four integral traces or, alternatively, spectra were xeroxed and peaks were cut out and weighed.

Titrimetric Method. Aliquots of 0.500 ml were removed from the thermostated reaction mixture at intervals and delivered to 15 ml of a 1:20 v/v mixture of anhydrous methanol–dry acetonitrile. The solution was boiled on a hot plate for 1 min, cooled to 25°, and 3 drops of thymol blue indicator (0.05 g of indicator in 50 ml of anhydrous methanol) was added. The solution was stirred and titrated with 0.2 *N* sodium methoxide in absolute methanol under an argon atmosphere. The end point was taken as the first appearance of a blue color. This end point was sharp and corresponded to the end point obtained by potentiometric titration with dual platinum electrode with one electrode in the buret tip and the other immersed in solution. A Beckman Model H2 pH meter was used to measure the potential difference in this nonaqueous titration.

Kinetic Analysis. For the second kinetic analysis, the differential expression that was assumed was eq 1 for the stoichiometry of eq 2. Equation 3 is the integrated expression for the second-order rate constant. In these expressions $[\mathbf{1}]_0$ is the concentration of **1** at zero time, $[\mathbf{2}]_t$ is the concentration of **2** at time t, and $[\mathrm{i}]_0$ is the concentration of *p*-tosyl isocyanate at zero time.

$$\frac{d[\mathbf{2}]}{dt} = k_2([\mathbf{1}]_0 - [\mathbf{2}]_t)([\mathrm{i}]_0 - [\mathbf{2}]_t) \quad (1)$$

$$\mathbf{1} + \mathrm{i} \longrightarrow \mathbf{2} + CO_2 \quad (2)$$

$$k_2 = \frac{1}{t}\frac{1}{[\mathrm{i}]_0 - [\mathbf{1}]_0}\left[\ln\frac{[\mathrm{i}]_0 - [\mathbf{1}]_t}{[\mathbf{1}]_0 - [\mathbf{1}]_t} - \ln\frac{[\mathrm{i}]_0}{[\mathbf{1}]_0}\right] \quad (3)$$

For the third-order analysis based on the stoichiometry of eq 2, eq 4 expresses the differential form and (5) the integrated form of the expression used. Least-squares analyses were employed for each run. Table I reports the number of points, the extent to which the reactions were followed, and the second- and third-order rate constants, as well as the concentrations of reactants used.

$$\frac{d[\mathbf{2}]}{dt} = k_3([\mathbf{1}]_0 - [\mathbf{2}]_t)([\mathrm{i}]_0 - [\mathbf{2}]_t)^2 \quad (4)$$

$$k_3 = \frac{1}{t}\frac{1}{[\mathrm{i}]_0 - [\mathbf{1}]_0}\left\{\frac{1}{[\mathrm{i}]_0 - [\mathbf{1}]_0}\left(\ln\frac{[\mathrm{i}]_0 - [\mathbf{1}]_t}{[\mathbf{1}]_0 - [\mathbf{1}]_t} - \ln\frac{[\mathrm{i}]_0}{[\mathbf{1}]_0}\right) - \frac{1}{[\mathrm{i}]_0 - [\mathbf{1}]_t} + \frac{1}{[\mathrm{i}]_0}\right\} \quad (5)$$

Reactions of (+)-(*R*)-Methyl *p*-Tolyl Sulfoxide ((+)-1), *p*-Tosyl Isocyanate, and *tert*-Butyl Methyl Sulfide (3). The optical rotation at 546 nm was monitored of an acetonitrile solution 0.132 *M* in (+)-**1**, 0.513 *M* in *p*-tosyl isocyanate, and 0.398 *M* in **3** at 25.0° (curve b, Figure 1). After 71 hr a maximum negative rotation of −6.471° was attained. The reaction was quenched at 75 hr by addition of 0.5 ml of water to 2 ml of reaction mixture. Chloroform was added and the dried ($MgSO_4$) solution was evaporated. The residue dissolved in dichloromethane was chromatographed on 50 g of silica gel packed in benzene. Elution with benzene–ethyl acetate mixtures gave methyl *p*-tolyl sulfide, *p*-toluenesulfonamide, acetamidine **4** (56% based on **1**; see below for characterization), and (−)-(*S*)-*N*-*p*-toluenesulfonylmethyl-*p*-tolylsulfimide ((−)-**2**), 48%, $[\alpha]^{25}_{546}$ −261° (*c* 2.84, acetone), 80% optically pure.

