[Chem. Pharm. Bull. 18(12)2518—2527(1970)]

UDC 547.314.2.04 : 547.379.2.04 : 547.571.04

Studies on Acetylenic Compounds. LIV.[1] Reactions of 2-Butynyl Phenyl Sulfone with Substituted Benzaldehydes

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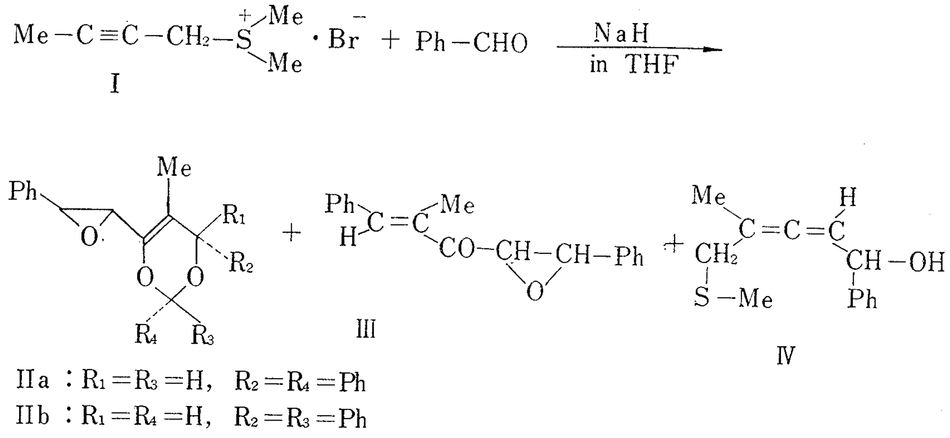
(Received June 30, 1970)

Treatment of 2-butynyl phenyl sulfone (V) and five benzaldehyde derivatives with sodium hydride afforded six kinds of products. Two 1:2 adducts of V and benzaldehyde derivatives were assigned to *cis*- and *trans*-1,3-dioxin (VI and VII, respectively), and the third group of compounds produced by condensation of VI and/or VII with benzaldehydes and subsequent dehydration were assigned to VIII. The fourth type of products were 1:1 addition compounds of V and benzaldehyde derivatives, and ascribed to 3-methyl-4-aryl-1-phenylsulfonyl-3-buten-2-one, IX. The condensation products of IX and the corresponding benzaldehydes were assigned to X. Moreover the direct condensation product of V and *m*-methoxybenzaldehyde was ascribed to the structure of XI. The plausible mechanisms of the reactions and the physical properties of these products are presented in detail.

The reactions of sulfur-stabilized carbanions (sulfur ylids)[3] have been the subject of recent intensive study in organic synthetic chemistry. In our laboratories the chemistry of sulfonium[4] and sulfoxinium[5] ylids have been investigated in relation to acetylenic compounds.

The reactions of propargylic sulfonium ylids, which were prepared from corresponding propargylic sulfonium salts, with substituted benzaldehydes were extensively studied in our laboratory.[4b,4c] The results of the reaction of 2-butynyldimethylsulfonium bromide (I) with benzaldehyde were summarized in Chart 1. The physical properties of the reaction products and the reaction mechanism were presented in some detail in the literature.[4c]



IIa : $R_1 = R_3 = H$, $R_2 = R_4 = Ph$
IIb : $R_1 = R_4 = H$, $R_2 = R_3 = Ph$

Chart 1

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1) Part LIII: A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **18**, 2507 (1970).
2) Location: *2-58, 1-chome, Hiromachi, Shinagawa-ku, Tokyo.*
3) A.W. Johnson, "Ylid Chemistry," Academic Press, New York and London, 1966, pp. 304—366.
4) *a*) A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **17**, 966, 974 (1969); *b*) *Idem, ibid.*, **18**, 490 (1970); *c*) *Idem, ibid.*, **18**, 497 (1970).
5) J. Ide and Y. Kishida, *Tetrahedron Letters*, **1966**, 1787; *idem, Chem. Pharm. Bull.* (Tokyo), **16**, 784 (1968).

As the continuation and extension of the reaction the chemistry of sulfonyl carbanions (sulfonyl ylids)[6] has been explored. This and a succeeding paper[7] will describe the reaction of propargylic sulfones with benzaldehyde derivatives. Although the reaction of sulfonyl-stabilized carbanions appeared in many papers,[8,9] a concept of "Sulfonyl Ylids"[6] in "Ylid Chemistry" has only referred to two reports,[9a] where the reactions resulted in elimination of sulfone groups. While, most of papers on sulfonyl carbanions have described normal carbanion reactions such as alkylation by alkylhalides, acylation by esters,[8a] alkylation by ketones and aldehydes,[8b] and addition to conjugated carbonyl systems.[8c] If the rigid definition of sulfonyl ylid suggests only the reaction accompanying the elimination of sulfone group, our acetylenic sulfone may not be included in such the category of sulfonyl ylids. But at least in a sense that the very interesting results so far obtained has ample analogy to the reaction of propargylic sulfonium ylids,[4b,4c] it may be regarded as sulfone ylid.

