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

Carl R. Johnson* and Robert A. Kirchhoff

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

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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]

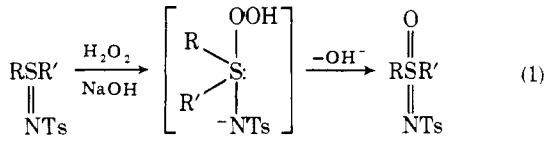
We would like to report here our finding that *N*-(*p*-tolylsulfonyl)sulfilimines (**1**) are readily oxidized in good yield to *N*-(*p*-tolylsulfonyl)sulfoximines (**2**) with alkaline hydrogen peroxide. These oxidations are achieved by adding 2 equiv of sodium hydroxide and hydrogen peroxide in water 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.

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Diels–Alder Reactions of 2*H*-Thiopyran

Ronald H. Fleming* and Barbara M. Murray

Department of Chemistry, Stephen F. Austin State University, Nacogdoches, Texas 75962

Received January 23, 1979

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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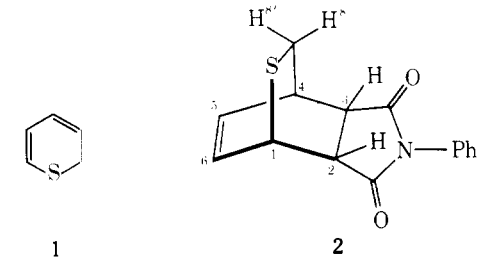
Table I. Chemical Shift Changes of 2 Induced by Eu(fod)$_3$

proton no.	Δδ/mol of [Eu(fod)$_3$]/mol of 2	proton no.	Δδ/mol of [Eu(fod)$_3$]/mol of 2
1	3.18	6	2.26
2	4.79	8	0.87
3	5.21	8′	0.81
4	4.64	ortho	4.69
5	2.58		

from the relatively unreactive *cis*-piperylene. We now have examples consistent with our predictions except that 2*H*-thiopyran is less reactive than predicted.

Results

We have prepared adducts **2**, **3**, and **4** from dienophiles *N*-phenylmaleimide, maleic anhydride, and methyl acrylate, respectively. Adduct **2** was shown to be the endo product by



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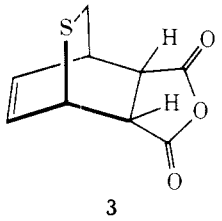
2



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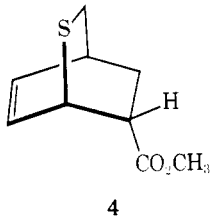


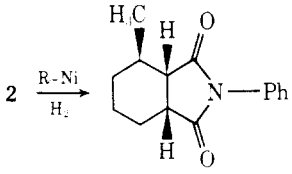
4

carrying out a Eu(fod)$_3$ shift reagent experiment and by chemically relating it to other substances of known stereochemistry.[2]

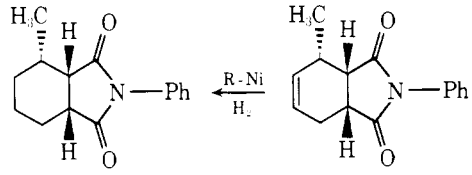
Data from the shift reagent experiment are summarized in Table I. As expected, for complexation of Eu(fod)$_3$ on carbonyl oxygens, the ortho, 2, and 3 position hydrogens were shifted the most. Also substantially shifted were the 1- and 4-hydrogens. For the expected endo product the vinyl hydrogens (5 and 6 positions) should be shifted more than the sulfur bridge hydrogens (8 and 8′ positions). The data are clearly consistent with the endo adduct **2**. The shift reagent complexes preferentially at the oxygen farthest from sulfur. The hydrogens on that side (3- and 4-positions) are shifted more than the corresponding hydrogens (1 and 2 positions) on the sulfur side of the molecule. Apparently the sulfur atom reduces the Lewis basicity of the nearer oxygen.

Compound **2** was reduced to **5** using Raney nickel and adsorbed hydrogen. An epimer of **5** was produced by Diels–Alder addition of *trans*-piperylene and *N*-phenylmaleimide to the known adduct **6** followed by reduction to **7** by Raney nickel catalyzed hydrogenation. Mass spectra of **5** and **7** showed the same parent ion and nearly identical fragmentation patterns. However, **5** and **7** gave different NMR spectra. The fact that **5** and **7** are isomeric confirms that **2** is indeed the endo adduct since the exo adduct would have been reduced to **7**. The synthesis of **5** also demonstrates the utility of 2*H*-thiopyran in producing the same stereochemical result as the unreactive *cis*-piperylene.

