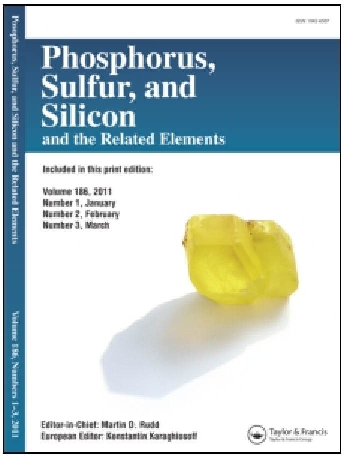

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MULTIPLE PATHWAYS IN THE BASE-CATALYZED REACTIONS OF *S*-ALLYL SULFONIUM COMPOUNDS

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MULTIPLE PATHWAYS IN THE BASE-CATALYZED REACTIONS OF *S*-ALLYL SULFONIUM COMPOUNDS

by

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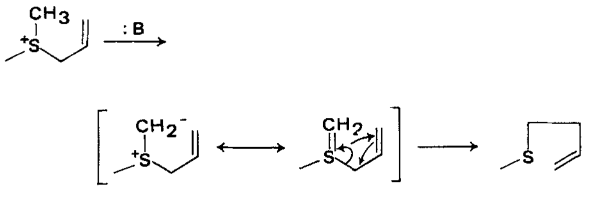
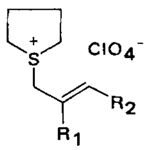
ABSTRACT

Various *S*-allyl sulfonium salts were allowed to react with bases (EtONa/EtOH, NaH/THF). From product analyses, it was found that modes of reaction depend on both the structure of sulfonium salts and the bases employed. Among the observations, it is worthy to note the formation of cyclopropane derivatives from some allyl sulfonium salts.

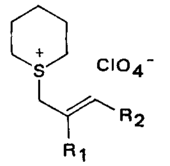
It is well known that allyl sulfonium compounds in the reaction with bases give almost quantitatively the corresponding homoallyl sulfides *via* 2,3-sigmatropic rearrangement. The driving force of this rearrangement is provided by the conversion of formally tetravalent sulfur to the divalent state. This concept serves to unify and rationalize a large number of reactions of sulfonium salts.[1]



For example, the intermediacy of sulfonium allylide has been implicated in several enzyme-catalyzed carbon-carbon bond-forming reactions,[1] *i.e.*, biosyntheses of squalene and phytoene, and the formation of the cyclopropane ring of chrysanthemic acid and the cyclopropene ring of sterculic acid.[2] Literature survey, however, indicates that the types of allyl sulfonium compounds and basic conditions investigated are still insufficient to establish a general rule about 2,3-sigmatropic rearrangement of sulfonium allylide. We have reported that the base-promoted reaction of sulfonium compounds is fairly sensitive to the structure of substrate and the types of base.[3] We have, thus, synthesized the following allyl sulfonium salts in order to examine their base-promoted reactions.

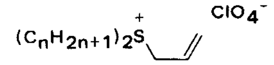


I



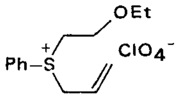
II

Ia, IIa; R_1=R_2=H
Ib, IIb; R_1=H, R_2=CH_3
Ic, IIc; R_1=CH_3, R_2=H

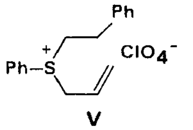


III

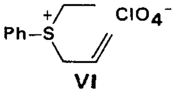
IIIa; n = 1
IIIb; n = 2
IIIc; n = 3



IV



V



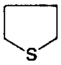
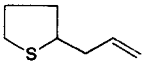
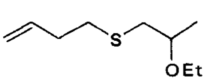
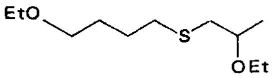
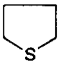
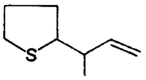
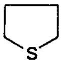
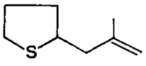
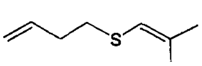
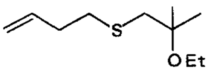
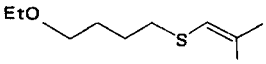
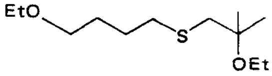
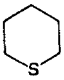
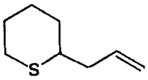
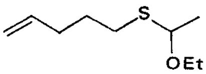
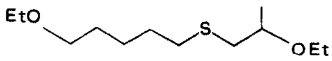
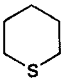
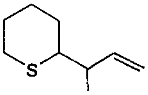
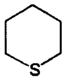
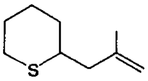
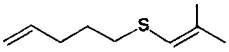
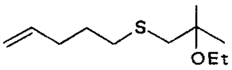
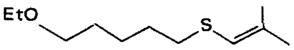
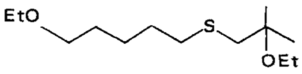
VI

Results and Discussion

Sulfonium perchlorates were generally obtained in good yields by the reactions of allyl iodide, β- or γ-methyl allyl chloride with the corresponding sulfides *via* silver perchlorate in acetonitrile.[4] The sulfonium salts thus prepared were allowed to react with bases, *i.e.*, EtONa in EtOH and NaH in THF. The product analyses are based on vpc, nmr, mass spectra, and elemental analyses. The results are summarized in Tables I, II, III, IV and V.

TABLE I

Products in the Reaction with EtONa (9 mmol/EtOH (50 ml) at 80°, 48 hr

Salt (3 mmol)	Products (%)[a]			
Ia	 trace	 **1**, 5%	 **2**, 25%	 **3**, 57%
Ib	 13%	 **4**, 41%		
Ic	 trace	 **5**, 13%	 **6**, 3%  **8**, 6%	 **7**, 42%  **9**, 18%
IIa	 5%	 **10**, 22%	 **11**, 29%	 **12**, 21%
IIb	 18%	 **13**, 37%		
IIc	 37%	 **14**, 3%	 **15**, 5%  **17**, 6%	 **6**, 6%  **18**[b], 3%

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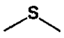
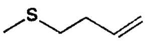
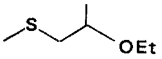
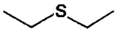
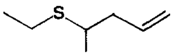
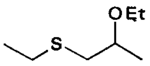
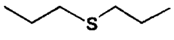
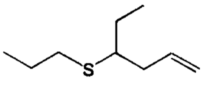
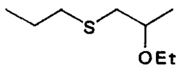
[a] Based on the starting salt

[b] This compound could not be collected. The structural assignment was based on the gc-mass spectra and the peak position of glc which is expected from a comparison of glc patterns of **Ic** and **IIc** products.

