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Studies on Acetylenic Compounds. LIII.[1] The Reactions of Acetylenic Sulfonium Salts with Acid Anhydride or Acid Chloride

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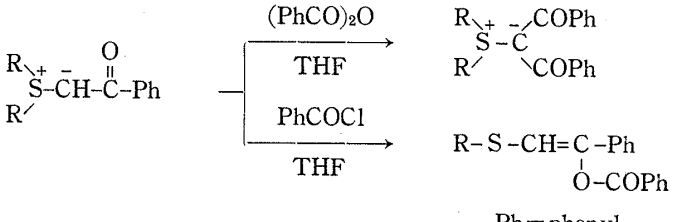
A series of new stable acetylenic sulfonium ylids, dimethylsulfonium 1-benzoyl-3-phenyl-2-propynylide derivatives, were prepared by the reaction of dimethyl 3-phenyl-2-propynylsulfonium bromide derivatives with benzoic anhydride. While, treatment of dimethyl 3-phenyl-2-propynylsulfonium bromide or dimethyl 2-butynylsulfonium bromide with benzoyl chloride gave methyl 3-phenyl-3,3-dibenzoyl-1-propynyl sulfide and methyl 3,3-dibenzoyl-1-butynyl sulfide, respectively. Treatment of dimethyl 2-propynylsulfonium bromide, however, afforded two different type compounds, methyl 1,1-dibenzoyl-2-propynyl sulfide and methyl 1,1-dibenzoyl-4-phenyl-4-oxo-2-butynyl sulfide.

Earlier reports have described on the base-catalyzed intramolecular rearrangements[3] of acetylenic sulfonium salts and the intermolecular reactions of acetylenic sulfonium salts with some electrophiles such as substituted benzaldehydes[4] or alicyclic ketones.[1]

This paper deals with the acylation reaction of acetylenic sulfonium salts as a continuation of our studies on sulfur ylid chemistry. Firstly, we will describe a formation of a series of new stable acetylenic sulfonium ylids by the reaction with benzoic anhydride and secondly, a double acylation reaction with benzoyl chloride.

It is of common knowldege that β-keto sulfonium ylid undergoes C-acylation with benzoic anhydride[5] and O-acylation with benzoyl chloride[5] as shown in Chart 1.

The stability of sulfonium ylids is enhanced by the presence of substituents such as carbonyl and other electron withdrawing groups, which situate in a β-position to the sulfur atom. Those substituents stabilize the ylids through the resonance hybridization of the negative charge of the ylid-carbanion.[5,6] Formation of stable



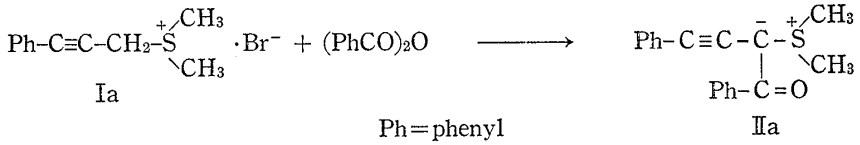
Ph=phenyl

Chart 1

1) Part LII: A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **18**, 991 (1970).
2) Location: *2-58, 1-chome, Hiromachi, Shinagawa-ku, Tokyo.*
3) A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **17**, 966 (1969).
4) A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **18**, 490, 497 (1970).
5) A.W. Johnson and R.T. Amel, *Tetrahedron Letters*, **1966**, 819.
6) *a*) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957); *b*) H.O. House and G. Rusmusson, *J. Org. Chem.*, **26**, 4278 (1961); *c*) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); *d*) H. Nozaki, K. Kondo and M. Takaku, *Tetrahedron Letters*, **1965**, 251; *e*) B.M. Trost, *J. Am. Chem. Soc.*, **89**, 138 (1967); *f*) Ch. Ruchardt, S. Eichler and P. Panse, *Angew. Chem.*, **75**, 858 (1963); *g*) G. Wittig and R. Haag, *Chem. Ber.*, **88**, 1654 (1955); *h*) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919); *i*) S. Trippett and D.M. Walker, *J. Chem. Soc.*, **1961**, 1266; *j*) G. Wittig and G. Felletschin, *Ann.*, **555**, 133 (1944); *k*) V. Horak and L. Kohout, *Chem. Ind.* (London), **1964**, 976.

ylids prepared from acetylenic compounds[7] has been known, but that of stable sulfonium ylid having a triple bond within the same molecule has not been reported.

