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Stable Sulfur Ylides. II.[1] Syntheses of Stable Sulfonium Allylides and Oxosulfonium Allylides

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Reaction of dimethyloxosulfonium- (I), dimethylsulfonium- (II), and tetramethylenesulfonium benzoylmethylide (III) with 2,2-diacetyl- and 2-acetyl-2-ethoxycarbonyl-1-ethoxyethylene (VI), in the presence of triethylamine afforded the corresponding 1-benzoyl-3,3-diacetyl- and -3-acetyl-3-ethoxycarbonylallylides (VII, VIII, and IX) in a good yield. Similar treatment of ethoxycarbonylmethyldimethyl- and ethoxycarbonyltetramethylene sulfonium bromides (IV and V) with VI gave the corresponding allylides (X and XI). These 3,3-diacetylallylides (VII and VIII) and 3-acetyl-3-ethoxycarbonylallylides (X) were hydrolyzed to the corresponding 3-acetylallylides (XII, XIII, and XIV) by treatment with dilute hydrochloric acid under a mild condition.

Two methods have been reported for the syntheses of stable allylic sulfur ylides. Kaiser, *et al.*,[3] Kishida, *et al.*,[4] and Hortmann, *et al.*[5] reported the preparation of stable oxosulfonium allylides by the Michael-type addition of dimethyloxosulfonium methylide to α-keto-acetylen derivatives. Syntheses of stable sulfonium allylides in the same manner were described by Trost,[6] Mukaiyama, *et al.*,[7] and by Payne.[8] On the other hand, Payne[8] and Tamura, *et al.*[9] described the reaction of alkoxyethylene derivativoes with ethyl dimethylsulfuranylideneacetate (EDSA) and dimethyoxosulfonium methylide to give the corresponding allylides.

Our previous paper[1] reported that dimethyloxosulfonium benzoylmethylide was converted into dimethyloxosulfonium 2-quinolylbenzoylmethylide when treated with quinoline 1-oxide in the presence of an acylating agent.

The present investigation was undertaken to synthesize the carbonyl-vinyl-stabilized sulfur ylides by the reaction of carbonyl-stabilized sulfur ylides with ethoxyethylenes under various conditions. These reactions have been found to proceed easily by the addition of triethylamine.

The reaction of dimethyloxosulfonium benzoylmethylide (I) with 1-ethoxy-2,2-diacetylethylene (VIa) in the presence of two equivalents of triethylamine gave dimethyloxosulfonium 1-benzoyl-3,3-diacetylallylide (VIIa) in 65% yield. The structure of VIIa was determined from analytical and spectral data. The infrared (IR) spectrum of VIIa showed carbonyl absorption bands at 1610 and 1660 cm^{-1}. These low frequency carbonyl absorption bands were suggestive of ylide carbonyl structure. The nuclear magnetic resonance (NMR) spectrum of VIIa showed signals at 2.15 ppm (6H, singlet) for acetyl protons, 3.65 ppm (6H, singlet) for dimethyloxosulfonium group, and 7.52 ppm (6H, multiplet) due to phenyl group and one vinyl proton. Similarly, dimethylsulfonium benzoylmethylide (II) or tetramethylenesulfonium

