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ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · FEBRUARY 1989

Impact Factor: 4.72 · DOI: 10.1021/jo00265a051

mycin by the Institute of New Antibiotics in the USSR, and as chloroorienticin A by the Shionogi Research Laboratories, Shionogi and Company, in Japan.

Acknowledgment. Orienticin A and eremomycin are gifts from Dr. Jun-ichi Shoji, Shionogi Research Laboratories, Osaka, Japan, and Professor Y. V. Dudnik, Institute of New Antibiotics, Moscow, USSR, respectively, and are gratefully acknowledged. We thank Verna Newton for typing the manuscript.

Preparation of "Free" Sulfoximines by Treatment of *N*-Tosylsulfoximines with Sodium Anthracenide

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Received July 28, 1988

Since the discovery of the sulfonimidoyl function in 1949, sulfoximines and related derivatives of sulfonimidic acid have received considerable attention.[1] A key feature is the variety of substitutions available to the sulfur-attached imino group. Unfortunately, direct methods for obtaining sulfoximines unsubstituted at nitrogen have serious limitations. The standard procedure involves the reaction of a sulfoxide with hydrazoic acid in a mixture of sulfuric acid and chloroform[2] (Scheme I, method A). In addition to the use of a potentially hazardous reagent,[3] this method is limited to compounds having sulfur substituents that are incapable of forming stable carbonium ions; under the acidic reaction conditions heterolysis of a carbon–sulfur bond usually occurs in cases where the alkyl group is tertiary and to some extent in secondary cases.[2,4] Treatment of a sulfoxide with *O*-(mesitylsulfonyl)hydroxylamine[5] (MSH, method B) provides a general and mild alternate route. The method is limited since MSH is quite difficult to prepare and to handle.[6]

A useful indirect method is the cleavage of the tosyl (*p*-tolylsulfonyl) group of a *N*-tosylsulfoximine (**1**). These compounds are readily available by treatment of a sulfoxide with tosyl azide (or Chloramine-T in the case of dimethyl sulfoxide) in the presence of a copper(II) salt[4] (route 1). They may also be prepared by oxidation of *N*-tosylsulfilimines[7] with alkaline hydrogen peroxide,[8] *m*-chloroperbenzoic acid (*m*CPBA) anion,[9] or sodium periodate–catalytic ruthenium dioxide[10] (route 2). *N*-Tosylsulfoximines have been obtained by reaction of a sulfonimidoyl fluoride[11] or a phenyl sulfonimidate[12] with an alkyllithium (route 3).

Scheme I

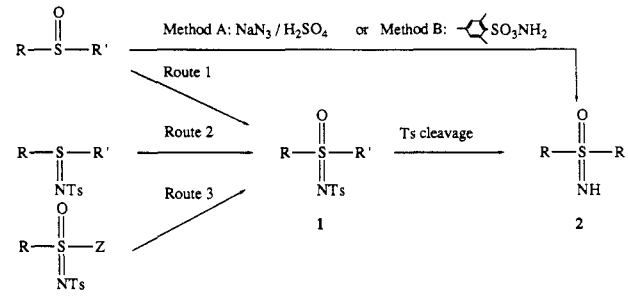

Table I. Isolated Yield of Sulfoximines 2 from Treatment of *N*-Tosylsulfoximes with Sodium Anthracenide in DME at 0 °C

entry	*N*-tosylsulfoximine 1 R	*N*-tosylsulfoximine 1 R′	yields of sulfoximine 2, %
a	CH_3	CH_3	93
b	$C(CH_3)_3$	$(CH_2)_3CH_3$	68
c	$(CH_2)_4$		88
d	CH_3		98
e	CH_3	$N[(CH_2)_3CH_3]_2$	92
f	CH_2CH_3	CCl_2CH_3	21[a]
g	CH_2Ph	CH_3	0[b]
h	Ph	CH_3	0

[a] Isolated product was *S*,*S*-diethylsulfoximine. [b] Starting material recovered.