Acylation of dimethyl 3-phenyl-2-propynylsulfonium bromide (Ia) with benzoic anhydride in the presence of sodium hydride in anhydrous tetrahydrofuran, followed by treatment with water gave dimethylsulfonium 1-benzoyl-3-phenyl-2-propynylide (IIa) of mp 164—165° in 42.8% yield.



Ia

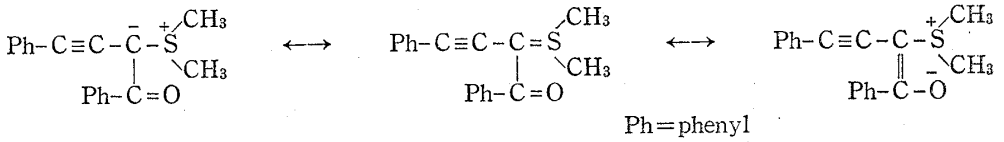
Ph=phenyl

IIa

Chart 2

The infrared (IR) spectrum of IIa showed a strong triple bond absorption band at 2175 cm^{-1} and an intense carbonyl band at 1582 cm^{-1}. The low carbonyl absorption band is consistent with common characteristics observed on the related systems.[4,5,6d,6e,8] The ultraviolet (UV) spectrum showed absorption maxima at 232 (ε=19600), 314 (13400) and 333 mμ (14060).

The observation of the low carbonyl band in the IR spectrum together with the UV maxima which red-shifted indicates a resonance contribution involving ylid, ylene, and betaine structures as shown in Chart 3.



Ph=phenyl

Chart 3

The nuclear magnetic resonance (NMR) spectrum showed a singlet at 2.70 ppm (6H) due to the dimethyl sulfonium group and an aromatic multiplet at 7.20—8.20 ppm (10H). The mass spectrum, suggesting the structure of IIa, showed a molecular ion peak at *m/e* 280 with the other intense peaks at *m/e* 265 (base peak, M–CH_3), *m/e* 218 $\left(M\text{-}S\langle^{CH_3}_{CH_3}\right)$, and *m/e* 105 [$(Ph\text{-}CO)^+$]. Although the structure of IIa was evident from its spectral properties, further proof of the carbon skeleton and ylid structure was made by desulfurization and acylation.

The compound, IIa, was treated with zinc-dust in acetic acid and a colorless oil of bp 150—160° (10^{-4} mmHg), $C_{18}H_{18}OS$, was obtained in 30% yield. The IR showed no triple bond absorption at 2200 cm^{-1} region, but showed an acetyl carbonyl band at 1756 cm^{-1}, an α,β-unsaturated ketone absorption at 1685 cm^{-1} and enol acetate band at 1202 cm^{-1}. The NMR spectrum showed signals at 2.10 ppm (3H, singlet) ascribable to a methyl group, 4.12 ppm (2H, singlet) due to the methylene protons, 6.58 ppm (1H, singlet) assignable to a vinyl proton, and an aromatic multiplet (10H). From these results, the structure of this reduction product would be either III or IV. Although there is no decisive evidence about the configura-

7) *a*) C. Kaiser, B.M. Trost, J. Beeson and J. Beinstock, *J. Org. Chem.*, **30**, 3972 (1965); *b*) J. Ide and Y. Kishida, *Tetrahedron Letters*, **1966**, 1787; *c*) S. Trippet, *J. Chem. Soc.*, **1962**, 4733; *d*) E. Winterfeldt and E.J. Dillinger, *Chem. Ber.*, **99**, 1558 (1966).