A second run was made that involved a solution of 2.08 g (20 mmol) of *tert*-butyl methyl sulfide (**3**), 1.54 g (10 mmol) of racemic sulfoxide **1**, and 1.97 g (10 mmol) of *p*-tosyl isocyanate in 10.0 ml of dry acetonitrile in which after 96 hr at 25,0° the reaction mixture was concentrated under a stream of dry nitrogen to about 4 ml. The crystals that separated were collected and washed with benzene to yield 0.804 g of sulfimide **2**, mp 124.5–125.5°, identified by ir spectrum. The mother liquor and washings were chromatographed on 100 g of silica gel packed in benzene. Elution with benzene gave methyl *p*-tolyl sulfide (0.40 g, 29%) identified by its characteristic odor and by ir, *p*-toluenesulfonamide (0.19 g, 11%), acetamidine **4**

(13) D. R. Rayner, unpublished results.

(0.761 g, 29%), and 0.554 g of additional sulfimide **2** (total yield 44%) identified by ir and nmr spectra and melting point. Upon prolonged standing in a sealed flask, the acetamidine **4** crystallized. Recrystallization of **4** from ether gave fine needles, mp 111–112°. Repeated crystallization from ether gave needles, mp 112.5–113.5°, undepressed by admixture with an authentic sample (see below). The ir spectrum of acetamidine **4** showed absorptions at 2.93 (w), 3.01 (w), 6.42 (s), 6.52 (s), 7.24 (m), 7.33 (m), 7.90 (m), 8.72 (s), and 9.14 μ (s). The nmr spectrum in deuteriochloroform–1% in tetramethylsilane gave the following chemical shifts (τ): 8.68 (s, 9, $(CH_3)_3C$), 7.69 (s, 3, C–CH_3), 7.61 (s, 3, ArCH_3), 3.98 (s (broad and position is concentration dependent), 1, NH), 2.47 (m, 4, ArH). The mass spectrum of **4** at 70 eV ionizing potential gave the following *m/e* values and relative intensities: 57 (22.9, $C_4H_9^+$), 65 (43.8), 72 (13.3, $C_4H_9NH^+$), 91 (100, C_7H_7), 106 (23.1), 107 (54.2), 147 (17.5), 155 (57.3, $C_7H_7SO_2^+$), 213 (18.5), 268 (11.5, $C_{13}H_{20}N_2O_2S_2^+$), 269 (2.1), 270 (0.8). *Anal.* Calcd for $C_{13}H_{20}N_2O_2S$: C, 58.17; H, 7.51; N, 10.44; S, 11.94. Found: C, 58.24; H, 7.46; N, 10.32; S, 11.85.

In another experiment, the nmr spectrum of an acetonitrile solution 0.90 *M* in **3**, 0.77 *M* in **1**, and 1.5 *M* in *p*-tosyl isocyanate was observed over a period of about 2 days. The appearance of a new *tert*-butyl absorption at τ 8.66 due to formation of acetamidine **4** or its precursor was observed. The reaction was 60–70% complete after 18 hr. Absorptions due to sulfimide **2** and methyl *p*-tolyl sulfide also developed.

In a control experiment, the nmr spectrum of a mixture of 1.8 mmol of sulfide **3**, and 3.1 mmol of *p*-tosyl isocyanate was observed to remain unchanged during a period of 7 days at 25°. Similarly, a solution of 1.08 g (10 mmol) of **3** and 2.0 g (10 mmol) of *p*-tosyl isocyanate refluxed in 10 ml of dry acetonitrile gave after 23 hr no products detectable by nmr except small amounts of decomposition products due to pyrolysis of sulfide **3**.

To test the possibility that *N*-*p*-toluenesulfonyl-*tert*-butylmethylsulfimide if formed might react with acetonitrile to produce the acetamide **4**, 1.06 g (3.9 mmol), of this sulfimide in 5 ml of dry acetonitrile (protected from moisture) was heated in an oil bath at 65° for 25 hr. Evaporation of the solvent gave essentially quantitative recovery of sulfimide.

