

Generation of Sulfur Ylides from Sulfonium Salts and Their Reactions. 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 acetonitrile in the presence and absence of benzaldehyde was carried out. Results were compared with results of the base method. In the presence of benzaldehyde, the electrochemical reduction gave epoxides as a result of the Corey–Chaykovsky reaction, thus confirming ylide formation. The electrochemical reduction of sulfonium salts without benzaldehyde yielded rearrangement products in high yield. On the contrary, upon base treatment of sulfonium salts without benzaldehyde, symmetrical epoxides derived from the benzyl group of the sulfonium salt are obtained as main products as a result of the auto oxidation of the sulfur ylide. The reaction mechanisms were elucidated based on the results obtained by a semi-empirical molecular orbital method.

Phosphorus and sulfur ylide (abbreviated as P–Y and S–Y hereafter), are important intermediates as carbanions in synthetic chemistry. S–Ys are extensively utilized in organic chemistry to achieve the stepwise insertion of a methylene or substituted methylene across the double bond of a carbonyl, an imine, or an electrophilic olefin to give an epoxide, aziridine or a cyclopropane, respectively. The reactivities of the carbanions depend on either the substituents on the carbanions or the sort of central heteroatom of the 15-group elements[1–3] (N, P, As etc.) or of the 16-group elements[4,5] (S, Se etc.) which carry the positive charge. In this study, we investigated the generation of S–Y by electrochemical reduction and their reactions. As intermediates in organic syntheses, especially the S–Y has been utilized for getting a wide variety of epoxides derivatives.[6,7] Because the sulfur atom of the S–Y has poor affinity with the oxygen atom, the popular Corey–Chaykovsky reaction with carbonyl compounds occurs, producing epoxides instead of the olefin. Among many reactions of ylides, the rearrangement reactions[8–10] of the S–Ys have stirred up interest in many researchers owing to their weaker affinity with carbon compared with those of P–Ys. The S–Y is stabilized by the (p–d) π conjugated system[11] i.e. the anionic charge is delocalized by d orbital on the sulfur atom. But theoretical calculations revealed the fact that the S–Y carbanion will interact with a S–C nonbonding orbital.[12] The substituent effect on carbanion is a great factor in S–Y stability, and the electron-withdrawing groups (EWG) stabilize S–Y by the delocalization of the negative charge on the carbanion.

Various synthetic methods of S–Y have been proposed by many researchers.[13–16] Generally it is found that (1) α-dehydroganation from sulfonium salt (abbreviated as S-salt) as the precursor of S–Y by base[17] and (2) addition reactions of alkylidene to a sulfide[18] are well-known methods to get the S–Ys. Although reaction (1) is the major method for obtaining the S–Y from S-salts, strong bases such as butyllithium and $DMSO^-$ are required to abstract an α-proton in the case of unstable ylides.[19,20] The method (2) is known to be simple and to give stable ylide in high yields. As a minor method, only a few papers has reported the utilization of an electrochemical reduction of S-salts[21–23] for generation of S–Ys.

We have reported the generation of P–Y by the electrochemical reduction of phosphonium salts[24] and we found that the P–Ys were obtained by a one-electron reductive process. In this experiment, we used the electrochemical reduction method for S-salts to produce S–Ys and we compared the reaction products with those obtained from the base method. We found that the 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 tried the Corey–Chaykovsky reactions of the S–Y generated by the electrochemical reduction method with benzaldehyde and obtained the corresponding epoxides as the main products. Without benzaldehyde, the S–Ys undergo the Sommelet–Hauser rearrangement easily, in a way similar to that reported on the nitrogen ylide along with the dimer formation of benzyl groups. Vedejs et al. reported a [2,3] Wittig rearrangement of S–Y that contains allylic substituent to give a macro-cyclic molecule.[25] Some theoretical studies from the view point of stereo chemistry are reported and the energy differences in the transition state are discussed.[26] In regard to the Sommelet–Hauser rearrangement, Okada et al.[27] reported the synthesis of thiepin derivatives through skeletal reconstruction of S–Y with two benzyl groups on the sulfur atom. An ab initio MO calculation at HF/6-31G* basis set was used to elucidate the reaction mechanism.[28] However, the sulfonium salts in their study have two benzyl groups and there is no competition between stable ylide and unstable ylide. In this report, we describe the electrochemical generations of S–Y with a benzyl group in S-salts and the route determination of the following Sommelet–Hauser rearrangement from benzyl tetrahydrothiophenium salt (BTHT) and from benzyl diethyl sulfonium salt (BDES) to detect the

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presence of any differences between ring structure and open chain structure. In order to clarify the mechanism of their reactions, all minimum or saddle points of the reaction profile were optimized. And also, the bond energies and spin density distributions were used to explain the reaction path found in the electrochemical reduction of the S-salts.

Experimental

Materials. Tetrahydrothiophene, diethyl sulfide, benzyl bromide, 4-methylbenzyl bromide, 4-bromobenzyl bromide, 4-cyanobenzyl bromide, 4-nitrobenzyl bromide, benzaldehyde, sodium amide, acetonitrile, and tetraethylammonium perchlorate are commercial products. All the liquid reagent materials were used after purification by distillation. ^{1}H NMR and ^{13}C NMR were recorded on JEOL JNM-A series spectrometers in $CDCl_3$ solvent. Mass spectra were obtained on a SHIMADZU GCMS-QP2010. The melting point was measured on a SEIKO INSTRUMENTS TG-DTA SSC/5200H. IR spectra were recorded on SHIMADZU FTIR-8700. Electric 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 ethyl ether solvent, the sulfonium salts were synthesized by the reaction of tetrahydrothiophene or diethyl sulfide with equimolar corresponding benzyl bromide and this *p*-substituent. Reaction conditions are at room temperature into an argon gas. The melting point, IR spectra, ^{1}H NMR, ^{13}C NMR spectra data and elemental analysis of the BTHT and BDES are shown below. The numbering systems of the compounds are specified as described in Chart 1.

BTHT. 1-Benzyltetrahydrothiophenium Bromide (a): White crystal; mp 119–121 °C; IR (KBr Tablet) 2945 (m), 2821 (m), 1850–1550 (w), 1497 (m), 1456 (m), 1418 (m), 1257 (m), 772 (m), 705 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (2H, d, H-5, J = 5.9 Hz), 7.22 (1H, t, H-7, J = 7.1 Hz), 7.20 (2H, t, H-6, J = 7.8 Hz), 4.40 (2H, s, H-3), 2.72 (4H, m, H-1), 1.85 (4H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.87 (C-1), 28.34 (C-2), 45.59 (C-3), 128.66 (C-4), 130.48 (C-5), 128.89 (C-6), 129.83 (C-7). Anal. Calcd for $C_{11}H_{15}BrS$: C 50.97, H 5.83%. Found: C 50.95, H 5.84%.

1-(4-Methylbenzyl)-tetrahydrothiophenium Bromide (b): White crystal; mp 127–130 °C; IR (KBr Tablet) 2939 (s), 2879 (m), 2826 (m), 1850–1550 (w), 1516 (m), 1410 (m), 1192 (m), 826 (m), 725 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (2H, d, H-6, J = 6.2 Hz), 7.13 (2H, d, H-5, J = 7.7 Hz), 4.41 (2H, s, H-3), 2.75 (4H, m, H-1), 2.29 (3H, s, R), 1.86 (4H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.81 (C-1), 28.46 (C-2), 45.80 (C-3), 139.58 (C-4), 128.53 (C-5), 129.03 (C-6), 125.28 (C-7), 20.78 (R). Anal. Calcd for $C_{12}H_{19}BrS$: C 52.75, H 6.27%. Found: C 52.80, H 6.19%.

1-(4-Bromobenzyl)-tetrahydrothiophenium Bromide (c): White crystal; mp 120–123 °C; IR (KBr Tablet) 2941 (m), 2831 (m), 1850–1550 (w), 1583 (s), 1483 (s), 1402 (m), 1220 (m), 1067 (m), 833 (m), 713 (m), 594 [C–Br] (s) cm^{-1}. ^{1}H NMR (400 MHz, D_2O) δ 7.47 (2H, d, H-5, J = 8.3 Hz), 7.23 (2H, d, H-6, J = 8.3 Hz), 4.33 (2H, s, H-3), 3.28 (4H, m, H-1), 2.12 (4H, m, H-2); ^{13}C NMR (100 MHz, D_2O) δ 42.44 (C-1), 28.15 (C-2), 44.90 (C-3), 127.38 (C-4), 132.57 (C-5), 131.96 (C-6), 123.75 (C-7). Anal. Calcd for $C_{11}H_{14}Br_2S$: C 39.08, H 4.17%. Found: C 39.01, H 3.87%.

