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A CONVENIENT SYNTHESIS OF VINYL SULFOXIMINES FROM β-HYDROXYALKYL SULFOXIMINES

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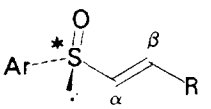
Summary: Previously unknown free and N-acylated vinyl sulfoximines were readily prepared via elimination of β-hydroxyalkyl methylphenylsulfoximines.

Studies on the chemistry of vinyl sulfoxides, 1, constitute a rich and varied literature Of particular interest has been the exploitation of sulfur atom chirality to direct the stereochemistry of bond formation at the α and/or β positions of the double bond.[2] The use of vinyl sulfoximines, 2, for analogous stereocontrol has been less intensively studied, although reports have appeared concerning the reactivity of 2 in Diels-Alder reactions[3] as well as 1,4-addditions of organometallic reagents[4] and various other nucleophiles.[5,6]



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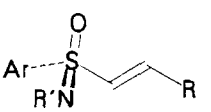


2

Several methods for preparing vinyl sulfoximines 2 have been reported, including amination and elimination of β-haloethylsulfoxides,[7] oxidation and elimination of β-haloethylsulfilimines,[3] and eliminations of β-hydroxyalkyl sulfoximines. Variants of the latter approach include acidic dehydration of carbinols,[5] basic elimination of mesylates,[4] and Peterson extrusion of lithiated carbinol trimethylsilyl ethers.[8] These methods provide access only to vinyl sulfoximines substituted at nitrogen with groups which are difficult or impossible to remove (2, R'= alkyl, p-toluenesulfonyl, phthalimido). We have recently described the preparation of free β-hydroxyalkyl sulfoximines via 1,2-addition of lithiated N-(trialkylsilyl)methylphenylsulfoximines to aldehydes and ketones.[9] We report herein the simple and convenient transformation of such addition products to the heretofore unknown free and N-acylated vinyl sulfoximines (2, R'= H, COR").

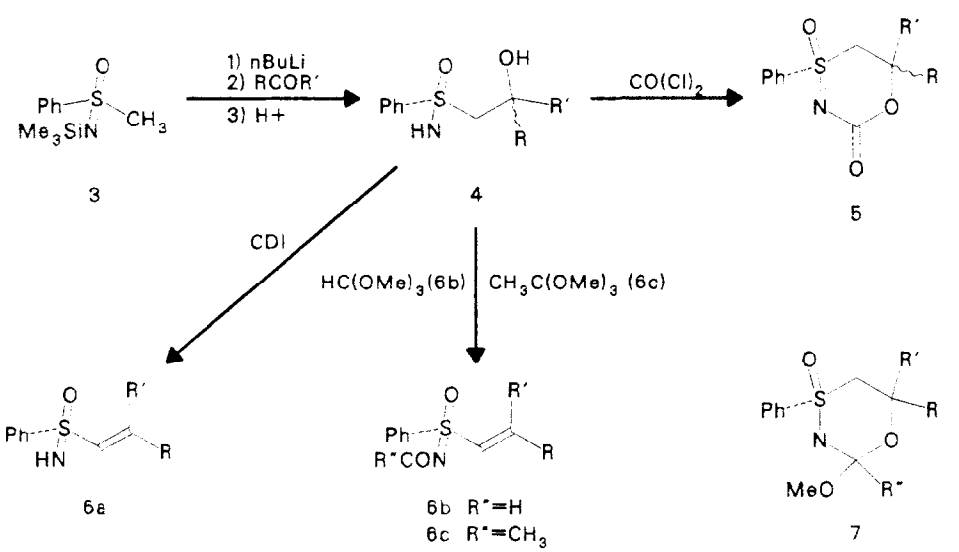
As reported previously, 1,2-addition of lithiated N-(trimethylsilyl)methylphenylsulfoximine 3 to aldehydes and ketones afforded the β-hydroxyalkyl sulfoximines 4 in excellent yields.[9] Whereas exposure of 4 to phosgene in dichloromethane gave 1,4,3-oxathiazin-2(6H)-one-4-oxides 5,[9] we have found that treatment with carbonyldiimidazole (CDI) in toluene yielded the free vinyl sulfoximines 6a. Heating of 4 in dimethylformamide dimethyl acetal

at 90°C was observed to promote a retroaldol cleavage to the corresponding carbonyl compound and methylphenylsulphoximine.[10] However, treatment of 4 with trimethyl orthoformate or trimethyl orthoacetate at 90°C in the presence of p-toluenesulfonic acid afforded the N-formyl and N-acetyl vinyl sulfoximines 6b and 6c. The vinyl sulfoximines prepared by these methods consisted of the E isomers in virtually all cases. While cyclic orthoesters of type 7 are likely intermediates in the formation of 6b and 6c, this point requires further elucidation. A number of examples are illustrated in the adjoining table; typical experimental procedures are described below.[11]