Adduct **3** was prepared similarly to the procedure used for **2** from maleic anhydride and **1**. Except for the aromatic region, the NMR spectra of **2** and **3** were nearly identical indicating that **3** was also the endo adduct.



5



7 **6**

To examine the regioselectivity of Diels–Alder additions to 2*H*-thiopyran, methyl acrylate was used as the dienophile. Since methyl acrylate is a less reactive dienophile than *N*-phenylmaleimide or maleic anhydride, the formation of adduct **4** required a longer time. The product **4** was distilled and collected by preparative gas chromatography. GC–MS showed one substance with an appropriate mass spectrum. The ^{1}H NMR spectrum of **4** showed a (H-1) doublet of doublets of doublets at δ 3.78 (1 H) consistent with the carbomethoxy at position 2 rather than position 3 and reminiscent of the corresponding signals of **2** and **3**. To determine the stereochemistry of the carbomethoxy group, **4** was subjected to Raney nickel catalyzed reduction to give methyl *trans*-3-methylcyclohexanecarboxylate. The various isomers of methyl methylcyclohexanecarboxylate were easily distinguished by comparison of their ^{13}C spectra with literature values.[3] The ^{1}H NMR spectrum of **4** and the ^{13}C NMR spectrum of its reduction product also indicated that about 10% of the exo isomer of **4** was present in the sample.

In order to estimate the reactivity of **1**, a competition experiment was done. Equal molar amounts of *N*-phenylmaleimide, piperylene, and **1** produced exclusively **6**. (In fact, *trans*-piperylene reacted with *N*-phenylmaleimide even at room temperature while **1** required 150 °C.) Thus, in spite of the electron-donating character of sulfur and the cyclic nature of **1**, *trans*-piperylene is still much more reactive than **1**. Nevertheless, in the cycloaddition of **1** with methyl acrylate, the sulfur appears to control the regioselectivity. The factors involved in the low reactivity and control of regioselectivity are under further study.

Experimental Section

Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc. ^{1}H NMR spectra were determined with a Varian HA-100 or a Perkin-Elmer R-20 spectrometer. The ^{13}C NMR spectrum was measured with a Varian CFT-20 spectrometer. IR spectra were determined with a Perkin-Elmer Model 700 spectrometer. Mass spectra and GC–MS were measured at Texas A&M University by Larry Burchfield or at the University of Houston by Fred Feyerherm. Gas chromatography was performed on a Varian A-90 P instrument using a ¼ in. × 10 ft 8% OV-17 on AnaKrom ABS (110/120 mesh) column.

***endo*-*N*-Phenyl-7-thiabicyclo[2.2.2]oct-5-ene-2,3-dicarboximide (2).** 2*H*-Thiopyran[4] (0.40 g, 4.1 mmol), *N*-phenylmaleimide (0.71 g, 4.1 mmol), and xylene (about 1 mL) were sealed in a glass tube under vacuum. The sample was heated at 150 °C for 2 h. Upon cooling, the product crystallized. It was filtered and dried. Purification by chromatography on silica gel using benzene gave **2** (0.59 g, 2.2 mmol, 53%), mp 225 °C. An analytical sample was prepared by recrystallization from benzene: mp 226 °C; NMR ($CDCl_3$) δ 2.58 (d of d, 1 H, J = 10.5, 3.0 Hz, H-8′), 3.03 (d of d, 1 H, J = 8.5, 2.5 Hz, H-3), 3.10 (d of d, 1 H, J = 10.5, 3.0 Hz, H-8), 3.51 (d of d, 1 H, J = 8.5, 3.4 Hz, H-2), 3.6 (m, 1 H, H-4), 3.96 (d of d of d, 1 H, J = 6.7, 3.4, 1.1 Hz, H-1), 6.14 (d of d of d, 1 H, J = 8.2, 6.7, 1.1 Hz, H-5), δ 6.45 (d of d of d, 1 H, J = 8.2, 6.7, 1.1 Hz, H-6), δ 7.0-7.4 (m, 5 H, aromatic); IR (KBr) 1710 (strong), 1780 (medium), 1390, 1200 cm^{-1} (strong); mass spectrum *m/e* 271 (parent). Anal. Calcd for $C_{15}H_{13}NO_2S$ (271.34): C, 66.40; H,

4.83; N, 5.16; S, 11.82. Found: C, 66.10; H, 5.23; N, 5.20; S, 11.93.