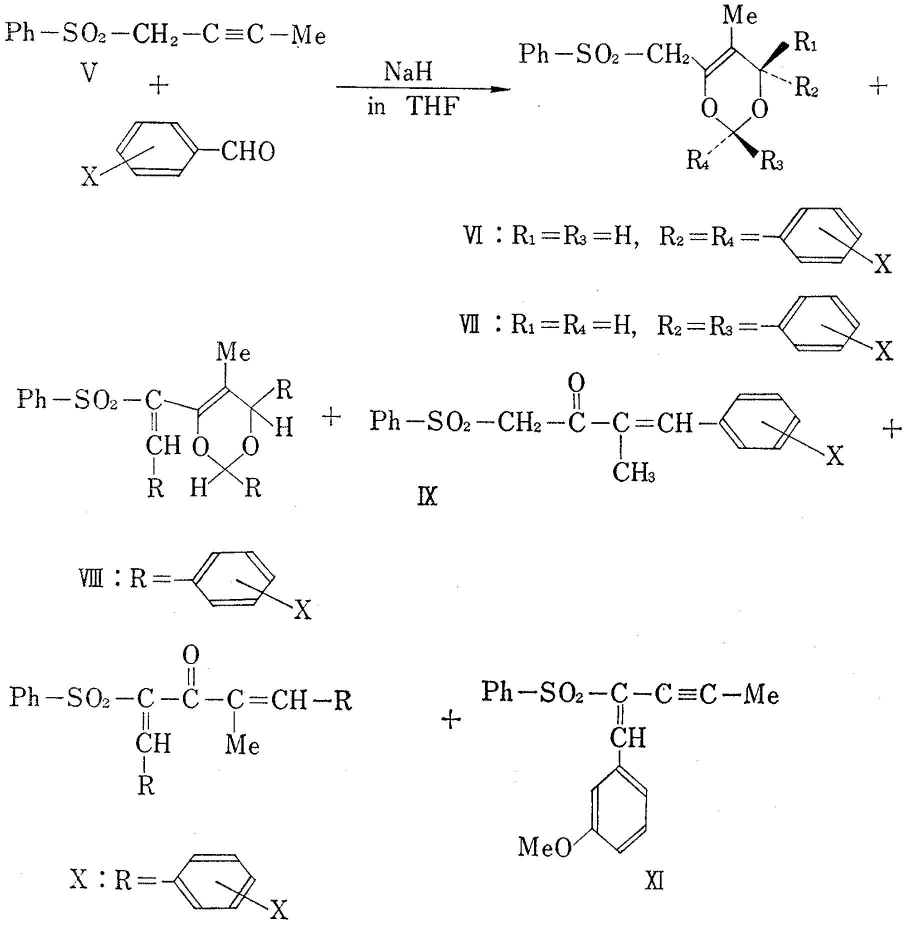

Chart 2

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[6] A.W. Johnson, "Ylid Chemistry," Academic Press, New York and London, 1966, pp. 351—352.

[7] M. Yoshimoto and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **18**, 2528 (1970); Studies on Acetylenic Compounds LV.

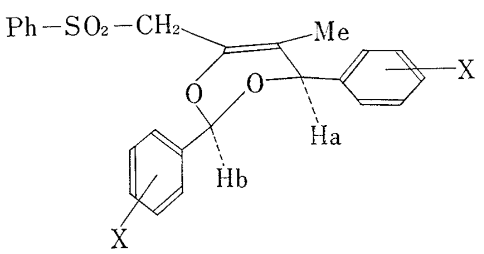
[8] *a*) W.E. Truce and R.H. Knospe, *J. Am. Chem. Soc.*, **77**, 5063 (1955); H.D. Becker and G.A. Russel, *J. Org. Chem.*, **28**, 1896 (1963); J. Martel, C. Huynh, E. Toromanoff and G. Nomine, *Bull. Soc. Chim. France*, **1967**, 982; *b*) H.O. House and J.K. Larson, *J. Org. Chem.*, **33**, 61 (1968); J.W. MacFarland and D.N. Buchanan, *J. Org. Chem.*, **30**, 2003 (1965); *c*) C.C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, 1962.

[9] *a*) E.J. Corey and M. Chaykovsky, *J. Org. Chem.*, **28**, 254 (1963); A.W. Johnson, *Chem. Ind.* (London), **1963**, 1119; *b*) Recently two intersting applications of sulfonyl ylids were reported about the syntheses of chrysanthemate. J. Martel and C. Huynh, *Bull. Soc. Chim. France*, **1967**, 985; J. Martel and G. Nomine, *Compt. Rend.* (*c*), **1969**, 2199; M. Julia and A.G. Roualt, *Bull. Soc. Chim. France*, **1967**, 1411.

Each mixture of 2-butynyl phenyl sulfone[10)] and various substituted benzaldehydes was treated with sodium hydride in tetrahydrofuran (THF) under nitrogen atmosphere. The products, separated by column partition chromatography on silica gel and fractional recrystallizations, were classified into six kinds of compounds (VI—XI). A characteristic difference of the reaction products from those of dimethyl-2-butynylsulfonium ylid with benzaldehyde was that the formers retained the sulfonyl group intact without one exception.

The first group of the products, VI, were shown to be 1:2 adducts of V and each substituted benzaldehyde by the elemental analyses and mass spectral data[11a)] ($M^+=406$ for VIa). The infrared (IR) spectra showed characteristic sulfone group absorptions (1300—1330, 1148—1150), intensive vinyl bands (near 1680 cm^{-1}) and no carbonyl groups, which suggested the existence of vinyl ethers. The ultraviolet (UV) spectra exhibited no other chromophore but

Table I. Spectral Data of VI



Compound	X	UV: λ_{max}^{EtOH} nm (log ε)			IR: ν_{max}^{Nujol} cm^{-1}			NMR: δppm				NOE: Δinteg. of H_b (Irradiate at H_a)(%)
					C=C	$-SO_2-$ asym.	$-SO_2-$ sym.	Me	$-CH_2-$	H_a	H_b	
a	H	266 (3.54)	273 (3.56)	289 (3.55)	1680	1300—1325	1148	1.40	4.10	5.37	5.67	21
c	*m*-OMe	267 (3.68)	273 (3.78)	281 (3.69)	1684	1305—1330	1149	1.40	4.05	5.28	5.58	21
d	*p*-Me	259	266	273a)	1678	1300—1325	1150	1.40	4.10	5.33	5.63	a)
e	*p*-Br	258 (3.40)	264 (3.37)	272 (3.24)	1686	1305—1330	1150	1.38	4.03	5.30	5.58	22

a) Degradation into IX_d and *p*-tolylaldehyde was observed during the measurements.