Three distinct procedures to cleave the tosyl group from *S*,*S*-dimethyl-*N*-tosylsulfoximine (**1a**) to give *S*,*S*-dimethylsulfoximine (**2a**) are found in the literature. Treatment with concentrated sulfuric acid gave **2a** in 40% yield,[13] while irradiation at 253.7 nm in benzene gave 7% of sulfoximine **2a**.[14] A 60% yield was obtained upon treatment of **1a** with sodium in liquid ammonia.[15] Although conceptually sound, some practical difficulties are encountered with the latter procedure since the sodium–liquid ammonia system is somewhat too powerful a reducing agent and requires exactly 2 equiv of sodium per equivalent of sulfoximine. We have found that this problem is circumvented by employing milder reducing reagents such as the sodium arenides.[16]

Tosyl-group cleavage is readily achieved upon treatment of *N*-tosylsulfoximines **1** with a 1,2-dimethoxyethane (DME) solution of sodium anthracenide at 0 °C to give the corresponding free sulfoximines **2** in high yields (Table I). The reaction has the characteristics of a titration.[16] Complete consumption of starting material is indicated by the persistence of the blue color of the anthracenide radical anion. The reagent does not seem to further interact with the product, as the blue color is maintained upon stirring of the reaction mixture with excess reagent at 0 °C for $^1/_2$ h. The yield obtained for entry **a** (Table I) demonstrates the superiority of this method compared to those mentioned above. This procedure allowed preparation of the

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first example of a *S*-*tert*-alkylsulfoximine (Table I, entry **b**). Entries **d** and **e** exemplify the application of the procedure to the sulfonimidamides. Such *N*-H sulfonimidamides have been previously known only with aromatic substituents on sulfur.[17] During the course of investigating the scope of the procedure, we encountered some limitations. The two halogen substituents of tosylsulfoximine **1f** are removed with the arene radical anion and only *S*,*S*-diethylsulfoximine was isolated in modest yield. The method failed when applied to benzyl- and phenylsulfoximines (Table I, entries **g** and **h**). In the former case the doubly activated methylene compound is deprotonated and in the latter case the phenylsulfonimidoyl function is degradated due to its electronic similarity with the arylsulfonyl substituent. These results imply that the method is limited to sulfoximino species bearing alkyl or dialkylamino substituents.

Experimental Section

1,2-Dimethoxyethane (DME) was distilled from sodium benzophenone ketyl. All other solvents and reagents employed were of commercial grade. Sodium anthracenide stock solutions[16] were prepared by sonification of sodium metal (2.7 g, 120 mmol) and anthracene (21.4 g, 120 mmol) in DME (200 mL) under argon at room temperature for 3 h.[18]

S,*S*-Dimethyl-*N*-[(4-methylphenyl)sulfonyl]sulfoximine (**1a**),[13] mp 166–167 °C, was prepared by the reaction of dimethyl sulfoxide (DMSO) with tosyl azide.[4] 1,1,2,3,4,5-Hexahydro-1-[[(4-methylphenyl)sulfonyl]imino]thiophene 1-oxide (**1c**),[19] mp 106–107 °C, was isolated in 85% yield by oxidation of 1,1,2,3,4,5-hexahydro-1-[[(4-methylphenyl)sulfonyl]imino]-thiophene[20] with basic *m*CPBA.[9] The phase-transfer-catalyzed Mann–Pope reaction[21] of butyl 1,1-dimethylethyl sulfide followed by basic *m*CPBA oxidation[9] gave *S*-butyl-*S*-(1,1-dimethylethyl)-*N*-[(4-methylphenyl)sulfonyl]sulfoximine (**1b**) in 90% overall yield: mp 83–84 °C; IR (KBr) 1319, 1302, 1154 (SO_2), 1220, 1092, 1073 (NSO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 1.44 (s, 9 H), 1.45 (m, 2 H), 1.84 (m, 2 H), 2.39 (s, 3 H), 3.4 (m, 2 H), 7.29 (d, 2 H), 7.84 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.39, 21.35, 21.81, 23.13, 24.59, 49.32, 63.74, 126.36, 128.99, 141.45, 142.56. Anal. Calcd for $C_{15}H_{25}NO_3S_2$: C, 54.35; H, 7.60. Found: C, 54.48; H, 7.73. Treatment of *N*-[(4-methylphenyl)sulfonyl]methanesulfonimidoyl chloride[12] with 2 equiv of morpholine in dichloromethane at 0 °C gave *S*-methyl-*S*-morpholino-*N*-[(4-methylphenyl)sulfonyl]sulfoximine (**1d**)[22] in 88% yield: mp 111–113 °C; IR (KBr) 1311, 1301, 1150 (SO_2), 1260, 1083 (NSO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 3.06 (s, 3 H), 3.24 (dt, J = 5 Hz, 12 Hz, 2 H), 3.35 (dt, J = 5 Hz, 12 Hz, 2 H), 3.77 (t, J = 12 Hz, 4 H), 7.29 (d, J = 8 Hz, 2 H), 7.85 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.36, 38.54, 46.04, 65.94, 126.59, 129.19, 140.40, 142.92. Anal. Calcd for $C_{12}H_{18}N_2O_4S_2$: C, 45.27; H, 5.68. Found: C, 45.26; H, 5.51. Similar treatment with dibutylamine gave *N*,*N*-dibutyl-*N'*-[(4-methylphenyl)sulfonyl]methanesulfonimidamide (**1e**) in 88% yield: mp 82–84 °C; IR (KBr) 1312, 1135 (SO_2), 1236, 1093, 1064 (NSO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 6 H), 1.31 (m, J = 7.3 Hz, 4 H), 1.56 (m, 4 H), 2.39 (s, 3 H), 3.07 (s, 3 H), 3.27 (dd, 4 H), 7.26 (d, J = 8.2 Hz, 2 H), 7.83 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.51, 19.77, 21.28, 30.28, 42.41, 47.78, 126.45, 129.02, 140.87, 142.43. Anal. Calcd for $C_{16}H_{28}N_2O_3S_2$: C, 53.30; H, 7.83. Found: C, 53.19; H, 7.86.

