[Chem. Pharm. Bull. 18(3) 490—496 (1970)]

UDC 547.279.2.04 : 547.462.8.04

Studies on Acetylenic Compounds. L.[1] The Formation of Stable Sulfonium Ylids from Acetylenic Sulfonium Salts

Atsusuke Terada and Yukichi Kishida

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

(Received August 28, 1969)

Dimethylsulfonium 2-oxo-3,4-diphenyl-*cis*-3-butenylide derivatives (IVa—e) were prepared from dimethyl 3-phenyl-2-propynylsulfonium bromide (III) and benzaldehyde derivatives and its addition mechanism were considered.

In the preceding paper,[1] we reported the intramolecular rearrangements of acetylenic sulfonium salts by base and proposed an existence of the equilibration of ylid, as an intermediate, between I and II as shown in Chart 1.

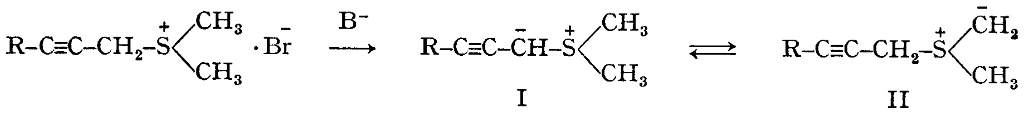


Chart 1

We have thought that the firstly formed ylid, I, should reasonably behave as a nucleophile. Then we turned our attention into the intermolecular reaction of the acetylenic sulfonium salts with some electrophiles such as aldehydes, ketones or acid halides to examine the aforementioned possibility.

Many workers[3] have revealed that the reaction of simple sulfonium ylid with aldehyde yields an epoxide. For example, Johnson, *et al.*[4] have reported that the reaction of benzylidendiphenylsulfurane with benzaldehyde gives stilbene oxide (Chart 2).

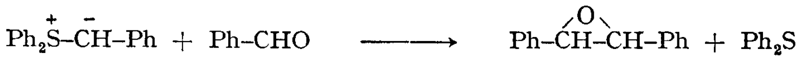


Chart 2

This paper deals with the reactions of the acetylenic sulfonium salts with substituted benzaldehydes in the presence of base whose results differ from the general pattern of the reported cases.[3]

Reaction of dimethyl 3-phenyl-2-propynylsufonium bromide (III) with benzaldehyde in the presence of sodium hydride in anhydrous tetrahydrofuran, followed by treatment with

---

1) Part XLIX: Y. Kishida, T. Hiraoka and M. Yoshimoto, *Chem. Pharm. Bull.* (Tokyo), **17**, 2126 (1969).
2) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
3) A.W. Johnson, "Ylid Chemistry," Academic Press, New York and London, 1966. p. 304
4) A.W. Johnson, V.J. Hruby and J.L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964).

water gave dimethylsulfonium 2-oxo-3,4-diphenyl-*cis*-3-butenylide (IV) in 64.3% yield.[5] The yellow crystalline stable ylid, IV, melted at 162—164° with slight degree of decomposition.

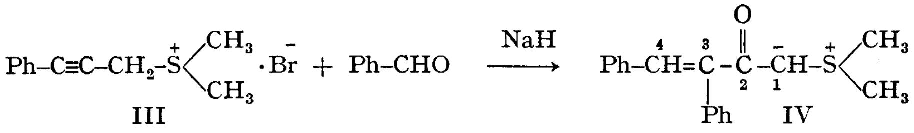
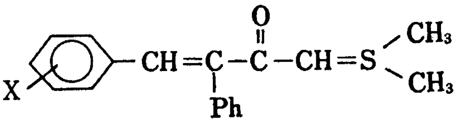


Chart 3

Table I.