***N*-*tert*-Butyl-*N'*-*p*-toluenesulfonylacetamidine (4).** After standing at 25° for 384 hr, a solution of 2.42 g (20.1 mmol) of *tert*-butyl methyl sulfoxide[7] (**5**) and 4.50 g (22.8 mmol) of *p*-tosyl isocyanate in 5.0 ml of dry acetonitrile was hydrolyzed by addition of 25 ml of water. Extraction with ether containing about 20% of dichloromethane followed by washing of the ether solution with 10% sodium hydroxide solution and then water gave 3.40 g of an oil upon evaporation to dryness which was identified as **4** by ir (63%). Chromatography on 100 g of silica gel packed in one-to-one ether–pentane and elution with ether–pentane mixtures gave crystalline acetamidine which after recrystallization from ether had mp 110.5–111.5°.

***N*-*p*-Toluenesulfonyl-*tert*-butylmethylsulfimide.** This material was prepared from *tert*-butyl methyl sulfide and chloramine-T by the usual method to give sulfimide (66%), crystallized from pentane–ethyl acetate, mp 88.7–90.0°. *Anal.* Calcd for $C_{12}H_{19}NO_2S_2$: C, 52.71; H, 7.00. Found: C, 52.59; H, 7.10.

***N*-*p*-Nitrobenzenesulfonyltetramethylenesulfimide (6).** Sodium *N*-chloro-*p*-nitrobenzenesulfonamide,[14] 5 g or 25 mmol, and 2.20 g (25 mmol) of tetrahydrothiophene in 200 ml of absolute ethanol was heated at reflux for 1 hr. The hot solution was filtered, cooled, and sulfimide **6** crystallized, wt 2.60 g (37%), mp 183.8–184.8°. Recrystallization of the material from chloroform gave mp 184.5–185.2°.

In a second preparation, 2.48 g (10 mmol) of *N*-sulfinyl-*p*-nitrobenzenesulfonamide[15] and 1.04 g of tetramethylene sulfoxide (10 mmol) in 15 ml of dry pyridine was stirred at 25° for 3 hr. The product was isolated by extraction, and recrystallization of **6** from benzene–chloroform gave 2.05 g (75%), mp 184–185°. The ir spectrum (Nujol) gave bands at 6.59 and 7.41 μ for the nitro group and bands at 7.82, 8.82, 9.27, and 10.28 μ related to the sulfimide and sulfonyl functions. *Anal.* Calcd for $C_{10}H_{12}N_2O_4S_2$: C, 41.65; H, 4.20. Found: C, 41.65; H, 4.11.

***N*-*p*-Nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (7).** By use of the first method employed to prepare **6** (see above), sulfimide **7** was prepared (26%), mp 165.5–166.5°. The ir spectrum of **7** in dichloromethane had strong bands at 6.53, 7.39, 7.69, 8.79, 9.16, 9.99, and 10.50 μ. *Anal.* Calcd for $C_{14}H_{14}N_2O_4S_2$: C, 49.69; H, 4.17. Found: C, 49.81; H, 4.12.

Reactions between Methyl *p*-Tolyl Sulfoxide (1), *p*-Tosyl Isocyanate, and *N*-*p*-Nitrobenzenesulfonyltetramethylenesulfimide (6). A solution of 0.57 g (2.0 mmol) of **6**, 0.62 g (4.0 mmol) of **1**, and 0.82 g (4.2 mmol) of *p*-tosyl isocyanate in 10 ml of dry acetonitrile was maintained under reflux for 3 hr. The cooled reaction mixture was then poured into 30 ml of 10% sodium hydroxide, diluted with 50 ml of distilled water, and extracted with two 50-ml portions of chloroform. The chloroform extracts were washed with two 25-ml portions of 10% sodium hydroxide and then water until the washings were of neutral pH. The dried solution ($MgSO_4$) was evaporated to dryness (rotary evaporator). The residual crystalline solid was recrystallized from 10 ml of hot ethyl acetate to yield 0.08 g of **6**. The mother liquor was chromatographed on 50 g of silica gel packed in ethyl acetate. Elution with ethyl acetate gave 0.18 g (13% yield) of *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (**7**), 0.54 g (44%) of **2**, 0.14 g of recovered **6**, and 0.09 g (17% yield) of *N*-*p*-toluenesulfonyltetramethylenesulfimide[11] in separate fractions which were identified by comparison of tlc, melting points, and ir spectra with authentic samples.

