[Chem. Pharm. Bull. 18(3) 505—510 (1970)] UDC 547.279.2.04 : 547.462.8.04

Rearrangements and Reactions of Stable Sulfonium Ylids from Acetylenic Sulfonium Salts

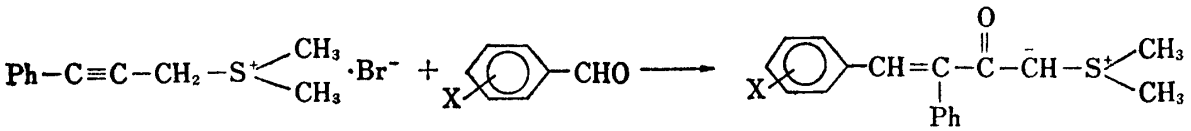
ATSUSUKE TERADA and YUKICHI KISHIDA

Central Research Laboratories, Sankyo Co., Ltd.[1]

(Received August 28, 1969)

Dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide derivatives (Ia—c) rearranged in boiling ethanol, in a Pummerer-type fashion, to produce 1,2-diphenyl-3-methylthiomethoxy-1,3-butadiene (IVa—c). Nucleophilicity of the ylid (I) was examined by the reactions described below. I-a still reacted with dimethyl acetylenedicarboxylate and ethyl propiolate to afford new stable ylids of dimethylsulfonium 1,2-dimethoxycarbonyl-4-oxo-5,6-diphenyl-1,5-hexadien-3-ylide (IX) and dimethylsulfonium 1-ethoxycarbonyl-4-oxo-5,6-diphenyl-1,5-hexadien-3-ylide (X), respectively. I also reacted with phenylisocyanate derivatives forming stable ylids, dimethylsulfonium 1-phenylcarbamoyl-2-oxo-3,4-diphenyl-3-butenylide derivatives (XIa—e).

In the preceding paper,[2] we reported the formation of a series of stable sulfonium ylids (Ia—e) by the reactions of dimethyl 3-phenyl-2-propynylsulfonium bromide with substituted benzaldehydes as outlined in Chart 1.



Ia : X=H
b : X=*p*-CH_3
c : X=*p*-Br
d : X=*p*-CH_3O
e : X=*p*-NO_2

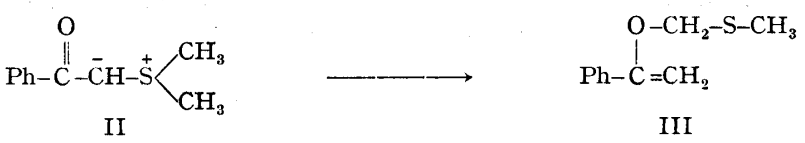
Chart 1

This paper deals with the rearrangements and further reactions of these stable sulfonium ylids (I).

Stevens and Sommelet–Hauser[3] rearrangements have been known as the reactions involving plausible N-ylid intermediates. Sulfonium salts, likewise, have been recognized to undergo the same type rearrangements to afford sulfide derivatives as presented in some occasions[4] including ours.[5] Triphenylchloromethylphosphonium chloride also undergoes the migration

1) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
2) A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **18**, 506 (1970).
3) *a*) P. de Mayo, "Molecular Rearrangements," Part I, Interscience Publishers, N.Y., 1963, p. 345; *b*) E.S. Gould, "Mechanism & Structure in Organic Chemistry," Henry Holt and Company, N.Y., 1959, p. 640.
4) *a*) T. Thomson and T.S. Stevens, *J. Chem. Soc.*, **1932**, 69; *b*) J.E. Baldwin, R.E. Hackler and D.P. Kelly, *Chem. Commun.*, **1968**, 537, 538, 1083; *c*) *Idem, J. Am. Chem. Soc.*, **90**, 4758 (1968); *d*) J.E. Baldwin and D.P. Kelly, *Chem. Commun.*, **1968**, 899; *e*) R.B. Bates and D. Feld, *Tetrahedron Letters*, **1968**, 417; *f*) B.M. Trost and R. LaRochelle, *ibid.*, **1968**, 3327; *g*) G.M. Blackburn, W.D. Ollis, J.D. Plackett, C. Smith, and I.O. Sutherland, *Chem. Commun.*, **1968**, 186; *h*) G.M. Blackburn and W.D. Ollis, *ibid.*, **1968**, 1261; *i*) G.M. Blackburn, W.D. Ollis, C. Smith and I.O. Sutherland, *ibid.*, **1969**, 99; *j*) W. Kirmse and M. Kupps, *Chem. Ber.*, **101**, 994, 1004 (1968).
5) A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **17**, 966 (1969).

of the phenyl group by the treatment with butyl lithium giving diphenyl butylphosphonium benzylides.[6] Meanwhile, Ratts and Yao[7] have recently reported a non base-catalyzed rearrangement of phenacylsulfonium ylid as shown in Chart 2.