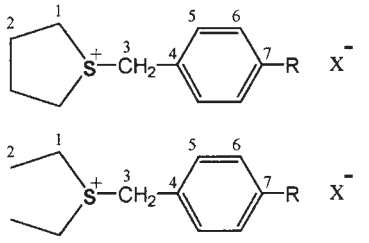
1-(4-Cyanobenzyl)-tetrahydrothiophenium Bromide (d): White crystal; mp 104–107 °C; IR (KBr Tablet) 2995 (w), 2810 (w), 2224 [CN] (m), 1850–1650 (w), 1590 (m), 1504 (m), 1409 (m), 1239 (m), 829 (m), 734 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, d, H-5, J = 8.5 Hz), 7.44 (2H, d, H-6, J = 8.7 Hz), 4.41 (2H, s, H-3), 2.75 (4H, m, H-1), 1.86 (4H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.04 (C-1), 31.43 (C-2), 45.93 (C-3), 142.73 (C-4), 132.48 (C-5), 129.63 (C-6), 118.29 (C-7), 112.01 (R). Anal. Calcd for $C_{12}H_{14}NBrS$: C 50.71, H 4.96, N 4.93%. Found: C 50.74, H 4.83, N 4.94%.

1-(4-Nitrobenzyl)-tetrahydrothiophenium Bromide (e): Yellow solid; mp 95–97 °C; IR (KBr Tablet) 2927 (w), 2814 (w), 1850–1650 (w), 1597 (m), 1540 [NO_2] (s), 1517 (s), 1226 (m), 800 (m), 752 (m) cm^{-1}. ^{1}H NMR (400 MHz, D_2O) δ 8.13 (2H, d, H-5, J = 8.5 Hz), 7.59 (2H, d, H-6, J = 8.8 Hz), 4.52 (2H, s, H-3), 3.45 (4H, m, H-1), 2.23 (4H, m, H-2); ^{13}C NMR (100 MHz, D_2O) δ 43.04 (C-1), 28.24 (C-2), 44.56 (C-3), 124.48 (C-4), 135.93 (C-5), 131.44 (C-6), 148.20 (C-7). Anal. Calcd for $C_{11}H_{14}NO_2BrS$: C 43.43, H 4.64, N 4.60%. Found: C 43.87, H 4.58, N 4.45%.

BDES. Benzyldiethylsulfonium Bromide (f): White crystal; mp 88–91 °C; IR (KBr Tablet) 2992 (m), 2881 (m), 1850–1550 (w), 1497 (m), 1456 (m), 1418 (m), 1267 (m), 775 (m), 707 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (2H, d, H-5, J = 7.3 Hz), 7.31 (2H, t, H-6, J = 7.2 Hz), 7.30 (1H, t, H-7, J = 7.8 Hz), 5.26 (2H, s, H-3), 3.72–3.64 (4H, m, H-1), 1.35 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.59 (C-1), 9.58 (C-2), 43.41 (C-3), 127.45 (C-4), 130.30 (C-5), 129.00 (C-6), 129.42 (C-7). Anal. Calcd for $C_{11}H_{17}BrS$: C 50.58, H 6.56%. Found: C 50.23, H 6.66%.

Diethyl-(4-methybenzyl)-sulfonium Bromide (g): White crystal; mp 90–93 °C; IR (KBr Tablet) 2956 (m), 2864 (m), 1850–1550 (w), 1510 (m), 1411 (m), 1192 (m), 826 (m), 725 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (2H, d, H-6, J = 7.2 Hz), 7.12 (2H, d, H-5, J = 7.7 Hz), 5.21 (2H, s, H-3), 3.70 (4H, m, H-1), 2.53 (3H, s, R), 1.38 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.82 (C-1), 9.98 (C-2), 43.77 (C-3), 134.74 (C-4), 130.25 (C-5), 130.66 (C-6), 124.13 (C-7), 21.23 (R). Anal. Calcd for $C_{12}H_{21}BrS$: C 52.36, H 6.96%. Found: C 52.41, H 6.78%.

Diethyl-(4-bromobenzyl)-sulfonium Bromide (h): White



(a) X = Br (d) R = CN, X = Br
(b) R = Me, X = Br (e) R = NO_2, X = Br
(c) R = Br, X = Br

(f) X = Br (i) R = CN, X = Br
(g) R = Me, X = Br (j) R = NO_2, X = Br
(h) R = Br, X = Br

Chart 1.

crystal; mp 115–118 °C; IR (KBr Tablet) 2931 (m), 2835 (m), 1850–1550 (w), 1587 (m), 1483 (m), 1400 (m), 1220 (m), 1064 (m), 833 (s), 711 (m), 594 [C–Br] (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, d, H-5, $J = 8.3$ Hz), 7.24 (2H, d, H-6, $J = 8.3$ Hz), 5.30 (2H, s, H-3), 3.72–3.60 (4H, m, H-1), 1.33 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.81 (C-1), 9.86 (C-2), 43.01 (C-3), 126.87 (C-4), 132.40 (C-5), 132.23 (C-6), 124.14 (C-7). Anal. Calcd for $C_{11}H_{16}Br_2S$: C 38.85, H 4.74%. Found: C 38.62, H 4.80%.

Diethyl-(4-cyanobenzyl)-sulfonium Bromide (i): White crystal; mp 114–116 °C; IR (KBr Tablet) 2994 (w), 2813 (w), 2226 [CN] (m), 1850–1650 (w), 1606 (m), 1506 (m), 1413 (m), 1228 (m), 846 (m), 829 (m), 738 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, d, H-5, $J = 8.4$ Hz), 7.33 (2H, d, H-6, $J = 8.6$ Hz), 4.40 (2H, s, H-3), 3.65–3.54 (4H, m, H-1), 1.47 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.39 (C-1), 9.50 (C-2), 35.22 (C-3), 143.10 (C-4), 132.11 (C-5), 129.31 (C-6), 118.39 (C-7), 111.79 (R). Anal. Calcd for $C_{12}H_{16}NBrS$: C 50.35, H 5.63, N 4.89%. Found: C 50.34, H 5.23, N 4.90%.

Diethyl-(4-nitrobenzyl)-sulfonium Bromide (j): Yellow solid; mp 97–99 °C; IR (KBr Tablet) 2926 (w), 2800 (w), 1850–1650 (w), 1604 (m), 1540 [NO_2] (s), 1510 (s), 1226 (m), 854 (m), 798 (m), 752 (m), 694 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (2H, d, H-5, $J = 8.8$ Hz), 7.39 (2H, d, H-6, $J = 8.8$ Hz), 4.45 (2H, s, H-3), 3.70 (4H, m, H-1), 1.42 (6H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.59 (C-1), 9.54 (C-2), 35.25 (C-3), 144.70 (C-4), 129.49 (C-5), 123.60 (C-6), 147.49 (C-7). Anal. Calcd for $C_{11}H_{16}NO_2BrS$: C 43.15, H 5.27, N 4.57%. Found: C 43.21, H 5.37, N 4.17%.

Electrochemical Reduction. In a 0.1 dL electrolytic cell which has a porous cup made of ceramics as a divider membrane, 0.2 mol of the S-salt was dissolved in 0.05 dL of acetonitrile at the cathodic side of the cell. In an anodic side, 0.01 dL of acetonitrile which contains 0.01 mol of tetraethylammonium perchlorate was used as the electrolyte. As the electrodes, two platinum plates (2×2 cm) were equipped in the cell. The cathodic reduction was carried out under condition of -2.5 V vs SCE at 22 °C under a nitrogen gas flow. After 1 F/mol of electricity based on the S-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 the case of the Corey–Chaykovsky reactions, an equimolar amount of benzaldehyde was dissolved in the cathodic solution and the same work up was carried out.

