mediates were reasonably stable at liquid nitrogen temperature.

The distribution of molecular weights of the polymeric products was striking in that only higher molecular weight silene self-condensation products were formed. Lower molecular weight species, *i.e.*, dimers and trimers resulting from the condensation of only two or three silene units, were not observed. Normally, one would expect to find a continuous distribution of chain lengths, so that the observation of a large yield of monomeric silene products should be accompanied by large amounts of dimer and trimer. The absence of these lower molecular weight polymeric species suggests that the intermediates involved are considerably less reactive than the silene intermediates responsible for the formation of monomeric products.

It is reasonable to assume that polymerization of silenes occurred in our system in the fashion described by Margrave and Wilson for the condensation of singlet $SiF_2$ to form triplet diradicals.[21]

$$\uparrow\downarrow \dot{S}iF_2 \xrightarrow{SiF_2} \uparrow \dot{S}iF_2\dot{S}iF_2 \uparrow \xrightarrow{SiF_2} \uparrow \dot{S}iF_2\dot{S}iF_2\dot{S}iF_2 \uparrow \xrightarrow{SiF_2} \text{etc.}$$

If the silene intermediates responsible for the formation of monomeric silicon atom products were also in the triplet state, one would expect them to be of approximately the same reactivity as the triplet diradicals formed in the polymerization process. The great difference in reactivity observed thus leads us to believe the monomeric products must have had a singlet state silene precursor.

**Acknowledgment.** We gratefully acknowledge the financial support of the Air Force Office of Scientific Research.

(21) J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, **4**, 145 (1971).

# Stereochemistry of Sulfur Compounds. III. Radical-Chain Mechanism for Racemization of Sulfinamides[1,2]

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*Received September 29, 1971*

**Abstract:** Optically pure (+)-*N*-phenyl-*p*-toluenesulfinamide ((+)-**1**), (+)-*N*-(α-naphthyl)-α-naphthalenesulfinamide ((+)-**2**), and (−)-*N*-methyl-*N*-phenyl-*p*-toluenesulfinamide ((−)-**3**) racemized at 25° in neutral, purified, deoxygenated benzene, and (−)-**3** at 25° in deoxygenated, purified hexamethylphosphoramide. The reactions exhibited radical-chain behavior characterized by varying induction periods, pseudo-first-order kinetics, and inhibition by di-*tert*-butyl nitroxide. That scission of the S–N bond was involved in racemization was demonstrated through crossbreeding of the nitrogen and sulfur parts of **1** and **2** to give 46% disproportionation products. Compound **3** inefficiently initiated styrene and methyl methacrylate polymerization at 25°. The mechanism consistent with these facts is one initiated by homolysis of the S–N bond, followed by a chain-radical displacement reaction of N· by N· on S.

In recent years different mechanisms of racemization at chiral sulfur centers in the *sulfin* oxidation state have been reported.[3-5] Sulfoxides have been racemized photochemically,[3a] by thermally induced homolytic cleavage and recombination,[3b] by reversible allylic rearrangement through allyl sulfenate esters,[3b,c] by reversible nucleophilic substitution at sulfur with nucleophilic acids,[3d] and by pyramidal inversion at high temperatures.[3b] The lowest energy pathway varied greatly with structure and catalyst. Sulfonium salts[4a] and sulfonium ylides[4b] racemized by simple pyramidal inversion at 25–50°. Alkyl sulfinate esters were shown to racemize and rearrange to sulfones in acetic acid through an ion-pair intermediate,[5b] and thiosulfinates racemized by an internal ligand-exchange mechanism involving an achiral point on the reaction coordinate.[5a]

From the variety of racemization mechanisms observed, the generalization emerges that chiral sulfur centers in the *sulfin* oxidation state offer virtually a new mechanism for each type of compound studied. This paper reports an extension of this generalization to optically active sulfinamides. The optical lability of sulfinamides in the solid state in the presence of sunlight was noted by others.[6] We have found that sulfinamides racemize in solution by a mechanism entirely different from those previously reported for sulfur in the *sulfin* oxidation state, and unique in the field of stereochemistry.

(1) This investigation was supported by the U. S. Public Health Service Research Grant No. GM12640-07 from the Department of Health, Education, and Welfare.

(2) The authors thank A. Nudelman [Ph.D. Thesis, UCLA, 1969] for preliminary observations.

(3) (a) K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4958, 4959 (1965); (b) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966); (c) E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, **88**, 3139 (1966); (d) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, **86**, 1452 (1964), and references cited therein.

(4) (a) D. Darwish and G. Tourigny, *ibid.*, **88**, 4303 (1966); (b) D. Darwish and R. L. Tomilson, *ibid.*, **90**, 5938 (1968).

(5) (a) P. Koch and A. Fava, *ibid.*, **90**, 3867 (1968); (b) E. Cuiffarin, M. Isola, and A. Fava, *ibid.*, **90**, 3594 (1968).

(6) S. Colonna, R. Giovini, and F. Montanari, *Chem. Commun.*, 865 (1968).

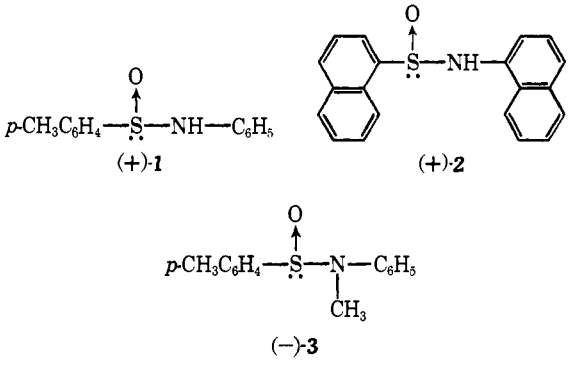
**Table I.** Racemization Kinetics of Sulfinamides at 25.0 ± 0.1° [a]

| Run no. | Substrate: Compd | Substrate: Concn, *M* | Solvent[b] | Induction period, sec × $10^{-4}$ [c] | First-order kinetics: % racemization used for *k* | First-order kinetics: No. of points[d] | First-order kinetics: $k \times 10^5$, $sec^{-1}$ [e] |
|---|---|---|---|---|---|---|---|
| 1 | (+)-**1** | 0.0171 | $C_6H_6$[f] | 0.472 | 7–97 | 26 | 9.47 ± 0.31 |
| 2 | (+)-**1** | 0.0191 | $C_6H_6$[g] | 0.132 | 1–99 | 23 | 19.1 ± 1.0 |
| 3 | (+)-**1** | 0.0173 | $C_6H_6$ | 1.08 | 6–87 | 17 | 7.18 ± 0.40 |
| 4 | (+)-**2** | 0.00915 | $C_6H_6$ | 10.04 | 14–77[h] | 14 | 2.17 ± 0.03 |
| 5 | (−)-**3** | 0.0159 | $C_6H_6$ | 0 | 0–94 | 36 | 91.8 ± 5.6 |
| 6 | (+)-**1** | 0.0249 | $C_6H_6$ | 0.554 | 11–99 | 22 | 9.81 ± 0.5 |
| 7 | (−)-**3** | 0.0169 | $[(CH_3)_2N]_3PO$ | 28.5 | 6–30[i] | 12 | 0.0235 ± 0.0023 |
| 8[j] | (+)-**1** | 0.0176 | $C_6H_6$ | | | | Small |
| 9[j] | (+)-**2** | 0.0109 | $C_6H_6$ | 0 | 1–6[h] | 5 | 0.0120 ± 0.001 |
| 10[j] | (−)-**3** | 0.0184 | $C_6H_6$ | 0 | 0–85 | 22 | 7.97 ± 0.55 |
| 11[k] | (+)-**1** | 0.0186 | $C_6H_6$ | 0.396 | 2–98 | 22 | 13.8 ± 0.57 |
| 12[k] | (+)-**2** | 0.00930 | $C_6H_6$ | 4.07 | 3–26[h] | 18 | 0.987 ± 0.015 |
| 13 | (+)-**1** | 0.00632 | $C_6H_6$ | 0.673 | 15–98 | 17 | 8.78 ± 0.35 |
| | (+)-**2** | 0.00632 | | | | | |
| 14 | (−)-**3** | 0.0171 | | | | | |
| | (+)-**1** | 0.0171 | $C_6H_6$ | 0 | 4–98 | 36 | 27.1 ± 0.67 |

[a] Observed at λ 589 nm except run 9, where λ 578 nm was used. [b] Distilled, deoxygenated solvent and buffer washed equipment unless specified otherwise. [c] See text. [d] Used in least-squares analysis for calculation of *k*. [e] Two standard deviations. [f] Distilled, deoxygenated solvent and buffer untreated equipment. [g] Distilled and solvent saturated with oxygen, buffer untreated equipment. [h] Stopped because solution absorbed too much light to get accurate readings. [i] Stopped because of long length of time necessary to follow reaction to completion. [j] Solutions 2.72 × $10^{-4}$ *M* in di-*tert*-butyl nitroxide. [k] Solutions 5.77 × $10^{-4}$ *M* in 2,6-di-*tert*-butylphenol.

