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Studies on Acetylenic Compounds. LI.[1] The Reactions of Acetylenic Sulfonium Salts with Benzaldehyde

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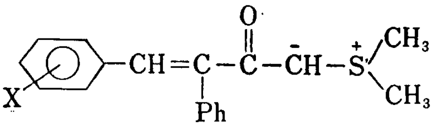
Treatment of dimethyl 2-butynylsulfonium bromide (II) with benzaldehyde gave *cis*- and *trans*-2,4-diphenyl-5-methyl-6-(2-phenyl-*trans*-1,2-epoxyethyl)-1,3-dioxin (III and IV), 1,5-diphenyl-2-methyl-*trans*-4,5-epoxy-*trans*-1-penten-3-one (V) and methyl 2-methyl-5-hydroxy-5-phenyl-2,3-pentadienyl sulfide (VI). Dimethyl 2-propynylsulfonium bromide (VIII), however, reacted with benzaldehyde to give only one product, 1,5-diphenyl-*trans*-4,5-epoxy-*trans*-1-penten-3-one (IX). A mechanistic assumption for the formation of these compounds from the acetylenic sulfonium bromides was given.

In the preceding paper,[1] we reported the formation of a series of stable sulfonium ylids (I) by the reaction of dimethyl 3-phenyl-2-propynylsulfonium bromide with the corresponding benzaldehyde derivatives.



I X=H, p-Br, p-CH_3, m-CH_3O, p-NO_2

Chart 1

In the continuation and extension of our studies on S-ylid chemistry, the reactions of dimethyl 2-butynyl- and dimethyl 2-propynylsulfonium bromides with benzaldehyde were investigated.

Contrary to our expectation, the sulfonium bromides gave no stable ylid by the aforementioned reaction, but afforded some interesting results.

Treatment of dimethyl 2-butynylsulfonium bromide (II) with benzaldehyde in the presence of sodium hydride in anhydrous tetrahydrofuran followed by careful silica gel chromatography afforded four compounds (III, IV, V and VI).

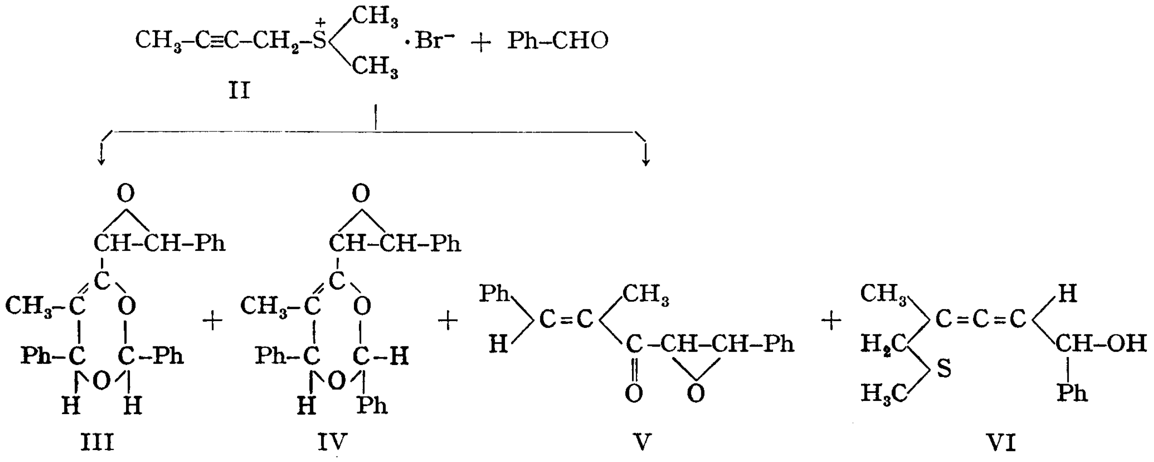


Chart 2

The first reaction product (III), obtained in 9.8% yield, melted at 131—132° and had an empirical formula, $C_{25}H_{22}O_3$. The ultraviolet (UV) spectrum showed an absorption maximum

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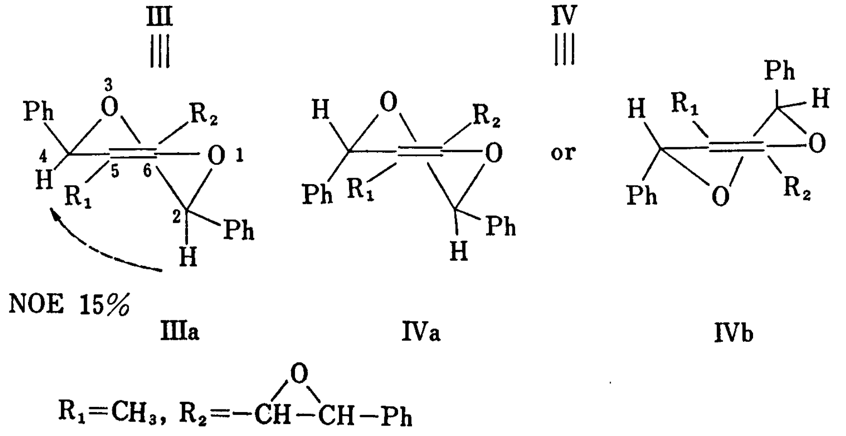
[1] Part L: A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), 18, 499 (1970).

