

[2,3] Sigmatropic Rearrangement of Unstable Sulfur Ylides from Allyl Sulfonium Salts. Comparative Study of Electrochemical Reduction with the Base Method and Mechanism Elucidation by the MO Method

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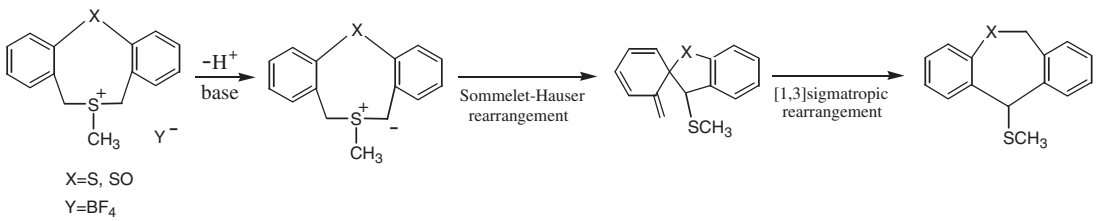
The cathodic reduction of sulfonium salts in acetonirile under the presence and absence of benzaldehyde were carried out and compared with the results of the base method. Under the presence of benzaldehyde, the electrochemical reduction gave epoxides as a result of a Corey–Chaykovsky reaction confirming ylide formation. The electrochemical reduction of sulfonium salt without benzaldehyde yields the same [2,3] sigmatropic rearrangement product as those obtained by the base method, in high yield. The reaction mechanism was studied by semi-emprical MO methods.

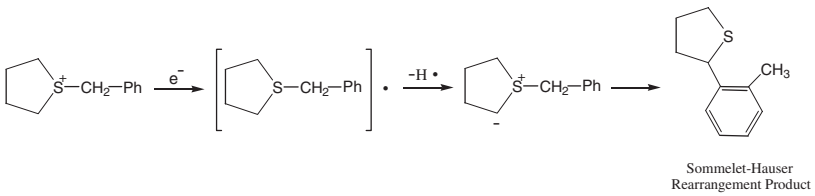
Organo-sulfur compounds have attracted attention as intermediates in the syntheses of various organic compounds.[1] Especially the sulfur ylides (abbreviated as S-Y hereafter) have played an important role as sources of versatile carbanions.[2] Corey–Chaykovsky reactions are well known as the important reaction for getting a wide variety of epoxides derivatives.[3,4] The reactions of S-Y with carbonyl compounds are different from those of phosphonium ylide, because the carbanion of S-Y attacks the carbonyl carbon and yields epoxides because of the weak affinity of sulfur atom to oxygen.

Besides their reactions with many electrophiles as carbanions, the S-Ys appear to be involved in two types of rearrangements as their characteristic reactions. Thomson and Stevens reported sulfur versions of the Stevens rearrangement which proceeded via a S-Y.[5] This rearrangement has been regarded as a radical process because the concerted mechanism is forbidden by the Woodward–Hoffmann rule. But by the MO calculation, we have found the possibilities of a sigmatropic process when the migrating groups are hydrogen, vinyl, and silyl groups which could use their hypervalent bonding.[6] On the contrary, the [2,3] sigmatropic rearrangements are allowed by the Woodward–Hoffmann rule, and many examples have been reported so far. Parham and Groen reported the [2,3] sigmatropic rearrangement of S-Y obtained from the reaction of allyl sulfide with dichlorocarbene.[7] In addition, Vedejs et al. reported [2,3] sigmatropic rearrangement of S-Y which contains allylic substituent to give macrocyclic molecules.[8] An ab initio theoretical study from a view point of stereochemistry is reported and the energy differences in the transition state are discussed.[9] And the rearrangement of benzyl dimethylsulfonium ion to *o*-methylbenzylmethylsulfide in the presence of amide ion is a normal Sommelet–Hauser rearrangement through the ylide as an intermediate.[10] Okada et al.[11] reported the synthesis of thiepin derivatives through skeletal reconstruction of S-Y with two benzyl groups on the sulfur atom (Scheme 1). Ab initio MO calculation at HF/6-31G* basis set was used to elucidate the reaction mechanism.[12] We have reported the Sommelet–Hauser rearrangement in electrochemically generated S-Y (Scheme 2).[13]

In this experiment, we used the electrochemical reduction



Scheme 1.



Scheme 2.

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method for allyl-substituted sulfonium salts to produce S-Ys and compared the reaction products with those obtained from the base method. We found that the allylic S-Y generation occurred under mild conditions at 22 °C under a nitrogen atmosphere. The electrochemical reduction method is found to be simple and clean for giving S-Ys, and easy work-up is also promised. We obtained the epoxides through the Corey–Chaykovsky reactions of the allylic S-Y generated by the electrochemical reduction method in the presence of benzaldehyde; the epoxides obtained are accompanied by a geometrical isomerization. But when there are the methyl groups at both terminals of the allyl group, the generated epoxides were hydrogenated to the alcohol. Without benzaldehyde, the S-Ys undergo the [2,3] sigmatropic rearrangement easily. The reactions of electrogenerated S-Ys with benzaldehyde and their [2,3] sigmatropic rearrangements were studied by using allyl-(ATHT) and allyl-(ADES) to see the difference between ring structure and open chain structure. In order to clarify the mechanism of their reactions, we optimized all minimum or saddle points of the reaction profile by a semi-emprical MO method. The bond energies and spin density distributions were also used to explain the reaction path in the electrochemical reduction of the sulfonium salts.

Experimental

Materials. Tetrahydrothiophene, diethyl sulfide, 3-bromopropene, 1-bromo-2-butene, 4-bromo-2-methyl-2-butene, benzaldehyde, and acetonitrile are commercial products and used were after being purified by distillation. Sodium amide and tetraethylammonium perchlorate were used without further purification. ^{1}H NMR and ^{13}C NMR were recorded on JEOL JNM-A series instruments in $CDCl_3$ solvent. Mass spectra were obtained on a SHIMADZU GCMS-QP2010. For preparative column chromatography, DB-5MS (30 m × 0.320 mm × 0.50 μm) were employed. Each melting point was exhibited on a SEIKO INSTRUMENTS TG-DTA SSC/5200H. IR spectra were recorded on a SHIMADZU FTIR-8700. Current was recorded on NIKKO KEISOKU DIGITAL COULOMB METER NDCM-1. Column chromatography for purification was performed using Mallinckrodt silica gel (100 mesh) with $CHCl_3$ as eluent.

Synthesis of the Sulfonium Salts. In diethyl ether, the sulfonium salts are synthesized by the reaction of tetrahydrothiophene or diethyl sulfide with equimolar amounts of the corresponding allyl bromides; 3-bromopropene, 1-bromo-2-butene or 4-bromo-2-methyl-2-butene under argon at r.t. The melting point, IR spectra, ^{1}H NMR, ^{13}C NMR spectra data, and elemental analysis of the ATHT and ADES are shown below. The numbering systems of the compounds are specified as described in Chart 1.