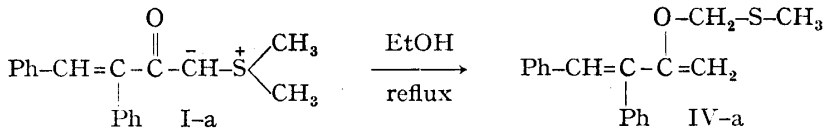


II III

Chart 2

Noticing the common partial structure, $-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H-\overset{+}{S}\!<\!\overset{CH_3}{CH_3}$, the rearrangements of I were attempted by the method of Ratts and Yao, using ethanol instead of water.

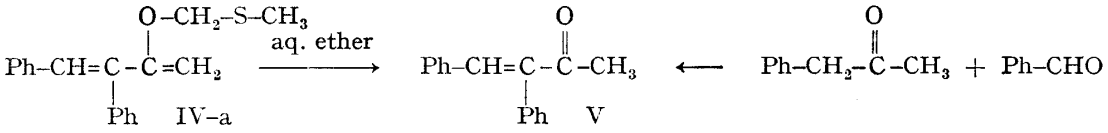
Refluxing of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (I-a), prepared from dimethyl 3-phenyl-2-propynylsulfonium bromide and benzaldehyde,[2] in ethanol for 8 hr gave 1,2-diphenyl-3-methylthiomethoxy-1,3-butadiene (IV-a) in 51% yield (Chart 3).



Ph I-a IV-a

Chart 3

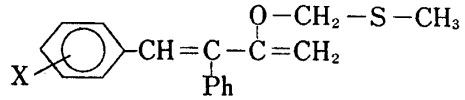
The structural assignment of IV-a was based on the following facts. The infrared (IR) spectrum showed no carbonyl absorption, but a new terminal methylene band at 924 cm^{-1}. The ultraviolet (UV) spectrum revealed maxima at 222.5 (ε=13280) (plateau) and 286 mμ (ε=10900). The nuclear magnetic resonance (NMR) spectrum[8] exhibited a singlet at 2.30 ppm (3H) due to the methyl group, typical AB type signals at 4.11 and 4.37 ppm (2H, J_{AB}= 2.5 cps) for the characteristic terminal methylene group, a singlet at 5.02 ppm (2H) ascribable to the methylene protons, and a multiplet at 6.82—7.45 ppm (11H) due to an olefinic proton together with two phenyl groups. The product, IV-a, was converted to the known ketone, 1,2-diphenyl-1-buten-3-one (V), by the treatemt with water–ether overnight. The product, V, was identical in all respects with an authentic sample[9] prepared from benzaldehyde and phenyl 2-propanone.



IV-a V

Chart 4

Table I.



N	X	bp (mp)[a]	Yield (%)	UV λ_{max}^{EtOH} mμ (ε)	
a	H	150—155 (0.0001)	51	222.5 (13280)(plateau)	286.0 (10900)
b	*p*-CH_3	148—150 (0.0001)	62	225.0 (13400)(plateau)	291.0 (18150)
c	*p*-Br	74—75[a]	30	228.0 (13030)(plateau)	292.5 (24600)

6) M. Schlosser, *Angew. Chem.*, **74**, 291 (1962).
7) *a*) K.W. Ratts and A.N. Yao, *J. Org. Chem.*, **33**, 70 (1968); *b*) E.B. Ruiz, *Acta Salmenticensi Ser. Cience*, **2**, 64 (1958); *Chem. Abstr.*, **54**, 7623 (1960).
8) The chemical shifts were expressed δ in ppm unit from the internal standard of tetramethylsilane in $CDCl_3$ solution.
9) R.A. Abramobitch and A. Obach, *Can. J. Chem.*, **37**, 502 (1959).

The sensitivity to water of IV-a may be due to the facile hydrolysis of the O,S-acetal structure. In the similar manner, 1,3-butadiene derivatives (enol ether) bearing various substituents in the phenyl group were prepared and the results are summarized in Table I. *p*-Nitro derivative, however, did give no rearrangement product, but only resin.