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

at 288 mμ (ε=5400) and the infrared (IR) spectrum revealed the characteristic epoxide bands at 1268, 889 and 837 cm^{-1}, and the band for double bond having four substituents at 1678 cm^{-1}. The nuclear magnetic resonance (NMR) spectrum exhibited a doublet at 1.57 ppm (3H, J=1 cps) due to the methyl protons, a AB type pattern at 3.69 and 4.42 ppm (2H, J=2 cps) for *trans* epoxide protons, a quartet at 5.42 ppm (1H, J=1 cps) due to the methine proton, a singlet at 6.02 ppm (1H) assignalbe to another methine proton and a multiplet centered at 7.43 ppm for three phenyl groups (15H). From these spectroscopic data and the elemental analysis, this compound, III, was assigned to be a cyclized product, 2,4-diphenyl-5-methyl-6-(2-phenyl-*trans*-1,2-epoxyethyl)-1,3-dioxin. The second product, IV, was isolated by careful chromatography on silica gel in poor yield (0.9%). The spectroscopic data of IV resembled closely to those of III. The UV spectrum showed an absorption maxmum at 288 mμ and the IR spectrum revealed the typical epoxide band at 1275, 895 and 848 cm^{-1}, and the band for double bond having four substitutuents at 1670 cm^{-1}. The NMR spectrum exhibited a doublet at 1.80 ppm (3H, J=1 cps) due to the methyl group, a AB type pattern at 3.83 and 4.45 ppm (2H, J=2 cps) for *trans* epoxide protons, a quartet at 5.27 ppm (1H, J=1 cps) assigned to the methine proton, a singlet at 5.87 ppm (1H) assignable to another methine proton adjacent to two oxygen atom and a multiplet centered at 7.40 ppm (15H) for three phenyl groups. Therefore, the spectroscopic analysis suggested that the two compounds (III and IV) should be conformational isomers of 2,4-diphenyl-5-methyl-6-(2-phenyl-*trans*-1,2-epoxyethyl)-1,3-dioxin to one another. The conformation of III and IV could be efficiently solved by investigating intramolecular "Nuclear Overhauser Effects" (NOE). If the protons attached to C-2 and C-4 positions have *cis* configuration, the C-4 proton signal intensity should be strongly enhanced by the irradiation at C-2 proton, but if the protons have *trans* the intensity at C-4 proton signal should be unchanged on the irradiation at C-2 proton. This was ideed observed on III, with a 15% increase in the signal intensity, but none of the change was noticed on IV. These NOE results suggested that the C-2 and C-4 protons in III have a relationship of 1,3-quasi-diaxial (*cis*) as depicted in III-a, and in IV have *trans* configuration as shown in IV-a or IV-b.



$R_1=CH_3$, $R_2=-\overset{}{CH}\overset{O}{-}CH-Ph$

Chart 3

These results coupled with a degradation reaction which will be described later, enable one to assign III and IV as *cis*- and *trans*-2,4-diphenyl-5-methyl-6-(2-phenyl-*trans*-1,2-epoxyethyl)-1,3-dioxin, respectively (Although these compounds (III and IV) should be present diastereomer owing to the existence of two kinds of asymetric center according to the epoxide and the dioxin moiety, we did not investigate about this point because of the difficulty). It is noteworthy that only few examples for the formation of 1,3-dioxin compounds[3] have

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[3] *a*) R. C. Elderfield, "Heterocyclic Compounds," Vol. 6, New York, John Wiley & Sons, Inc., London, 1957, p. 58; *b*) J.A. Lambrech, Brit. Patent 776423 (1957); *c*) *Idem*, U.S. Patent 2816898 (1957); *d*) D. O'Meara and G.N. Richards, *Chem. Ind.* (London), **1958**, 40.