Chlorination of *S*,*S*-diethyl-*N*-[(4-methylphenyl)sulfonyl]sulfoximine[4] with hexachloroethane[23] gave *S*-(1,1-dichloroethyl)-*S*-ethyl-*N*-[(4-methylphenyl)sulfonyl]sulfoximine (**1f**) in 52% yield: mp 92–93 °C; IR (KBr) 1323, 1164 (SO_2), 1221, 1078 (NSO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (t, 3 H), 2.42 (s, 3 H), 2.48 (s, 3 H), 3.84 (m 2 H), 7.28 (d, 2 H), 7.86 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.43, 29.55, 49.20, 61.21, 126.49, 129.29, 140.24, 143.14. Anal. Calcd for $C_{11}H_{15}Cl_2NO_3S_2$: C, 38.38; H, 4.39. Found: C, 38.50; H, 4.51.

General Method for Tosyl Group Cleavage. To a magnetically stirred solution or suspension of *N*-tosylsulfoximine **1** in DME (5–10 mL/mmol) under argon at 0 °C was added dropwise a solution of sodium anthracenide (ca. 0.6 N) until a blue color persists for a few minutes. Then workup A, B, or C was applied.

Workup A (for 2 mmol, general application, **2a,c,d,g**): the blue reaction mixture was quenched at 0 °C with 3 N hydrochloric acid (10 mL) and poured into dichloromethane (20 mL). After the mixture was washed with dichloromethane (3 × 10 mL) and diethyl ether (1 × 10 mL), the aqueous layer was made basic with granular sodium carbonate. The water was removed in vacuo at ca. 50 °C. The dry residue was stirred with dichloromethane (20 mL), and the extract was dried over magnesium sulfate. The free sulfoximine **2** was obtained upon removal of the solvent.

Workup B (for 2 mmol, acid sensitive sulfoximine **2b**): the blue reaction mixture was quenched at 0 °C with saturated aqueous ammonium chloride (3 mL), and the solvent was removed in vacuo. The residue was taken up in ethyl acetate and filtered to removed the bulk of the anthracene. The crude free sulfoximine **2** was then obtained by flash chromatography on silica gel with ethyl acetate/petroleum ether, 2/1.

Workup C (for 2 mmol, dichloromethane soluble sulfonimidamide **2e** conjugate acid): the blue reaction mixture was quenched with methanol (2 mL), and the solvent was removed in vacuo. The residue was taken up in diethyl ether and extracted with 3 N aqueous sulfuric acid (3 × 10 mL). Isolation of the free sulfoximine **2** from the combined acidic aqueous extracts was then performed as in workup A.