8) *a*) A.J. Speziale, C.C. Tung, K.W. Ratts and A. Yao, *J. Am. Chem. Soc.*, **87**, 3460 (1965); *b*) K.W. Ratts and A. Yao, *J. Org. Chem.*, **31**, 1185, 1689 (1966); *c*) K.W. Ratts, *Tetrahedron Letters*, **1966**, 4707; *d*) H. Nozaki, M. Takaku and K. Kondo, *Tetrahedron*, **32**, 2145 (1966); *e*) A. König, H. Metzger and K. Sealert, *Chem. Ber.*, **98**, 3712, 3724, 3733 (1965); *f*) H. Nozaki, D. Tunemoto, S. Matubara and K. Kondo, *Tetrahedron*, **23**, 545 (1967).

tion of this compound, the UV of this reduction product, having an absorption maximum at 251 mμ (log ε=4.13), would favor the probable structure of III, comparing with that of 1-phenyl-2-buten-1-one.[9] It was clear for the compound to have the skeleton of Ph–C–C–C–C–Ph by this desulfurization.

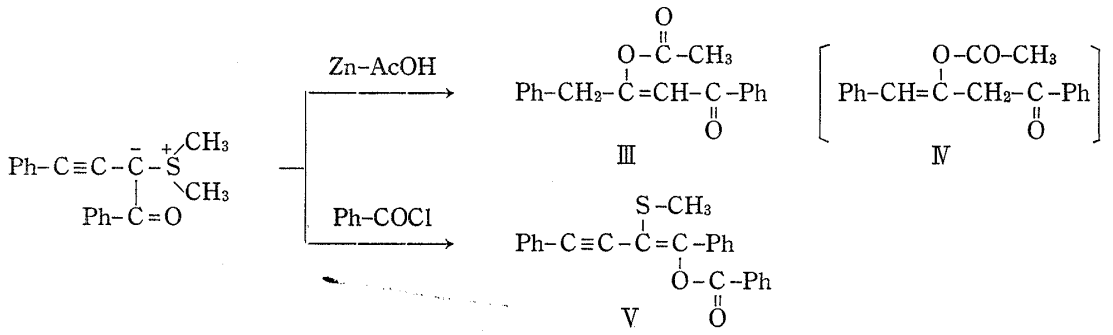


Chart 4

We could assume that the reduction of the acetylenic sulfonium ylid (IIa) with zinc dust in acetic acid would proceed through an anion radical which would have been produced by the transfer of the electrons from the metal surface to the sulfur atom.[10]

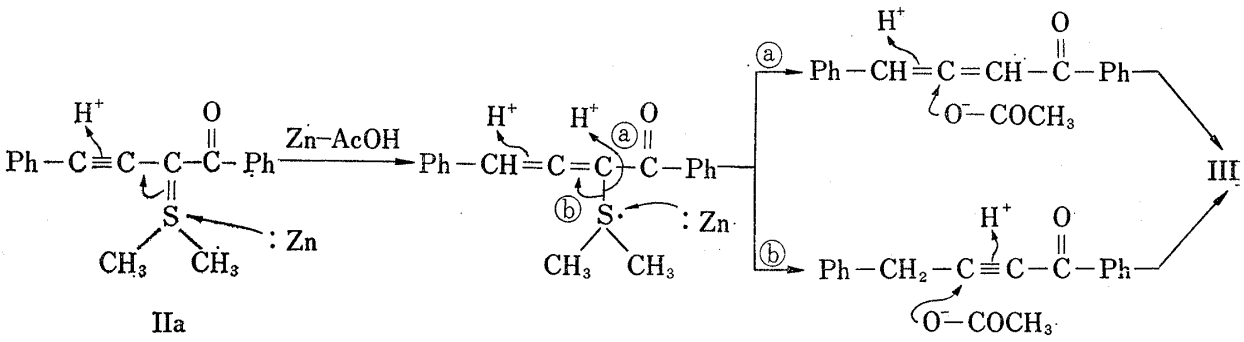


Chart 5

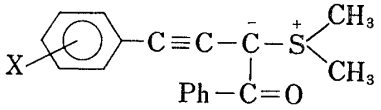
There have been a few examples for the reduction of the sulfur ylids with zinc dust in acetic acid.[4,7b,11]

