[Chem. Pharm. Bull.
17(5) 966—973 (1969)]

UDC 547.538.24-279.1.04

Studies on Acetylenic Compounds. XLVII.[1] The Rearrangement of Acetylenic Sulfonium Salts

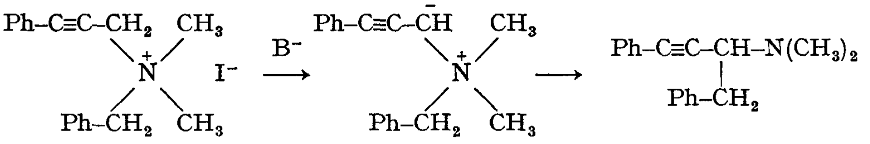
Atsusuke Terada and Yukichi Kishida

Central Research Laboratories, Sankyo Co., Ltd.[2]

(Received September 7, 1968)

Treatment of acetylenic sulfonium salts, dimethyl 3-phenyl-2-propynylsulfonium bromide (VII), dimethyl 2-butynylsulfonium bromide (XII) and methyl bis(3-phenyl-2-propynyl)sulfonium methyl sulfate (XIX), with base gave *S*$_N$*i'* reaction products, methyl 2-phenyl-2,3-butadienyl sulfide (VIII), methyl 2-methyl-2,3-butadienyl sulfide (XIII) and methyl 1-(2-phenylethynyl)-2-phenyl-2,3-butadienyl sulfide (XXII), respectively. Similarly, methyl (2-propenyl)(3-phenyl-2-propynyl)sulfonium methyl sulfate (XXIII) was converted to methyl 1-(2-phenylethynyl)-3-butenyl sulfide (XXVII) by *S*$_N$*i'* reaction. The reaction of methyl benzyl 3-phenyl-2-propynylsulfonium methyl sulfate (XXXIII) with base, however, afforded the usual Stevens type rearrangement product, methyl 1-benzyl 3-phenyl-2-propynyl sulfide (XXXVI). A mechanistic assumption for the rearrangements of acetylenic sulfonium salts was given.

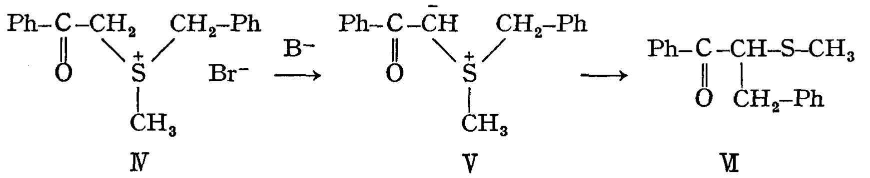
The Stevens rearrangement[3] of quarternary ammonium salts has been extensively studied. Iwai and Hiraoka[4] have reported the rearrangement of acetylenic ammonium salts (Eq. 1). This electrophilic intramolecular 1,2 rearrangement has been thought[5] to proceed presumably *via* an intermediate ylid (II) leading to the amine (III).



(1)

I II III

Sulfonium salts, likewise, rearrange *via* ylids to sulfides.[6] For example, Thompson and Stevens[7] have reported that methyl benzyl phenacylsulfonium bromide (IV), when treated with sodium methoxide, gave methyl 1-benzylphenacyl sulfide (VI) *via* ylid (V) (Eq. 2).



(2)

IV V VI

---

[1] Part XLVI: Y. Kishida and A. Terada, *Chem. Pharm. Bull.* (Tokyo), **16**, 1351 (1968).

[2] Location: *2-58, 1-chome, Hiromachi, Shinagawa-ku, Tokyo.*

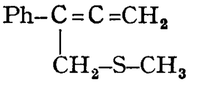
[3] *a*) H.E. Zimmerman, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, **1963**, p. 378; *b*) M.S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, **1956**, p. 279; *c*) E.S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt & Company, Inc., **1960**, p. 640.

[4] I. Iwai and T. Hiraoka, *Chem. Pharm. Bull.* (Tokyo), **11**, 1556 (1963).

[5] Gould[3c] has asserted that the Stevens rearrangements are convenient to regard carbanion rearrangements as internal nucleophilic substitutions (*S*$_N$*i* reactions), with the negatively charged carbon atom as the attacking nucleophile.

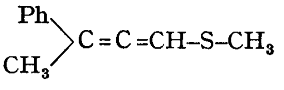
In the course of the study of S–ylid chemistry, we found novel rearrangements of sulfonium salts, $S_{N}i'$ reactions of the Stevens type rearrangements, which had not been reported on the rearrangements of ammonium salts.

Treatment of dimethyl 3-phenyl-2-propynylsulfonium bromide (VII), prepared from 3-phenyl-2-propynyl bromide and dimethyl sulfide, with sodium hydride in anhydrous tetrahydrofuran or aqueous sodium hydroxide gave an oily substance of bp 73—75° (0.0001 mmHg) in 78.4 and 11.4% yield, respectively, whose elemental analysis agreed with $C_{11}H_{12}S$. (see Chart 1). On the basis of the reaction mechanism of the Stevens type rearrangement, the structure of this oil would be assumed as one of the following (VIII, IX, X and XI).