been known. The third substance (V) of bp 130—135° (0.0001 mmHg) (bath temp.) obtained in 8.0% yield from II, had an empirical formula, $C_{16}H_{16}O_2$. The IR spectrum showed an α,β-unsaturated ketone band at 1675 cm^{-1} and an epoxide band at 1220 and 950 cm^{-1}, and the UV spectrum revealed an absorption maximum at 288 $m\mu$ (ε=16600). The NMR spectrum exhibited a doublet at 2.15 ppm (3H, J=1 cps) due to the methyl group attached to the double bond, a AB type pattern at 4.07 and 4.18 ppm (2H, J=2 cps) for *trans* epoxide, a quartet at 7.69 ppm (1H, J=1 cps) assigned to the vinyl proton and a multiplet centered at 7.42 ppm for two phenyl groups. From these results, the structure of V was assigned to be 1,5-diphenyl-2-methyl-*trans*-4,5-epoxy-1-penten-3-one. Although there is no decisive evidence about the configuration of the compound, the configuration at C-1 conld be solved again by the NOE. When the C-1 proton signal was irradiated, the C-2 methyl proton signal intensity was unchanged, suggesting that the configuration at C-1 of compound V would be *trans*; 1,5-diphenyl-2-methyl-*trans*-4,5-epoxy-*trans*-1-penten-3-one. Considering the reaction mechanism, the compound, V, would be generated presumably from III or IV. The compound, V, however, could not be obtained from III under the conditions employed. But refluxing of III in ethanol afforded benzaldehyde and V. Benzaldehyde was identified by analytical gas chromatography, and the latter was identical in all respects with V, whose structure had already determined by the spectroscopic data. The conversion of IV to a ring-opened product such as V, however, could not be attempted, owing to the shortage of the sample available. Thus, it was concluded that the product, III, was not the precursor of V, but the reaction products, III and V, from II were intercorrelated by the chemical reaction.

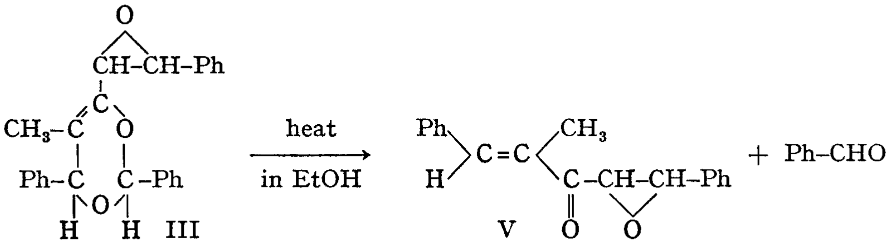

Chart 4

The final product, VI, of bp 115—120° (0.0001 mmHg) (bath temp.), obtained in 11.6% yield from II, agreeded with an empirical formula, $C_{13}H_{16}OS$. The IR spectrum showed a hydroxyl band at 3385 cm^{-1} and a typical allenic band at 1960 cm^{-1}. The NMR spectra in deuteriochloroform at 60 and 100 Mc are shown in Fig. I and II. From these spectra, it can be seen that the methyl protons appeared as a sharp quartet at 1.80 ppm at 60 Mc, but as a sharp triplet at 1.78 ppm at 100 Mc. This fact suggested that the possibility of the existence of two kinds of methyl groups whose chemical shifts differed from to one another.

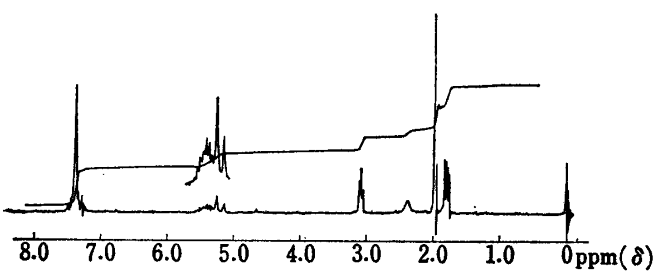

Fig. 1. The NMR Spectrum of VI at 60 Mc

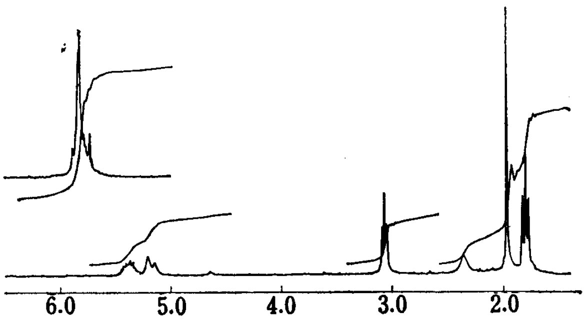

Fig. 2. The NMR Spectrum of VI at 100 Mc

The other signals, however, had almost similar patterns at 60 and 100 Mc (see Fig 1 and 2). The spectrum at 100 Mc, for example, showed a triplet at 1.78 ppm (3H) due to methyl protons,

