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Reduction of Vinylogous Thioesters with Lithium Aluminum Hydride. I.[1] Reduction of β-Phenylthio-α,β-unsaturated Cyclic Ketones

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5,5,Dimethyl-3-phenoxy-2-cyclohexenone (Ib) was reduced with lithium aluminum hydride (LAH) to give the 1,2-addition product (IIIa). 2-Methyl-3-phenoxy-2-cyclopentenone (IIa) gave a mixture of the allyl alcohol (IVa) and 1,2-addition product (IVb). On the other hand, vinylogous thioesters, 5,5-dimethyl-3-phenylthio-2-cyclohexenone (Ic) and 2-methyl-3-phenylthio-2-cyclopentenone (IIb) were reduced in ether to give the corresponding 1,2-addition products. In tetrahydrofuran, the 1,2-addition product (IIIb) from Ic was further reduced to the 3-phenylthio alcohol (VIa). The product (IVa) from IIb transformed on standing at room temperature into the vinyl sulfide (VII) and the enone (VIII).

Keywords——vinylogous ester; vinylogous thioester; reduction; lithium aluminum hydride; β-phenoxy-α,β-unsaturated cyclic ketone; 3-phenylthio-2-cyclohexenone; 3-phenylthio-2-cyclopentenone; β-phenylthio-α,β-unsaturated cyclic ketone

We previously reported the reduction of various cyclic vinylogous esters (VE) with an excess of lithium aluminum hydride (LAH), and the results are summarized in Chart 1.[2] The difference of behavior of six- and five-membered VE toward LAH could be explained in terms of the hard and soft acids and bases (HSAB) principle.[3]

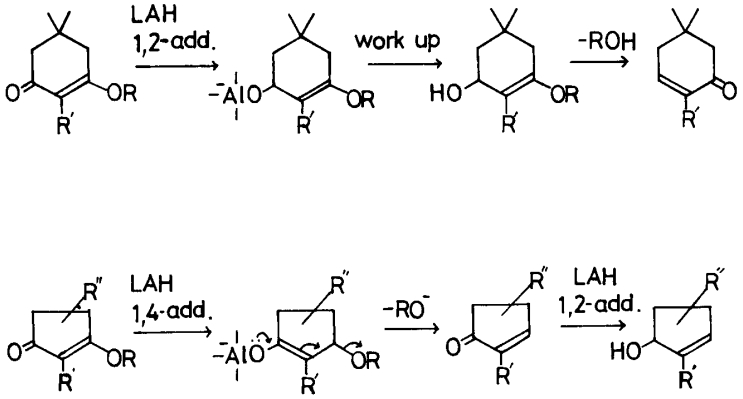


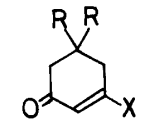
Chart 1

Based on this ground work, we have investigated the reduction of vinylogous thioesters (VTE) with LAH. Omote *et al.*[4] studied the reduction of various VTE with LAH and sodium borohydride, and reported that LAH attacked the carbonyl group in all cases. However, they did not use cyclic VTE as a substrate except for 3-ethylthio-2-cyclohexenone (Ia), which gave only 2-cyclohexenone in 35.5% yield upon reduction with LAH followed by treatment with concentrated hydrochloric acid.

In this paper we intend to report on the reduction of six- and five-membered β-

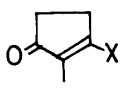
phenylthio-α,β-unsaturated ketones. First the reduction of phenyl cyclic VE, 5,5-dimethyl-3-phenoxy-2-cyclohexenone (Ib) and 2-methyl-3-phenoxy-2-cyclopentenone (IIa), was investigated. When Ib was reduced in ether or tetrahydrofuran (THF) with an excess of LAH followed by work-up with ammonium chloride–water, the product was 5,5-dimethyl-3-phenoxy-2-cyclohexenol (IIIa); this was subsequently treated with a catalytic amount of sulfuric acid in acetone to give 5,5-dimethyl-2-cyclohexenone (Id), as expected. On the other hand, IIa was treated successively with LAH and hydrochloric acid to give a mixture of 2-methyl-2-cyclopentenone (IIc) and 2-methyl-2-cyclopentenol (IVa) in the ratio of *ca.* 3 : 2 (see Experimental). The formation of IIc is attributable to 1,2-addition of LAH, and that of IVa is attributable to 1,4-addition followed by 1,2-addition of LAH. Thus Ib showed behavior similar to that of β-alkoxy cyclic enones,[2] but in the case of IIa the β-phenoxy group disturbed the 1,4-addition, and the 1,2-addition product was favored.