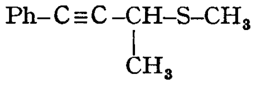
$\mathrm{Ph{-}C(CH_2{-}S{-}CH_3){=}C{=}CH_2}$

VIII



$\mathrm{(Ph)(CH_3)C{=}C{=}CH{-}S{-}CH_3}$

IX



$\mathrm{Ph{-}C{\equiv}C{-}CH(CH_3){-}S{-}CH_3}$

X

$\mathrm{Ph{-}C{\equiv}C{-}CH_2{-}CH_2{-}S{-}CH_3}$

XI

The infrared spectrum showed no triple bond absorption at 2200 cm^{-1} region, which excluded the possibility of the two structures X and XI, but showed a new allenic absorption band at 1955 cm^{-1}, substanciating the possibility of two other structures VIII and IX. The structure IX, however, was excluded by another absorption band at 858 cm^{-1}, which was characteristic of an allenic terminal methylene group, leaving only methyl 2-phenyl-2,3-butadienyl sulfide (VIII) for the possible structure. This was further confirmed by the nuclear magnetic resonance (NMR) spectrum. The NMR spectrum of VIII in deuteriochloroform showed a singlet at 2.01 ppm ($-S-CH_3$), a triplet at 3.59 ppm (J=2 cps, $-S-CH_2-C=C=$), a triplet at 5.18 ppm (J=2 cps, $-C=C=CH_2$), and an aromatic multiplet at 7.40 ppm (center).

Similarly, treatment of dimethyl 2-butynylsulfonium bromide (XII), prepared from 2-butynyl bromide and dimethyl sulfide, with sodium hydride in anhydrous tetrahydrofuran afforded an allenic substance, methyl 2-methyl-2,3-butadienyl sulfide (XIII), bp 70—75° (20 mmHg) in 20.6% yield (see Chart 1). The infrared spectrum of XIII showed a typical allenic moiety at 1950 cm^{-1}, together with an allenic terminal methylene at 850 cm^{-1}. The NMR spectrum in deuteriochloroform showed a singlet at 2.00 ppm ($-S-CH_3$), a triplet at 1.78 ppm (J=3 cps, $-C=C-CH_3$), a triplet at 3.03 ppm (J=1.7 cps, $-S-CH_2-C=$) and a multiplet centered at 4.63 ppm ($-C=C=CH_2$).

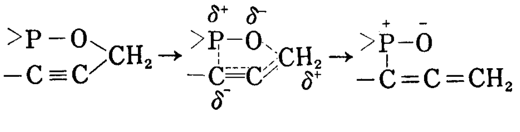
These rearrangements can be explained by a $S_{N}i'$ mechanism[8] as indicated in Chart 1, or alternatively, by a sigmatropic reaction[10] involving the covalent formulation (XVII) of the ylid intermediate.

---

6) A.W. Johnson, "Ylid Chemistry," Academic Press, New York and London 1966, p. 304.

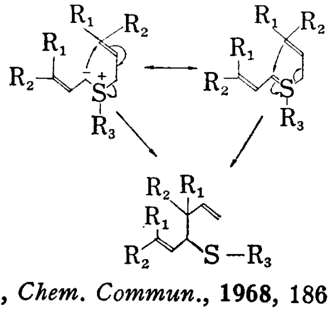
7) T. Thompson and T.S. Stevens, *J. Chem. Soc.*, **1932**, 69.

8) Mark[9] has reported the similar $S_{N}i'$ mechanism in the system of $>P-O-CH_2-C\equiv C-$ as illustrated below.



9) V. Mark, *Tetrahedron Letters*, **1962**, 281.

10) Recently, Blackburn, *et al.*,[11] have reported the similar sigmatropic reaction of allylic sulfur ylid as illustrated below:



11) G.M. Blackburn, W.D. Ollis, J.D. Plackett, C. Smith and I.O. Sutherland, *Chem. Commun.*, **1968**, 186.