TABLE II

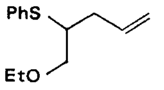
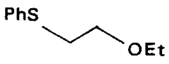
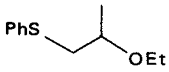
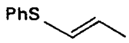
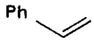
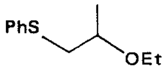
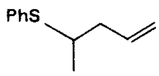
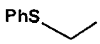
Products in the Reaction with EtONa (9 mmol)/EtOH (50 ml) at 80°, 48 hr

Salt (3 mmol)	Products (%)[a]		
IIIa	 trace	 **19**, 30%	 **20**, 22%
IIIb	 trace	 **21**, 33%	 **22**, 58%
IIIc	 3%	 **23**, 66%	 **24**, 22%

[a] Based on the starting salt.

TABLE III

Products in the Reaction with EtONa (9 mmol/EtOH (50 ml) at 80°, 48 hr

Salt (3 mmol)	Products (%)[a]		
IV	 **25**, 80%	 5%	
V	 **26**, 67%	 3%	 90%
VI	 **26**, 52%	 **27**, 14%	 9%

[a] Based on the starting salt.

TABLE IV

Products in the Reaction with NaH (9 mmol)/THF (50 ml) at 55°, 48 hr[a]

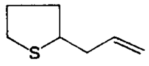
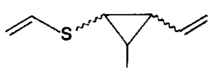
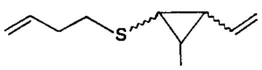
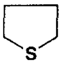
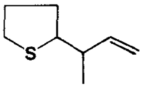
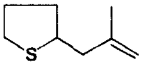
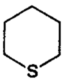
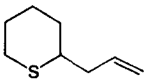
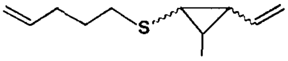
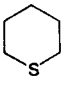
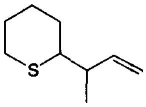
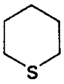
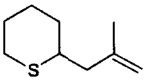
Salt (3 mmol)	Products (%)[b]			
Ia	 42%	 1%	 **28**, 10%	 **29**, 6%

TABLE IV—*continued*

Salt (3 mmol)	Products (%)[b]		
Ib	 16%	 43%	
Ic	 13%	 41%	
IIa	 39%	 trace	 **30**, 9%
IIb	 38%	 42%	
IIc	 51%	 33%	

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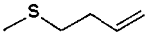
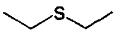
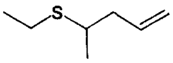
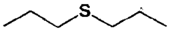
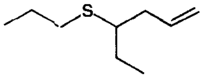
[a] Sulfonium salts were found to decompose thermally to give sulfide and uncharacterized gaseous products. For example, under these conditions tetramethylene sulfide was obtained in 0.4% for **Ic**, and pentamethylene sulfide was obtained in 32% for **IIa** and 13% for **IIc**.

[b] Based on the starting salt. 18% of the starting salt was recovered in the case of **Ib**.

TABLE V

Products in the Reaction with NaH (9 mmol)/THF (50 ml) at 55°, 48 hr

Salt (3 mmol)	Products (%)[a]		
IIIa	 80%		
IIIb[c]	 12 (18)[b]%	 25 (33)[b]%	 **31** 10 (4)[b]%
IIIc[c]	 71%	 19%	

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[a] Based on the starting salt. 20% of the starting salt was recovered in the case of **IIIb**.

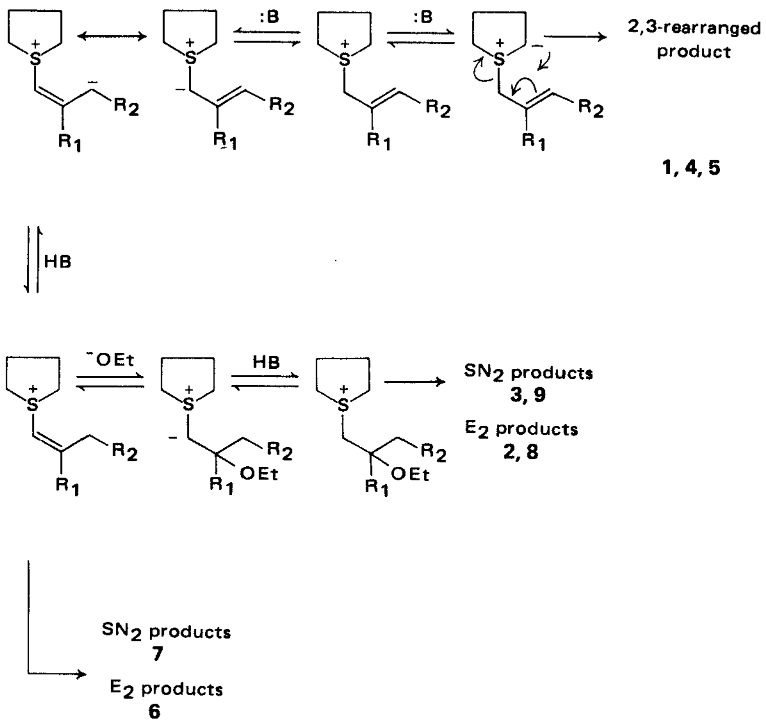
[b] The yields when the concentration of the starting salt was lowered to one fifth.

[c] Small amounts of unidentified products were detected in vpc at high retention time.

In EtONa/EtOH System

In a series of cyclic sulfonium salts, the following reaction Scheme I can best account for the reaction products.

