Notes

Sulfonimidoyl Chlorides by Oxidation of Sulfinamides with *tert*-Butyl Hypochlorite

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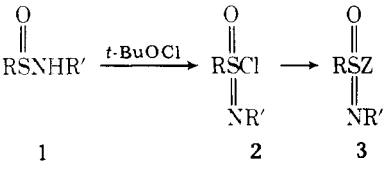
We have shown that sulfinamides (**1**) can be oxidized to sulfonimidoyl chlorides (**2**) by chlorine or *N*-chlorobenzotriazole.[1] In this paper the oxidization of sulfinamides (**1**) by *tert*-butyl hypochlorite to sulfonimidoyl chlorides (**2**) and their subsequent conversion to sulfonimidamide or sulfonimidate derivatives are discussed (eq 1 and Table I). The



(1)

1 **2** **3**

a, R = C_6H_5; R′ = CH_3
b, R = $C_6H_5CH_2$; R′ = C_6H_5
c, R = C_6H_5; R′ = C_6H_5
d, R = C_6H_5; R′ = $C_6H_5CH_2$

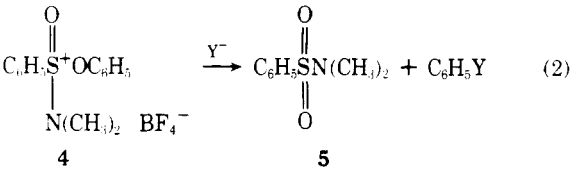
tert-butyl hypochlorite method appears to have several advantages. The experimental procedure is very simple. The sulfinamide and hypochlorite are separately dissolved or suspended in carbon tetrachloride, cooled to 0 °C, and then mixed. The reaction is kept at 0 °C in the dark for 0.5–1 h. The solvent, excess reagent, and *tert*-butyl alcohol are readily removed by vacuum evaporation at room temperature or below. The sulfonimidoyl chlorides were usually produced in nearly quantitative yield as shown by NMR.

In the chlorine oxidation, hydrogen chloride is the byproduct; certain sulfonimidoyl chlorides decompose in the presence of hydrogen chloride to give amine hydrochlorides and sulfinyl chlorides.[2] Since *tert*-butyl alcohol is the byproduct in the hypochlorite oxidation, the reaction remains neutral. With excess chlorine, compound **1b** gave *N*-(*p*-chlorophenyl)-α-toluenesulfonimidoyl chloride on warming to room temperature, with an occasional violent reaction.[1] However, NMR analysis showed that **2b** was produced without ring or benzylic chlorination from **1b** by oxidation with excess *tert*-butyl hypochlorite. The advantage that *tert*-butyl hypochlorite has over *N*-chlorobenzotriazole is that the *tert*-butyl alcohol is more easily removed than benzotriazole. (If base is added to the reaction mixture, the benzotriazole will react with the sulfonimidoyl chloride.)[3]

In addition to the standard reactions resulting in the formation of amides or esters (Table I) several other reactions of the sulfonimidoyl chlorides and derivatives were examined. The ester **3a** (Z = OC_6H_5) was alkylated at nitrogen with trimethyloxonium fluoroborate to give **4**; such sulfonium salts have not been previously described. We anticipated that **4** might act as an arylating reagent as the leaving group would be the highly stable *N*,*N*-dimethylbenzenesulfonamide (**5**) (eq 2). These expectations were not realized. In heterogeneous reactions of **4** with benzene, sodium iodide, and sodium phenoxide no products of arylation (biphenyl, iodobenzene, and diphenyl ether) were observed. The compound also failed to yield any *N*-benzylaniline on treatment with benzylamine.

