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SHORT COMMUNICATIONS

New [2,3]-Sigmatropic Rearrangement of Allylsulfinylcarbanions

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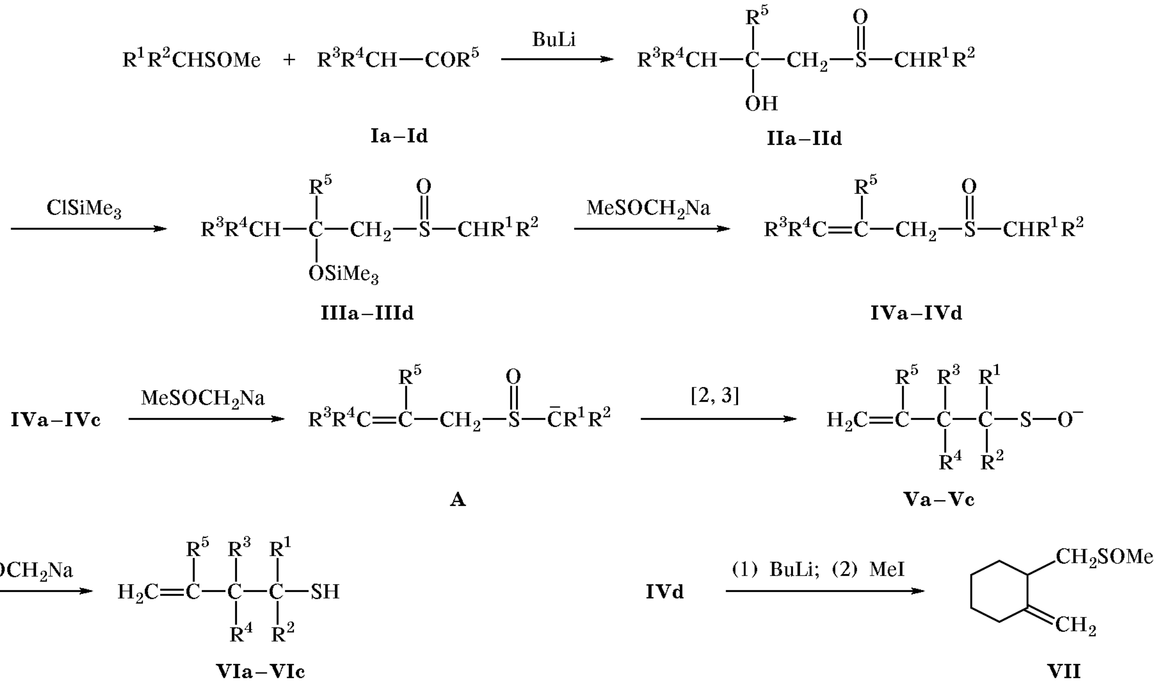
[2,3]-Sigmatropic rearrangements of unsaturated sulfoxides, in particular of aryl- or *tert*-butyl allyl sulfoxides [1], involve the oxygen atom and lead to formation of allyl alcohols. The activation barriers to such transformations are usually high [2], and the rearrangements require severe temperature conditions and removal of intermediate unsaturated alkanesulfenates from the reaction zone. Carbanionic rearrangements of alkyl allyl sulfoxides have not been studied previously.

We have found that carbonyl compounds **I** react with lithium derivatives of methyl butyl and methyl cyclohexyl sulfoxides to give β-hydroxy sulfoxides **II**. Treatment of the latter with chlorotrimethylsilane yields trimethylsilyl derivatives **III** whose reaction with dimethyl sulfoxide sodium salt under severe conditions (130°C, DMSO) involves new carbanionic [2,3]-sigmatropic rearrangement of allyl sulfoxides **IV** into sulfenates **V** and leads to formation of highly substituted previously inaccessible thiols **VI** [3] (Scheme 1).

[2,3]-Sigmatropic rearrangement of carbanion **A** [$R^1 = R^2 = R^4 = H$, $R^3R^5 = (CH_2)_4$] derived from sulfoxide **IVd** occurs under mild conditions (–78°C,

Scheme 1.