Base Method. In acetonitrile solvent, 0.2 mol of the S-salts were dissolved; after an equimolar amount of sodium amide was added, the solution 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 method 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 from BTHT and BDES are summarized in the Tables 1 and 2, respectively; they are numbered [1]–[15] and their yields are recorded in the same column. Their structures were determined based on physical properties, spectral data, and elemental analyses as listed in the following. Different products are obtained according to the difference in the reduction method and *p*-substituent on the benzyl groups. When the substituent group is an electron-donating group (EDG), the electrochemical reduction of BTHT gave the rearranged product in high yield. Conversely, when the substituent group on the benzyl group is an electron-withdrawing group (EWG), the electrochemical reduction generated radical coupling products of the benzyl group in the yields of 50–90% and the rest was mostly the reactant.

In the base method, all of the BTHT generated S–Ys and the autoxidation of the S–Ys led to the formation of symmetric epoxides, along with minor amounts of the rearrangement products. However, in the case of the BDES salts with a *p*-methyl or bromo-substituent, the rearrangement reaction dominated with minor amounts of the epoxide. All isolated epoxides had the *Z*-conformations and there were no peaks corresponding to *E*-isomers in ^1H or ^{13}C NMR spectra.

In the electrochemical reduction of BDES, the same rearrangement occurred, along with coupling reactions as for BTHT, but the yields are high compared to those from BTHT, especially in the case of rearrangement of S–Y with Me and Br substituents.

Products from BTHT. 2-Tetrahydrothionyl-2-methylbenzene [1]: Yellow liquid; bp 165–168 °C; IR (KBr Coat) 3024 (m), 2947 (m), 2860 (m), 1850–1650 (w), 1602 (m), 1493 (m), 1440 (m), 1317 (m), 1195 (m), 760 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–6.82 (4H, m, H-6,7,8,9), 4.61 (1H, t, H-4, $J = 8.1$ Hz), 3.01–2.76 (2H, m, H-1), 2.25–2.09 (2H, m, H-2), 2.21 (3H, s, H-11), 1.92–1.73 (2H, m, H-3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.67 (C-1), 31.22 (C-2), 33.88 (C-3), 49.01 (C-4), 141.95 (C-5), 126.31 (C-6), 127.84 (C-7), 130.04 (C-8), 125.61 (C-9), 135.09 (C-10), 19.92 (C-11); MS m/z 178 [M^+], 163 [$M^+ - CH_3$] (15), 135 (43), 91 (87). Anal. Calcd for $C_{11}H_{14}S$: C 74.10, H 7.91%. Found: C 74.04, H 7.66%.

2-Tetrahydrothionyl-2,5-dimethylbenzene [2]: Yellow liquid; bp 181–183 °C; IR (KBr Coat) 3016 (m), 2925 (m), 2860 (m), 1850–1650 (w), 1612 (m), 1500 (m), 1440 (m), 1379 (m), 1037 (m), 810 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–6.80 (3H, m, H-6,8,9), 4.59 (1H, t, H-4, $J = 8.1$ Hz), 3.03–2.74 (2H, m, H-1), 2.32–2.11 (2H, m, H-2), 2.22–2.20 (6H, s, H-11,12), 1.95–1.82 (2H, m, H-3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.35 (C-1), 30.66 (C-2), 32.94 (C-3), 48.38 (C-4), 140.20 (C-5), 127.03 (C-6), 132.41 (C-7), 129.96 (C-8), 127.22 (C-9), 135.34 (C-10), 20.97 (C-11), 19.02 (C-12); MS m/z 192 [M^+], 177 [$M^+ - CH_3$] (15), 163 (29), 149 (43), 133 (59) 117 (75). Anal. Calcd for $C_{12}H_{16}S$: C 74.55, H 8.86%. Found: C 74.57, H 8.30%.

2-Tetrahydrothionyl-2-methyl-5-bromobenzene [3]: Yellow liquid; bp 186–188 °C; IR (KBr Coat) 2947 (m), 2860 (m), 1850–1650 (w), 1589 (m), 1487 (m), 1440 (m), 1404 (m), 1070 (m), 1010 (m), 810 (m), 808 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64–6.85 (4H, m, H-6,8,9), 4.56 (1H, t, H-4, $J = 8.1$ Hz), 3.03–2.88 (2H, m, H-1), 2.27–2.04 (2H, m, H-2), 2.21 (3H, s, H-11), 1.92–1.76 (2H, m, H-3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.38 (C-1), 30.60 (C-2), 33.08 (C-3), 48.07 (C-4), 143.20 (C-5), 129.43 (C-6), 119.72 (C-7), 131.74 (C-8), 129.62 (C-9), 134.49 (C-10), 19.10 (C-11); MS m/z 257 [M^+], 242 [$M^+ - CH_3$] (15), 163 [$M^+ - CH_3Br$] (94), 150 (107), 134 (123), 118 (139). Anal. Calcd for $C_{11}H_{13}BrS$: C 51.37, H 5.09%. Found: C 51.79, H 4.61%.

4,4′-Dicyanobibenzyl [4]: White crystal; mp 190–193 °C; IR (KBr Tablet) 3057 (m), 2933 (m), 2223 [CN] (s), 1850–1650 (w), 1602 (m), 1504 (m), 1413 (m), 1176 (m), 835 (m), 557 (m) cm^{-1}.

Table 1. Reduction Products and Their Yields from BTHT Salts (%)

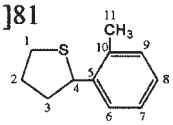
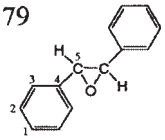
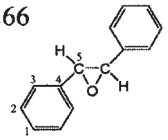
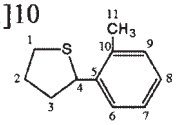
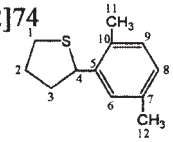
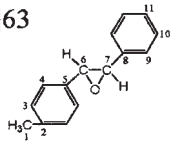
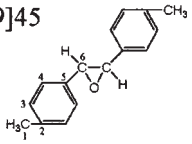
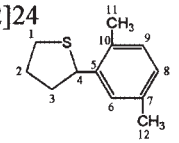
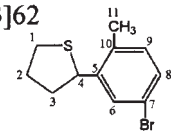
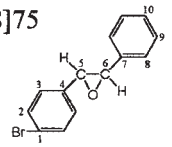
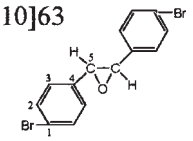
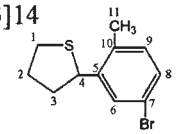
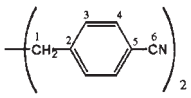
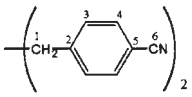
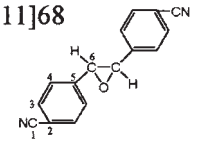
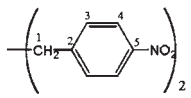
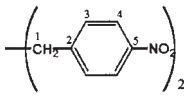
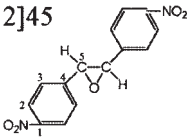
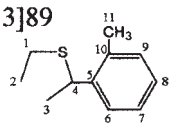
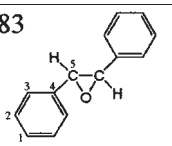
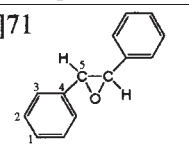
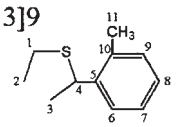
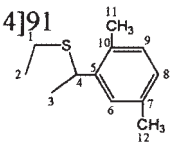
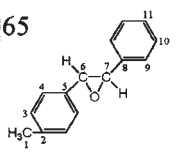
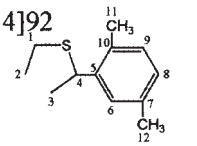
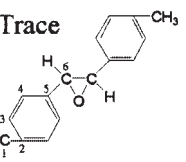
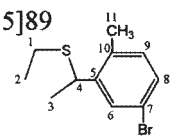
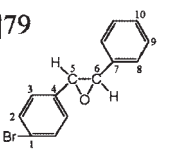
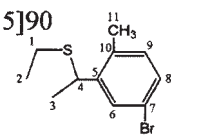
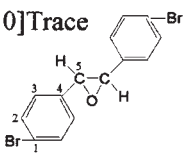
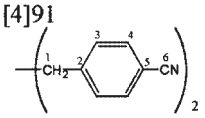
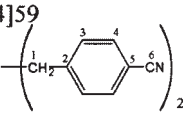
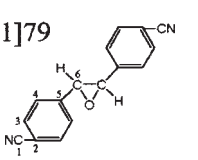
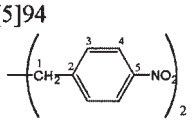
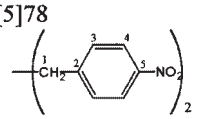
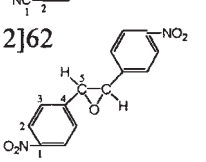
Salt	Synthetic methods			
	Electro reduction	Electro reduction with PhCHO	Base method main products	Base method side products
(a)	[1]81 	[6]79 	[6]66 	[1]10 
(b)	[2]74 	[7]63 	[9]45 	[2]24 
(c)	[3]62 	[8]75 	[10]63 	[3]14 
(d)	[4]89 	[4]55 	[11]68 	—
(e)	[5]92 	[5]72 	[12]45 	—