Table I. Transformation of Sulfinamides 1 to Sulfonimidoyl Derivatives 3

sulfinamide 1	Derivative 3 Z	mp, °C	% yield from 1
a	$NHCH_3$	94.5–96	60
a	OCH_3	oil	70
a	$OCH(CH_3)_2$	oil	81
b	$N(CH_3)_2$	77–80	84
b	OC_6H_5	117–118	57
c	OC_6H_5	56.5–58	66
c	OC_6H_4-*p*-CH_3	oil	57
d	OC_6H_5	50.5–52	62



(2)

4 **5**

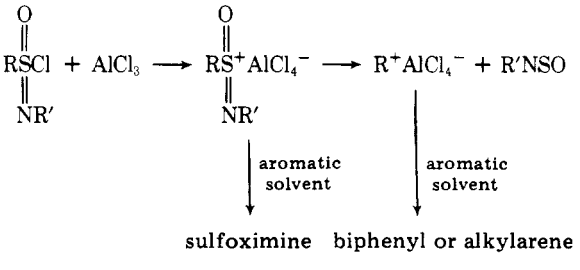
Reaction with water produced *N*,*N*-dimethylbenzenesulfonamide.

Sulfonyl chlorides are known to give sulfones under Friedel–Crafts conditions. Sulfonimidoyl chlorides were reacted with aromatic substrates under Friedel–Crafts conditions with the idea of obtaining sulfoximines. When *N*-methylbenzenesulfonimidoyl chloride (**2a**) was reacted with anisole in the presence of aluminum chloride, a 36% yield of *S*-(4-methoxyphenyl)-*N*-methyl-*S*-phenylsulfoximine was obtained along with a neutral material believed to be a mixture of *o*- and *p*-phenylanisole. When boron triflouride was used as a catalyst, a similar result was obtained, but the yield of sulfoximine decreased. The reaction *N*-phenyl-α-toluenesulfonimidoyl chloride (**2b**) with anisole and aluminum chloride gave an 89% yield of a mixture of (2- and 4-methoxyphenyl)phenylmethane. These reactions can be explained by the loss of a thionyl amine to give a carbonium ion which then reacts with the aromatic substrate (Scheme I).

The loss of thionyl amine is not surprising; methanesulfonyl chloride with aluminum chloride produces methyl chloride and phenylmethanesulfonyl chloride, upon heating, yields benzyl chloride and sulfur dioxide.[4]

Although the reactions were not explored in detail it appears that *N*-methylbenzenesulfonimidoyl chloride (**2a**) also loses *N*-methylthionylamine in the presence of cupric ion or under the influence of light. When **2a** was irradiated at 3000 Å or treated with cupric ion in the presence of phenylacetylene the desired addition products were not obtained.[1] Each of these attempted addition reactions has successful analogues with sulfonyl chlorides. The successful addition of *N*-(phenylsulfonyl)benzenesulfonimidoyl chloride to styrene and

Scheme I



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phenylacetylene in the presence of cuprous chloride has been reported.[5]

Experimental Section

***N,N'*-Dimethylbenzenesulfonimidamide (3a, Z = $NHCH_3$).** *N*-Methylbenzenesulfinamide[1] (120 mg) was dissolved in several milliliters of carbon tetrachloride. An excess of *tert*-butyl hypochlorite was added. The reaction mixture was allowed to stand at room temperature for 1.5 h. The solvent, excess reagent, and *tert*-butyl alcohol were evaporated under vacuum without heating by using a protected vacuum pump (cold trap and sodium hydroxide trap). The product was obtained as a colorless oil; IR (neat) 1595 (w), 1320 (s), 1165 (s), 1000 cm^{-1}; NMR (CCl_4) δ 3.1 (s, 3 H), 7.4–8.3 (m, 5 H). The imidoyl chloride was dissolved in ether and the solution was cooled to −30 °C. Methylamine was bubbled into the solution. The solvent and excess amine were evaporated under reduced pressure. The product was dissolved in ether and filtered to remove the amine hydrochloride. The ether was removed. The product was recrystallized from ethanol to yield 86 mg (60% overall yield from sulfinamide) of product, mp 94.5–96 °C. Its infrared spectrum was identical with that of an authentic sample.