## Results

Sulfinamides (+)-**1**, (+)-**2**, and (−)-**3** were found to racemize in a variety of solvents at 25°. In purified benzene and hexamethylphosphoramide (HMPA), racemization was the only detectable reaction in the absence of light, and rotations at infinite time were 0.000 ± 0.002°.[7] In the first section, the kinetics of racemization of the sulfinamides are described. The second section describes the results of crossbreeding experiments with different sulfinamides. The third section describes sulfinamide initiated polymerization reactions.



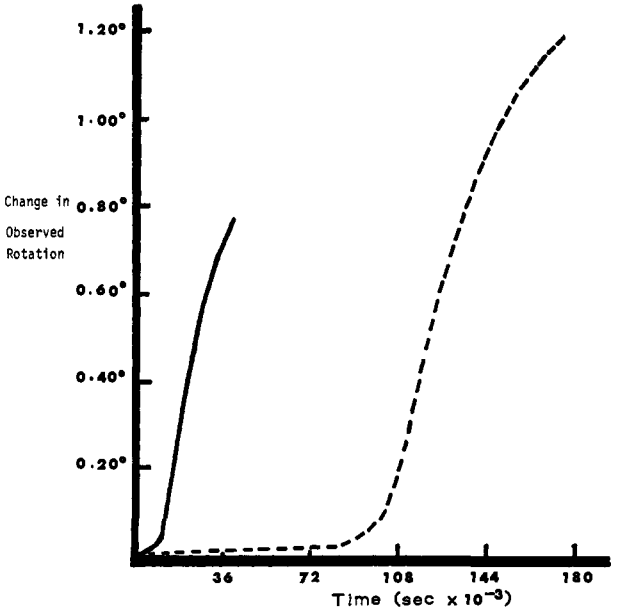




Figure 1. Plots of change of rotation of sulfinamides against time in benzene at 25.0°: solid line, (+)-**1** in run 3; dashed line, (+)-**2** in run 4.

**Kinetics.** Table I describes the results of kinetic runs carried out in a thermostated polarimeter cell. Rotations taken on stock solutions from which the cells were filled demonstrated that the solutions in and out of the cells behaved identically. Changes in rotation observed were from 2.50 to 0.17°, most being greater than 0.300°. Deoxygenated, purified benzene served as the standard medium. When the polarimeter cell and other equipment were washed with pH 7 buffer, the rate constants were reproducible within ±3%, and the induction periods within ±20% (see below).

A long induction period was observed in some of the runs before racemization occurred at an appreciable rate (see Figure 1 for examples). The length of this induction period was determined by extrapolating the linear portion of a plot of per cent racemization *vs.* time (7–22 points were used in extrapolation) to provide an intercept on the time axis. The difference between this extrapolated and the initial time is defined as the induction period, and represents in principle the time required for racemization to begin at its maximum rate. In the runs without induction periods (see Figure 2 as an ex-

(7) In ethanol, (+)-1 underwent ethanolysis as a reaction competitive with racemization. Thus 58% of (±)-**1** and 24% of (−)-ethyl *p*-toluenesulfinate were produced from (+)-*N*-phenyl-*p*-toluenesulfinamide ((+)-**1**). This ethanolysis coupled with the preparation of (+)-1 from (−)-(*S*)-menthyl *p*-toluenesulfinate [(a) A. Nudelman and D. J. Cram, *J. Amer. Chem. Soc.*, 90, 3869 (1968)] and the ethanolysis of the same sulfinate ester to give (+)-ethyl *p*-toluenesulfinate [(b) H. Phillips, *J. Chem. Soc.*, 127, 2552 (1925)] completes a three-reaction, triligostatic stereochemical cycle with four chiromers. These three similar reactions probably went with predominant inversion.

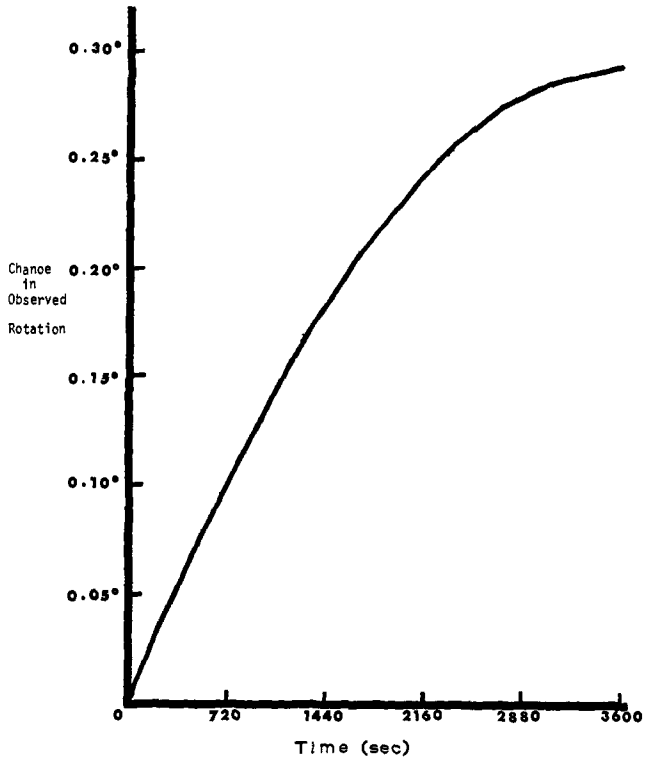
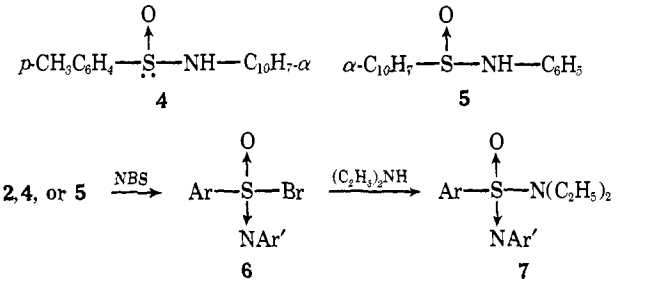



Figure 2. Plot of change of rotation of (−)-**3** against time in benzene at 25.0° (run 5).

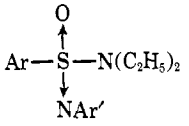
ample), and for that portion of the racemization that occurred after the induction period, the loss in rotation followed first-order kinetics, in most runs with ±6% probable error or less for several half-lives. Table I records the times for the induction periods, the numbers of points taken for the first-order rate constants, and the per cent racemization covered by the first-order behavior. First-order racemization was judged to start at the earliest time at which points could be included in calculation of the first-order rate constant without increasing the probable error. The per cent racemization that occurred before first-order behavior emerged ranged from 0 to 15%. Run 6 with (+)-**1** as substrate was carried out on a preparative scale, and the combined stock solution and cell material produced over 95% accounting of starting material as (±)-**1** by isolation at the end of the run.

**Crossbreeding Experiment.** To determine if the mechanism of racemization involved scission of the S–N bonds of the sulfinamides, a crossbreeding experiment was carried out in benzene in which (+)-**1** and (+)-**2** were racemized at the same concentrations in the same solution of deoxygenated benzene. The reaction was followed kinetically (run 13), and showed good first-order behavior from 15 to 98% racemization after an induction period of 6730 sec.