Table II. Yields, Melting Points and Elemental Analyses of VI.

Compound	X	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd.			Found.		
					C	H	S	C	H	S
a	H	33	138—139	$C_{24}H_{22}O_4S$	70.91	5.46	7.89	70.77	5.34	7.97
c	*m*-OMe	35	117—118	$C_{26}H_{26}O_6S$	66.94	5.62	6.86	66.81	5.61	6.89
d	*p*-Me	66	115—117	$C_{26}H_{26}O_4S$	71.86	6.03	7.38	71.45	6.05	7.51
e	*p*-Br	21	116—118	$C_{24}H_{20}O_4SBr_2$a)	51.10	4.57	5.68	51.80	4.28	5.28

a) Calcd. for Br, 28.30, Found, 28.03

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10) G. Pourcelot and P. Cadiot, *Bull. Soc. Chim. France*, **1966**, 3024.

11) *a)* Mass spectra were determined on a JEOL JMS-01SG; *b)* NMR spectra were obtained in the deuteriochloroform solution on a Varian A-60 and a Varian HA-100 spectrometer with tetramethylsilane as an internal standard, NOE data were measured on the degassed sample; *c)* All melting points were uncorrected.

the phenylsulfone group (Table I). The nuclear magnetic resonance (NMR) spectrum[11b)] of each compound showed a methyl group on a double bond, a methylene attached to strong electron attracting groups (corresponding to the methylene of V, which appeared at 3.92 ppm) (see Experimental) and two low field methines. The nuclear Overhauser effects (NOE) were observed on the methine protons, that is, the irradiation of Ha (upper field protons) induced the remarkable increment of integrated intensity in the peaks of Hb (lower field protons). From these data and the comparison with IIa[4c)] the structure of *cis*-2,4-diaryl-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin was given for VI, whose conformation might be deduced as shown in Table I based on the NOE data. Moreover 1:2 adduct (mp 115—117°)[11c)] of V and *p*-tolylaldehyde, which was tentatively assigned to be *cis*-2,4-di-(*p*-tolyl)-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VId) by comparison with the spectroscopic data of VIa, VIc and VIe without having any NOE data, spontaneously degradated very rapidly into a ketone, 3-methyl-1-phenylsulfonyl-4-*p*-tolyl-3-buten-2-one (IXd) and *p*-tolylaldehyde even during the measurements of UV and NMR spectra. The *cis*-2,4-diphenyl-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VIa) from V and benzaldehyde degradated on heating in ethanol containing a trace of *p*-toluenesulfonic acid, and the corresponding ketone, 3-methyl-4-phenyl-1-phenylsulfonyl-3-buten-2-one (IXa) and benzaldehyde were obtained (Chart 3). The assignment of IXd and IXa will be described later in the structure proof for the fourth type reaction products. The relationship of VIa to IXa was also confirmed by mass spectral (MS) measurements, *i.e.*, MS datum of VIa exhibited a very weak molecular ion peak (m/e=406), a very strong (M-PhCHO) peak (300), a base peak (106) due to ($PhCHO^+$) and others, and the significant peaks below 300 almost superimposed on the peaks of IXa, which suggested the evidence for the easy decomposition of VIa into IXa and benzaldehyde as shown in Fig. 1 and Fig. 2.

