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Allyl Benzenesulfenates in Isomeric Forms

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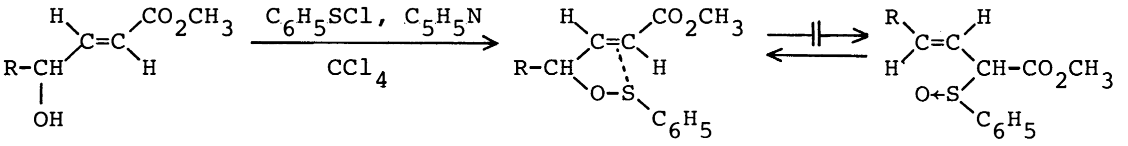
Allyl benzenesulfenates containing an electron-withdrawing group at the conjugated position were prepared in isomeric forms which would be stabilized by partial bonding between the C=C bond and two lone pairs of electrons on the sulfur atom.

The thermal interconversion of allyl sulfenate-sulfoxide[1)] is characterized as a [2,3] sigmatropic process by way of a five-membered ring transition state, and the equilibrium is usually much in favor to the sulfoxide.[2)] If the mixture is treated with a thiophile, the sulfenate ester is irreversibly converted into the allyl alcohol, and this method has been widely applied to organic synthesis.[3-5)] Isolation of sulfenate esters sometimes requires the presence of a nitro group[6-7)] which may prevent the S-O bond fission. Allyl sulfenate esters are furthermore susceptible to the C-O bond fission owing to the sigmatropic rearrangement.[2,8)] From the mechanistic standpoint of the [2,3] sigmatropic rearrangement it is of importance to isolate thermally stable allyl benzenesulfenates and to examine the structure in the ground state. Here we wish to report the preparation of isomeric allyl benzenesulfenates (1) containing an electron-withdrawing group.

Treatment of methyl (2*E*)-4-hydroxy-2-alkenoates (2a-d)[4)] with benzenesulfenyl chloride and pyridine in CCl_4 for 15 min at room temperature under argon atmosphere[6)] readily produced 1 as a liquid. The isolated yield through column chromatography was rather low because 1 was to a considerable extent hydrolyzed to 2 by silica gel or alumina. Even if a solution of 1 was allowed to stand at room temperature for a few days, the corresponding allylic sulfoxide (3) was not detected. That is to say, the rate of this [2,3] sigmatropic rearrangement is slow at room temperature. Although the similar treatment of (2*E*)-4-hydroxy-2-alkenenitrile would give the corresponding sulfenate ester, it was completely hydrolyzed during purification by chromatography even on neutralized alumina.



2 1 (A + B) 3

1	R	Isolated Yield/%	A/B
a[9)]	C_2H_5	50	5/5
b	*n*-C_3H_7	46	4/6
c	*n*-C_5H_{11}	43	4/6
d	*n*-C_8H_{17}	35	3/7

Although 1 showed one spot on TLC, careful PHLC analysis revealed the presence of two components which could not be isolated even by repetition of preparative PHLC. The ^1H-NMR spectrum also indicated that 1 contained two components (1A and 1B) exhibiting essentially same absorptions except in the δ_H values. The component 1A exhibited the CH= and OCH_3 absorptions in a lower field, but the CH_3 and CH_2 ones in a higher field than 1B. Formation of allyl sulfoxide is ruled out by the absence of the characteristic S→O streching frequency in the 1010-1130 cm^{-1} range of the IR spectrum and also by no M^+-16 peak in the mass spectrum. The absence of sulfinate ester is suggested by no *m/e*=141 ($C_6H_5SO_2$) peak, and definitely by elemental analysis. The presence of a (*Z*)-isomer is ruled out by the finding that all *J* values are identical between 1A and 1B. The occurrence of these two isomers does not seem to result simply from steric effects, that is, steric restraint for rotation around a C-O bond. These differences in the δ_H values may arise from the anisotropy of the benzene ring.

Since methyl *o*-nitrobenzenesulfenate is known to be stabilized by partial bonding between the sulfur atom and the oxygen atom of the nitro group,[7] 1 is assumed to be stabilized in formation of a five-membered ring by the similar interaction between the sulfur atom and the C=C bond, and two lone pairs of electrons may cause the observed isomerism. In order to confirm this assumption the ^{1}H-NMR spectra of 1a were determined using various solvents (Table 1).

