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FORMATION OF 4-METHYLTHIO-2-PHENYL-1-BUTENE DERIVATIVES BY THE REACTION OF β-HYDROXY-β-PHENYLSULFONIUM SALT WITH BASE

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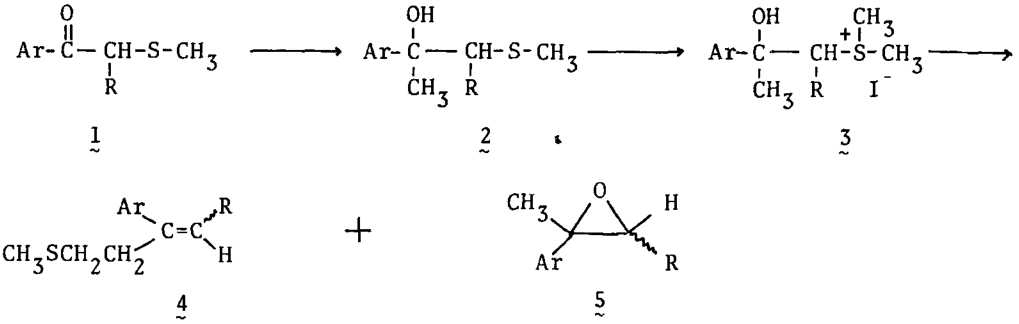
β-Hydroxysulfonium salt and related compounds, most often prepared by condensation of nucleophilic alkylidene sulfur reagent with ketones, have been proposed as efficient intermediates for synthesis of oxirans[1,2,3]. During the investigation of an alternative general synthetic method for oxirans starting from α-sulfenylated ketones through β-hydroxysulfonium intermediates[4], we found a formation of 4-methylthio-2-phenyl-1-butene derivatives on treatment of β-hydroxy-β-phenylsulfonium iodides with base as abnormal products, without formation of the usually expected oxirans in some cases, or together with oxirans. We wish to report these results in this paper.

β-Hydroxy-β-phenylsulfonium iodides (3) were prepared by the Grignard reaction of the α-sulfenylated ketones (1)[5] with methylmagnesium bromide, followed by the S-methylation of β-hydroxy sulfides (2) with methyl iodide in MeOH under reflux as outlined in the following scheme. The sulfonium iodide (3a) was treated with t-BuOK in DMSO at room temperature for 3 hr to give 2-(3,4-dimethoxy)-phenyl-4-methylthio-1-butene (4a) in 60 % yield without formation of the expected styrene oxide (5a). In this way, the 2-(4-methoxy)phenyl-1-butene (4b) was



a: Ar=3,4-$(CH_3O)_2C_6H_3$-, R=H; b: Ar=4-$(CH_3O)C_6H_4$-, R=H;

c: Ar=4-$(CH_3O)C_6H_4$-, R=CH_3; d: Ar=4-$(CH_3)C_6H_4$-, R=H;

e: Ar=4-$(CH_3)C_6H_4$-, R=CH_3; f: Ar=C_6H_5-, R=CH_3;

obtained in 45 % yield. Furthermore, **3c**-**3f** were also treated with *t*-BuOK to give two kinds of products (**4c**: 23 %)[6], (**4d**: 19 %), (**4e**: 10 %)[6], (**4f**: 6 %)[6] and the usually expected oxirans (**5c**: 30 %; *trans*/*cis*=3:2), (**5d**: 45 %), (**5e**: 45 %; *trans*/*cis*=2:1), (**5f**: 50 %; *trans*/*cis*=2:1), respectively[7]. Thus, the yield of **4** was found to vary with the electronic effect of the substituent on the benzene ring. The NMR (CCl_4) spectra were listed in Table 1. It is apparent that **4** was formed through dehydration of **3**, followed by concomitant [2,3] sigmatropic rearrangement of S-ylide intermediates (**6**) as shown in the following scheme.

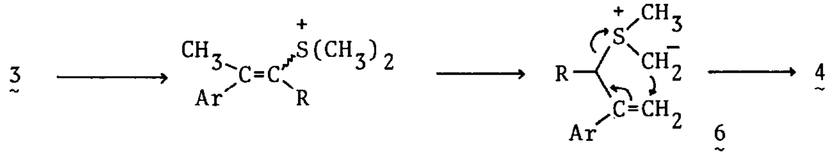


Table 1. NMR (CCl_4) spectra of **4**[8]

Compound	ppm
4a	2.02 (SCH_3), 2.25-2.81 (CH_2-CH_2), 3.75 (OCH_3), 3.85 (OCH_3), 4.93 (C=CH, d, J=2 Hz), 5.13 (C=CH, d, J=2 Hz), 6.55-6.88 (Ar-H)
4b	2.03 (SCH_3), 2.39-2.83 (CH_2-CH_2), 3.71 (OCH_3), 4.96 (C=CH, d, J=2 Hz), 5.18 (C=CH, d, J=2 Hz), 6.72, 7.23 (Ar-H, each d, J=8 Hz)
4c	1.78 (CH_3, d, J=7 Hz), 2.02 (SCH_3), 2.2-2.93 (CH_2-CH_2), 3.70 (OCH_3), 5.63 (C=CH, q, J=7 Hz), 6.72, 7.12 (Ar-H, each d, J=9 Hz)
4d	2.01 (SCH_3), 2.3 (Ar-CH_3), 2.4-2.87 (CH_2-CH_2), 4.98 (C=CH, d, J=2 Hz) 5.18 (C=CH, d, J=2 Hz), 7.00, 7.18 (Ar-H, each d, J=8 Hz)
4e	1.80 (CH_3, d, J=7 Hz), 2.01 (SCH_3), 2.28 (Ar-CH_3), 2.32-2.80 (CH_2-CH_2), 5.65(=CH, q, J=7 Hz), 6.98, 7.10 (Ar-H, each d, J=8 Hz)
4f	1.81 (CH_3, d, J=7 Hz), 2.02 (SCH_3), 2.25-2.92 (CH_2-CH_2), 5.70 (C=CH, q, J=7 Hz), 7.25 (Ar-H)

References and Footnotes

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6. The geometry of the double bond was not determined.
7. Although separation of **4** from the mixture was easily achieved by column chromatography on silica gel using benzene-hexane (1:1), the oxirans (**5c**-**5f**) were not obtained as a pure state. The ratio of *trans*/*cis* was determined based on methyl signals appeared in their NMR (CCl_4) spectra.
8. All compounds gave satisfactory high resolution mass spectral data.

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