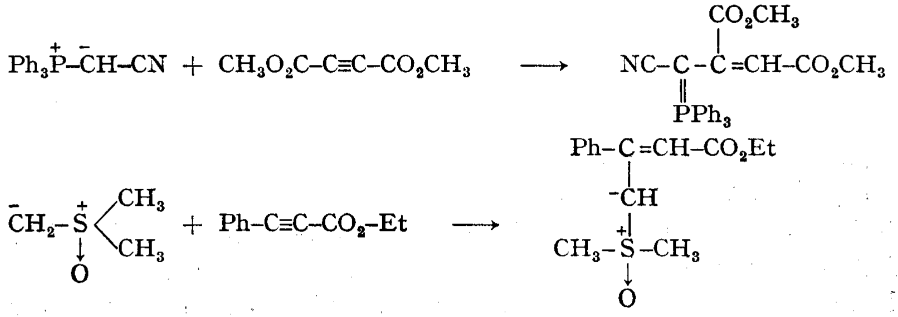
N	X	mp	Yield (%)	UV (ε)		
a	H	162—164	64.3	284 (12800)	296 (13200)	318 (14900)
b	p-Br	191—193	75.0	289 (17800)	299 (18050)	322 (19350)
c	p-CH_3	172—174	20.0	298 (15300)	319 (20130)	
d[a]	m-MeO	110—111	trace	289	324	
e[a]	p-NO_2	117—119	27.5	280.5 (12690)	356 (15800)	

a) hydrate form

Likewise, several benzaldehyde derivatives reacted with the sulfonium bromide, III, in a similar way to afford a novel series of stable sulfonium ylids (IVa—e) and the results are summarized in Table I. The infrared (IR) spectrum of IV in chloroform showed an intense carbonyl band at 1512 cm^{-1} and hydroxyl absorption at 3305 cm^{-1}, but in nujol only carbonyl band at 1537 cm^{-1}. The low frequency carbonyl absorption band is consistent with the observations on the related system.[8] The ultraviolet (UV) spectrum showed absorption maxima at 284 (ε=12800), 296 (ε=13200) (shoulder) and 318 mμ (ε=14900). The behavior of the hydroxyl band in the IR spectrum and the UV maxima which red-shifted indicate a resonance contribution between ylid and ylene structures as shown in Chart 4.

---

[5] Among the stable ylids, 2-(α-cyanotriphenylphosphonium)-1,2-dimethoxycarbonylethylene[6] and dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide[7] have been typical examples for the formation of stable ylids, starting from an acetylenic compound and an unstable ylid.



[6] S. Trippett, *J. Chem. Soc.*, 4733 (1962).

[7] *a*) C. Kaiser, B.M. Trost, J. Beeson and J. Beinstock, *J. Org. Chem.*, 30, 3927 (1965); *b*) J. Ide and Y. Kishida, *Tetrahedron Letters*, **1966**, 1787.

[8] *a*) A.J. Speziale, C.C. Tung, K.W. Ratts and A.N. Yao, *J. Am. Chem. Soc.*, **87**, 3460 (1965); *b*) K.W. Ratts and A.N. Yao, *J. Org. Chem.*, **31** 1185, 1689 (1966); *c*) A.W. Johnson and R.T. Amel, *Tetrahedron Letters*, **1966**, 819; *d*) B.M. Trost, *J. Am. Chem. Soc.*, **89** 138 (1967); *e*) K.W. Ratts, *Tetrahedron Letters* **1966**, 4707; *f*) H. Nozaki, M. Takaku and K. Kondo, *Tetrahedron*, **22**, 2145 (1966); *g*) A. König, H. Metzger and K. Seelert, *Chem. Ber.*, **98**, 3712, 3724, 3733 (1965); *h*) H. Nozaki, D. Tunemoto, S. Matubara and K. Kondo, *Tetrahedron*, **23** 545 (1967); *i*) H. Nozaki, K. Kondo and M. Takaku, *Tetrahedron Letters*, **1965**, 251.