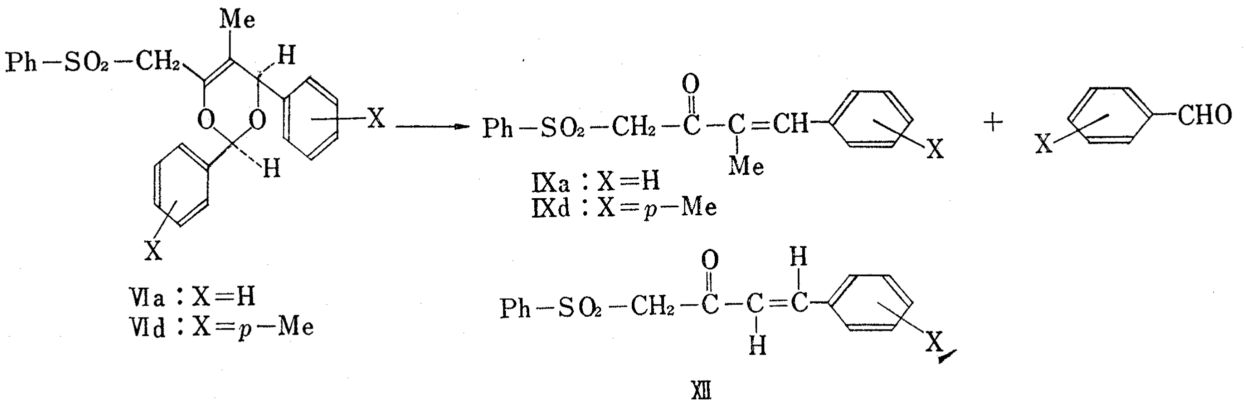


Chart 3

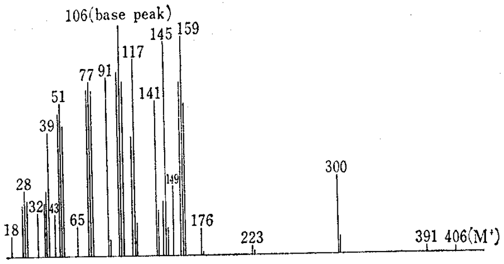


Fig. 1. Mass Spectru m of VIa

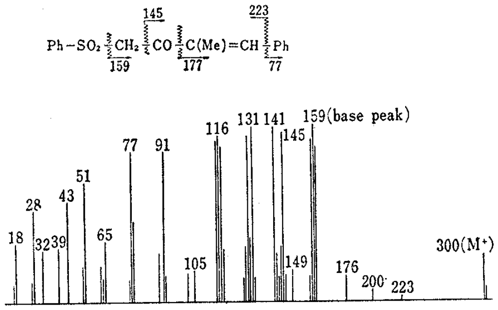
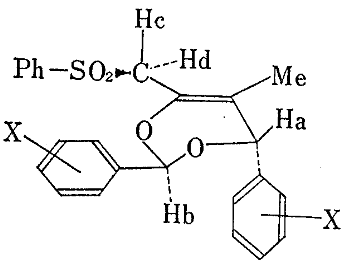


Fig. 2. Mass Spectrum of IXa

The second type of products were assumed to be *trans*-2,4-diaryl-5-methyl-6-phenylsulfonylmethyl-1,3-dioxins (VII), which are the stereoisomers of *cis*-1,3-dioxins (VI), based on the following. The spectroscopic data of VII were very similar to those of VI, but in detail there were noticed the differences of chemical shifts between the corresponding NMR peaks, which might be due to the different configurations and conformations. Moreover the methylene peaks of VIIb and VIIc appeared as broad singlets and that of VIIe as AB quartet in 60 Mc NMR. A 100 Mc NMR gave the more detailed data as shown in Table III and Fig. 3. The decisive data to distinguish *trans-* from *cis*-1,3-dioxin was obtained by NOE measurements.

Table III. Spectral Data of VII



Compound	X	UV: λ_{max}^{EtOH} nm (log ε)	IR: ν_{max}^{Nujol} cm^{-1}			NMR: δppm (60Mc)				NMR & NMDR (100MC)			
			C=C	$-SO_2-$ *asym.*	$-SO_2-$ *sym.*	Me	$-CH_2-$	H_a	H_b	H_c (δppm)	H_d	J_{cd} (Herz)	J_{ac}
b	*o*-Cl	259 266 273 (2.93) (2.88) (2.07)	1680	1305—1335	1148	1.63	4.20[a)]	5.60[b)]	5.80[b)]	4.14	4.24	15.0	1.5
c	*m*-OMe	267 273 281 (3.68) (3.78) (3.69)	1687	1317	1146	1.65	4.07	5.08	5.42				
e	*p*-Br	266[c)] 274 283	1691	1310—1324	1150—1163	1.65	4.03[a)]—4.23	5.08	5.33	4.03	4.23	15.0	1.7

a) The measurements of NMDR on 100MC NMR spectrometer[11b)] elucidated the fine couplings of Hc, Hd and Ha as indicated in other columns and Fig. 3.

b) The steric hindrance induced by the two *o*-chlorophenyl groups might afford the different conformation of VIIb from those of VIIc and VIIe, and the resulting effects of deshielding the benzene rings could shift the peaks of Ha and Hb to the lower field.

c) Degradation into IXe and *p*-bromobenzaldehyde was observed during the measurement in EtOH.

Irradiation at Ha peaks of VII showed no increment of the integrated intensity on Hb peaks, which suggested the *trans* configuration of Ha to Hb. The corresponding *trans*-dioxin (IIb) from I and benzaldehyde indicated an analogous NOE datum.[4c)]

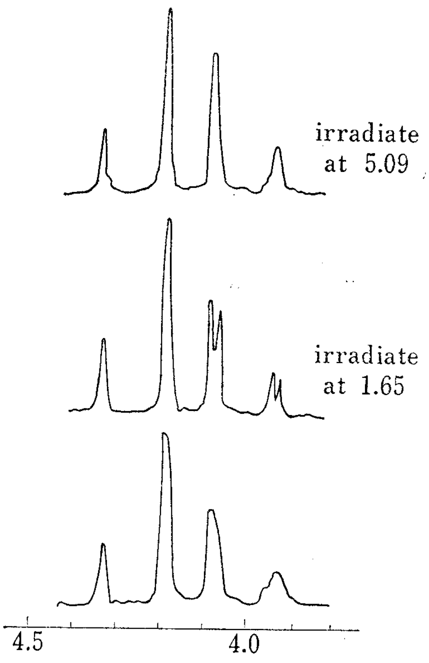


Fig. 3. NMDR Datum of VIIe

The third group of products (VIII) were deduced to be condensation compounds of dioxins VI and/or VII with a further mole of the substituted benzaldehydes by elemental analyses and the following spectral data. The analogous IR of VIII to VI and VII indicated the existence of dioxin skeleton and the UV showed an appearance of new chromophore. In NMR, each methyl peak shifted to higher filed than those of VI and VII, which would be due to a shielding effect of the new benzene ring introduced at a proper position, and the methylene peaks attached to the sulfone group of VI and VII disappeared. The configuration and conformation of VIII were not investigated.