A postulated mechanism for the rearrangement is given in Chart 5. The initial equilibrium favors the starting ylid, but the presence of VI leads *via* the ylene contribution (VII) to the product of enol ether. Thus the present rearrangement reaction of I-a to IV-a makes a close analogy to the Pummerer rearrangement[10] which leads to acetoxy sulfides[11] from a mechanistic point of veiw (see Chart 6).

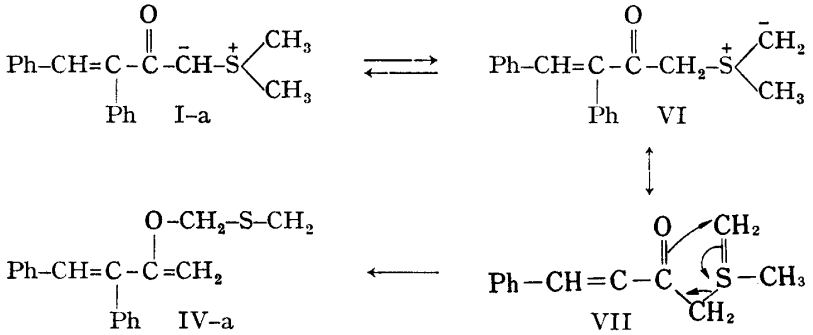


Chart 5

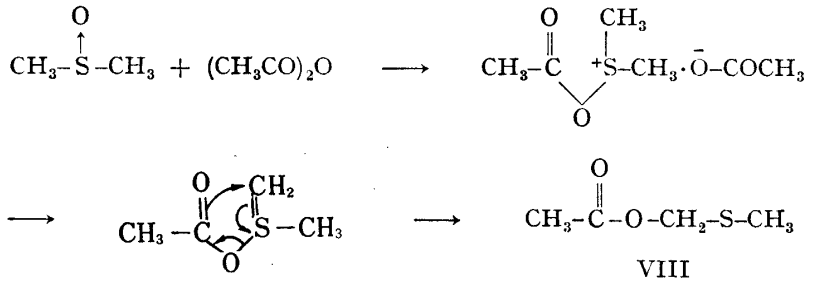


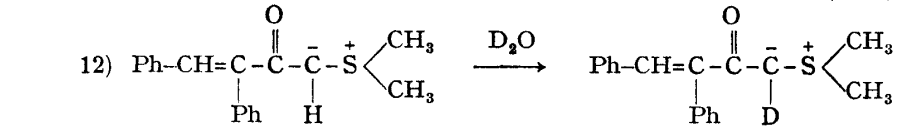
Chart 6

While, the compounds (Ia—e) seem to possess the ylid-like structure rather than the ylenes from the facile proton exchange with deuterium ion at the ylid-carbanion as described in the preceding paper.[2,12] Therefore, the ylid carbanion in I may be estimated to have yet an appreciably strong base character so as to be able to react with the electrophiles in the Michael type addition or with acylating reagents.

When I-a was treated with dimethyl acetylenedicarboxylate in ethanol at room temperature, a new stable ylid, dimethylsulfonium 1,2-dimethoxycarbonyl-4-oxo-5,6-diphenyl-1,5-hexadien-3-ylide (IX), mp 139—140°, was obtained in 53% yield, although the reaction in tetrahydrofuran gave no product. The IR spectrum showed absorption bands at 1725 and 1713 cm^{-1} ($-CO_2CH_3\times2$) and 1680 cm^{-1} (α,β-unsaturated ketone), and the UV spectrum showed absorption maxima at 264.5 ($\varepsilon=14500$) and 285 mμ ($\varepsilon=13680$) (shoulder). The NMR spectrum exhibited a singlet at 3.16 ppm due to dimethylsulfonium group ($-S^+(CH_3)_2$), two singlets at 3.55 and 3.73 ppm for the two methyl esters, a sharp singlet at 5.83 ppm assignable

10) *a*) R. Pummerer, *Chem. Ber.*, **42**, 2282 (1909); *b*) *Idem*, *ibid.*, **43**, 1401 (1910); *c*) C.R. Johnson and W.G. Phillips, *J. Am. Chem. Soc.*, **91**, 682 (1969).

11) F.G. Bordwell and B.M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

12) 

to vinyl proton at C-1, a slightly broader singlet at 6.74 ppm due to the vinyl proton at C-6 and a multiplet at 6.98—7.31 ppm for two phenyl groups.