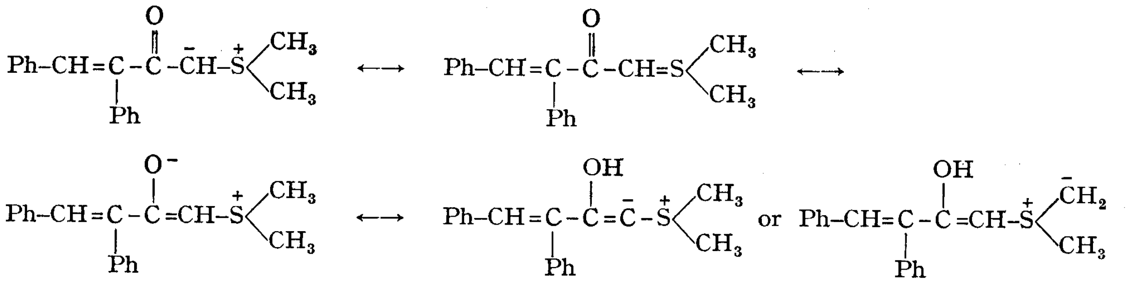


Chart 4

The nuclear magnetic resonance (NMR) spectrum in deuteriochloroform exhibited the signals at 2.90 (6H, singlet) due to the dimethylsulfonium groups, 3.49 (1H, slightly broader singlet) assignable to C-1 proton, 7.08 (5H, approximately singlet) and 7.32 (5H, approximately singlet) for two phenyl groups, and 7.65 ppm (1H, singlet) assignable to C-4 vinyl proton. Addition of deuterium oxide to a solution of IV in deuteriochloroform caused the disappearance of the signal at 3.49 ppm, whereas none of the change was observed at other signals. From these results, the signal at 3.49 ppm was assigned to the ylid proton at C-1. The absorption due to the ylid portion of IV is in good agreement with the values reported for other stabilized sulfonium ylids.[8] The mass spectrum of IV, suggesting the structure of dimethylsulfonium 2-oxo-3,4-diphenyl-*cis*-3-butenylide, showed an intense molecular ion at *m/e* 282 and the other most intense peaks at *m/e* 220 (base peak, M–$S(CH_3)_2$) and at *m/e* 179 [$(Ph\text{–}CH{=}C\text{–}Ph)^+$].

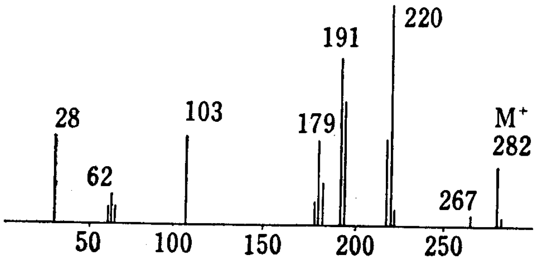


Fig. 1. Mass Spectrum of IV

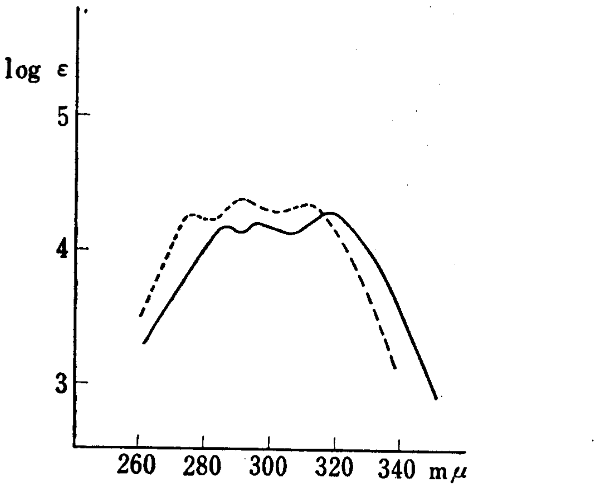


Fig. 2

——: IV ------: *trans*-stilbene

The configuration of two phenyl groups at the olefinic bond were tentatively assigned to be *trans* in comparison with *trans*-stilbene in the UV spectra.