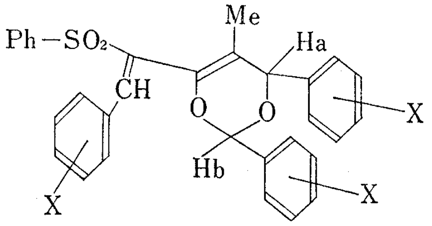
The fourth type of products were 1:1 addition products of V and the benzaldehyde derivatives, which

Table IV. Yields, Melting Points and Elemental Analyses of VII

Compound	X	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. C	H	S	Found. C	H	S
b	*o*-Cl	6.0	151—152	$C_{24}H_{20}O_4SCl_2$[a]	60.63	4.24	6.75	60.61	4.31	6.70
c	*m*-OMe	10	105—106	$C_{26}H_{26}O_6S$	66.94	5.62	6.86	66.78	5.66	6.98
e	*p*-Br	5.0	113—115	$C_{24}H_{20}O_4SBr_2$[b]	51.10	4.57	5.68	50.72	4.28	5.41

a) Calcd. for Cl,14.91, Found, 14.80
b) Calcd. for Br, 28.30, Found, 28.52

Table V. Spectral Data of VIII



Compound	X	UV: λ_{max}^{EtOH} nm (log ε)		IR: ν_{max}^{Nujol} cm^{-1} C=C–O	C=C	–SO₂– *asym.*	–SO₂– *sym.*	NMR: δppm Me	Ha	Hb
b	*o*-Cl	266 (4.22)		1667	1625	1297—1317	1147—1163	1.15	5.52	5.98
c	*m*-OMe	274 (4.34)	310 (3.77)	1682	1614	1310—1320	1140—1160	1.15	5.37	5.80
e	*p*-Br	224 (4.61)	278 (4.36)	1672	1616	1304—1324	1145—1158	1.07	5.33	5.80

Table VI. Yields, Melting Points and Elemental Analyses of VIII

Compound	X	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd., C	H	S	Found. C	H	S
b	*o*-Cl	8.0	154—155	$C_{31}H_{23}O_4SCl_3$[a]	62.57	3.88	5.36	62.51	3.83	5.37
c	*m*-OMe	5.3	138—139	$C_{34}H_{32}O_7S$	69.84	5.52	5.48	69.66	5.63	5.60
e	*p*-Br	3.5	135—136	$C_{31}H_{23}O_4SBr_3$[b]	50.92	3.18	4.40	50.87	3.20	4.43

a) Calcd. for Cl, 17.79, Found, 17.81
b) Calcd. for Br, 32.84, Found, 32.97

corresponded to III obtained from I and benzaldehyde. The structure of the compounds (IX) was deduced from the following spectral data and the comparison with III and XII.[12] The strong absorption maxima in the regions of near 210 and near 300 nm in UV, and

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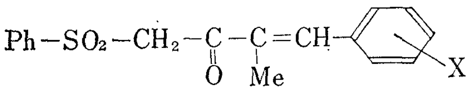
12) The preparation and the spectroscopic data of XII which was synthesized both by the reaction of phenyl 2-propynyl sulfone with benzaldehyde derivatives and by an alternative unambiguous method are to be shown in a forthcoming paper.[7]

α,β-unsaturated ketone as well as sulfonyl absorption in IR suggested the existence of phenyl sulfone group and cinnamoyl moiety. Moreover, the NMR exhibiting a methyl, a methylene, and a very low field olefin proton peaks, the last of which was not assigned convincingly because of the overlapping with the peaks of aromatic protons, but assumed to be β-proton of α,β-unsaturated ketone group, supported the structure of the 1:1 addition products (IX) to be 4-aryl-3-methyl-1-phenylsulfonyl-3-buten-2-one. The configuration of the cinnamoyl moiety was tentatively assumed to be *trans* in comparison with the structure of XII.

Table VII. Spectral Data of IX



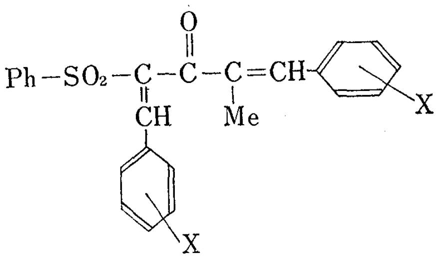
Compound	X	UV: λ_{max}^{EtOH} nm (log ε)	IR: ν_{max}^{Nujol} cm^{-1}				NMR: δppm	
			C=O	C=C	-SO$_2$- *asym.*	*sym.*	Me(J_{Herz})	-CH$_2$-
a	H	290 (4.29)	1648	1620	1300—1320	1161	2.02 (1.2)	4.63
d	*p*-Me	302 (4.33)	1646	1622	1300—1320	1160	2.02 (1.1)	4.62
e	*p*-Br	296 (4.37)	1676	1620	1284—1320	1140	1.98 (1.2)	4.62

Table VIII. Yields, Melting Points and Elemental Analyses of VII

Compound	X	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd.				Found.			
					C	H	S	Br	C	H	S	Br
a	H	4.5	99—100	$C_{17}H_{16}O_3S$	67.99	5.37	10.66		67.82	5.52	10.65	
d	*p*-Me	8.0	118—119	$C_{18}H_{18}O_3S$	68.78	5.77	10.20		68.65	6.00	10.24	
e	*p*-Br	3.5	103—104	$C_{17}H_{15}O_3SBr$	53.87	3.99	8.46	21.07	53.50	4.05	8.43	20.92

The fifth products were condensation products accompanying dehydration between IX and a further mole of corresponding benzaldehyde derivatives, based on the following. The

Table IX. Spectral Data of X



Compound	X	UV: λ_{max}^{EtOH} nm (log ε)	IR: ν_{max}^{Nujol} cm^{-1}				NMR: δppm (J_{Herz})
			C=O	C=C	-SO$_2$- *asym.*	*sym.*	Me
a	H	279 (4.49)	1640	1613	1300—1320	1148	2.07 (1.2)
b	*o*-Cl	285 (4.30)	1647	1626	1297—1317	1152	1.83 (1.2)

IR and UV bore marked resemblance to those of IX, which suggested the maintenance of cinnamoyl moiety. Moreover the disappearance of a methylene peak in NMR indicated the position of condensation. Therefore the structure of the fifth type products was assigned to be X and the relationship of X to IX was comparable with that of VIII to VI and VII. The MS of Xa confirmed this assignment (Fig. 3). The configuration of the two double bonds was not determined.