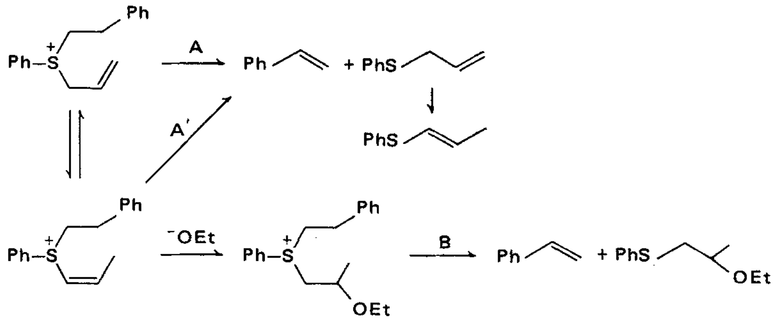
SCHEME I



All the pathways appear to be competitive, and the product distribution depends on the effect of R_1 and R_2 groups. In the case of unsubstituted allyl sulfonium salts (**Ia** and **IIa**), the main path is the isomerization of the double bond, and the resulting vinyl sulfonium salts undergo typical Michael addition of ethoxide anion.[5] The adducts are then subjected to the SN_2 attack of ethoxide anion on the ring α-carbon and E_2 reactions[3] to give **3** and **12**, and **2** and **11**, respectively. On the other hand, in the cases of γ-methyl allyl sulfonium salts, (**Ib** and **IIb**), the double bond isomerization would be unfavorable because the methyl group (R_2=CH_3) is expected to destabilize an adjacent carbanion. Thus, the reactions proceed mainly through 2,3-sigmatropic rearrangement to give **4** and **13**, respectively. In the case of β-methyl allyl sulfonium salts (**Ic** and **IIc**), the double bond migration to give vinyl sulfonium salts would be more favored than in the case of γ-methyl allyl sulfonium salts. However, the addition of ethoxide ion to the resulting vinyl double bond may suffer some steric hindrance from the γ-methyl groups, thus to give much lower yields of **8**, **9**, **17** and **18**, as compared to the cases of **Ia** and **IIa**. As a consequence, the major paths become the direct SN_2 and E_2 reactions of the vinyl sulfonium intermediate to give **6**, **7**, **15** and **16**. Tetra- and pentamethylene sulfides are also the main products in the reactions of **Ib**, **IIb** and **IIc**, respectively. The formation of these sulfides may be accounted for by SN_2 attack of ethoxide on either methylene carbon of the starting allyl group or the side chain methylene carbon of the ethoxide adduct, or both (see also the footnote in Table IV).

For acyclic sulfonium salts (**IIIa**, **IIIb** and **IIIc**), 2,3-sigmatropic rearrangement and ethoxide addition to the intermediate vinyl double bond are the major pathways in all the cases. Similar reactions were observed for the compounds of **IV** and **VI**; **IV** gave mainly 2,3-sigmatropic rearrangement (**25**) and **VI** gave both the 2,3-rearranged (**27**) and ethoxide addition products (**26**). However, **V** did not give 2,3-rearranged product, but styrene and ethoxide adduct were the main products. The formation of styrene may be explained by Scheme II.

SCHEME II



A small amount (3%) of phenylpropenyl sulfide may be formed by either path A or A′. In path A, the phenylallyl sulfide initially formed was checked to be readily isomerized to the propenyl isomer under the present reaction conditions. These pathways, however, do not account for a quantitative yield of styrene. Rather, it may be clear that styrene was formed by the elimination from the ethoxide adduct of intermediate vinyl sulfonium salt.

In NaH/THF System

This system is known to be typical for the occurrence of 2,3-sigmatropic rearrangement of sulfonium allylide.[1] Expected difference from the above EtONa/EtOH system is non-formation of ethoxide adduct. In addition to these expected results, it was found unexpectedly that the compounds, **Ia**, **IIa**, and **IIIb**, gave cyclopropane derivatives. To our knowledge, it is the first example of cyclopropane ring formation in the reaction of allyl sulfonium salt with bases, although Corey and his coworkers[6] have reported cyclopropane ring formation by an intramolecular cyclization of cyclic sulfonium allylide.

The structural assignment of **28**, **29**, **30**, and **31** are based on their nmr (Figure I) and mass spectra.