The four possible products, **1**, **2**, **4**, and **5**, could not be analyzed for directly by tlc, column chromatography, or mass spectroscopy because of their thermal lability. An indirect and satisfactory analysis was developed as follows. The four compounds were prepared by a known procedure,[8] and each was oxidized with *N*-bromosuccinimide to the corresponding sulfonimidoyl bromide[9] (**6**), which in turn was treated with diethylamine to produce the corresponding sulfonimidamide (**7**), a class of compounds well known.[10] The overall yields (after chromatography) for these conversions were not uniform: from **1**, 69%; from **2**, 28%; from **4**, 53%; from **5**, 66%. These compounds separated cleanly by glpc, and their retention times correlated with their molecular weights. In a control experiment, a mixture of **1** and **2** was converted to **7** by this procedure, and no crossbred products were detectable by glpc.




The product mixture of racemic sulfinamides from run 13 was similarly converted to a mixture of compounds of structure **7**. This mixture was separated into its *four components* by glpc, and each component was characterized by comparison of its mass spectrum with that of authentic sulfonimidamides **8**, **9**, **10**, and **11**. By use of an internal standard the mixture was quantitatively analyzed by glpc. The results were corrected for the difference in yields for conversion of the four sulfinamides to their corresponding sulfonimidamides (see above), and the yields (total = 100%) of racemic




**8**, Ar = *p*-$CH_3C_6H_4$; Ar′ = $C_6H_5$
**9**, Ar = α-$C_{10}H_7$; Ar′ = α-$C_{10}H_7$
**10**, Ar = *p*-$CH_3C_6H_4$; Ar′ = α-$C_{10}H_7$
**11**, Ar = α-$C_{10}H_7$; Ar′ = $C_6H_5$

sulfinamides were calculated to be 39% **1**, 21% **2**, 27% **4**, and 13% **5**. An authentic mixture of **1**, **2**, **4**, and **5** of these per cent compositions was then prepared, converted to **8**–**11**, and the mixture analyzed by glpc. The yields of the conversion (in the presence of one another) of **1** → **8**, **2** → **9**, **4** → **10**, and **5** → **11** were calculated, and these yields coupled with the glpc data were used to calculate the relative amounts of **1**, **2**, **4**, and **5** actually produced in run 13. The values were as follows: total yield 54%; relative (mol %) yields, 34% **1**, 20% **2**, 34% **4**, and 12% **5**. Addition of the relative yields of crossbred sulfinamides **4** and **5** indicates that *46% of the racemic product involved ligand interchange at sulfur.* Interestingly, 68% of the sulfinamides present after racemization came from **1** and only 32% from **2**. Apparently, **2** accounted for most of the material lost in producing the 54% absolute yield of sulfinamides. Clearly, the S–N bond was cleaved during the racemization. Unlike most crossbreeding experiments, the racemic and ligand-exchanged products were just as

(8) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem., Int. Ed. Engl.*, 1, 89 (1962), and references therein.

(9) H. Takei, I. Watanabe, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **38**, 1989 (1965).

(10) L. N. Markovskii, E. S. Levchenko, A. A. Kisilenko, and A. V. Kirsanov, *J. Org. Chem. USSR*, **3**, 2168 (1967).

capable of ligand exchange as the starting material. Thus, much of the product must have been through several cycles of ligand exchange.

In the mass spectra of sulfonimidamides **8**, **9**, and **11**, the molecular ion of greatest intensity was P − 120. For **10**, the P − 120 had the second greatest intensity. This apparent efficient production of a neutral fragment of mass 120 probably resulted from migration of the S-aryl group from sulfur to nitrogen. The 120 fragment is attributed to $(C_2H_5)_2NSO$. Similar migrations from sulfur to oxygen have been noted in the mass spectra of sulfoxides,[11] sulfones,[11] and sulfonamides.[12]

**Initiation of Polymerization of Styrene and Methyl Methacrylate by (−)-*N*-Methyl-*N*-phenyl-*p*-toluenesulfinamide ((−)-3).** In run 15, a 0.0878 *M* solution of (−)-**3** in deoxygenated, inhibitor-free styrene after 836 hr at ambient temperature produced a 19% yield of polymer of molecular weight greater than 10,000, whose nitrogen and sulfur content were within error of 0. A parallel control experiment with the same sample of styrene alone gave only 1.5% polymer. In run 16, a 1.11 *M* solution of (−)-**3** in styrene produced, after 289 hr at ambient temperature, an 87% yield of polymer of molecular weight greater than 10,000, and with nitrogen and sulfur content within error of 0. A parallel control experiment with the same sample of styrene alone after 361 hr gave 0.8% of polymer. In runs 15 and 16, the methanol-soluble materials containing **3** were optically inactive. Clearly, (−)-**3** racemized in styrene, acted as a poor initiator for its polymerization, and showed poor, if any, chain transfer properties.

In run 17, (−)-**3** at ambient temperature and at 0.0188 *M* concentration initiated the polymerization of inhibitor free, deoxygenated, methyl methacrylate. After 2928 hr a 4.2% yield of polymer (average molecular weight ~4620) was obtained, whereas a parallel control run with the same monomer in the absence of (−)-**3** gave no polymer. Recovery of (−)-**3** from run 17 showed it to be >90% optically pure.

## Discussion

The major facts of the Results section are summarized as follows. Racemization involves scission of the S–N bond and leads to crossbred products when different sulfinamides are racemized in the presence of one another (run 13). In benzene, the reactions of (+)-*N*-phenyl-*p*-toluenesulfinamide ((+)-**1** in runs 1, 2, 3, 6, and 11) and (+)-*N*-α-naphthyl-α-naphthalenesulfinamide ((+)-**2** in runs 4 and 12) have induction periods, while (−)-*N*-methyl-*N*-phenyl-*p*-toluenesulfinamide ((−)-**3** in run 5) does not. The racemization rate of the N,N-disubstituted amide ((−)-**3**) exceeds the rates of the N-monosubstituted amides ((+)-**1** and (+)-**2**) by 1 order of magnitude (compare run 6 with runs 4 and 5). A very low concentration of di-*tert*-butyl nitroxide (0.000272 *M*) completely inhibits the racemization of (+)-**1** (run 8) and diminishes the rates of racemization of (+)-**2** (run 9) and (−)-**3** (run 10) by over a power of 10. Sulfinamide (−)-**3** acts as an initiator for the racemization of (+)-**1** (run 14), as well as for polymerization of styrene (runs 15 and 16) and methyl methacrylate (run 17). Aside from the induction periods, the racemizations followed first-order kinetics. Oxygen reduces the induction period for racemization of (+)-**1** (compare runs 1 and 2). The presence of 2,6-di-*tert*-butylphenol in 0.000577 *M* concentration reduces the induction period for racemization of (+)-**1** (compare runs 3 and 11) and of (+)-**2** (compare runs 4 and 12). Racemization rates exhibit a large solvent dependence, with nonpolar solvents giving rates several orders of magnitude faster than polar solvents (compare runs 5 and 7, or runs 16 and 17).

A radical-chain mechanism most satisfactorily accommodates these facts. In the envisioned mechanism (Chart I), the initiation reaction (rate constant, $k_i$) occurs by reversible homolysis of the S–N bond, which also contributes to the reaction rate, but in the absence of inhibitors only minimally. Racemization mainly is caused by the propagation step (rate constant, $k_p$) which is a radical substitution reaction in which the attacking and leaving groups are identical. The question of whether ArSO· or ArRN· serves as the chain carrier is unsettled, although the latter possibility explains more facts, and is the more attractive. The nature of the termination step is unclear, but probably involves reaction of two chain carriers with one another with a rate constant, $k_t$. Equations 1–5 summarize schemes based on either radical as the chain carrier. The following sections show compatibility between the facts and this mechanism, and incompatibility with other mechanisms.