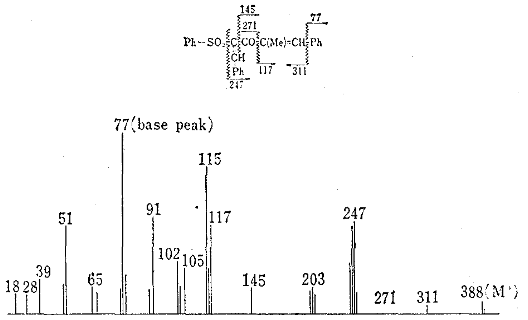


Fig. 4. Mass Spectrum of Xa

Table X. Yields, Melting Points and Elemental Analyses of X

Compounds	X	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. S	Calcd. Cl	Found. C	Found. H	Found. S	Found. Cl
a	H	20	135—136	$C_{24}H_{20}O_3S$	74.20	5.19	8.25		73.60	5.19	8.15	
b	*o*-Cl	25	113—114	$C_{24}H_{18}O_3SCl_2$	63.02	3.97	7.01	15.51	62.53	3.78	6.96	15.50

The sixth type product was only obtained in the reaction of 2-butynyl phenyl sulfone (V) with *m*-methoxybenzaldehyde and it was characterized as the condensation-dehydration compound of V and the aldehyde. The maintenance of triple bond (2210 cm^{-1}) and sulfone group (1290—1317, 1151), an appearance of a double bond (1607) in IR, and disappearance

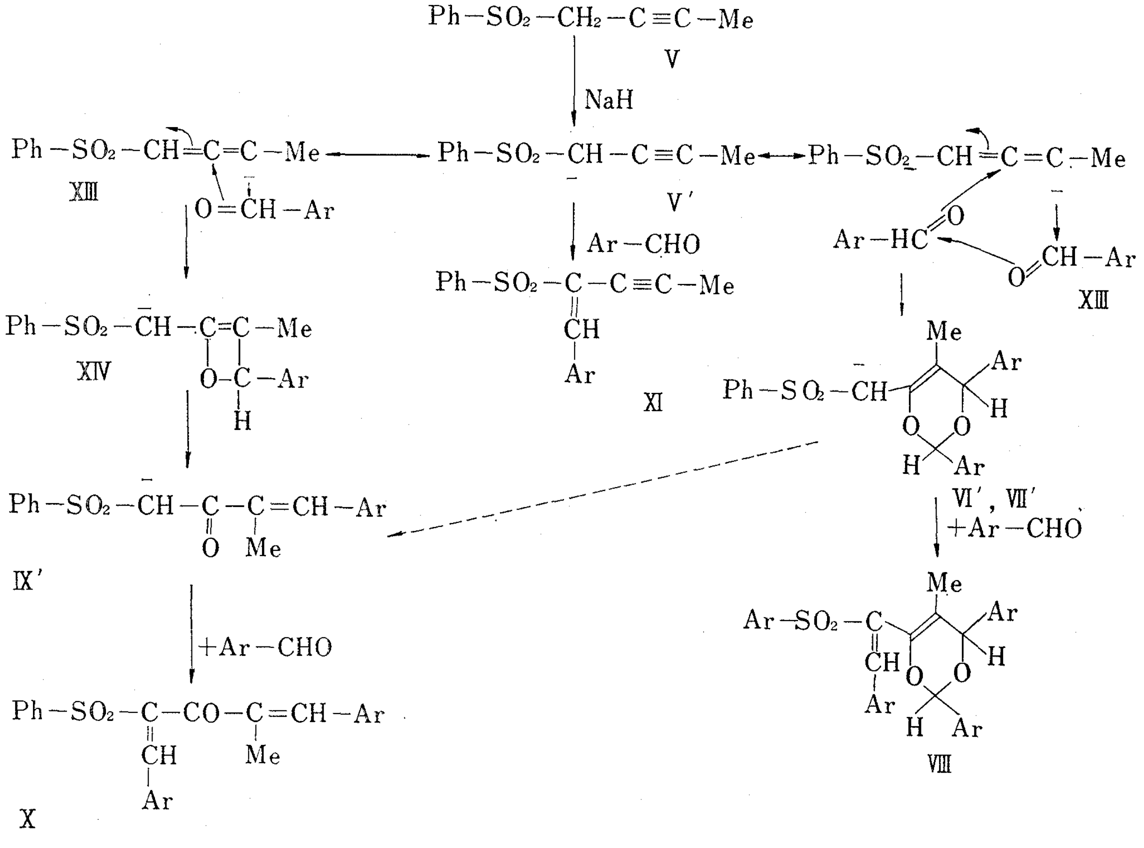


Chart 4

of a methylene peak in NMR suggested the position of the condensation. The assigned structure for XI was supported by the bathochromic shift and hyperchromic effect observed in its UV spectrum, comparing with the original system of V.