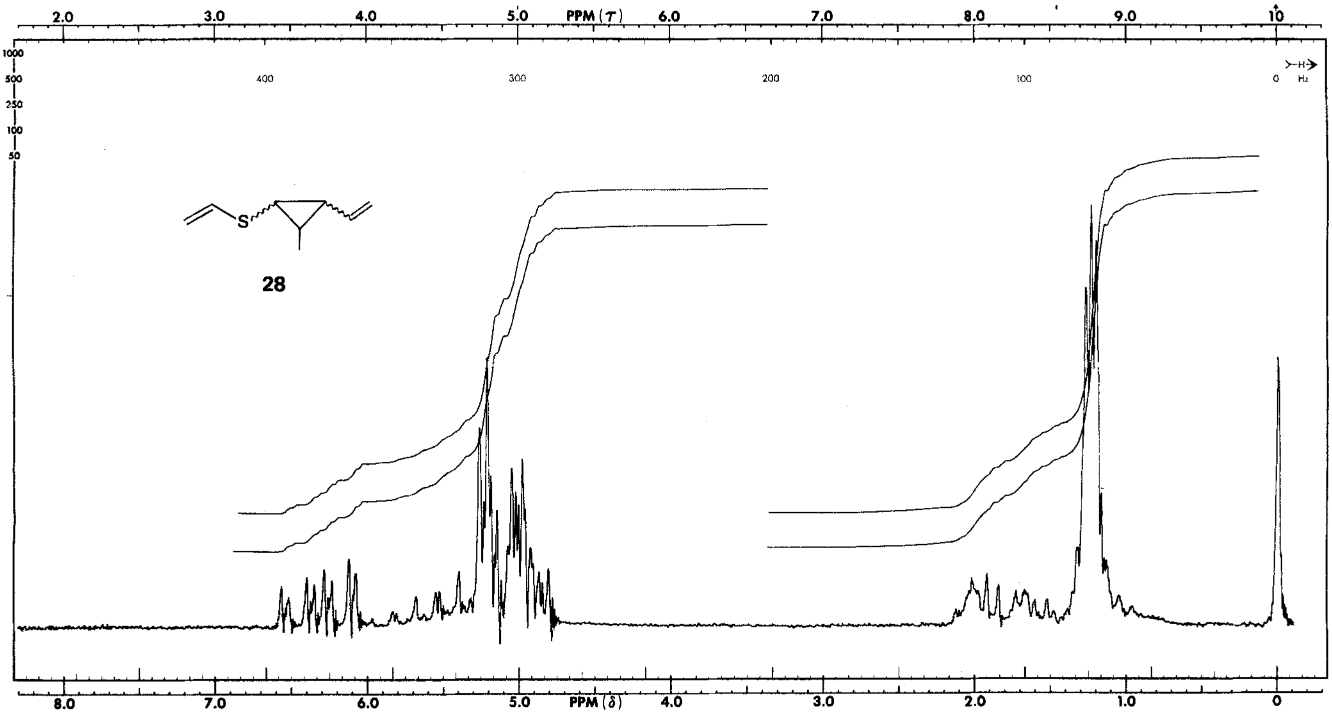


FIGURE Ia

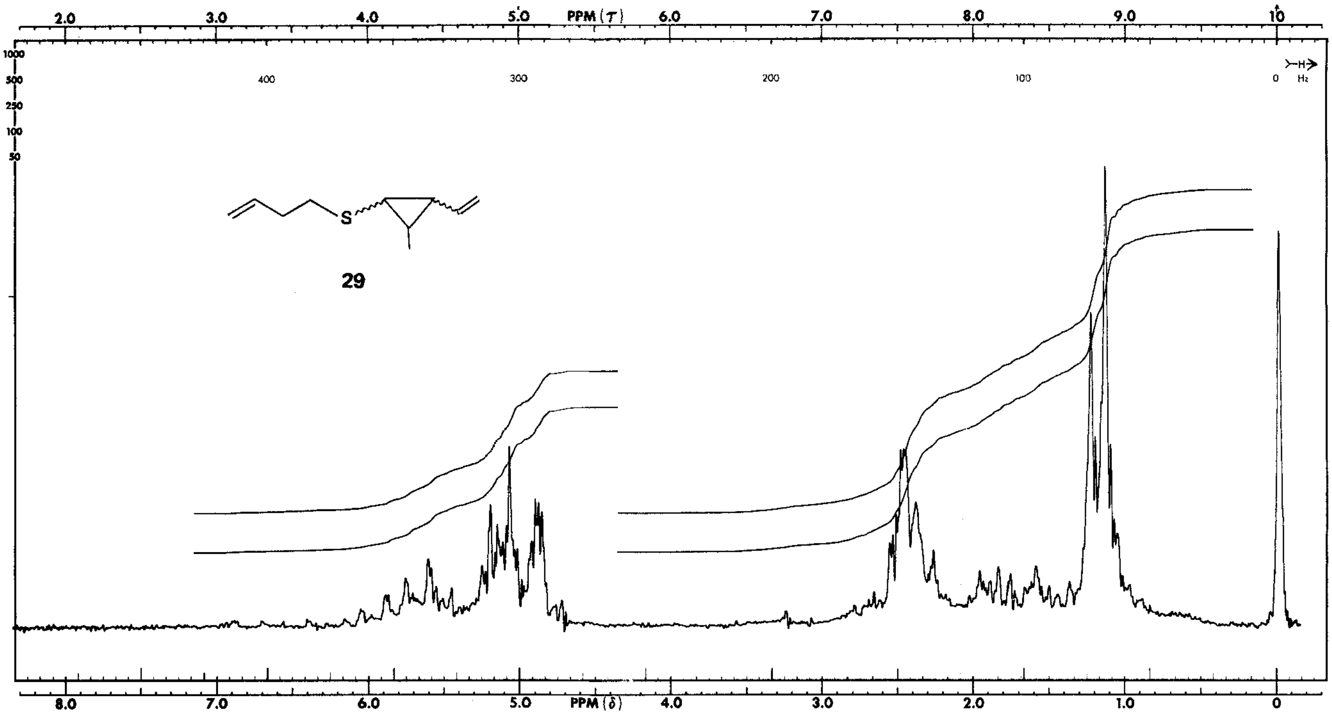


FIGURE Ib

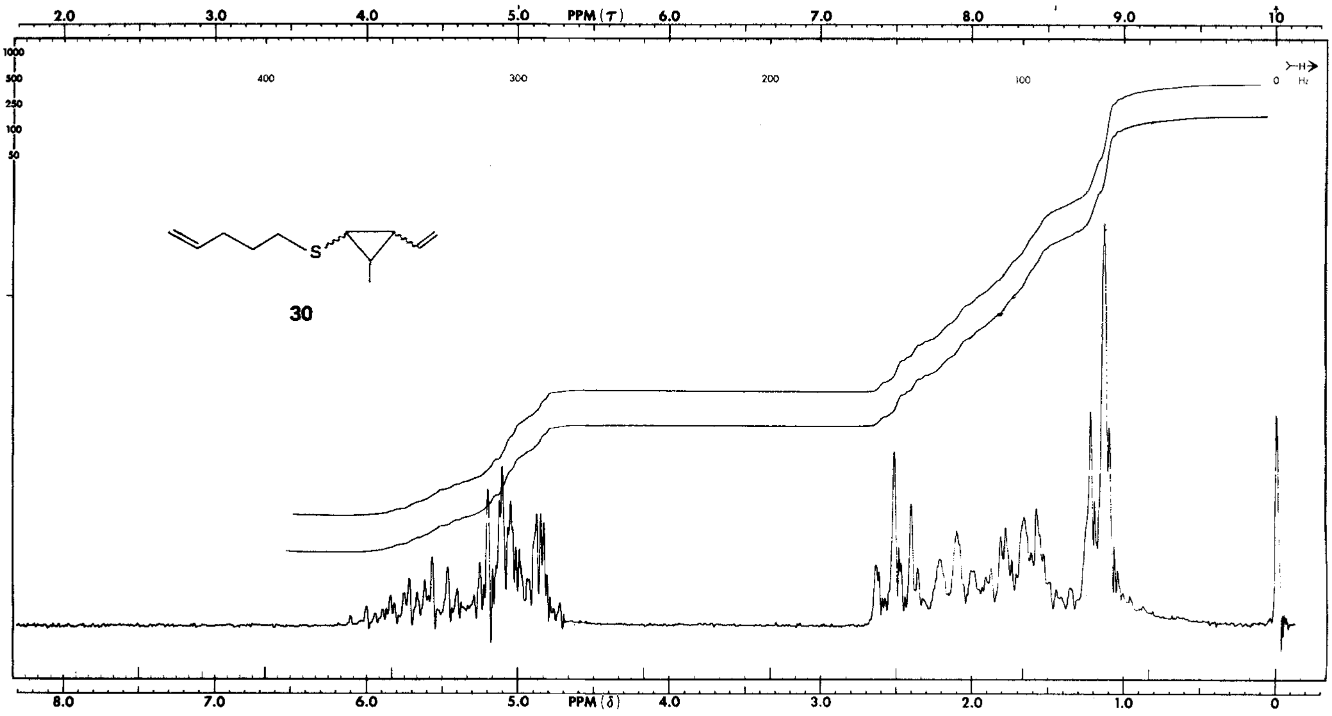
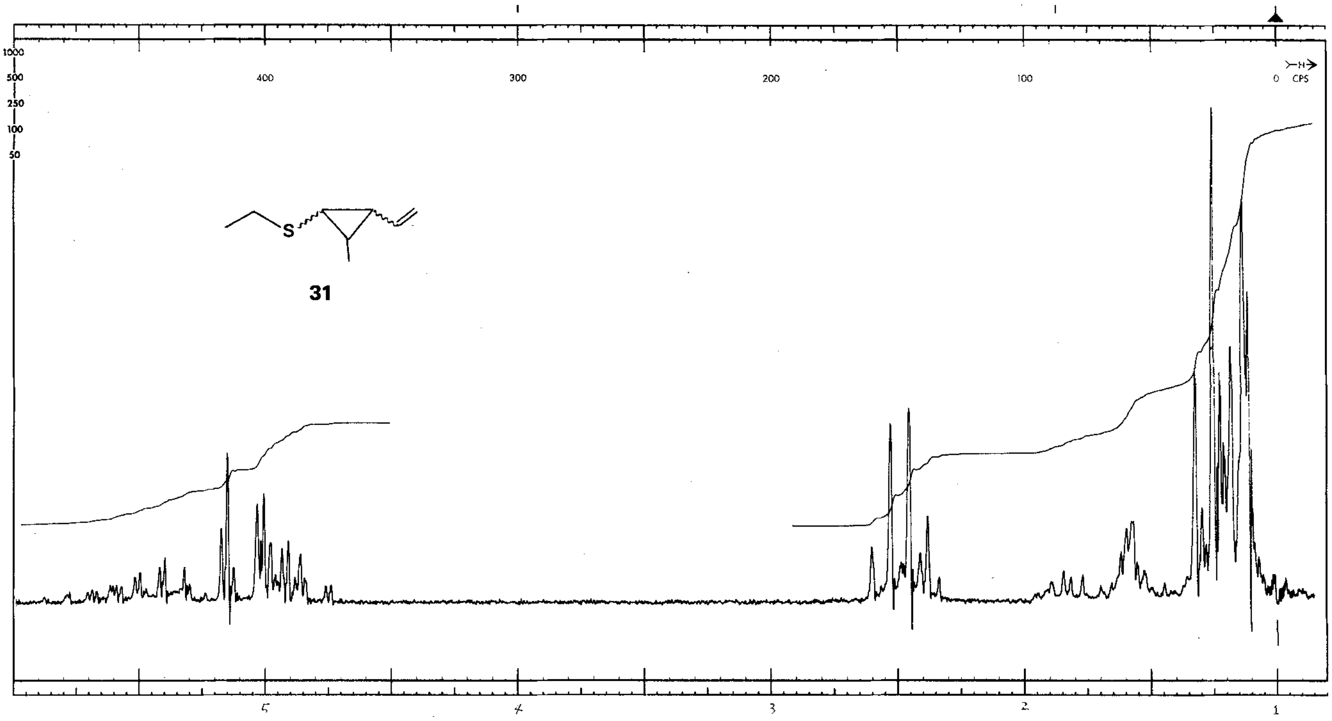