***endo*-7-Thiabicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Acid Anhydride (3).** 2*H*-Thiopyran[4] (0.50 g, 5.1 mmol), maleic anhydride (0.50 g, 5.1 mmol) and xylene (about 1 mL) were sealed in a glass tube under vacuum. The sample was heated at 150 °C for 2 h and cooled to give a black tarry mixture. Isolation and purification by chromatography on silica gel using benzene gave 3 (0.19 g, 0.97 mmol, 19%). An analytical sample was prepared by repeated recrystallization from methylcyclohexane: mp 148–148.5 °C; NMR ($CDCl_3$) δ 2.62 (d of d, 1 H, J = 10, 3 Hz, H-8′), 3.10 (d of d, 1 H, J = 10, 3 Hz, H-8), 3.22 (d of d, 1 H, J = 9, 3 Hz, H-3), 3.65 (m, 1 H, H-4), 3.70 (d of d, 1 H, J = 9, 3 Hz, H-2), 4.02 (d of d of d, 1 H, J = 7, 4, 2 Hz, H-1), δ 6.28 (d of d of d, 1 H, J = 8, 7, 2 Hz, H-5), 6.58 (d of d of d, 1 H, J = 8, 7, 2 Hz, H-6); IR (KBr) 1770 cm^{-1} (very strong), 1850, 1220, 1070 cm^{-1} (all strong); mass spectrum *m/e* 196 (parent). Anal. Calcd for $C_9H_8O_3S$ (196.22): C, 55.09; H, 4.11; S, 16.34. Found: C, 55.04; H, 4.17; S, 16.58.

Methyl *endo*-7-Thiabicyclo[2.2.2]oct-5-ene-2-carboxylate (4). 2*H*-Thiopyran[4] (1.69 g, 17.2 mmol) and methyl acrylate (1.55 g, 18.0 mmol) were sealed in a glass tube under vacuum and heated at 150 °C for 36 h. Distillation (bp 100–170 °C (1 torr)) gave **4** (1.28 g, about 80% pure by NMR, 32%) which was further purified by preparative gas chromatography at 180 °C: NMR ($CDCl_3$) δ 1.75–1.97 (m, 2 H, H-3, 3′), 2.27–2.68 (m, 1 H, H-8′), 2.85–3.35 (m, 3 H, H-2, -4, -8), 3.64 (s, 3 H, $-OCH_3$), 3.78 (d of d of d, 1 H, J = 8, 5, 2 Hz, H-1), 6.06–6.60 (m, 2 H, H-5, -6); IR (neat) 1735, 1210, 1180 cm^{-1} (all strong); mass spectrum *m/e* 184 (parent). Anal. Calcd for $C_9H_{12}O_2S$ (184.26): C, 58.67; H, 6.56; S, 17.40. Found: C, 58.43; H, 6.79; S, 17.64.

***cis,trans*-3-Methyl-*N*-phenylcyclohexane-1,2-dicarboximide (5).** Adduct **2** (0.25 g, 0.92 mmol), Raney nickel[5] (about 2 mL), and ethanol (15 mL) were heated at reflux for 10 min and filtered through Celite. The Celite was washed with hot ethanol and the ethanol portions were concentrated at reduced pressure. The product was recrystallized (methylcyclohexane, charcoal) to give 0.12 g (0.49 mmol, 54%) of product: mp 108.5–110 °C; NMR ($CDCl_3$) δ 1.24 (d, 3 H, J = 6 Hz), 1.0–2.0 (broad signal, 6 H), 2.25 (broad signal, 1 H), 2.57 (m, 1 H), 3.1 (broad signal, 1 H), 7.36 (m, 5 H); mass spectrum *m/e* 243 (parent).

***cis,cis*-3-Methyl-*N*-phenylcyclohex-4-ene-1,2-dicarboximide (6).** *N*-Phenylmaleimide (1.00 g, 5.8 mmol) and *trans*-piperylene (0.59 g, 8.7 mmol) were sealed in a tube under vacuum and heated for 1 h at 150 °C. The resulting solid was recrystallized (methylcyclohexane, charcoal) to give 0.96 g (4.0 mmol, 69%) of product, mp 116.5–117 °C (lit.[6] mp 116–117 °C).