Although the structure of IV was evident from its spectral properties, IV was unambiguously identified by converting it to the known ketone, 1,2-diphenyl-3-butanone (V), which was identical in all respects with an authentic sample[9] prepared from benzyl chloride and phenyl-2-propanone, using zinc dust in acetic acid. The IR spectrum of V showed a carbonyl band at 1705 cm^{-1}, and the NMR spectrum exhibited a singlet at 2.30 ppm (3H) due to the methyl protons, a ABC pattern [Ha=2.90 ppm (quartet), Hb=3.55 ppm (quartet), Hc=3.95 ppm (triplet), *J*ab=14 cps, *J*ac=7 cps, *J*bc=7 cps] and a multiplet centered at 7.28 ppm due to two phenyl groups.

---

9) S. Ishiwata and K. Suzuki, *Yakugaku Zasshi*, **71**, 1274 (1951).
10) H.O. House, "Modern Synthetic Reactions," W.A. Benjamin, Inc., N.Y., 1965, p. 51.

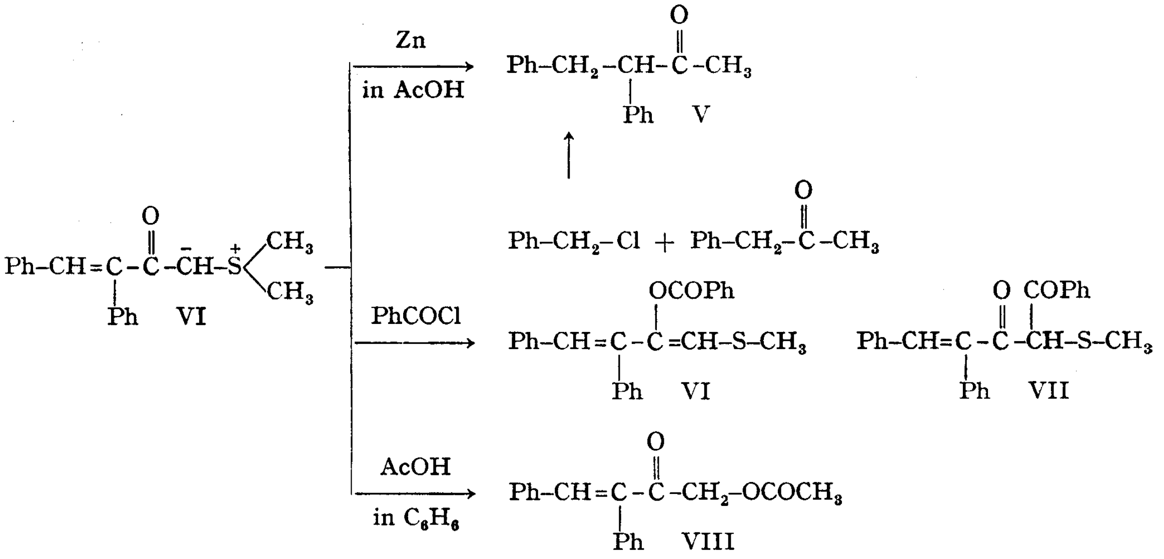


Chart 5

One could assume that this reduction would proceed through an anion radical[10] with two stage reactions as shown in Chart 6.