FIGURE Ic



31

FIGURE Id

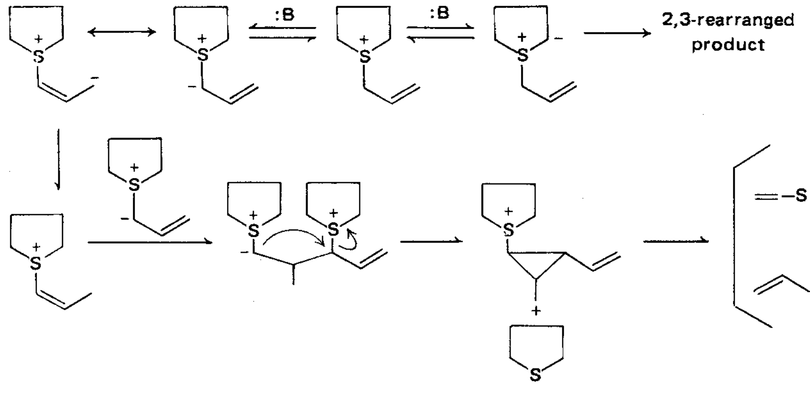
The mechanism of cyclopropane formation can be reasonably accounted for in Scheme III.

In Scheme III. the pathways for 2,3-rearrangement and the double-bond migration are similar as described in the schemes of I and II. Major difference is the bimolecular addition of sulfonium allylide anion to the intermediate vinyl double bond instead of the addition of ethoxide anion in the EtONa/EtOH system. The adduct anion is then cyclized to form a cyclopropyl sulfonium salt which further undergoes elimination reactions. For five-membered sulfonium compound with a strong base, it is known that a fragmentation of ring to form ethylene and vinyl sulfide accompanies with an ordinal elimination reaction,[3] thus to give two cyclopropyl derivatives in the case of **Ia**.

Similar bimolecular cyclopropyl ring formation has been observed by Becker and Gosselck in the reaction of vinyl sulfonium salt with mono- and di-sulfone stabilized carbanion.[7]

There are very similar trends the formation of ethoxide adducts in EtONa/EtOH system and the cyclopropyl derivatives in NaH/THF system. The cyclopropyl derivatives were only obtained from the compounds (**Ia**, **IIa** and **IIIb**) which also give higher yields of ethoxide adducts. Thus, the ease of double bond migration to give vinyl isomer and the steric

SCHEME III



hindrance to the addition of a nucleophile to the vinyl double bond may be the determining factors in both reactions. If these factors are favored, the two bimolecular reactions compete with the unimolecular 2,3-sigmatropic rearrangement. Relative importance of these unimolecular and bimolecular reactions should depend also on the reactivity of α-carbanion of the other alkyl portion than allyl group. The CH_3 group of **IIIa** forms the most active carbanion among the compounds examined, thus the 2,3-rearranged product was exclusively formed. The corresponding CH_2 groups of **IIIb** and **IIIc** are known to be far more less acidic than CH_3 group ($\sim 10^2$ times),[8] thus lower yields of 2,3-rearranged products were obtained. Non-formation of cyclopropane ring from **IIIc** may be due to a larger steric hindrance of propyl than that of ethyl group (in **IIIb**). Bimolecular nature of the reaction of cyclopropane ring formation may accord with the concentration effect of sulfonium salt. In the case of **IIIb**, when the concentration was lowered to one fifth, the yield of cyclopropane derivatives was found to be only 4%, and the yield of the competitive unimolecular path (2,3-rearrangement) increased considerably (33%).

The conclusions drawn from the above results and discussions are the following: (1) 2,3-sigmatropic rearrangement is the main path of the reactions of sulfonium allylide when the α-carbanion is active such as derived from a methyl group, or when the double-bond migration of a allyl group to form the vinyl isomer is hindered by some factors. (2) If the conditions of (1) are not satisfied, other pathways such as the formation of cyclopropane derivatives involving nucleophilic addition of carbanion to the vinyl double bond may well compete with that of 2,3-sigmatropic rearrangement.