The plausible mechanism for the formation of six kinds of products was described in Chart 4. The firstly formed propargyl carbanion (V′), which whould be stabilized by the neighboring sulfone group and acetylenic linkage, may not be very reactive and then it might isomerize to a more reactive allene carbanion (XIII).[13] In fact V′ would be responsible for giving the product, XI, although only in the reaction with *m*-methoxybenzaldehyde. The probable intermediate, XIII, which could react with electrophiles without disturbance of the conjugated system, might give the corresponding 1:1 reaction product (IX) *via* an oxetene intermediate (XIV) and the corresponding *trans*- and *cis*-1,3-dioxin intermediates (VI′, VII′), reacting with one mole and two moles of each substituted benzaldehyde, respectively. The four membered ring intermediate (XIV) would collapse very easily to a stable carbanion, IX′ as shown by arrows and IX′ would react with a further mole of the aldehydes to afford the condensed compound (X). Similarly VI′ and/or VII′ might give the condensed product VIII on reacting with a further mole of the aldehydes. VIa was converted to IXa in refluxing ethanol, but the conversion had never been achieved on treatment with sodium hydride in THF which was the identical conditions with the original reaction of V and benzaldehyde. This denied the route of VI′ to IX′ definitely. Of couse VId easily degradated to afford IXd and *p*-tolyaldehyde even during the measurements of UV in ethanol and NMR in dueteriochloroform, but this case was assumed to proceed from VI directly to IX and not *via* VI′. A pertinent evidence for the existence of the intermediate XIV has been indicated by isolating the corresponding compound in the reaction of 2-butynyl phenyl sulfone, V, with cyclohexanone. The reaction of propargyl sulfones with cyclohexanone and cyclopentanone will be published in a forthcoming paper.

Experimental

2-Butynyl Phenyl Sulfide[14]——To a sodium ethoxide solution (prepared from 250 ml of abs. EtOH and 9.4 g; 0.41 mole of sodium) was added 44.1 g (0.40 mole) of thiophenol. To the resulting phenylmercaptide solution was added dropwise 53.2 g (0.40 mole) of 2-butynyl bromide. The reaction mixture was heated under reflux for 30 min. After cooling, the precipitated NaBr was removed on a glass filter and the filtrate was condensed at reduced pressure under 50°. To the condensate was added ether, and the organic solution was washed with H_2O three times until neutral, dried over anhyd. Na_2SO_4, and evaporated to dryness. The distillation of the residue gave the title compound of bp 107—109° (5 mmHg). Yield, 53.4 g (82.4%). Redistillation for analytical sample indicated bp 89—90° (3 mmHg) (bath temp.). (lit.,[14] bp 109°/2 mmHg, Yield, 78%). UV λ_{max}^{EtOH} nm (log ε): 252 (3.723). IR ν_{max}^{liquid} cm^{-1}: 2270 (C≡C), 1585. NMR δppm in $CDCl_3$: 1.78 (3H, triplet, $J=2.4$ Hz, $-CH_3$), 3.58 (2H, quartet, $J=2.4$ Hz, $-CH_2-$), 7.15—7.50 (5H, multiplet, C_6H_5-).

2-Butynyl Phenyl Sulfone (V)[10]——a) To a solution of 2-butynyl phenyl sulfide (48.6 g, 0.30 mole) in 300 ml of AcOH was added dropwise 136 g of 30% H_2O_2 (1.20 mole) with stirring for 20 min. The resulting mixture was heated at 55—65° for 5 hr and, after cooling, poured into 1500 ml of crushed ice–water. The precipitated needles were collected on a glass–filter. Recrystallization from ether–*n*-hexane or only *n*-hexane gave prisms of the title compound, mp, 63.5°. Yield, 40 g (69%). (lit.,[10] mp 62°, Yield, 72%). UV λ_{max}^{EtOH} nm (log ε): 259 (2.898), 265 (3.043), 272 (2.977). IR ν_{max}^{Nujol} cm^{-1}: 2240 (C≡C), 1585, 1315 and 1151 ($-SO_2-$). NMR δppm in $CDCl_3$: 1.78 (3H, triplet, $J=2.6$ Hz, $-CH_3$), 3.92 (2H, quartet, $J=2.6$ Hz, $-CH_2-$), 7.50—8.15 (5H, multiplet, C_6H_5-).

b) To a solution of 2-butynyl phenyl sulfide (32.4 g, 0.20 mole) in 1.0 liter of CH_2Cl_2 was added a mixture of *m*-chloroperbenzoic acid (69.2 g, 0.40 mole) and CH_2Cl_2 (1.3 liter) for 1 hr at 5—8° in ice bath. Stirring was continued for 1 hr at 5—8° and then the mixture was diluted with ether. The organic mixture

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13) C.J.M. Stirling, *J. Chem. Soc.*, **1964**, 5856; I. Iwai, "Mechanism of Molecular Migrations," Vol. 2, ed. by B.S. Thyagarajan, Interscience Publishers, Inc., New York, N.Y., 1969, pp. 78—84; J.H. Wotiz, *J. Am. Chem. Soc.*, **72**, 1637 (1950).

14) G. Pourcelot and P. Cadiot, *Bull. Soc. Chim. France*, **1966**, 3016.

was washed with satd. $NaHCO_3$ solution, H_2O and, dried over anhyd. Na_2SO_4. Evaporation of the solvent and recrystallization from EtOH gave colorless prisms of mp 62—63°. Yield, 23.8 g (61.3%).

