

Competitive Intramolecular [4+2] Cycloaddition and [2+2] Cycloaddition of Sulfonyllallene

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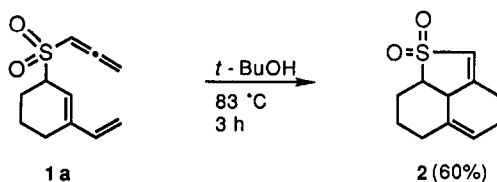
Summary: Thermal reaction of sulfonyl allenes proceeded by the intramolecular Diels-Alder ([4+2]) reaction and/or [2+2] cycloaddition reaction depending upon the substitution pattern, in which the effect is switching of the reaction pathway depending on a C(2) position.

Recently, we have reported a remarkable substituent effect in the intramolecular cycloaddition reaction of allenyl 3-vinyl-2-cyclohexenyl ethers¹. The reaction proceeded by intramolecular Diels-Alder reaction and/or tandem [2+2] cycloaddition, [3,3]-sigmatropic rearrangement ([2+2]+[3,3]) depending upon the substitution pattern.

As a continuation of our systematic studies on allene intramolecular cycloaddition reactions, we investigate the intramolecular cycloaddition reaction of sulfonyllallenes. We have already reported intermolecular Diels-Alder reaction of phenyl sulfonyllallene², while this is the first report of the intramolecular Diels-Alder reaction of sulfonyllallene.

Thus, thermal reaction of **1a**³ exclusively afforded the Diels-Alder adduct (**2**)⁵ in 60% yield upon heating in refluxing *t*-BuOH for 4 hours (Scheme 1). In contrast, the 2-methyl derivative (**1b**)⁴ afforded a mixture of the [2+2] adduct (**3**)⁶ and the [4+2] adduct (**4**)⁷ in a 8/1 ratio. While, **5**⁸ underwent selectively the [2+2] cycloaddition reaction to give **6**⁹ as the sole product (Scheme 2). The structure of [2+2] adduct (**3**) was determined by the spectroscopic data⁶ and the single-crystal X-ray analysis (Fig. 1). As shown in X-ray analysis, the most remarkable structural feature of the [2+2] cycloadduct (**3**) is the presence of an unusually long C-C bond of nearly 1.6 Å in the cyclobutane ring (C(5)-C(6) : 1.590 Å ; C(5)-C(8) : 1.58 Å).

Scheme 1



Scheme 2

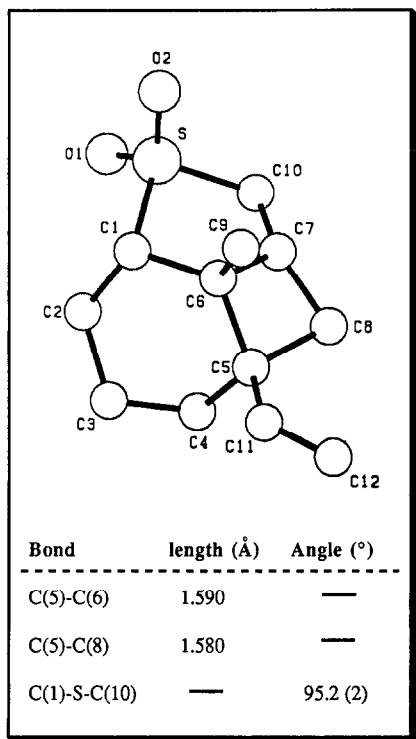
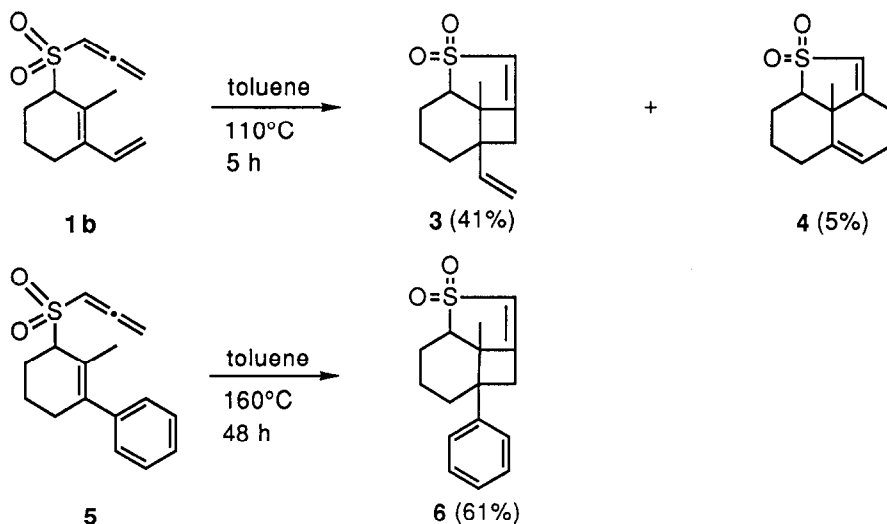


Figure 1. The X-ray crystal structure of **3**.