Methyl *N*-Methylbenzenesulfonimidate (3a, Z = OCH_3). *N*-Methylbenzenesulfinamide (180 mg) was cooled to 0 °C in carbon tetrachloride and a solution of an excess of *tert*-butyl hypochlorite in carbon tetrachloride, cooled to 0 °C, was added. The reaction mixture was kept at 0 °C for 1 h. The solvent, excess reagent, and *tert*-butyl alcohol were evaporated under reduced pressure without heating. The sulfonimidoyl chloride, an oil, was dissolved in 40 mL of carbon tetrachloride. To it, excess solid sodium methoxide was added. The reaction was stirred for 1 h at room temperature and then filtered. The solvent was evaporated without heating. The product, 150 mg, was obtained pure (as shown by NMR) in 70% yield from the sulfinamide. The product, an oil which decomposes slowly at room temperature, had NMR (CCl_4) δ 2.8 (s, 3 H), 3.5 (s, 3 H), 7.5–7.7 (m, 3 H), 7.9–8.2 (m, 2 H).

Isopropyl *N*-Methylbenzenesulfonimidate (3a, Z = $OCH(CH_3)_2$). *N*-Methylbenzenesulfinamide (173 mg) was treated, as above, with excess *tert*-butyl hypochlorite in carbon tetrachloride. The imidoyl chloride was added to a suspension of sodium isopropoxide (prepared from 1.9 mL of 2-propanol and an excess of sodium hydride) in benzene at 0 °C. After the addition the reaction was stirred for 1.5 h at room temperature and then filtered. The solvent was evaporated to give pure product (192 mg, 81% yield from sulfinamide) as shown by NMR. The structure was supported by acid hydrolysis to *N*-methylbenzenesulfonamide in 90% yield. This isopropyl ester decomposes much slower than the above methyl ester. After 8 days, no noticable decomposition was observed by NMR. After several months, about 50% decomposition was observed: NMR (CCl_4) δ 1.1 (two overlapping doublets appearing nearly as a triplet, 6 H), 2.9 (s, 3 H), 4.5 (quint, 1 H), 7.3–7.6 (m, 3 H), 7.7–8.1 (m, 2 H). Upon irradiation of the proton at δ 4.5 the overlapping doublets became two singlets. When the protons at δ 1.1 are irradiated the proton at δ 4.5 becomes a singlet.

***N*-Phenyl-α-toluenesulfonimidoyl Chloride (2b).** *N*-Phenyl-α-toluenesulfinamide (80 mg) [mp 141–145 °C (lit.[6] mp 144–145 °C) was treated with excess *tert*-butyl hypochlorite as above for 30 min in the dark. The solvent was evaporated under reduced pressure with aluminum foil around the flask to protect against light until all the *tert*-butyl hypochlorite and solvent were removed. The imidoyl chloride was a light yellow solid and appeared to be stable at room temperature. NMR showed the product was pure: NMR (CCl_4) δ 5.0 (AB q, 2 H), 7.0–7.8 (m, 10 H).

***N',N'*-Dimethyl-*N*-phenyl-α-toluenesulfonimidamide (3b, Z = NMe_2).** Excess dimethylamine was condensed in 150 mL of ether at −78 °C. All of the *N*-phenyl-α-toluenesulfonimidoyl chloride from the preceding reaction, in ether at −78 °C, was added to the dimethylamine. The reaction was allowed to warm to room temperature and stand for 2 h. It was then washed with water five times. The solvent was evaporated to obtain 89 mg (84% yield) of the product, mp 77–80 °C (TLC showed only trace impurity). After it was recrystallized from methanol, it melted at 79–80 °C (lit.[1] 79–80 °C).

