Rearrangements and Reactions of Stable Sulfonium Ylids
from Acetylenic Sulfonium Salts

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Dimethylsulfonium 2-oxo-3,4-diphenyl-3-butenylidene derivatives (Ia—c) rearranged in boiling ethanol, in a Pummerer-type fashion, to produce 1,2-diphenyl-3-methylthio-methoxy-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-butenylidene 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.

Chart 1

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

Stevens and Sommelet-Hauser³⁾ 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 occasions⁴⁾ 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 benzyldes.⁶⁾ Meanwhile, Ratts and Yao⁷⁾ have recently reported a non base-catalyzed rearrangement of phenacysulfonium ylid as shown in Chart 2.

Noticing the common partial structure, $-\text{C}(=\text{O})-\text{CH}-\text{S}^+ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$, 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).

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 ($\epsilon=13280$) (plateau) and $286\text{ m}\mu$ ($\epsilon=10900$). The nuclear magnetic resonance (NMR) spectrum⁸⁾ 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 treatment with water-ether overnight. The product, V, was identical in all respects with an authentic sample⁹⁾ prepared from benzaldehyde and phenyl 2-propanone.

TABLE I.

N	X	bp (mp) ^{a)}	Yield (%)	UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ (ϵ)
a	H	150—155 (0.0001)	51	222.5 (13280)(plateau) 286.0 (10900)
b	<i>p</i> -CH ₃	148—150 (0.0001)	62	225.0 (13400)(plateau) 291.0 (18150)
c	<i>p</i> -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. Ciencia*, **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 CDCl₃ solution.

9) R.A. Abramobitch and A. Obach, *Can. J. Chem.*, **37**, 502 (1959).

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, treatment 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 ($\epsilon=15280$) (shoulder) and 327 $\text{m}\mu$ ($\epsilon=24770$). 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 ($-\text{S}^+(\text{CH}_3)_2$), typical AB type signals at 5.34 and 8.12 ppm (2H , $J_{\text{AB}}=15$ 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 ($\epsilon=26400$) and 283 $\text{m}\mu$ ($\epsilon=27870$). The NMR spectrum exhibited a singlet at 2.74 ppm due to dimethyl-

Chart 8

XI	X	mp	Yield (%)	UV $\lambda_{\text{max}}^{\text{EtOH}}$ $\text{m}\mu$ (ϵ)
a	H	210—212	94	230.5 (26400) 283.0 (27870)
b	<i>p</i> -Br	203—204	96	231.0 (25000) 288.0 (32100)
c	<i>m</i> -Cl	192—193	80	234.0 (25240) 288.0 (29200)
d	<i>p</i> -CH ₃	191—193	78	230.0 (28090) 284.0 (25240)
e	<i>p</i> -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.

Experimental¹³⁾

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). Distillation 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-dinitrophenylhydrazones: 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. Recrystallization 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 temperature 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.

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