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Stable Sulfur Ylides. V.[1] Syntheses of α-Acylfuran Derivatives by Thermal and Photochemical Reaction of Allylides

MITSUAKI WATANABE, MITSUKI BABA, TOSHIO KINOSHITA,
and SUNAO FURUKAWA

Faculty of Pharmaceutical Sciences, Nagasaki University[2]

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The reactions of tetramethylenesulfonium acylmethyl bromides (I) with 1-ethoxy-2,2-diacylethylenes (II) in the presence of triethylamine in chloroform under reflux afforded α-acylfuran derivatives (IV) and tetramethylenesulfonium 1,3,3-triacylallylides (III). The thermolysis or irradiation of these allylides (III) were converted to corresponding furan derivatives (IV). In the case of irradiation of dimethylsulfonium (and dimethyloxosulfonium) 1-benzoyl-3-acetyl-3-ethoxycarbonylallylide (VIIIcB and VIcB) gave 2-methyl-3-ethoxycarbonyl-5-benzoylfuran (IVcB) and 2-ethoxy-3-acetyl-5-benzoylfuran (X) which was could not be obtained by thermolysis of VIcB and VIIIcB.

The irradiation of dimethyloxosulfonium 1-benzoyl-3-acetylallylide (XI) in methanol using Pyrex filter gave dimethyloxosulfonium 1-oxo-4-acetyl-2-naphthylide (XII) in 8% yield.

Syntheses of furan derivatives by use of sulfur ylides have been studied by several groups.[3] Recently Tamura, *et al.*,[4] reported that the reaction of 1-ethoxy-2,2-diacetylethylene with equimolar of dimethyloxosulfonium methylide in dimethylsulfoxide at room temperature afforded 2-methyl-3-acetyl-4-ethoxy-4,5-dihydrofuran and 2-methyl-3-acetylfuran.

Our previous paper[5] reported the syntheses of carbonyl-vinyl-stabilized sulfur ylides (IIIcA, VIcA, VIcB, VIIIbA, VIIIbB, VIIIcA, and VIIIcB). In this paper, we examined in detail the reaction conditions of the syntheses of carbonyl-vinyl-stabilized sulfur ylides and these ylides gave corresponding α-acylfuran derivatives in fair yield by thermal and irradiation reactions.

The reaction of tetramethylenesulfonium ethoxycarbonylmethyl bromide (Ib) with 1-ethoxy-2,2-diacetylethylene (IIA) in the presence of triethylamine in chloroform under reflux for 5 hr gave 2-methyl-3-acetyl-5-ethoxycarbonylfuran (IVbA), mp 96—98° (lit. mp 75—77°,[3d] mp 107—109°[4]), the infrared absorption (IR), ultraviolet absorption (UV), and nuclear magnetic resonance (NMR) spectral data are in good agreement with the reported data.[3d] The reaction of tetramethylenesulfonium acetylmethyl bromide (Ia) with IIA or 1-ethoxy-2-acetyl-2-ethoxycarbonylethylene (IIB) in the same manner afforded 2-methyl-3,4-diacetylfuran (IVaA) or 2-methyl-3-ethoxycarbonyl-5-acetylfuran (IVaB) in 18% or 20% yield, respectively. Similar reaction of tetramethylenesulfonium benzoylmethyl bromide (Ic) with 1-ethoxy-2-acetyl-2-benzoylethylene (IIC) gave 2-phenyl-3-acetyl-5-benzoylfuran (IVcC) in 20% yield. When the mixture (Ic and IIC) was refluxed for 2 hr, tetramethylenesulfonium 1,3-dibenzoyl-3-acetylallylide (IIIcC, 26%) was obtained accompanied with

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[1] Part IV: M. Watanabe, M. Kodera, T. Kinoshita, and S. Furukawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 2598 (1975).

