676-85-7; *N,N*-dichlorobutylamine, 14925-83-8; *N*-butylmethanesulfonamide, 3989-40-0; *N*-butylmethanesulfonimidamide, 69726-82-5; butyl isocyanate, 111-36-4; dichloramine-T, 473-34-7; *N*-methylsulfonyl-*p*-toluenesulfonamide, 14653-91-9; *N*-*p*-tolylsulfonylmethanesulfonimidamide, 69726-83-6; *N,N*-dimethyl-*N'*-(*p*-tolylsulfonyl)methanesulfonimidamide, 69726-84-7; *p*-toluenesulfinamide, 6873-55-8; *N*-(*p*-tolylsulfonyl)chloromethanesulfinamide, 69726-78-9; *N*-(*p*-tolylsulfonyl)dichloromethanesulfinamide, 69726-79-0; *N*-(*p*-tolylsulfonyl)trichloromethanesulfinamide, 69726-85-8; *N,N'*-dimethylbenzenesulfonimidamide, 17247-02-8; *N*-methylbenzenesulfinamide, 69726-27-8; benzenesulfinyl chloride, 4972-29-6; benzenesulfinamide, 16066-31-2; benzenesulfonamide, 98-10-2; *N,N*-dimethylbenzenesulfonimidamide, 69726-86-9; *N*-phenylbenzenemethanesulfinamide, 40723-04-4; *N*-phenylbenzenemethanesulfonamide, 19127-51-6; *N,N*-dimethyl-*N'*-phenylbenzenemethanesulfonimidamide, 69726-31-4; *N*-phenylbenzenemethanesulfonimidamide, 69726-87-0; *N*-(*p*-chlorophenyl)benzenemethanesulfinamide, 69726-88-1; *N*-(*p*-chlorophenyl)phenylmethanesulfonamide, 69726-89-2; phenylmethanesulfonyl chloride, 1939-99-7; *p*-chloroaniline, 106-47-8; *N,N*-dimethyl-*N'*-(*p*-chlorophenyl)benzenemethanesulfonimidamide, 69726-90-5; *N*-(*p*-chlorophenyl)benzenemethanesulfonimidamide, 69726-91-6; *N*-(2,4,6-trichlorophenyl)benzenemethanesulfinamide, 69726-92-7; *N,N*-dimethyl-*N'*-(2,4,6-trichlorophenyl)benzenemethanesulfonimidamide, 69726-93-8; *N*-(2,4,6-trichlorophenyl)benzenemethanesulfonamide, 69726-94-9; α-chlorotoluene, 100-44-7; 2,4,6-trichloro-*N*-sulfinylbenzenamine, 2845-63-8; 4-acetamidobenzenesulfinyl chloride, 69726-95-0; 4-acetamidobenzenesulfinic acid, 710-24-7; *N*-methyl-4-acetamidobenzenesulfinamide, 69726-96-1; *N,N,N'*-trimethyl-4-acetamidobenzenesulfonimidamide, 69726-97-2; *N,N,N'*-trimethyl-4-aminobenzenesulfonimidamide, 69726-98-3; *N*-methyl-*N'*-2-pyrimidyl-4-acetamidobenzenesulfonimidamide, 69726-99-4; *N*-methyl-*N'*-2-pyrimidyl-4-aminobenzenesulfonimidamide, 69727-00-0; *N*-(2-pyrimidyl)-4-acetamidobenzenesulfinamide, 69727-01-1; 2-aminopyrimidine, 109-12-6; *N*-(2-pyrimidyl)-4-acetamidobenzenesulfonimidamide, 69727-02-2; *N*-butyl-*N'*-(*p*-toluenesulfinyl)urea, 13630-85-8; methanol-*O*-*d*, 1455-13-6; *N*-*p*-tolylsulfonylmethanesulfonamide, 14653-91-9; 1,1-diethoxyethene, 2678-54-8; *p*-toluenesulfonamide, 70-55-3; *N*-(*p*-tolylsulfonyl)chloromethanesulfonamide, 69727-03-3; 1-chloro-*N*-(*p*-tolylsulfonyl)ethanesulfonamide, 69727-04-4; *N*-(*p*-tolylsulfonyl)methyl-d_1-sulfonamide, 69727-05-5.

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Nucleophilic Substitution at Sulfur in Sulfonimidoyl Compounds: Synthesis of Sulfoximines