$R^1 = R^5 = H$, $R^2 = Pr$, $R^3 = R^4 = Me$ (**a**); $R^1 = R^4 = H$, $R^2 = Pr$, $R^3R^5 = (CH_2)_4$ (**b**); $R^1R^2 = (CH_2)_5$, $R^3 = R^4 = Me$, $R^5 = H$ (**c**); $R^1 = R^2 = R^4 = H$, $R^3R^5 = (CH_2)_4$ (**d**).

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butyllithium, THF/HMPA) and yields, after alkylation with methyl iodide, the corresponding γ-unsaturated sulfoxide **VII**.

Thiols VIa–VIc and sulfoxide VII. β-Hydroxy sulfoxides **IIa**–**IId** and their trimethylsilyl derivatives **IIIa**–**IIId** were synthesized by the procedure reported in [1]. Compounds **IIIa**–**IIIc** were brought into subsequent transformations without preliminary purification. A mixture of 24 mmol of NaH and 20 ml of anhydrous DMF was stirred for 5 min at 130°C, and a solution of 8 mmol of compound **IIIa**–**IIIc** in 5 ml of DMSO was added. The mixture was kept for 20 min, cooled, diluted with 50 ml water, and treated with methylene chloride. The extract was evaporated, and the residue was purified by column chromatography on silica gel using pentane as eluent.

A solution of sulfoxide **IVd** [4] in 8 ml of THF was cooled to –70°C, and a 1 N solution of butyllithium (3 mmol) in hexane was added. The mixture was kept for 1 h at room temperature, and 9 mmol of methyl iodide was added. The mixture was diluted with 5 ml of water and extracted with carbon tetrachloride. The extract was evaporated, and the residue was purified by column chromatography on silica gel using chloroform as eluent.

3,3-Dimethyl-1-heptene-4-thiol (VIa). Yield 58%. ^{1}H NMR spectrum, δ, ppm: 5.8 m (1H), 5.0 m (2H), 2.6 m (1H), 2.4 s (1H), 1.8–1.6 m (2H), 1.25 s (6H), 1.2–0.8 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 146.3, 113.2, 67.2, 53.6, 35.3, 24.4, 21.5, 13.7.

1-(2-Methylenecyclohexyl)butane-1-thiol (VIb). Yield 65%. ^{1}H NMR spectrum, δ, ppm: 4.8–4.5 m (2H), 2.8–2.2 m (3H), 2.1–0.9 m (15H). ^{13}C NMR spectrum (CDCl$_3$), δ_C, ppm: 150.3, 108.6, 54.4, 50.8, 38.8, 33.5, 29.2, 28.4, 22.3, 20.1, 13.7.

1-(1,1-Dimethyl-2-propenyl)cyclohexane-1-thiol (VIc). Yield 61%. ^{1}H NMR spectrum, δ, ppm: 5.7 m (1H), 5.2–4.7 m (2H), 2.4 s (1H), 2.1–1.2 m (10H), 1.12 s (6H). ^{13}C NMR spectrum, δ_C, ppm: 144.5, 113.2, 57.0, 44.5, 33.4, 25.9, 22.4, 22.3.

1-Methylsulfinylmethyl-2-methylenecyclohexane (VII) (a mixture of diastereoisomers, 62:38, GLC). Yield 97%. ^{1}H NMR spectrum, δ, ppm: 4.81 s, 4.77 s, 4.68 s, 4.64 s, 3.1–2.9 m, 2.8–2.6 m, 2.62 s, 2.60 s, 2.3–1.9 m, 1.8–1.3 m. ^{13}C NMR spectrum, δ, ppm: 150.6, 149.1, 107.7, 106.3, 58.6, 39.3, 39.0, 37.8, 37.3, 35.3, 34.4, 34.3, 32.9, 28.3, 28.2, 24.5, 24.1.

The ^{1}H and ^{13}C NMR spectra were measured on a Varian VXR-300 spectrometer at 300 and 75 MHz, respectively; TMS was used as internal reference.

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