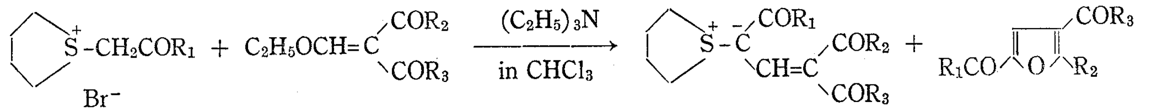
[2] Location: *1-14 Bunkyo-machi, Nagasaki, 852, Japan.*

[3] *a*) T.M. Harris, C.M. Harris, and J.C. Cleary, *Tetrahedron letters*, **1968**, 1427; *b*) H. Takei, M. Higo, K. Saito, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **41**, 1738 (1968); *c*) M. Higo and T. Mukaiyama, *Tetrahedron Letters*, **1970**, 2565; *d*) Y. Hayashi, M. Kobayashi, and H. Nozaki, *Tetrahedron*, **26**, 4353 (1970).

[4] Y. Tamura, H. Taniguchi, T. Miyamoto, M. Tsunekawa, and M. Ikeda, *J. Org. Chem.*, **39**, 3519 (1974).

[5] M. Watanabe, T. Kinoshita, and S. Furukawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 82 (1975).

TABLE I. Reactions of Sulfonium Salts with Ethoxyethylene Derivatives



I II III IV

	R_1
Ia :	CH_3
Ib :	OC_2H_5
Ic :	C_6H_5

	R_2	R_3
IIA :	CH_3	CH_3
IIB :	CH_3	OC_2H_5
IIC :	C_6H_5	CH_3

	R_1	R_2	R_3
IIIaC :	CH_3	C_6H_5	CH_3
IIIbC :	OC_2H_5	C_6H_5	CH_3
IIIcA :	C_6H_5	CH_3	CH_3
IIIcC :	C_6H_5	C_6H_5	CH_3

	R_1	R_2	R_3
IVa A :	CH_3	CH_3	CH_3
IVa B :	CH_3	CH_3	OC_2H_5
IVb A :	OC_2H_5	CH_3	CH_3
IVb B :	OC_2H_5	CH_3	OC_2H_5
IVc A :	C_6H_5	CH_3	CH_3
IVc B :	C_6H_5	C_6H_5	CH_3

Starting material		Reaction		Reaction product			
I	II	Temp (°C)	Time (hr)	III	Yield (%)	IV	Yield (%)
Ia	IIA	reflux	5		—	IVaA	18
Ia	IIB	reflux	5		—	IVaB	20
Ia	IIC	25	3	IIIaC	74		—
Ib	IIA	reflux	5		—	IVbA	30
Ib	IIB	reflux	5		—	IVbB	15
Ib	IIC	reflux	5	IIIbC	49		—
Ic	IIA	25	3	IIIcA	34	IVcA	35
Ic	IIA	reflux	5	IIIcA	25	IVcA	45
Ic	IIC	25	3	IIIcC	94		—
Ic	IIC	reflux	2	IIIcC	26	IVcC	14
Ic	IIC	reflux	5		—	IVcC	20

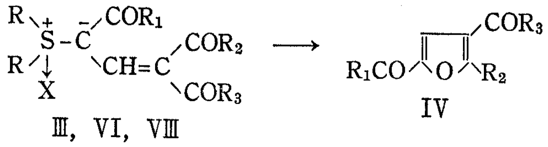
furan derivatives (IVcC, 14%). While a mixture of Ic and IIC standing at room temperature for 2 hr gave IIIcC as sole product in 94% yield. Table I shows the stable ylides (III) and furan derivatives (IV) produced by the reaction of several tetramethylenesulfonium salts (I) with ethoxyethylene derivatives (II).

As described procedure in a previous paper,[5] the reaction of IIC with dimethyloxosulfonium benzoylmethylide (Vc), dimethylsulfonium ethoxycarbonylmethyl bromide (VIIb), or dimethylsulfonium benzoylmethyl bromide (VIIc) gave corresponding carbonyl-vinyl-stabilized sulfur ylides (VIcC, VIIIbC, or VIIIcC) in 84%, 85%, or 80% yield in the presence of triethylamine in chloroform at room temperature, respectively. These structures were determined by the elemental and spectral analyses (Table IV).