Carl R. Johnson,* Ernst U. Jonsson, and Anthony Wambsgans

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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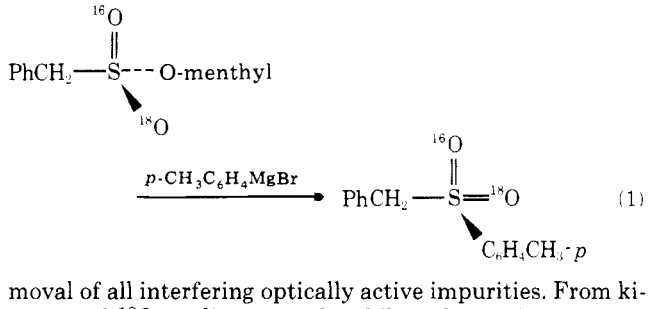
Nucleophilic substitution at tetracoordinate, hexavalent sulfur is shown to occur with inversion at sulfur. Oxidation of (*S*)-*N*-methylbenzenesulfinamide (**1**) with chlorine gave (*R*)-*N*-methylbenzenesulfonimidoyl chloride (**3**) (retention at sulfur). Reaction of **3** with sodium phenoxide gave (*S*)-phenyl *N*-methylbenzenesulfonimidate (**5**) (inversion). Methyllithium and **5** gave (*S*)-*N,S*-dimethyl-*S*-phenylsulfoximine (**4**) (inversion). Reduction of **4** with aluminum amalgam gave **1**. The reactions of alkyllithiums with phenyl benzenesulfonimidate provide sulfoximines that are difficult or impossible to prepare by standard methods.

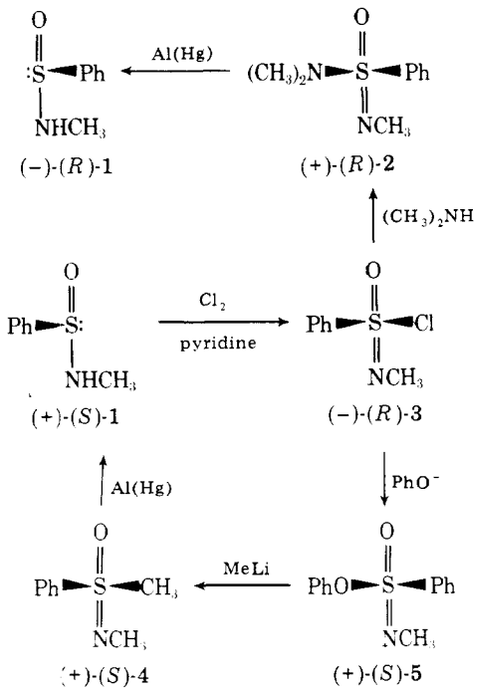
Nucleophilic substitution at sulfur, a common reaction of organosulfur compounds, has been extensively studied for dicoordinate and tricoordinate sulfur. In the latter case the stereochemical course has been studied in detail.[2,3] On the other hand, the stereochemical course of nucleophilic substitution at tetracoordinate sulfur has been little studied. One reason is obviously the lack of easily obtainable optically active tetracoordinate sulfur compounds for stereochemical studies of substitution. In the singular report by Sabol and Andersen,[4] ^{18}O-labeled sulfonate with chirality at sulfur due to isotopic label was subjected to treatment with a Grignard reagent to produce an optically active sulfone (eq 1). Their results implied an inversion mechanism, but because of extraordinarily low rotations, the interpretation relied on the complete removal of all interfering optically active impurities. From kinetic and ^{18}O studies on nucleophilic substitution at tetracoordinate sulfur in sulfonates and cyclic sulfate esters, a one-step synchronous mechanism is suggested and there is no



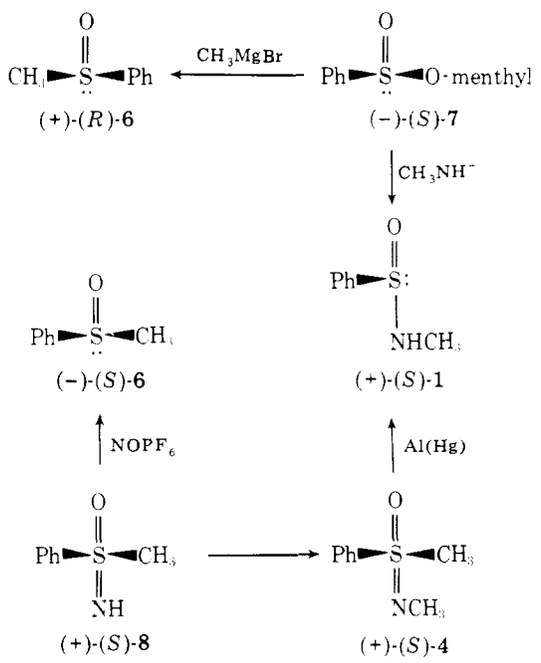
(1)

0022-3263/79/1944-2061$01.00/0

Scheme I



Scheme II



evidence to support a pentacovalent intermediate.[5] From the kinetic data for the hydrolysis of sulfonyl chlorides and sulfonates, Vizgert[6] proposed a S_N2-like mechanism for these reactions.

With a convenient method of preparing sulfonimidoyl chlorides in our hands,[7] and having the possibility of starting with an optically active precursor, it was a logical extension to prepare optically active sulfonimidoyl compounds and examine the stereochemical course of nucleophilic reactions at sulfur in sulfonimidoyl compounds.

Nucleophilic Displacement at Sulfur in Sulfonimidoyl Derivatives. In the present investigation definite evidence for an inversion mechanism at tetracoordinate hexavalent sulfur is given.[8] The reactions which complete new cycles of reactions at asymmetric sulfur are useful in establishing configurational relationships and in the preparation of optically active sulfur compounds. Scheme I summarizes the stereochemical courses of the new reactions which have been found to occur with stereospecificity. In Scheme II are formulated transformations establishing the absolute configurations of **1** and **4**, which allow the stereochemical courses of the reactions in Scheme I to be assigned.