Phenyl *N*-Phenyl-α-toluenesulfonimidate (3b, Z = OPh). *N*-Phenyl-α-toluenesulfinamide (1.012 g) in carbon tetrachloride (27 mL) at 0 °C was oxidized by *tert*-butyl hypochlorite (1.66 g in 10 mL of solvent) as previously noted. The product in 55 mL of benzene was stirred overnight with solid sodium phenoxide (3.04 g). The reaction was washed with water, followed by an aqueous sodium hydroxide wash. The product was recrystallized from carbon tetrachloride and then from methanol. Recrystallization of the material from the mother liquors from methanol gave more product. The total yield from the sulfinamide was 0.810 g (57% yield), mp 116–118 °C. Recrystallization from methanol gave analytically pure product: mp 117–118 °C; IR (KBr) 1595, 1330, 1230, 1075, 845, 775, 750, 690 cm^{-1}; NMR (CCl_4) δ 4.6 (s, 2 H), 6.7–7.7 (m, 15 H).

Anal. Calcd for $C_{19}H_{17}NO_2S$: C, 70.56; H, 5.29; N, 4.33. Found: C, 70.78; H, 5.54; N, 4.21; C, 70.83; H, 5.37; N, 4.17.

***p*-Tolyl *N*-phenylbenzenesulfonimidate (3c, Z = OC_6H_4-*p*-CH_3).** *N*-Phenylbenzenesulfinamide (0.370 g) was treated with *tert*-butyl hypochlorite (1.27 g) as above. The imidoyl chloride in benzene was stirred with excess sodium *p*-cresolate overnight. The reaction mixture was washed first with water and then with a sodium hydroxide solution. The solvent was evaporated to yield an oil which failed to crystallize. The material was chromatographed on a silica gel column and then on a preparative TLC silica gel plate to give as an oil a 57% yield of the product: IR (neat) 1600, 1490, 1445, 1325, 1235, 1190, 1155, 1110, 1060, 1020, 1000, 935, 900, 850, 830, 780, 755, 735, 685 cm^{-1}; NMR (CCl_4) δ 2.3 (s, 3 H), 6.5–8.2 (m, 14 H).

Anal. Calcd for $C_{19}H_{17}NO_2S$: C, 70.56; H, 5.30; N, 4.33. Found: C, 70.28; H, 5.48; N, 4.06.

Phenyl *N*-Phenylbenzenesulfonimidate (3c, Z = OPh). *N*-Phenylbenzenesulfinamide (0.172 g) was converted to the imidoyl chloride which was treated with an excess of sodium phenoxide as above. The product was chromatographed on silica gel by eluting with a 1:1 carbon tetrachloride–benzene mixture. The product, mp 56.5–58 °C (0.16 g, 66%), was further purified by recrystallization from methanol.

Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.86; H, 4.89; N, 4.53. Found: C, 70.04; H, 5.08; N, 4.60.

Phenyl *N*-Benzylbenzenesulfonimidate (3d, Z = OPh). *N*-Benzylbenzenesulfinamide[7] (1.02 g) was treated with *tert*-butyl hypochlorite (1.046 g) in carbon tetrachloride at 0 °C in the dark for 1 h. The solvent and excess reagent were evaporated. The imidoyl chloride [(IR (neat) 1445, 1290, 1155 cm^{-1}; NMR (CCl_4) δ 4.7 (s), 7.1–7.7 (m), 8.0–8.4 (m)] was dissolved in benzene and an excess of sodium phenoxide was added. The reaction was stirred overnight. The benzene solution was washed with water and then with a sodium hydroxide solution. The solvent was evaporated. The product was chromatographed on silica gel to yield 0.94 g (a 62% yield from the sulfinamide) of pure material which was recrystallized from methanol to give product of mp 50.5–52 °C.

Anal. Calcd for $C_{19}H_{17}NO_{25}$: C, 70.56; H, 5.30; N, 4.33. Found: C, 70.82; H, 5.58; N, 4.30.