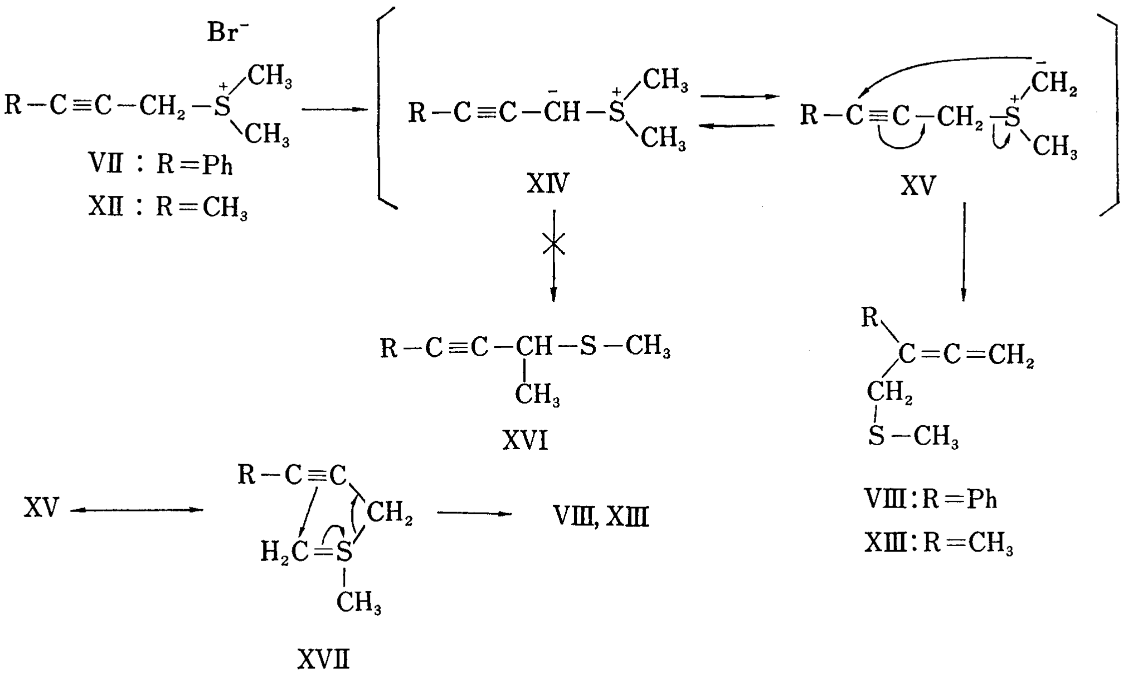


Chart 1

The initial equilibrium favors the starting ylid (XIV), but the equilibration to XV or XVII can lead to the product. In these reactions, none of 1,2 rearrangement product *i.e.*, methyl 1-methyl-3-phenyl-2-propynyl sulfide (XVI) was detected, differing from the case of Eq. 2.

Contrary to our expectation, dimethyl 2-propynylsulfonium bromide (XVIII) gave no rearrangement product, but yielding only a polymerized product by the similar procedure. This exceptional behavior of XVIII in basic medium can be understood, if one can imagine the formation of an allenic carbene:

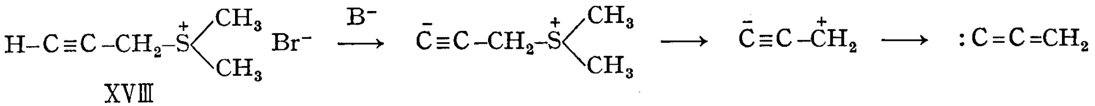


Chart 2

While, treatment of methyl bis(3-phenyl-2-propynyl)sulfonium methyl sulfate (XIX), prepared from bis(3-phenyl-2-propynyl)sulfide[12] and dimethyl sulfate, with aqueous sodium

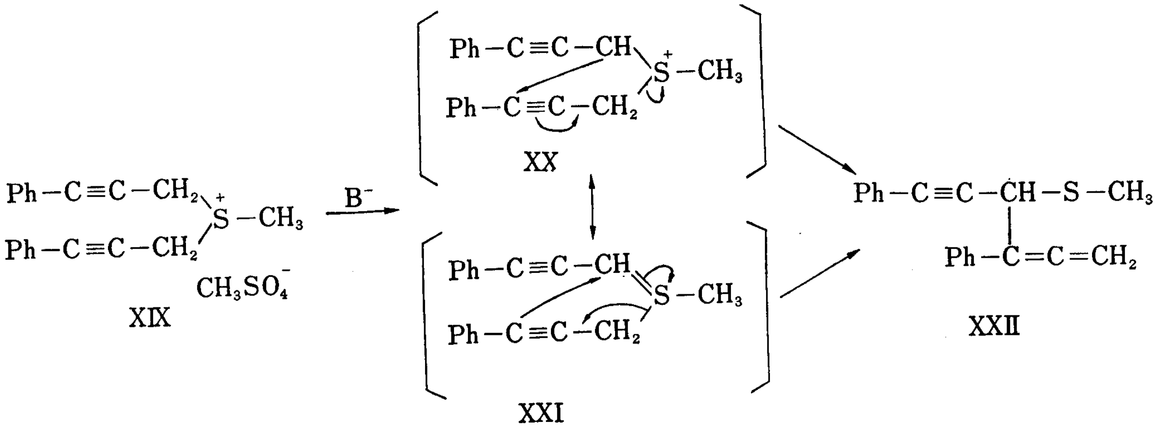


Chart 3

---

[12] I. Iwai and J. Ide, *Chem. Pharm. Bull.* (Tokyo), **12**, 1094 (1964).

hydroxide afforded an oily product (XXII) in 89.8% yield after careful silicagel column chromatography. This oil could not distilled even under highly reduced pressure (0.0001 mmHg), owing to the unstable nature for polymerization or decomposition. The ultraviolet spectrum of XXII showed the characteristic absorption band of phenylacetylene at 245 (ε=24200) and 254 mμ (ε=21300), and the infrared spectrum revealed the absorption at 2210 cm^{-1} due to the triple bond, an allenic band at 1955 cm^{-1} and an allenic terminal methylene band at 860 cm^{-1}.