Table 1. Summary of crystal data, intensity collection and least-squares processing of compound **3**

formula	C ₁₂ H ₁₆ O ₂ S
formula weight	224.3
crystal system	monoclinic
space group	P2 ₁ / c
a / Å	7.254 (2)
b / Å	14.911 (2)
c / Å	12.056 (2)
β / deg	120.03 (1)
V / Å ³	1128.9 (4)
Z	4
D _{calcd} / g cm ⁻³	1.320
m (Cu Kα) / cm ⁻¹	22.9
diffractometer	Rigaku AFC-5R
radiation	Ni-filtered Cu Kα (λ=1.54178 Å)
2θ _{max} / deg	120
scan mode	2θ-ω
crystal size / mm	0.3 x 0.15 x 0.15
total no. of unique reflections	1674
no. of observed reflections	
with F _o > 3 σ(F _o)	1448
R	0.045
R _w	0.068
S (goodness of fit)	1.345
no. of reflections used at the last stage of refinement	1413

Apparently, the substituent at C(2) plays the most important role in controlling the periselectivity of the sulfonyllallene cycloaddition reactions. The obvious effect of C(2) substituents is the one probably exerted on the conformational equilibrium of the 1,3-butadiene moiety in the sulfonyllallenes. The *s-cis* conformation of the butadiene moiety may be severely disfavored by the substituent at C(2). In this regard, the ^1H NMR spectra showed some instructive evidences. While the vinylic proton signal (Ha) of the unsubstituted compound (**1a**) appeared at about δ 6.4, the compound having the 2-substituent (**1b**) exhibited the Ha signal at the much lower field (δ 6.86). This remarkable low-field shift of the vinylic proton signal can be attributed to the deshielding effect of the proximate C(2) and C(3) double bond experienced in the *s-trans*-butadiene conformer (Fig. 2).

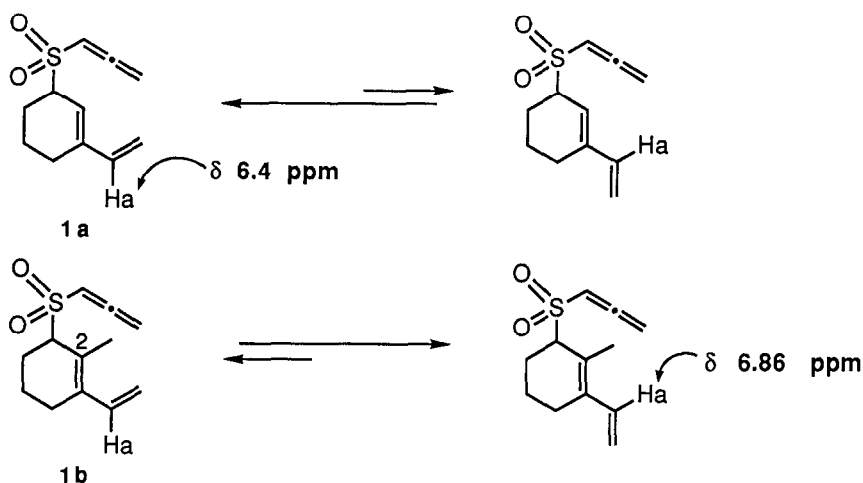


Figure 2

Hence, when there is no severe steric hindrance to the *s-cis*-butadiene conformation as in **1a**, the [4+2] cycloaddition reaction takes place preferentially to give the less strained Diels-Alder adduct. However, when the [4+2] transition state is sterically congested by the C(2) substituent as in **1b**, the [2+2] cycloaddition is enforced to give the [2+2] adduct.

The latter case was quite different in comparison with that of the intramolecular cycloaddition of allenyl ethers. Obviously, the structural conditions in the sulfonyllallene such as **1b** provide an energetically favorable situation for this exceptional behaviour of the spatial proximity of the C(2) and C(3) double bonds and a decrease in the internal bond angle (95.2° ; see Fig. 1) at the sulfonyllallene moiety ("the reactive rotamer effect"¹⁰).

While, the sulfonyl moiety affected the reaction pathway, the [2+2] cycloadduct (**3**) can be expected to proceed by a stepwise manner via diradical intermediate [A] rather than that of [B] which is sterically congested between sulfonyl oxygen and H_b as depicted in Fig. 3.