ATHT. 1-Allyltetrahydrothiophenium Bromide (a): White crystal; mp 71.3–73.2 °C; IR (KBr Tablet) 2947 (m), 2077 (w), 1850–1650 (w), 1633 (m), 1456 (m), 1421 (m), 1259 (m), 1001 (m), 952 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81–5.73 (1H, m, H-4), 5.65 (2H, d, H-6, J = 9.8 Hz) 5.43 (1H, d, H-7, J = 9.8 Hz), 4.32 (2H, d, H-3, J = 7.3 Hz), 3.79–3.49 (4H, m, H-1), 2.32–2.26 (4H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.96 (C-1), 31.40 (C-2), 44.80 (C-3), 126.93 (C-4), 124.92 (C-5). Anal. Calcd for $C_7H_{13}BrS$: C, 40.20; H, 6.26%. Found: C, 39.98; H, 6.51%.

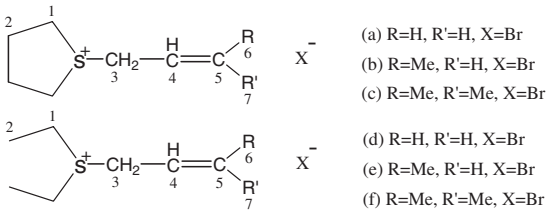


Chart 1.

1-(2-Butenyl)tetrahydrothiophenium Bromide (b): (*E*)-Isomer; White crystal; mp 75.4–76.8 °C; IR (KBr Tablet) 2951 (m), 2066 (m), 1850–1680 (w), 1662 (m), 1458 (m), 1419 (m), 1258 (m), 975 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22–6.17 (1H, m, H-4), 5.52 (1H, s, H-6), 4.35–4.34 (2H, d, H-3, J = 9.7 Hz), 3.79–3.55 (4H, m, H-1), 2.40–2.37 (4H, m, H-2), 1.86 (3H, s, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.00 (C-1), 28.69 (C-2), 44.16 (C-3), 139.11 (C-4), 111.63 (C-5), 17.93 (C-7). Anal. Calcd for $C_8H_{15}BrS$: C, 43.05; H, 6.77%. Found: C, 42.89; H, 6.58%.

1-(3-Methyl-2-butenyl)tetrahydrothiophenium Bromide (c): White crystal; mp 79.0–81.2 °C; IR (KBr Tablet) 2937 (m), 2362 (w), 1850–1680 (w), 1662 (m), 1446 (m), 1415 (m), 1245 (m), 846 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47–5.44 (1H, m, H-4), 4.36 (2H, d, H-3, J = 9.8 Hz), 3.80–3.48 (4H, m, H-1), 2.37–2.35 (4H, m, H-2), 1.86 (3H, s, H-6), 1.81 (3H, s, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.11 (C-1), 28.88 (C-2), 42.93 (C-3), 146.82 (C-4), 111.60 (C-5), 19.22 (C-6), 25.61 (C-7). Anal. Calcd for $C_9H_{17}BrS$: C, 45.57; H, 7.22%. Found: C, 45.68; H, 7.16%.

ADES. 1-Allyldiethylsulfonium Bromide (d): White crystal; mp 68.3–70.6 °C; IR (KBr Tablet) 2939 (m), 2061 (m), 1850–1650 (w), 1635 (m), 1456 (m), 1423 (m), 1263 (m), 995 (m), 952 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64–5.62 (1H, m, H-4), 5.54 (2H, d, H-6, J = 16.3 Hz) 5.32 (1H, d, H-7, J = 9.8 Hz), 4.29 (2H, d, H-3, J = 7.32 Hz), 3.44–3.41 (4H, m, H-1), 1.24–1.20 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.03 (C-1), 9.26 (C-2), 41.06 (C-3), 126.96 (C-4), 123.53 (C-5). Anal. Calcd for $C_7H_{15}BrS$: C, 39.82; H, 7.16%. Found: C, 39.96; H, 6.99%.

1-(2-Butenyl)diethylsulfonium Bromide (e): (*E*)-Isomer; White crystal; mp 70.4–71.5 °C; IR (KBr Tablet) 2950 (m), 2064 (m), 1850–1680 (w), 1662 (m), 1456 (m), 1419 (m), 1259 (m), 975 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35–6.30 (1H, m, H-4), 5.58 (1H, s, H-6), 4.57 (2H, d, H-3, J = 9.7 Hz), 3.76–3.66 (4H, m, H-1), 1.83 (3H, s, H-7) 1.27–1.24 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.32 (C-1), 8.90 (C-2), 40.51 (C-3), 138.76 (C-4), 115.45 (C-5), 17.25 (C-7). Anal. Calcd for $C_8H_{17}BrS$: C, 42.67; H, 7.61%. Found: C, 42.60; H, 7.87%.

1-(3-Methyl-2-butenyl)diethylsulfonium Bromide (f): White crystal; mp 73.1–74.3 °C; IR (KBr Tablet) 2930 (m), 1850–1680 (w), 1662 (m), 1450 (m), 1415 (m), 1261 (m), 979 (w), 839 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56–5.50 (1H, m, H-4), 4.56 (2H, d, H-3, J = 9.8 Hz), 3.78–3.66 (4H, m, H-1), 1.86 (3H, s, H-6), 1.80 (3H, s, H-7) 1.27–1.24 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.45 (C-1), 10.10 (C-2), 38.27 (C-3), 147.35 (C-4), 109.45 (C-5), 19.36 (C-6), 25.62 (C-7). Anal. Calcd for $C_9H_{19}BrS$: C, 45.19; H, 8.01%. Found: C, 45.39; H, 8.07%.

Electrochemical Reduction. In a 0.1 dL electrolytic cell which has a porous cup made of ceramics as a divided membrane, 0.2 mol of the sulfonium salt was dissolved in 0.05 dL in acetonitrile at the cathodic side of the cell. In the anodic side, 0.01 dL of acetonitrile that contains 0.01 mol of tetraethylammonium perchlorate was used as electrolyte. As the electrodes, two platinum plates (2 × 2 cm) were installed in the cell. The cathodic reduction was carried out under condition of −2.5 V vs SCE at 22 °C in ni-

trogen gas flow. After 1 F/mol electricity based on the sulfonium salts was passed, the reaction products were dissolved in diethyl ether and extracted with the same amount of water to remove inorganic salts. And the organic solution was dried over Na_2SO_4. After the solvent was removed by evaporation, the products were purified by column chromatography on silica gel adsorbent using $CHCl_3$ as eluent. In case of the Corey–Chaykovsky reactions, an equimolar amount of benzaldehyde was dissolved in the cathodic solution and the same work-ups were carried out.