The product, IIa, was further characterized to have the ylid structure by the typical acylation reaction of a sulfonium ylid having β-carbonyl group. Treatment of IIa with benzoyl chloride gave the corresponding benzoate (V) of mp 124.5° in 40% yield. The UV showed the absorption maxima at 234 (ε=33900), 273.4 (15500) and 329 mμ (17820) and the IR showed only one carbonyl band at 1739 cm^{-1}, C–O stretching band at 1235 cm^{-1}, and a triple bond absorption at 2135 cm^{-1}. The NMR spectrum exhibited a singlet at 2.50 ppm (3H) due to only one S-methyl group and an aromatic multiplet at 7.22—8.33 ppm (15H). The fate of another methyl group attached to sulfur was not pursued. This result of O-acylation is characteristic of a sulfonium ylid having β-carbonyl group[5,7d] Thus the structure of IIa was established to have the ylid structure as shown in Chart 3.

Parallel reactions were undertaken with some derivatives of Ia and the results are summarized in Table I.

9) In the UV of 1-phenyl-2-buten-1-one, the absorption maximum appeared at 252 mμ (log ε=4.20).
10) *a*) H.O. House, "Modern Synthetic Reactions," W.A. Benjamin, Inc., N.Y., 1965, p. 51; *b*) F.D. Popp and H.P. Schultz, *Chem. Rev.*, **62**, 19 (1962).
11) E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964).

TABLE I



II

II	X	Yield (%)	mp	UV λ_{max}^{EtOH} mμ (ε)
a	H	42.8	164—165	232 (19600) 314 (13400) 333 (14060)
b	*p*-CH_3	17.0	180—180.5	233 (19900) 309 (13480) 330 (13600)
c[a)]	*p*-CH_3O	15.3	146—147	234 (16700) (plateau) 246 (16300) (plateau) 310 (14000)
d[a)]	*p*-Br	40.0	166—167	235 (19600) 318 (16200) (shoulder) 342 (18160)

a) hydrate form

Likewise, dimethyl 2-butynyl and dimethyl 2-propynylsulfonium bromide were treated with benzoic anhydride, but, in these cases the corresponding stable ylids were not isolated because of their instability.

Acylation of Ia using benzoyl chloride was found to proceed differently from that using benzoic anhydride.

Treatment of Ia with benzoyl chloride in the presence of sodium hydride and triethylamine (see Experimental part) afforded a dibenzoyl compound of mp 126°, $C_{24}H_{18}O_2S$, in 40.6% yield. The IR showed a weak triple bond absorption band at 2204 cm^{-1} and a carbonyl absorption at 1739 cm^{-1}. The NMR spectrum exhibited a singlet at 2.48 ppm (3H), due to the S-methyl group and an aromatic multiplet at 7.25—8.30 ppm (15H). From these