Thus, the reduction of Ic was carried out in ether and THF. In ether the product was 5,5-dimethyl-3-phenylthio-2-cyclohexenol (IIIb), which was subsequently treated with a catalytic amount of sulfuric acid to give 5,5-dimetyl-3-phenylthiocyclohexanone (V). The formation of V may be due to the Michael addition of thiophenol to Id which occurred in this reaction medium. When Id was treated with thiophenol under acidic conditions in acetone, it gave V in 65.7% yield.



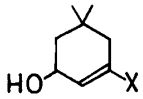
I

a: R=H, X=SEt
b: R=Me, X=OPh
c: R=Me, X=SPh
d: R=Me, X=H
e: R=Me, X=Br



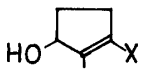
II

a: X=OPh
b: X=SPh
c: X=H
d: X=Br



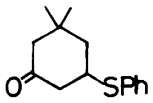
III

a: X=OPh
b: X=SPh

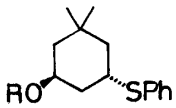


IV

a: X=H
b: X=OPh
c: X=SPh

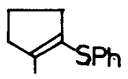


V

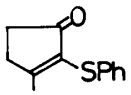


VI

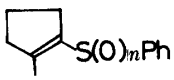
a: R=H
b: R=*p*-nitrobenzoyl



VII



VIII



IX

a: n=2
b: n=1

Chart 2

When the reduction of Ic was carried out in THF, the product was found to be 5,5-dimethyl-3-phenylthiocyclohexanol (VIa). From the coupling constants of the C_1- and C_3-protons, the hydroxy and phenylthio groups were concluded to be axial and equatorial, respectively. Compound VIa may be produced by intramolecular hydride attack from the C_1-axial O-aluminum hydride of IIIb at the C_3-position. The different reduction behavior of Ic in ether and THF may be explicable in terms of the different solubilities of a complex derived from IIIb and aluminum hydride, but further studies are required to confirm this.

Next a five-membered VTE, IIb, was reduced in ether. From the spectral data (see Experimental), the product was suggested to be 2-methyl-3-phenylthio-2-cyclopentenol (IVc). Thus the five-membered VTE, IIb, was found to give only the 1,2-addition product in contrast to the five-membered VE. The difference in the mode of addition of LAH must be due to differences in the electronic or steric character of oxygen and sulfur atoms. Compound IVc

was unstable and gradually changed on standing at room temperature to yield mainly two compounds, 2-methyl-1-phenylthiocyclopentene (VII) and 3-methyl-2-phenylthio-2-cyclopentenone (VIII), whose structures were assigned on the basis of spectroscopic evidence (see Experimental).

Experimental

All melting points and boiling points are uncorrected. Infrared (IR) spectra were determined by using a JASCO IRA-1 diffraction grating spectrophotometer; absorption data are given in cm^{-1}. Ultraviolet (UV) spectra were obtained in MeOH with a Hitachi 200—10 or 220 spectrophotometer, and absorption maxima are given in nm. Gas chromatography (GC) was carried out using a Shimadzu GC-6AM instrument with a stainless steel column packed with 5% SE-30. The velocity of N_2 gas flow was 40 ml/min. Mass spectra (MS) were measured with a JEOL D-200 (70 eV, direct inlet system) spectrometer. GC-MS were taken with a JEOL D-300 instrument. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL PMX-60, Varian EM-360, and Varian XL-200 spectrometers with tetramethylsilane as an internal standard. The chemical shifts, coupling constants (J), and half-width ($W_{1/2\,h}$) values are given in δ, Hz, and Hz, respectively. All solvents were removed by evaporation under reduced pressure after drying of the solution over anhyd. Na_2SO_4.