Starting from (−)-menthyl (*S*)-benzenesulfinate (**7**) with known absolute configuration, the sulfoxide (*R*)-**6** has been shown earlier to have the *R* configuration and the reaction to proceed by inversion.[8] By a similar reaction Montanari et al.[9] and Nudelman and Cram[10] have shown that displacement on sulfinates by the lithium salts of amines occurs with inversion of configuration at sulfur but, if the amide ion is a strong base, i.e. generated from an alkylamine, racemization takes place, probably by a displacement by amide ion.[10] By adding the lithium salt of methylamine at 0 °C to an excess of (*S*)-**7**, sulfinamide (±)-**1** with 24% optical purity was obtained; therefore (+)-**1** must have the *S* configuration. Optically pure sulfinamide (+)-(*S*)-**1** was obtained by a novel reaction by Schroeck and Johnson[11] from optically pure sulfoximide (*S*)-**4** by reduction with aluminum amalgam in aqueous tetrahydrofuran in good yield. This reduction and a similar reduction[11] proceed with retention of configuration. The absolute configuration of (+)-**4** was deduced from the reactions (+)-**8** → (+)-**4** and (+)-**8** → (−)-**6**. When nitrosonium hexafluorophosphate was added to (+)-**8**, (−)-(*S*)-methyl phenyl sulfoxide (**6**) was obtained; this novel reaction from Cram's laboratory[2] has been shown to proceed with retention and 99% stereospecificity. Our small loss of optical purity is probably due to impurities in the isolated sulfoxide, because even after chromatography on silica gel and distillation three times, the sulfoxide turned yellow on standing. This reaction establishes the *S* configuration of (+)-**8**; in the methylation of (+)-(*S*)-**8** to (+)-**4** no substitution at sulfur is involved and therefore, the configuration is preserved and is *S*.

Hydrogen chloride is formed during the oxidation and because sulfoxides are known to be racemized by catalytic amounts of hydrogen chloride,[12] racemization is also very likely for sulfinamides. When hydrogen chloride was added to optically active *N*-methylbenzenesulfinamide (**1**), a fast racemization took place in ether. Pyridine was therefore added as a hydrogen chloride scavenger during the oxidation step. The optically active *N*-methylbenzenesulfonimidoyl chloride (**3**) was obtained by oxidation in ether at −78 °C, but **3** was not isolated because racemization took place very fast at higher temperatures. This caused problems in the reaction of the chloride **3** with sodium phenoxide to produce the ester **5** because the reaction required a temperature of about 0 °C. After many unsuccessful experiments with different solvents and temperatures the optically active ester (+)-**5** was obtained by adding the cold ether solution of (−)-**3** to an excess of sodium phenoxide dissolved in dimethylformamide kept at 0 °C. After workup and chromatography a product with 69% optical purity was obtained. The loss of optical purity during the two-step reaction sequence is probably caused by racemization of the acid chloride prior to reaction with phenoxide. By recrystallization of (+)-**5** to constant specific rotation and melting point a sample with at least 97% optical purity was obtained.

The ester (+)-**5** of essentially maximum rotation, when subjected to treatment with an excess of methyllithium in ether at 0 °C, gave, after chromatography on silica gel and sublimation, a 66% yield of sulfoximide (+)-**4** with 96% optical purity. This reaction exemplifies a new route to N-substituted sulfoximides which will be discussed later. Transformation **4** → **1** closes this cycle of reactions.

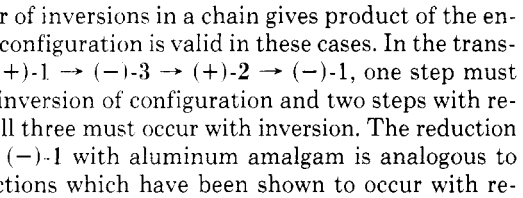
A third cycle of transformations was completed by the sequence (+)-**1** → (−)-**3** → (+)-**2** → (−)-**1**. The acid chloride **3** was generated at −78 °C in ether and the solution was added

without filtering to an excess of dimethylamine in ether cooled to −78 °C. After workup a 56% yield (not maximized) of (+)-2 was obtained which was recrystallized from ethanol–water to maximum rotation. The third reaction in the cycle was accomplished with the aluminum amalgam reduction of (+)-2 (94% optically pure) to yield 37% of (−)-1 with 91% optical purity.