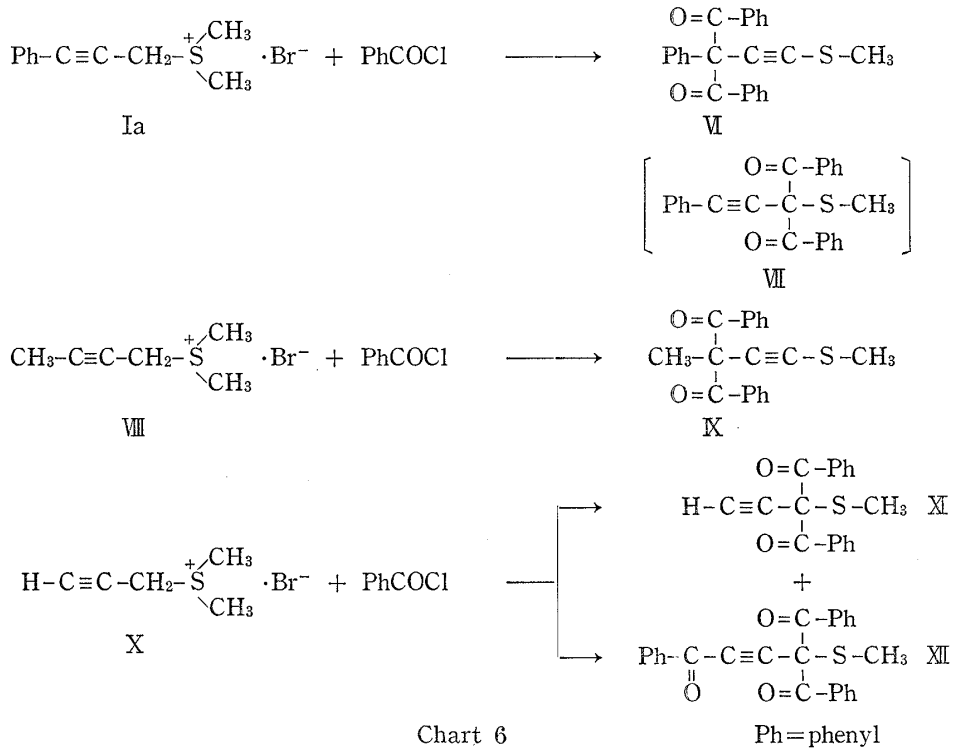


Chart 6

Ph=phenyl

data only two structures, VI or VII, were possible for this compound. However, the UV showed no typical phenylacetylene absorption, but exhibited the absorption maxima at 234 (ε=27700), 273 (12600) and 330 mμ (14700) which excluded the structure VII. The structure of VI was confirmed by oxidation with hydrogen peroxide in acetic acid. When this compound was treated with hydrogen peroxide in acetic acid, an acetylenic sulfone compound (XIII) was obtained.

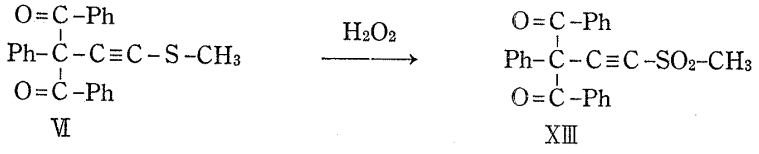


Chart 7

In the IR of XIII, the intensity of triple bond absorption (2198 cm^{-1}) increased as compared with that of VI. This fact indicated that the structure of VI had a conjugated acetylenic system with sulfur.[12] Thus, the structure of VI was established to be methyl 3-phenyl-3,3-dibenzoyl-1-propynyl sulfide.

Similarly, treatment of dimethyl 2-butynylsulfonium bromide (VIII) with benzoyl chloride gave a compound (IX). This substance, obtained in a very low yield (1.1%) and melted at 125—125.5, was assigned to be methyl 3,3-dibenzoyl-1-butynyl sulfide on the basis of the following facts which were similar to the case of VI. The IR showed a triple bond absorption band at 2225 cm^{-1} and a carbonyl band at 1732 cm^{-1}. The NMR spectrum revealed a singlet at 2.13 ppm (3H) due to the S-methyl group, a singlet at 2.42 ppm (3H) assignable to the methyl group and an aromatic multiplet at 7.27—8.43 ppm (10H).