Table 2. Reduction Products and Their Yields from BDES Salts (%)

Salt	Synthetic methods			
	Electro reduction	Electro reduction with PhCHO	Base method main products	Base method side products
(f)	[13]89 	[6]83 	[6]71 	[13]9 
(g)	[14]91 	[7]65 	[14]92 	[9]Trace 
(h)	[15]89 	[8]79 	[15]90 	[10]Trace 
(i)	[4]91 	[4]59 	[11]79 	—
(j)	[5]94 	[5]78 	[12]62 	—

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (4H, d, H-4, $J = 8.1$ Hz), 7.20 (4H, d, H-3, $J = 14.8$ Hz), 2.92 (4H, s, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.13 (C-1), 118.82 (C-2), 130.21 (C-3), 132.23 (C-4), 146.03 (C-5), 110.14 (C-6); MS m/z 232 [M^+], 205 [$M^+ - CN$] (27), 175 (57), 130 (102), 117 (115). Anal. Calcd for $C_{16}H_{12}N_2$: C 82.97, H 5.20, N 12.01%. Found: C 82.73, H 5.21, N 12.06%.

4,4′-Dinitrobibenzyl [5]: Yellow crystal; mp 165–168 °C; IR (KBr Tablet) 3111 (m), 2937 (m), 1850–1650 (w), 1606 (m), 1593 (m), 1512 [NO_2] (s), 1340 (m), 1107 (m), 852 (m), 752 (m), 698 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (4H, d, H-4, $J =$ 8.5 Hz), 7.22 (4H, d, H-3, $J = 12.7$ Hz), 3.01 (4H, s, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.88 (C-1), 148.07 (C-2), 123.74 (C-3), 129.30 (C-4), 146.59 (C-5); MS m/z 272 [M^+], 226 [$M^+ - NO_2$] (46), 178 (94), 136 (136). Anal. Calcd for $C_{14}H_{12}N_2O_4$: C 61.76, H 4.44, N 10.29%. Found: C 61.69, H 4.26, N 10.06%.

***trans*-Stilbene Oxide [6]:** White crystal; mp 65–67 °C; IR (KBr Tablet) 3030 (m), 2933 (m), 1850–1650 (w), 1609 (m), 1492 (m), 1452 (m), 1271 (m), 1026 (m), 891 (m), 750 (m), 696 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (2H, s, H-1), 7.19 (4H, d, H-3, $J = 2.2$ Hz), 6.94 (4H, t, H-2, $J = 10.5$ Hz), 3.70 (2H, s, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.12 (C-1), 128.22 (C-2), 125.08 (C-3), 136.69 (C-4), 62.39 (C-5); MS m/z 196 [M^+], 177 (19), 166 (30), 151 (45), 104 (92), 90 (106). Anal. Calcd for $C_{14}H_{12}O$: C 85.68, H 6.16%. Found: C 85.46, H 5.92%.

***trans*-4-Methylstilbene Oxide [7]:** White crystal; mp 43–45 °C; IR (KBr Tablet) 3038 (m), 2960 (m), 1850–1650 (w), 1517 (m), 1450 (m), 1271 (m), 1109 (m), 1070 (m), 817 (m), 769 (m), 738 (m), 698 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.01 (5H, m, H-9,10,11), 6.96 (4H, d, H-2,3, $J = 11.5$ Hz), 3.61 (1H, s, H-7), 3.58 (1H, s, H-6), 2.10 (3H, s, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.84 (C-1), 137.11 (C-2), 128.91 (C-3), 125.19 (C-4), 132.58 (C-5), 62.47 (C-6), 62.33 (C-7), 129.31 (C-8), 126.47 (C-9), 128.18 (C-10), 128.02 (C-11); MS m/z 210 [M^+], 195 [$M^+ - CH_3$] (15), 181 (29), 166 (44), 152 (58), 103 (107). Anal. Calcd for $C_{15}H_{14}O$: C 85.68, H 6.71%. Found: C 85.73, H 6.70%.

***trans*-4-Bromostilbene Oxide [8]:** White crystal; mp 83–85 °C; IR (KBr Tablet) 3041 (m), 2979 (m), 1850–1650 (w), 1593 (m), 1488 (m), 1460 (m), 1423 (m), 1070 (m), 1008 (m), 839 (m), 788 (m), 748 (m), 513 [C–Br] (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (2H, d, H-3, $J = 8.3$ Hz), 7.24–7.22 (5H, m, H-2,9,10), 7.09 (2H, d, H-8, $J = 8.8$ Hz), 3.70–3.66 (2H, m, H-5,6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.93 (C-1), 131.65 (C-2), 126.98 (C-3), 136.52 (C-4), 61.89 (C-5), 62.57 (C-6), 135.99 (C-7), 125.31 (C-8), 128.38 (C-9), 128.32 (C-10); MS m/z 275 [M^+], 194 [$M^+ - Br$] (81), 176 (99), 166 (109), 150 (125), 104 (171). Anal. Calcd for $C_{14}H_{11}BrO$: C 61.11, H 4.03%. Found: C 61.43, H 4.01%.

***trans*-4,4′-Dimethylstilbene Oxide [9]:** White crystal; mp 80–82 °C; IR (KBr Tablet) 3039 (m), 2864 (m), 1850–1650 (w), 1608 (m), 1514 (m), 1278 (m), 1018 (m), 879 (m), 839 (m), 806 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (4H, d, H-3,4, $J = 8.3$ Hz), 7.00 (4H, d, H-4, $J = 8.5$ Hz), 3.66 (2H, s, H-6), 2.19 (3H, s, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.06 (C-1), 137.81 (C-2), 129.06 (C-3), 125.29 (C-4), 134.11 (C-5), 62.60 (C-6), 27.56 (C-7); MS m/z 224 [M^+], 209 [$M^+ - CH_3$] (15), 195 (29), 180 (44), 165 (59), 104 (124). Anal. Calcd for $C_{16}H_{16}O$: C 85.68, H 6.71%. Found: C 85.29, H 7.69%.

***trans*-4,4′-Dibromostilbene Oxide [10]:** White crystal; mp 101–104 °C; IR (KBr Tablet) 3003 (m), 2933 (m), 1850–1650 (w), 1591 (m), 1487 (m), 1438 (m), 1402 (m), 1074 (m), 1010 (m), 835 (m), 522 [C–Br] (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (2H, d, H-2, $J = 8.5$ Hz), 7.07 (2H, d, H-3, $J = 8.5$ Hz), 3.64 (2H, s, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.33 (C-1), 131.72 (C-2), 127.09 (C-3), 135.72 (C-4), 62.17 (C-5); MS m/z 275 [$M^+ - Br$] (81), 194 [$M^+ - Br_2$] (162), 176 (178), 166 (190), 150 (206), 104 (250). Anal. Calcd for $C_{14}H_{10}Br_2O$: C 85.68, H, 6.71%. Found: C 85.29, H 7.69%.

***trans*-4,4′-Dicyanostilbene Oxide [11]:** White crystal; mp 103–106 °C; IR (KBr Tablet) 3033 (m), 2933 (m), 2223 [CN] (s), 1850–1650 (w), 1604 (m), 1541 (m), 1498 (m), 1402 (m), 1110 (m), 835 (m), 827 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (4H, d, H-2, $J = 9.0$ Hz), 7.40 (4H, d, H-3, $J = 8.7$ Hz), 3.83 (2H, s, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.37 (C-1), 118.37 (C-2), 132.72 (C-3), 126.14 (C-4), 141.39 (C-5), 62.07 (C-5); MS m/z 246 [M^+], 220 [$M^+ - CN$] (26), 210 (36), 193 (53), 147 (99), 135 (111), 104 (142). Anal. Calcd for $C_{16}H_{10}N_2O$: C 78.04, H 4.09, N 11.38%. Found: C 77.68, H 4.58, N 11.09%.