Base Method. In acetonitrile solvent, 0.2 mol of the sulfonium salts were dissolved and an equimolar amount of sodium amide was added. Then the mixture was refluxed for 2 h. The work-up method was the same as in the case of the electrochemical reduction method.

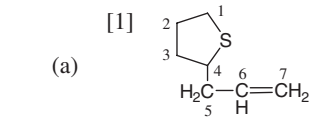
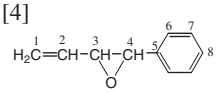
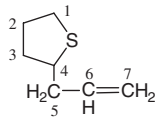
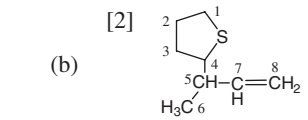
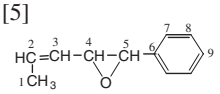
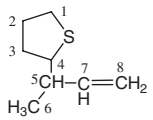
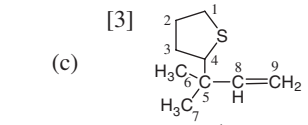
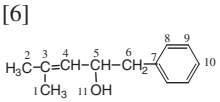
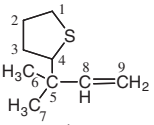
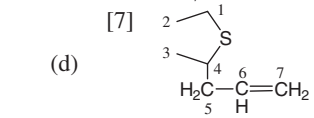
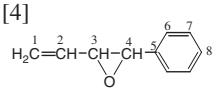
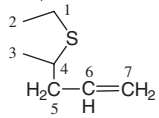
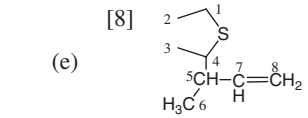
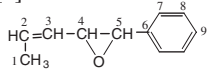
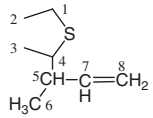
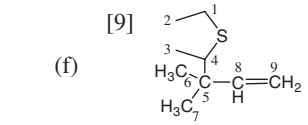
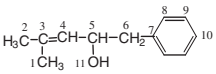
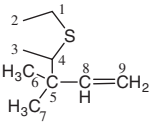
Computational Method. Semi-empirical calculations were carried out using PM3 Hamiltonian implemented in Prime Power 200 at Chubu university computer center. Each transition state possesses only one imaginary frequency for the vibrational analysis, corresponding to the appropriate coordinate of the reaction. An IRC calculation was performed for the transition state to confirm that it is a true transition state.

Reaction Products. The reaction products are the same in both electrochemical and base methods. And also the yields in the methods are comparable. When the sulfonium salt is reacted by each method, the rearranged products are obtained in high yield and the yields become higher as the numbers of terminal methyl groups increased. The products [2] and [8] were the mixtures of (*R*)- and (*S*)-isomers which can be differentiated by ^{1}H NMR and ^{13}C NMR. However, they could not be separated by column chromatography, so the combined yields are shown in Table 1. During the electrochemical reduction of sulfonium salts in the presence of benzaldehyde, the epoxide was formed with geometrical isomer. And when the methyl groups exist at the two terminals of the allyl group, the generated epoxide is hydrogenated to the alcohol. The reaction products from ATHT and ADES are summarized in Table 1; they were numbered as [1]–[9] and their yields are recorded in the same table. The ratio of geometrical isomer in epoxide is determined by the peak area in GC–MS spectra because it can not be isolated. Their structures are determined based on the physical properties, spectral data, and elemental analyses listed below.

Products from ATHT. **2-Allyltetrahydrothiophene [1]:** Yellow liquid; bp 145–147 °C; IR (KBr Coat) 2958 (m), 2927 (m), 2860 (m), 1850–1650 (w), 1685 (m), 1458 (m), 1377 (m), 1260 (m), 952 (m), 912 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (1H, m, H-6), 5.76–5.69 (2H, m, H-7), 5.01–4.93 (1H, m, H-4), 3.31 (2H, t, H-5, $J = 7.8$ Hz), 2.79 (2H, t, H-1, $J = 7.6$ Hz), 2.28–1.97 (2H, m, H-2), 1.81–1.51 (2H, m, H-3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.38 (C-1), 29.89 (C-2), 32.01 (C-3), 47.89 (C-4), 36.39 (C-5), 136.39 (C-6), 115.84 (C-7); MS m/z 129 [M$^+$], 113 (16), 100 (29), 87 (34). Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.43%. Found: C, 65.16; H, 9.81%.

2-(1-Methylallyl)tetrahydrothiophene [2]: Mixture of (*R*)- and (*S*)-isomers. Yellow liquid; bp 146–148 °C; IR (KBr Coat) 3076 (m), 2947 (s), 2862 (m), 1850–1650 (w), 1637 (m), 1440 (m), 1371 (m), 995 (m), 914 (m) cm^{-1}; MS m/z 141 [M$^+$], 129 (12), 113 (28), 100 (41), 87 (54). Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92%. Found: C, 67.50; H, 10.06%. Main fraction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, m, H-7), 5.77–5.70 (2H, m, H-8), 4.99–4.89 (1H, m, H-4), 3.22–3.01 (1H, m, H-5),

Table 1. Reduction Products and Their Yields by ATHT and ADES

Salt	Synthetic methods and yield					
	Electro reduction	Yield/%	Electro reduction with PhCHO	Yield/%	Base method	Yield/%
(a)	[1] 	75	[4] 	*E* 45 *Z* 37	[1] 	88
(b)	[2] 	76	[5] 	2*E*,4*E* 31 2*E*,4*Z* 22	[2] 	79
(c)	[3] 	84	[6] 	62	[3] 	92
(d)	[7] 	52	[4] 	*E* 43 *Z* 32	[7] 	62
(e)	[8] 	74	[5] 	2*E*,4*E* 31 2*E*,4*Z* 21	[8] 	75
(f)	[9] 	74	[6] 	64	[9] 	90

2.78–2.71 (2H, m, H-1) 2.32–2.01 (2H, m, H-2), 1.95–1.82 (2H, m, H-3), 1.03–1.00 (3H, d, H-6, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.02 (C-1), 30.98 (C-2), 32.10 (C-3), 54.87 (C-4), 34.90 (C-5), 19.26 (C-6), 142.42 (C-7), 114.10 (C-8). Minor fraction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, m, H-7), 5.77–5.70 (2H, m, H-8), 4.99–4.89 (1H, m, H-4), 3.22–3.01 (1H, m, H-5), 2.78–2.71 (2H, m, H-1) 2.32–2.01 (2H, m, H-2), 1.95–1.82 (2H, m, H-3), 1.03–1.00 (3H, d, H-6, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.92 (C-1), 30.62 (C-2), 32.22 (C-3), 54.92 (C-4), 35.34 (C-5), 19.84 (C-6), 142.32 (C-7), 114.01 (C-8).