Then dimethyl 2-propynylsulfonium bromide (X) was treated with benzoyl chloride under the similar conditions as described above, and two products were isolated from the reaction mixture by careful silica gel chromatography. The first product (XI), mp 98—101°, had a molecular formula, $C_{18}H_{14}O_2S$. The IR showed a ethynyl group absorption at 3290 and 2120 cm^{-1} and a carbonyl absorption band at 1738 cm^{-1}. The NMR spectrum exhibited a singlet at 2.42 ppm due to the S-methyl group, a singlet at 3.56 ppm (1H) assigned to the ethynyl proton and an aromatic multiplet at 7.30—8.43 ppm (10H). From these data, XI was assigned to be methyl 1,1-dibenzoyl-2-propynyl sulfide. The structure of the second product was assigned to be methyl 1,1-dibenzoyl-4-phenyl-4-oxo-2-butynyl sulfide by the IR and NMR spectra coupled with the elemental analysis ($C_{25}H_{18}O_3S$). The IR showed typical strong triple bond absorption at 2190 cm^{-1} which indicated that the triple bond was in a conjugation with carbonyl group and a carbonyl band at 1749 cm^{-1}. The NMR spectrum exhibited a singlet at 2.56 ppm (3H) due to the methyl group adjacent to the sulfur atom and an aromatic multiplet at 6.98—8.41 ppm (15H).

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

Experimental[13]

General Procedure for the Synthesis of Dimethylsulfonium 1-Benzoyl-3-phenyl-2-propynylide Derivatives (II)——To a mixture of dimethyl 3-phenyl-2-propynylsulfonium bromide (1.0 mole), benzoic anhydride (1.0 mole) and 3 liter of anhyd. tetrahydrofuran was added in one portion sodium hydride (1—1.5 mole)

12) L.H. Allan, G.D. Meakins and M.C. Whiting, *J. Chem. Soc.*, **1955**, 1874.

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

(50% oily mixture) at 3—5° under N_2. Stirring was continued for 30 min at the same temperature and further 5 hr at room temperature. The reaction mixture was poured into 20 liter of ice–water and the resulting crystalline substance was collected by filtration and recrystallized from AcOEt to give dimethylsulfonium 1-benzoyl-3-phenyl-2-propynylide.

Dimethylsulfonium 1-Benzoyl-3-phenyl-2-propynylide (IIa)——The reaction from dimethyl 3-phenyl-2-propynylsulfonium bromide (2.6 g, 10 mmole), benzoic anhydride (2.3 g, 10 mmole), sodium hydride (0.7 g) (50% oily mixture) in 30 ml of anhyd. tetrahydrofuran under N_2 gave 1.2 g of the title compound, mp 164—165°. *Anal.* Calcd. for $C_{18}H_{16}OS$: C, 77.10; H, 5.74; S, 11.43. Found: C, 77.06; H, 5.89; S, 11.35.

Dimethylsulfonium 1-Benzoyl-3-tolyl-2-propynylide (IIb)——The same sort of the reaction from dimethyl 3-tolyl-2-propynylsulfonium bromide (2.71 g, 10 mmole) instead of the dimethyl 3-phenyl-2-propynylsulfonium salt in the above mentioned experiment gave 0.5 g of pale yellow needles of the title compound, mp 180—180.5°. IR ν_{max}^{Nujol} cm^{-1}: 2180 (C≡C), 1584 (C=O). UV λ_{max}^{EtOH} $m\mu$ (ε): 233 (19900), 309 (13480), 330 (13600). *Anal.* Calcd. for $C_{19}H_{18}OS$: C, 77.50; H, 6.16; S, 10.89. Found: C, 77.23; H, 6.25; S, 10.75.

Dimethylsulfonium 1-Benzoyl-3-(*p*-methoxyphenyl)-2-propynylide (IIc)——The reaction from dimethyl 3-(*p*-methoxyphenyl)-2-propynylsulfonium bromide (2.87 g, 10 mmole), instead of the dimethyl 3-phenyl-2-propynylsulfonium salt in the above–mentioned experiment gave pale yellow needles of the title compound (0.5 g), mp 146—147°. IR ν_{max}^{Nujol} cm^{-1}: 2170 (C≡C), 1501. UV λ_{max}^{EtOH} $m\mu$ (ε): 234 (16700) (plateau), 246 (16300) (plateau), 310 (14000). *Anal.* Calcd. for $C_{19}H_{18}O_2S \cdot H_2O$: C, 69.50; H, 6.14; S, 9.74. Found: C, 69.45; H, 6.24; S, 9.65.