In separate experiments, 0.27 g (0.94 mmol) of **6** and 0.50 g (2.5 mmol) of *p*-tosyl isocyanate in 5 ml of dry acetonitrile were heated at 80° under dry nitrogen for 22 hr without reaction. Similarly, 0.62 g (4.0 mmol) of **1** and 0.28 g (1.0 mmol) of sulfimide **6** in 5.0 ml of dry acetonitrile gave no reaction products after 20 hr at 80°. Also, 0.29 g (1.0 mmol) of **6** and 0.31 g (1.0 mmol) of **2** in 5.0 ml of dry acetonitrile gave no new products when heated at 80° for 3 hr. Sulfimide **2** (0.21 *M* in acetonitrile) was chemically unchanged when refluxed for 5 hr. Possible changes in the above solutions were monitored by tlc and nmr.

In an additional experiment, a solution of 0.144 g (0.50 mmol) of **6**, 0.079 g (0.51 mmol) of **1**, and 0.101 g (0.51 mmol) of *p*-tosyl isocyanate made up to 10.000 ml with dry acetonitrile was placed in a bath at 25.0° for 163 hr. Absolute methanol (1.0 ml) was added, the solution was evaporated, and the solid was recrystallized from ethyl acetate–acetone to yield 0.103 g of recovered sulfimide **6**. The mother liquor was chromatographed on 20 g of silica gel packed in ethyl acetate with elution by ethyl acetate. An intermediate fraction was found to contain both *N*-*p*-toluenesulfonyl and *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (**7**) (by nmr and ir). The latter nitro compound comprised only about 1% of the mixture (by nmr) but was positively identified. The combined yield of sulfimides **2** and **7** was 0.037 g (25%).

Reaction of Diethyl Sulfide, Methyl *p*-Tolyl Sulfoxide (1), and *p*-Tosyl Isocyanate in Acetonitrile. A solution of 0.903 g (10 mmol) of diethyl sulfide, 1.571 g (10 mmol) of **1**, and 1.937 g (9.8 mmol) of *p*-tosyl isocyanate in 10 ml of dry acetonitrile was allowed to stand for 26 hr at 25° after which time 1.0 ml of absolute methanol was added. The excess solvent was evaporated under a stream of nitrogen. The residue, dissolved in benzene–methylene chloride, was chromatographed on 200 g of silica gel packed in 1:1 benzene–ethyl acetate. Elution with benzene–ethyl acetate mixtures gave 0.064 g (2%) of sulfimide **2**, 0.083 g (5%) of recovered sulfoxide **1**, and 2.121 g (82%) of *N*-*p*-toluenesulfonyldiethylsulfimide, mp 144–145°. This latter compound was identified by comparison of its tlc, ir spectrum, and melting point with authentic material (mp 145.8–146.5° crystallized from benzene) prepared from diethyl sulfide and chloramine-T.

An acetonitrile solution which was 0.146 *M* in diethyl sulfide and 0.047 *M* in (+)-**1** was maintained at 25.0° for a period of 168 hr without any change in optical rotation (+1.245 ± 0.005° at 546 nm). Disproportionation to diethyl sulfoxide and methyl *p*-tolyl sulfide was *not* observed. The constitution of a solution of 0.314 g (1.0 mmol) of racemic **2** and 0.137 g (1.5 mmol) of diethyl sulfide in 2.0 ml of dry acetonitrile allowed to stand at 25° for 239 hr did not change as judged by tlc on silica plates with development by ethyl acetate. Finally, 1.05 g (5.32 mmol) of *p*-tosyl isocyanate in 10.0 ml of dry diethyl sulfide was heated under reflux in a dry nitrogen atmosphere in an oil bath held at 100° for 21 hr without change as indicated by tlc analysis. In particular, no *N*-*p*-toluenesulfonyldiethylsulfimide was produced.