Similarly, treatemt of I-a with ethyl propiolate at room temperature in ethanol gave a new stable ylid, dimethylsulfonium 1-ethoxycarbonyl-4-oxo-5,6-diphenyl-1,5-hexadien-3-ylide (X), mp 127—128° in 71% yield. Its IR spectrum showed absorption bands at 1678 cm^{-1} (CO_2Et) and 1655 cm^{-1} (α,β-unsaturated ketone), and the UV spectrum showed absorption maxima at 274 (ε=15280) (shoulder) and 327 mμ (ε=24770). The NMR spectrum exhibited a triplet at 1.22 ppm and a quartet at 4.11 ppm due to the ethyl ester, a singlet at 3.03 ppm assigned to dimethylsulfonium group ($-\overset{+}{S}(CH_3)_2$), typical AB type signals at 5.34 and 8.12 ppm (2H, J_{AB}=15 cps) for the two vinyl protons which are in *trans*, a singlet at 6.71 ppm assignable to the vinyl proton at C-6 and two singlets at 7.13 and 7.31 ppm for two phenyl groups.

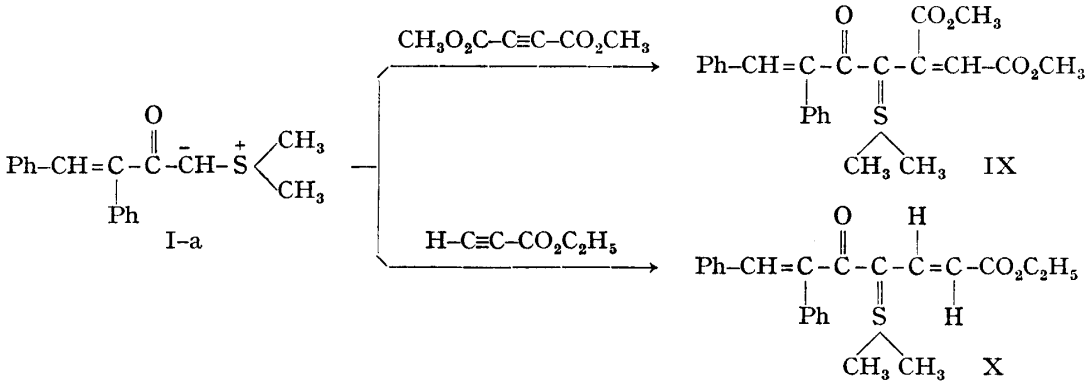
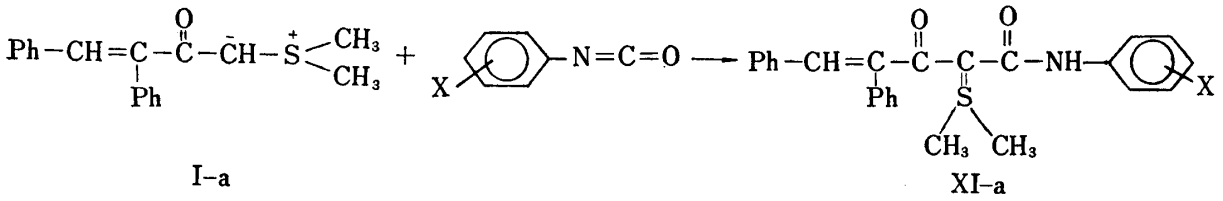


Chart 7

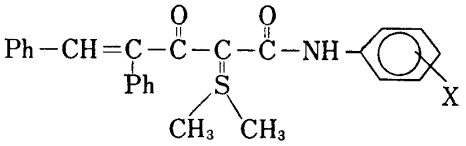
Likewise, I-a reacted with phenylisocyanate at room temperature in tetrahydrofuran to afford a new stable sulfonium ylid,dimethylsulfonium 1-phenylcarbamoyl-2-oxo-3,4-diphenyl-3-butanylide (XI), mp 210—212° in 94% yield. The IR spectrum showed absorption bands at 3320 cm^{-1} (NH), 1648 cm^{-1} (α,β-unsaturated ketone) and 1600 and 1540 cm^{-1} due to secondary amide group. The UV spectrum revealed absorption maxima at 230.5 (ε=26400) and 283 mμ (ε=27870). The NMR spectrum exhibited a singlet at 2.74 ppm due to dimethyl-



I-a XI-a

Chart 8

Table II.