In discussing the stereochemical courses of the reactions in Schemes I and II we note that, using the nomenclature system introduced by Garwood and Cram,[13] the cycle in Scheme II is a diligostatic antipodal five-reaction stereochemical cycle involving two inversions and one ligand metathesis. Due to the ligand metathesis, which is the formal equivalent of an inversion, 1 and 4 have the same absolute configuration and are *S*. From this and the stereochemical course of the aluminum amalgam reduction, the stereochemical courses of the remaining reactions in Scheme I can be assigned. These make up three cycles: (+)-1 → (−)-3 → (+)-5 → (+)-4 → (+)-1, (+)-1 → (−)-3 → (+)-2 → (−)-1, and (+)-1 ← (+)-4 ← (+)-5 ← (−)-3 → (+)-2 → (−)-1. The cycle 1 → 3 → 2 → 1 is a three-reaction cycle which includes simultaneous double ligand substitution and has to be treated according to Cram's system as involving two reaction cycles, one triligostatic podal two-reaction stereochemical cycle, and one triligostatic antipodal three-reaction stereochemical cycle involving one inversion. A similar analysis is applicable to the remaining two cycles and therefore the classical rule that an odd number of inversions in a chain gives product of the enantiomeric configuration is valid in these cases. In the transformation (+)-1 → (−)-3 → (+)-2 → (−)-1, one step must occur with inversion of configuration and two steps with retention or all three must occur with inversion. The reduction of (+)-2 to (−)-1 with aluminum amalgam is analogous to other reductions which have been shown to occur with retention at sulfur and, therefore, it can be concluded that compound (+)-2 has the *R* configuration. This conclusion is compatible with the stereochemical course of reaction (+)-1 → (−)-3, which is expected to proceed with retention since this reaction can be considered as an electrophilic substitution occurring on sulfur without perturbation of the tetrahedral structure. Thus, the nucleophilic displacement reaction at tetracoordinate hexavalent sulfur, (−)-3 → (+)-2, must proceed with inversion of configuration. In the cycle 1 → 3 → 5 → 4 → 1, transformations (+)-1 → (−)-3 and (+)-4 → (+)-1 occur with retention (above) and therefore (−)-3 → (+)-5 and (+)-5 → (+)-4 both must proceed by the same stereochemical course. The conversion of (−)-3 to (+)-5 very likely proceeds with the same stereochemical course as for the similar conversion (−)-3 → (−)-2, and thus, both occur with inversion and exhibit the configurational notations as given in Scheme I.

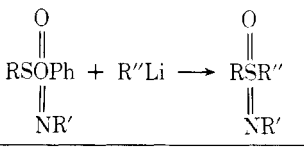
An exhaustive description of the possible stereochemical mechanisms for substitution at tetrahedral sulfur by way of trigonal bipyramids or square pyramids are given by Cram et al.[2]

Preparation of Sulfoximines from Sulfonimidates. In connection with the above stereochemical cycles, in searching for a route to sulfoximines from sulfonimidoyl chlorides, *N*-methylbenzenesulfonimidoyl chloride was treated with methylmagnesium iodide. Only the reduction product, *N*-methylbenzenesulfinamide, was obtained (eq 2). The reduction is not unusual, as some benzenesulfonyl chlorides are reduced partly to sulfinic acids by organomagnesium and -lithium compounds; however, some sulfones are produced.[14]



(2)

Table I. Reaction of Alkyllithiums with Phenyl Sulfonimidates



R	R′	R″	% yield of sulfoximine
Ph	Me	Me	73
Ph	Me	*n*-Bu	74
Ph	Me	$PhCH_2$	30
Ph	Me	CH_2=$CHCH_2$	71
Ph	Me	c-C_5H_{11}	46
Ph	Ph	Me	45
Ph	Ph	*n*-Bu	67

Methylmagnesium iodide and dimethylmagnesium failed to react with phenyl *N*-methylbenzenesulfonimidate. In each case there was nearly total recovery of the starting ester. An attempt to activate methylmagnesium iodide with *N,N,N′,N′*-tetramethylethylenediamine in its reaction with the sulfonimidate ester did not give sulfoximine.

It was found that alkyllithiums react with phenyl *N*-methylbenzenesulfonimidate to give acceptable yields of sulfoximines (Table I). This method provides a route to sulfoximines which are difficult or impossible to prepare by the usual routes. For example, *N*-aryl sulfoximines are difficult to prepare except in the *S,S*-dimethyl series.[15] *S*-Benzyl- and *S*-allylsulfoximines are readily subject to rearrangement and/or C–S bond heterolysis under the usual conditions of synthesis.

Experimental Section

(+)-(*S*)-*N*-Methylbenzenesulfinamide (1) from Menthyl (−)-(*S*)-Benzenesulfinate. To menthyl benzenesulfinate (2.50 g, 9 mmol), $[\alpha]^{25}_D$ −202.8° (*c* 1.77 acetone) [lit.[16] $[\alpha]^{25}_D$ −205.5° (acetone)], dissolved in 25 mL of dry ether and cooled in an ice bath, was added with stirring a slurry of the lithium salt of methylamine (prepared by adding an excess of gaseous methylamine to 10 mL of butyllithium (1.7 M) diluted with 40 mL of dry benzene). The reaction mixture was stirred for 30 min at 0 °C and then quenched by the addition of a saturated ammonium chloride solution. The organic layer was removed and the water phase was extracted once with pentane. These extracts containing unreacted ester and menthol were discarded. The water layer was extracted three times with dichloromethane, and the organic layer was washed with water, dried, and filtered. The solvent was evaporated, yielding 0.27 g of sulfinamide 1:$[\alpha]^{25}_D$ +41.8° (*c* 1.74, acetone) (24% optically pure). The product was pure by TLC and the IR spectrum of this material was identical with that of an authentic racemic sample. No attempt was made to improve the stereospecificity or the yield.