**Chart I**

$$\underset{\text{optically active or racemic}}{\overset{*}{\text{ArS}}\text{ONRAr}} \underset{}{\overset{k_i}{\rightleftharpoons}} \underset{\text{achiral}}{\text{ArSO}\cdot} + \underset{\text{achiral}}{\text{ArRN}\cdot} \qquad (1)$$

$$\underset{\text{achiral}}{\text{ArSO}\cdot} + \underset{\text{optically active}}{\overset{*}{\text{ArS}}\text{ONRAr}} \xrightarrow{k_p} \underset{\text{achiral}}{\text{ArSO}\cdot} + \underset{\text{racemic}}{\text{ArSONRAr}} \qquad (2)$$

or

$$\underset{\text{achiral}}{\text{ArRN}\cdot} + \underset{\text{optically active}}{\overset{*}{\text{ArS}}\text{ONRAr}} \xrightarrow{k_p} \underset{\text{achiral}}{\text{ArRN}\cdot} + \underset{\text{racemic}}{\text{ArSONRAr}} \qquad (3)$$

$$2\text{ArSO}\cdot \xrightarrow{k_t} \text{by-products} \qquad (4)$$

or

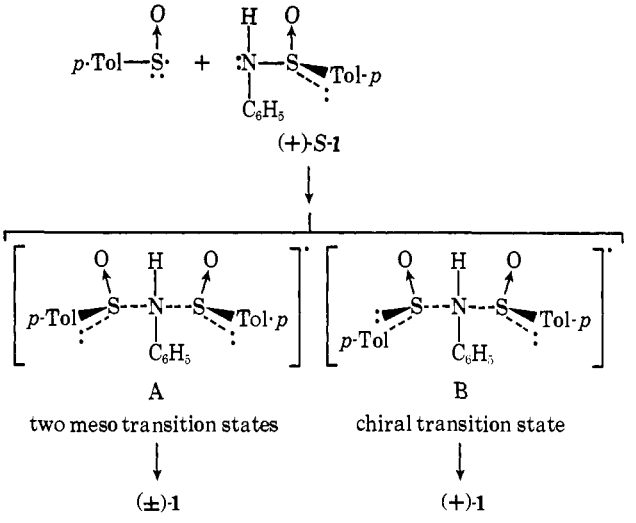
$$2\text{ArRN}\cdot \xrightarrow{k_t} \text{by-products} \qquad (5)$$

**Structural Features of Racemization and Crossbreeding Reactions.** About 46% of the product sulfinamides obtained when optically active sulfinamides **1** and **2** were racemized in the presence of one another did not have structures **1** or **2**, but were derived by combinations of the ArSO of **1** with the NRAr of **2**, or the ArSO of **2** with the NRAr of **1**. This result is compatible with eq 1, 2, and 3, and the mechanistic scheme of Chart I. Although the reverse of the initiation step could account for the observed cross products, probably very little of the reaction occurred this way. The racemization and crossbreeding reactions seemed to occur at comparable rates, and eq 1 taken alone cannot account for the induction period, and inhibition of the racemization of **1** and **2**. Thus, the main crossbreeding reaction component is better explained by either eq 2 or 3, as are the racemizations.

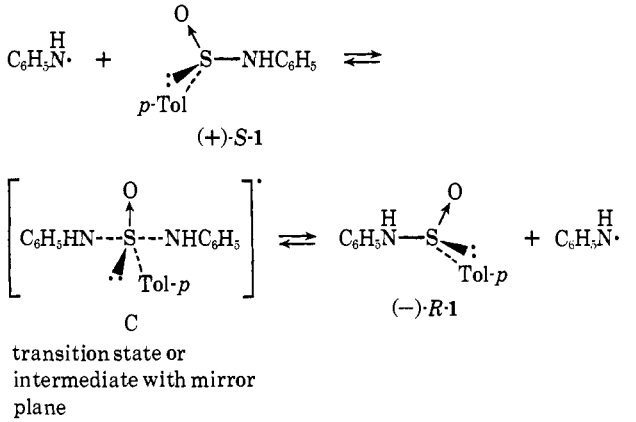
If eq 2 applies, then ArSO· is the chain carrier, and the reaction is a radical substitution on nitrogen. Two diastereomeric transition states are possible. One is meso (A), and regenerates starting material if it decom-

(11) J. H. Bowie, D. H. Williams, S. O. Lawesson, J. O. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, **22**, 3515 (1966).
(12) G. Spiteller and R. Karchnitz, *Monatsch. Chem.*, **94**, 964 (1963).

poses one way, and the enantiomer of starting material if it decomposes the other. The other is chiral (B), and regenerates the optically active starting material even if ligand exchange on sulfur does occur. With this mechanism, only the reaction going by transition state A would be visible. These possibilities are formulated with (+)-*S*-**1** as substrate.[7a] For mechanism (+)-**1** → A → (±)-**1** to apply, ArSO· would have to be achiral, or equilibrating with its enantiomer faster than it goes to A. Since nitrogen is pseudoasymmetric, two meso structures are possible, both leading to (±)-**1**. The two meso forms are not distinguished in A since this additional complication has little bearing on the outcome of the reaction. The analogy closest to this mechanism of which the authors are aware is the radical displacements on oxygen seen in the induced decomposition of benzoyl peroxide in ether.[13]




If eq 3 applies, then ArRN· is the chain carrier, and the reaction is a radical substitution on sulfur. For racemization to occur, the substitution either has to go with inversion of configuration by way of transition state C, or has to involve a radical intermediate containing the same components as C and equivalent symmetry properties. The simpler, former possibility is formulated.




The closest analogy to mechanism (+)-**1** → C → (±)-**1** of which we are aware is in the work of Pryor and Guard.[14] These authors demonstrated the existence of radical substitution reactions by phenyl radical on alkyl disulfides.

**Kinetic Features of Racemization Reaction.** The two mechanisms of Chart I are compatible with the observed kinetics of the racemization reaction, which are not unlike the radical-chain mechanism for polymerization of vinyl polymers.[15] Equation 6 formulates the kinetics of racemization as a rate expression in which [ArSONRAr] is the concentration of sulfinamide that acts as initiator, and [ArS*ONRAr] the concentration of optically active sulfinamide.[16] Either optically active or racemic sulfinamide can initiate racemization. Thus, [ArSONRAr] remains constant throughout a given run, eq 6 reduces to 7, and the rate of racemization is pseudo-first order. The observed kinetics of racemization were first order, in some runs over as much as 98% of the reaction (run 2). The concentrations of substrates listed in Table I are close enough together to allow the first-order rate constants to be used for gross comparisons between runs.

$$\text{racemization rate} = \frac{k_p k_i^{1/2}}{\sqrt{2} k_t^{1/2}}[\text{ArSONRAr}]^{1/2}[\text{ArS}^*\text{ONRAr}] \quad (6)$$

$$\text{racemization rate} = k_{obsd}[\text{ArS}^*\text{ONRAr}] \quad (7)$$

**Initiation and Inhibition of Racemization.** All of the substrates except the N,N-disubstituted sulfinamide (**3**) had substantial induction periods. The mechanism of Chart I accounts for this phenomenon as the period necessary for the chain-carrying radical to consume inhibitor impurities and reach a steady-state concentration. The inhibition for long periods of time of racemization by di-*tert*-butyl nitroxide at a concentration of 0.000272 *M* in runs 8 and 9 suggests that homolysis of ArSONHAr is a very slow reaction (eq 1) compared to the chain reaction. The nitroxide scavenges the chain carrier as it develops, and inhibits the chain reaction. That only a very low concentration of nitroxide is needed for essentially complete inhibition suggests that the steady-state concentrations of the chain carrier are very low, and the chains very long.

The N,N-disubstituted substrate (**3**) behaved differently than **1** and **2**. The substance exhibited no observable induction period, and the rate of racemization was decreased by a power of 10 by introduction of nitroxide at 0.000272 *M* concentration (run 10). No induction period was observed in this run. These facts are explained in terms of the mechanisms of Chart I as follows. Racemization of (−)-**3** in the absence of nitroxide occurs mainly by the chain reaction (run 5). The absence of an induction period indicates a steady state is reached rapidly, and adventitious inhibitors are quickly scavenged. In the presence of nitroxide (run 10), the chain reaction is inhibited, and the racemization of (−)-**3** occurs mainly by homolysis and recombination within the solvent cage. This latter reaction is first order in (−)-**3**, has no induction period, and is not inhibited by

(13) E. S. Huyser, "Free-Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, pp 262–264.

(14) W. A. Pryor and H. Guard, *J. Amer. Chem. Soc.*, **86**, 1150 (1964).

(15) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter IV.

(16) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1965, pp 241–244, for a detailed discussion of chain reaction mechanisms.

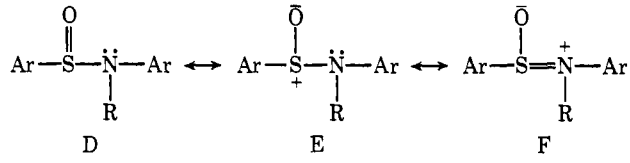
nitroxide. Only radicals that escape the cage initiate the much faster chain reaction (run 5), but are scavenged by nitroxide (run 10).