In order to prove the thermolysis process, following reactions were examined. Dimethylsulfonium 1-benzoyl-3,3-diacetyallylide (VIIIcA) was heated at 150° in the absence of solvent for 3 hr to produce 2-methyl-3-acetyl-5-benzoylfuran (IVcA) with evolution of dimethylsulfide. The structure of IVcA was determined on the bases of elemental, IR (carbonyl absorption at 1720 cm^{-1} and 1667 cm^{-1}), and NMR (acetyl at 2.46 ppm, methyl at 2.73 ppm, β-position of furan at 7.44 ppm, and phenyl at 7.52—8.04 ppm) data. Similar thermolyses were examined to several allylides and the results are summarized in Table II. By the thermolyses at 150° for 2—3 hr, all of the allylides (III, VI, and VIII) were converted to furan derivatives in good yield except few allylides.

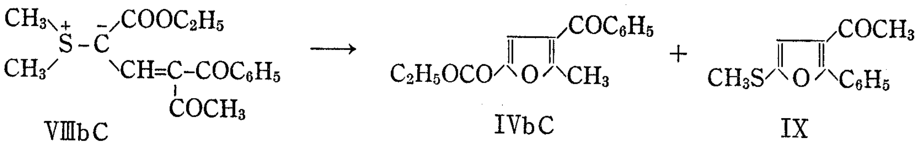
When dimethylsulfonium 1-ethoxycarbonyl-3-acetyl-3-benzoylallylide (VIIIbC) was heated at 150° for 4 hr, two compounds (IVbC and IX) were obtained. The structures of these compounds were established by elemental analyses and spectral data. But analogous compound of IX could not be obtained by the thermolyses of other allylides. Thermolysis of VIIIbC was examined under several conditions: starting material was recovered quantitatively in xylene solution for 3 hr, in decalin solution IVbC was obtained as sole product. These

Table II. Thermolyses of Allylides



	Starting material					Reaction			Product			Yield (%)
	R	X	R_1	R_2	R_3	Temp (°C)	Time (hr)		R_1	R_2	R_3	
IIIaC	$-(CH_2)_4-$	—	CH_3	CH_3	C_6H_5	150	2	IVaC	CH_3	CH_3	C_6H_5	22
IIIcA	$-(CH_2)_4-$	—	C_6H_5	CH_3	CH_3	150	3	IVcA	C_6H_5	CH_3	CH_3	30
IIIcC	$-(CH_2)_4-$	—	C_6H_5	C_6H_5	CH_3	150	2	IVcC	C_6H_5	C_6H_5	CH_3	trace
VIcA	CH_3	O	C_6H_5	CH_3	CH_3	160	3	IVcA	C_6H_5	CH_3	CH_3	70
VIcB	CH_3	O	C_6H_5	CH_3	OC_2H_5	150	3	IVcB	C_6H_5	CH_3	OC_2H_5	50
VIIIbA	CH_3	—	OC_2H_5	CH_3	CH_3	150	3	IVbA	OC_2H_5	CH_3	CH_3	65
VIIIbB	CH_3	—	OC_2H_5	CH_3	OC_2H_5	150	3	IVbB	OC_2H_5	CH_3	OC_2H_5	75
VIIIcA	CH_3	—	C_6H_5	CH_3	CH_3	150	3	IVcA	C_6H_5	CH_3	CH_3	85
VIIIcC	CH_3	—	C_6H_5	C_6H_5	CH_3	150	2	IVcC	C_6H_5	C_6H_5	CH_3	trace

Table III. Thermolysis of VIIIaC



Reaction number	Solvent	Reaction		IVbC Yield(%)	IX Yield(%)	Recovery of VIIIbC (%)
		Temp (°C)	Time (hr)			
1	—	150	1	33	—	28
2	—	150	2	30	10	—
3	—	150	4	35	trace	—
4	xylene	120	3	—	—	100
5	xylene	150	3	—	—	100
6	xylene	150	24	33	10	—
7	decalin	190	4	39	—	—

results are shown on Table III. Hydrolysis of IVbB[3a)] or IVbC with sodium ethoxide in ethanol gave the corresponding carboxylic acid derivative (IVbB′ or IVbC′).