(−)-(*S*)-Methyl Phenyl Sulfoxide (6) from (+)-(*S*)-*S*-Methyl-*S*-phenylsulfoximine (8). A similar procedure as given by Cram et al.[2] was followed. To 1.14 g (7.3 mmol) of sulfoximide 8, $[\alpha]^{25}_D$ +34.7° (*c* 1.15, acetone, 95% optically pure), in nitromethane at 0 °C was added 1.40 g (8.0 mmol) of nitrosonium hexafluorophosphate. After workup the residual oil was chromatographed on silica gel (ether) to yield 0.41 g of an oil which was distilled three times under reduced pressure to give 0.18 g of a colorless oil (became pale yellow on standing): $[\alpha]^{25}_D$ −130.0° (*c* 1.06, absolute ethanol, 87% optically pure). The IR was identical with that of an authentic sample.

(+)-(*R*)-*N,N,N′*-Trimethylbenzenesulfonimidamide (2). A solution of 0.310 g (2 mmol) of *N*-methylbenzenesulfinamide, $[\alpha]^{25}_D$ +174° (*c* 1.0, acetone), mp 48–53 °C, and 0.16 mL of pyridine in 20 mL of dry ether was cooled in dry ice. Dry chlorine was added slowly to excess (yellow color). The reaction mixture was poured (without filtering) into an ether solution of dimethylamine cooled to −78 °C. After 2 h at room temperature the solution was filtered and evaporated to a small volume. A white solid (0.12 g) crystallized and from the filtrate was obtained 0.10 g more, mp 75–76 °C. The two crops were combined and recrystallized from ethanol–water: mp 75–76 °C;

$[\alpha]^{25}_D$ +50.9° (c 1.22, chloroform); IR ($CHCl_3$) 1270 and 1190 cm^{-1} (N=S=O); NMR ($CDCl_3$) δ 7.93 (m, 2), 7.57 (m, 3), 2.88 (s, 3), 2.70 (s, 6).

Anal. Calcd for $C_9H_{14}N_2OS$: C, 54.52; H, 7.12; S, 16.17. Found: C, 54.37; H, 7.05; S, 16.19.

(−)-(*R*)-*N*-Methylbenzenesulfinamide (1) from (+)-(*R*)-*N,N,N'*-Trimethylbenzenesulfonimidamide. To 0.198 g (1 mmol) (+)-(*R*)-*N,N,N'*-trimethylbenzenesulfonimidamide, $[\alpha]^{25}_D$ +47.8° (c 1.47, chloroform, 94% optical purity), dissolved in 10 mL of 10% aqueous tetrahydrofuran was added 0.27 g (10 mmol) of aluminum amalgam. The reaction mixture was kept at 25 °C by means of a water bath and the reaction was monitored by TLC (silica gel–ether). After about 10 h most of the starting material had disappeared, and the mixture was filtered (Celite) and evaporated almost to dryness. Water was added and the aqueous layer was extracted with dichloromethane. After drying and evaporating the solvent, the residual yellow oil was chromatographed on silica gel–ether to give a white solid (57 mg), mp 36–40 °C, $[\alpha]^{25}_D$ −157.5° (c 1.34, acetone, 91% optically pure). The IR spectrum was identical with that of an authentic sample of racemic 1.

(+)-(*S*)-*N*-Methylbenzenesulfinamide (1). To a cold solution of 0.845 g (0.0050 mol) of sulfoximine **4**, $[\alpha]_D$ + 183° (c 1.2, acetone), in 40 mL of 90% tetrahydrofuran–10% water mixture (by volume) was added 1.35 g (0.050 g-atom) of freshly amalgamated aluminum foil. The mixture was allowed to warm up in a cold water bath to 10–15 °C. The reaction was followed by TLC (silica gel–ether); the sulfinamide moves up the plate faster than the sulfoximine. After 3 h at 10–15 °C much of the metal remained, but the reaction appeared to be over. This was confirmed by the infrared spectrum of a filtered and dried sample. The mixture was filtered through Celite, washing well with tetrahydrofuran. The colorless solution was evaporated to an oil; it smelled strongly of benzenethiol. Water was added, and the mixture was extracted with several portions of methylene chloride. TLC analysis showed only two components; no starting material. The methylene chloride solution was dried ($MgSO_4$), concentrated in vacuo, and chromatographed on a 1.5 ft × 0.5 in. column of silica gel with ether. The benzenethiol eluted very quickly (0.071 g, 13%) and was identified by comparative spectra. The sulfinamide (**1**) was obtained with clean separation as a white crystalline solid (0.572 g, 74%) upon evaporation of the solvent in vacuo: mp 49–52 °C; $[\alpha]_D$ + 173° (c 1.03, acetone); IR (melt) 695, 752, 1045, 1080, 3230 cm^{-1}; NMR (CCl_4) δ 7.9–7.3 (m, 5, Ph), 5.45 (br q, 1, *J* = 4 Hz, NH), 2.44 (d, 3, *J* = 4 Hz, NCH_3). Its spectral properties were identical with those of an authentic racemic sample prepared by the reaction of methylamine with benzenesulfinyl chloride.