***trans*-4,4′-Dinitrostilbene Oxide [12]:** Yellow crystal; mp 128–130 °C; IR (KBr Tablet) 3118 (m), 3030 (m), 1850–1650 (w), 1600 (m), 1506 [NO_2] (s), 1352 (m), 1012 (m), 1107 (m), 850 (m), 813 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (4H, d, H-2, $J = 8.6$ Hz), 7.45 (4H, d, H-3, $J = 8.8$ Hz), 3.92 (2H, s, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.29 (C-1), 123.60 (C-2), 126.91 (C-3), 147.06 (C-4), 63.08 (C-5); MS m/z 287 [M^+], 239 [$M^+ - NO_2$] (46), 223 (64), 211 (76), 194 (93), 176 (111), 150 (137), 104 (183). Anal. Calcd for $C_{14}H_{10}N_2O_3$: C 58.75, H 3.52, N 9.79%. Found: C 58.35, H 3.47, N 9.45%.

Products from BDES. 1-(2-Methylphenyl)-diethyl Sulfide [13]: Yellow liquid; bp 160–162 °C; IR (KBr Coat) 3024 (m), 2947 (m), 2860 (m), 1850–1650 (w), 1602 (m), 1493 (m), 1440 (m), 1317 (m), 1195 (m), 760 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–6.99 (4H, m, H-6,7,8,9), 4.15 (1H, d, H-3, $J =$ 7.1 Hz), 2.29 (2H, d, H-2, $J = 8.1$ Hz), 2.30 (3H, s, H-11), 1.45 (3H, m, H-4), 1.12–1.08 (3H, m, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.82 (C-1), 14.46 (C-2), 21.77 (C-3), 38.98 (C-4), 141.52 (C-5), 126.34 (C-6), 128.25 (C-7), 130.12 (C-8), 126.19 (C-9), 135.01 (C-10), 19.17 (C-11); MS m/z 180 [M^+], 165 [$M^+ - CH_3$] (15), 149 (31), 134 (46), 119 (61), 103 (77). Anal. Calcd for $C_{11}H_{16}S$: C 73.27, H 8.94%. Found: C 73.25, H 8.61%.

1-(2,4-Dimethylphenyl)-diethyl Sulfide [14]: Yellow liquid; bp 163–165 °C; IR (KBr Coat) 3016 (m), 2925 (m), 2860 (m), 1850–1650 (w), 1612 (m), 1500 (m), 1440 (m), 1379 (m), 1037 (m), 810 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–6.75 (3H, m, H-6,8,9), 4.08 (1H, d, H-3, $J = 7.3$ Hz), 2.26 (2H, d, H-2, $J = 9.5$ Hz), 2.21 (3H, s, H-11), 2.18 (3H, s, H-12) 1.41 (3H, m, H-4), 1.01 (3H, m, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.71 (C-1), 14.31 (C-2), 21.65 (C-3), 38.83 (C-4), 141.11 (C-5), 127.05 (C-6), 131.62 (C-7), 129.88 (C-8), 126.78 (C-9), 135.22 (C-10), 19.17 (C-11), 20.78 (C-12); MS m/z 194 [M^+], 179 [$M^+ - CH_3$] (15), 163 (31), 149 (45), 133 (61), 117 (77), 105 (89). Anal. Calcd for $C_{12}H_{18}S$: C 74.16, H 9.34%. Found: C 74.57, H 9.15%.

1-(2-Methyl-4-bromophenyl)-diethyl Sulfide [15]: Yellow liquid; bp 177–180 °C; IR (KBr Coat) 2947 (m), 2860 (m), 1850–1650 (w), 1589 (m), 1487 (m), 1440 (m), 1404 (m), 1070 (m), 1010 (m), 810 (m), 808 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–6.84 (4H, m, H-6,8,9), 4.20 (1H, d, H-3, $J = 7.1$ Hz), 2.35 (2H, d, H-2, $J = 11.9$ Hz), 2.19 (3H, s, H-11), 1.40 (3H, m, H-4), 1.03 (3H, m, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.83 (C-1), 14.38 (C-2), 21.62 (C-3), 38.80 (C-4), 143.95 (C-5), 129.38 (C-6), 119.84 (C-7), 131.73 (C-8), 129.33 (C-9), 133.95 (C-10), 18.67 (C-11); MS m/z 259 [M^+], 244 [$M^+ - CH_3$] (15),

165 [$M^+ - CH_3Br$] (94), 150 (109), 134 (125), 118 (141). Anal. Calcd for $C_{11}H_{15}BrS$: C 50.97; H, 5.83%. Found: C, 51.19; H, 5.44%.

Discussion

Organosulfides have been applied as synthetic raw materials for S-salts, sulfoxides, sulfones, and the other sulfur compounds. Among them, S-salts are important compounds for the synthesis of S–Ys. Under gentle conditions and without catalyst, we prepared S-salts by the reaction of alkyl halides with aliphatic sulfides. The electrophilic reaction of alkyl halides to the sulfur atom of sulfides is the rate-determining step. And the reaction is fast when the alkyl halide gives a stable carbocation.

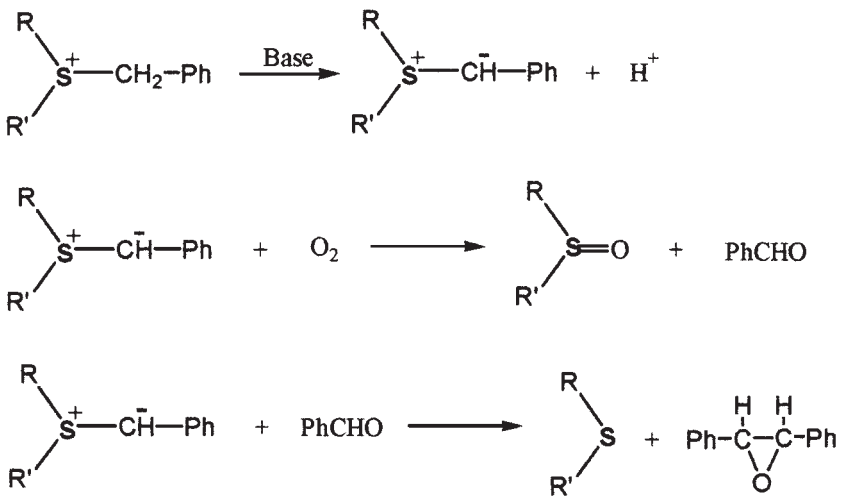
The generation of S–Ys by a base such as sodium amide has been confirmed by reactions with many carbonyl compounds.[29] However, without the presence of carbonyl compounds, the ylides gave symmetrical epoxides derived from the benzyl groups on the salt as a result of an oxidation reaction caused by coexisting oxygen as shown in Scheme 1. Along with the epoxides, the rearrangement compounds [1]–[3] and [13]–[15] were found as minor products; their yields obtained from ^{1}H NMR are shown in Tables 1 and 2. In the case of the S–Ys having an EWG on a benzyl group, stable ylides formed by standing for a long period and a small amount of epoxide was produced via autoxidization. The generated benzaldehyde reacted with residual S–Y immediately after its formation, so no benzaldehyde was detected during the autoxidization.

Electrochemical generation of S–Y progresses as a one-electron reduction process, since S-salt disappeared nearly 100% when 1 F/mol of electric current has been passed. In the presence of benzaldehyde, the electrochemical reduction of S-salts which have EDG substituents such as methyl and bromo groups gives epoxides in high yields as a result of the Corey–Chaykovsky reaction. On the contrary, the main products of this reaction without benzaldehyde proved to be interesting rearrangement products that are numbered as [1]–[3] and [13]–[15] in Tables 1 and 2.