Reaction of Dimethyl Sulfide, Methyl *p*-Tolyl Sulfoxide (1), and *p*-Tosyl Isocyanate. The nmr spectrum was monitored for a solution of 0.717 g (11.5 mmol) of dimethyl sulfide, 1.566 g (10.2 mmol) of **1**, and 1.927 (10.0 mmol) of *p*-tosyl isocyanate in 10.0 ml of dry acetonitrile. The nmr chemical shifts of *S*-methyl groups of the reactants and possible products in acetonitrile are summarized in the text. As time progressed, the absorptions due to *N*-*p*-toluenesul-

(14) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1948, p 824.

(15) (a) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6**, 149 (1967); (b) E. S. Levchenko and A. V. Kirsanov, *Zh. Obshch. Khim.*, **32**, 161 (1962).

fonyldimethylsulfimide and methyl *p*-tolyl sulfide increased in relative intensity. Also, a small intensity line appeared and subsequently disappeared at τ 7.49. At completion of the reaction (less than 6 hr), the nmr showed only *N*-*p*-toluenesulfonyldimethylsulfimide as the sole sulfimide product together with methyl *p*-tolyl sulfide. Absolute methanol (1.0 ml) was added to the reaction mixture which was then evaporated. The crystalline residue was triturated with benzene. The solid was collected and dried, 1.80 g, 78% yield of *N*-*p*-toluenesulfonyldimethylsulfimide. Recrystallization from methanol gave pure material, mp 157.5–158.5°, identified by comparison with authentic material. The benzene mother liquor contained a lesser amount of additional *N*-*p*-toluenesulfonyldimethylsulfimide and methyl *p*-tolyl sulfide.

The nmr spectrum of an acetonitrile solution of 0.124 g (2.0 mmol) of dimethyl sulfide and 0.277 g (1.4 mmol) of *p*-tosyl isocyanate in 10.0 ml of dry acetonitrile exhibited lines attributable to the two solutes and to the solvent only. No change in the spectrum occurred over a period of 96 hr at 25°.

Reaction of Methyl *p*-Tolyl Sulfoxide (1), *p*-Tosyl Isocyanate, and Triphenylphosphine (11). Triphenylphosphine (2.62 g, 10.0 mmol) and methyl *p*-tolyl sulfoxide (1.54 g, 10.0 mmol) were dissolved in 10.0 ml of dry acetonitrile. Then 0.99 g (5.0 mmol) of *p*-tosyl isocyanate was added to the solution. Dry nitrogen was bubbled through the solution to remove oxygen. The reaction mixture was then stirred under nitrogen for 24 hr at 45°. The reaction was quenched with 5 ml of water and the mixture extracted with dichloromethane. The organic layer was washed with two 50-ml portions of 10% aqueous sodium hydroxide solution. Acidification of the aqueous layer and extraction into dichloromethane gave, upon evaporation of the solvent, 0.77 g of *p*-toluenesulfonamide (the hydrolysis product of isocyanate). The organic layer containing the remainder of the reaction mixture was dried over sodium sulfate and evaporated onto 10 g of silica gel. This was added dry to the top of a column packed with 200 g of silica gel in 98% pentane–2% 2-propanol. Elution with various mixtures of pentane, ethyl acetate, and 2-propanol gave 0.74 g (79%) of methyl *p*-tolyl sulfide (**10**) and 2.34 g (83%) of triphenylphosphine oxide (**12**), mp 154.5–156° from benzene–hexane. Both **10** and **12** gave nmr and ir spectral identical with those of authentic samples.

In a control experiment, a solution of **11** (0.65 g) and **1** (0.38 g) in 3 ml of oxygen-free acetonitrile was held at 45° for 60 hr, and the products were isolated as in the above experiment. Neither **10** nor **12** was detected in the chromatographic fractions. Only 0.45 g (69%) of **11** and 0.32 g (84%) of **1** were obtained and were identified by their ir spectra.

In a second control experiment, a solution of 0.66 g of **11** and 0.50 g of *p*-tosyl isocyanate in 5 ml of oxygen-free acetonitrile was heated at 45° for 45 hr. The solution was quenched with saturated aqueous sodium chloride and the mixture was extracted with dichloromethane. The ir spectrum of this solution showed bands only characteristic of **11**, and *p*-toluenesulfonamide, and none characteristic of **12** (*e.g.*, P–O absorption) or *N*-*p*-toluenesulfonyltriphenylphosphinimide (**13**, see below).