5,5-Dimethyl-3-phenoxy-2-cyclohexenone (Ib)——3-Bromo-5,5-dimethyl-2-cyclohexenone[5] (Ie, 11.7 g, 57.6 mmol) was added to an ethanolic mixture of phenol (5.43 g, 57.8 mmol) and NaOH (3 g, 75.0 mmol) with ice-cooling. After being stirred overnight at room temperature (r.t.), the mixture was diluted with water and extracted with Et_2O. The organic layer was washed with brine, dried and evaporated to give a residue, which crystallized on cooling. The product was recrystallized from Et_2O–hexane. 4.5 g (36.2%). mp 76—77 °C (lit.[6] mp 80—82 °C). IR (Nujol): $\nu_{C=O}$1650, $\nu_{C=C}$1610. NMR (CCl_4): 1.16 (6H, s), 2.11 and 2.45 (each 2H, s), 4.94 (1H, s), 6.7—7.6 (5H, m). *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.18; H, 7.53.

5,5-Dimethyl-3-phenylthio-2-cyclohexenone (Ic)——Ie (5.35 g, 26.3 mmol) was added to an ethanolic mixture of PhSH (2.9 g, 26.3 mmol) and NaOH (1.37 g, 34.2 mmol) with ice-cooling. After being stirred for 39 h at r.t., the mixture was diluted with water and extracted with benzene. The organic layer was washed with 5% NaOH and brine, then dried. Ie (0.54 g, 10.1%) was recovered by distillation (4 mmHg) of the residue obtained after removal of the solvent. Ic was crystallized and recrystallized from hexane. mp 47—48 °C (lit.[7] mp 50—51 °C). IR (Nujol): $\nu_{C=O}$1650, $\nu_{C=C}$1575. NMR (CCl_4): 1.12 (6H, s), 2.10 and 2.32 (each 2H, s), 5.30 (1H, s), 7.31 (5H, s). *Anal.* Calcd for $C_{14}H_{16}OS$: C, 72.41; H, 6.90. Found: C, 72.15; H, 6.89.

3-Bromo-2-methyl-2-cyclopentenone (IId)——A $CHCl_3$ solution of PBr_3 (29 g, 107 mmol) was added to a suspension of 2-methylcyclopentane-1,3-dione (4.02 g, 35.8 mmol) in $CHCl_3$. The mixture was refluxed for 1 d and then poured into ice-water. The organic layer was washed with 10% NaOH and brine. Crude IId was obtained after removal of the solvent. 4.3 g (68.5%). GC (100 °C), t_R 4.0 min. NMR ($CDCl_3$): 1.76 (3H, t, J=2, C_2–CH_3), 2.3—2.6 (2H, m), 2.7—3.1 (2H, m).

2-Methyl-3-phenoxy-2-cyclopentenone (IIa)——IId (2.49 g, 14.2 mmol) was added to a homogeneous ethanolic soln. of PhOH (1.35 g, 14.3 mmol) and NaOH (0.77 g, 19 mmol) with stirring under ice-cooling. After being stirred for 14 h at r.t., the mixture was poured into ice-water. The Et_2O extract was washed with brine, dried and concentrated to give IIa as colorless plates, 2.05 g (76.5%), which were recrystallized from hexane–Et_2O. mp 91.5—92 °C. IR (Nujol): $\nu_{C=O}$1680, $\nu_{C=C}$1640. NMR (CCl_4): 1.57 (3H, t, J=1.9, C_2–CH_3), 2.39 (4H, s), 6.9—7.6 (5H, m). *Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.23; H, 6.22.

Reduction of Ib——a) Using Et_2O as a Solvent: An Et_2O soln. (10 ml) of Ib (0.5 g, 2.3 mmol) was added to a suspension of LAH (0.5 g, 13.2 mmol) in Et_2O (40 ml) under an Ar atmosphere with ice-cooling. After being stirred at r.t. for 0.5 h, the mixture was refluxed for 1.5 h. NH_4Cl (3.5 g, 65.4 mmol) and then H_2O were added to the mixture to decompose the complex. The filtrate was concentrated to give 5,5-dimethyl-3-phenoxy-2-cyclohexenol (IIIa). NMR (CCl_4): 0.93 and 1.00 (each 3H, s), 3.9—4.4 (1H, br s, $W_{1/2\,h}$=14, C_1-H), 4.69 (1H, br s, $W_{1/2\,h}$=6, C_2-H), 6.6—7.3 (5H, m). This product was dissolved in a mixture of 10% H_2SO_4 (0.5 ml) and acetone (10 ml), and refluxed for 2 h. The mixture was diluted with ice-water and extracted with Et_2O. The organic layer was washed with 5% NaOH and brine, and dried. The material obtained after removal of the solvent was pure 5,5-dimethyl-2-cyclohexenone (Id) as judged from the NMR spectrum. 0.2 g (70.1% from Ib). NMR (CCl_4): 1.07 (6H, s), 2.19 (4H, s), 5.90 (1H, dt, J=10.5, 2.0, C_2-H), 6.70 (1H, dt, J=10.5, 4.5, C_3-H). Id was identified by comparison with an authentic sample.[2] The conversion of IIIa to Id was also observed upon addition of trifluoroacetic acid (1 drop) to a CCl_4 soln. of IIIa in an NMR tube.