It is noteworthy that there have been only few examples for the reduction of S-ylid compounds with zinc dust in acetic acid.[11]

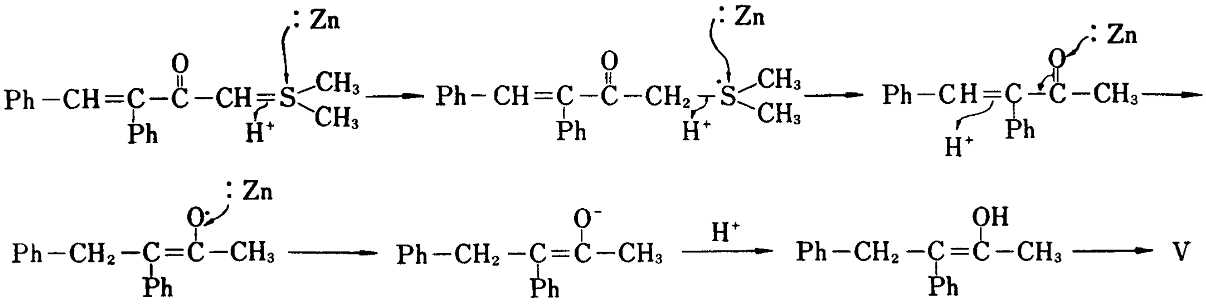


Chart 6

The product, IV was further characterized by the following reactions. Treatment of IV with benzoyl chloride at 90—100° gave the corresponding benzoate of bp 190—195° (0.0001 mmHg)(bath temp.) in 47% yield. The UV spectrum showed the absorption maxima at 231 (ε=26200), 307.5 (ε=20400) and 319 mμ (ε=22270) and the NMR spectrum exhibited a singlet at 2.19 (3H) due to the methyl group, two singlets at 5.68 (1H) and 6.67 (1H) assignable to the vinyl protons and a multiplet at 6.90—8.40 (15H) due to the three phenyl groups. On the basis of these results, the structure of this benzoate would be either VI or VII (Chart 5). The IR spectrum showed only one carbonyl band at 1735 cm^{-1} and C–O stretching band at 1240 cm^{-1}, which excludes the possibility of the structure, VII. Thus, the benzoate was concluded to be methyl 2-benzoxy-3,4-diphenyl-1,3-butadienyl sulfide (VI). The two singlets at 5.68 and 6.67 ppm in the NMR spectrum are assignable to vinyl protons adjacent to sulfur and phenyl groups, but which is which could not be assigned. The fate of methyl group attached to sulfur was not pursued. This *O*-acylation is characteristic of a sulfonium ylid having β-carbonyl group.[12]

---

11) *a*) E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964); *b*) J. Ide and Y. Kishida, *Tetrahedron Letters*, **1966**, 1787.

12) *a*) A.W. Johnson and R.T. Amel, *Tetrahedron Letters*, **1966**, 819; *b*) E. Winterfeldt and H.J. Dillinger, *Chem. Ber.*, **99**, 1558 (1966).

Reaction of IV with acetic acid in benzene solution caused a substitution reaction to give light red prisms of mp 93—93.5° in 30% yield. On the basis of the following evidence, this was assigned to be 2-oxo-3,4-diphenyl-3-butenyl acetate (VIII). The IR spectrum showed bands at 1700 cm^{-1} (α,β-unsaturated ketone) and 1750 cm^{-1} ($-OCOCH_3$), and the UV spectrum exhibited the absorption maxima at 223 (ε=18600) and 297 mμ (ε=24400). The NMR spectrum exhibited the signals at 2.15 (3H, singlet) due to a methyl group, 4.83 (2H, singlet) assignable to the methylene protons attached to the acetoxy group, 7.73 (1H, singlet) assigned to the vinyl proton and 7.00—7.56 ppm (10H, multiplet) due to two phenyl groups. Recently, DeGraw and Cory(13) have reported this substitution reaction using dimethylsulfoxonium ylid.

The compound, IV, was subjected to the reaction with benzaldehyde in anhydrous tetrahydrofuran in an expect to yield the epoxide derivative by the method of Johnson(4) and others,(8) but a 70% recovery of unchanged starting material was the result. This lack of reactivity parallels that the ylid, IV, is quite stable.

A mechanistic assumption for the formation of the new stable ylid (IV) from III and benzaldehyde would be expressed as following.