Reaction of *N*-*p*-Toluenesulfonylmethyl-*p*-tolylsulfimide (2), *p*-Tosyl Isocyanate, and Triphenylphosphine (11). Triphenylphosphine (**11**) (0.26 g, 1.0 mmol) and 0.30 g (1.0 mmol) of sulfimide **2** were dissolved in 5 ml of dry acetonitrile. Dry nitrogen was bubbled through the solution for 10 min. Then 0.20 g (1.0 mmol) of *p*-tosyl isocyanate was dissolved in the solution. The reaction mixture was kept under nitrogen at 45° for 48 hr. The nmr spectrum of an aliquot showed substantial (~70%) conversion of sulfimide **2** to methyl *p*-tolyl sulfide (**10**). The aliquot was returned to the mixture and the reaction continued under the same conditions for an additional 48 hr. Saturated aqueous ammonium chloride solution was added to hydrolyze unreacted *p*-tosyl isocyanate to *p*-toluenesulfonamide. The mixture was extracted with five 10-ml portions of chloroform. The combined organic layers were dried over sodium sulfate and evaporated to give 0.66 g of material. This was dissolved in 10 ml of dichloromethane and evaporated onto 6 g of silica gel, which was then added dry to a column of 60 g of silica gel packed in 98% pentane–2% 2-propanol. Elution with mixtures of pentane, ethyl acetate, and 2-propanol gave, in the order listed, fractions containing the following products: methyl *p*-tolyl sulfide (0.065 g, 70% yield), a liquid identified by its characteristic odor and by ir; *p*-toluenesulfonamide (0.13 g, 75% recovery); *N*-*p*-toluenesulfonyltriphenylphosphinimide (**13**) (0.098 g, 23% yield); triphenylphosphine oxide **12** (0.090 g, 30% yield); and the reactant sulfimide **2** (0.020 g, 7% recovery); all were identified by comparison of ir spectra and melting points with those of authentic samples. Solid products were recrystallized and their melting points were undepressed when mixed with authentic samples. The substance *N*-*p*-toluenesulfonyltriphenylphosphinimide, mp 179–180° from benzene, was prepared by the method of Mann and Chaplin.[16]

Attempted Hydrolysis of *N*-*p*-Toluenesulfonyltriphenylphosphinimide (13) to Triphenylphosphine Oxide (12). A 0.10 g sample of *N*-*p*-toluenesulfonyltriphenylphosphinimide was dissolved in 5 ml of dry acetonitrile. Saturated aqueous ammonium chloride (10 ml) was added to the solution, which was extracted with dichloromethane, dried over magnesium sulfate, and evaporated to give 0.1 g of solid. The ir spectrum of this material in dichloromethane was identical with that of the starting material. The strong absorption band at 8.4 μ associated with the phosphine oxide was absent from this spectrum. Hence the **12** isolated was not formed by hydrolysis of **13** under isolation conditions.

Control Experiment. Reaction of Triphenylphosphine with *N*-*p*-Toluenesulfonylmethyl-*p*-tolylsulfimide (2). A solution of 0.307 g (1.0 mmol) of sulfimide **2** and 0.262 g (1.0 mmol) of triphenylphosphine in 5.0 ml of dry acetonitrile was stirred under nitrogen at 50° for 7 days. The solvent was removed and the solid residue extracted with ether. Material insoluble in ether was filtered. The ether filtrate was evaporated to dryness leaving 0.25 g of a white solid, mp 79–80°, pure by tlc, which gave an ir spectrum in dichloromethane identical with that of triphenylphosphine. The melting point of a sample was undepressed on admixture with an authentic sample of triphenylphosphine. The material insoluble in ether (0.29 g) gave an ir spectrum in dichloromethane identical with that of the starting sulfimide **2**, and its melting point, 124–125° from dichloromethane–pentane, was undepressed on admixture with an authentic sample of **2**. No peaks were observed in either spectrum corresponding to absorption by either phosphine oxide or phosphine imide functional groups.