***S*,*S*-Dimethylsulfoximine (2a).** Treatment of 1.24 g (5 mmol) of **1a** dissolved in DME (20 mL) with sodium anthracenide followed by workup A gave 472 mg (93%) of white crystals, mp 56–57 °C (lit.[13] mp 52–53 °C).

1,1,2,3,4,5-Hexahydro-1-iminothiophene 1-Oxide (2c). Tosylsulfoximine **1c** (547 mg, 2 mmol) was dissolved in DME (10 mL) and treated with sodium antracenide. Workup A gave, after bulb-to-bulb distillation (120 °C, 0.1 Torr), 210 mg (88%) of **2c**[24] as a colorless oil.

***S*-Methyl-*S*-morpholinosulfoximine (2d).** Treatment of 3.18 g (10 mmol) of **1d** suspended in DME (15 mL) with sodium anthracenide and workup A gave 1.61 g (98%) of **2d** as a colorless oil, which upon standing gave crystals: mp 70–71 °C; IR (KBr) 3269 (NH), 1247, 1107 (NSO) cm^{-1}; ^1H NMR ($CDCl_3$) δ (br, 1 H), 2.81 (s, 3 H), 3.23 (m, 4 H), 3.77 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 34.18, 46.97, 66.57. Anal. (as the *picrate* salt, mp 120–121 °C). Calcd for $C_{11}H_{15}N_5O_9S$: C, 33.59; H, 3.84. Found: C, 33.42; H, 4.08.

***S*,*S*-Diethylsulfoximine.** A solution of 689 mg (2 mmol) of **1f** in DME (10 mL) was treated with sodium anthracenide followed by workup A to give 51 mg (21%) of *S*,*S*-diethylsulfoximine.[25]

***S*-Butyl-*S*-(1,1-dimethylethyl)sulfoximine (2b).** Treatment of **1b** (663 mg, 2 mmol) in DME (20 mL) with sodium anthracenide and workup B (flash chromatography on silica gel with ethyl acetate/petroleum ether, 2/1) gave a yellow oil. Bulb-to-bulb distillation (120 °C, 1 Torr) gave 241 mg (68%) of **2b** as a colorless oil: IR (film) 3289 (NH) 1212, 972 (NSO) cm^{-1}; ^1H NMR ($CDCl_3$) δ .98 (t, 3 H), 1.43 (s, 9 H), 1.48 (m, 2 H), 1.91 (m, 2 H), 2.26 (br, 1 H), 2.94 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.46, 21.80, 22.73, 23.56, 46.41, 59.99. Anal. Calcd for $C_8H_{19}NOS$: C, 54.19; H, 10.80. Found: C, 53.91; H, 10.68.

***N*,*N*-Dibutylmethanesulfonimidamide (2e).** Treatment of a DME solution (10 mL) of **1e** (720 mg, 2 mmol) with sodium anthracenide followed by workup C gave 380 mg (92%) of **2e** as

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a colorless oil (bp 112-115 °C, 0.1 Torr): IR (film) 3343, 3285, 3203 (NH) 1253, 1019 (NSO) cm^{-1}; ^1H NMR ($CDCl_3$) δ .94 (t, 6 H), 1.33 (m, 4 H), 1.55 (m, 4 H), 2.05 (br, 1 H), 2.85 (s, 3 H), 3.18 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.66, 19.93, 31.19, 38.71, 48.48. Anal. Calcd for $C_9H_{22}N_2OS$: C, 52.39; H, 10.75. Found: C, 52.51; H, 10.85.

Acknowledgment. This work was supported by a grant from the National Science Foundation. O.L. is a student from Ecole Supérieure de Chimie Industrielle de Lyon. We acknowledge the cooperative program between our institutions.