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[4] *a*) J. Ide and Y. Kishida, *Tetrahedron Letters*, **1966**, 1787; *b*) *Idem*, *Chem. Pharm. Bull.* (Tokyo), **15**, 360 (1967); *c*) *Idem*, *ibid.*, **16**, 784 (1968); *d*) *Idem*, *ibid.*, **16**, 793 (1968).
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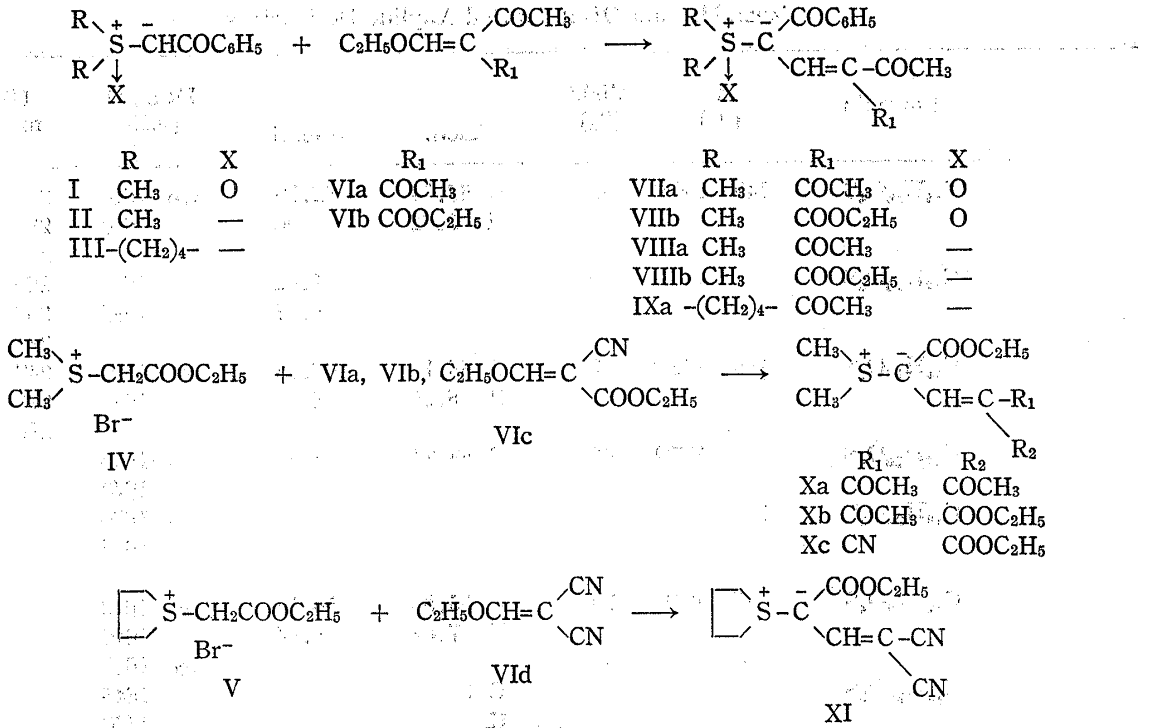

Chart 1

Table I. Reaction of I with VIa or VIb in the Presence of Various Bases

Reaction No.	Base	Time (hr)	Reactant	Product	Yield (%)
1	triethylamine (in $CHCl_3$)	3	VIa	VIIa	65
2	triton B (in $CHCl_3$)	0.5	VIa	VIIa	40
3	triethylamine (in $CHCl_3$)	3	VIb	VIIb	59
4	pyridine (in $CHCl_3$)	2	VIb	VIIb	47
5	triton B (in $CHCl_3$)	2	VIb	VIIb	71
6	diethylamine (in $CHCl_3$)	5	VIb	VIIb	no reaction
7	piperidine (in $CHCl_3$)	3	VIb	VIIb	no reaction
8	NaOH (in CH_3OH)	2	VIb	VIIb	trace

benzoylmethylide (III) was converted into the corresponding allylide (VIIIa or IXa) by reaction with VIa. Treatment of I or II with 1-ethoxy-2-acetyl-2-ethoxycarbonylethylene (VIb) afforded VIIb or VIIIb.

Table I shows the yield of VIIa and VIIb in the presence of various bases, and Table II summarizes the analytical and spectral data of these allylides.

The reaction of ethoxycarbonylmethyldimethylsulfonium bromide (IV) with VIa, VIb, and VIc in the presence of four equivalents of triethylamine gave the corresponding allylides (Xa, Xb, and Xc). Similarly, XI was obtained by the reaction of ethoxycarbonylmethyltetramethylenesulfonium bromide (V) with VId. The analytical and spectral data of these allylides are also summarized in Table II.

In order to obtain dimethyloxo- and dimethylsulfonium 1-benzoyl-2-methylthio-3,3-diacetylallylides, I and II were treated with bis(methylthio)-2,2-diacetylethylene which was expected to react in the same manner as alkoxyethylene derivatives. Unfortunately, no reaction occurred and starting materials were recovered.

It has been known that sulfur ylides are atable to bases, but relatively unstable to acids. Johnson and Amel[10] reported that stable dimethylsulfonium dibenzoylmethylide was hy-

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[10] A.W. Johnson and R.T. Amel, *J. Org. Chem.*, 34, 1240 (1969).