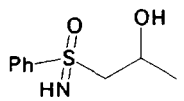
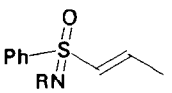
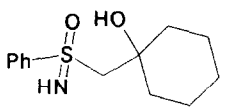
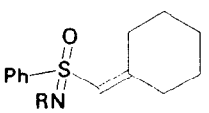
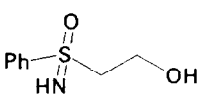
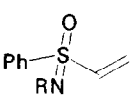
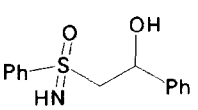
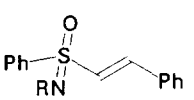
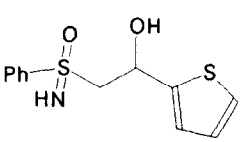
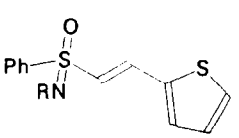
Method A (entry 1). Carbonyldiimidazole (1.94 g, 12 mmol) was added to a magnetically stirred solution of S-phenyl-S-(2-hydroxypropyl)sulfoximine (1.99 g, 10 mmol) in 10 mL of of toluene; moderate warming of the resulting mixture was observed. After 12 h at ambient temperature the mixture was diluted with water and extracted repeatedly with methylene chloride, which was dried over magnesium sulfate. Filtration, evaporation of solvents in vacuo and MPLC chromatography on silica gel with 1/1 EtOAc/CH_2Cl_2 as eluent afforded S-phenyl-S-(1-propenyl)sulfoximine (1.59 g, 88% yield) as a colorless oil consisting exclusively of the E isomer as judged by 400 MHz proton NMR.

Method B (entry 2). A solution of the above β-hydroxy sulfoximine (1.70 g, 8.5 mmol) in 10 mL of trimethyl orthoformate containing 16 mg (0.08 mmol) of p-toluenesulfonic acid was heated at 90°C for 2.5 h. Evaporation of solvents in vacuo and MPLC chromatography of the residue with 4/1 EtOAc/cyclohexane as eluent gave N-formyl-S-phenyl-S-(1-propenyl)sulfoximine (1.25 g, 71% yield) as a colorless oil consisting of a 12/1 mixture of E and Z isomers.

Method C (entry 3). A solution of the above β-hydroxy sulfoximine (1.89 g, 9.5 mmol) in 10 mL of trimethyl orthoacetate containing 25 mg (0.13 mmol) of p-toluenesulfonic acid was heated at 90°C for 0.5 h. Evaporation of solvents in vacuo and MPLC chromatography of the residue with neat EtOAc as eluent afforded N-acetyl-S-phenyl-S-(1-propenyl)sulfoximine (1.95 g, 92% yield) as a colorless oil consisting exclusively of the E isomer.



PREPARATION OF VINYL SULFOXIMINES FROM β-HYDROXYALKYL SULFOXIMINES

SM	PRODUCT	METHOD	YIELD[1]
		1. A (R=H)	88%[2]
		2. B (R=CHO)	71%[3]
		3. C (R=$COCH_3$)	92%[2]
		4. A (R=H)	66%
		5. B (R=CHO)	92%
		6. C (R=$COCH_3$)	96%
		7. C (R=$COCH_3$)	40%
		8. C (R=$COCH_3$)[4]	96%[2]
		9. C (R=$COCH_3$)	92%[2]

[1] AFTER CHROMATOGRAPHIC PURIFICATION [2] E ISOMER ONLY [3] E/Z: 12/1 [4] MP 120-121°C

In conclusion, we have described a facile preparation of previously unknown free and N-acylated vinyl sulfoximines. Their accessibility should extend considerably the range of compounds available for the study of vinyl sulfoximine reactivity.

References and Notes

1. Present address: Korea Research Institute of Chemical Technology, Daeduk-danji, South Korea.

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5. (a) C. R. Johnson, J. P. Lockard and E. R. Kennedy, J. Org. Chem., 1980, 45, 264; (b) C. R. Johnson and J. P. Lockard, Tetrahedron Lett., 1971, 22, 4589.

6. (a) R. Annunziata, M. Cinquini and S. Colonna, J. Chem. Soc., Perkin Trans. 1, 1980, 2422; (b) R. Annunziata and M. Cinquini, ibid., 1979, 1684.

7. S. Colonna and C. J. M. Stirling, J. Chem. Soc., Perkin Trans. 1, 1974, 2120.

8. I. Erdelmeier, H.-J. Gais and H. J. Lindner, Angew. Chem., Int. Ed. Engl., 1986, 25, 935.

9. K.-J. Hwang, E. W. Logusch, L. H. Brannigan and M. R. Thompson, J. Org. Chem., in press.

10. For an analogous cleavage of N-methyl sulfoximines, see: C. R. Johnson and J. R. Zeller, Tetrahedron, 1984, 40, 1225.

11. All compounds had spectral data consistent with assigned structures and gave satisfactory elemental analyses. ^{1}H NMR spectra were recorded in deuteriochloroform on Varian EM 360 (60 MHz) and XL 400 (400 MHz) spectrometers. Shifts reported as ppm downfield from tetramethylsilane. Entry 1: 1.85 (3H,dm,J=7), 2.85 (1H,broad m), 6.40 (1H,dm,J=15), 7.00 (1H,dq,J=15,7), 7.66 (3H,m), 8.00 (2H,m); analysis ($C_9H_{11}N_1O_1S_1$+0.08CH_2Cl_2): calculated, C 57.99, H 5.98; found, C 57.88, H 6.14. Entry 2: 1.97 (3H,dm,J=7), 6.40 (1H,dm,J=15), 7.00 (1H,dq,J=15,7), 7.56 (3H,m), 7.88 (2H,m), 8.56 (1H,s); analysis ($C_{10}H_{11}N_1O_2S_1$): calculated, C 57.40, H 5.30; found, C 57.34, H 5.52. Entry 3: 1.90 (3H,dm,J=7), 2.13 (3H,s), 6.40 (1H,dm,J=15), 7.00 (1H,dq,J=15,7), 7.66 (3H,m), 8.00 (2H,m); analysis ($C_{11}H_{13}N_1O_2S_1$+0.20H_2O): calculated, C 58.23, H 5.95, found, C 58.25, H 5.95.

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