b) Using THF as a Solvent: In a manner similar to that described in a), but with THF instead of Et_2O as a solvent, Id was obtained in a yield of 55.4%.

Reduction of IIa——An Et_2O soln. of IIa (0.3 g, 1.6 mmol) was added to a suspension of LAH (0.35 g, 9.2 mmol) in Et_2O with ice-cooling. After being stirred at r.t. for 30 min, the mixture was refluxed for 1.5 h, and then worked up as usual using NH_4Cl (2.5 g, 46 mmol) to give a mixture containing 2-methyl-2-cyclopentenol (IVa) and 2-methyl-3-

phenoxy-2-cyclopentenol (IVb) in the ratio of *ca.* 1 : 2. NMR (CCl_4): 1.6 (1.5H, nearly s, C_2-Me of IVa), 1.85 (3H, s, C_2-Me of IVb), 4.55 (0.5H, br s, $W_{1/2\,h}=14$, C_1-H of IVa), 5.03 (1H, br s, $W_{1/2\,h}=14$, C_1-H of IVb), 5.60 (0.5H, br s, $W_{1/2\,h}=7$, C_3-H of IVa). Next, 5% HCl (2 ml) was added to an acetone soln. (10 ml) of the mixture (200 mg) of IVa and IVb. The mixture was warmed on a water bath at 40 °C for 5 min, and then diluted with Et_2O. The Et_2O soln. was washed with 5% NaOH and brine. The residue (91 mg) obtained after removal of the solvent consisted of IVa and 2-methyl-2-cyclopentenone (IIc) in a ratio of *ca.* 2 : 3. NMR (CCl_4): 1.70 (s), 4.43 (br s, $W_{1/2\,h}=14$, C_1-H of IVa), 5.36 (br s, $W_{1/2\,h}=6.5$, C_3-H of IVa), 7.30 (br s, $W_{1/2\,h}=9$, C_3-H of IIc). An aq. soln (10 ml) of CrO_3 (81 mg, 0.8 mmol) and conc. H_2SO_4 (2 drops) was added to an acetone soln. (10 ml) of the mixture of IVa and IIc with stirring and ice-cooling. After being stirred at r.t. for 2 h, the reaction mixture was poured into ice-water and extracted with $CHCl_3$. The NMR spectrum of the residue (42.2 mg) was consistent with that of IIc.[8] IIc-2,4-dinitrophenylhydrazone (DNPH): mp 198—201 °C (from EtOH, lit.[9] mp 219—220 °C). Ms *m/e*: 276 (M^+, base peak).