Table II. 3,3-Disubstituted Allylide Derivatives

Compound No.	Formula	mp (°C)	Yield (%)	Analysis (%) Calcd.	Analysis (%) Found	IR cm^{-1} (KBr)	UV λ_{max}^{EtOH} nm (log ε)
VIIa	$C_{16}H_{18}O_4S$	149—150[a]	65	C 62.74 H 5.92	62.79 5.90	ν_{CO} 1610 1660	238 (3.97) 280 (4.04) 360 (3.93)
VIIb	$C_{17}H_{20}O_5S$	137[a]	59	C 60.71 H 5.99	61.02 6.01	ν_{CO} 1631 1695	260 * 293 388
VIIIa	$C_{16}H_{18}O_3S$	160—162[b]	67	C 66.19 H 6.25	66.13 6.18	ν_{CO} 1615 1690	247 (3.94) 275 (3.97) 386 (4.28)
VIIIb	$C_{17}H_{20}O_4S$	127[c]	62	C 63.74 H 6.29	63.99 6.35	ν_{CO} 1605 1670	248 (4.06) 384 (4.32)
IXa	$C_{18}H_{20}O_3S$	156—157[c]	25	C 68.34 H 6.37	68.07 6.33	ν_{CO} 1630 1655	249 (3.96) 277 (3.97) 390 (4.23)
Xa	$C_{12}H_{18}O_4S$	97—98[d]	70	C 55.80 H 7.03	56.13 6.94	ν_{CO} 1613 1640	245 (3.76) 295 (4.01)
Xb	$C_{13}H_{20}O_5S$	81—82[d]	40	C 54.16 H 6.99	54.46 6.70	ν_{CO} 1620 1645 1700	265 (4.00) 374 (4.34)
Xc	$C_{12}H_{17}O_4NS$	139[e]	14	C 53.13 H 6.32 N 5.16	52.81 6.32 4.94	ν_{CO} 1663 1675 ν_{CN} 2190	257 (3.63) 339 (4.65)
XI	$C_{12}H_{14}O_2N_2S$	174[b]	18	C 57.59 H 5.64 N 11.20	57.56 5.69 11.48	ν_{CO} 1670 ν_{CN} 2200	260 (3.77) 340 (4.59)

recrystallized from *a*) acetone–ether, *b*) acetone, *c*) benzene–ether, *d*) ether, *e*) methanol–ether
* sparingly soluble (log ε could not be calculated)

drolyzed to phenacyldimethylsulfonium chloride and benzoic acid with dilute hydrochloric acid. When VIIa was treated with 10% hydrochloric acid in ethanol at room temperature, a new vinyl stabilized sulfur ylide, *trans*-dimethyloxosulfonium 1-benzoyl-3-acetylallylide (XIIa) was obtained. The structure of XIIa was determined from analytical and spectral data. The NMR spectrum of XIIa showed three protons of acetyl at 2.12 ppm and a new doublet signal at 5.98 ppm (1H, J=16 Hz), compared with that of VIIa. By the use of the spin decoupling technique, another hidden signal which coupled with the proton at 5.98 ppm, was found at 7.64 ppm.