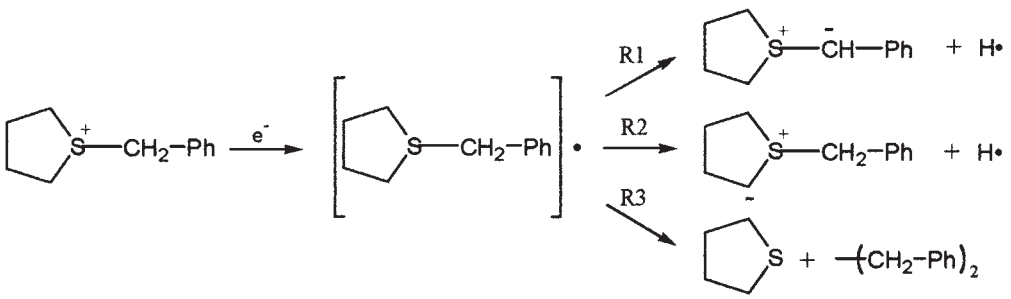
In the electrochemical reduction method without the presence of benzaldehyde, the rearrangement compound is the main product, and no oxidation of the ylide to produce aldehydes occurred. This fact may be ascribed to retardation of oxidization because of the reductive surroundings of the cathode. On the other hand, S-salts which have an EWG, such as a nitro and a cyano group, gave benzyl dimers, and no generation of S–Ys could be confirmed.

The electrochemical reduction might proceed through a 3-way mechanism as described in Scheme 2. The two routes designated R1 and R2 route are based on the positional difference of hydrogen abstraction. Furthermore, R3 corresponds to a dimerization route of benzyl radicals generated from the radical intermediate from the S-salt.

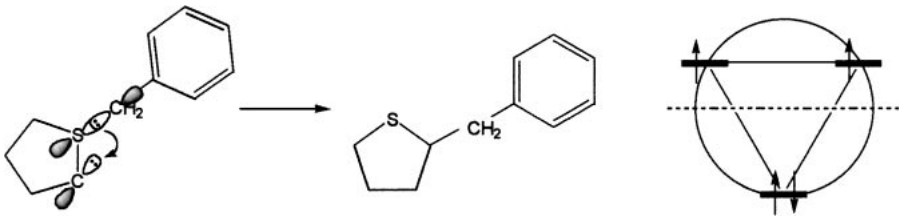
The reaction with benzaldehyde progresses following the R1 route. In the case of S–Ys, nucleophilic reaction to a carbonyl group creates an epoxide and is different from the reaction of P–Y because of the weaker affinity of S to oxygen atom than



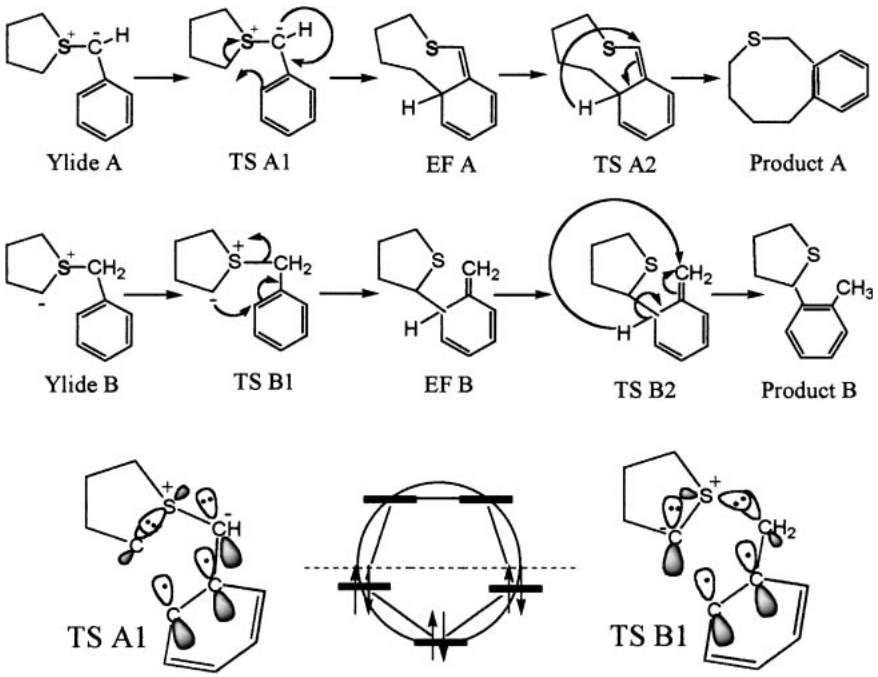
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

that of P atom. For cleaving the intermediate four-membered ring and forming C–C double bond, high activation energy is required because of steric strain, and sulfide is eliminated through a S_N2 type reaction of oxygen to carbon atom. Generally, sulfides are known as good leaving groups, and this is a reason why epoxides are formed by the R1 route. In all electrochemical reductions, the hydrogen molecule generation was observed at the cathodic electrode, indicating the coupling reaction of generated hydrogen atoms.

Besides the reactions of S–Y with electrophiles such as carbonyl compounds, imines and olefins, characteristic rearrangement reactions have fascinated many investigators. The [1,2]-Stevens rearrangement found in N–Ys are also reported with S–Y[30] having an aryl group at the β-position. This rearrangement could be a radical process, because sigmatropic rearrangements which include four electrons in three orbitals pictured in Scheme 3 are forbidden by the Woodward–Hoffmann rule.

The products [1]–[3] and [13]–[15] found in this study come from the [2,3] sigmatropic Sommelet–Hauser rearrangement of S–Ys by the R2 route. Regarding N–Y, many Sommelet–Hauser rearrangements have been reported so far.[31] The migration of one of the substituents on the heteroatom, in this case the nitrogen atom, to the ortho position of the aromatic ring of the benzyl group occurred. In the case of S–Y, a similar [2,3] Wittig rearrangement and the Sommelet–Hauser rearrangement of S-Ylide which has two benzyl groups on sulfur atom have been reported.[27] However, there is no report on Sommelet–Hauser rearrangements of S–Y which has only one benzyl group which enforce the rearrangement through unstable S–Y. In this experiment, Sommelet–Hauser rearrangement products are formed through an unstable ylide R2 which may exist in equilibrium with stable ylide R1. Although the starting ylide is unstable in R2 route, the transition state of the rearrangement is stabilized because both the cation on the S atom and the anion can delocalize into benzene rings in the R2 route. A possible rearrangement through stable S–Y in R1 route shown in the equation may give eight-membered products through transition state A1. Both routes R1 and R2 will give transition states obeying the Woodward–Hoffmann rule, i.e., 5 orbitals and 6 electrons as shown in Scheme 4.

In order to elucidate the reason why this S–H rearrangement proceeds through the unstable Ylide B instead of stable Ylide A, we calculated the energy surfaces and the geometries of all the reactants, intermediates and transition states on the surface of the R1 and R2 routes by using the PM3 Hamiltonian; an energy diagram of the reaction of BTHT that has no substituent on the benzyl group is presented 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.