Reduction of Ic——a) Using Et_2O as a Solvent: An Et_2O soln. of Ic (0.3 g, 1.3 mmol) was added to a suspension of LAH (0.3 g, 7.9 mmol) in Et_2O at r.t. during 30 min. The mixture was refluxed for 1 h. The complex was destroyed by adding sat. NH_4Cl soln. and the filtrate was dried and evaporated to give crude 5,5-dimethyl-3-phenylthio-2-cyclohexenol (IIIb). 0.34 g. IR (neat): ν_{OH}3370, $\nu_{C=C}$1635, 1590. NMR (CCl_4): 0.84 and 0.91 (each 3H, s), 3.21 (1H, br s, OH), 3.9—4.4 (1H, m, $W_{1/2\,h}=15$, C_1-H), 5.75 (1H, br s, $W_{1/2\,h}=7$, C_2-H). MS *m/e*: 217 (M^+-OH, base peak). Next, 10% H_2SO_4 (0.5 ml) was added to an acetone soln. of crude IIIb (0.1 g), and the mixture was refluxed for 1 h. The residue obtained after concentration was dissolved in Et_2O and the organic layer was washed with 5% NaOH and brine. The product was purified by SiO_2 column chromatography. 5,5-Dimethyl-3-phenylthiocyclohexanone (V) was eluted with benzene. 33 mg. Oil. IR (neat): 2970—2810, 1704. NMR (CCl_4): 0.89 and 1.05 (each 3H, s), 1.2—2.8 (6H, m), 3.36 (1H, tt, $J=11$, 5, C_3-H), 7.24 (5H, s). V-2,4-DNPH: mp 173—175 °C (from EtOH). *Anal.* Calcd for $C_{20}H_{22}N_4O_4S$: C, 57.96; H, 5.35; N, 13.52. Found: C, 57.74; H, 5.27; N, 13.35. A mixture of Id (102.6 mg, 0.83 mmol), PhSH (91 mg, 0.83 mmol), conc. H_2SO_4 (0.1 ml), and acetone (*ca.* 10 ml) was refluxed for 1.5 h, then concentrated. The residue was diluted with Et_2O. The organic layer was washed with 5% NaOH, and brine, then evaporated to give an oily residue, which was fractionated through an SiO_2 column. The material obtained from the benzene fraction was identified as V by comparison of the physical data with those of an authentic sample. 127 mg (65.7%).

b) Using THF as a Solvent: A THF soln. of Ic (1 g, 4.3 mmol) was added to a suspension of LAH (0.5 g, 13.2 mmol) in THF at r.t. The mixture was refluxed for 3 h, then NH_4Cl (3.5 g, 65.4 ml) and water were added to destroy the complex. The filtrate was concentrated to give 5,5-dimthyl-3-phenylthiocyclohexanol (VIa, 0.8 g, 78.7%). Oil. GC (250 °C), t_R: 5.3 min (*cf.*, Ic: 6.3 min). NMR (CCl_4): 0.94 and 1.14 (each 3H, s), 3.65 (1H, tt, $J=10.5$, 4.5, C_3-H), 4.22 (1H, t, $J=4$, C_1-H), 7.35 (5H, d like). VIa was benzoylated with *p*-nitrobenzoyl chloride (1.2 mol eq) in pyridine to give VIa-*p*-nitrobenzoate (VIb), mp 93.5—95.5 °C (from Et_2O–hexane). NMR ($CDCl_3$): 1.00 and 1.17 (each 3H, s), 1.2—2.5 (6H, m), 3.62 (1H, tt, $J=12$, 4, C_3-H), 5.49 (1H, t, $J=4$, C_1-H), 7.2—7.5 (5H, m, PhS), 8.24 and 8.37 (each 2H, d, $J=9$). *Anal.* Calcd for $C_{21}H_{23}NO_4S$: C, 65.45; H, 5.97; N, 3.64. Found: C, 65.53; H, 5.81; N, 3.39.

2-Methyl-3-phenylthio-2-cyclopentenone (IIb)——IId (4.17 g, 23.8 mmol) was added to an aq. mixture of PhSH (2.62 g, 23.8 mmol) and NaOH (1.24 g, 31 mmol) under stirring with ice-cooling. The material that precipitated during overnight stirring was filtered off and recrystallized from aq. EtOH. 3.79 g (78.0%). mp 99—101 °C. GC (200 °C), t_R: 4.5 min. MS *m/e*: 204 (M^+, base peak). IR (Nujol): $\nu_{C=O}$1680, $\nu_{C=C}$ 1595. NMR (CCl_4): 1.76 (3H, nearly s, C_2-Me), 2.27 (4H, s), 7.2—7.7 (5H, m). *Anal.* Calcd for $C_{12}H_{12}OS$: C, 70.55; H, 5.92. Found: C, 70.31; H, 5.86.

2,4-DNPH: mp 215—216 °C. *Anal.* Calcd for $C_{18}H_{16}N_4O_4S$: C, 56.23; H, 4.20; N, 14.58. Found: C, 55.99; H, 4.12; N, 14.37. MS *m/e*: 384 (M^+, base peak).