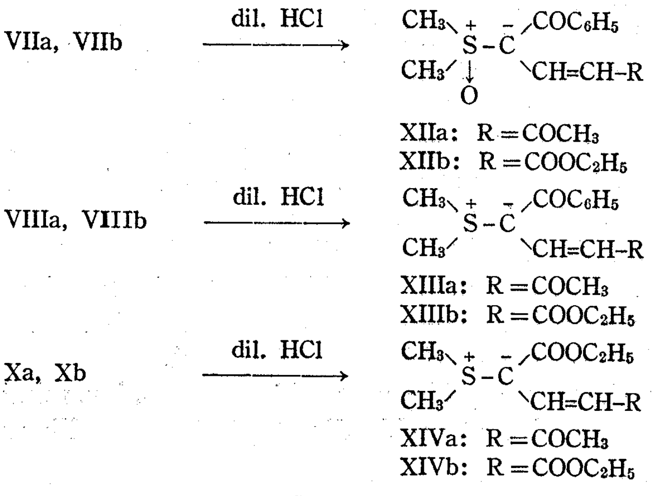

Chart 2

TABLE III. 3-Substituted Allylide Derivatives

Compound No.	Formula	mp (°C)	Yield (%)	Analysis (%) Calcd.	Analysis (%) Found	IR cm^{-1} (KBr)	UV λ_{max}^{EtOH} nm (log ε)	NMR ($CDCl_3$) -CH=CH- ppm (Hz)
XIIa	$C_{14}H_{16}O_3S$	174—175[a]	70	C 63.62 H 6.10	63.99 6.17	ν_{CO} 1629 1655	240 (3.94) 292 (4.00) 348 (4.26)	5.98 (J=16) 7.64 (J=16)
XIIb	$C_{15}H_{18}O_4S$	150[a]	35	C 61.21 H 6.17	61.61 6.02	ν_{CO} 1690	237 (4.03) 286 (4.07) 326 (4.20)	5.72 (J=15) 7.70 (J=15)
XIIIa	$C_{14}H_{16}O_2S$	168[a]	70	C 67.73 H 6.50	67.40 6.45	ν_{CO} 1642	231 (3.86) 358 (4.52)	5.81 (J=15) 7.76 (J=15)
XIIIb	$C_{15}H_{18}O_3S$	171[a]	46	C 64.73 H 6.52	64.96 6.04	ν_{CO} 1675	228 (3.96) 336 (4.43)	5.36 (J=15) 7.84 (J=15)
XIVa	$C_{10}H_{16}O_3S$	143[b]	85	C 55.54 H 7.46	55.82 7.30	ν_{CO} 1630 1645	270 (3.68) 351 (4.60)	5.90 (J=15) 7.88 (J=15)
XIVb	$C_{11}H_{18}O_4S$	92—93[b]	35	C 53.65 H 7.37	53.37 7.30	ν_{CO} 1625 1670	280 (3.90) 327 (4.55)	5.40 (J=15) 7.84 (J=15)

recrystallized from a) acetone–ether, b) ether

Similarly, treatment of VIIb, VIIIa, VIIIb, Xa and Xb with dilute hydrochloric acid gave easily corresponding *trans*-3-monoacetylallylide derivatives, respectively. The analytical and spectral data of these ylides are summarized in Table III.

Experimental

All the melting points were uncorrected. NMR spectra were measured with a JNM-PS-100 (JEOL) spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded with an IRA-2 (JASCO) spectrophotometer.

Preparation of VIIa, VIIb, VIIIa, VIIIb, and IX——The following preparation of dimethyloxosulfonium 1-benzoyl-3-acetyl-3-ethoxycarbonylallylide (VIIb) illustrates the general procedure: To a solution of dimethyloxosulfonium benzoylmethylide (0.98 g, 0.005 mole) and 1-ethoxy-2-acetyl-2-ethoxycarbonylethylene (0.93 g, 0.005 mole) in 30 ml of $CHCl_3$, Et_3N (1.0 g, 0.01 mole) in 10 ml of $CHCl_3$ was added, the mixture was refluxed for 2 hr, and the deep red solution was evaporated under a reduced pressure. The residue was purified by column chromatography (silica gel) and elution of the column with benzene–acetone (10: 1) gave 1.0 g (59%) of VIIb. A sample was recrystallized from acetone–ether to give yellow crystals, mp 137°. NMR ($CDCl_3$) ppm: 3.68 (6H, dimethyloxosulfonium), 2.21 (3H, acetyl), 7.81 (1H, vinyl), 1.21 and 4.0 (5H, ester), 7.4—7.7 (5H, aromatic).

Preparation of Xa, Xb, Xc, and XI——The following preparation of dimethylsulfonium 1-ethoxycarbonyl-3,3-diacetylallylide (Xa) illustrates the general procedure: To a solution of ethoxycarbonylmethyldimethylsulfonium bromide (2.29 g, 0.01 mole) and 1-ethoxy-2,2-diacetylethylene (1.56 g, 0.01 mole) in 30 ml of $CHCl_3$, Et_3N (4.0 g, 0.04 mole) in 10 ml of $CHCl_3$ was added, the mixture was stirred for 5 hr at room temperature, and the red solution was washed with water and dried over Na_2SO_4. The solvent was evaporated and the precipitated solid was collected and recrystallized from ether to give 1.8 g (70%) of Xa, mp 97—98°. NMR ($CDCl_3$) ppm: 2.99 (6H, dimethylsulfonium), 2.26 (6H, acetyl), 1.13 and 4.21 (5H, ester), 8.17 (1H, vinyl).

Preparation of XIIa, XIIb, XIIIa, XIIIb, XIVa, and XIVb——The following preparation of dimethylsulfonium 1-ethoxycarbonyl-3-acetylallylide (XIVa) illustrates the general procedure: A mixture of 10% HCl (20 ml) and Xa (2.58 g, 0.01 mole) was stirred at room temperature for 2 hr. The reaction mixture was basified with 10% Na_2CO_3, extracted with $CHCl_3$, and the extract was dried over Na_2SO_4. Evaporation of the solvent under a reduced pressure and the residue was recrystallized from acetone–ether to give 2.4 g (85%) of XIVa, mp 143° (reported[8]) mp 144—146°). NMR ($CDCl_3$) ppm: 2.95 (6H, dimethylsulfonium), 2.15 (3H, acetyl), 1.30 and 4.19 (5H, ester), 5.90 and 7.88 (2H, vinyl, J=15 Hz).

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