Dimethylsulfonium 1-Benzoyl-3-(*p*-bromophenyl)-2-propynylide (IId)——The reaction from dimethyl 3-(*p*-bromophenyl)-2-propynylsulfonium bromide (3.36 g, 10 mmole), instead of the dimethyl 3-phenyl-2-propynylsulfonium salt in the above–mentioned experiment, but, conducted in 40 ml of anhyd. tetrahydrofuran likewise gave pale yellow needles of the title compound (1.5 g), mp 166—167°. IR ν_{max}^{Nujol} cm^{-1}: 2170 (C≡C), 1584 (C=O). UV λ_{max}^{EtOH} $m\mu$ (ε): 235 (19600), 318 (16200) (shoulder), 342 (18160). *Anal.* Calcd. for $C_{18}H_{15}OSBr \cdot H_2O$: C, 57.30; H, 4.54; S, 8.49; Br, 21.17. Found: C, 57.54; H, 4.66; S, 8.57; Br, 20.98.

1,4-Diphenyl-3-acetoxy-2-buten-1-one (III)——To a solution of dimethylsulfonium 1-benzoyl-3-phenyl-2-propynylide (0.56 g, 2 mmole) in 10 ml of AcOH was added zinc–dust (0.654 g, 10 mmole) at 15—18° with stirring. Stirring was continued for 48 hr at room temperature. The inorganic substance was filtered off and the filtrate was poured into ice–water and extracted with AcOEt. The combined extracts were washed with H_2O, satd. aq. solution of $NaHCO_3$, H_2O and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and a residual oily substance (0.5 g) was chromatographed on silica gel (15 g) with hexane–benzene (2:1) to afford 0.2 g of an oil. Distillation of this oil gave a pale yellow oil, bp 150—160° (10^{-4} mmHg) (bath temp.). *Anal.* Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.16; H, 5.62.

1,4-Diphenyl-1-benzoxy-2-methylthio-1-buten-3-yn (V)——A mixture of dimethylsulfonium 1-benzoyl-3-phenyl-2-propynylide (0.56 g, 2 mmole), benzoyl chloride (0.25 g, 2 mmole) and 10 ml of anhyd. tetrahydrofuran was stirred at room temperature to give a solid. Recrystallization from ether–hexane afforded 0.5 g of the title compound, mp 124—125.5°. *Anal.* Calcd. for $C_{24}H_{18}O_2S$: C, 77.82; H, 4.90; S, 8.64. Found: C, 78.13; H, 4.96; S, 8.48.

Methyl 3-Phenyl-3,3-dibenzoyl-1-propynyl Sulfide (VI)——To a suspension of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.60 g, 10 mmole) and benzoyl chloride (1.41 g, 10 mmole) in 30 ml of anhyd. tetrahydrofuran was added sodium hydride (0.5 g) (50% oily mixture) at 3—5° under N_2 atmosphere. After 5 min, triethylamine (1.01 g, 10 mmole) was added to the mixture at 3—5°. Stirring was continued for 1 hr at the same temperature and further 5 hr at room temperature. The reaction mixture was poured into 300 ml of ice-water and the resulting crystalline substance was collected by filtration. Recrystallization from EtOH gave pale yellow needles of the title compound (1.5 g), mp 125—126°. *Anal.* Calcd. for $C_{24}H_{18}O_2S$: C, 77.83; H, 5.06; S, 8.64. Found: C, 77.71; H, 5.06; S, 8.54.

