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Simple Synthesis and the Diels-Alder Reaction of 3-(*p*-Tolylthio)-2-(trimethylsilyloxy)-1,3-butadiene

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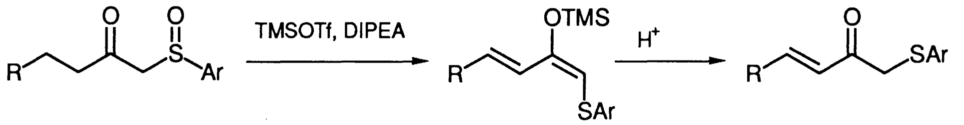
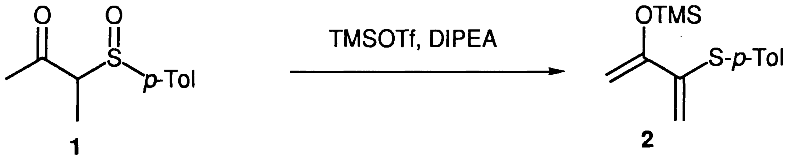
The reaction of 3-(*p*-tolylsulfinyl)-2-butanone with trimethylsilyl trifluoromethanesulfonate in the presence of diisopropylethylamine gave 3-(*p*-tolylthio)-2-(trimethylsilyloxy)-1,3-butadiene (**2**) quantitatively. The Diels-Alder reactions of **2** and the related dienes with methyl acrylate were studied.

We have recently reported a new transformation of ß-keto sulfoxides into γ,δ-unsaturated β-keto sulfide derivatives via 1-arylthio-2-(trimethylsilyloxy)-1,3-diene derivatives (Eq 1).[1] The novel mechanistic feature of this reaction involves the first example of remote participation of the sulfinyl moiety beyond the ß-carbonyl group. We now describe an extension of the method to an α-methyl substituted β-keto sulfoxide, which provides a simple access to a synthetically useful 2,3-heteroatom-disubstituted 1,3-diene.



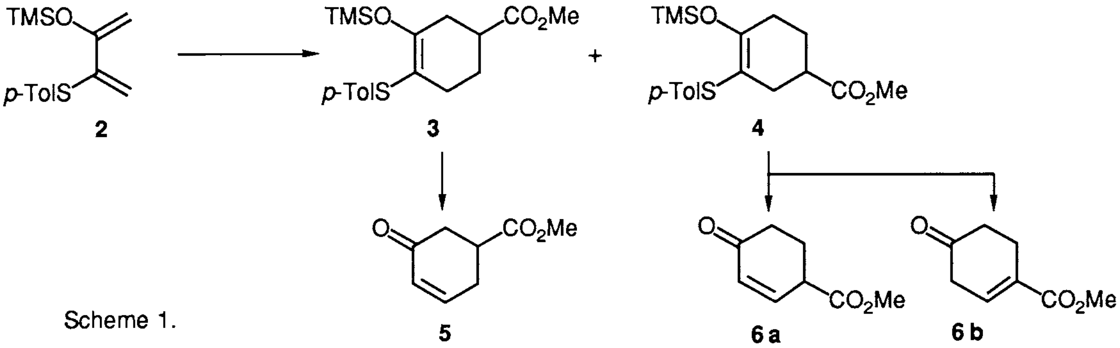
(1)

3-(*p*-Tolylsulfinyl)-2-butanone (**1**)[2] was treated with trimethylsilyl trifluoromethanesulfonate (3 equiv.) and diisopropylethylamine (DIPEA) (4 equiv.) in dichloromethane at 0 °C for 0.5 h. The aqueous alkaline work-up gave the quantitative yield of 3-(*p*-tolylthio)-2-(trimethysilyloxy)-1,3-butadiene (**2**)[3] which could be distilled and stored in a refrigerator for a few weeks. This simple but hitherto unknown diene **2** may not be obtained from the parent ketone, 3-arylthio-3-buten-2-one because it is known to be considerably unstable and to undergo dimerization.[4] Thus, the present method offers an easy access to this type of silyl enol ethers.



(2)