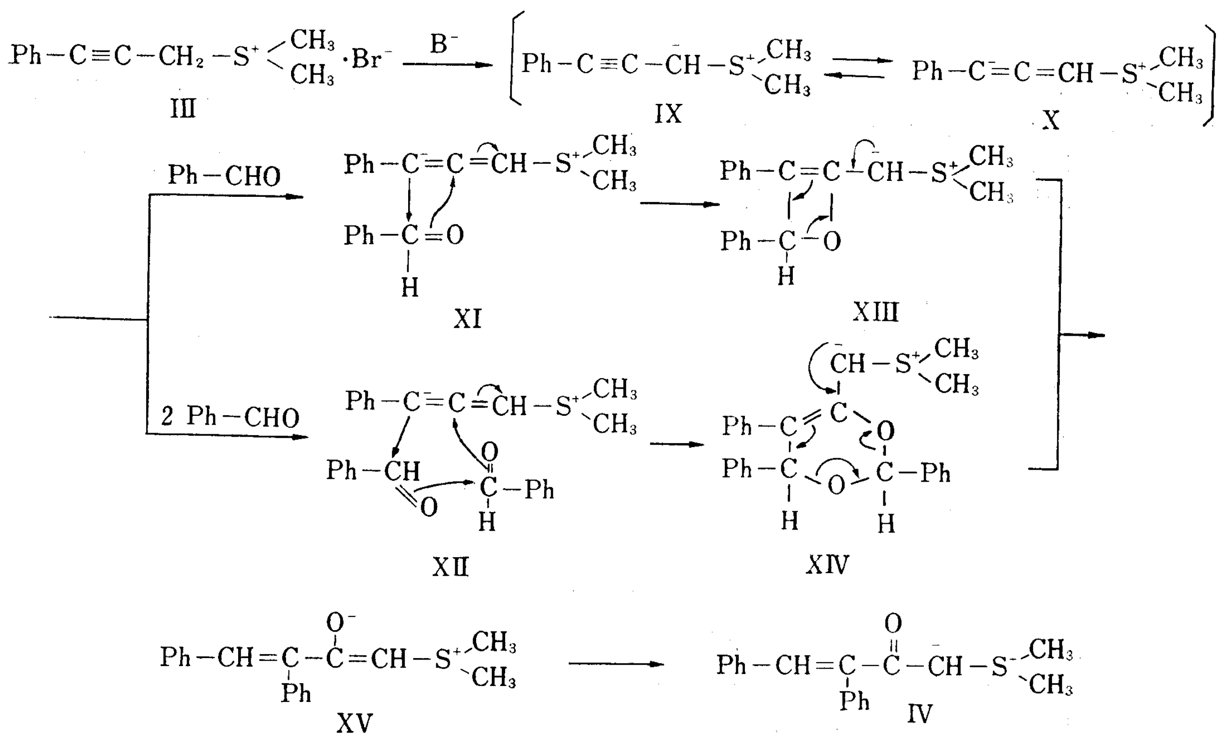


Chart 7

The ylid (IX), formed from the parent sulfonium bromide (III) by base, was converted into an unstable allenic betaine (X). Then the attack of the resulting anion to one or two molar benzaldehyde followed by the attack to the allenic center carbon at C-2 give a four- or six-membered ring intermediate (XIII or XIV). The ylid anion would be functioning as a driving force to the C–O bond fission to give the product (IV). In this assumption, we considered two structures as the intermediates (XIII and XIV). Although it is very difficult to determine which is the real intermediate, in the absence of the kinetic information, the six-membered ring intermediate (XIV) would be favorable rather than the four-membered ring one (XIII) by the following reasons. The yield of IV was only 21.3% in a reaction of 1:1 molar ratio of benzaldehyde to dimethyl 3-phenyl-2-propynylsulfonium bromide (III). The yield, however, increased to 64.3% when two molar aldehyde was used in the reaction. Moreover,

---

13) J.I. DeGraw and M. Cory, *Tetrahedron Letters*, **1968**, 2501.

the intermediacy of the six-membered ring compound, XIV, woudl be evident by an unequivocal synthesis of a 1,3-dioxin having six-membered ring, but not ylid, from dimethyl 2-butynylsulfonium bromide and benzaldehyde, which will be described in the following paper.