General Procedure for the Reaction of 2-Butynyl Phenyl Sulfone (V) with Substituted Benzaldehydes——To a mixture of 2-butynyl phenyl sulfone (1.94 g, 10 mmole), each substituted benzaldehyde (20 mmole) and dry THF (40 ml) was added sodium hydride (0.24 g, 10 mmole) in several portions with vigorous stirring under N_2 atmosphere in ice–water bath keeping the temperature at 0—10°. The resulting mixture, turning into orange and then dark red, was allowed to stand with stirring at 0—5° for 30 min and then at r.t. (20—25°) for 1.5 hr. The mixture was poured into 500 ml of crushed ice–water with stirring and extracted with AcOEt. The combined extracts were washed with satd. NaCl solution, dried over anhyd. Na_2SO_4, and evaporated. The oily residue was chromatographed on silica gel (100 g).

(a) Benzaldehyde: First Fraction: Elution with benzene and recrystallization from acetone gave 1,5-diphenyl-4-methyl-2-phenylsulfonyl-1,4-pentadien-3-one (Xa).

Second Fraction: Elution with benzene and recrystallization from acetone afforded *cis*-2,4-diphenyl-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VIa).

Third Fraction: Elution with a mixture of benzene and $CHCl_3$ (95:5) and recrystallization from acetone gave 3-methyl-4-phenyl-1-phenylsulfonyl-3-buten-2-one (IXa).

(b) *o*-Chlorobenzaldehyde: First Fraction: Elution with benzene and recrystallization from acetone gave *trans*-2,4-di(*o*-chlorophenyl)-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VIIb).

Second Fraction: Elution with a mixture of benzene and $CHCl_3$ (99:1) and recrystallization from EtOH afforded 2,4-di-(*o*-chlorophenyl)-5-methyl-6-(1-phenylsulfonyl-2-*o*-chlorophenylethenylethenyl)-1,3-dioxin (VIIIb).

Third Fraction: Elution with a mixture of benzene and $CHCl_3$ (97:3) and recrystallization from EtOH gave 1,5-di(*o*-chlorophenyl)-4-methyl-2-phenylsulfonyl-1,4-pentadien-3-one (Xb).

(c) *m*-Methoxybenzaldehyde: First Fraction: Elution with benzene and recrystallization from ether gave 5-*m*-methoxyphenyl-4-phenylsulfonyl-4-penten-2-yn (XI) of mp 102—103°. Yield, 100 mg (4%). *Anal.* Calcd. for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; S, 10.27. Found: C, 69.17; H, 5.20; S, 10.39. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 300 (4.314), 227 (4.199) (shoulder). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 2210 (C≡C), 1607, 1290—1315 and 1151 ($-SO_2-$). NMR δppm in $CDCl_3$: 2.10 (3H, singlet, $C-CH_3$), 3.81 (3H, singlet, $O-CH_3$), aromatic region (10H).

Second Fraction: Elution with a mixture of benzene and $CHCl_3$ (95:5) and recrystallization from acetone afforded 2,4-di-(*m*-methoxyphenyl)-5-methyl-6-(1-phenylsulfonyl-2-*m*-methoxyphenylethenyl)-1,3-dioxin (VIIIc).

Third Fraction: Elution with a mixture of benzene and $CHCl_3$ (90:10) and recrystallization from acetone gave *trans*-2,4-di-(*m*-methoxyphenyl)-5-methyl-6-phenylsulfonylemthyl-1,3-dioxin (VIIc).

Fourth Fraction: Elution with a mixture of benzene and $CHCl_3$ (80:20) and recrystallization from acetone afforded *cis*-2,4-di(*m*-methoxyphenyl)-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VIc).

(d) *p*-Tolylaldehyde: First Fraction: Elution with benzene and recrystallization from acetone gave *cis*-2,4-di-(*p*-tolyl)-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VId).

Second Fraction: Elution with a mixture of benzene and $CHCl_3$ (95:5) and recrystallization from acetone afforded 3-methyl-1-phenylsulfonyl-4-*p*-tolyl-3-buten-2-one (IXd).

(e) *p*-Bromobenzaldehyde: First Fraction: Elution with benzene and recrystallization from EtOH gave 2,4-di-(*p*-bromophenyl)-5-methyl-6-(1-phenylsulfonyl-2-*p*-bromophenylethenyl)-1,3-dioxin (VIIIe).

Second Fraction: Elution with a mixture of benzene and $CHCl_3$ (98:2) and recrystallization from EtOH gave *trans*-2,4-di-(*p*-bromophenyl)-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VIIe).

Third Fraction: Elution with a mixture of benzene and $CHCl_3$ (95:5) and recrystallization from EtOH gave *cis*-2,4-di-(*p*-bromophenyl)-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VIe).

Fourth Fraction: Elution with a mixture of benzene and $CHCl_3$ (90:10) and recrystallization from acetone afforded 4-*p*-bromophenyl-3-methyl-1-phenylsulfonyl-3-buten-2-one (IXe).

3-Methyl-4-phenyl-1-phenylsulfonyl-3-buten-2-one (IXa) from *cis*-2,4-Diphenyl-5-methyl-6-phenylsulfonylmethyl-1,3-dioxin (VIa)——A mixture of VIa (40 mg), EtOH (5 ml) and a trace of *p*-TsOH was heated under reflux for 5 hr, during the time, the conversion of VIa to IXa had been detected by TLC. Evaporation of the solvent and recrystallization from acetone gave pure IXa (25 mg), which was identified by mixed melting test and IR spectrum comparison with an authentic sample. The vapor partition chromatograph analysis identified the sample from the mother liquor with an authentic benzaldehyde.

Acknowledgement The authors are very grateful to Dr. A. Terada of this laboratory for his valuable suggestion and kind discussion, and to Mr. N. Ishida for his technical assistance. Their thanks are also due to Mr. H. Kuwano for the measurements of nuclear Overhauser effects, and to the members of physical chemistry laboratory for the spectroscopic measurements and microanalyses.