When equal molar concentrations of (+)-**1** and (−)-**3** were racemized in the same medium (run 14), no induction period was observed, and loss of optical activity followed first-order kinetics. Clearly **3** acted as an initiator for **1**. The homolysis of **3** should occur faster than that of **1**, since **3** gives $CH_3N \cdot C_6H_5$ and **1** gives the less stable $HN \cdot C_6H_5$ radical. If the ArSO· radical is the chain-carrying species (eq 2) and termination is by eq 4, and if the first-order dependence is taken to indicate that both substrates are attacked by ArSO· with nearly the same rate constants, then the observed pseudo-first order rate constant for the mixture of **1** and **3** should depend only on the concentration of **3**. The concentration of **3** was nearly the same in runs 14 and 5, and yet the rate constant in run 14 was a factor of 4 lower than that in run 5. This fact suggests that ArSO· is not, and ArN·R is the chain-carrying radical (eq 3).[17] With this mechanism, both $C_6H_5 \cdot NH$ and $C_6H_5 \cdot NCH_3$ would have to serve as chain carriers in run 14, and the observed first-order rate constant would be a composite of many compensating components.

That oxygen reduces the induction period for racemization of **1** (run 2) suggests that oxygen can contribute directly as an initiator of the chain reaction, possibly by attack on S to generate $C_6H_5 \cdot NH$. Less marked was the reduction of the induction period by 2,6-di-*tert*-butylphenol of **1** and **2** (runs 11 and 12). Possibly, the phenol by reacting with ArSO· inhibits the reverse reaction of eq 1, in which chain carrier is consumed by its original partner radical to give starting material. The phenol might react with the nonchain-carrying partner radical. Thus, a steady-state concentration of chain carrier would be reached earlier in the presence of this phenol.

**Solvent Effects.** The rate of racemization of (−)-**3** in hexamethylphosphoramide (run 7) was lower by a factor of about 4000 compared to a comparable run (5) in benzene. Likewise, (−)-**3** racemized much faster in styrene than in methyl methacrylate, and (+)-**1** faster in benzene than in ethanol (results of preliminary experiments). Changes this large are rare for homolytic reactions such as those of equations 1, 2, and 3 of Chart I. The fact that the nonpolar solvent favors reaction over the polar solvent indicates the starting state is much more polar and more heavily solvated than the rate-controlling transition states. The mechanisms of Chart I are in accord with this solvent effect. The sulfinamide linkage is very polar, not unlike the amide linkage, and is expected to be highly solvated by polar solvents. The polarity can be visualized with resonance structures such as E and F. The products of homolysis (reaction 1) are far less polar, and thus the transition state for homolysis is less polar than the ground state. The transition states for propagation (structures A, B, or C) are also far less polar than the starting state, and these transition states are located half way along the reaction coordinate. For sulfinamides to racemize by the mechanisms of Chart I in polar solvents, sulfinamide at both initiation and propagation stages would have to desolvate in passing to the transition states, and the rate depressed as is observed.[18]

(17) The authors are indebted to referee II for this argument.




## Experimental Section

**General.** Melting points are uncorrected, and all temperatures are in degrees Celsius. Nuclear magnetic resonance spectra were obtained on Varian A-60D or HA-100 instruments on dilute solutions (5–20%) in deuteriochloroform or DMSO-$d_6$ with tetramethylsilane as internal standard. Infrared spectra were recorded on a Beckman IR-5 spectrophotometer. Optical rotations were measured at 25° with a Perkin-Elmer 141 polarimeter and a 1-dm thermostated cell. Mass spectra were obtained with an AEI Model MS-9. Silica gel used for column chromatography was Baker chromatographic grade. All solvents were reagent grade unless otherwise specified. Solutions were dried with anhydrous sodium sulfate. Thin-layer chromatograms used were Brinkman silica gel G coated on Pyrex plates or Brinkman prepared silica gel plates with fluorescent indicator. The chromatograms were developed by uv light or by spraying with a 10% solution of phosphomolybdic acid in ethanol followed by heating on a hot plate for about 1 min. In the latter case, the tlc plate was carefully observed while being heated because changes in color hue or intensity were often characteristic of a compound. Colors varied from yellow to blue, purple, or brown. The rate of color development was also a characteristic of different compounds.

**Known Starting Materials.** The (+)-*N*-phenyl-*p*-toluenesulfinamide ((+)-**1**) used[7a] gave mp 129–130° dec, $[\alpha]^{25}D$ +220.5° (*c* 1.47, $CHCl_3$), was 98.3% optically pure,[7a] and was stored at −20°. The (−)-menthyl α-naphthalenesulfinate was prepared as reported.[19] and gave mp 120–121°, $[\alpha]^{25}D$ −424.6° (*c* 1.14, acetone). The (−)-*N*-methyl-*N*-phenyl-*p*-toluenesulfinamide ((−)-**3**) used[20] gave mp 79–80°, $[\alpha]^{25}_{578}$ −109.9° (*c* 2.53, $CHCl_3$), and was stored at −20° in the dark.

(+)-*N*-α-**Naphthyl-α-naphthalenesulfinamide** ((+)-**2**). To 2.14 g of α-naphthylamine in 150 ml of anhydrous ether stirred under a nitrogen atmosphere was added 9.4 ml of a 1.6 *M* solution of butyllithium in hexane. The resulting dark green solution was stirred briefly and added dropwise over 25 min to a solution of 4.93 g of (−)-menthyl α-naphthalenesulfinate (see above) in 150 ml of anhydrous ether stirred at 0° under a nitrogen atmosphere. The mixture was stirred 3 hr at 0° and quenched at 0° with water saturated with ammonium chloride. The mixture was shaken with dichloromethane, and the organic layer was washed with distilled water, dried, and chromatographed on 250 g of silica gel. Ether–pentane and pentane–dichloromethane–isopropyl alcohol solvent mixtures were used to elute the product, thirty 400-ml fractions being collected. Fractions 24–28 contained 1.6 g (34%) of a red solid, which was decolorized (charcoal) in ethanol at 25° and recrystallized twice from ethanol to give a constant rotation of $[\alpha]^{25}D$ +561° (*c* 0.62, $CHCl_3$) for the white plates, mp 129–130° dec, which was stored at −20°. This sulfinamide ((+)-**2**) gave the following nmr spectrum ($(CD_3)_2SO$): τ 1.70–3.08 (m, 14. ArH), 0.62 (s, 1, NH). *Anal.* Calcd for $C_{20}H_{15}NOS$: C, 75.68; H, 4.76. Found: C, 75.63; H, 4.70.

**Kinetic Runs.**[21] Spectral grade benzene was distilled from lithium aluminum hydride and deoxygenated by four freeze–thaw cycles (liquid nitrogen to room temperature) evacuated to about 10 μ, and was stored under pure nitrogen in a dry box until used. Except in runs 1 and 2, in which the equipment was not pretreated, the volumetric flask and polarimeter cell (1 dm) were washed with a pH 7.0 buffer, freshly distilled water, acetone, and purified benzene

(18) We gratefully acknowledge the value of discussions of the results of this paper with Professor W. A. Pryor.

(19) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, T. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, 86, 5637 (1964).

(20) T. R. Williams, R. E. Booms, and D. J. Cram, *ibid.*, 94, 4684 (1972).

(21) The raw kinetic data for representative runs shown in Table II appear in Figures 1 and 2. Table II will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5438. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

several times before use. The solutions were prepared in a dry box, immediately transferred to the jacketed polarimeter cell, and the first reading recorded after approximately 5 min at λ 589 nm. In representative runs the rotations of the stock solutions were checked against the rotation in the polarimeter cell after partial reaction, and the two were found to be identical. At the end of runs 5 and 7, tlc (50% ether–pentane eluent, uv developer) analysis revealed the presence of only **3**. In run 6, 57.6 mg of (+)-**1** in 10 ml of purified benzene was used. The final colorless solutions in flask and cell were combined, the solvent was removed below 25°, and the residue recrystallized from benzene–pentane at −25°. White plates, 50 mg (86%), were collected, mp 137–138° dec. The sample was shown to be identical with (±)-**1**[7a] by tlc (2% methanol–chloroform eluent, uv developer) and ir analysis. In a control experiment, 52 mg of (±)-**1**[7a] was recrystallized from benzene–pentane to give 42.6 mg (82%), mp 137–138° dec, tlc behavior identical with the above sample.