Experimental Section

Materials

Ethanol and tetrahydrofuran were purified by distillation in the usual manner. Commercial sodium hydride was used (Wako Chemical Co., 50% mineral oil).

Preparation of Sulfonium Salts

Allyl iodide (0.02 mol) in 10 ml of anhydrous acetonitrile was added dropwise to a stirred solution of 40 ml of acetonitrile containing silver perchlorate (0.02 mol) and the corresponding sulfide (0.02 mol) at 0°C. After stirring for 15 hrs at room temperature, the precipitated silver iodide was filtered off, and the solvent was evaporated under reduced pressure. The residue was washed with ether several times until tlc showed a single spot. Then methylene dichloride (50 ml) was added and filtered to remove silver perchlorate. The filtered solution was treated with charcoal, and the solvent was distilled off and dried in a desiccator. β- and γ-Methyl allyl sulfonium perchlorates were prepared similarly from the corresponding chlorides and sulfides, by stirring for 3 days at 40°C. Yields and physical properties are summarized in Table VI.

TABLE VI

Yields, Melting Points, NMR Data, and Elemental Analyses of Sulfonium Salts

			Found (Calcd) %			δ ppm (TMS)
Salt	Yields (%)	Mp °C	C	H	S	Solvent[b]
Ia	86	Oil	36.34 (36.76)	6.01 (5.73)	13.95 (13.99)	A. 2.20-2.85 (m; 4H) 3.20-3.90 (m; 4H) 4.11 (d; 2H) 5.48-6.45 (m; 3H)
Ib	80	Oil	39.23 (39.59)	6.05 (6.23)	13.23 (13.21)	C. 1.83 (d; 3H) 2.00-2.70 (m; 4H) 3.10-3.70 (m; 4H) 3.95 (d; 2H) 4.95-5.84 (m; 1H) 5.84-6.52 (m; 1H)
Ic	77	55-6[a]	39.40 (39.59)	6.12 (6.23)	13.92 (13.21)	A. 1.97 (s; 3H) 2.20-2.85 (m; 4H) 3.34-4.00 (m; 4H) 4.17 (s; 2H) 5.24-5.50 (m; 2H)

TABLE VI—*continued*

			Found (Calcd) %			δ ppm (TMS)	
Salt	Yields (%)	Mp °C	C	H	S	Solvent[b]	
IIa	87	Oil	40.08 (39.59)	6.71 (6.23)	13.50 (13.21)	A.	1.50-2.70 (m; 6H) 3.05-3.96 (m; 4H) 4.27 (d; 2H) 5.50-6.54 (m; 3H)
IIb	71	57-8[a]	41.82 (42.10)	6.94 (6.69)	12.23 (12.49)	A.	1.83 (d; 3H) 1.50-2.70 (m; 6H) 2.80-3.90 (m; 4H) 4.32 (d; 2H) 5.32-6.62 (m; 2H)
IIc	68	126-8[a]	39.19 (39.20)	6.24 (6.69)	12.04 (12.49)	A.	1.94 (s; 3H) 1.45-2.48 (m; 2H) 2.68-3.10 (m; 4H) 3.27-3.78 (m; 4H) 4.32 (d; 2H) 5.22-5.51 (m; 2H)
IIIa	84	Oil	30.00 (29.63)	5.60 (5.47)	15.91 (15.82)	A.	3.03 (s; 6H) 4.23 (d; 2H) 5.52-6.46 (m; 3H)
IIIb	75	Oil	35.81 (36.44)	6.43 (6.55)	13.81 (13.90)	A.	1.50 (t; 6H) 3.41 (q; 4H) 4.20 (d; 2H) 5.50-6.42 (m; 3H)
IIIc	80	124-5[a]	41.20 (41.78)	7.57 (7.40)	12.39 (12.39)	C.	1.12 (t; 6H) 1.45-2.34 (m; 4H) 3.32 (t; 4H) 4.12 (d; 2H) 5.45-6.20 (m; 3H)
IV	85	Oil	47.57 (48.37)	6.21 (5.93)	9.93 (10.64)	C.	1.12 (t; 3H) 3.16-4.35 (m; 6H) 4.59 (d; 2H) 5.24-6.38 (m; 3H) 7.55-8.28 (m; 5H)
V	83	60-1[a]	58.25 (57.54)	5.43 (5.40)	9.44 (9.04)	C.	3.04 (t; 2H) 4.10 (t; 2H) 4.33 (d; 2H) 5.10-5.74 (m; 3H) 7.20 (s; 5H) 7.40-8.07 (m; 5H)
VI	80	Oil	48.17 (47.40)	5.94 (5.42)	11.64 (11.48)	C.	1.42 (t; 3H) 3.86 (q; 2H) 4.54 (d; 2H) 5.34-6.28 (m; 3H) 7.50-8.25 (m; 5H)

[a] Uncorrected. Recrystallized from CH_2Cl_2/ether.

[b] A; Acetone-d_6, C; Chloroform-d_3, D; Carbon tetrachloride.

Reactions with bases and product analyses

Sulfonium salts (3 mmol) and bases (9 mmol) in 50 ml of solvents were stirred for 48 hrs at the desired temperature, then the solution was poured into 100 ml ice water and extracted twice with 100 ml ether. After the extract was dried over $CaCl_2$, ether was distilled off and the residue was subjected to gas-chromatography using a column (2 m) packed with Celite 545 covered with silicone DC high vacuum grease 20%, or Carbowax 20 M, 20%. Hydrogen was used as a carrier gas. The yields were determined from the relative peak areas of products to that of known amounts of appropriate internal standards. Fraction of all peaks were collected and identified by nmr, mass spectra, and elemental analyses.

Nmr spectra were recorded on a Varian A-60 D spectrometer; chemical shifts are given in δ with TMS as the internal standard. Mass spectra were taken on the JEOL JMS-07 gc-mass spectrometer at an ionizing voltage of 75 ev and an ionizing current of 300 μA.

Spectral properties and elemental analyses of the reaction products are followings;

Compound **1**; nmr (CCl_4) δ 1.17-2.45 (m, 6H), 2.58-3.00 (m, 2H), 3.05-3.65 (m, 1H), 4.80-5.24 (m, 2H), 5.46-6.18 (m, 1H); ms, m/e 128 (M^+), 87, 41

Anal. Calc for $C_{11}H_{12}S$: C, 65.56; H, 9.41; S, 25.00.
Found: C, 65.84, H, 9.53; S, 24.31.