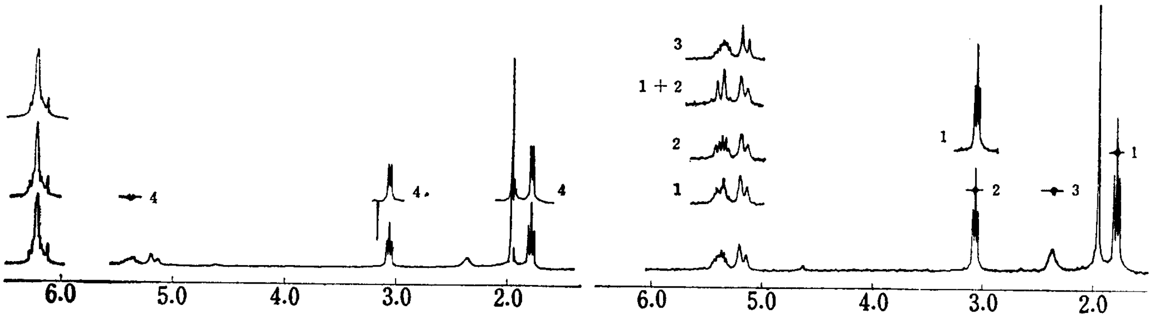

Fig. 3. The NMR Spectrum of VI

a singlet at 2.35 ppm (1H) for hydroxyl proton, a triplet at 3.06 ppm (2H), a doublet at 5.18 ppm (1H, J=6 cps), a multiplet at 5.38 ppm (1H) assigned to the vinyl proton and an aromatic multiplet at 7.31 ppm (5H). The nuclear magnetic double resonance (NMDR) spectra are shown in Fig 3. Double irradiation at 5.38 ppm changed the peak at 1.78 ppm (triplet) into a doublet (as a matter of fact, it showed the existence of two singlets), and the signal at 3.06 ppm (triplet) into a doublet (it also showed two singlets). Reversely, the peak at 5.38 ppm (multiplet) changed into tripleting doublet and octet, respectively, when the signals at 1.78 (triplet) and 3.06 ppm (triplet) were irradiated. Triple irradiation at 1.78 (triplet) and 3.06 ppm (triplet) changed the peak at 5.38 ppm (multiplet) into a doublet (J=6 cps) indicating the coupling with the signal at 5.18 ppm (J=6 cps). These spectroscopic data suggested that VI was a mixture of two isomers.[4] In order to convert VI into a unimolecular compound, we attempted the oxidation of VI with manganese dioxide leading to an allenic ketone (VII).

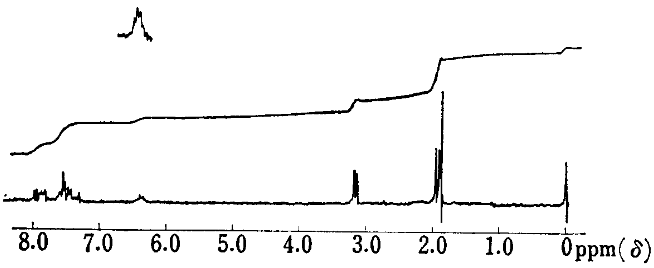

Fig. 4. The NMR Spectrum of VII at 60 Mc

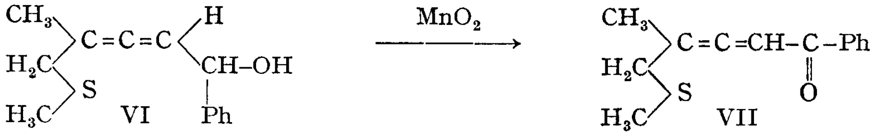

Chart 5

The IR spectrum showed the α,β-unsaturated ketone band at 1658 cm^{-1} and the characteristic allenic band at 1953 cm^{-1}, and the UV spectrum revealed the absorption maximum at 252.5 mμ. The NMR spectrum in deuteriochloroform exhibited a singlet at 1.88 ppm (3H) due to the S-methyl group, a doublet at 1.93 ppm (3H, J=3 cps) assignable to the methyl protons attached to the double bond, a doublet at 3.17 ppm (2H, J=2 cps) assigned to the methylene protons adjacent to the sulfur atom, a multiplet at 6.40 ppm (1H) due to the vinyl proton and an aromatic multiplet centered at 7.65 ppm (5H) as shown in Fig. 4. The oxidized product, VII, was assigned to be methyl 2-methyl-5-oxo-5-phenyl-2,3-pentadienyl sulfide. The elemental analysis, spectral and chemical data, and the reaction mechanism which was analogous to our previous findings of the Stevens type $S_{Ni'}$ reaction[5] indicated that VI was a mixture of the racemic–diastereomeric allenes, VI-a and VI-b. Thus VI was concluded to be methyl 2-methyl-5-hydroxy-5-phenyl-2,3-pentadienyl sulfide.