Table V shows the analytical and the spectral data of furan derivatives obtained here.

From the experiments presented above, it may be assumed that the zwitterionic intermediate exists in this thermal reaction. Similar intermediates have been described by Tamura, *et al.*[6)] and Gaudiano, *et al.*,[7)] respectively.

The photochemical reactions of stable ylides have been described by Corey, *et al.*,[8)] Trost,[9)] and Nozaki, *et al.*[10)] Kishida, *et al.*[11)] reported that the irradiation of dimethyloxosulfonium 2-phenyl-3-ethoxycarbonylallylide in tetrahydrofuran for 10 hr gave 1,4-diphenyl-2,5-diethoxycarbonylbenzene in 0.9% yield.

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6) Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi, and M. Ikeda, *J. Org. Chem.*, **38**, 4324 (1973).

7) G. Gaudiano, A. Umani-Ronchi, P. Bravo, and M. Acempora, *Tetrahedron Letters*, **1967**, 107.

8) E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964).

9) B.M. Trost, *J. Am. Chem. Soc.*, **88**, 1587 (1966).

10) H. Nozaki, M. Takaku, D. Tunemoto, Y. Yamamoto, and K. Kondo, *Nippon Kagaku Zasshi*, **88**, 1 (1967).

11) Y. Kishida, T. Hiraoka, and J. Ide, *Chem. Pharm Bull.* (Tokyo), **17**, 591 (1969).

Irradiation of dimethyloxosulfonium 1-benzoyl-3,3-diacetylallylide (VIcA) or dimethylsulfonium 1-benzoyl-3,3-diacetylallylide (VIIIcA) in methanol for 1 hr gave IVcA in 38.3% or 13% yield, respectively. The same product (IVcA) was obtained by the thermolysis of VIcA as described above.