Compound **2**; nmr (CCl_4) δ 1.12 (t, 3H), 1.18 (d, 3H), 2.02-2.82 (m, 6H), 3.10-3.68 (m, 3H), 4.74-5.20 (m, 2H), 5.45-6.18 (m, 1H); ms, m/e 174 (M^+), 101, 73, 60, 45, 41

Anal. Calc for $C_9H_{18}SO$: C, 62.02; H, 10.41; S, 18.40.
Found: C, 61.90; H, 10.50; S, 18.65.

Compound **3**; nmr$(CDCl_3)$ δ 1.18 (t, 6H), 1.25 (d, 3H), 1.52-1.88 (m, 4H), 2.30-2.84 (m, 4H), 3.30-3.82 (m, 7H); ms, m/e 220 (M^+), 174, 148, 101, 73, 45

Anal. Calc for $C_{11}H_{24}SO_2$: C, 59.95; H, 10.98;
S, 14.55. Found: C, 59.74; H, 11.10; S, 14.93.

Compound **4**; nmr (CCl_4) δ 1.06 (d, 3H), 1.38-2.50 (m, 5H), 2.64-3.00 (m, 2H), 3.00-3.46 (m, 1H), 4.78-5.20 (m, 2H), 5.38-6.14 (m, 1H); ms; m/e 142 (M^+), 87,55

Anal. Calc for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.54.
Found: C, 67.42; H, 10.10; S, 22.47.

Compound **5**; nmr (CCl_4) δ 1.70 (s, 3H), 1.45-2.38 (m, 6H), 2.62-3.00 (m, 2H), 3.14-3.72 (m, 1H), 4.56-4.84 (m, 2H); ms, m/c 142 (M^+), 87, 55

Anal. Calc for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.54.
Found: C, 68.11; H, 10.13; S, 22.26.

Compound **6**; nmr (CCl_4) δ 1.72 (s, 3H), 1.77 (s, 3H), 2.00-2.88 (m, 4H), 4.75-5.25 (m, 2H), 5.44-6.30 (m, 2H); ms, m/e 142 (M^+)

Anal. Calc for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.54.
Found: C, 67.16; H, 10.30; S, 22.00.

Compound **7**; nmr (CCl_4) δ 1.15 (t, 3H), 1.72 (s, 3H), 1.77 (s, 3H), 1.34-2.00 (m, 4H), 2.32-2.72 (m, 2H), 3.16-3.62 (m, 4H), 5.42-6.62 (m, 1H); ms, m/e 188 (M^+), 101, 88, 59.

Anal. Calc for $C_{10}H_{20}SO$: C, 63.78; H, 10.70; S, 17.03.
Found: C, 63.25; H, 10.65; S, 16.68.

Compound **8**; nmr (CCl_4) δ 1.08 (t, 3H), 1.18 (s, 6H), 2.02-2.80 (m, 6H), 3.30 (q, 2H), 4.82-5.38 (m, 2H), 5.42-6.08 (m, 1H); ms, m/e 188 (M^+), 101, 87, 59.

Anal. Calc for $C_{10}H_{20}SO$: C, 63.78; H, 10.70; S, 17.03.
Found: C, 63.19; H, 10.39; S, 16.70.

Compound **9**; nmr (CCl_4) δ 1.08 (t, 3H), 1.14 (t, 3H), 1.18 (s, 6H), 1.48-1.85 (m, 4H), 2.30-2.70 (m, 4H), 3.18-3.64 (m, 6H); ms, m/e 234 (M^+), 188, 101, 87, 73, 59, 55.

Anal. Calc for $C_{12}H_{26}SO_2$: C, 61.49; H, 11.18; S, 13.68.
Found: C, 61.10; H, 10.98; S, 13.75.

Compound **10**; nmr $(CDCl_3)$ δ 0.85-2.40 (m, 8H), 2.50-2.92 (m, 3H), 4.64-5.42 (m, 2H), 5.42-6.25 (m, 1H); ms, m/e 142 (M^+), 101, 41.

Anal. Calc for $C_8H_{14}S$; C, 67.54; H, 9.92; S, 22.54.
Found: C, 67.53; H, 10.39; S, 21.98.

Compound **11**; nmr (CCl_4) δ 1.12 (t, 3H), 1.15 (d, 3H), 1.46-2.36 (m, 4H), 2.36-2.82 (m, 4H), 3.18-3.75 (m, 3H), 4.78-5.25 (m, 2H), 5.45-6.18 (m, 1H); ms, m/e 188 (M^+), 101, 87, 73, 59.

Anal. Calc for $C_{10}H_{20}SO$: C, 63.78; H, 10.70; S, 17.03.
Found: C, 64.10; H, 11.00; S, 17.54.

Compound **12**; nmr $(CDCl_3)$ δ 1.18 (t, 6H), 1.23 (d, 3H), 1.36-1.88 (m, 6H), 2.26-2.92 (m, 4H), 3.28-3.75 (m, 7H); ms, m/e 234 (M^+), 188, 73, 59.

Anal. Calc for $C_{12}H_{26}SO_2$: C, 61.49; H, 11.18; S, 13.68.
Found: C, 60.93; H, 11.30; S, 14.32.

Compound **13**: nmr (CCl_4) δ 1.07 (d, 3H), 1.18-2.28 (m, 7H), 2.28-2.84 (m, 3H), 4.76-5.20 (m, 2H), 5.40-6.10 (m, 1H); ms, m/e 156 (M^+), 101, 55.

Anal. Calc for $C_9H_{16}S$: C, 69.17; H, 10.32; S, 20.58.
Found: C, 70.20; H, 9.93; S, 20.00.

Compound **14**; nmr (CCl_4) δ 1.71 (s, 3H), 1.05-2.24 (m, 8H), 2.34-3.00 (m, 3H), 4.55-4.82 (m, 2H); ms, m/e 156 (M^+), 101, 55.

Anal. Calc for $C_9H_{16}S$: C, 69.17; H, 10.32; S, 20.58.
Found: C, 68.11; H, 10.15; S, 21.00.

Compound **15**: nmr (CCl_4) δ 1.70 (s, 3H), 1.75 (s, 3H), 1.42-2.38 (m, 4H), 2.55 (t, 2H), 4.72-5.20 (m, 2H), 5.30-6.22 (m, 2H); ms, m/e 156 (M^+), 101, 55, 45, 41.

Anal. Calc for $C_9H_{16}S$: C, 69.16; H, 10.32; S, 20.51.
Found: C, 69.00; H, 10.00; S, 20.10.

Compound **16**; nmr (CCl_4) δ 1.14 (t, 3H), 1.71 (s, 3H), 1.74 (s, 3H), 1.30-1.90 (m, 6H), 2.34-2.72 (m, 2H), 3.12-3.62 (m, 4H), 5.42-5.62 (m, 1H); ms, m/e 202 (M^+), 115, 88, 59.