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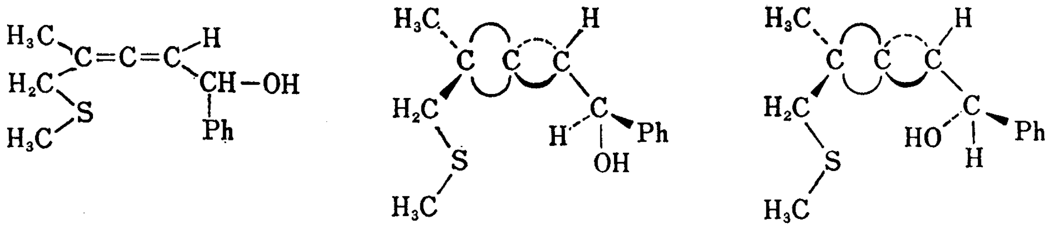
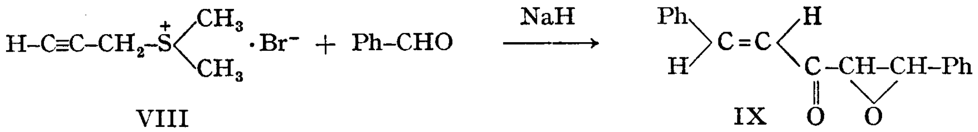
[4] D.R. Taylor, *Chem. Rev.*, **67**, 317 (1967).
[5] A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **17**, 966 (1969).



VI VIa VIb

Chart 6

Expecting the same results, this reaction was extended to the reaction of dimethyl 2-propynylsulfonium bromide (VIII) with benzaldehyde. Treatment of VIII with benzaldehyde in the presence of sodium hydride in anhydrous tetrahydrofuran followed by silica gel chromatography afforded only one product (IX) in 14% yield, differing from the case of the reaction of II with benzaldehyde. The compound, IX, had an empirical formula, $C_{17}H_{14}O_2$ and melted at 83—84°. The IR spectrum showed an absorption at 1682 cm^{-1} due to α,β-unsaturated ketone, 1611 cm^{-1} for double bond and 863 and 832 cm^{-1} due to the epoxide. The UV spectrum revealed an absorption maxima at 222.7 (ε=15100), 230.5 (ε=12990) (shoulder) and 302 mμ (ε=25300). The NMR spectrum exhibited a AB type pattern at 3.76 and 4.10 ppm (2H, J=2 cps) due to the *trans* epoxide protons, another AB type pattern at 7.00 and 7.88 ppm (2H, J=16 cps) for *trans* vinyl protons and an aromatic multiplet centered at 7.45 ppm (10 H).



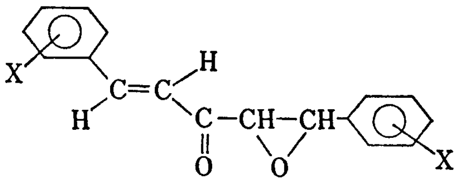
VIII IX

Chart 7

From these data and the results of the reaction of II giving V, IX was assigned to be 1,5-diphenyl-*trans*-4,5-epoxy-*trans*-1-penten-3-one.

In the similar manner, epoxypentenone derivatives bearing various substituents in the phenyl group were prepared and the results are summarized in Table I.

Table I.



(IX)	X	Yield(%)	mp(bp)	UV λ_{max}^{EtOH} mμ (ε)		
a	H	14	83—84	222.7 (15200)	230.5 (12900)(shoulder)	302.0 (25300)
b	p-Br	16.3	164—165	228.9 (21100)	234.5 (19200)(shoulder)	310.0 (28059)
c	o-Cl	25	111—111.5	229.0 (12900)	236.5 (10700)(shoulder)	295.3 (20300)
d	p-CH_3	7.6	112—114	225.0 (17000)	236.0 (10700)(shoulder)	313.0 (26540)
e	m-CH_3O	16.3	200—210(0.0001)	245.0 (11000)	297.5 (19400)	
f	p-NO_2	8	215—216	274.0 (15100)	303.0 (15300)	386.0 (31480)

The behavioral differences between the formation of ylid (I) reported previously[1)] and the epoxides (III, IV, V and IX) in this paper would be due to an assumption that the phenyl group of ylid, I, contributes greatly to the resonance stabilization of the ylid structure. However, such a resonance stabilization would not be exerted in the corresponding compounds (X, R=CH_3, H) to I, so that II or VIII gives no ylid proudct.

The mechanistic assumption for the formation of these compounds (III, IV, V, VI and IX) from II or VIII would be expressed as follows:

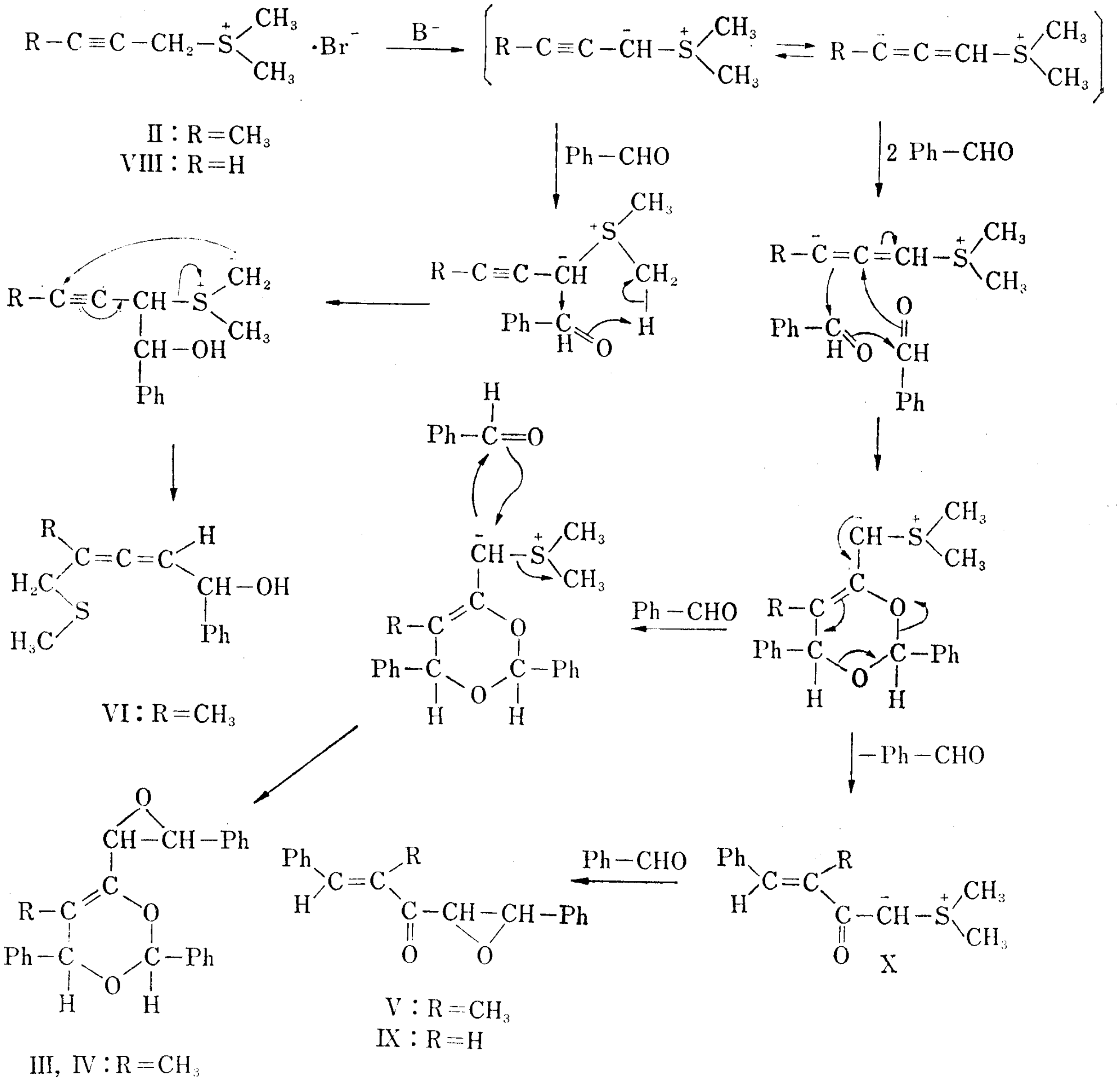


Chart 8

The difference in the reactivity between α- and γ-postion of the acetylenic sulfonium compounds $(\mathrm{R{-}\overset{\gamma}{C}{\equiv}C{-}\overset{\alpha}{C}H_2{-}\overset{+}{S}{<}})$ is not clear at present.

Experimental[6]

Reaction of Dimethyl 2-Butynylsulfonium Bromide with Benzaldehyde——To a suspension of dimethyl 2-butynylsulfonium bromide (3.9 g, 0.02 mole) and benzaldehyde (6.36 g, 0.06 mole) in anhyd. tetrahydrofuran (40 ml) was added at one portion sodium hydride (0.96 g, 0.02 mole) (50% oily mixture) at 3—5° under N_2 atmosphere with stirring. An exothermic reaction took place after 30 min. Stirring was continued for 1 hr at 3—5° and then for 24 hr at room temperature. The reaction mixture was poured into 300 ml of ice-water, extracted with AcOEt, washed with satd. NaCl solution, dried over Na_2SO_4 and evaporated.

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[6] All melting and boiling points are uncorrected. NMR spectra were taken using Varian A-60 and HA-100 spectrometer and the chemical shifts were expressed in ppm unit from the internal standard of tetramethylsilane.

The residue (8.6 g) was chromatographed on 150 g of silica gel. Elution with hexane–benzene (3:2) gave III which was recrystallized from ether to give colorless prisms (0.726 g, 9.8%) of mp 137—138°. *Anal.* Calcd. for $C_{25}H_{22}O_3$: C, 81.05; H, 5.95. Found: C, 80.91; H, 5.89.

