An unusually easy [1,3]-migration of the PhS group in 3-methyl-4-phenylthiohept-2-en-1-ols

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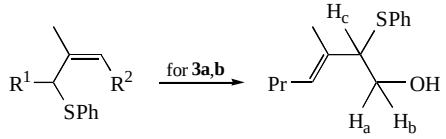
Hydride reduction of the 2(*Z*)- and 2(*E*)-isomers of methyl and *tert*-butyl 3-methyl-4-phenylthioheptenoates under standard conditions is accompanied by [1,3]-migration of the PhS group and in both cases (*E*)-3-methyl-2-phenylthiohept-3-en-1-ol **5** is produced, whose structure is confirmed by spectroscopic methods, instead of the expected (*Z*)-3-methyl-4-phenylthiohept-2- **3a** and (*E*)-2-enol **3b**; compounds **3a**,**b** obtained under specially developed conditions undergo isomerisation to compound **5** during chromatography on SiO_2 or on storage in the light of their solutions in $CDCl_3$ or in C_6D_6.

In a series of papers dealing with the mechanism and stereochemistry of [1,3]-migration of the PhS group in allyl sulfides, Warren *et al.* showed that this reaction readily occurs in compounds **1** with a C=C terminal bond, but does not occur in compounds **2** with an internal C=C bond (see *e.g.* ref. 1).



5

1 R^1 = Alk, R^2 = H
2 R^1 = Alk, R^2 = Alk^1
3a 2(*Z*), R^1 = Pr, R^2 = CH_2OH
3b 2(*E*), R^1 = Pr, R^2 = CH_2OH
4a 2(*Z*), R^1 = Pr, R^2 = COOR
4b 2(*E*), R^1 = Pr, R^2 = COOR
(R = Me, Bu^t)

On the contrary, we observed a very readily occurring [1,3]-migration of the PhS group in compounds **3** with functionalised substituents R^2. For example, hydride reduction of esters **4a**,**b**, (**4a** is a key intermediate in the synthesis of the sex pheromone of *Callosobruchus analis* beetles),[2] under standard conditions is accompanied by [1,3]-migration of the PhS group to give alcohol **5** in both cases, instead of the expected alcohols **3a**,**b**, respectively. The structure of compound **5** was confirmed by spectroscopic methods.

Specifically, the mass spectrum of compound **5** contains a molecular ion peak with *m*/*z* 236, and its IR spectrum contains an OH group absorption band (3600 cm^{-1}). The ^1H NMR spectrum recorded on a Bruker DRX-500 spectrometer in $CDCl_3$ contains two one-proton doublets of triplets (δ 1.96 and 1.97) for the allyl CH_2 group, while the signals of the CH_2OH and CHSPh group protons are observed as a strongly coupled ABC group at δ 3.72–3.77. An iterative computation of the spectrum with the CALM program,† made it possible to determine (RMS = 0.083) the following parameters for this part of the spectrum: δ_a = 3.762, δ_b = 3.723, δ_c = 3.728, J_{AB} = –11.4 Hz, J_{AC} = 7.29 Hz, J_{BC} = 7.00 Hz. The configuration of compound **5** was confirmed by NOE spectra obtained by the NOESY method, which showed the spatial proximity of the methyl group at the C-3 atom with the protons at C-5, as well as the proximity of the vinyl proton at C-4 with protons at C-1 and C-2, which is possible only if compound **5** has the 3(*E*)-configuration.

A thorough development of conditions for the reduction of compounds **4a**,**b** made it possible to obtain individual alcohols **3a**,**b**,[2] which can be stored unchanged for one month, in the native state or as ethereal solutions, at 4–5 °C in a light-protected vessel. In the light at *ca.* 20 °C, 40% of compound **3a** dissolved in $CDCl_3$ isomerises into compound **5**. The same degree of isomerisation of compound **3a** dissolved in C_6D_6 is reached in 24 h. After a solution of compound **3a** in $CDCl_3$ had been stored for 1 week at *ca.* 20 °C, its ^1H NMR spectrum contained only signals of compound **5**. Similarly, 20% of compound **3b** was converted into **5** at *ca.* 20 °C after 24 h in a C_6D_6 solution, and 40% was converted in a $CDCl_3$ solution.‡

Flash chromatography of compound **3a** on Silpearl grade SiO_2 is also accompanied by [1,3]-migration of the PhS group to give a mixture of compounds **3a**:**3b**:**5** in the ratio 1:1.6:7 (^1H NMR spectroscopic data).

It should be noted that the [1,3]-migration of the PhS group reported here has hardly ever been observed for **3a**,**b** analogues with R^1 = $Me_2C{=}CH(CH_2)_2CMe{=}CHCH_2$ (Ner).[3]

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† CALM, small venture 'Rezonans', Moscow, 1993, carried out by Yu. A. Strelenko.

‡ The rate of isomerisation of compounds **3a**,**b** depends on the specimen of $CDCl_3$ and C_6D_6 used.