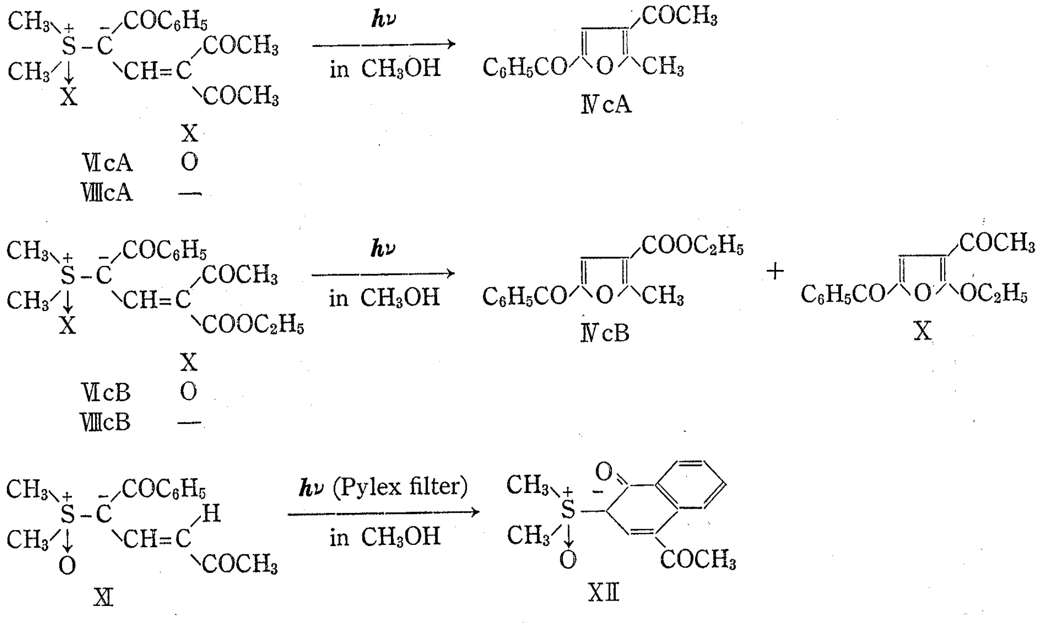


Chart 1

On the other hand, irradiation of dimethyloxosulfonium 1-benzoyl-3-acetyl-3-ethoxycarbonylallylide (VIcB) in methanol for 50 min gave two products which were purified by chromatography on silica gel. The first substance (IVcB), $C_{15}H_{14}O_4$, obtained in 21.7% yield, melted at 48°. The second substance (X), $C_{15}H_{14}O_4$, obtained in 44.7% yield, melted at 110—111°. IVcB was identified with an authentic sample, which was obtained by thermolysis of VIcB, by mixed melting point and comparison of IR spectra. The NMR spectrum of X showed signals at 1.60 ppm (3H, triplet) and 4.78 ppm (2H, qualtet) due to ethoxy group, 2.46 ppm (3H, singlet) due to acetyl group, and 7.48—7.96 ppm (6H, multiplet) due to phenyl and β-position of furan. The IR spectrum of X showed two carbonyl absorption at 1661 cm^{-1} and 1635 cm^{-1}. Thus the structure of X was established as 2-ethoxy-3-acetyl-5-benzoylfuran. Similarly, dimethylsulfonium 1-benzoyl-3-acetyl-3-ethoxycarbonylallylide (VIIIcB) was converted to IVcB and X in 17.3% and 12.3% yield, respectively. The compound (X) was not obtained by the thermal reaction of VIcB.

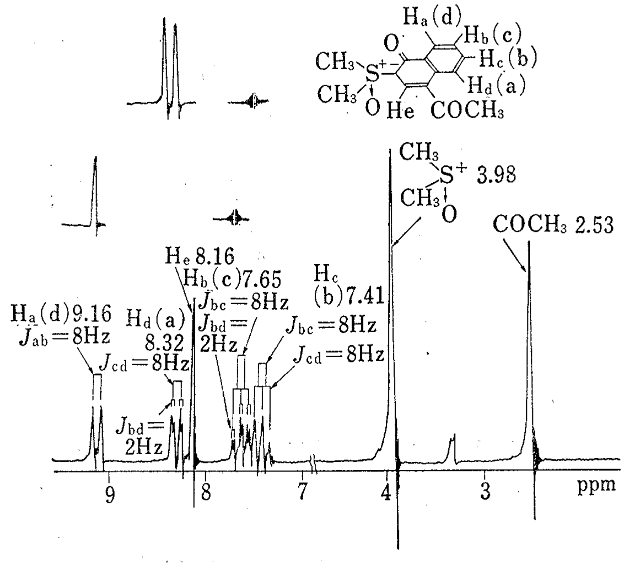


Fig. 1. NMR Spectrum of XII in DMSO-d_6

Although the compounds (VIcB and VIIIcB) were considered two isomers (*E* and *Z* type), these were ascertained as sole component by NMR spectra. The thermal reaction of these compounds gave only one product, so *E* type isomer was suggested. In the irradiation reaction of VIcB (and VIIIcB), two isomeric furan derivatives were obtained, so that the carbon-carbon double bond should be rotated followed by cyclized to furan ring.

When the same photochemical reaction was carried out on dimethyloxosulfonium 3-monoacylallylide in place of 3,3-diacylallylides, a novel product was obtained. The irradiation of *trans*-dimethyloxosulfonium 1-benzoyl-3-acetylallylide[5] (XI) in methanol using Pyrex filter for 3 hr gave a new system ylide (XII) in 8% yield. The NMR spectrum (Fig. 1) of XII showed signals at 2.53 ppm (3H, singlet, acetyl), 3.98 ppm (6H, singlet, dimethylsulfonium group), and 7.41—9.16 ppm (5H, aromatic ring). The five aromatic protons were distinguished as following description: H*a*(*d*), 9.16 ppm (doublet), H*b*(*c*), 7.65 ppm (triple-doublet), H*c*(*b*), 7.41 ppm (double-doublet), H*d*(*a*), 8.32 ppm (double-doublet), H*e*, 8.16 ppm (singlet). The IR spectrum of XII showed carbonyl absorption at 1620 cm^{-1} and 1570 cm^{-1}, these low frequency were suggestive of ylide carbonyl structure. Above results suggested that XII was dimethyloxosulfonium 1-oxo-4-acetyl-2-naphthylide.