Reaction of *N*-*p*-Nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (7), *p*-Tosyl Isocyanate, and Triphenylphosphine. Sulfimide **7** (0.66 g, 2.0 mmol), *vide supra*, and triphenylphosphine (0.52 g, 2.0 mmol) were dissolved in 5.0 ml of dry acetonitrile. Dry nitrogen was bubbled through the solution for 10 min. Subsequently, 0.50 g (2.5 mmol) of *p*-tosyl isocyanate was added to the solution which was then kept under nitrogen at 45° for 120 hr. The reaction was quenched with saturated sodium chloride solution and extracted with five 10-ml portions of dichloromethane. The combined organic layers were dried over magnesium sulfate and then evaporated onto 15 g of silica gel. This was added dry to a column of 150 g of silica gel packed in 98% pentane–2% 2-propanol. Elution with various mixtures of pentane, ether and 2-propanol gave fractions containing methyl *p*-tolyl sulfide **10** (0.110 g, 40% yield), identified by its odor and by ir, *p*-toluenesulfonamide (0.165 g, 40% yield), *p*-nitrobenzenesulfonamide, mp 179–181° (0.016 g, 5% yield), *N*-*p*-toluenesulfonyltriphenylphosphinimide (**13**) (0.221 g, 26% yield), triphenylphosphine oxide (**12**) (0.244 g, 44% yield), *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (**7**) (0.067 g, 11% recovery), and *N*-*p*-nitrobenzenesulfonyltriphenylphosphinimide (**14**) (0.169 g, 18% yield, mp 228–230°), all identified by melting points and by ir. Melting points of admixtures with authentic samples were undepressed. Imide **14** was also prepared by another procedure as seen below.

In another experiment, sulfimide **7** (0.34 g, 1.0 mmol) and 0.26 g (1.0 mmol) of **11** were dissolved in dry acetonitrile which had been flushed with nitrogen. Then *p*-tosyl isocyanate (1.98 g, 10.0 mmol) was introduced into the solution which was then stirred at 50° under nitrogen for 125 hr. The reaction was quenched with 10 ml of saturated sodium chloride solution and the mixture extracted with dichloromethane. The organic layer was extracted with 25 ml of 10% sodium hydroxide. Acidification of the basic layer, extraction with dichloromethane, and evaporation to dryness left 1.8 g of a light yellow solid. The ir spectrum of this material in dichloromethane was identical with that of *p*-toluenesulfonamide, but tlc (silica gel, 1:1 ether–pentane) showed it to be a mixture of *p*-toluenesulfonamide and *p*-nitrobenzenesulfonamide. The organic layer, which had been washed with base, was dried and evaporated onto 7 g of silica gel. This was added to a column consisting of 68 g of silica gel packed in pentane–2% 2-propanol. Elution with various mixtures of pentane, ethyl acetate, and 2-propanol gave the following product distribution: methyl *p*-tolyl sulfide (**10**) (0.10 g, 73%), *N*-*p*-toluenesulfonyltriphenylphosphinimide (**13**) (0.031 g, 7.2%), triphenylphosphine oxide (**12**) (0.032 g, 11.5%), unreacted sulfimide **7** (0.045, 13%), and *N*-*p*-nitrobenzenesulfonyltriphenylphosphinimide (**14**) (0.106, 25%).

(16) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

N-p-Nitrobenzenesulfonyltriphenylphosphinimide (14). A mixture of 0.6 g (2.6 mmol) of *N,N*-dichloro-*p*-nitrobenzenesulfonamide, prepared by chlorination of the sulfonamide in a procedure analogous to that for the preparation of dichloramine-T,[17] and 0.6 g (2.5 mmol) of triphenylphosphine was covered with 15 ml of carbon tetrachloride. The solution became bright red immediately. The mixture was refluxed for 15 min and then allowed to cool. The reaction mixture was never completely homogeneous during any phase of the reaction. The slightly yellow precipitate was collected by filtration and dried, 0.7 g, mp 220–225°. Recrystallization of the compound from dichloromethane–pentane gave 0.4 g (36%) of light yellow prisms, mp 229–231°. The ir spectrum in dichloromethane was very similar to that of *N-p*-toluenesulfonyltriphenylphosphinimide (13) with the exception of two sharp bands at 6.6 and 7.4 μ due to absorption by a nitro group. *Anal.* Calcd for $C_{24}H_{19}N_2O_4PS$: C, 62.33; H, 4.14. Found: C, 62.53; H, 4.04.