2-(1,1-Dimethylallyl)tetrahydrothiophene [3]: Yellow liquid; bp 148–150 °C; IR (KBr Coat) 3080 (m), 2929 (s), 2860 (m), 1850–1650 (w), 1637 (m), 1487 (m), 1414 (m), 1377 (m), 1002 (m), 912 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (1H, m, H-8), 5.98–5.91 (2H, m, H-9), 4.99–4.89 (1H, m, H-4), 2.80–2.72 (2H, m, H-1) 2.16–2.11 (2H, m, H-2), 1.97–1.82 (2H, m, H-3), 1.06 (6H, s, H-6,7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.53 (C-1), 31.29 (C-2), 31.72 (C-3), 59.70 (C-4), 31.98 (C-5), 25.02 (C-6), 24.93 (C-7), 145.56 (C-8), 111.41 (C-9); MS m/z 156 [M$^+$], 141 [M$^+$ − CH_3] (15), 129 (27), 113 (43), 100 (56), 87 (69). Anal. Calcd for $C_9H_{16}S$: C, 69.16; H, 10.32%. Found: C, 69.31; H, 10.33%.

3,4-Epoxy-4-phenyl-1-butene [4]: Mixture of (*E*)- and (*Z*)-isomers; Yellow liquid; bp 180–208 °C; IR (KBr Coat) 3085 (m), 3031 (m), 2991 (m), 1850–1650 (w), 1637 (m), 1496 (m), 1456 (m), 1440 (m), 1388 (m), 985 (m), 925 (m), 871 (s), 752 (s), 698 (s) cm^{-1}. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89%. Found: C, 81.99; H, 7.10%. (*E*)-isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.10 (3H, m, H-6,7,8), 5.60–5.52 (1H, m, H-2), 5.36–5.25 (1H, m, H-1, cis), 5.17–5.07 (1H, m, H-1, trans), 3.59 (1H, d, H-4, $J = 2.0$ Hz), 3.19 (1H, t, H-3, $J = 2.2$ Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 119.20 (C-1), 134.94 (C-2), 59.87 (C-3), 62.59 (C-4), 131.92 (C-5), 125.24 (C-6), 127.95 (C-7), 128.23 (C-8); MS m/z 146 [M$^+$], 131 [M$^+$ − CH_3] (15), 117 (29), 105 (41), 89 (56). (*Z*)-isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.10 (3H, m, H-6,7,8), 5.60–5.52 (1H, m, H-2), 5.36–5.25 (1H, m, H-1, cis), 5.17–5.07 (1H, m, H-1, trans), 4.05 (1H, d, H-4, $J = 4.4$ Hz), 3.47 (1H, t, H-3, $J = 4.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.57 (C-1), 131.92 (C-2), 58.47 (C-3), 59.44 (C-4), 136.83 (C-5), 126.17 (C-6), 127.44 (C-7), 127.87 (C-8); MS m/z 146 [M$^+$], 131 [M$^+$ − CH_3] (15), 117 (29), 105 (41), 89 (56).

4,5-Epoxy-5-phenyl-2-pentene [5]: Mixture of (2*E*,4*E*)- and (2*E*,4*Z*)-isomers. Yellow liquid; bp 161–200 °C; IR (KBr Coat) 3075 (m), 3029 (m), 2991 (m), 1850–1650 (w), 1635 (m), 1492 (m), 1465 (m), 1440 (m), 1388 (m), 984 (m), 921 (m), 875 (s), 752 (s), 696 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%. Found: C, 82.62; H, 7.25%. (4*E*)-isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.08 (3H, m, H-7,8,9), 5.25–5.22 (1H, t, H-3, $J = 4.3$ Hz), 4.95–4.86 (1H, m, H-2), 3.58–3.55 (1H, d, H-5, $J = 4.2$ Hz), 3.13–3.11 (1H, t, H-4, $J = 10.0$ Hz) 1.59–1.55 (3H, d, H-1, $J = 11.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.49 (C-1), 124.50 (C-2), 135.32 (C-3), 59.60 (C-4), 62.48 (C-5), 125.11 (C-6), 129.22 (C-7), 127.22 (C-8), 127.95 (C-9); MS m/z 160 [M$^+$], 145 [M$^+$ − CH_3] (15), 131 (29), 117 (43), 105 (55), 91 (69). (4*Z*)-isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.08 (3H, m, H-7,8,9), 5.82–5.70 (1H, t, H-3, $J = 4.3$ Hz), 4.95–4.86 (1H, m, H-2), 3.99–3.98 (1H, d, H-5, $J = 4.1$ Hz), 3.44–3.41 (1H, t, H-4, $J = 12.8$ Hz), 1.42–1.40 (3H, d, H-1, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.66 (C-1), 126.15 (C-2), 131.21 (C-3), 58.40 (C-4), 59.32 (C-5), 126.07 (C-6), 128.06 (C-7), 127.72 (C-8), 128.06 (C-9); MS m/z 160 [M$^+$], 145 [M$^+$ − CH_3] (15), 131 (29), 117 (43), 105 (55), 91 (69).

2-Methyl-5-phenyl-2-pentene-4-ol [6]: Yellow liquid; bp 124–126 °C; IR (KBr Coat) 3398 (s), 2972 (m), 2914 (m), 1850–1750 (w), 1701 (m), 1492 (m), 1450 (m), 1363 (m), 1026 (m), 758 (m), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.19 (3H, m, H-8,9,10), 5.13 (1H, d, H-3, $J = 6.8$ Hz), 4.59 (1H, t, H-4, $J = 6.6$ Hz), 2.44–2.38 (2H, m, H-6), 1.80 (1H, s, OH) 1.69 (3H, s, H-2, trans) 1.56 (3H, s, H-1, cis); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.73 (C-1), 17.78 (C-2), 144.17 (C-3), 119.17 (C-4), 73.89 (C-5), 38.04 (C-6), 135.18 (C-7), 125.72 (C-8), 127.17 (C-9), 128.13 (C-10); MS m/z 176 [M$^+$], 161 [M$^+$ − CH_3] (15), 143 (33), 128 (48), 117 (59), 107 (69), 103 (73), 91 (85). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%. Found: C, 82.14; H, 8.73%.