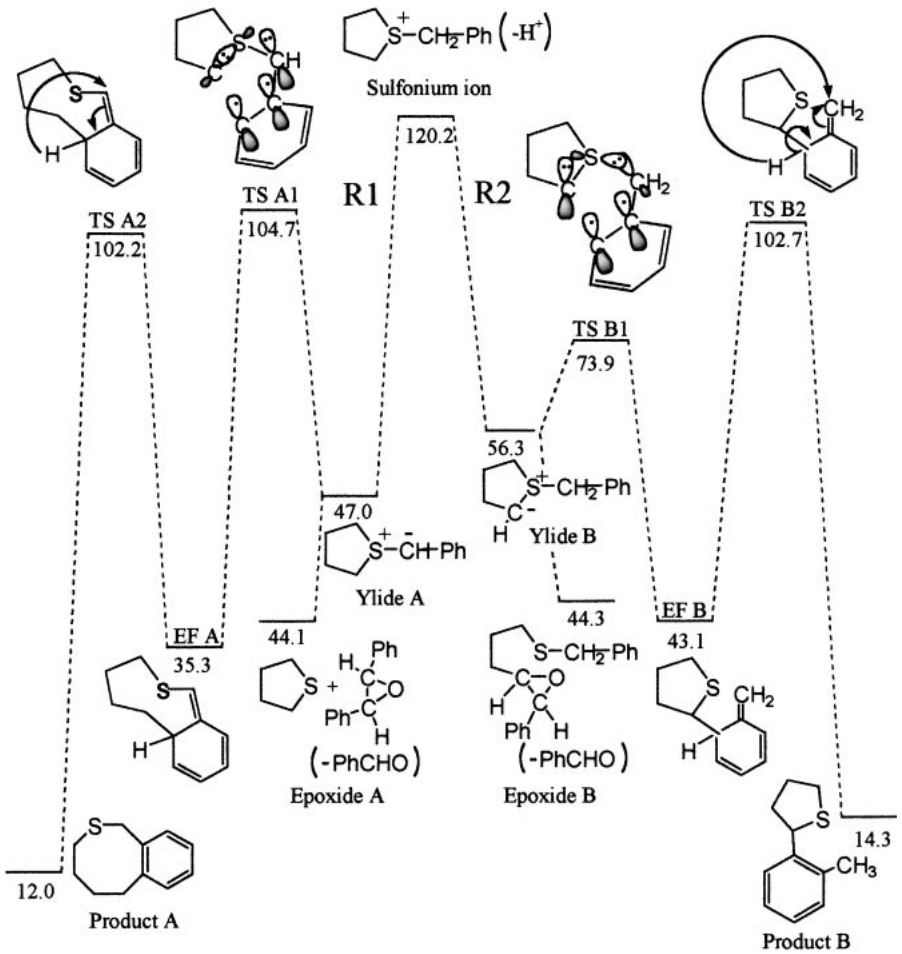


Fig. 1. Energy surfaces of the Sommelet–Hauser rearrangement.

The difference in the heat of formations between stable Ylide A and unstable Ylide B is 9.3 kcal/mol. The possible reaction products of each, Ylide A and Ylide B, with benzaldehyde are indicated as Epoxide A and Epoxide B; the heats of formation were nearly equal. However the experimental results showed that the reaction product of S–Y with benzaldehyde is Epoxide A; therefore, the stable Ylide A must have reacted immediately after its formation with benzaldehyde. For without benzaldehyde Ylide A cannot rearrange to form Product A, because the activation energy of TS A1 is obviously 30.1 kcal/mol higher than that of TS B1. And the activation energy of the following hydrogen migration is lower by 7.4 kcal/mol in TS B2 than in TS A2, indicating the preferential formation of Product B. And it is clear that the dramatic stability difference between TS A1 and TS B1 is the main factor of route determination.

The R2 route from Ylide B to EFB is the real path of this rearrangement and involves a sigmatropic rearrangement reaction with cleavage of the S–C11 σ bond. And the π electrons on the benzene ring can interact with the partial positive charge generated on C11. This resonance stabilization decreases the activation energy to TS B1 from unstable Ylide B. On the contrary, the interaction of the partial positive charge generated on C4 atoms of TS A1 with benzene ring is not large enough to stabilize the transition state TS A1. The differences of electron density changes between Ylide A and TS A1, and also between Ylide B and TS B1, are shown in Fig 2. The electron densities

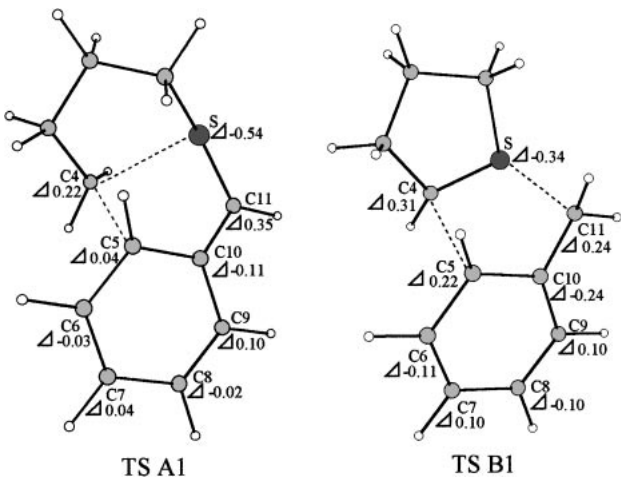


Fig. 2. The differences of electron densities between Ylide A and TS A1, Ylide B and TS B1.

on the benzene ring appear to be larger in the TS B1 than in the TS A1. In the case of TS B1, the electrons at anion and cation on S atom delocalize more to the benzene ring than in the case of TS A1. This is the reason why TS B1 is more stable than TS A1 and why no rearrangement via R1 route occurs.

The weaker bond strength of ② bond in radical intermediate compared to ① bonds may be an another factor to control the

reaction path. The bond strengths of ④ and ⑤ do not differ so much; therefore the C–H bond fission does not contribute to the route determination. The hydrogen migration from this intermediate EFB to TS B2 is a [1,3] sigmatropic rearrangement and is suprafacial, as the dihedral angle of C3–C4–C5–H1 changes from -68.2° to -121.1°. C10–C11 becomes a single bond upon the migration, thus leading to the regeneration of the benzene ring. The geometrical figures of the R1 and R2 route are shown in the Figs. 3 and 4 and the relevant dihedral angles are listed in Table 3. We also calculated the two-centered bond

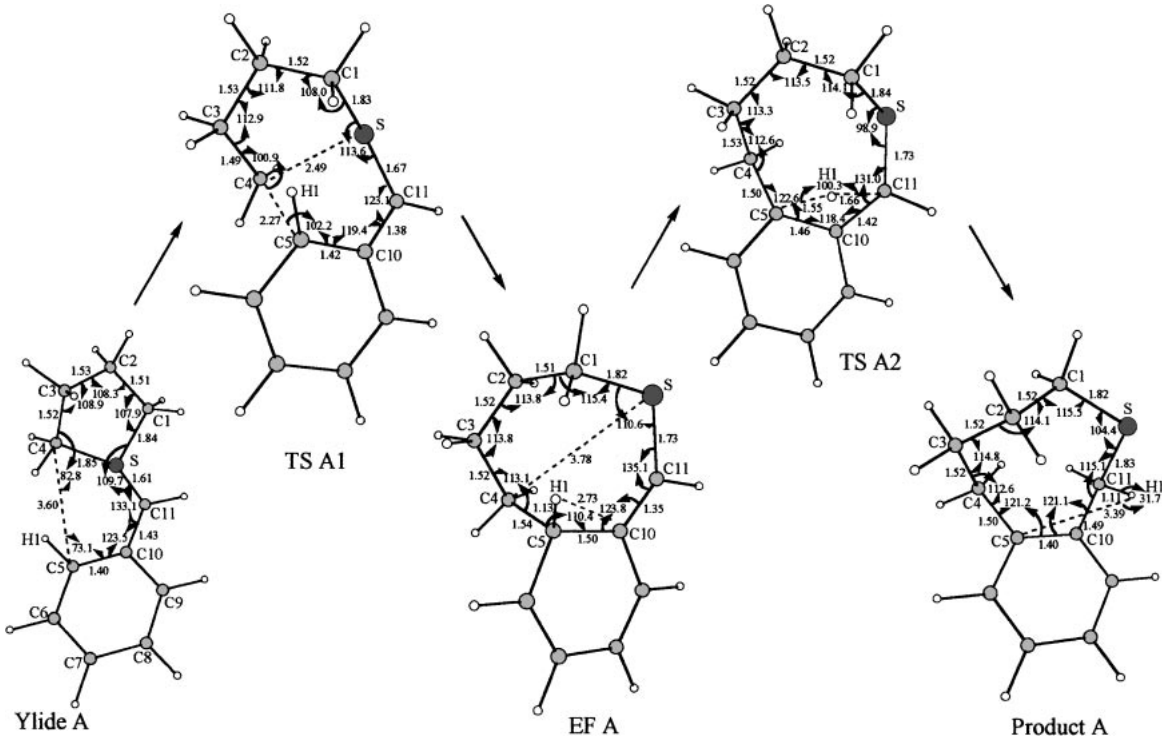


Fig. 3. Optimized structures of the R1 route.