Experimental[14]

Dimethylsulfonium 2-Oxo-3,4-diphenyl-*cis*-3-butenylide (IVa)——To a suspension of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.57 g, 0.01 mole) and benzaldehyde (2.12 g, 0.02 mole) in 20 ml of anhyd. tetrahydrofuran was added sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 3—5° under N_2. An exothermic reaction took place after 30 min and the stirring was continued for 1 hr at the same temperature and further for 24 hr at 25—30°. The reaction mixture was poured into 200 ml of ice-water and the precipitate was collected to give 1.803 g of almost pure ylid. Recrystallization from AcOEt gave pale yellow needles, mp 162—164°. *Anal.* Calcd. for $C_{18}H_{18}OS$: C, 76.55; H, 6.42; S, 11.35. Found: C, 76.38; H, 6.04; S, 11.02.

Dimethylsulfonium 2-Oxo-3-phenyl-4-(*p*-bromophenyl)-3-butenylide (IVb)——To a suspension of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.6 g, 0.01 mole) and *p*-bromobenzaldehyde (3.7 g, 0.02 mole) in 30 ml of anhyd. tetrahydrofuran was added sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 8—9° under N_2 atmosphere. The stirring was continued for 30 min at 8—10° and then at room temperature for 5 hr. The reaction mixture was poured into 200 ml of ice-water and the precipitate was collected to give 2.7 g of almost pure ylid. Recrystallization from EtOH gave pale yellow prisms, mp 191—193°. *Anal.* Calcd. for $C_{18}H_{17}OSBr$: C, 59.83; H, 4.74; Br, 22.11; S, 8.87. Found: C, 60.05; H, 4.94; Br, 21.91; S, 8.61.

Dimethylsulfonium 2-Oxo-3-phenyl-4-(*p*-methylphenyl)-3-butenylide (IVc)——To a suspension of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.6 g, 0.01 mole) and *p*-methylbenzaldehyde (2.4 g, 0.02 mole) in 30 ml of anhyd. tetrahydrofuran was added sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 5—6° under N_2 atmosphere. The stirring was continued for 30 min at the same temperature and then at room temperature for 5 hr. The reaction mixture was poured into 300 ml of ice-water and the precipitate was collected by filtration to give 0.6 g of almost pure ylid. Recrystallization from AcOEt gave colorless needles, mp 172—174°. *Anal.* Calcd. for $C_{19}H_{20}OS$: C, 76.98; H, 6.80; S, 10.81. Found: C, 76.84; H, 6.81; S, 10.74.

Dimethylsulfonium 2-Oxo-3-phenyl-4-(*m*-methoxyphenyl)-3-butenylide (IVd)——To a suspension of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.6 g, 0.01 mole) and *m*-methoxybenzaldehyde (2.7 g, 0.02 mole) in 30 ml of anhyd. tetrahydrofuran was added sodium hydride (0.75 g, 0.015 mole) (50% oily mixture) at 5—8° under N_2 atmosphere. The stirring was continued for 30 min at the same temperature and then at room temperature for 5 hr. The reaction mixture was poured into ice-water and the precipitate was collected to give pale green solid (0.01 g). Recrystallization from AcOEt–hexane gave pale green needles, mp 110—111°. *Anal.* Calcd. for $C_{19}H_{20}O_2S \cdot H_2O$: C, 69.06; H, 6.70. Found: C, 69.64; H, 6.47.