XI	X	mp	Yield (%)	UV λ_{max}^{EtOH} mμ (ε)	
a	H	210—212	94	230.5 (26400)	283.0 (27870)
b	*p*-Br	203—204	96	231.0 (25000)	288.0 (32100)
c	*m*-Cl	192—193	80	234.0 (25240)	288.0 (29200)
d	*p*-CH_3	191—193	78	230.0 (28090)	284.0 (25240)
e	*p*-NO_2	141—143	90	229.0 (27870)	266.5 (27790)

sulfonium group, a singlet at 6.81 ppm assignable to the vinyl proton, a multiplet at 7.15—7.80 ppm for three phenyl groups and a slightly broader singlet at 12.20 ppm for amide proton. In the similar manner, carbamoyl derivatives bearing various substituents in the phenyl group were prepared in high yields and the results are summarized in Table II.

Experimental[13]

1,2-Diphenyl-3-methylthiomethoxy-1,3-butadiene (IV-a)——A solution of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (1.0 g) in 20 ml of anhyd. EtOH was heated under reflux for 8 hr. After cooling, the solvent was evaporated under reduced pressure to give an oil (1.0 g), which was chromatographed on silica gel (30 g) and eluted with benzene to afford an oil (0.8 g). Distillation of this oil gave the title compound (0.51 g), bp 150—155° (0.0001 mmHg) (bath temp.). *Anal.* Calcd. for $C_{18}H_{18}OS$: C, 76.57; H, 6.43; S, 11.32. Found: C, 76.38; H, 6.42; S, 11.17.

1-(*p*-Tolyl)-2-phenyl-3-methylthiomethoxy-1,3-butadiene (IV-b)——A solution of dimethylsulfonium 2-oxo-3-phenyl-4-(*p*-tolyl)-3-butenylide (0.5 g) in 10 ml of anhyd. EtOH was heated under reflux for 12 hr. After cooling, the solvent was evaporated under reduced pressure to give an oil (0.5 g). This oil was chromatographed on silica gel (10 g) and eluted with benzene to afford an oil (0.4 g). Distilation of this oil gave the title compound (0.31 g), bp 148—150° (0.0001 mmHg) (bath temp.). *Anal.* Calcd. for $C_{19}H_{20}OS$: C, 77.00; H, 6.80; S, 10.80. Found: C, 76.97; H, 6.86; S, 10.80.

1-(*p*-Bromophenyl)-2-phenyl-3-methylthiomethoxy-1,3-butadiene (IV-c)——A solution of dimethylsulfonium 2-oxo-3-phenyl-4-(*p*-bromophenyl)-3-butenylide (1.0 g) in 20 ml of EtOH was heated under reflux for 20 hr. After cooling, the solvent was evaporated under reduced pressure to give an oil (1.0 g). Distillation of this substance afforded an oil, bp 165—170° (0.0001 mmHg) (bath temp.), which crystallized on standing. Recrystallization from hexane afforded the title compound as white needles, mp 75—78° (0.3 g). *Anal.* Calcd. for $C_{18}H_{17}OSBr$: C, 59.84; H, 4.74; S, 8.85; Br, 22.12. Found: C, 59.81; H, 4.88; S, 8.82; Br, 21.77.

1,2-Diphenyl-1-buten-3-one (V)——A solution of 1,2-diphenyl-3-methylthiomethoxy-1,3-butadiene (0.51 g) in 95% ether was allowed to stand overnight. The solvent was evaporated under reduced pressure to give an oil. This oil solidified in the refrigerator overnight, the solid was collected by filtration and recrystallized from aqueous EtOH giving the title compound (0.38 g), mp 54—55°. 2,4-dinitrophenylhydrazone: mp 198—199°. *Anal.* Calcd. for $C_{22}H_{18}O_4N_4$: C, 65.66; H, 4.51; N, 13.93. Found: C, 65.60; H, 4.61; N, 14.14.

Dimethylsulfonium 1,2-Dimethoxycarbonyl-4-oxo-5,6-diphenyl-1,5-hexadien-3-ylide (IX)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (0.564 g), dimethyl acetylenedicarboxylate (0.3 g) and 15 ml of anhyd. EtOH was stirred at room temperature for 3 hr. The solvent was evaporated under reduced pressure at 35—40° to give a solid. Recrystallization from ether gave 0.45 g of pale yellow needles of the title compound, mp 139—140°. *Anal.* Calcd. for $C_{24}H_{24}O_5S$: C, 67.90; H, 5.69; S, 7.55. Found: C, 67.64; H, 5.79; S, 7.56.