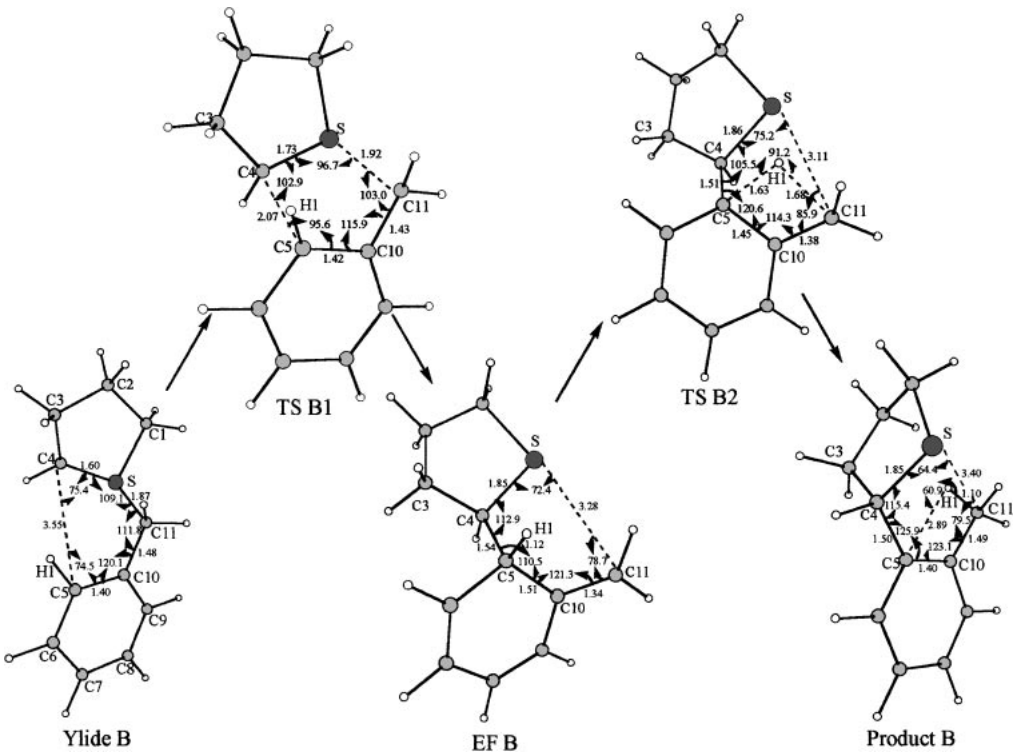


Fig. 4. Optimized structures of the R2 route.

Table 3. Dihedral Angles of Optimized Structures in R1 and R2 Route

	R1					R2				
	Ylide A	TS A1	EF A	TS A2	Product A	Ylide B	TS B1	EF B	TS B2	Product B
S–C11–C10–C5	−17.5	−12.5	2.3	−40.7	88.5	−84.2	−56.7	−41.9	−28.6	23.7
C4–S–C11–C10	−50.5	−23.8	−27.3	14.7	−60.7	76.9	27.8	5.2	−2.1	−40.9
C4–S–C10–C5	−61.9	−36.6	−33.9	−17.0	−18.6	3.2	−19.1	−35.1	−35.8	−28.6
S–C4–C5–C10	35.5	45.0	73.3	52.4	−1.0	39.8	51.6	83.3	74.7	2.9
C4–C5–C10–C11	−50.0	−43.3	−52.7	−30.6	−26.8	2.5	−24.1	−67.4	−72.3	−61.4
C11–C10–C5–H1	−1.7	−45.4	−46.5	−41.3	22.8	1.4	−40.4	−35.9	4.6	26.0
C3–C4–C5–H1	−23.1	−22.1	−1.7	−47.5	−106.6	29.9	−21.8	−68.2	−121.1	47.5

energies and spin densities of the radical intermediates from BTHT and BDES to elucidate the bond fission on the radical intermediate. The results are summarized in Tables 4–7 and Figs. 5, 6 where the atom numbers and bond numbers are defined.

When S–Y has a benzyl group with a strong EWG such as a CN, or a NO_2 group, the electrochemical reduction does not generate S–Y, judging from the complete recovery of benzaldehyde, and radical coupling products of benzyl groups were obtained in high yield. The S–benzyl bond of trivalent sulfur radicals obtained by one electron reduction of the S-salt is weakened because of the dispersion of electron spin density to neighboring carbon atoms by the strong EWG. This fact can be substantiated by the theoretical calculations as follows.

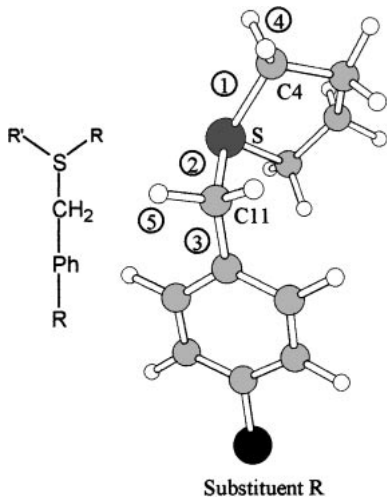


Fig. 5. Geometries and definitions of BTHT.

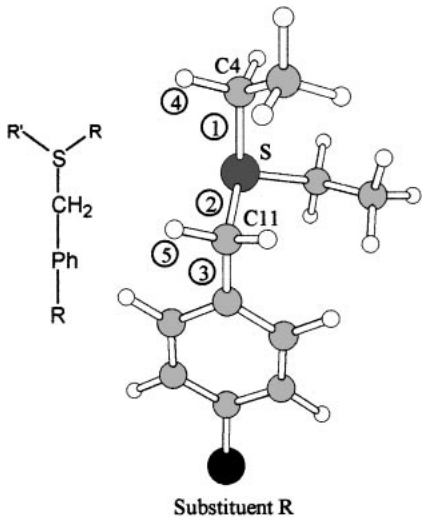


Fig. 6. Geometries and definitions of BDES.

Table 4. The Bond Energies (eV) of Radical Intermediates from BTHT

	Substituent R				
	H	Me	Br	CN	NO_2
①	−11.35	−11.36	−11.35	−11.35	−11.35
②	−7.92	−7.90	−7.78	−7.65	−7.51
③	−14.83	−14.84	−14.88	−14.99	−15.16
④	−12.74	−12.74	−12.75	−12.75	−12.76
⑤	−12.67	−12.67	−12.67	−12.68	−12.70

Table 5. The Spin Densities of Radical Intermediates from BTHT

	Substituent R				
	H	Me	Br	CN	NO_2
S	0.33	0.29	0.33	0.30	0.31
C4	0.28	0.28	0.26	0.24	0.21
C11	0.50	0.50	0.51	0.52	0.52

Table 6. The Bond Energies (eV) of Radical Intermediates from BDES

	Substituent R				
	H	Me	Br	CN	NO_2
①	−10.77	−10.57	−10.64	−10.71	−10.81
②	−8.50	−8.71	−8.53	−8.34	−8.14
③	−14.75	−14.71	−14.76	−14.86	−15.01
④	−12.68	−12.68	−12.68	−12.68	−12.68
⑤	−12.66	−12.66	−12.67	−12.68	−12.69

Table 7. The Spin Densities of Radical Intermediates from BDES

	Substituent R				
	H	Me	Br	CN	NO_2
S	0.23	0.23	0.24	0.24	0.26
C4	0.28	0.29	0.27	0.25	0.22
C11	0.44	0.41	0.43	0.44	0.45

In the two-centered bond energies, the ② bond of radical intermediates of BTHT and BDES were significantly decreased by the effect of a CN or NO_2 group in the *p*-position of the benzyl group. In addition, it is clear that the ③ bond is strengthened. A very characteristic dispersion of radical spin density for each substituent is shown in Tables 4 and 6. Concerning each radical intermediate with EDG group, the highest spin density is found on C11. In fact, the reduction of S-salts in the presence of benzaldehyde, the S–Y generation, occurred via the R1 route, i.e., the hydrogen radical was abstracted from this carbon. While the radical intermediates with EWG have the same amounts of spin density on C11, the bond strength on ② bond decreases considerably, about 6–7 kcal/mol; this fact allows the cleavage of benzyl radical which is stabilized by the EWG group.

Summary

The electrochemical reduction of sulfonium salts having a benzyl group with *p*-EDG gave a stable S-Ylide A. This fact was confirmed by a Corey–Chaykovsky reaction of the ylide with benzaldehyde. In the absence of benzaldehyde, the Sommelet–Hauser rearrangement of the ylide occurred. On the contrary, the same reduction of sulfonium salt having a benzyl group with *p*-EWG formed the coupling products of the benzyl group instead of forming S-Ylide. The results were compared with those obtained by the normal base method. By using semi-empirical MO calculations, we compared the reaction path of the ylide generations and the two routes of the possible Sommelet–Hauser rearrangement.

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