In run 7, reagent grade hexamethylphosphoramide was distilled from 13× molecular sieves (dried at 750° for 6 hr), and deoxygenated and stored as was benzene. In runs 8–10, a standard solution of 0.980 mg of freshly distilled di-*tert*-butyl nitroxide[22] (bp 56–57° (11 mm)) was prepared. At the end of all three runs, tlc revealed the presence of only sulfinamide. For runs 11 and 12, a standard solution of 2.971 mg of 2,6-di-*tert*-butylphenol[23] in 25 ml of purified benzene was prepared.

The crossbreeding experiment of run 13 was conducted with 73 mg of (+)-**1** and 100.2 mg of (+)-**2** in 50 ml of purified benzene under the standard conditions. The final mixture after 98% racemization was a deep red color, and had become totally optically inactive after 30 hr. The volumetric flask and polarimeter cell samples were combined after 56 hr, and the solvent was evaporated rapidly in the absence of oxygen under reduced pressure at 25° to yield a thick red oil. To this oil under a nitrogen atmosphere were added 0.19 ml of diethylamine and 30 ml of dry carbon tetrachloride. The mixture was cooled to 0–5° and 124 mg of *N*-bromosuccinimide was added. The resulting solution was stirred 3 hr at 0–5° and 16 hr at 25°. Dichloromethane was added to dissolve all the organic material, the solution was washed with distilled water, dried, and evaporated, and the residue was chromatographed on 40 g of silica gel. Twenty-five 75-ml fractions were eluted with 10% ether–pentane. Fractions 3–6 contained a red oil which showed the presence of the desired products by tlc analysis (50% ether–pentane eluent, uv developer). These fractions were combined, analyzed, and preparatively separated by glpc (see later section). Each of the four products was collected as a separate entity (see later section) and identified by mass spectrometry (see later section).

**Preparative Scale Racemization of (+)-*N*-Phenyl-*p*-toluenesulfinamide ((+)-1) in Ethanol.** In 50 ml of ethanol, freshly distilled from magnesium ethoxide (and deoxygenated as was benzene, see above), was dissolved 204.4 mg of optically pure (+)-**1** (solution was 0.0177 *M*). The sample was prepared and sealed in a volumetric flask with vacuum grease and wax in a dry box, and allowed to stand at ambient temperature for 360 hr. The final solution was light purple in color, and tlc analysis (50% ether–pentane, uv developer) showed the presence of only **1** and a faster moving spot. The solution gave $[\alpha]^{25}D$ −13.2° (*c* 0.41, ethanol). The solvent was evaporated at reduced pressure, and the residue was chromatographed on 10 g of silica gel with ether–pentane mixtures as developer. Twelve 50-ml fractions were collected, the second of which contained 39 mg (24%) of (−)-ethyl *p*-toluenesulfinate, $[\alpha]^{25}D$ −51.0°, $[\alpha]^{25}_{546}$ −61.0° (*c* 0.50, $CHCl_3$). The nmr spectrum of the material in $CDCl_3$ gave τ 8.72 (t, 3, $CH_2CH_3$ methyl), 7.59 (s, 3, $ArCH_3$), 6.08 (m, 2, $CH_2CH_3$ methylene), 2.30–2.81 (m, 4, ArH). This material was distilled, bp 88–92° (0.15 mm), to give a pale yellow oil of the same rotation as was obtained before distillation. *Anal.* Calcd for $C_9H_{12}O_2S$: C, 58.67; H, 6.56. Found: C, 58.71; H, 6.66.

From fractions 10 and 11 of the chromatograph was isolated 119 mg (58%) of (±)-**1**, identified by tlc (50% ether–pentane, uv developer) and by ir spectrum.

**(±)-*N*-Phenyl-α-naphthalenesulfinamide ((±)-5).** To 2.7 g of magnesium turnings in 50 ml of anhydrous ether was added under a nitrogen atmosphere about 10% of a solution composed of 22.8 g of α-bromonaphthalene in 50 ml of dry ether and several iodine crystals. The mixture was heated briefly to initiate reaction and the remainder of the α-bromonaphthalene solution was added over a 60-min period. The solution was refluxed for 3 hr, and to it was added a solution of 13.9 g of *N*-sulfinylaniline[8] in 50 ml of dry ether over a 60-min period at 13–15°. The resulting solution was stirred at this temperature for 15 min and quenched with ice-cold 10% ammonium chloride solution. The reaction mixture was filtered and the solid collected was washed well with dichloromethane. The filtrate was extracted with distilled water, dried, and evaporated at reduced pressure. The yellow residue was recrystallized at low temperature from benzene to yield 12 g of white plates, mp 118.5–120° dec; nmr ($DCCl_3$) τ 3.8 (s, 1, NH), 1.7–3.0 (m, 12, Ar-H). *Anal.* Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90. Found: C, 71.83; H, 4.78.

**(±)-*N*-(α-Naphthyl)-*p*-toluenesulfinamide ((±)-4).** Using a procedure similar to the above, from 10 g of *p*-bromotoluene and 10.0 g of *N*-sulfinyl-α-naphthylamine[24] was obtained 6.8 g (46%) of (±)-**4** as white plates (from benzene), mp 113–114° dec. The nmr spectrum of the substance in $(CD_3)_2SO$ gave the following signals: τ 7.78 (s, 3, $ArCH_3$), 0.5 (s, 1, NH), 1.72–2.97 (m, 11, ArH). *Anal.* Calcd for $C_{17}H_{13}NOS$: C, 72.57; H, 5.37. Found: C, 72.73; H, 5.28.

**(±)-*N*-(α-Naphthyl)-α-naphthalenesulfinamide ((±)-2).** By the above procedure, from 12.06 g of α-bromonaphthalene and 10 g of *N*-sulfinyl-α-naphthylamine[8,24] was obtained 10.7 g (64%) of (±)-**2** as white cubes from benzene, mp 128–130° dec. The nmr spectrum of the substance in $(CD_3)_2SO$ gave the following signals: τ 0.6 (s, 1, NH), 1.72–2.93 (m, 14, ArH). *Anal.* Calcd for $C_{20}H_{15}NOS$: C, 75.68; H, 4.76. Found: C, 75.72; H, 4.83.

**(±)-*N*,*N*-Diethyl-*N*′-phenyl-*p*-toluenesulfonimidamide ((±)-8).** To a solution of 3.0 g (0.013 mol) of *N*-phenyl-*p*-toluenesulfinamide ((±)-**1**) in 85 ml of carbon tetrachloride cooled to 0–5° was added 2.32 g (0.013 mol) of *N*-bromosuccinimide. The resulting solution was stirred 40 min at this temperature during which time a dark orange color developed. Added was 2.67 ml (0.026 mol) of diethylamine by syringe and the mixture was stirred 3 hr at 0–5° and 4 hr at 25°. After extraction with distilled water and drying, the reaction mixture was chromatographed on 350 g of silica gel. The product was eluted with 10% ether–pentane. Thirty-five 100-ml fractions were collected. Fractions 19–32 contained a yellow oil which crystallized upon standing. These fractions were combined to yield 2.7 g (69%) of material which was decolorized in petroleum ether on charcoal and recrystallized twice. Collected were white cubes, mp 59–60.5°; nmr ($DCCl_3$) τ 9.05 (t, 6, $CH_2CH_3$ methyl), 7.6 (s, 3, $ArCH_3$), 6.72 (q, 4, $-CH_2CH_3$ methylene), 2.0–3.15 (m, 9, ArH). *Anal.* Calcd for $C_{17}H_{22}N_2OS$: C, 67.52; H, 7.33. Found: C, 67.38; H, 7.17.

**(±)-*N*,*N*-Diethyl-*N*′-(α-naphthyl)-α-naphthalenesulfonimidamide ((±)-9).** By a similar prodedure, 3.0 g of (±)-**2** was converted into 1.03 g (28%) of (±)-**9** as white needles, mp 95.5–97.5° (to a green liquid); nmr ($DCCl_3$) τ 9.0 (t, 6, $CH_2CH_3$ methyl), 6.53 (q, 4, $CH_2CH_3$ methylene), 0.9–2.8 (m, 14, ArH). *Anal.* Calcd for $C_{24}H_{24}N_2OS$: C, 74.10; H, 6.23. Found: C, 74.17; H, 6.10.