Anal. Calc for $C_{11}H_{22}SO$: C, 65.29; H, 10.96; S, 15.84.
Found: C, 64.98; H, 10.55; S, 16.00.

Compound **17**; nmr (CCl_4) δ 1.10 (t, 3H), 1.20 (s, 6H), 1.36-2.26 (m, 4H), 2.28-2.68 (m, 4H), 3.35 (q, 2H), 4.68-5.20 (m, 2H), 5.40-6.10 (m, 1H); ms, m/e 202 (M^+) 187, 115, 87, 59.

Anal. Calc for $C_{11}H_{22}S$: C, 65.29; H, 10.96; S, 15.84.
Found: C, 64.98; H, 10.56; S, 16.00.

Compound **18**: This compound was not collected. See footnote (b) in Table I.

Compound **19**: nmr (CCl_4) δ 2.06 (s, 3H), 2.22-2.75 (m, 4H), 4.82-5.28 (m, 2H), 5.50-6.20 (m, 1H); ms, m/e 102 (M^+), 87, 61.

Anal. Calc for $C_5H_{11}S$: C, 58.76; H, 9.86; S, 31.37.
Found: C, 58.38; H, 9.50; S, 31.00.

Compound **20**: nmr (CCl_4) δ 1.14 (t, 3H), 1.17 (d, 3H), 2.08 (s, 3H), 2.24–2.80 (m, 2H), 3.22–3.78 (m, 3H); ms, m/e 134 (M^+), 73, 61, 45.

Anal. Calc for $C_6H_{14}S$: C, 53.63; H, 10.51; S, 23.88.
Found: C, 53.55; H, 10.40; S, 23.50.

Compound **21**: nmr (CCl_4) δ 1.25 (t, 3H), 1.25 (d, 3H), 2.00–3.22 (m, 5H), 4.84–5.30 (m, 2H), 5.50–6.25 (m, 1H); ms, m/e 130 (M^+), 115, 87, 61.

Anal. Calc for $C_4H_{14}S$: C, 64.55; H, 10.83; S, 24.62.
Found: C, 64.63; H, 10.56; S, 24.19.

Compound **22**: nmr ($CDCl_3$) δ 1.18 (t, 3H), 1.26 (t, 3H), 1.18 (d, 3H), 2.12–3.02 (m, 4H), 3.28–3.88 (m, 3H); ms, m/e 148 (M^+).

Anal. Calc for $C_7H_{16}SO$: C, 56,70; H, 10.88; S, 21.62.
Found: C, 56.88; H, 10.75; S, 20.93.

Compound **23**: nmr (CCl_4) δ 1.02 (t, 3H), 1.14 (t, 3H), 1.34–2.07 (m, 6H), 2.07–2.84 (m, 3H), 4.70–5.25 (m, 2H), 5.40–6.15 (m, 1H); ms, m/e 158 (M^+).

Anal. Calc for $C_9H_{18}S$: C, 68.29; H, 11.46; S, 20.25.
Found: C, 68.00, H, 11.10; S, 19.95.

Compound **24**: nmr (CCl_4) δ 0.80–1.38 (m, 9H), 1.38–1.95 (m, 2H), 2.10–2.68 (m, 4H), 3.28–3.72 (m, 3H); ms, m/e 162 (M^+).

Anal. Calc for $C_8H_{18}SO$: C, 59.21; H, 11.18; S, 19.76.
Found: C, 59.00; H, 10.98; S, 19.70.

Compound **25**: nmr ($CDCl_3$) δ 1.15 (t, 3H), 2.22–2.65 (m, 2H), 3.06–3.68 (m, 3H), 4.90–5.32 (m, 2H), 5.50–6.34 (m, 1H), 7.15–7.62 (m, 5H); ms, m/e 222 (M^+).

Anal. Calc for $C_{13}H_{18}SO$: C, 70.22; H, 8.16; S, 14.42.
Found: C, 71.06; H, 8.79; S, 14.50.

Compound **26**: nmr ($CDCl_3$) δ 1.14 (t, 3H), 1.23 (d, 2H), 2.60–3.20 (m, 2H), 3.20–3.86 (m, 3H), 7.15–7.52 (m, 5H); ms, m/e 196 (M^+).

Anal. Calc for $C_{11}H_{16}S$: C, 67.30; H, 8.22; S, 16.33.
Found: C, 66.97; H, 8.27; S, 17.11.

Compound **27**: nmr (CCl_4) δ 1.33 (d, 3H), 2.05–2.56 (m, 2H), 3.02–3.64 (m, 1H), 4.90–5.32 (m, 2H), 5.45–6.32 (m, 1H), 7.15–7.62 (m, 5H); ms, m/e 178 (M^+).

Anal. Calc for $C_{11}H_{14}S$: C, 74.10; H, 7.91; S, 17.98.
Found: C, 74.10; H, 8.44; S, 17.95.

Compound **28**: nmr (CCl_4) δ 0.92–1.30 (m, 3H, 1H), 1.30–2.16 (m, 1H, 1H), 4.74–5.86 (m, 5H), 5.94–6.60 (m, 1H); ms, m/e 140 (M^+), 125, 113, 81.

Anal. Calc for $C_8H_{12}S$: C, 68.51; H, 8.63; S, 22.86.
Found: S, 22.92.

Compound **29**: nmr ($CDCl_3$) δ 0.84–1.32 (m, 3H, 1H), 1.32–2.02 (m, 1H, 1H), 2.12–2.98 (m, 4H), 4.72–6.22 (m, 6H); ms, m/e 168 (M^+), 153, 127, 81.

Anal. Calc for $C_{10}H_{16}S$: S, 19.05. Found: S, 18.42.

Compound **30**: nmr (CCl_4) δ 0.83–1.32 (m, 3H, 1H), 1.32–2.27 (m, 4H, 1H, 1H), 2.28–2.27 (m, 2H), 4.70–6.12 (m, 6H); ms, m/e 182 (M^+), 157, 155, 101, 81.

Anal. Calc for $C_{11}H_{18}S$: S, 17.59. Found: S, 17.30.

Compound **31**: nmr (CCl_4) δ 0.92–1.47 (m, 3H, 1H), 1.25 (t, 3H), 1.47–2.00 (m, 1H, 1H), 2.27–2.78 (m, 2H), 4.72–6.16 (m, 3H); ms, m/e 142 (M^+), 127, 116, 113, 81.

Anal. Calc for $C_8H_{14}S$: S, 22.54. Found: S, 22.40.

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