Reduction of IIb——IIb (281.7 mg, 1.38 mmol) was reduced in the usual way in Et_2O with LAH (309 mg, 8.14 mmol) for 13 h at r.t. The ether layer obtained after work-up with NH_4Cl (2.14 g, 40.0 mmol) was concentrated to give 2-methyl-3-phenylthio-2-cyclopentenol (IVc) as an oily residue. 244.4 mg. GC (200 °C), t_R: 1.8 min. IR (neat): 3480, 1585. NMR (CCl_4): 1.2—2.7 (4H, m), 1.85 (3H, s), 3.7 (1H, br s, –OH), 4.6 (br s, $W_{1/2\,h}=13$, C_1-H), 7.3 (5H, nearly s). MS *m/e* (%): 206 (M^+, 62), 188 (M^+-H_2O, 40), 97 (M^+-SPh, base peak). IVc (226.4 mg) was left to stand for 5 d at r.t., yielding mainly two products as determined by GC. The products were fractionated through an SiO_2 column. 2-Methyl-phenylthiocyclopentene (VII, 81 mg) and 3-methyl-2-phenylthio-2-cyclopentenone (VIII, 120 mg) were eluted with benzene and $CHCl_3$, respectively.

VII: IR (neat): 1580. GC (200 °C), t_R 1.9 min. NMR (CCl_4): 1.1—1.6 (2H, m), 1.86 (3H, br s), 2.1—2.7 (4H, m), 7.07 (5H, s). MS *m/e*: 190 (M^+, base peak), 81 (M^+-SPh).

VIII: IR (neat): 1710. GC (200 °C), t_R: 4.3 min. NMR ($CDCl_3$): 2.25 (3H, s), 2.43 and 2.65 (each 2H, A_2B_2 type, $J=4.5$), 7.23 (5H, s), MS *m/e* (%): 204 (M^+, base peak), 109 (PhS^+, 14.6).

VIII-2,4-DNPH: mp 162 °C (recrystallized from EtOH). MS *m/e* (%): 384 (M^+, 56.9), 202 ($C_{12}H_{12}SN^+$, base peak). *Anal.* Calcd for $C_{18}H_{16}N_4O_4S$: C, 56.23; H, 4.20; N, 14.58. Found: C, 56.23; H, 4.17; N, 14.23.

Oxidation of VII with *m*-Chloroperbenzoic Acid (mCPBA)——mCPBA (138.4 mg, 0.8 mmol) was added to a $CHCl_3$ soln. of VII (125.7 mg, 0.66 mmol) with stirring under ice-cooling, and the mixture was stirred for a further 45 min. After being washed with sat. $NaHCO_3$ and brine, the organic layer was dried and concentrated to give an oily residue, 155 mg, which was fractionated through an SiO_2 column. 2-Methyl-1-phenylsulfonylcyclopentene (IXa, 31.7 mg, 21.0%) and 2-methyl-1-phenylsulfinylcyclopentene (IXb, 33.3 mg, 24.1%) were eluted with 10% Et_2O–

hexane and Et_2O, respectively.

IXa: mp 49—51 °C (recrystallized from hexane). IR (Nujol): ν_{SO}1150. NMR (CCl_4): 1.5—2.1 (2H, m), 2.12 (3H, s), 2.3—2.8 (4H, m), 7.2—8.0 (5H, m). MS *m/e* (%): 222 (M^+, 78), 79 ($M^+ - PhSO_2H_2$, base peak). *Anal.* Calcd for $C_{12}H_{14}O_2S$: C, 64.86; H, 6.35. Found: C, 64.77; H, 6.34. GC (200 °C), t_R: 4.6 min.

IXb: Oil (microdistilled), bp < 150 °C (2 mmHg). IR (neat): ν_{SO}1020, 1040. NMR (CCl_4): 1.6—2.1 (2H, m), 2.20 (3H, s), 2.3—2.9 (4H, m), 7.1—8.1 (5H, m). MS *m/e* (%): 206 (M^+, 32), 190 ($M^+ - O$, 47), 110 (86), 55 (base peak). *Anal.* Calcd for $C_{12}H_{14}OS \cdot 2/5\ H_2O$: C, 67.51; H, 6.80. Found: C, 67.47; H, 6.65. GC (200 °C), t_R: 4.2 min.

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References and Notes

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