Methyl 3-Phenyl-3,3-dibenzoyl-1-propynyl Sulfone (XIII)—To a mixture of methyl 3-phenyl-3,3-dibenzoyl-1-propynyl sulfide (0.91 g, 3 mmole), AcOH (8 ml) and 10 ml of dioxane was added dropwise 30% H_2O_2 at room temperature. After the addition was completed, the reaction mixture was stirred for 5 hr at 40° and poured into 100 ml of ice–water. The resulting precipitate was collected by filtration and washed with cold–H_2O to give 0.9 g of a yellow solid. Recrystallization from benzene afforded methyl 3-phenyl-3,3-dibenzoyl-1-propynyl sulfone (0.24 g) as colorless prisms, mp 168—169°. *Anal.* Calcd. for $C_{24}H_{18}O_4S$: C, 71.62; H, 4.51; S, 7.96. Found: C, 71.91; H, 4.53; S, 7.89.

Methyl 3,3-Dibenzoyl-1-butynyl Sulfide (IX)——To a suspension of dimethyl 2-butynylsulfonium bromide (2.93 g, 15 mmole) and benzoyl chloride (2.15 g, 15 mmole) in 40 ml of anhyd. tetrahydrofuran was added sodium hydride (0.75 g) (50% oily mixture) at 3—5° under N_2 atmosphere. After 5 min, triethylamine (1.6 g) was added to the mixtur at 3—5°. Stirring was continued for 1 hr at the same temperature and then 24 hr at room temperature. The reaction mixture was poured into 400 ml of ice–water and extracted with AcOEt. The combined extracts were washed with satd. aq. solution of NaCl until neutral to litmus, dried over Na_2SO_4, and evaporated to dryness. The oily residue (2.5 g) was chromatographed on 30 g of silica gel using hexane–benzene (2:1) to afford 0.24 g of a solid. Recrystallization from ether afforded 33 mg of methyl 3,3-dibenzoyl-1-butynyl sulfide, mp 125—125.5°. *Anal.* Calcd. for $C_{19}H_{16}O_2S$: C, 73.99; H, 5.23; S, 10.39. Found: C, 73.83; H, 5.15; S, 10.41.

Methyl 1,1-Dibenzoyl-2-propynyl Sulfide (XI) and Methyl 1,1-Dibenzoyl-4-phenyl-4-oxo-2-butynyl Sulfide (XII)——To a suspension of dimethyl 2-propynylsulfonium bromide (2.71 g, 15 mmole) and benzoyl chloride (4.3 g, 36 mmole) in 35 ml of anhyd. tetrahydrofuran was added sodium hydride (0.75 g) (50% oily support) at 3° under N_2 atmosphere. After 5 min, triethylamine (3.1 g) was added to the mixture at 3—5°. Stirring was continued for 1 hr at the same temperature and then 5 hr at room temperature. The reaction mixture was poured into 350 ml of ice–water and extracted with AcOEt. The combined extracts were washed with satd. aq. solution of NaCl until neutral to litmus, dried over Na_2SO_4, and evaporated to dryness. The oily residue (3.0 g) was chromatographed on 50 g of silica gel using hexane–benzene (2:1) to give a solid (0.41 g). Recrystallization from ether afforded methyl 1,1-dibenzoyl-2-propynyl sulfide (XI) as pale yellow prisms, mp 106—107°. *Anal.* Calcd. for $C_{18}H_{14}O_2S$: C, 73.45; H, 4.79; S, 10.89. Found: C, 73.55; H, 4.85; S, 10.78. Further elution with hexane–benzene (1:1) gave a solid. Recrystallization from EtOH afforded methyl 1,1-dibenzoyl-4-phenyl-4-oxo-2-butynyl sulfide (XII) as colorless needles, mp 153—155°. *Anal.* Calcd. for $C_{25}H_{18}O_3S$: C, 75.35; H, 4.55; S, 8.04. Found: C, 75.19; H, 4.76; S, 8.09.