(*N,N*-Dimethylamino)phenoxyphenyloxosulfonium Tetrafluoroborate (4). Trimethyloxonium tetrafluoroborate (131 mg) and phenyl *N*-methylbenzenesulfonimidate (195 mg) were stirred in 5 mL of dichloromethane at room temperature for 24 h. The solution was filtered through a glass filter under nitrogen pressure. The residue was washed with about 10 mL of dichloromethane chloride. The filtrates were combined. To this solution about 30 mL of carbon tetrachloride was added. Immediately a white precipitate began forming. The flask was cooled to −20 °C for several hours. The product was filtered under nitrogen on a glass filter. It was vacuum dried without heating. The yield was 163 mg (59%). The product melted with decomposition in the range 79–91 °C: IR (Nujol mull), 1610, 1590, 1300, 1000–1180 (br), 975, 925, 860, 800, 760, 745 cm^{-1}; NMR (CCl_4) δ 3.3 (s, 6 H), 7.6 (s, 5 H), 7.9–8.1 (m, 3 H), 8.2–8.5 (m, 2 H).

Anal. Calcd for $C_{14}H_6BF_4NO_2S$: C, 48.16; H, 4.62; N, 4.01. Found: C, 47.91; H, 4.90; N, 4.19.

Acknowledgment. This work was supported by the National Science Foundation.

Registry No.—**1a**, 69726-27-8; **1b**, 40723-04-4; **1c**, 14933-97-2; **1d**, 6829-91-0; **2a**, 15934-21-1; **2b**, 33872-07-0; **2c**, 69726-28-9; **2d**, 69726-29-0; **3a** (Z = $NHCH_3$), 17247-02-8; **3a** (Z = OCH_3), 16181-36-5; **3a** (Z = $OCH(CH_3)_2$), 69726-30-3; **3b** (Z = NMe_2), 69726-31-4; **3b** (Z = OPh), 69726-32-5; **3c** (Z = OC_6H_4-*p*-CH_3), 69726-33-6; **3c** (Z = OPh), 69726-34-7; **3d** (Z = OPh), 69726-35-8; **4**, 69726-37-0; phenyl *N*-methylbenzenesulfonimidate, 15934-34-6; trimethoxonium tetrafluoroborate, 420-37-1; *tert*-butyl hypochlorite, 507-40-4; sodium methoxide, 124-41-4; sodium isopropoxide, 683-60-3; sodium phenoxide, 139-02-6; *S*-(4-methoxyphenyl)-*N*-methyl-*S*-phenylsulfoxime, 69726-38-1; anisole, 100-66-3; (2-methoxyphenyl)phenylmethane, 883-90-9; (4-methoxyphenyl)phenylmethane, 834-14-0; sodium *p*-cresolate, 1121-70-6.

References and Notes

(1) C. R. Johnson, E. U. Jonsson, and C. C. Bacon, *J. Org. Chem.*, companion paper, this issue.
(2) E. S. Levchenko, L. N. Markovskii, and A. V. Kirsanov, *Zh. Org. Khim.*, **3**, 1273 (1967).

(3) F. Wudl, C. K. Bush, and T. B. K. Lee, *J. Chem. Soc., Chem. Commun.*, 151 (1972).
(4) W. E. Truce and C. W. Vriesen, *J. Am. Chem. Soc.*, **75**, 5032 (1953).
(5) Ya. N. Derkach, N. A. Pasmurtseva, L. N. Markovskii, and E. S. Levchenko, *Zh. Org. Khim.*, **9**, 1411 (1973).
(6) H. Gilman and H. L. Morris, *J. Am. Chem. Soc.*, **48**, 2399 (1926).
(7) L. C. Raiford and S. E. Hazlet, *J. Am. Chem. Soc.*, **57**, 2172 (1935).