(+)-(*S*)-Phenyl *N*-Methylbenzenesulfonimidate (5). (+)-(*S*)-*N*-Methylbenzenesulfinamide, $[\alpha]^{25}_D$ +170.1 (c 1.8, acetone) (0.31 g, 2 mmol), and 0.20 mL of pyridine were dissolved in 30 mL of dry ether in a 50-mL flask. The flask was cooled in dry ice and chlorine from a tank was added to a slight excess (yellow color). The cold ether solution was added with stirring in one portion to 1.2 g (10 mmol) of sodium phenoxide dissolved in 40 mL of dimethylformamide cooled in an ice bath. After stirring for 30 min at 0 °C, the reaction mixture was poured into 2 M sodium hydroxide. The aqueous layer was extracted with ether four times and the combined ether extracts were washed twice with water, dried over magnesium sulfate, and treated with decolorizing carbon. After filtering and evaporating the solvent, 0.35 g of a light yellow solid was obtained, mp 96–99 °C. This material was recrystallized twice by dissolving in hot methanol and adding an equivalent volume of pentane to give 0.20 g of **5**, mp 106–107 °C, $[\alpha]^{25}_D$ +81.1° (c 1.71, acetone). The IR spectrum of this material was identical with that of an authentic racemic sample, mp 87–89 °C. In one experiment the crude product was chromatographed on silica gel with elution by hexane–ether (4:1 v/v) to give a white solid, mp 96–99 °C, $[\alpha]^{25}_D$ +62.8° (c 1.82, acetone). After recrystallization (four times) to constant melting point and specific rotation, the following values were obtained: mp 106–107 °C; $[\alpha]^{25}_D$ +81.7° (c 1.51, acetone).

(+)-(*S*)-*N,S*-Dimethyl-*S*-phenylsulfoximine (4) from (+)-(*S*)-Phenyl *N*-Methylbenzenesulfonimidate (5). To 0.20 g of (+)-(*S*)-**5**, $[\alpha]^{25}_D$ +81.1° (c 1.71 acetone, 99% optical purity), mp 106–107 °C, dissolved in 10 mL of dry ether and cooled in an ice bath was added 2 mL of methyllithium (excess). The ice bath was removed and the reaction mixture was stirred for 30 min. 2-Propanol and then water was added to destroy excess methyllithium. The ether layer was separated and the aqueous solution was extracted three times with dichloromethane. The organic layers were combined and washed with water, dried, and evaporated. The yellow oil, 0.122 g, was purified by chromatography on a short column of silica gel and eluted with ether to give 97 mg of **4** (IR identical with that of an authentic sample). It was sublimed [70 °C (0.05 mm)] on to a cold finger to give a colorless oil, 90 mg (66%), $[\alpha]^{25}_D$ +174.8° (c 1.15, acetone, 96% optical purity).

***N,S*-Dimethyl-*S*-phenylsulfoximine.** To 0.247 g of phenyl *N*-methylbenzenesulfonimidate (racemic **5**) in 10 mL of ether at room temperature was added 2.5 mL of methyllithium (1.7 M, 4 equiv). A vigorous reaction took place and the solution turned red. After stirring for 10 min 2-propanol was added and the reaction mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried over $MgSO_4$, and evaporated. The remaining oil was chromatographed on a short column of silica gel with ether to give 0.123 g (73%) of sulfoximide (spectral properties identical with an authentic sample).

***S*-Butyl-*N*-methyl-*S*-phenylsulfoximine.** A procedure similar to that above was used. From 0.496 g of ester there was obtained after chromatography 0.310 g (74%) of the sulfoximine as an oil: IR (neat 1240 and 1145 cm^{-1} (N=S=O); NMR ($CDCl_3$) δ 7.97–7.50 (m, 5), 3.37–3.17 (m, 2), 2.67 (s, 3), 2.00–0.87 (m, 7).

Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.49; H, 8.15. Found: C, 62.40; H, 7.90.

***S*-Benzyl-*N*-methyl-*S*-phenylsulfoximine.** To 0.496 g (2 mmol) of racemic **5** dissolved in benzene and cooled in an ice bath was added 15 mL of benzyllithium (6 mmol) in benzene with stirring. After 15 min water was added, and the aqueous layer was extracted with dichloromethane; the organic layer was washed with water, dried, and evaporated. The remaining yellow oil, which showed six spots by TLC, was dissolved in 25 mL of ether and the ether layer was extracted with 4 M sulfuric acid. The water layer was extracted once more with ether and the ether extracts were discarded. The water layer was made basic with dilute sodium hydroxide, then extracted three times with dichloromethane. The dichloromethane extracts were washed with water, dried, and evaporated to yield 0.148 g (30%) of a white solid which was recrystallized from carbon tetrachloride to give product: mp 101–102 °C; IR (Nujol) 1240, 1145, 1100, and 1080 cm^{-1}; NMR ($CDCl_3$) δ 2.77 (s, 3), 4.40 (s, 2), 7.67–7.00 (m, 10).