Dimethylsulfonium 2-Oxo-3-phenyl-4-(*p*-nitrophenyl)-3-butenylide (IVe)——To a suspension of dimethyl 3-phenyl-2-propynylsulfonium bromide (2.6 g, 0.01 mole) and *p*-nitrobenzaldehyde (3.0 g, 0.02 mole) in 30 ml of anhyd. tetrahydrofuran was added sodium hydride (0.7 g, 0.014 mole) (50% oily mixture) at 0—3° under N_2 atmosphere. An exothermic reaction took place after 2 min and the color of the reaction mixture developed to red-brown. The reaction mixture was stirred for 30 min at 5—10° and poured into 300 ml of ice-water to give pale yellow solid (0.9 g). Recrystallization from AcOEt gave pale yellow needles, mp 117—119°. *Anal.* Calcd. for $C_{18}H_{17}O_3NS \cdot H_2O$: C, 62.59; H, 5.54; N, 4.06; S, 9.25. Found: C, 62.93; H, 5.72; N, 4.12; S, 9.20.

1,2-Diphenyl-3-butanone (V) from Dimethylsulfonium 2-Oxo-3,4-diphenyl-cis,3-butenylide——To a solution of dimethylsulfonium 2-oxo-3,4-diphenyl-*cis*,3-butenylide (0.282 g) in 5 ml of AcOH was added zinc-dust (0.327 g) at 18—20° with stirring. Stirring was continued for 48 hr at room temperature. The reaction mixture 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 residual oily substance (0.2 g) was chromatographed on silica gel (4 g) and eluted with hexane–benzene (5:1) to afford 0.115 g of the title compound. 2,4-dinitrophenylhydrazone of 1,2-diphenyl-3-butanone melted at 115—117° after recrystallization from EtOH. *Anal.* Calcd. for $C_{22}H_{20}O_4N_4$: C, 65.33; H, 4.99; N, 13.86. Found: C, 65.03; H, 5.00; N, 13.85.

Methyl 2-benzoxy-3,4-diphenyl-1,3-butadienyl Sulfide (VI)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-*cis*,3-butenylide (0.564 g) and benzoyl chloride (10 ml) was heated at 90—100° for 3 hr. The reaction mixture was poured into ice-water and extracted with ether. The combined extracts were washed with H_2O and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give an oily

---

[14] 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.

substance. This oil was chromatographed on alumina (Woelm, grade I, 30 g) and eluted with hexane–benzene (1:1) to afford 0.421 g of gummy oil. Distillation of this oil *in vacuo* gave a pale yellow oil, bp 190—195° (0.0001 mmHg) (bath temp.). *Anal.* Calcd. for $C_{24}H_{20}O_2S$: C, 77.15; H, 5.38; S, 8.89. Found: C, 76.76; H, 5.44; S, 8.85.

1-Acetoxy-3,4-diphenyl-3-buten-2-one (VIII)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-*cis*,3-butenylide (0.42 g), AcOH (0.1 g) and 5 ml of anhyd. benzene was refluxed for 3 hr. After cooling, the reaction mixture was poured into ice-water. The organic layer was separated and the aqueous layer was extracted with benzene. The combined extracts were washed with satd. aq. solution of $NaHCO_3$, H_2O and dried over Na_2SO_4. The solvent was evaporated under diminished pressure to give an oil (0.4 g). This oil was chromatographed on silica gel (12 g) and eluted with hexane–benzene (1:3) to give a solid (0.14 g). Recrystallization from benzene–hexane (1:10) afforded pale red prisms of mp 93—93.5°. *Anal.* Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.90; H, 5.78.

Acknowledgement The authors express their deep gratitude to Dr. I. Iwai, Associate Director of this laboratories, for his interest and encouragement throughout this work and also to Dr. T. Hiraoka of this laboratory for his valuable suggestion and helpful discussion in this work. We are indebted to Mr. N. Ishida for technical assistance.