Dimethylsulfonium 1-Ethoxycarbonyl-4-oxo-5,6-diphenyl-1,5-hexadien-3-ylide (X)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (0.564 g), ethyl propiolate (0.20 g) and 15 ml of anhyd. EtOH was stirred at room temperature for 24 hr. The solvent was evaporated under reduced pressure at 30—35° to give a solid. Recrystallization from benzene–hexane afforded 0.54 g of pale yellow needles of the title compound, mp 127—128°. *Anal.* Calcd. for $C_{22}H_{22}O_3S$: C, 72.11; H, 6.05; S, 8.73. Found: C, 72.51; H, 6.48; S, 8.31.

Dimethylsulfonium 1-Phenylcarbamoyl-2-oxo-3,4-diphenyl-3-butenylide (XI-a)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (1.13 g), phenylisocyanate (0.48 g) and 20 ml of anhyd. tetrahydrofuran was stirred at room temperature for 12 hr. The solvent was evaporated under reduced pressure to give a solid. Recrystallization from benzene afforded 1.5 g of colorless needles of the title compound, mp 210—212°. *Anal.* Calcd. for $C_{25}H_{23}O_2NS$: C, 74.79; H, 5.78; N, 3.49; S, 7.98. Found: C, 74.65; H, 5.85; N, 4.11; S, 7.76.

Dimethylsulfonium 1-(*p*-Bromophenylcarbamoyl)-2-oxo-3,4-diphenyl-3-butenylide (XI-b)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (1.13 g), *p*-bromophenylisocyanate (0.80 g) and 25 ml of anhyd. tetrahydrofuran was stirred at room temperature overnight. The solvent was evaporated under reduced pressure to give a solid. Recrydstallization from benzene gave 1.85 g of colorless needles of the title compound, mp 203—204°. *Anal.* Calcd. for $C_{25}H_{22}O_2NSBr$: C, 62.49; H, 4.59; S, 6.67; N, 2.91; Br, 16.63. Found: C, 62.55; H, 4.66; S, 6.53; N, 2.88; Br, 16.81.

13) All melting and boiling points are uncorrected. NMR-spectra were taken using Varian A-60 spectrometer.

Dimethylsulfonium 1-(*m*-Chlorophenylcarbamoyl)-2-oxo-3,4-diphenyl-3-butenylide (XI-c)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (1.13 g), *m*-chlorophenylisocyanate (0.614 g) and 35 ml of anhyd. tetrahydrofuran was stirred at room temperature for 24 hr. The solvent was evaporated under reduced pressure to give a solid. Recrystallization from benzene–hexane afforded 1.4 g of colorless needles of the title compound, mp 191—193°. *Anal.* Calcd. for $C_{25}H_{22}O_2NSCl$: C, 68.87; H, 5.08; N, 3.21; S, 7.35; Cl, 8.13. Found: C, 68.31; H, 5.26; N, 3.37; S, 7.26; Cl, 8.22.

Dimethylsulfonium 1-(*p*-Tolylcarbamoyl)-2-oxo-3,4-diphenyl-3-butenylide (XI-d)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (1.13 g), *p*-tolylisocyanate (0.532 g) and 35 ml of anhyd. tetrahydrofuran was stirred at room temperatufe for 24 hr. The solvent was removed under reduced pressure to give a solid. Recrystallization from benzene gave 1.3 g of colorless needles of the title compound, mp 191—193°. *Anal.* Calcd. for $C_{26}H_{25}O_2NS$: C, 75.16; H, 6.07; N, 3.37; S, 7.70. Found: C, 74.99; H, 6.20; N, 3.52; S, 7.72.

Dimethylsulfonium 1-(*p*-Nitrophenylcarbamoyl)-2-oxo-3,4-diphenyl-3-butenylide (XI-e)——A mixture of dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylide (0.40 g), *p*-nitrophenylisocyanate (0.25 g) and 15 ml of anhyd. tetrahydrofuran was stirred at room temperature for 24 hr. The solvent was removed under reduced pressure to give a solid. Recrystallization from AcOEt afforded 0.56 g of pale yellow needles of the title compound, mp 141—143°. *Anal.* Calcd. for $C_{25}H_{22}O_4N_2S$: C, 67.25; H, 4.97; N, 6.28; S, 7.16. Found: C, 67.10; H, 4.85; N, 6.11; S, 7.20.

Acknowledgement The authors are very grateful to Dr. I. Iwai, Associate Director of this Laboratories for his continued interest and encouragement in this work and also to Dr. T. Hiraoka of this laboratory for his valuable suggestion and helpful discussion in this work.