Tetrahedron Letters, Vol.31, No.32, pp 4621-4624, 1990
Printed in Great Britain

0040-4039/90 \$3.00 + .00
Pergamon Press plc

A Novel 1,5-Rearrangement of a Sulfonyl Group in a 1-Sulfenylated 2,4-Alkadiene

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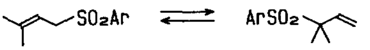
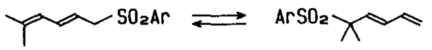
Abstract: 1-Substituted 1-methylthio-2,4-pentadien-1-yl sulfones (4) smoothly underwent a 1,5-rearrangement of a sulfonyl group by the action of silica gel. Its application to a new synthesis of conjugated dienones is also described.

To date, many chemists have investigated 1,3-rearrangement of allylic sulfonyl groups (eq. 1), which is accelerated by an acid, Pd(0), or a radical initiator.[1] Especially, an acid-catalyzed facile rearrangement of the sulfonyl group can be attained in sulfenylated systems,[1a,i,j,l] which are utilized for synthesizing various organic compounds.



(eq.1)

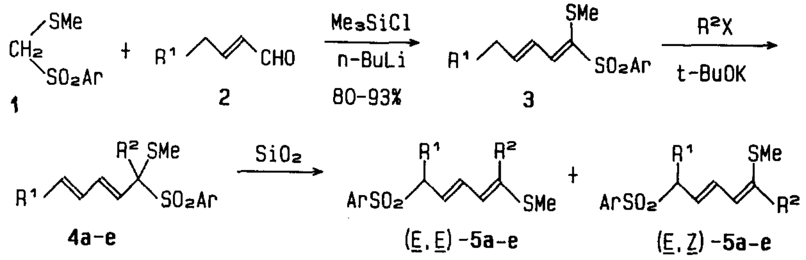


(eq.2)

In contrast, the corresponding 1,5-rearrangement of sulfonyl group (eq. 2) is unprecedented. Here we wish to describe a preliminary result of our investigation on this 1,5-rearrangement in a sulfenylated system which is applicable to a new synthetic method of conjugated dienones.

The starting compound of the present 1,5-rearrangement was obtained by alkylation of (*E,E*)-1-arylsulfonyl-1-methylthio-1,3-alkadiene (3),[2] easily obtainable from aryl methylthiomethyl sulfone (1)[3] as outlined in Scheme 1: On treatment of **3a** with ethyl iodide and potassium *t*-butoxide, a smooth reaction took place in THF at $-20\ ^{\circ}$C. The ^{1}H NMR (270 MHz) spectrum of the crude product exhibited regiospecific formation of the expected **4a**. The crude **4a** was placed on a silica gel column, followed by elution with benzene to give a 1,5-rearrangement product (**5a**).[4] It is noteworthy that **4a** was not detected in any fraction. Alkylation of 3 (Ar=p-Tol, R'=H) with benzyl iodide followed by column chromatography on silica gel gave the corresponding 1,5-rearrangement product. A phenyl analog (**4d** or **4e**) also rearranged in a similar manner to afford the corresponding 5. These results are summarized in Scheme 1.

Scheme 1



a:	Ar = p-Tol	R^1 = H	R^2 = Et	72%[¶]	(95 : 5)[§]
b:	Ar = p-Tol	R^1 = H	R^2 = $PhCH_2$	81%	(84 : 16)
c:	Ar = p-Tol	R^1 = Et	R^2 = $PhCH_2$	76%	(84 : 16)
d:	Ar = Ph	R^1 = H	R^2 = Et	62%	(96 : 4)
e:	Ar = Ph	R^1 = H	R^2 = $PhCH_2$	67%	(92 : 8)

[¶] overall yield from 3

[§] (E,E)-5 : (E,Z)-5

For the present rearrangement, a dissociation-recombination mechanism is conceivable because silica gel functions as an acid catalyst.[5] Further support for this mechanism was furnished by cross-over experiments. When a ca. 1:1 mixture of **4b** and **4d** was passed through a silica gel column (elution with benzene), a partial scrambling was observed (**5a**:**5b**:**5d**:**5e**=14:46:45:10). When **4b** was subjected to a column chromatography on silica gel which was treated with benzenesulfinic acid (2 equiv) prior to use, **5e** was given in 37% overall yield from the corresponding **3** together with **5b** (46%).