Table 1. Solvent Effects on δ_H in ^{1}H-NMR Spectra of 1a

Solv.	Isomer	δ_H /ppm					
		CH_3	CH_2	-CH-	CH-C$\underline{H}$=C	C=C$\underline{H}$-CO	OCH_3
CCl_4	A	0.89	1.64	4.7-4.8[a]	6.83	5.97	3.71
	B	0.96	1.73		6.52	5.55	3.62
$CDCl_3$	A	0.89	1.68	4.8-4.9[a]	6.92	6.05	3.76
	B	0.96	1.77		6.69	5.76	3.68
CD_3OD	A	0.85	1.64	4.8-4.9[a]	6.91	5.91	3.72
	B	0.92	1.73		6.71	5.71	3.66
CD_3CN	A	0.85	1.65	4.8-4.9[a]	6.91	5.91	3.73
	B	0.93	1.75		6.73	5.73	3.68

a) Assignment between A and B was impossible.

The difference in the δ_H (CH-C$\underline{H}$=C & C=C$\underline{H}$-CO) values between 1Aa and 1Ba decreased with increasing polarity of the solvent used. This finding suggests the interaction between the sulfur atom and the C=C bond. The importance of such an interaction also implied by the fact that the similar treatment of methyl 4-hydroxyalkanoate did not generate the corresponding sulfenate ester in a stable form. Although the exact structure of 1A and 1B cannot be displayed at the present stage, they may resemble interestingly the previously-proposed structure in the transition state of the [2,3] sigmatropic rearrangement.[1,10] Therefore, the interaction between sulfur and carbon atoms in the ground state usually promotes the rearrangement, but the electron-withdrawing group prevents the S-C bond formation.

The present observation seems to provide significant information regarding to the [2,3] sigmatropic rearrangement.

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References

1) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, J. Am. Chem. Soc., 90, 4869 (1968).

2) R. Tang and K. Mislow, J. Am. Chem. Soc., 92, 2100 (1979).

3) D. A. Evans and G. C. Andrews, Acc. Chem. Res., 7, 147 (1974) and references therein.

4) R. Tanikaga, Y. Nozaki, K. Tanaka, and A. Kaji, Chem. Lett., 1982, 1703.

5) R. Annunziata, M, Cinquini, F. Cozzi, and L. Raimondi, J. Chem. Soc., Chem. Commun., 1986, 366.

6) S. R. Sandler and W. Karo, "Organic Functional Group Preparations," Academic Press, New York (1972), Vol. 3, p. 168.

7) W. C. Hamilton and S. J. LaPlaca, J. Am. Chem. Soc., 86, 2289 (1964).

8) H. J. Reich and S. Wollowitz, J. Am. Chem. Soc., 104, 7051 (1982).

9) ^{1}H-NMR (CDCl$_3$/TMS): 1Aa; δ = 0.89 (t, 3 H, J = 7.4 Hz), 1.68 (dq, 2 H, J = 6.5, 7.4 Hz), 3.76 (s, 3 H), 4.8-4.9 (m, 1 H), 6.05 (d, 1 H, J = 16 Hz), 6.92 (dd, 1 H, J = 16, 6 Hz), and 7.4-7.9 (m, 5 H); 1Ba; δ = 0.96 (t, 3 H, J = 7.4 Hz), 1.77 (dq, 2 H, J = 6.5, 7.4 Hz), 3.68 (s, 3 H), 4.8-4.9 (m, 1 H), 5.76 (d, 1 H, J = 16 Hz), 6.69 (dd, 1 H, J = 16, 6 Hz), and 7.4-7.9 (m, 5 H).
IR (neat): 1Aa+1Ba: ν = 1730, 1280, 1150 (C=C-C=O), and 930 cm^{-1} (-O-S-).
MS: 1Aa+1Ba; m/e = 252 (0%, M$^+$), 143 (4, M$^+$-C$_6$H$_5$S), 127 (100, M$^+$-C$_6$H$_5$SO), 125 (45, C$_6$H$_5$SO), and 109 (3, C$_6$H$_5$S).
Found: C, 61.43; H, 6.71%. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39%.

10) H. Kosugi, M. Kitaoka, A. Takahashi, and H. Uda, J. Chem. Soc., Chem. Commun. 1986, 1268.

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