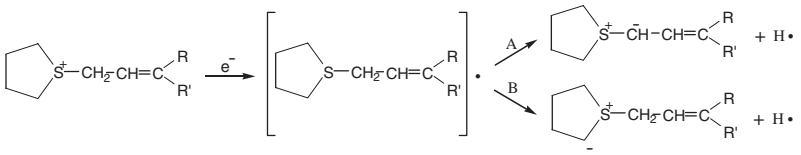
Products from ADES. Ethyl 1-Methyl-3-butenyl Sulfide [7]: Yellow liquid; bp 140–142 °C; IR (KBr Coat) 3082 (m), 2960 (m), 2825 (m), 1850–1650 (w), 1643 (m), 1438 (m), 1375 (m), 1261 (m), 914 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (1H, m, H-6), 5.76–5.69 (2H, m, H-7), 5.03–4.98 (1H, m, H-4), 2.52–2.47 (2H, m, H-5), 2.51–2.44 (2H, m, H-1), 1.20–1.17 (6H, m, H-2,3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.97 (C-1), 14.75 (C-2), 20.69 (C-3), 41.24 (C-4), 24.27 (C-5), 135.67 (C-6), 116.78 (C-7); MS m/z 131 [M$^+$], 117 (14), 105 (26), 91 (40). Anal. Calcd for $C_7H_{12}S$: C, 64.55; H, 10.83%. Found: C, 64.45; H, 11.03%.

1,2-Dimthyl-3-butenyl Ethyl Sulfide [8]: Mixture of (*R*)- and (*S*)-isomers. Yellow liquid; bp 142–144 °C; IR (KBr Coat) 3078 (m), 2945 (s), 2862 (m), 1850–1650 (w), 1647 (m), 1440 (m), 1374 (m), 999 (m), 914 (m) cm^{-1}; MS m/z 145 [M$^+$], 131 (14), 117 (14), 105 (26), 91 (40). Anal. Calcd for $C_8H_{14}S$: C, 66.60; H, 11.18%. Found: C, 66.50; H, 11.06%. Main fraction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (1H, m, H-7), 5.80–5.73 (2H, m, H-8), 4.99–4.94 (1H, m, H-4), 2.51–2.49 (2H, m, H-1), 2.49 (2H, t, H-5, $J = 7.6$ Hz), 1.19–1.16 (6H, m, H-2,3), 1.03–1.00 (3H, d, H-6, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.53 (C-1), 14.69 (C-2), 17.25 (C-3), 44.96 (C-4), 24.72 (C-5), 18.21 (C-6), 140.91 (C-7), 114.39 (C-8). Minor fraction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (1H, m, H-7), 5.80–5.73 (2H, m, H-8), 4.99–4.94 (1H, m, H-4), 2.51–2.49 (2H, m, H-1), 2.49 (2H, t, H-5, $J = 7.6$ Hz), 1.19–1.16 (6H, m, H-2,3), 1.03–1.00 (3H, d, H-6, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.29 (C-1), 15.46 (C-2), 17.64 (C-3), 44.84 (C-4), 24.97 (C-5), 18.21 (C-6), 141.39 (C-7), 114.33 (C-8).

1,2,2-Trimethyl-3-butenyl Sulfide [9]: Yellow liquid; bp 143–146 °C; IR (KBr Coat) 3082 (m), 2968 (s), 2927 (m), 2871 (m), 1850–1650 (w), 1637 (m), 1456 (m), 1413 (m), 1373 (m), 1066 (m), 1002 (m), 912 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, m, H-8), 5.91–5.83 (2H, m, H-9), 5.01–4.96 (1H, m, H-4), 2.60–2.52 (2H, m, H-1), 1.26–1.23 (6H, m, H-2,3), 1.11 (6H, s, H-6,7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.77 (C-1), 14.74 (C-2), 17.76 (C-3), 50.71 (C-4), 26.19 (C-5), 25.19 (C-6), 23.71 (C-7), 146.23 (C-8), 111.58 (C-9); MS m/z 159 [M$^+$], 144 [M$^+$ − CH_3] (15), 131 (28), 117 (42), 105 (54), 91 (68). Anal. Calcd for $C_9H_{16}S$: C, 68.28; H, 11.46%. Found: C, 68.20; H, 11.82%.

Discussion

In our previous report,[13] the generation of S-Y from benzyl sulfonium salts by the electrochemical reduction has been confirmed in two ways: by the reaction with benzaldehyde giving



Scheme 3.

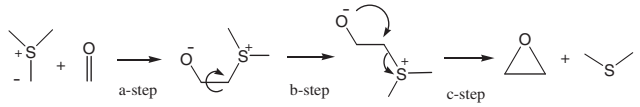
epoxides as a result of Corey–Chaykovsky reaction, and also by the Sommelet–Hauser rearrangement that is a [2,3] sigmatropic rearrangement of a substituent on the S atom onto benzene ring. Their reaction occurred under gentle conditions. In this study, we found generation of S-Y from allyl sulfonium salts by the electrochemical reduction.

Without catalyst, we prepared allyl sulfonium salts by the electrophilic reaction of allyl halides with aliphatic sulfides; sulfonium salts [b] and [e] were obtained as (*E*)-isomer only. This S-salt is more difficult to synthesize than benzyl sulfonium salts because of the unstability of the carbocations supplied by the allyl halides.

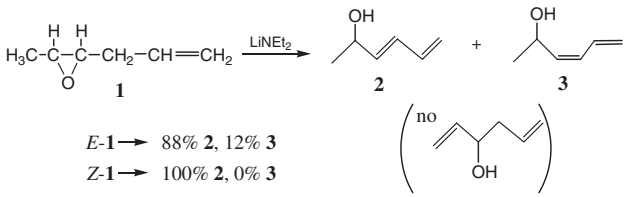
The generation of S-Ys by a base such as sodium amide has been confirmed by reactions with many carbonyl compounds. And without the presence of carbonyl compounds, we have reported that the benzyl S-Y give symmetrical epoxides derived from the benzyl groups on the salt as a result of an oxidation reaction caused by coexisting oxygen.[13] However, the allyl S-Y gave only the rearrangement compounds and no epoxide derived from the oxidation of the allyl group on the S-Y, because the allyl group has weak affinity to oxygen and is not oxidized to aldehyde.

Electrochemical generation of S-Y progresses as one-electron reduction, since sulfonium salts disappeared completely when 1 F/mol of electric current has been passed. And the electrochemical reduction might proceed through 2-way mechanisms to generate S-Ys as described in Scheme 3. The two routes were designated as A and B route based on the positional difference of hydrogen abstraction. In the presence of benzaldehyde, the electrochemical reduction of sulfonium salts, (a), (b), (d), and (e), gave epoxides in high yields as epoxidation of S-Y with benzaldehyde followed the A route.