Anal. Calcd for $C_{14}H_{15}NOS$: C, 68.56; H, 6.13. Found: C, 68.32; H, 6.20.

***S*-Allyl-*N*-methyl-*S*-phenylsulfoximine.** Phenyllithium (7 mL of 1.8 M) was added to tetraallyltin (1.053 g) in ether (15 mL) to prepare allyllithium. The reaction was stirred under N_2 for 2 h. After cooling the allyllithium to 0 °C, phenyl *N*-methylbenzenesulfonimidate (0.507 g in 15 mL of ether) was added to it. The reaction was stirred for 2 h at 0 °C and then stored in the refrigerator at 3 °C for 24 h. Water was added to the reaction, and it was extracted several times with an ether–benzene mixture. The solvent was evaporated, and the material was chromatographed on silica gel. The product (0.284 g, 71% yield) was eluted with 30% ether in benzene. The product, an oil, had NMR and IR spectral properties identical with that of the compound prepared by another route in this laboratory: IR (neat) 1650 (w), 1580 (v w), 1445, 1240 (s), 1145 (s), 1105, 1080, 995 (w), 935, 885, 855, 785 (w), 750, 690 cm^{-1}; NMR (CCl_4) δ 2.6 (s, 3 H), 3.7 (d, 2 H), 4.8–5.3 (m, 2 H), 5.5–6.2 (m, 1 H), 7.3–8.0 (m, 5 H).

***S*-Cyclopentyl-*N*-methyl-*S*-phenylsulfoximine.** Cyclopentyllithium was prepared from chlorocyclopentane, lithium, and copper powder in a 54% yield in pentane. It was titrated by the method employing benzoic acid. Phenyl *N*-methylbenzenesulfonimidate [mp 84–87 °C (lit.[7] 88–89 °C), 0.738 g, 3.0 mmol) was covered with pentane and then cooled to 0 °C under nitrogen. Cyclopentyllithium (12.7 mmol in 30 mL of pentane) was added to the ester. The reaction was stirred at 0 °C for 1 h and then at room temperature for 15 h. After the addition of water, the pentane was evaporated. The material was extracted with benzene and was washed with a sodium hydroxide solution. After evaporation of the solvent, the product was chromatographed on silica gel with an ether–benzene mixture. The product was obtained as a colorless oil (0.309 g, yield 46%). A small amount was molecularly distilled through a short-path apparatus [100 °C (0.05 mm)]: IR (neat) 1455, 1230 (v s), 1150, 1105, 1085, 863, 760, 720, 693 cm^{-1}; NMR (CCl_4) δ 1.2–2.3 (m, 8 H), 2.5 (s, 3 H), 3.0–3.8 (br, 1 H) 7.3–8.1 (m, 5 H).

Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67; N, 6.27. Found: C, 64.61; H, 7.42; N, 6.38.

***S*-Methyl-*N,S*-diphenylsulfoximine.** Phenyl *N*-phenylbenzenesulfonimidate (0.430 g) was reacted in ether with methyllithium (about 16 mL of 1.1 M) for 4 h at 0 °C. Water was added to the reaction mixture. The material was extracted with an ether–benzene mixture and was washed with a sodium hydroxide solution. The product was eluted from a silica gel column with 25% ether in benzene. The product was obtained as an oil (145 mg, 45% yield). It was molecularly distilled (oil bath about 80 °C, pressure about 0.05 mm) to remove traces of solvent for analysis. The product, a viscous oil, crystallized on slight warming (mp 95–96.5 °C): IR (neat) 1600, 1495,

1290, 1260, 1200. 1095, 1040, 1020, 790, 740, 688 cm^{-1}; NMR (CCl_4) δ 3.1 (s, 3 H), 6.8–7.3 and 7.3–7.7 (two m, 8 H), 7.8–8.2 (m, 2 H).

Anal. Calcd for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; N, 6.05. Found: C, 67.57; H, 5.64; N, 6.10.

S-Butyl-N,S-diphenylsulfoximine. Phenyl N-phenylbenzenesulfonimidate (1.290 g, 4.17 mmol) in approximately 100 mL of anhydrous ether was cooled to 0 °C and butyllithium (15 mL of 1.29 M, 19.42 mmol) was added. The reaction was stirred under nitrogen at 0 °C for 90 min. Water was added slowly to the reaction and it was extracted with benzene. After the solvent was removed, the material was chromatographed on a silica gel column with an ice cold 25% ether–75% carbon tetrachloride mixture employing the "dry column technique" (nylon tubing was used for the column). The product was extracted from the silica gel section by washing it with solvent. The product, obtained as an oil (0.760 g, 67% yield), was shown to be pure by NMR. It was dissolved in a carbon tetrachloride–pentane mixture and cooled. The product crystallized from the solution. Seed crystals were removed. The mother liquor was evaporated and 666 mg of the product was recrystallized from methanol to give 338 mg (mp 47–48 °C). It was then recrystallized from carbon tetrachloride–pentane to yield a sample for analysis (mp 47.5–48.5 °C): IR (KBr) 1600, 1490, 1285, 1260, 1200, 1090, 1035, 1015, 793, 750, 690 cm^{-1}; NMR (CCl_4) δ 0.7–1.1 (nearly a triplet, 3 H), 1.1–2.1 (m, 4 H), 2.9–3.4 (m, 2 H), 6.6–7.3 and 7.3–7.7 (two m, 8 H), 7.7–8.2 (m, 2 H).