The progress of the rearrangement could be pursued by ^1H NMR (270 MHz).[6] As summarized in Fig. 1, **4b** rapidly disappeared and mainly two rearrangement products appeared in an approximate ratio of 3:2 after 4 min. One is **5b** and the other is assigned as **6b** from its NMR.[7] The amount of **6b** reached to a maximum after ca. 1 h and then decreased little by little. While, **5b** gradually increased and, at the final stage, became the exclusive product. These results showed that **4b** dissociates to a

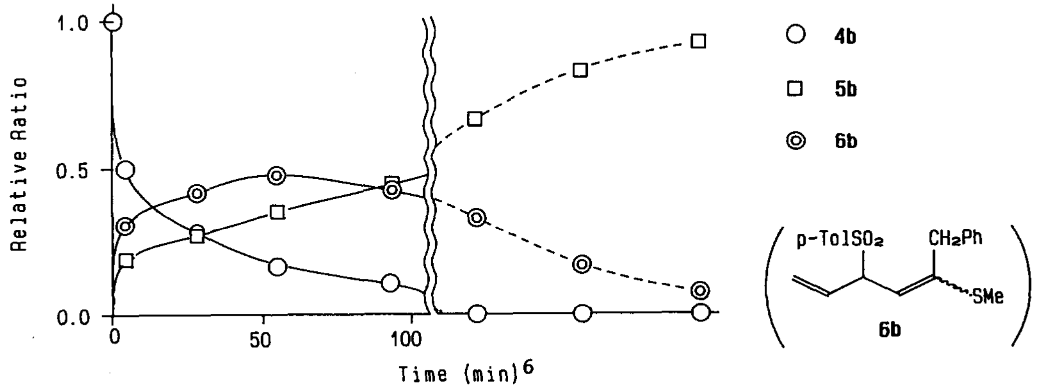
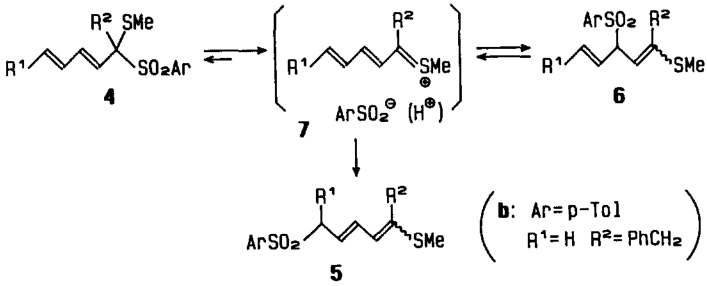


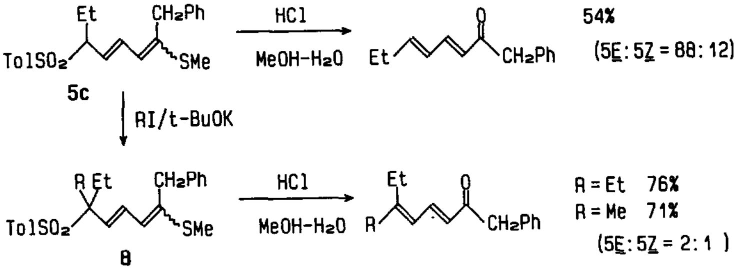
Fig. 1 Rearrangement of **4b**

cationic intermediate (7b) and p-toluenesulfinate ion (or p-toluenesulfinic acid) which recombine to mainly produce 5b and 6b. The latter product (6b) can dissociate to regenerate 7b and p-toluenesulfinate ion. Exclusive formation of 5b at the final stage is interpreted in terms of the stability of 5 under these conditions. Indeed, 5b was recovered perfectly unchanged by passing through the column packed with the silica gel which was treated with benzenesulfinic acid.

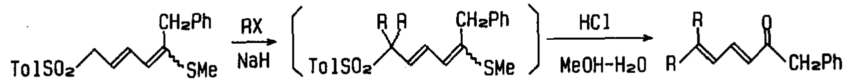


One of the distinct features of the present rearrangement is the predominant formation of (E,E)-5 (Scheme 1).[8] This may be attributable to the preferable geometry (7) of the intermediary cation which is more stabilized by donation of the lone electron pair on the sulfur atom.

Finally, we wish to describe the reaction conditions for the conversion of 5 to conjugated dienones.[9] When 5c was treated with hydrogen chloride (1 equiv) in refluxing $MeOH-H_2O$ (9:1) for 24 h, hydrolysis occurred and 1-phenyl-3,5-octadien-2-one was produced in 54% yield. We found that the dialkylated derivative of 5 is more easily hydrolyzed. Alkylation of 5c with alkyl iodide and t-BuOK in THF (-20 °C) produced 8. Without any purification, 8 was hydrolyzed on treatment with HCl (1 equiv) in refluxing $MeOH-H_2O$ (9:1) for ca. 2 h to give the corresponding conjugate dienone.