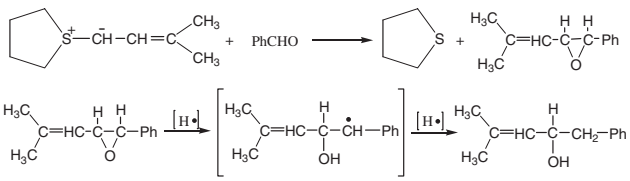
In the case of allyl S-Ys, the epoxides obtained from the A route isomerized, giving (*E*)- and (*Z*)-isomers, although the benzyl S-Ys gave (*E*)-epoxide stereoselectively. The detailed mechanisms of Corey–Chaykovsky reaction of S-Ys have been calculated by Aggarwal et al.[14] using the B3LYP density function. The reaction of S-Ys with aldehyde proceeds in three-step reactions through the most stable route, which is shown in Scheme 4, and the stereoselectivity is determined on the b-step, where the charged groups rotate to anti from gauche form. In the case of benzyl S-Ys, the rotation barrier is high and on b-step, *erythro*-betaine is stabler than *threo*-betaine and only the (*E*)-epoxide is obtained stereoselectively. And in the reaction of allyl S-Y, the reason of the contamination



Scheme 4.



Scheme 5.



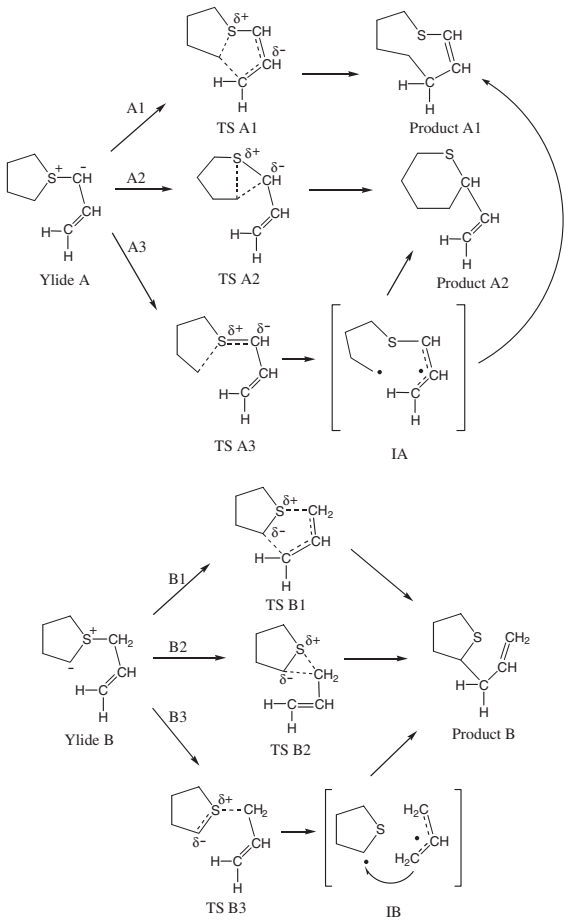
Scheme 6.

of (*E*)- and (*Z*)-epoxides is because the rotation barrier from *erythro*-betaine to *threo*-betaine is smaller than in the case of benzyl S-Y, because of the allyl group being a less bulky group than the benzyl group.

But on sulfonium salts (c) and (f), which have the methyl groups at both ends of the allyl group, this reduction gives alcohols only which were considered as the addition compounds of H atom to the epoxide. Production of alcohol by the base-catalyzed α- or β-proton elimination pathway from epoxide have been reported by R. P. Thummel et al.[15,16] as shown in Scheme 5. Electrochemical reduction of epoxides has not been reported so far. The active H radical comes from the sulfonium salts or the other activated minor products at the cathode might cause the hydrogenation of epoxides, because the usual hydrogen molecule generation was not observed at the cathodic electrode in this reaction. And the electron donative property of methyl groups helps the electrophilic radical addition reaction to the strained epoxide. The reduction process is shown in Scheme 6.

Without benzaldehyde, the products of [1]–[3] and [7]–[9] were found to be the rearrangement products formed through an unstable ylide B, as shown in Scheme 7. The yield of product [7] is rather low because of its poor stability. A possible rearrangement mechanism through stable ylide A is shown in route A1 that may give eight-membered products. Both routes A1 and B1 will give transition states obeying the Woodward–Hoffmann rule, i.e., 5 orbitals and 6 electrons. But to proceed via unstable Ylide B giving only intriguing product B indicates that unstable Ylide B may exist in equilibrium with stable Ylide A. The B route is supposed to proceed through the most stable TS to rearrange.

Without any substituent on the allyl group, it would be difficult to differentiate between the [2,3] Sommelet–Hauser route B1 and the [1,2] Stevens rearrangement route B2, al-



Scheme 7.

though from Ylide A the different products A1 and A2 are expected. We have reported the mechanisms about the [1,2] Stevens rearrangement of P-Y and As-Y and found that sigmatropic route might be more preferable than radical route with the migrating groups[6] such as hydrogen, vinyl, and silyl groups. In this study, we should take into consideration the [1,2] Stevens rearrangement A2, B2 and radical routes A3, B3, which will proceed through the intermediate IA and IB, as the alternative routes. However in the reaction, the sigmatropic [2,3] Sommelet–Hauser route is supposed to be most preferable because the activation energies to transition states TS A1 or TS B1 on sigmatropic route are expected to be reduced by allylic substituent. In order to elucidate the rearrangement mechanisms, we calculated the energy surfaces and the geometries of all the reactants, intermediates and transition states on the surface of the A and B routes by using the PM3 Hamiltonian; an energy diagram of the reaction of ATHT that has no substituent on the allyl group is shown in Fig. 1. In this figure, the heat of formation of proton was subtracted from that of sulfonium ion; also, from the heats of formation of each epoxide, that of benzaldehyde was taken away.

The difference in the heat of formations between stable Ylide A and unstable Ylide B is 9.9 kcal/mol. For the reaction of S-Y with benzaldehyde, the experimental product is Epoxide A, though the heats of formation of the two products were nearly equal. Because this reaction is similar to that of the benzyl S-Y;[13] the stable Ylide A must react with benzaldehyde immediately after its formation. On the other hand, the rearrangement reaction proceeds via unstable Ylide B, giving only intriguing Product B. At the PM3 level, the Sommelet–Hauser rearrangement at B route is easier by about 28–34 kcal/mol than any other route, and it is clear that the dramatic stability of TS B1 is the main factor of route determination.