**(±)-*N*,*N*-Diethyl-*N*′-(α-naphthyl)-*p*-toluenesulfonimidamide ((±)-10).** By a similar procedure, 3.0 g of (±)-**4** was converted to 2.0 g (53%) of (±)-**10** as white cubes (from ether–pentane), mp 99.5–101.5°; nmr ($DCCl_3$) τ 9.07 (t, 6, $CH_2CH_3$ methyl), 7.6 (s, 3, $ArCH_3$), 6.73 (q, 4, $CH_2CH_3$ methylene), 1.33–2.81 (m, 11, ArH). *Anal.* Calcd for $C_{21}H_{24}N_2OS$: C, 71.55; H, 6.86. Found: C, 71.33; H, 6.66.

**(±)-*N*,*N*′-Diethyl-*N*′-phenyl-α-naphthalenesulfonimidamide ((±)-11).** By a similar procedure, 3.0 g of (±)-**5** was converted to 2.5 g (66%) of (±)-**11** as pale yellow cubes from petroleum ether, mp 67–69.5°; nmr ($DCCl_3$) τ 9.0 (t, 6, $CH_2CH_3$ methyl), 6.52 (q, 4, $CH_2CH_3$ methylene), 0.9–3.1 (m, 12, ArH). *Anal.* Calcd for $C_{20}H_{22}N_2OS$: C, 70.97; H, 6.55. Found: C, 71.06; H, 6.25.

**Gas Chromatographic Separation of Four Sulfonimidamides, 8–11.** Analysis of the sulfonimidamides **8–11** by glpc (F&M Model 720, 1 ft × 0.24 in. aluminum column of 5% SE 30 on DMCS treated Chromosorb W, column temperature programmed at 2°/min from 125 to 250°, flow rate of 60 cc of helium/min) showed the following relative retention times: **8**, 0.45; **11**, 0.69; **10**, 0.79; **9**, 1.00. The separation was base-line in each case.

**Control Oxidation of Mixture of (±)-1 and (±)-2.** To a solution of 100.6 mg ($3.17 \times 10^{-4}$ mol) of *N*-(α-naphthyl)-α-naphthalenesulfinamide ((±)-**2**), 72.7 mg ($3.14 \times 10^{-4}$ mol) of *N*-phenyl-*p*-toluenesulfinamide ((±)-**1**), 0.19 ml ($1.90 \times 10^{-3}$ mol) of diethylamine, and 30 ml of dry carbon tetrachloride cooled to 0–5° under

(22) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and A. Henderson, *Org. Syn.*, **48**, 62 (1968).

(23) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

(24) A. Michaelis and H. Buntrock, *Ann. Chim. (Paris)*, 274, 253 (1893).

a nitrogen atmosphere was added 124 mg ($6.95 \times 10^{-4}$ mol) of *N*-bromosuccinimide. A bright yellow color resulted in about 10 min. The resulting solution was stirred 3 hr at 0–5° and overnight at room temperature. Dichloromethane was added to dissolve all the organic material and the solution was extracted with distilled water, dried, and chromatographed on 40 g of silica gel. Twenty 75-ml fractions were eluted with 10% ether–pentane. Fractions 3–6 contained a red oil which showed the presence of sulfonimidamides by tlc analysis (50% ether–pentane eluent, uv developer). These fractions were combined and analyzed by the glpc method previously described. No crossproducts were seen, only the oxidized starting materials, **8** and **9**. None of the other chromatographic fractions contained sulfonimidamides.

**Procedure for Analytical Glpc Analysis.** With the glpc technique and conditions described previously, standard solutions of internal standard (*o*-terphenyl) and compounds **8, 9, 10,** and **11,** individually, were analyzed to determine the relative response curves of each of the four possible products. The cut-and weigh integration procedure described by Varian-Aerograph[25] was employed without tracing the chromatograms. In multiple injections the determinations of all standard solutions were reproducible to ±2.5%. Unknown product mixtures were analyzed in the same manner employing these relative response curves.

**Quantitative Crossbreeding Experiment.** In 50 ml of neutral purified benzene were dissolved 118.5 mg ($5.13 \times 10^{-4}$ mol) (±)-**1** and 162.6 mg ($5.13 \times 10^{-4}$ mol) of (±)-**2**. The solution was allowed to set 30 hr in a dry box at room temperature. The final color was dark red-brown. The solvent was removed at reduced pressure at room temperature to yield a thick red oil. To this oil under a nitrogen atmosphere were added 0.32 ml ($3.08 \times 10^{-3}$ mol) of diethylamine and 30 ml of dry carbon tetrachloride. The mixture was cooled to 0–5° and 201 mg ($1.13 \times 10^{-3}$ mol) of *N*-bromosuccinimide was added and the resulting solution was stirred 3 hr at 0–5° and overnight at room temperature. Dichloromethane was added to dissolve all the organic material, and the solution was extracted with distilled water, dried, and chromatographed on 60 g of silica gel eluted with 5% ether–pentane. Twenty 75-ml fractions were collected. Fractions 10–18 contained a thick red oil which showed the presence of the desired products by tlc analysis (50% ether–pentane eluent, uv developer). These fractions were combined and analyzed by the analytical glpc method described above.

**Control Oxidation of Simulated Crossbreeding Mixture of 1, 2, 4, and 5.** A mixture of 96.5 mg ($4.18 \times 10^{-4}$ mol) of (±)-**1**, 36.5 mg ($1.37 \times 10^{-4}$ mol) of (±)-**5**, 80.5 mg ($2.86 \times 10^{-4}$ mol) of (±)-**4**, 71.6 mg ($2.26 \times 10^{-4}$ mol) of (±)-**2**, and 10 ml of dry dichloromethane was swirled until no solid remained. The solvent was immediately removed at reduced pressure to yield a thick paste. To this mixture under a nitrogen atmosphere were added 0.66 ml ($6.42 \times 10^{-3}$ mol) of diethylamine and 30 ml of dry carbon tetrachloride. The solution was cooled to 0–5° and 418 mg ($2.53 \times 10^{-3}$ mol) of *N*-bromosuccinimide was added; the resulting solution was stirred 3 hr at 0–5° and overnight at room temperature. Dichloromethane was added to dissolve all the organic material and the solution was extracted with distilled water, dried, and chromatographed on 60 g of silica gel eluted with 5% ether–pentane. Twenty-five 75-ml fractions were collected. Fractions 5–21 were shown to contain the desired products by tlc analysis (50% ether–pentane eluent, uv developer) and were combined and analyzed by the analytical glpc method described previously.

**Mass Spectra.** Spectra of authentic samples of sulfonimidamides **8, 9, 10,** and **11** were taken on a Model 21-491 mass spectrometer at 70 eV by direct insertion. The four authentic spectra were then compared with the spectra of the four compounds isolated by glpc from the conversion of the crossbred products of run 13 to the sulfonimidamides, **8–11**. The relative intensities of the major peaks of the authentic compounds are listed, and the relative intensities of the corresponding compounds ultimately obtained in run 13 are then listed parenthetically. For **8**, the base peak was at *m/e* 182, and its intensity was set equal to 100. The same was true for the compound from run 13. The peaks were as follows: 305, 1 (1); 304, 3 (3); 303, 10 (10); 302, 52 (45); 230, 19 (17); 183, 17 (17); 182, 100 (100); 167, 40 (37); 140, 9 (11); 139, 88 (105); 91, 29 (31). For **9**, the base peak was at *m/e* 268, and its intensity was set equal to 100. The same was true for the compound from run 13. The peaks were as follows: 391, 2 (2); 390, 5 (4); 389, 18 (17); 388, 57 (53); 269, 25 (23); 268, 100 (100); 267, 27 (34); 175, 10 (10); 142, 20 (21); 127, 8 (10). For **10**, the base peak was *m/e* 352, and its intensity was set equal to 100. The same was true for the compound from run 13. The peaks were as follows: 355, 3 (4); 354, 8 (9); 353, 25 (26); 352, 100 (100); 280, 8 (7); 233, 17 (19); 232, 91 (77); 217, 37 (42); 142, 49 (47); 141, 16 (14); 139, 11 (9); 91, 9 (9). For **11**, the base peak was *m/e* 218, and its intensity was set equal to 100. The same was true for the compound from run 13. The peaks were as follows: 341, 2 (1); 340, 5 (6); 339, 16 (17); 338, 59 (57); 266, 8 (11); 219, 24 (20); 218, 100 (100); 217, 24 (25); 176, 11 (7); 175, 70 (64); 127, 20 (33).