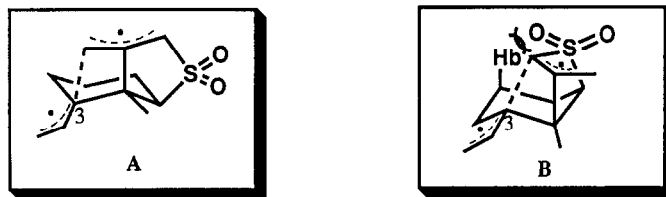


Figure 3. Diradical intermediate in [2+2] cycloaddition

References and Notes

- Hayakawa, K.; Aso, K.; Shiro, M.; Kanematsu, K. *J. Am. Chem. Soc.*, **1989**, *111*, 5312.
- a) Hayakawa, K.; Nishiyama, H.; Kanematsu, K. *J. Org. Chem.*, **1985**, *50*, 512.
b) A. Padwa, W. H. Bullock ; D. N. Kline ; J. Perumattam, *J. Org. Chem.*, **1989**, *54*, 2862 and references cited therein.
- Data for the synthetic **1a** : ^1H NMR (60 MHz, CDCl_3) δ 6.43 (dd, $J = 11.4, 17.4$ Hz, 1H), 6.07 (t, $J = 6.0$ Hz, 1H), 5.92-5.78 (m, 1H), 5.45 (d, $J = 6.0$ Hz, 2H), 5.26 (d, $J = 16.8$ Hz, 1H), 5.14 (d, $J = 11.4$ Hz, 1H), 4.17-3.58 (m, 1H), 2.55-1.50 (m, 6H) ; IR (CHCl_3) 1950, 1300, 1110 cm^{-1} .
- Data for the synthetic **1b** : ^1H NMR (60 MHz, CDCl_3) δ 6.86 (dd, $J = 11.4, 17.4$ Hz, 1H), 6.09 (t, $J = 6.6$ Hz, 1H), 5.43 (d, $J = 6.6$ Hz, 2H), 5.29 (d, $J = 17.4$ Hz, 1H), 5.17 (d, $J = 11.4$ Hz, 1H), 3.96-3.44 (m, 1H), 2.08 (s, 3H), 2.56-0.63 (m, 6H) ; IR (CHCl_3) 1960, 1300, 1110 cm^{-1} .
- Data for the synthetic **2** : ^1H NMR (270 MHz, CDCl_3) δ 6.33 (t, $J = 1.6$ Hz, 1H), 5.51 (bt, $J = 1.8$ Hz, 1H), 3.66 (bd, $J = 6.6$ Hz, 1H), 3.43-3.34 (m, 1H), 2.72-2.65 (m, 1H), 2.47-1.59 (m, 9H) ; IR (CHCl_3) 1640, 1280, 1090 cm^{-1} ; MS (m/z) 210 (M^+).
- Data for the synthetic **3** : ^1H NMR (270 MHz, CDCl_3) δ 6.31 (d, $J = 1.3$ Hz, 1H), 5.95 (dd, $J = 17.2, 10.6$ Hz, 1H), 5.21 (d, $J = 10.6$ Hz, 1H), 5.06 (d, $J = 17.2$ Hz, 1H), 3.50 (dd, $J = 15.2, 2.3$ Hz, 1H), 3.17 (dd, $J = 8.8, 4.5$ Hz, 1H), 2.67 (dd, $J = 15.2, 1.0$ Hz, 1H), 2.28-2.17 (m, 1H), 1.91-1.81 (m, 1H), 1.73-1.59 (m, 3H), 1.48 (bs, 3H), 1.45-1.32 (m, 1H) ; ^{13}C NMR (67.8 MHz, CDCl_3) δ 162.26 (s), 141.26 (d), 121.41 (d), 114.29 (t), 70.84 (d), 50.35 (s), 46.73 (s), 40.38 (t), 34.63 (t), 23.72 (t), 21.95 (q), 17.88 (t) ; IR (CHCl_3) 1650, 1280, 1140 cm^{-1} ; MS (m/z) 224 (M^+).
- Data for the synthetic **4** : ^1H NMR (270 MHz, CDCl_3) δ 6.25 (s, 1H), 5.47-5.44 (m, 1H), 2.99 (dd, $J = 11.2, 4.6$ Hz, 1H), 2.60-2.54 (m, 2H), 2.45-2.12 (m, 3H), 1.52 (s, 3H), 2.01-1.46 (m, 3H) ; IR (CHCl_3) 1640, 1280, 1090 cm^{-1} ; MS (m/z) 224 (M^+).
- Data for the synthetic **5** : ^1H NMR (60 MHz, CDCl_3) δ 7.57-6.95 (m, 5H), 6.19 (t, $J = 6.0$ Hz, 1H), 5.47 (d, $J = 6.0$ Hz, 2H), 3.99-3.61 (m, 1H), 2.58-0.86 (m, 6H), 1.82 (s, 3H) ; IR (CHCl_3) 1960, 1310, 1130 cm^{-1} .
- Data for the synthetic **6** : ^1H NMR (270 MHz, CDCl_3) δ 7.40-7.21 (m, 3H), 7.08-7.03 (m, 2H), 6.38 (d, $J = 1.3$ Hz, 1H), 3.83 (dd, $J = 15.2, 1.7$ Hz, 1H), 3.33 (dd, $J = 7.4, 3.2$ Hz, 1H), 3.05 (dd, $J = 15.2, 1.0$ Hz, 1H), 2.52-2.43 (m, 1H), 2.05-1.96 (m, 1H), 1.96-1.73 (m, 2H), 1.60-1.52 (m, 2H), 1.33 (s, 3H) ; IR (CHCl_3) 1650, 1280, 1130 cm^{-1} ; MS (m/z) 274 (M^+).
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(Received in Japan 22 December 1990)