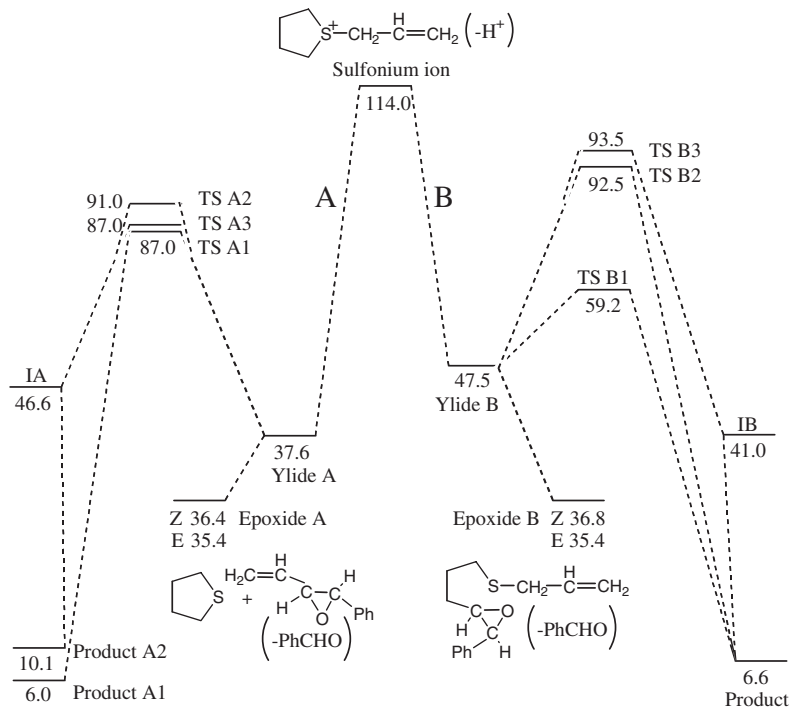


Fig. 1. Energy surfaces in the A and B routes.

The B route, from unstable Ylide B via TS B1 to Product B, must be the real path of this rearrangement; it involves a cleavage of the S–7C σ bond. In case of having a benzyl group on the S-Y, the rich π electrons of phenyl group may be expected to interact with the partial positive charge generated on 7C at TS B1 resulting in much stable transition state. We calculated the differences of electron density changes for allyl S-Y between Ylide A and TS A1, and also between Ylide B and TS B1 (represented as ΔAl) and compared with those of benzyl S-Y (represented as ΔBn) as shown in Fig. 2. As a result, it emerged that the partial positive charge on S atom of TS B1 was delocalized to allyl group almost equally with the case of benzyl group; in addition, the delocalization of partial negative charge on 4C to 5C appeared to be larger in the allyl group than in the benzyl group. This resonance stabilization by delocalization of the electron at anionic and cationic charge on TS B1 decreases the activation energy to TS B1 from unstable Ylide B. On the contrary, the partial positive charge on S atom of TS A1 was distributed locally to adjacent atoms and was not enough to stabilize TS A1. This is the reason why no rearrangement via A route occurs.

As another possible mechanism in B route, the [1,2] Stevens rearrangement gave the TS B2 with higher activation energy than the TS B1, but this route is more favored than TS B3, radical route, by 1.0 kcal/mol although it is forbidden by the Woodard–Hoffmann rule, i.e., 3 orbitals and 4 electrons. To elucidate the factor of stabilization of TS B2, we compared

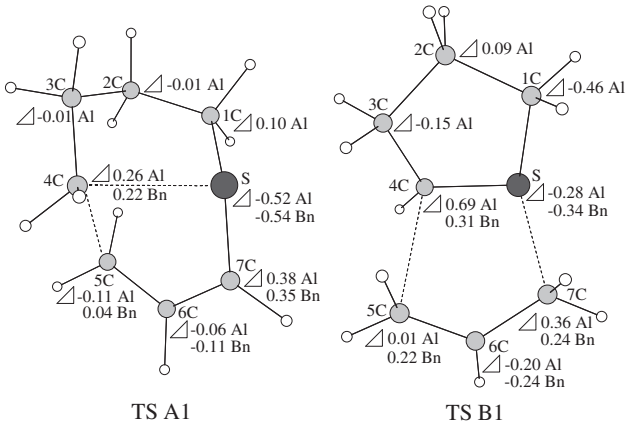


Fig. 2. The differences of electron densities between Ylide A and TS A1, and between Ylide B and TS B1. Al is allyl S-Y and Bn is benzyl S-Y.

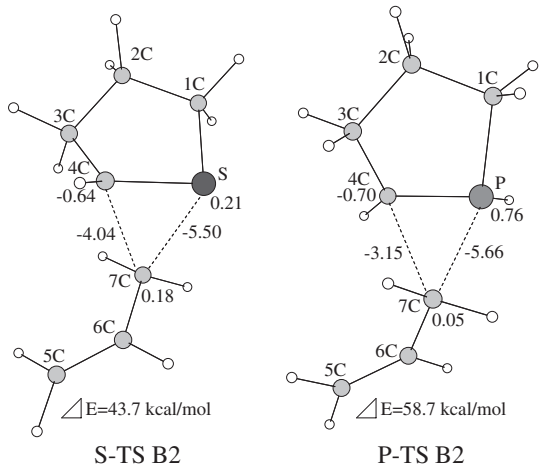


Fig. 3. Electron densities of the S-TS B2 and P-TS B2.

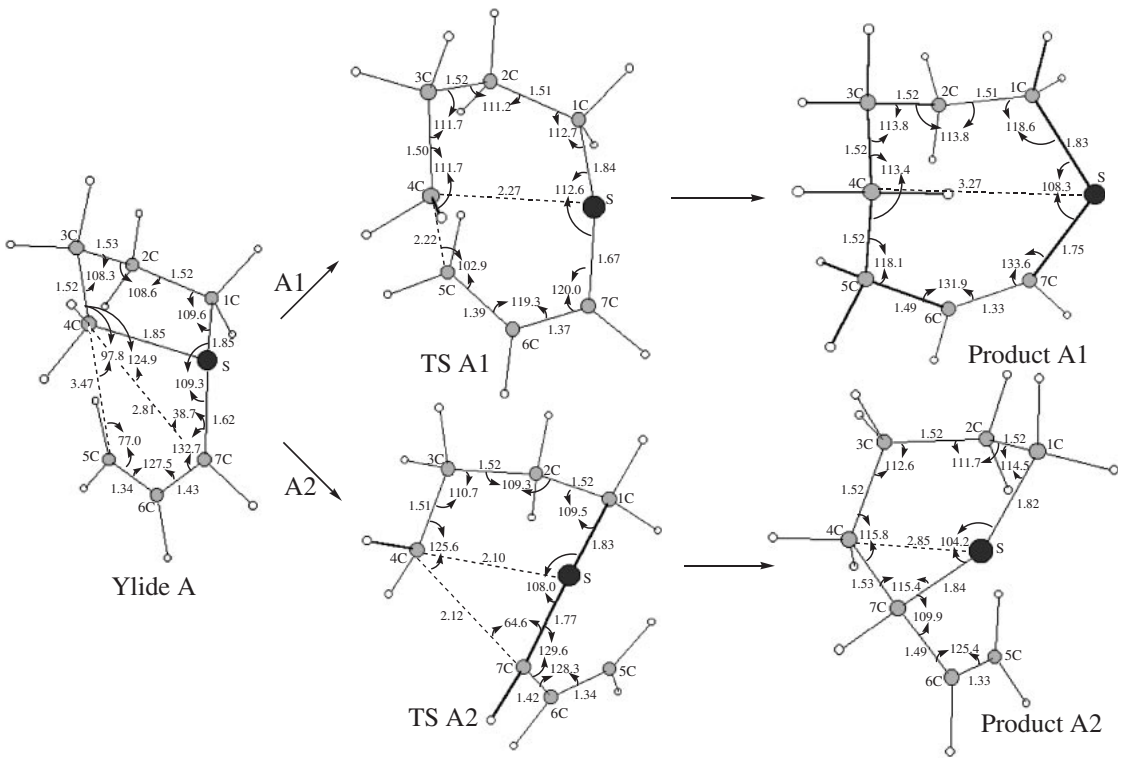


Fig. 4. Optimized structures of the A route.