The NMR spectrum of XXII in deuteriochloroform exhibited the signals at 2.30 ppm (3H, singlet) due to the S-methyl protons, 7.30 ppm (10H, multiplet) assignable to the two phenyl groups, a triplet at 4.80 ppm (1H, J=2 cps) assigned to the methyne proton adjacent to the S-methyl group and a triplet at 5.31 ppm (2H, J=2 cps) for the allenic terminal methylene protons. On the basis of these data and the reaction mechanism, the allenic compound, XXII, was concluded to be methyl 1-(2-phenylethynyl)-2-phenyl-2,3-butadienyl sulfide.

A plausible S_Ni' mechanism would be operative for the formation of XXII as in the case mentioned before (VII→VIII and XII→XIII). An alternative sigmatropic reaction mechanism involving the covalent formulation (XXI) of the ylid intermediate is also possible.

When methyl (2-propenyl) (3-phenyl-2-propynyl)sulfonium methyl sulfate (XXIII), prepared from (2-propenyl) (3-phenyl-2-propynyl)sulfide and dimethyl sulfate, was treated with aqueous sodium hydroxide, an oily product (XXVII) of bp 90—95° (0.0001 mmHg) (bath temp.) was obtained in 27.2% yield.

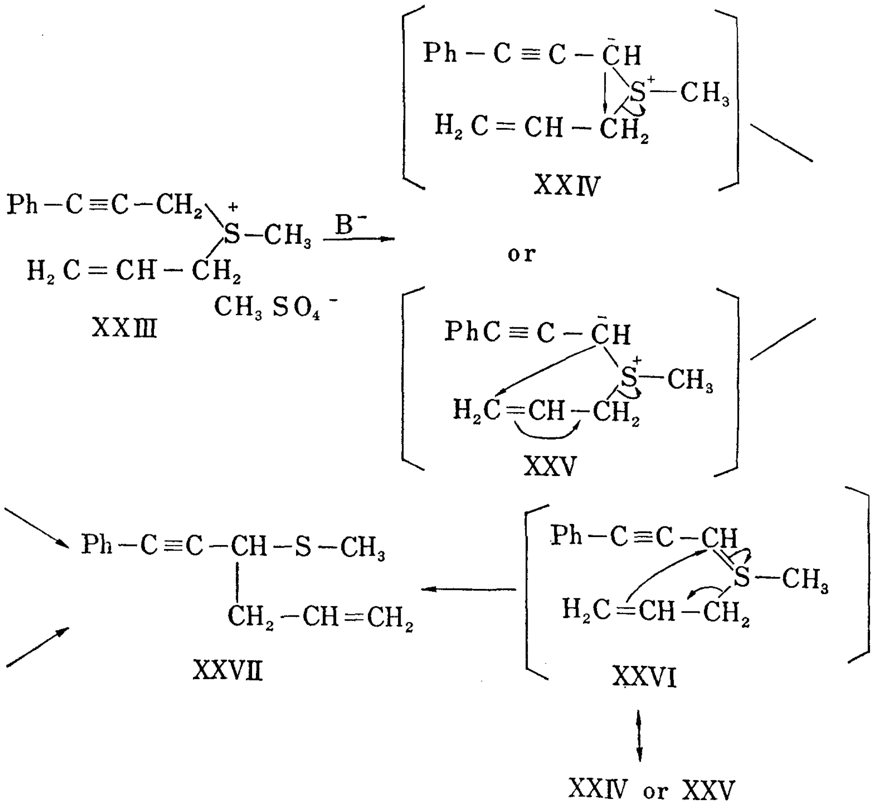


Chart 4

The infrared spectrum still showed a triple bond at 2200 cm^{-1} and a terminal vinyl group at 918 and 990 cm^{-1}, and the ultraviolet spectrum also revealed the characteristic absorption of phenylacetylene group at 242.5 (ε=13800) and 250 mμ (ε=13200). The NMR spectrum in deuteriochloroform exhibited the signals at 2.26 ppm (3H, singlet) due to the S-methyl protons, a triplet at 3.70 ppm (1H, J=7.0 cps) assigned to the methyne proton adjacent to S-methyl group, a multiplet at 2.55 ppm (2H) for the methylene protons adjacent to vinyl group, a multiplet centered at 5.50 ppm which is characteristic of the vinyl group and an aromatic multiplet centered at 7.30 ppm. From these data, the oily product, XXVII, was assigned to be methyl 1-(2-phenyethynyl)-3-butenyl sulfide. This assignment was further supported by the nuclear magnetic double resonance data, the mass spectrum (*m/e* 202, molecular ion peak) and the characterization as the crystalline chloroplatinate, $C_{26}H_{28}S_2PtCl_6$, mp 123°.

A mechanistic assumption for the formation of XXVII from XXIII would be expressed as the usual Stevens type rearrangement (XXIV) or as S_Ni' reaction (XXV).[13]

In order to investigate this reaction path, dimethyl 3-phenyl-2-propenylsulfonium bromide (XXVIII), prepared from 3-phenyl-2-propenyl bromide and dimethyl sulfide, was treated with dimethyl sulfinyl carbanion to afford methyl 2-phenyl-3-butenyl sulfide (XXX) of bp 129—130° (10 mmHg) in 87.1% yield.