Elution with hexane–benzene (2:3) afforded 0.067 g (0.9%) of IV as an oil whose structure was assigned by spectroscopic data. IR ν_{max}^{Nujol} cm^{-1}: 1670 (C=C), 1275, 895, 848 ($\overset{\diagup O \diagdown}{CH-CH}$). UV λ_{max}^{EtOH} mμ (ε): 287.5 (qualitative). NMR δ ppm ($CDCl_3$): 1.80 (3H, doublet, $J=1$ cps, CH_3), 3.83 (1H, doublet, $J=2$ cps, $\overset{\diagup O \diagdown}{CH-CH}$), 4.45 (1H, doublet, $J=2$ cps, $\overset{\diagup O \diagdown}{CH-CH}$), 5.27 (1H, quartet, $J=1$ cps, –CH=), 5.87 (1H, singlet, –CH–), 7.40 (15H, multiplet, aromatic protons). Further elution with the same solvent system afforded V which was distilled *in vacuo* to give 0.422 g (8.0%) of an oil, bp 130—135° (0.0001 mmHg) (bath temp.). 2,4-Dinitrophenylhydrazone: mp 185—186°. *Anal.* Calcd. for $C_{24}H_{20}O_5N_4$: C, 64.86; H, 4.54; N, 12.61. Found: C, 64.67; H, 4.57; N, 12.46.

Elution with hexane–benzene (1:4) afforded VI which was distilled *in vacuo* to give 0.51 g (11.6%) of an oil, bp 105—110° (0.0001 mmHg) (bath temp). *Anal.* Calcd. for $C_{13}H_{16}OS$: C, 70.89; H, 7.32; S, 14.55. Found: C, 70.73; H, 7.33; S, 14.20.

Methyl 2-Methyl-5-oxo-5-phenyl-2,3-pentadienyl Sulfide (VII)——A mixture of methyl 2-methyl-5-hydroxy-5-phenyl-2,3-pentadienyl sulfide (a mixture of racemic diastereomers) (0.14 g, 0.000636 mole), MnO_2 (1.4 g) and 10 ml of acetone was stirred for 4 hr at room temperature. The inorganic substance was filtered off and the filtrate was evaporated under reduced pressure to give 0.138 g of the title compound as an oil. Distillation *in vacuo* afforded a pale yellow oil, bp 105—108° (0.0001 mmHg) (bath temp.). 2,4-Dinitrophenylhydrazone: mp 202—204°. *Anal.* Calcd. for $C_{19}H_{18}O_4N_4S \cdot H_2O$: C, 54.80; H, 4.80. Found: C, 54.49; H, 4.43.

1,5-Diphenyl-2-methyl-*trans*-4,5-epoxy-*trans*-1-penten-3-one (V) from *cis*-2,4-Diphenyl-5-methyl-6-(2-phenyl-*trans*-1,2-epoxyethyl)-1,3-dioxin (III)——A mixture of *cis*-2,4-diphenyl-5-methyl-6-(2-phenyl-*trans*-1,2-epoxyethyl)-1,3-dioxin (0.1 g) and abs. EtOH (10 ml) was refluxed for 10 hr. After cooling, the solvent was evaporated under reduced pressure and the oily residue was chromatographed on silica gel (20 g). Elution with hexane–benzene (1:2) afforded 38 mg of the title compound, whose IR, UV, and NMR spectra were superimposable on that of the product prepared from dimethyl 2-butynylsulfonium bromide and benzaldehyde.

1,5-Diphenyl-*trans*-4,5-epoxy-*trans*-1-penten-3-one (IX-a)——To a stirred suspension of dimethyl 2-propynylsulfonium bromide (2.71 g, 0.015 mole) and benzaldehyde (1.6 g, 0.0151 mole) in anhyd. tetrahydrofuran (30 ml) was added at one portion sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 5° under N_2. Stirring was continued for 30 min at 5—8° and then for 30 min at room temperature. The reaction mixture was poured into ice–water and extracted with AcOEt. The combined extracts were washed with satd. NaCl solution, dried over Na_2SO_4 and evaporated. The oily residue (2.5 g) was chromatographed on silica gel (50 mg) and eluted with benzene–hexane (1:1) afforded crystalline substance (0.295 g). Recrystallization from ether–hexane (1:1) gave 0.15 g of colorless prisms of the title compound, mp 83—84°. *Anal.* Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.40; H, 5.69.

1,5-Bis(*p*-bromophenyl)-*trans*-4,5-epoxy-*trans*-1-penten-3-one (IX-b)——To a stirred suspension of dimethyl 2-propynylsulfonium bromide (2.71 g, 0.015 mole) and *p*-bromobenzaldehyde (8.325 g, 0.045 mole) in anhyd. tetrahydrofuran (30 ml) was added at one portion sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 3—5° under N_2 atmosphere with stirring. An exothermic reaction took place after 1 min. Stirring was continued for 10 min at 5—8° and then for 1 hr at room temperature. The reaction mixture was poured into ice–water (300 ml) and extracted with AcOEt. The combined extracts were washed with satd. NaCl solution, dried over Na_2SO_4 and evaporated. The oily residue was scratched on a small amount of benzene to solidify. The soild was filtered and recrystallized from benzene gave 1.0 g of colorless prisms title compound, mp 164—165°. *Anal.* Calcd. for $C_{17}H_{12}O_2Br_2$: C, 50.03; H, 2.97; Br, 39.16. Found: C, of the 50.09; H, 3.11; Br, 39.22.