Anal. Calcd for $C_{16}H_{19}NOS$: C, 70.29; H, 7.01; N, 5.12. Found: C, 69.90; H, 6.85; N, 5.08. Found: C, 70.17; H, 7.26.

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Registry No.—(+)-(S)-**1**, 33957-73-2; (−)-(R)-**1**, 33993-55-4; (+)-(R)-**2**, 33993-54-3; (+)-(S)-**4**, 33993-53-2; (±)-**4**, 69831-03-4; (+)-(S)-**5**, 33993-56-5; (±)-**5**, 33903-52-5; (−)-(S)-**6**, 18453-46-8; (−)-(S)-**7**, 34513-32-1; (+)-(S)-**8**, 33903-50-3; S-benzyl-N-methyl-S-phenylsulfoximine, 69766-04-7; S-allyl-N-methyl-S-phenylsulfoximine, 69766-05-8; S-cyclopentyl-N-methyl-S-phenylsulfoximine, 69766-06-9; S-methyl-N,S-diphenylsulfoximine, 69766-07-0; S-butyl-N,S-diphenylsulfoximine, 69766-08-1; S-butyl-N-methyl-S-phenylsulfoximine, 69766-09-2; phenyl N-phenylbenzenesulfonimidate, 69766-10-5.

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Preparation and Reactions of N-(p-Tolylsulfonyl)sulfilimines

Carl R. Johnson,* Kaoru Mori, and Akira Nakanishi

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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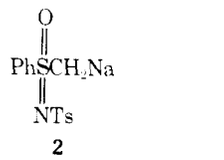
N-(p-Tolylsulfonyl)sulfilimines are prepared in high yield by a phase-transfer-catalyzed process from solid Chloramine-T trihydrate to a solution of a sulfide in dichloromethane. α-Lithio derivatives of N-(p-tolylsulfonyl)-sulfilimines are shown to be useful nucleophilic alkylidene transfer reagents for the conversion of aldehydes and ketones to oxiranes. In the case of benzalacetophenone, 1,2 addition occurred to yield the oxirane. The facile [2,3] sigmatropic rearrangement of allylic sulfilimines to sulfinamides is noted.

N-(Tolylsulfonyl)sulfilimines[1] have been prepared most commonly by the reaction of Chloramine-T (the sodium salt of N-chloro-p-toluenesulfonamide) with sulfides in aqueous media, often with methanol or acetone as a cosolvent. The use of aqueous systems sometimes leads to significant formation of byproduct sulfoxides. In some cases, the reactions give poor results due to insolubility of the sulfide in the aqueous medium. We have found phase-transfer catalysts are effective in these reactions. The sulfide and approximately 0.05 mol % of phase-transfer catalyst were dissolved in dichloromethane and Chloramine-T trihydrate was added as a *solid phase*.[2] The reactions were generally complete in 1 to 2 h at ambient temperature (Table I).

Our earlier demonstration of the utility of carbanions derived from N-tosylsulfoximines (e.g., **2**) as nucleophilic alkylidene transfer reagents prompted our examination of the related sulfilimine-stabilized carbanions (e.g., **3**). We found that the lithiated sulfilimines prepared by addition of butyllithium to a dimethyl sulfoxide solution of the sulfilimine were highly satisfactory reagents for the conversion of aldehydes and ketones to oxiranes (eq 1). Subsequent to our first mention of these reagents,[4] the corresponding sodium anions derived from N-tosylsulfilimines have been explored as reagents for carbonyl to oxirane conversions by Tamura and co-workers.[5] Early in our work we found that the rapidly generated lithium reagents consistently gave higher yields than the



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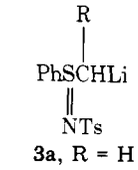

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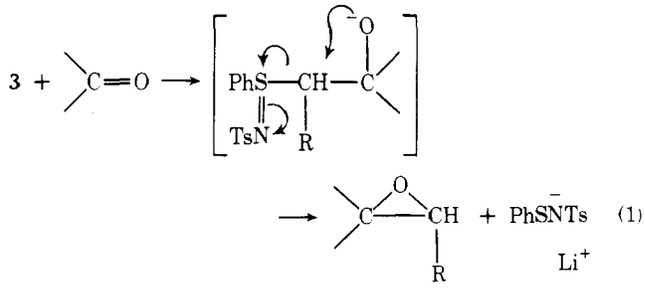
b, R = Ph



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