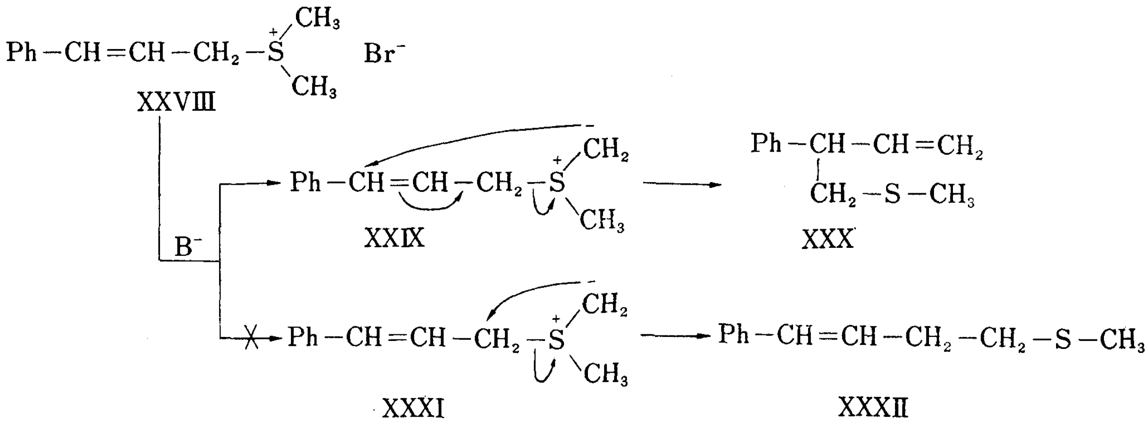


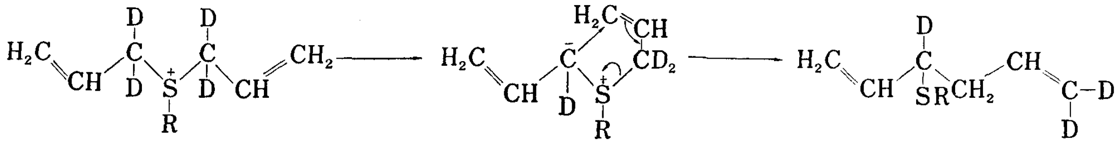
Chart 5

The structure of XXX was assigned by the infrared and NMR spectra coupled with elemental analysis ($C_{11}H_{14}S$). The infrared spectrum showed typical terminal vinyl band at 918 and 995 cm^{-1}. The NMR spectrum exhibited the signals at 2.02 ppm (3H, singlet) due to the S-methyl protons, a doublet at 2.83 ppm (2H, J=7.0 cps) for the methylene protons adjacent to S-methyl group, an approximate quartet at 3.52 (1H, J_1=7.0 cps, J_2=7.0 cps), multiplets centered at 5.05, 5.10 and 6.05 ppm (3H) due to the vinyl protons and an aromatic multiplet centered at 7.40 ppm. Thus, it could be concluded that dimethyl 3-phenyl-2-propenylsulfonium bromide (XXVIII) was converted to methyl 2-phenyl-3-butenyl sulfide (XXX) only by S_Ni' reaction (XXIX) under the conditions employed. Therefore, S_Ni' reaction was operative and the usual Stevens type rearrangement was extruded in this case. Alternatively, the transformation of XXIII to XXVII may be explained as a sigmatropic reaction as aforementioned for XVII and XXI.

When methyl benzyl 3-phenyl-2-propynylsulfonium methyl sulfate (XXXIII), prepared from benzyl 3-phenyl-2-propynyl sulfide and dimethyl sulfate, was treated with sodium hydride in anhydrous tetrahydrofuran or aqueous sodium hydroxide, two products were isolated by means of preparative gas chromatography. The first product (XXXV), mp 51°, had a mole-

---

[13] Recently, Kirmse and M. Kupps[14] have reported the similar S_Ni' reaction using α-deuterated diallylsulfonium salt as illustrated below:



[14] W. Kirmse and M. Kupps, *Chem. Ber.*, **101**, 1004 (1968).

cular formula, $C_{14}H_{14}$, which was identical in all respects with an authentic sample of dibenzyl. The mechanism for the formation of XXXV is not clear at present.