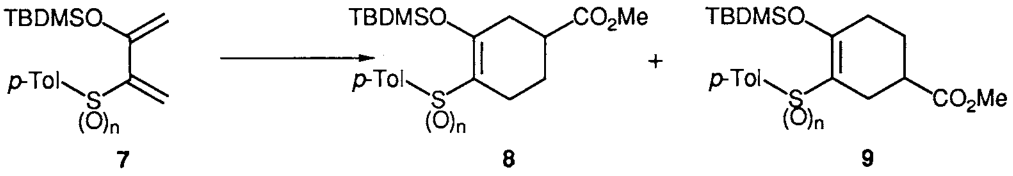
As a preliminary study, the reactivity of the 2,3-heteroatom-disubstituted diene as a partner in the Diels-Alder cycloaddition was investigated. Treatment of **2** with excess methyl acrylate at 80 °C for 8 h afforded the Diels-Alder cycloadducts **3** and **4** (77% combined yield) along with the hydrolyzed products (9%). The ratio of the regioisomeric adducts (**3** and **4**) was determined to be 72 : 28 on the basis of the ^{1}H NMR integration of the methoxy protons at δ 3.70 (**3**) and 3.64 (**4**) ppm, respectively. The structural assignment of the cycloadducts was made by the transformation into the cyclohexenone derivatives using the well known three-step sequence. The mixture of **3** and **4** was subjected to mild hydrolysis with $MgBr_2{\cdot}OEt_2$ in CH_2Cl_2 to give the keto sulfides which was oxidized with $NaIO_4$, followed by desulfenylation in refluxing CCl_4 afforded the separable mixture of the cyclohexenone derivatives **5** (72%), **6a** (16%), and **6b**(12%). This indicated that the regioselectivity of the



Scheme 1.

Diels-Alder reaction was controlled mostly by the sulfenyl group. This behavior is in line with the analogous system of 2-methoxy-3-phenylthio-1,3-butadiene reported by Trost and his co-workers.[5)]

In order to determine the ratio of the regioisomeric Diels-Alder adducts directly, the more stable 2-(*t*-butyldimethylsilyloxy)-3-(*p*-tolylthio)-1,3-butadiene **7a** was chosen. Thus, **7a**, prepared from **1** with *t*-butyldimethylsilyl trifluoromethanesulfonate and DIPEA, was allowed to react with methyl acrylate at 80 °C for 8 h, and the two separable cycloadducts **8a** and **9a**[6)] were obtained in the same ratio of 72 : 28 as the case of **2** with methyl acrylate (62% yield). We also performed the Diels-Alder reaction of the corresponding sulfoxide **7b** and sulfone **7c** which were obtained from **7a** by oxidation with *m*-chloroperbenzoic acid. The Diels-Alder reactions of **7b** and **7c** with methyl acrylate under the identical conditions furnished the cycloadducts **8b** and **9b** (ratio 25 : 75; 72% yield), and **8c** and **9c** (ratio 28 : 72; 99% yield), respectively.[7)] As expected, changing the tolylthio group to the electon-withdrawing groups reversed the regioselectivity; the para adducts with respect to the silyloxy group were formed as the major products.



Scheme 2. **a** : n=0; **b**: n=1; **c**: n=2

References

1) H. Kosugi, K. Hoshino, and H. Uda, presented in part at the 18th Symposium on Heteroatom Chemistry, Narashino, December, 1990, Abstract p 153, and submitted for publication.

2) **1** was prepared from commercially available 3-chloro-2-butanone in two steps (90% overall yield): i) p-$CH_3C_6H_4SH$, Et_3N, THF, r.t., 18 h; ii) $NaIO_4$, $MeOH$-H_2O, r.t., 15 h.

3) **2**: bp 100-110 °C(oil bath temperature)/0.07 mmHg; ^1H NMR($CDCl_3$) 0.22(9H, s), 2.32(3H, s), 4.42(1H, t, J=1.0), 5.01(1H, d, J=1.0), 5.20(1H, d, J=1.0), 5.87(s), 7.10(2H, d, J=8.1), and 7.27(2H, d, J=9.1); ^{13}C NMR -0.05, 21.06, 95.61, 117.69, 129.82, 130.71, 131.56, 137.20, 140.50, and 153.23.

4) K. Takaki, M. Okada, M. Yamada, and K. Negoro, *J. Org. Chem.*, **47**, 1200 (1980).

5) B. M. Trost, J. Ippen, and W. C. Vladuchick, *J. Am. Chem. Soc.*, **99**, 8116, (1977); B. M. Trost, W. C. Vladuchick, and A. J. Bridge, *ibid.*, **102**, 3554 (1980). For the theoretical argument of 2,3-disubstituted dienes in the Diels-Alder reaction see: S. D. Kahn, C. F. Pau, L. E. Overman, and W. J. Hehre, *ibid.*, **108**, 7381 (1986).

6) The structural assignment was based on the transformation of **8a** and **9a** into **5**, and **6a** and **6b**, respectively.

7) The ratios of the regioisomers were determined on the basis of the ^1H NMR integration of the methoxy signals. For the cycloadducts from sulfoxide **7b**, the ^1H NMR spectrum shows four methoxy signals (δ 3.56, 3.63, 3.64, and 3.69 ppm) due to the chiral sulfur atom. The authentic sulfoxides **8b** (δ 3.63 and 3.69) and **9b** (δ 3.56 and 3.64) for the NMR assignment of the methoxy signals were obtained as mixtures of the diastereoisomers from **8a** and **9a**, respectively, by oxidation with MCPBA. The authentic sulfones **8c** and **9c** were also prepared from **8a** and **9a**, respectively.

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