Further work is in progress on the chemical reactivity of carbonyl-vinyl-stabilized sulfur ylides.

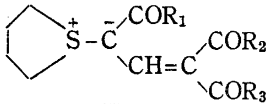
Experimental

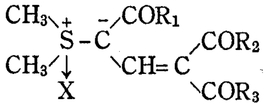
All the melting points are uncorrected. NMR spectra were recorded on a JNM-PS-100 (JEOL) spectrometer using tetramethylsilane as an internal standard. IR spectra were taken on an IRA-2 (JASCO) spectrophotometer. UV spectra were taken on an EPS-2 (Hitachi) spectrophotometer. A Nikko high-pressure 100 W mercury lamp was employed in all irradiations.

The analytical and spectral data of allylides and furan derivatives listed in Table IV and Table V, respectively.

Reactions of I with II——The following reaction of tetramethylenesulfonium benzoylmethyl bromide (Ic) with 1-ethoxy-2-acetyl-2-benzoylethylene (IIC) illustrates the general procedure: To a solution of Ic (5.7 g, 0.02 mole) and IIC (4.4 g, 0.02 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 refluxed for 2 hr, and the solution was washed with water and dried over Na_2SO_4. The solvent was evaporated and the residue was dissolved in a small amount of benzene, and chromatographed over a silica gel column. The first compound obtained from elution with benzene was recrystallized from

TABLE IV. Some Properties of Carbonyl-vinyl-stabilized Sulfur Ylides


III


VI, VIII

Compound number					Formula	mp (°C)		Analysis (%)		IR (KBr) cm^{-1}	UV λ_{max}^{EtOH} nm (log ε)
	X	R_1	R_2	R_3				Calcd.	Found		
IIIaC	—	CH_3	C_6H_5	CH_3	$C_{18}H_{20}O_3S$	142—144[a)]	C H S	68.34 6.37 10.13	68.21 6.38 9.87	ν_{co} 1627 1598	255.5 (4.09) 349 (4.29)
IIIbC	—	OC_2H_5	C_6H_5	CH_3	$C_{19}H_{22}O_4S$	123—124[b)]	C H S	65.88 6.40 9.26	65.90 6.54 9.14	ν_{co} 1655 1635 1618	254 (4.17) 344 (4.33) 390 (4.07)
IIIcC	—	C_6H_5	C_6H_5	CH_3	$C_{23}H_{22}O_3S$	145—146[a)]	C H S	73.00 5.86 8.47	73.02 5.81 8.18	ν_{co} 1626 1580	251 (4.24) 350 (4.27)
VIcC	O	C_6H_5	C_6H_5	CH_3	$C_{21}H_{20}O_4S$	167—168[a)]	C H S	68.47 5.47 8.68	68.16 5.41 8.53	ν_{co} 1635 1589 1565	252 (4.20) 284 (4.03) 388 (4.03)
VIIIbC	—	OC_2H_5	C_6H_5	CH_3	$C_{17}H_{20}O_4S$	138—139[a)]	C H S	63.74 6.29 10.01	63.92 6.05 9.97	ν_{co} 1655 1620	253 (4.19) 342 (4.28) 380 (4.07)
VIIIcC	—	C_6H_5	C_6H_5	CH_3	$C_{21}H_{20}O_3S$	187—188[a)]	C H S	71.58 5.72 9.10	71.71 5.64 9.10	ν_{co} 1625 1587 1570	254 (4.29) 342 (4.09)

recrystallized from *a*) benzene *b*) ether

ether to give 0.81 g (14%) of IVcC, mp 115°. The second compound obtained from elution with benzene–acetone (10: 1) was recrystallized from benzene to give 1.96 g (26%) of IIIcC, mp 145—146°.