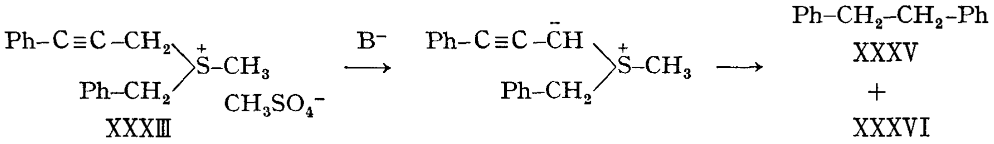
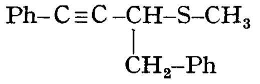
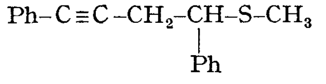


Chart 6



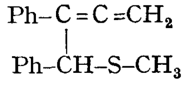
XXXVI

$$Ph-C\equiv C-\underset{CH_2-Ph}{\underset{|}{C}H}-S-CH_3$$



XXXVII

$$Ph-C\equiv C-CH_2-\underset{Ph}{\underset{|}{C}H}-S-CH_3$$



XXXVIII

$$Ph-\underset{Ph-CH-S-CH_3}{\underset{|}{C}}=C=CH_2$$

The structure of the second product would be assumed as one of the following substances (XXXVI, XXXVII and XXXVIII) from the reaction mechanism. The infrared spectrum showed no allenic absorption band at 1950 cm^{-1} region, which excluded the possibility of the structure XXXVIII. The NMR spectrum showed signals at 1.85 ppm (3H, singlet) due to S-methyl group, approximate two singlets centered at 7.17 and 7.28 ppm assignable to two phenyl groups and a AB_2 pattern at 3.90 (1H, quartet, $J=6.8$ cps) and 3.14 ppm (2H, doublet, $J=6.8$ cps). This NMR assignment was further confirmed by decoupling. These data were consistent with two other structures XXXVI and XXXVII. The structure XXXVII, however, would be excluded by the following reasons: 1) The initial ylid anion should be generated at the methylene group adjacent to phenylacetylene group rather than that of the benzyl, because of the stronger electron withdrawing character of the former than the latter, σ^* value: $\sigma^*_{Ph}=+0.6$, $\sigma^*_{Ph-C\equiv C-}=1.35$[1b)]. 2) If the loss of proton occurred at the benzyl methylene group, S_Ni' reaction would predominate rather than the usual Stevens rearrangement leading to XXXVIII, considering the results of VII→VIII and XII→XIII. The structure XXXVIII, which was excluded as mentioned above, however, was one of the possible S_Ni' rearrangement product. Thus the structure of the second product was tentatively assigned to be methyl 1-benzyl-3-phenyl-2-propynyl sulfide.

As conclusion, S_Ni' reactions (VII→VIII and XII→XIII) are limited to the dimethylsulfonium salt derivatives. This rearrangement is quite analogous to the Sommelet–Hauser rearrangement of benzyltrimethylammonium bromide in liquid ammonia by sodamide.[15]

The acetylenic ammonium salt, however, did not undergo this rearrangement. On the other hand, in the presence of the acceptors of carbanion such as propynyl and allyl group, the initial carbanion formed at the methylene group adjacent to phenylacetylene substituent worked itself as nucleophile to accomplish 1,2 rearrangement.

Experimental[16]

Dimethyl 3-Phenyl-2-propynylsulfonium Bromide (VII)——A solution of 3-phenyl-2-propynyl bromide (19.6 g) and dimethyl sulfide (7.0 g) in 20 ml of benzene was stirred for 8 hr at room temperature. The resulting crystalline substance was collected by filtration and recrystallized from EtOH to give colorless needles of mp 139—141° (20 g). *Anal.* Calcd. for $C_{11}H_{13}BrS$: C, 51.36; H, 5.06; Br, 31.13; S, 12.45. Found: C, 51.08; H, 5.06; Br, 31.10; S, 12.45. UV λ_{max}^{EtOH} mμ (ε): 246 (16900), 255 (13300) (shoulder). IR ν_{max}^{Nujol} cm^{-1}: 2210. NMR (δ) (in D_2O): 3.05 (6H, singlet, $-S(CH_3)_2$), 4.60 (2H, singlet, $-CH_2-S-$), 7.60 (5H, multiplet, aromatic protons).

Methyl 2-Phenyl-2,3-butadienyl Sulfide (VIII)——a) To a stirred suspension of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.6 g) in 20 ml of anhydrous tetrahydrofuran was added 0.48 g of sodium

---

15) S.W. Kantor and C.R. Hauser, *J. Am. Chem. Soc.*, 73, 4122 (1951).

16) All melting and boiling points are uncorrected. The NMR spectra were taken on Varian A-60 and HA-100 spectrometer with tetramethylsilane as an internal standard.

hydride (50% oily mixture) at 3—5° under N_2 and continued to stir at room temperature for 2 days. The reaction mixture was poured into 100 ml of ice-water and extracted with ether. The combined extracts were washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 3.0 g of pale yellow oil, which was distilled *in vacuo* to afford a pale yellow oil (1.38 g), bp 73—75° (0.0001 mmHg). *Anal.* Calcd. for $C_{11}H_{12}S$: C, 74.97; H, 6.84; S, 18.16. Found: C, 74.69; H, 6.98; S, 17.91.

b) A mixture of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.6 g), 10% NaOH (4.5 ml), 15 ml of H_2O and 15 ml of benzene was heated on the steam bath for 3 hr. After cooling, benzene layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give an oil, which was distilled *in vacuo* to afford VIII (0.2 g).