Concerning the Pathway of Xylyl Rotation in 9-(2,6-Xylyl)-9,10-dihydroanthracenes

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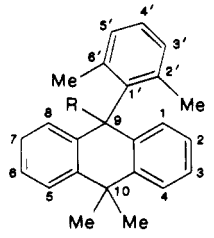
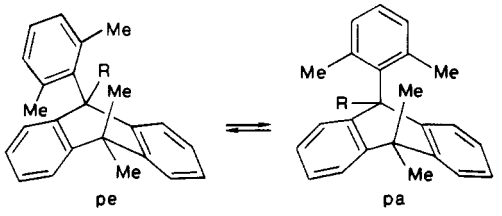
Received June 29, 1988

Nakamura and Oki[1] have examined the proton NMR behavior of 9-aryl-9,10-dihydroanthracenes (as well as 9-arylxanthenes) in a study directed towards the measurement of the $C(sp^2)$–$C(sp^3)$ rotational barrier of the aryl substituent. At elevated temperatures, the methyl groups of the xylyl substituent in **1** and **2** coalesce, and inversion



1: R = H ($\Delta G^{\ddagger}$ = 19.6 kcal/mol)
2: R = OH ($\Delta G^{\ddagger}$ = 15.4 kcal/mol)

barriers of 19.6 and 15.4 kcal/mol, respectively, were determined.[1a] In formulating their proposed pathway for this rotation, the authors made two assumptions: (1) the 9,10-dihydroanthracene ring in **1** and **2** undergoes rapid boat-to-boat ring inversion and (2) the xylyl substituent occupies the pseudoequatorial (pe) rather than the pseudoaxial (pa) position in the most stable conformation. On



this basis, they reasoned that xylyl rotation could not take place from the pe conformation due to a prohibitive barrier between the xylyl methyls and peri hydrogens on the aromatic rings of the dihydroanthracene. Hence they suggested that xylyl rotation must first involve an inversion to the pa form whereupon the rotation actually takes place. As noted above, a lower inversion barrier was observed for **2**, and this was attributed to a destabilization of the ground-state geometry by the interaction of the xylyl methyl(s) with the OH substituent. More recently, the traditional concept of boat-to-boat inversion for 9,10-dihydroanthracene (DHA) and many of its derivatives has been challenged by molecular mechanics calculations.[2-5] In fact, MM2 predicts a planar conformation for DHA itself[2] but with very little energy required to reach the fully puckered state (i.e., 145° angle between the planes of the benzene rings), and so one might expect a broad range of geometries on a time average. Calculations suggest a much greater tendency toward planarity for symmetrically disubstituted trans derivatives as well as gem disubstituted compounds.[3] Monosubstituted DHA's, on the other hand, show a parabolic potential well with the minima indicating some degree of ring puckering proportional to the size of the substituent (which is always pa).[4] Most importantly, the conformational description of these systems provided by theory has been supported by carbon-13 NMR studies.[5] In view of these results, we thought it worthwhile to further examine the question of aryl rotation in **1** and **2** by molecular mechanics.

In contrast to the previous suggestions of puckered DHA rings and pe xylyl substituents for **1** and **2**, *the MM2 global minima are nearly planar in each case*! DHA puckering is minor, 4° and 10° respectively, with the xylyl ring perpendicular and very slightly pe (see Figure 1a).

We also calculated the barriers to xylyl rotation and found values of 20.1 and 17.0 kcal/mol for **1** and **2** respectively, in good agreement with the experimental values of 19.6 and 15.4 kcal/mol; however, the pathway for this rotation is quite complex. As shown in Figure 2, the initial rotation of the xylyl group in **1** is accompanied by a slight increase in DHA ring pucker (Figure 2b) with the xylyl group becoming slightly more pe. However, after a rotation of ca. 40°, there is an abrupt change in the DHA ring with the xylyl group "flipping" into the pa position. Continued rotation passes through a maximum of about 60° and then on to the 90° position, which represents a local minimum whereupon the DHA ring is highly puckered (132°) (see Figure 1b). At this point, of course, the nonbonded interactions between the xylyl methyls and the pa 10-methyl is at a minimum. Further rotation regenerates this unfavorable interaction between the xylyl methyl and pa 10-methyl and the xylyl "flips" back down to the very slightly pe state (i.e., nearly planar) where the rotation is completed. Hence the overall process must be viewed as a "geared" rotation involving a combination of xylyl movement and DHA ring puckering.

A rather similar curve was obtained for the rotation of **2** except that the beginning geometry (i.e., the global minimum) starts out at higher energy. Hence calculations support the suggestion that the lower barrier to rotation in **2** is due to a destabilization of the ground state:[1a] the transition-state energies in both **1** and **2** are of comparable energy.

Finally, we examined rotational barriers with the DHA ring constrained to (a) the nearly planar conformation with the xylyl group slightly pseudoequatorial and (b) the

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