Preparations of VI and VIII——The following preparation of dimethyloxosulfonium 1,3-dibenzoyl-3-acetylallylide (VIcC) illustrates the general procedure: To a solution of dimethyloxosulfonium benzoylmethylide (3.9 g, 0.02 mole) and IIC (4.4 g, 0.02 mole) in 30 ml of $CHCl_3$, Et_3N (2.0 g, 0.02 mole) in 10 ml of $CHCl_3$ was added, the mixture was stirred at room temperature for 3 hr, and the deep red solution was evaporated under a reduced pressure. The residue was purified through a silica gel column. The column was eluted with benzene–acetone (10: 1) to afford 6.2 g (84%) of VIcC. A sample was recrystallized from benzene to give yellow crystals, mp 167—168°.

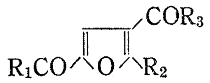
Thermolyses of III, VI, and VIII——The following thermolysis of dimethylsulfonium 1-ethoxycarbonyl-3,3-diacetylallylide (VIIIbA) illustrates the general procedure: VIIIbA (2.6 g, 0.01 mole) was heated at 150° for 3 hr in oil bath. To the resultant oil, H_2O was added and this was extracted with $CHCl_3$ and the extract was dried over Na_2SO_4. The solvent was evaporated and the residue was purified through a silica gel column. The compound obtained from elution with benzene was recrystallized from ether to give 1.5 g (65%) of IVbA, mp 96—98°.

Thermolysis of VIIIbC——A solution of 1.6 g (0.005 mole) of VIIIbC in 20 ml of xylene was refluxed for 24 hr. The solvent was removed under a reduced pressure and the residual oil was purified through an alumina column. The compound obtained from elution with benzene was recrystallized from ether to give 0.1 g (10%) of IX, mp 128—129°. From the mother liquor, IVbC was obtained in 33% yield as viscous oil.

Hydrolyses of IVbB and IVbC——To a solution of Na (0.12 g, 0.005 mole) dissolved in EtOH (10 ml), 1.1 g (0.005 mole) of IVbB was added and the mixture was refluxed for 3 hr. After the solvent was evaporated, H_2O was added to the residue and this aqueous solution was acidified with 10% HCl. The precipitated solid was collected and recrystallized from ether to give 0.7 g (80%) of IVbB′, mp 255°. Similarly, when IVbC was treated by the same manner described above, IVbC′ was obtained in 85% yield.

Irradiations of VIcA and VIIIcA——The following irradiation of dimethyloxosulfonium 1-benzoyl-3,3-diacetylallylide (VIcA) illustrates the general procedure: A solution of 0.92 g (0.003 mole) of VIcA in 200 ml of MeOH was irradiated with ultraviolet lamp for 1 hr. The solvent was evaporated under a reduced pressure.