Dimethyl 2-Butynylsulfonium Bromide (XII)——A mixture of 2-butynyl bromide (13.3 g) and dimethyl sulfide (13.0 g) was stirred at room temperature for 2 days. The resulting crystalline substance was collected by filtration and recrystallized from EtOH to give white leaflets (18 g), mp 140—143°. *Anal.* Calcd. for $C_6H_{11}BrS$: C, 36.92; H, 5.64; Br, 41.02; S, 16.41. Found: C, 36.71; H, 5.66; Br, 41.09; S, 16.21. IR ν_{max}^{Nujol} cm^{-1}: 2230. NMR (δ) (D_2O): 2.91 (6H, singlet, $-S(CH_3)_2$), 1.97 (3H, triplet, $-CH_3$, $J=2.5$ cps), 4.25 (2H, quartet, $J=2.5$ cps, $-CH_2-$).

Methyl 2-Methyl-2,3-butadienyl Sulfide (XIII)——To a suspension of dimethyl 2-butynylsulfonium bromide (2.93 g) in 30 ml of anhydrous tetrahydrofuran was added sodium hydride (0.75 g) (50% oily mixture) at 3—5° under N_2 atmosphere. The reaction mixture was stirred at 50—60° for 5 hr, poured into 150 ml of ice-water and extracted with ether. The combined extracts were washed successively with H_2O and satd. NaCl solution until neutral to litmus, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was distilled *in vacuo* to give 0.35 g of pale yellow oil, bp 70—75° (20 mmHg). Chloroplatinate of XIII showed mp 124—127° (decomp.). *Anal.* Calcd. for $C_{14}H_{26}Cl_6PtS$: C 25.22; H, 3.90; S, 9.60. Found: C, 25.20; H, 3.95; S, 9.23.

Dimethyl 2-Propynyl Bromide (XVIII)——A mixture of 2-propynyl bromide (24.0 g) and dimethyl sulfide (12.5 g) in 60 ml of benzene was stirred at room temperature for 24 hr. The resulting crystalline substance was collected by filtration and recrystallized from EtOH to give colorless prisms of XVIII (7.5 g). IR ν_{max}^{Nujol} cm^{-1}: 2125. *Anal.* Calcd. for C_5H_9BrS: C, 33.15; H 4.98; Br, 44.20; S, 17.67. Found: C, 33.12; H, 5.01; Br, 44.60; S, 17.67.

Methyl 1-(2-Phenylethynyl)-2-phenyl-2,3-butadienyl Sulfide (XXII)——Methyl bis(3-phenyl-2-propynyl)-sulfonium methyl sulfate (XIX) was prepared from bis(3-phenyl-2-propynyl)sulfide (2.62 g) and methyl sulfate (1.26 g) by heating at 80—85° for 3 hr. XIX was analysed as chloroplatinate, mp 148—150°. *Anal.* Calcd. for $C_{38}H_{34}Cl_6PtS_2$: C, 47.40; H, 3.53; Cl, 22.03; S, 6.65. Found: C, 47.00; H, 3.52; Cl, 21.46; S, 7.05.

XIX was dissolved in 15 ml of H_2O and 15 ml of benzene, and 10% NaOH (4.5 ml) was added to the solution. The reaction mixture was heated to reflux for 3 hr. After cooling, benzene layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give 3.3 g of brown colored liquid which was chromatographed on silicagel (50 g) and eluted with hexane-benzene (3:1) to afford 2.48 g of an oil. A small portion of this oil was rechromatographed on silicagel eluting with hexane to give analytically pure sample. *Anal.* Calcd. for $C_{19}H_{16}S$: C, 82.52; H, 5.83; S, 11.60. Found: C, 81.94; H, 5.84; S, 11.60.

(2-Propenyl)(3-phenyl-2-propynyl)sulfide——To a solution of NaOEt in EtOH, prepared from Na (2.3 g) and 15 ml of EtOH, was added dropwise a solution of allylmercaptane (7.4 g) in 5 ml of benzene at 5° and then a solution of 3-phenyl-2-propynyl bromide (19.5 g) in 20 ml of benzene at room temperature. The reaction mixture was refluxed for 3 hr and poured into 100 ml of ice-water. The organic layer was separated and aqueous layer was extracted with benzene. The combined extracts were washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was distilled *in vacuo* to gvie 13.0 g of an oil, bp 102—103° (0.0001 mmHg). IR ν_{max}^{liq} cm^{-1}: 2205, 990, 920. UV λ_{max}^{EtOH} $m\mu$ (ε): 242 (17300), 250 (15800), 272.5 (1770), 280 (1070). Chloroplatinate showed mp 118—123°. *Anal.* Calcd. for $C_{26}H_{30}Cl_6PtS_2$: C, 38.23; H, 3.68; Cl, 26.16; S, 7.86. Found C, 38.16; H, 3.69; Cl, 25.60; S, 8.12.

Methyl 1-(2-Phenylethynyl)-3-butenyl Sulfide (XXVII)——Methyl (2-propenyl)(3-phenyl-2-propynyl)-sulfonium methyl sulfate (XXIII) was prepared from (2-propenyl)(3-phenyl-2-propynyl)sulfide (1.88 g) and dimethyl sulfate (1.26 g) by heating at 80—85° for 3 hr. XXIII was analysed as chloroplatinate, mp 118—123°. *Anal.* Calcd. for $C_{26}H_{30}Cl_6PtS_2$: C, 38.23; H, 3.68; S, 7.86. Found: C, 38.16; H, 3.69; S, 8.12.

