

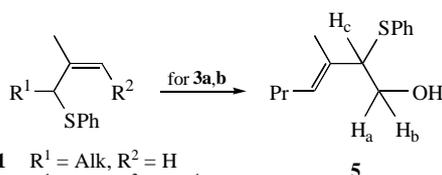
An unusually easy [1,3]-migration of the PhS group in 3-methyl-4-phenylthiohept-2-en-1-ols

Natal'ya Ya. Grigor'eva,* Paata G. Tsiklauri and Aleksei V. Buevich

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.
Fax: +7 095 135 5328; e-mail: gny@cacr.ioc.ac.ru

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 SiO₂ or on storage in the light of their solutions in CDCl₃ or in C₆D₆.

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).



- 1** R¹ = Alk, R² = H
2 R¹ = Alk, R² = Alk¹
3a 2(*Z*), R¹ = Pr, R² = CH₂OH
3b 2(*E*), R¹ = Pr, R² = CH₂OH
4a 2(*Z*), R¹ = Pr, R² = COOR
4b 2(*E*), R¹ = Pr, R² = COOR
 (R = Me, Bu¹)

On the contrary, we observed a very readily occurring [1,3]-migration of the PhS group in compounds **3** with functionalised substituents R². 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 CDCl₃ contains two one-proton doublets of triplets (δ 1.96 and 1.97) for the allyl CH₂ group, while the signals of the CH₂OH 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 CDCl₃ isomerises into compound **5**. The same degree of isomerisation of compound **3a** dissolved in

C₆D₆ is reached in 24 h. After a solution of compound **3a** in CDCl₃ 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 C₆D₆ solution, and 40% was converted in a CDCl₃ solution.[‡]

Flash chromatography of compound **3a** on Silpearl grade SiO₂ 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 R¹ = Me₂C=CH(CH₂)₂CMe=CHCH₂ (Ner).³

The authors are grateful to the Russian Foundation for Basic Research (grant no. 94-03-08904), the State Foundation for the Support of Leading Scientific Schools and the International Science Foundation (grant no. NGO 000) for the financial support of this study, and to Yu. A. Strelenko for the CALM program.

References

- P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2125.
- N. Ya. Grigor'eva, P. G. Tsiklauri, O. A. Pinsker and A. V. Buevich, *Izv. Akad. Nauk, Ser. Khim.*, 1998 (in press).
- N. Ya. Grigor'eva, O. A. Pinsker and A. M. Moiseyenko, *Mendeleev Commun.*, 1994, 129.

Received: Moscow, 5th January 1998

Cambridge, 11th February 1998; Com. 8/004741

[†] 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 CDCl₃ and C₆D₆ used.