1,5-Bis(*o*-chlorophenyl)-*trans*-4,5-epoxy-*trans*-1-penten-3-one (IX-c)——To a suspension of dimethyl 2-propynylsulfonium bromide (2.71 g, 0.015 mole) and *o*-chlorobenzaldehyde (6.33 g, 0.045 mole) in 40 ml of anhyd. tetrahydrofuran was added at one portion sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 3—5° under N_2 atmosphere with stirring. An exothermic reaction took place after 1 min. Stirring was continued for 5 min at 5—8° and then for 1 hr at room temperature. The reaction mixture was poured into 300 ml of ice–water and extracted with AcOEt. The combined extracts were wahesd with satd. NaCl solution, dried over Na_2SO_4 and evaporated. The oily residue (7.5 g) was chromatographed on 140 g of silica gel and eluted with hexane–benzene (1:2) to give 1.2 g of the title compound. Recrystallization from AcOEt gave colorless prisms (1.1 g) of mp 111—111.5°. *Anal.* Calcd. for $C_{17}H_{12}O_2Cl_2$: C, 63.97; H, 3.79; Cl, 22.21. Found: C, 63.97; H, 3.94; Cl, 22.27.

1,5-Di(*p*-tolyl)-*trans*-4,5-epoxy-*trans*-1-penten-3-one (IX-d)——To a suspension of dimethyl 2-propynylsulfonium bromide (2.71 g, 0.015 mole) and *p*-methylbenzaldehyde (5.4 g, 0.045 mole) in 30 ml of anhyd. tetrahydrofuran was added at one portion sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 3—5° under N_2 atmosphere with stirring. An exothermic reaction took place. Stirring was continued for 1 hr at 20—25°. The reaction mixture was poured into 300 ml of ice–water and extracted with AcOEt. The combined extracts were washed with satd. NaCl solution, dried over Na_2SO_4 and evaporated. The oily residue (7.0 g) was chromatographed on 150 g of silica gel and eluted with hexane–benzene (1:2) to give 400 mg of the title compound. Recrystallization from AcOEt–hexane gave colorless needles, mp 112—114.° *Anal.* Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.75; H, 6.32.

1,5-Bis(*m*-methoxyphenyl)-*trans*-4,5-epoxy-*trans*-1-penten-3-one (IX-e)——To a suspension of dimethyl 2-propynylsulfonium bromide (2.71 g, 0.015 mole) and *m*-methoxybenzaldehyde (6.12 g, 0.045 mole) in 30 ml of anhyd. tetrahydrofuran was added at one portion sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 3—5° under N_2 atmosphere with stirring. An exothermic reaction took place after 10 min. Stirring was continued for 10 min at 5° and then for 1 hr at 20—25°. The reaction mixture was poured into 300 ml of ice–water and extracted with AcOEt. The combined extracts were washed with satd. NaCl solution, dried over Na_2SO_4 and evaporated. The oily residue (5.0 g) was chromatographed on 180 g of silica gel and eluted with benzene–chloroform (4:1) to give an oil (0.8 g). Distillation of this oil gave the title compound, bp 200—220° (0.0001 mmHg) (bath temp.). *Anal.* Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.20; H, 5.86.

1,5-Bis(*p*-nitrophenyl)-*trans*-4,5-epoxy-*trans*-1-penten-3-one (IX-f)——To a suspension of dimethyl 2-propynylsulfonium bromide (2.71 g, 0.015 mole) and *p*-nitrophenylbenzaldehyde (6.86 g, 0.045 mole) in 30 ml of anhyd. tetrahydrofuran was added at one portion sodium hydride (0.75 g, 0.015 mole) at 3—5° under N_2 atmosphere with stirring. Stirring was continued for 10 min at 3—5° and then for 1 hr at 20—25°. The reaction mixture was poured into 300 ml of ice–water and extracted with AcOEt. The combined extracts was washed with satd. NaCl solution, dried over Na_2SO_4 and evaporated. The oily residue was chromatographed on 150 g of silica gel and eluted with benzene to give a solid. Recrystallization from acetone gave 0.35 g of pale yellow prisms of the title compound, mp 215—216°. *Anal.* Calcd. for $C_{17}H_{12}O_6N_2$: C, 60.00; H, 3.55; N, 8.23. Found: C, 59.81; H, 3.50; N, 8.49.

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