(17) R. B. Krauss and E. Crede, *J. Amer. Chem. Soc.*, 39, 2720 (1917).

Cycloallyl–Bicycloalkyl Cation Interconversions[1]

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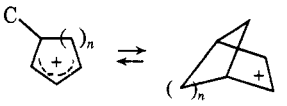
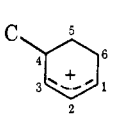
Abstract: A remarkable series of observable cation rearrangements involving the reversible interconversions of substituted cyclohexenyl and 2-bicyclo[2.2.1]heptyl (norbornyl) cations has been observed. The reactions are discussed in detail, with regard to both the thermodynamics of the reactions and their mechanisms. Two of the bicyclic cations involved in the sequence, the 3-*exo*-methyl and 3-*endo*-methyl cations **6** and **8**, provide a dramatic example of the extreme stereospecificity of the 3,2-hydride shift in tertiary norbornyl cations (rate difference $>10^5$ at 25°).

In thermochemical calculations relating to carbonium ions, chemists today have access to good data relating to (a) the stability of solution carbonium ions relative to their neutral progenitors and (b) an increasing body of data on the relative stability of isomeric gas-phase carbonium ions. There is, however, scant information relating the energies of various isomeric solution carbonium ions and, in specific cases like the $C_nH_{2n-3}^+$ cations discussed in this paper, *no* real previous information. In the position (thermodynamic stabilities) of the following equilibrium, the results are as follows

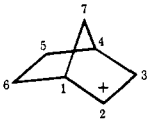


n = 1, strongly favor cycloallyl cation
n = 2, isoenergetic
n = 3, predict to favor the bicycloalkyl cation system

This paper reports an investigation of the n = 2 case: the cyclohexenyl (A) and 2-bicyclo[2.2.1]heptyl (B)



A



B

cations. Previously, we have reported[2] evidence for the 2-bicyclo[2.1.1]hexyl cation system as a high-energy intermediate in some cyclopentenyl cation rearrangements. In addition to the thermodynamic aspects, certain of the 2-bicyclo[2.2.1]heptyl cations have very interesting properties in their own right and these are fully discussed.

(1) Presented in part at the Adelaide Symposium of the Royal Australian Chemical Institute, May 16–19, 1972.
(2) T. S. Sorensen and K. Rajeswari, *J. Amer. Chem. Soc.*, 93, 4222 (1971).

Results

In practice, the parent C-7 systems A and B are separated by too high a transition state barrier to allow interconversions between the two. Only when one comes to a tetramethyl-substituted case (or higher substitution) does one get facile interconversions. The following sequence (Figure 1) has been observed (the basic skeleton is outlined in each case).

Starging with cation **1**, the total sequence can be observed and one eventually ends up with an excellent yield of **10**. The further rearrangement of **10** to cyclopentenyl cations has previously been reported by Deno.[3,4] These authors actually obtained cation **10** by adding 2-methylfenchol or 2-methylborneol to sulfuric acid.[5]

The sequence can be entered at any stage and this has facilitated the determination of several of the rate constants. For example, both the **1** → **2,3,4** → **5** and the **5** → **6,7** → **8,9** reactions have to be treated as consecutive first-order processes. Generating the **2,3,4** cation mixture directly allows one to independently determine the second rate constant and also to better characterize these ions. Actually, in order to prove the structures of the various cations, each system has been independently prepared by reasonably unambiguous means. These are outlined below in Scheme I.

The cations **11** and **12** (Figure 1) were also prepared, because they seemed like possible intermediates in the main sequence and we wished to test their reactivity. Although they do enter the main sequence at the indicated points, they probably represent "dead-end" paths (*vide infra*). They were prepared from the alcohols **23** and **24**.

(3) N. C. Deno and J. J. Houser, *J. Amer. Chem. Soc.*, 86, 1741 (1964).
(4) N. C. Deno and R. R. Lastomirsky, *ibid.*, 90, 4085 (1968).
(5) From our results, this is expected, since at 0° in H_2SO_4 the conversion of **2**, **3**, **4** to **5** and of **5** to **10** would be rapid.