Oxidation of *N*-(*p*-Tolylsulfonyl)sulfilimines to *N*-(*p*-Tolylsulfonyl)sulfoximines with Alkaline Hydrogen Peroxide

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The anions derived from *N*-(*p*-tolylsulfonyl)sulfoximines are of considerable synthetic utility as alkylidene transfer reagents for the conversion of aldehyde and ketones into oxiranes.[1] Routes to *N*-tosylsulfoximines include treatment of the corresponding NH sulfoximine with *p*-toluenesulfonyl chloride, the copper-catalyzed reaction of sulfoxides with *p*-toluenesulfonyl azide,[1,2] and the oxidation of *N*-(*p*-tolylsulfonyl)sulfilimines.[3] These latter compounds are themselves readily available from the reaction of sulfides with Chloramine-T.[4,5] *N*-(Arylsulfonyl)-*S,S*-dimethylsulfoximines are available by copper-catalyzed reactions of Chloramine-T and related compounds with dimethyl sulfoxide.[1,6]

The oxidation of *N*-(*p*-tolylsulfonyl)sulfilimines to the corresponding sulfoximines has generally been carried out with aqueous potassium permanganate.[3,4] One literature report describes the use of the sodium salt of *m*-chloroperoxybenzoic acid to effect this oxidation.[7] Recently, Swern reported on the high yield oxidation of *N*-acyl- and *N*-(arylsulfonyl)dimethylsulfilimines to the corresponding sulfoximines with ruthenium tetroxide; the reaction may be accomplished with catalytic amounts of ruthenium tetroxide if sodium metaperiodate or sodium hypochlorite is added to the reaction mixture.[8]

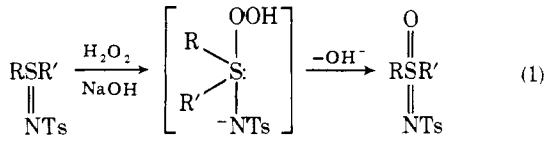
We would like to report here our finding that *N*-(*p*-tolylsulfonyl)sulfilimines (**1**) are readily oxidized in good yield to *N*-(*p*-tolylsulfonyl)sulfoximines (**2**) with alkaline hydrogen peroxide. These oxidations are achieved by adding 2 equiv of sodium hydroxide and hydrogen peroxide in water to a refluxing solution of the *N*-(*p*-tolylsulfonyl)sulfilimine in methanol. The mixture is allowed to reflux for 2 h and then worked up by pouring into water and extracting the *N*-(*p*-tolylsulfonyl)sulfoximine with chloroform. In some instances, the *N*-(*p*-tolylsulfonyl)sulfoximine crystallizes from the reaction mixture in pure form on cooling. This oxidation procedure is applicable to a variety of *N*-(*p*-tolylsulfonyl)sulfilimines as shown in Table I.

Table I. Preparation of *N*-(*p*-Tolylsulfonyl)sulfoximines

sulfoximine **2**		yield,	mp,	lit.[a] mp,
R	R′	%	°C	°C
Ph	CH_3	98	107–109	107–109
Ph	C_2H_5	88	123–125	
Ph	i-C_3H_7	80	98.5–99.5	
Ph	c-C_5H_9	44	142–143	142.5–143.5
Ph	c-C_6H_{11}	65	145–147	145.5–146
Ph	CH_2Ph	29	151–152	148–149
CH_3	CH_3	78	169–179	169–170
C_2H_5	C_2H_5	88	93–94	89–91
n-C_4H_9	n-C_4H_9	60	57–58	

[a] Reference 1.