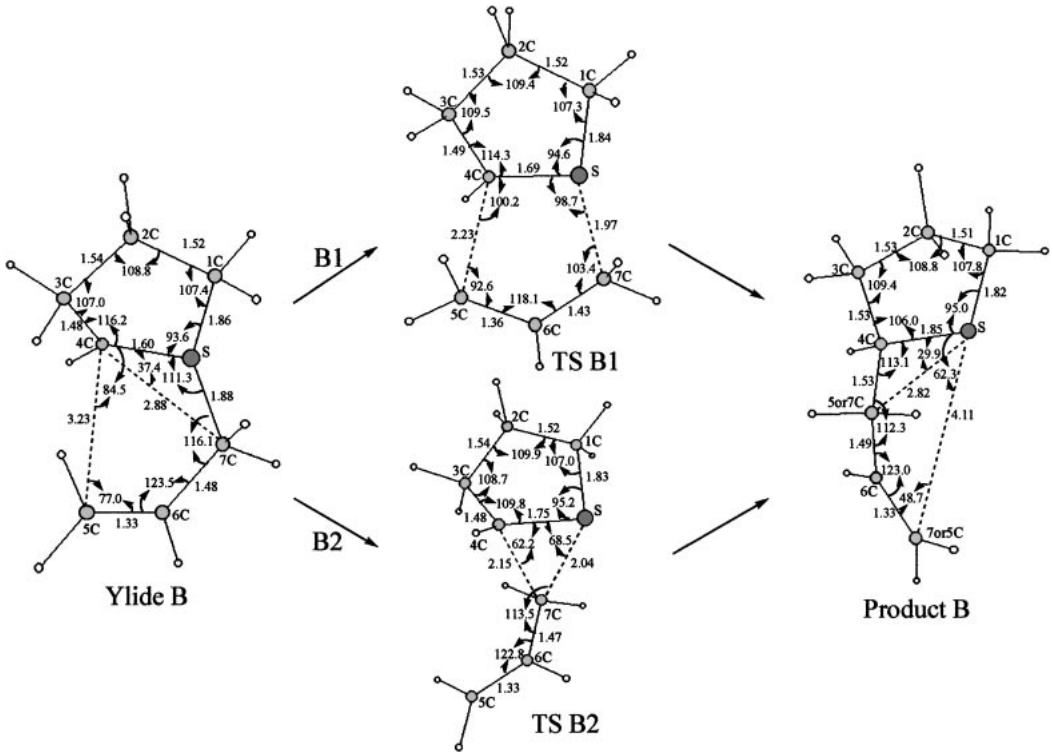


Fig. 5. Optimized structures of the B route.

Table 2. Dihedral Angles of Optimized Structures in A and B Routes

	A					B			
	Ylide A	TS A1	TS A2	Product A1	Product A2	Ylide B	TS B1	TS B2	Product B
S–C7–C6–C5	3.98	12.11	−1.02	1.26	−90.23	−70.80	−59.42	−138.25	−63.17
C4–S–C7–C6	49.26	22.27	116.76	0.16	129.81	32.27	26.81	75.24	22.14
C4–S–C6–C5	49.40	34.06	122.49	1.17	86.54	−25.36	−21.30	−16.99	−38.13
S–C4–C5–C6	40.41	40.86	99.76	1.81	54.67	−21.90	−24.89	−10.39	−74.31
C4–C5–C6–C7	−26.22	−40.37	−37.79	−2.74	−21.43	48.18	52.91	57.29	134.18

the electron density of TS B2 of S-Y (S-TS B2) with that of P-Y (P-TS B2) which might be difficult to migrate using sp^3 hybrid orbital in the allyl group; the results are shown in Fig. 3. In the P-TS B2, the neutralized 7C has low affinity with the negatively charged 4C, on the contrary, the positively charged 7C on S-TS B2 has high affinity with the 4C atom. For the cationic sigmatropic route, the activation energy of S-TS B2 is lower than P-TS B2 by 15.0 kcal/mol. However, the activation energies of TS-B2 and TS B3 are much higher than that of TS B1 of the Sommelet–Hauser rearrangement.

The most favorable B route from TS B1 to Product B is a [2,3] sigmatropic rearrangement and is suprafacial, as the dihedral angle of C4–S–C7–C6 changes from 32.3° to 26.8°, keeping the tetrahydrothiophene ring upon the migration. The geometrical figures of the A and B routes are shown in Figs. 4 and 5 and the relevant dihedral angles are listed in Table 2.

In the case of allyl S-Ys which have the methyl substituents at the end of allyl group, the mechanism is evidently the B1 route, that is, the [2,3] sigmatropic Sommelet–Hauser route, judging from the products obtained. As a result, it is obvious that the [2,3] sigmatropic rearrangement of allyl group is a predominant route in the electrochemical reduction of the S-salt.

Summary

The electrochemical reductions of allyl sulfonium salts gave allyl S-Ys with one-electron transfer reactions. The presence of S-Ys was verified by Corey–Chaykovsky reactions with benzaldehyde, giving (*E*)- and (*Z*)-mixture of the corresponding epoxides. The reactions of sulfonium salts having the methyl groups at both ends of the allyl group gives alcohols which were considered to be the addition compounds of H atom generated at cathodes to the epoxides. Without the presence of benzaldehyde, the S-Ys gave Sommelet–Hauser rearrangement products in good yields. And this rearrangement was ascertained in the reaction of sulfonium salts with strong base, sodium amide, and the yields of the two methods are not so different. By the base method, no oxidation of S-Ys was observed. This fact is different from the case of the S-Ys having a benzyl group on the S atom. The MO calculations by using semi-empirical PM3 Hamiltonian clarified that the most plausible route among the possible rearrangements was the Sommelet–Hauser rearrangement.

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