Table V. Some Properties of Furan Derivatives



Compound number				Formula	mp (°C)	Analysis (%)			IR (KBr) ν_{co} cm^{-1}	UV λ_{max}^{EtOH} nm (log ε)
	R_1	R_2	R_3				Calcd.	Found		
IVaA	CH_3	CH_3	CH_3	$C_9H_{10}O_3$	94— 95$^{a)}$	C H	65.05 6.07	64.89 6.14	1720	277(4.42)
IVaB	CH_3	CH_3	OC_2H_5	$C_{10}H_{12}O_4$	75— 77$^{a)}$	C H	61.21 6.17	61.25 6.03	1718	275(4.20)
IVaC	CH_3	C_6H_5	CH_3	$C_{14}H_{12}O_3$	84— 86$^{a)}$	C H	73.67 5.30	73.40 5.22	1650	257(4.20) 278(4.28)
IVbA	OC_2H_5	CH_3	CH_3	$C_{10}H_{12}O_4$	96— 98$^{a)}$	C H	61.21 6.17	61.28 6.18	1720 1667	259(4.22)
IVcA	C_6H_5	CH_3	CH_3	$C_{14}H_{12}O_3$	122—123$^{a)}$	C H	73.67 5.30	73.52 5.39	1720 1667	259(4.22)
IVcB	C_6H_5	CH_3	OC_2H_5	$C_{15}H_{14}O_4$	48$^{b)}$	C H	69.75 5.46	69.92 5.45	1717 1647	259(4.00) 293(4.29)
IVcC	C_6H_5	C_6H_5	CH_3	$C_{19}H_{14}O_3$	115$^{a)}$	C H	78.60 4.85	78.86 4.80	1670 1635	320(4.29)
IVbB′	OH	CH_3	OH	$C_7H_6O_5$	255$^{a)}$	C H	49.42 3.56	49.81 3.68	1700	251(4.16)
IVbC′	OH	C_6H_5	CH_3	$C_{13}H_{10}O_4$	134$^{c)}$	C H	67.82 4.38	67.52 4.28	1690 1654	252(4.30)
IX	($S-CH_3$)	C_6H_5	CH_3	$C_{13}H_{12}O_2S$	128—129$^{a)}$	C H S	67.23 5.21 13.78	67.16 5.14 13.72	1692	253(3.99)
X	C_6H_5	OC_2H_5	CH_3	$C_{15}H_{14}O_4$	110—111$^{a)}$	C H	69.75 5.46	69.61 5.50	1661 1635	261(4.15) 321(4.30)

recrystallized from *a*) ether *b*) petroleum ether *c*) ether–cyclohexane

The precipitated solid was collected and recrystallized from ether to give 0.26 g (38%) of IVcA, mp 122—123°. Similarly, when VIIIcA was treated by the same manner described above, IVcA was obtained in 13% yield.

Irradiations of VIcB and VIIIcB——The following irradiation of dimethyloxosulfonium 1-benzoyl-3-acetyl-3-ethoxycarbonylallylide (VIcB) illustrates the general procedure: A solution of 1.0 g (0.003 mole) of VIcB in 200 ml of MeOH was irradiated with ultraviolet lamp for 50 min. After the solvent was evaporated, the residue was dissolved in a small amount of benzene. The solution was chromatographed over a silica gel column, elution with benzene gave oil. The starting material was recovered in 33% yield from elution with benzene–acetone (20: 1). Above oily product was rechromatographed over a silica gel column, elution with benzene gave crystals, which were recrystallized from petroleum ether to give 0.17 g (22%) of IVcB, mp 48°. The compound obtained from elution with benzene–acetone (20: 1) was recrystallized from ether to give 0.35 g (45%) of X, mp 110—111°. Similarly, when VIIIcB was treated by the same manner described above, IVcB and X were obtained in 17.3% and 12.3% yield, respectively, accompanied with the starting material (9%).

Irradiation of XI——A solution of 1.58 g (0.006 mole) of XI in 200 ml of MeOH was irradiated with ultraviolet lamp using Pyrex filter for 3.5 hr. After the solvent was evaporated under a reduced pressure, the residue was washed with a small amount of ether and recrystallized from acetone to give 0.13 g (8%) of XII, mp 272°. *Anal.* Calcd. for $C_{14}H_{14}O_3S$: C, 64.11; H, 5.38; S, 12.20. Found: C, 63.71; H, 5.29; S, 11.99. Mass Spectrum *m/e* (%): 262 (M^+, 71), 247 (M^+-CH_3, 100), 232 (M^+-2CH_3, 9), 217 (M^+-3CH_3, 12), 112 ($217-C_6H_5CO$, 14), 43 (CH_3CO^+, 33). UV λ_{max}^{EtOH} nm (log ε): 231 (4.45), 259 (4.27), 264 (4.27), 330 (4.27), 349 (4.27), 365 (4.12).

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