The success of these oxidation reactions with nucleophilic oxidants can be attributed to the highly electonegative *N*-tosyl substituent, which increases the electrophilic character of the sulfilimine sulfur. We suggest that these oxidants proceed via an intermediate sulfurane (eq 1). Results with two other in-



(1)

expensive nucleophilic oxidants, sodium hypochlorite and *tert*-butyl hydroperoxide/base, have not been satisfactory.[9]

Experimental Section

***S,S*-Diethyl-*N*-(*p*-tolysulfonyl)sulfoximine.** *S,S*-Diethyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2.31 g, 0.01 mol) was dissolved in 30 mL of refluxing methanol. A solution of 0.8 g [0.02 mol of sodium hydroxide and 2.1 mL of 30% hydrogen peroxide (~0.02 mol)] in 8 mL of water was added. The mixture after stirring and refluxing for 5 h was poured into 75 mL of water and extracted twice with 30-mL portions of chloroform. The combined chloroform extracts were washed with 20 mL of water, dried over $MgSO_4$, and evaporated. The residue was recrystallized from ethanol to yield 2.4 g (88%) of product, mp 93–94 °C.

Registry No.—**1**(R = Ph; R′ = CH_3), 10330-22-0; **1** (R = Ph; R′ = C_2H_5), 10330-18-4; **1** (R = Ph; R′ = i-C_3H_7), 18922-56-0; **1** (R = Ph; R′ = c-C_5H_9), 69765-76-0; **1** (R = Ph; R′ = c-C_6H_{11}), 56561-39-8; **1** (R = Ph; R′ = CH_2Ph), 24702-30-5; **1** (R = CH_3; R′ = CH_3), 13150-75-9; **1** (R = C_2H_5; R′ = C_2H_5), 13553-69-0; **1** (R = n-C_4H_9; R′ = n-C_4H_9), 17627-00-8; **2** (R = Ph; R′ = CH_3), 42153-74-2; **2** (R = Ph; R′ = C_2H_5), 69765-77-1; **2** (R = Ph; R′ = i-C_3H_7), 69780-68-3; **2** (R = Ph; R′ = c-C_5H_9), 33332-99-9; **2** (R = Ph; R′ = c-C_6H_{11}), 33367-88-3; **2** (R = Ph; R′ = CH_2Ph), 38764-59-9; **2** (R = CH_3; R = CH_3), 22236-45-9; **2** (R = C_2H_5; R′ = C_2H_5), 42153-72-0; **2** ($R = nC_4H_9$, R′ = n-C_4H_9), 69765-78-2; H_2O_2, 7722-84-1.

References and Notes

(1) C. R. Johnson, R. A. Kirchhoff, R. J. Reischer, and G. F. Katekar, *J. Am. Chem. Soc.*, **95**, 4287 (1973).
(2) H. Kwart and A. A. Kahn, *J. Am. Chem. Soc.*, **89**, 1950 (1967).
(3) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950).
(4) T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, **77**, 409 (1977).
(5) For a convenient phase-transfer method see C. R. Johnson, K. Mori, and A. Nakanishi, *J. Org. Chem.*, companion paper, this issue.
(6) R. W. Heintzelman and D. Swern, *Synthesis*, 731 (1976); D. Carr, T. P. Seden, and R. W. Turner, *Tetrahedron Lett.*, 477 (1969); M. Moriyama, T. Numata, and S. Oae, *Org. Prep. Proced. Int.*, **6**, 207 (1974).
(7) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. G. Garwood, *J. Am. Chem. Soc.*, **92**, 7369 (1970); a detailed study of the oxidation of sulfilimines to sulfoximines with *m*-chloroperoxybenzoate anion has been completed; S.-L. Huang and D. Swern, *J. Org. Chem.*, submitted for publication.
(8) H. S. Veale, J. Levin, and D. Swern, *Tetrahedron Lett.*, 503 (1978).
(9) This work was supported by a grant from the National Science Foundation.

Diels–Alder Reactions of 2*H*-Thiopyran

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During the course of our investigation of functionialized cyclic dienes, we have examined the Diels–Alder reaction of 2*H*-thiopyran (**1**).[1] Our original thinking led us to predict that 2*H*-thiopyran would be a relatively reactive diene because of the electron-donating character of sulfur and further that the sulfur atom could be used to control regioselectivity. We also predicted that the Alder endo effect would lead to products having the same carbon skeleton stereochemistry as expected

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