Dialkylation of 5b was achieved by the reaction with excess NaH (3.0 equiv) and alkyl halide (3.0 mol-equiv) in DMF (from -20 °C to room temperature). Under the similar conditions described above, the dialkylated product was hydrolyzed as follows.



5b

RX = MeI 71%; RX = EtI 71%; 2RX = Br(CH₂)₅Br 53%

Now we are studying scope and limitation of the present conjugated dienone synthesis and the detailed results will be reported in due course.

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2. A THF solution of 1 and trimethylsilyl chloride (2.2 mol-equiv) was successively treated with n-butyllithium (2.2 equiv; -78 °C/2 h) and then with an enal (2; -78 °C/2 h). The crude 3 consists of its (1E,3E)- and (1Z,3E)-isomers. When the crude 3 was stirred along with iodine (2 mol-equiv) in diethyl ether or diisopropyl ether at room temperature for 3-5 h, a smooth isomerization took place to give (1E,3E)-3 in a pure form (80-93% yield based on 1).
3. Preparation of 1: Ogura, K.; Yahata, N.; Watanabe, J.; Takahashi, K.; Iida, H. Bull. Chem. Soc. Jpn. 1983, 56, 3543. Now 1 (Ar=p-Tol) is commercially available. For organic synthetic methods using 1, see Ogura, K. Pure Appl. Chem. 1987, 59, 1033.
4. Acetic acid and p-toluenesulfonic acid also catalyzed this rearrangement in $CHCl_3$.
5. The geometry of the 1,5-rearrangement products reported herein was determined by ^{1}H NMR analysis (proton-proton coupling constants and the NOE magnitude) to be E,E.
6. A solution of the crude 4b (10 mg) in $CDCl_3$ (0.4 ml) was placed in an NMR tube, and then silica gel (Merck; 30 mg) was added. The ^{1}H NMR spectrum of the resulting mixture was measured at regular time intervals (22.5 °C). After 100 min, the tube was occasionally shaken and then its ^{1}H NMR spectrum was measured.
7. The ^{1}H NMR signals of 6b: δ 2.24 (3H, s), 2.46 (3H, s), 3.23 (1H, d, J=16.2 Hz), 3.50 (1H, d, J=16.2 Hz), 4.54 (1H, dd, J=10.0, 7.4 Hz), 5.04 (1H, d, J=16.8 Hz), 5.05 (1H, d, J=10.2 Hz), 5.30 (1H, dd, J=10.2, 1.0 Hz), and 5.94 (1H, ddd, J=17.2, 10.0, 7.3 Hz).
8. In the corresponding 1,3-rearrangement of a sulfonyl group, the major isomer was tentatively assigned to be Z.[1i] At the present time, the structure of the rearrangement product was re-examined on the base of the NOE experiments which showed that the major isomer was determined to be E. For example, (E)-3-methylthio-4-phenyl-2-buten-1-yl p-tolyl sulfone (MeS protons: δ 2.11) exhibited 4.3% NOE enhancement between its benzyl CH_2 and sulfonyl CH_2, while a NOE enhancement (7.0%) was observed between olefinic proton and benzyl CH_2 of its (Z)-isomer (MeS protons: δ 1.89).
9. Several methods have been established for preparing a wide range of conjugated dienones: (a) Surber, W.; Theus, V.; Colombi, L.; Schinz, H. Helv. Chim. Acta, 1956, 39, 1299. (b) Cookson, R. C.; Gopalan, R. J. Chem. Soc. Chem. Commun. 1978, 608. (c) Kuwajima, I.; Hoshino, S.; Tanaka, T.; Shimizu, M. Tetrahedron Lett. 1980, 21, 3209. (d) Villieras, J.; Ramband, M. Synth. Commun. 1983, 13, 300. (e) Molander, G. A.; Singaram, B.; Brown, H. C. J. Org. Chem. 1984, 49, 5024. (f) Hanessian, S.; Hodges, P. J.; Sahoo, S. P.; Roy, P. J. Tetrahedron Lett. 1986, 27, 2949. (g) Jabri, N.; Alexakis, A.; Normant, J. F. Tetrahedron 1986, 42, 1369. (h) Trost, B. M.; Schmidt, T. J. Am. Chem. Soc. 1988, 110, 2301. (i) Ma, D.; Yu, Y.; Lu, X. J. Org. Chem. 1989, 54, 1105.

(Received in Japan 7 May 1990)