***cis,cis*-3-Methyl-*N*-phenylcyclohexane-1,2-dicarboximide (7).** Adduct **6** (0.25 g), Raney nickel (about 2 mL), and ethanol (15 mL) were heated at reflux for 10 min and filtered through Celite. The Celite was washed with hot ethanol (2 × 15 mL), and the ethanol portions were concentrated at reduced pressure. Two recrystallizations (methylcyclohexane, charcoal) gave white needles: mp 90 °C; NMR ($CDCl_3$) δ 2.22 (d, 3 H, J = 7 Hz), 1.0–2.4 (broad signal, 7 H), 2.98 (m, 2 H), 7.04 (m, 5 H); mass spectrum *m/e* 243 (parent); mmp (with **5**) 85–87 °C.

Reduction of 4. Adduct **4** (0.55 g), Raney nickel (about 6 mL), and ethanol (15 mL) were heated at reflux for 45 min and filtered through Celite. The Celite was washed with hot ethanol, and the combined ethanol fractions were concentrated at reduced pressure. The resulting liquid was purified by preparative gas chromatography (column temperature 150 °C) to give methyl 3-methylcyclohexanecarboxylate.

Acknowledgments. Generous financial support from the Robert A. Welch Foundation is acknowledged. We thank Dr. Robert R. Schumaker for taking ^{13}C and 100 MHz ^1H NMR spectra. The assistance of Russell Wiles, an undergraduate research student, is gratefully acknowledged.

Registry No.—1, 289-72-5; **2**, 69927-41-9; **3**, 69979-92-6; **4**, 69927-42-0; **5**, 53288-19-0; **6**, 69979-93-7; **7**, 53288-20-3; *N*-phenylmaleimide, 941-69-5; maleic anhydride, 108-31-6; methyl acrylate, 96-33-3; *trans*-piperylene, 2004-70-8; *trans*-methyl methylcyclohexanecarboxylate, 7605-53-0.

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Absolute Configurations and Rotations of *trans*-3,5-Dimethylcyclohexanone, *trans*-3,5-Dimethylcyclohexene, and *trans*-1,3-Dimethylcyclohexane

Harlan L. Goering,* W. Warren Schmidt, and Victor D. Singleton, Jr.

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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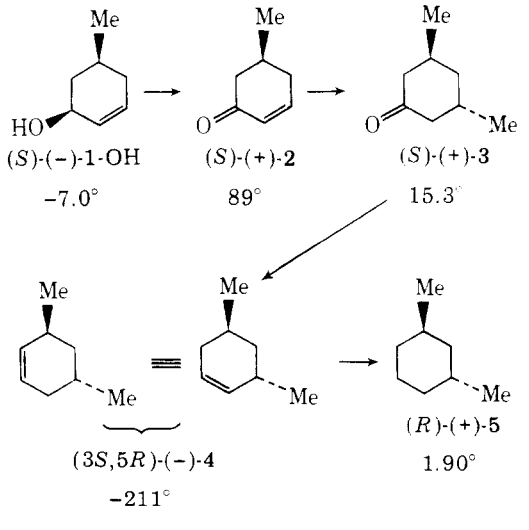
In another study it became important to know the absolute configuration and rotation of *trans*-3,5-dimethylcyclohexene (**4**). This paper describes the correlations that provide this information. We have also converted active **4** to *trans*-1,3-dimethylcyclohexane (**5**) to establish the absolute rotation and configuration of the latter.

The optical configuration and rotation of **4** were correlated with 5-methyl-2-cyclohexenone (**2**) as outlined in Scheme I. Optically active 5-methyl-2-cyclohexenone (**2**) was prepared from active *cis*-5-methyl-2-cyclohexenol (1-OH)[1] by oxidation with manganese dioxide as reported earlier.[2] It has been shown[2] that this reaction proceeds with complete preservation of optical configuration. The absolute rotation for 1-OH (7.0°)[1,3] was originally determined by complete resolution, and in this work we have confirmed this value by direct determination of enantiomeric compositions of active 1-OH with a chiral NMR shift reagent, tris(heptafluorobutyrylcamphorato)europium, Eu(hfbc)$_3$.[4] For example, a sample of 1-OH, $[\alpha]^{25}_D$ −2.32°, was found to be 34 ± 0.5% optically pure and a sample of (−)-1-OAc, found to be 52% optically pure with Eu(hfbc)$_3$, was converted to (+)-**2**, $[\alpha]^{25}_D$ 46°, which corresponds to 52% optical purity.[5] These experiments confirm the original absolute rotation for **2**[2,5] as well as for 1-OH.[1] Attempts to determine enantiomeric compositions of active **2** and **3** with chiral NMR shift reagents[4] were unsuccessful. The absolute configuration of **2** was established earlier[2] by corre-

Scheme I



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