XXIII was dissolved in 15 ml of H_2O and 15 ml of benzene, and 10% NaOH was added to the solution. The reaction mixture was heated to reflux for 3 hr. After cooling, benzene layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give 1.90 g of a pale yellow oil which was chromatographed on silica gel (60 g) and eluted with hexane-benzene (20:1) to afford 1.07 g of an oil. Distillation of this oil gave 0.55 g of XXVII, bp 90—95° (0.0001 mmHg) (bath temp.). Chloroplatinate of XXVII showed mp 130—133°. *Anal.* Calcd. for $C_{28}H_{34}Cl_6PtS_2$: C, 39.90; H, 4.03; S, 7.60. Found: C, 39.58; H, 3.99; S, 7.85.

Dimethyl 3-Phenyl-2-propenylsulfonium Bromide (XXVIII)——A mixture of 3-phenyl-2-propenyl bromide (9.9 g), dimethyl sulfide (3.1 g) and 20 ml of anhyd. benzene was stirred for 8 hr at room temperature. The resulting crystalline substance was collected by filtration and recrystallized from EtOH to give colorless prisms (8.0 g), mp 87—91°. *Anal.* Calcd. for $C_{11}H_{15}BrS$: C, 50.96; H, 5.79; Br, 30.84; S, 12.35. Found: C, 50.74; H, 5.84; Br, 31.01; S, 12.20.

Methyl 2-Phenyl-3-butenyl Sulfide (XXX)——To a solution of methylsulfinyl carbanion which was prepared from 0.48 g of sodium hydride and 50 ml of dimethyl sulfoxide by stirring at 75° under N_2 and which was once cooled to room temperature, was added 50 ml of anhyd. tetrahydrofuran to prevent freezing and then a solution of dimethyl 3-phenyl-2-propenylsulfonium bromide (2.6 g) in 50 ml of dimethyl sulfoxide at 5°. The reaction mixture was stirred at 20—25° for 2 hr, poured into 600 ml of ice-water and extracted with ether. The etherial solution was washed with H_2O, satd. NaCl solution and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was distilled *in vacuo* to give an oil (1.55 g), bp 129—130° (10 mmHg). *Anal.* Calcd. for $C_{11}H_{14}S$: C, 74.15; H, 7.87; S, 17.97. Found: C, 73.81; H, 8.13; S, 17.92.

Benzyl 3-Phenyl-2-propynyl Sulfide——To a solution of KOH (5.6 g) in 100 ml of EtOH was added benzyl mercaptane (13.8 g) and then 3-phenyl-2-propynyl bromide (19.5 g) at 25°. The reaction mixture was refluxed for 3 hr, poured into 1000 ml of ice-water and extracted with ether. The combined extracts were washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave an liquid which was distilled *in vacuo* to afford an oil (18 g), bp 178—180° (0.3 mmHg). IR $\nu_{\max}^{\text{liq}}$ cm^{-1}: 2210. UV $\lambda_{\max}^{\text{EtOH}}$ $\text{m}\mu$ (ε): 246 (18100), 250 (16200). *Anal.* Calcd. for $C_{16}H_{14}S$: C, 80.68; H, 5.88; S, 13.51. Found: C, 80.40; H, 6.07; S, 13.51.

Methyl 1-Benzyl-3-phenyl-2-propynyl Sulfide (XXXVI) and Dibenzyl——Methyl benzyl 3-phenyl-2-propynylsulfonium methyl sulfate (XXXIII) was prepared from benzyl 3-phenyl-2-propynyl sulfide (3.6 g) and dimethyl sulfate (1.9 g) by heating at 80° for 3 hr. XXXIII was analysed as chloroplatinate, mp 154—155°. *Anal.* Calcd. for $C_{34}H_{34}Cl_6PtS_2$: C, 44.63; H, 3.72; S, 7.00. Found: C, 44.40; H, 3.78; S, 7.06.

XXXIII was dissolved in 15 ml of H_2O and 15 ml of benzene, and 10% NaOH was added to the solution. The reaction mixture was heated to reflux for 3 hr. After cooling, benzene layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. Evaporation of solvent afforded 2.3 g of an oil. This oil was subjected to preparative gas chromatography on 3/4 in. × 240 in. column packed with 20% SE-30 on 60—80 mesh Chromosorb P at 280° with a flow of 0.4 liter of helium per min to give dibenzyl (relative retention time 19 min) (15 mg), which was identical in all respects with an authentic sample, and 47 mg of XXXVI (relative retention time 25 min). Chloroplatinate showed mp 158—161°. *Anal.* Calcd. for $C_{36}H_{38}Cl_6PtS_2 \cdot H_2O$: C, 45.01; H, 4.20. Found: C, 45.05; H, 4.64.

Acknowledgement We are very grateful to Dr. T. Hiraoka for his kind assistance and valuable discussion. We are also thankful to Mr. N. Ishida for his technical assistance.