**Polymerization Experiments.** The styrene used was washed with 5% sodium hydroxide and distilled water, dried over magnesium sulfate, and distilled at reduced pressure, bp 34–35° (7–8 mm). The methyl methacrylate monomer was washed twice with 5% sodium hydroxide and twice with distilled water, dried first over sodium sulfate and then over calcium hydride, and finally distilled from calcium hydride, bp 45–46° (92–93 mm). Both monomers were stored at −20° until used.

The procedure for preparing the actual polymerization samples involved use of a high-vacuum distillation apparatus. The thick-walled glass sample tubes used were pretreated as in the standard racemization runs. The monomer was degassed twice (two freeze–thaw cycles) before being distilled directly into the sample tubes cooled in liquid nitrogen. After sealing, the tubes were warmed to room temperature and allowed to stand in a closed cabinet wrapped in aluminum foil for the duration of the polymerization experiment. In all cases the polymerization conditions were as similar as possible to the racemization conditions in neutral distilled deoxygenated benzene previously described. Isolation of polystyrene samples was according to a known procedure,[26] and polymethyl methacrylate samples according to a second.[27]

**Initiation of Styrene Polymerization with (−)-*N*-Methyl-*N*-phenyl-*p*-toluenesulfinamide ((−)-3). Run 15.** A control and **3**-initiated run were carried out and worked up identically. Into a sample tube containing 344 mg of (−)-**3** ($[\alpha]^{25}_{578}$ −107.6° (*c* 0.89, chloroform, 97.9% optically pure)) was distilled 15 ml of purified styrene. After warming to room temperature the tube was allowed to set for 836 hr. After this period the sample was dissolved in 200 ml of benzene, and 1600 ml of methanol was added. The precipitated 2.53 g (18.5%) of polymer was collected, mp 170–185°. The product was identical with known polystyrene by tlc (50% ether–pentane eluent, uv developer), ir, and nmr, and was racemic. The polymer was analyzed for sulfur and nitrogen: S, 0.12 ± 0.20%; N, 0.00 ± 0.20%. An average molecular weight of >10,000 was determined osmometrically by Galbraith Laboratories. The methanol–benzene filtrate was evaporated at reduced pressure at 25° to yield a yellow semisolid residue (293 mg) which was optically inactive. The residue was chromatographed on 25 g of silica gel eluted first with ether–pentane mixtures and finally with methanol. No telomeric material was obtained.

The control run made with 16 ml of styrene without added (−)-**3** but otherwise carried out the same way for the same length of time gave 213 mg (1.5%), mp 240–250°, of polystyrene.

**Run 16.** Into a sample tube containing 4.10 g of partially optically active (−)-**3** was distilled 15 ml of purified styrene. After warming to 25°, the tube was allowed to set for 289 hr. After this period, the sample was slightly yellow colored and completely immobile. The tube was ground in 250 ml of benzene with slight warming. After filtration, 1750 ml of methanol was added and the precipitated polymer was collected, washed three times very thoroughly with methanol, and dried at reduced pressure. Collected was 12.2 g (87% yield) of white material, mp 195–205° (softens at 140°), identical with known polystyrene by tlc (50% ether–pentane eluent, uv developer), ir, and nmr. The methanol–benzene filtrate was evaporated at reduced pressure at <40° and carefully chromatographed on 75 g of silica gel eluted first with ether–pentane mixtures and finally with methanol. No telomeric material was obtained. A parallel control with only styrene was run 361 hr, and gave 122 mg (0.8%) of polystyrene, mp 240–250°.

**Initiation of Methyl Methacrylate Polymerization with (−)-*N*-Methyl-*N*-phenyl-*p*-toluenesulfinamide ((−)-3). Run 17.** Into a sample tube containing 8.3 mg of optically pure (−)-**3**, $[\alpha]^{25}_{578}$ −109.9° (*c* 2.53, $CHCl_3$), was distilled 1.8 ml of purified methyl methacrylate. After warming to room temperature, the sample was allowed to set for 2928 hr. After 336 hr, the solution flowed

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(26) R. Boundy and R. Boyer, "Styrene, Its Polymers, Copolymers, and Derivatives," Reinhold, New York, N. Y., 1952, p 316.

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only with vigorous shaking; no color ever developed. The tube was opened and the contents were dissolved in 50 ml of acetone. The solution was filtered, 100 ml of 30–60° petroleum ether was added, and the precipitated polymer was collected, washed well with petroleum ether, and thoroughly dried under vacuum. Isolated was 70 mg (4.2%) of optically inactive white material identical with known polymethyl methacrylate by ir. The polymer was analyzed for sulfur and nitrogen: S, 0.00 ± 0.20%; N, 0.00 ± 0.20%. An average molecular weight of 4620 was determined osmometrically by Galbraith Laboratories. The acetone–petroleum ether soluble portion (<10 mg) was almost entirely (−)-**3** by tlc (50% ether–pentane eluent, uv developer), and ir, and had a specific rotation of $[\alpha]^{25}D$ −100° (*c* 0.65, chloroform), >90% optically pure.

A control run conducted in the absence of (−)-**3** was carried out in parallel. Into a sample tube was distilled 1.8 ml of purified methyl methacrylate. After warming to room temperature and setting 2928 hr, the tube was opened and the residual monomer was removed by low-temperature vacuum distillation. No material remained in the pot. The monomer collected was identical with known material by tlc (50% ether–pentane eluent, uv developer) and ir.

# Dimerization and Trimerization of Norbornadiene by Soluble Rhodium Catalysts

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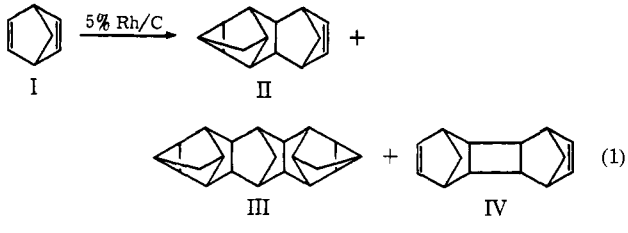
**Abstract:** Norbornadiene is dimerized and trimerized by catalytic amounts of $[(C_6H_5)_3P]_3RhCl$, giving eight structurally complex molecules, which have been isolated and characterized. Their structures are assigned as V–XII by X-ray crystallography, by proton nmr spectroscopy, and by analysis of their chemical reactions. The structure of a crystalline derivative of one dimer, VI, was determined previously; that of another, VII, is determined here. The stereochemistries of the four stereoisomers of structure II were assigned by comparing their proton nmr spectra and by chemically interconverting them. These interconversions were effected by the addition of hydriodic acid to XIII followed by its elimination giving V, as shown in Scheme I, and by the addition of bromine to XVI followed by dehydrohalogenation and reduction giving XVII, as shown in Scheme II. The structure of the saturated dimer was assigned as IX, rather than XXII, because it was possible to synthesize it by treating XIII with hydriodic acid. The structures of the products, V–XII, although complex, share a common architecture, suggesting that in rhodium-catalyzed reactions an intermediate intervenes that gives a variety of products.

Rhodium is a useful element in organic synthesis for it catalyzes a number of reactions, such as cycloadditions, that cannot be effected in other ways. None of these reactions is understood well although those that involve XY adding to olefins, or rearranging, where Y is H,[2] CHO,[3] or alkenyl[4] and X is hydrogen, have been known the longest and studied the most. Less is known about such reactions when X and Y are both carbon. The first of these, discovered in our laboratory in 1966, was a cycloaddition, the quantitative dimerization and trimerization of norbornadiene (I) to structures II, III, and IV effected by rhodium on carbon (eq 1).[5] Since its discovery few rhodium-catalyzed reactions (other than that giving IV) have been found in which the starting materials and products are related by 2 + 2 cycloadditions. Examples are now known of additions of olefins to olefins giving cyclobutanes[6,7] and of cyclopropanes to olefins giving cyclopentanes,[8] and when thermodynamics requires it, the reverse.[9] No rhodium-catalyzed reactions have been described, other than those giving II and III, in which the starting materials and products are formally related by a Diels–Alder reaction although a few have been discovered in our laboratory.[7] Other related reactions that have been found are some electrocyclic reactions[10] and the apparent subtraction of a carbene from a cyclopropane.[11]

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