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Studies on Acetylenic Compounds. XLIV.[1] Sulfoxonium Ylide Chemistry. I. Formation of Stable Sulfoxonium Ylides from Acetylenic Compounds

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Dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide derivatives (III-a—f) were prepared from ethyl phenylpropionate derivatives and dimethylsulfoxonium methylide (II) and its addition mechanism were considered. III-a was reacted with dimethyl acetylenedicarboxylate, ethyl propionate, benzoyl chloride to afford dimethylsulfoxonium 1,2-dimethoxycarbonyl-5-ethoxycarbonyl-4-phenyl-1,4-pentadien-3-ylide (VII), dimethylsulfoxonium 1,5-diethoxycarbonyl-4-phenyl-1,4-pentadien-3-ylide (VIII) and dimethylsulfoxonium 1-benzoyl-3-ethoxycarbonyl-2-phenylallylide (IX), respectively. Dimethylsulfoxonium 1-phenylcarbamoyl-3-ethoxycarbonyl-2-phenylallylide derivatives (X-a—i) were prepared from III and phenylisocyanate derivatives.

The stability of ylides is enhanced by the presence of substituents, such as carbonyl and other electron withdrawing groups, which situate in an alpha position to the ylide-carbanion. Thus, those substituents stabilize the ylides through resonance hybridization of negative charge of the ylide-carbanions.[3-15]

Among those stabilized ylides, involving phosphonium, sulfonium and, in rare case, sulfoxonium,[16-19] 2-(α-cyanotriphenylphosphonium)-1,2-dimethoxycarbonylethylene[20] has been

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[1] Part XLIII: I. Iwai and N. Nakamura, *Chem. Pharm. Bull.* (Tokyo), **14**, 1277 (1966).

[2] Location: *Hiromachi, Shinagawa-ku, Tokyo.*

[3] O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).

[4] H.O. House and G. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961).

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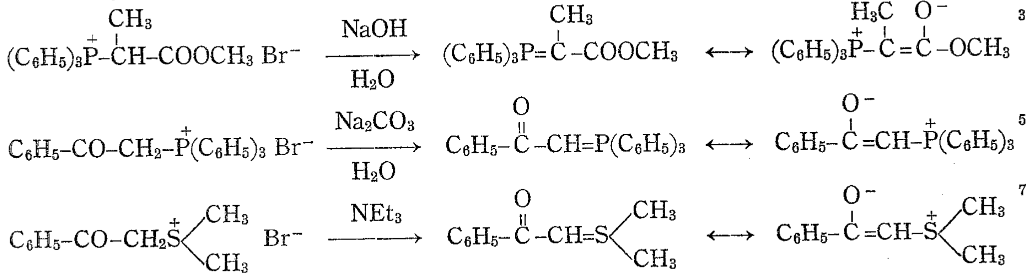

$$(C_6H_5)_3\overset{+}{P}\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}COOCH_3\ Br^- \xrightarrow[H_2O]{NaOH} (C_6H_5)_3P{=}\overset{CH_3}{\overset{|}{C}}\text{-}COOCH_3 \longleftrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\overset{H_3C}{\overset{|}{C}}{=}\overset{O^-}{\overset{|}{C}}\text{-}OCH_3$$

3,4)

$$C_6H_5\text{-}CO\text{-}CH_2\text{-}\overset{+}{P}(C_6H_5)_3\ Br^- \xrightarrow[H_2O]{Na_2CO_3} C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}P(C_6H_5)_3 \longleftrightarrow C_6H_5\text{-}\overset{O^-}{\overset{|}{C}}{=}CH\text{-}\overset{+}{P}(C_6H_5)_3$$

5)

$$C_6H_5\text{-}CO\text{-}CH_2\overset{+}{S}(CH_3)_2\ Br^- \xrightarrow{NEt_3} C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}S(CH_3)_2 \longleftrightarrow C_6H_5\text{-}\overset{O^-}{\overset{|}{C}}{=}CH\text{-}\overset{+}{S}(CH_3)_2$$

7,8)

[9] Ch. Ruchardt, S. Eichler, and P. Panse, *Angew. Chem.*, **75**, 858 (1963).

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[16] E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1641 (1964).

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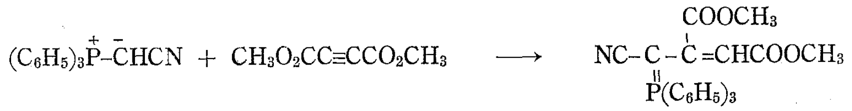
a typical pattern for the formation of a stable ylide starting from an acetylenic compound and a ylide.



$$(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HCN + CH_3O_2CC{\equiv}CCO_2CH_3 \longrightarrow NC\text{-}\underset{\underset{P(C_6H_5)_3}{\|}}{C}\text{-}\overset{\overset{COOCH_3}{|}}{C}{=}CHCOOCH_3$$

We intended to synthesize directly some stable sulfoxonium ylides, which possess α,β-unsaturated carbonyl groups adjacent to the ylide-carbanions, by Michael type addition of dimesulfoxonium methylide[21,22] to α-keto or alkoxycarbonyl acetylenic compounds.

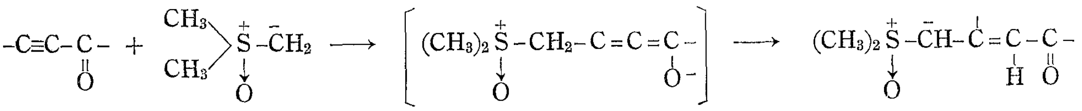


Chart 1

In this paper[23] are described, therefore, some aspects of addition mechanisms of dimethylsulfoxonium methylide to ethyl phenylpropionate derivatives and the formation of stable sulfoxonium ylides from propiolic acid derivatives and other electrophiles.

A reaction of ethyl phenylpropionate (I) with dimethyl sulfoxonium methylide (II) in dimethylsulfoxide, followed by treatment with water gave dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (III-a), mp 130—131° in 91% yield, which has also been prepared by Kaiser and co-workers.[18]

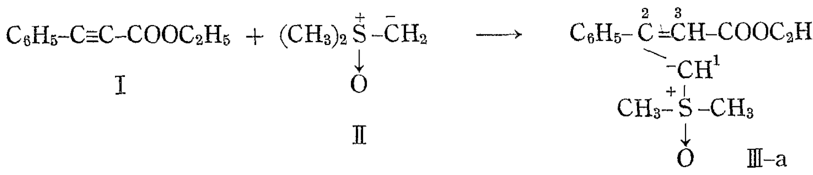


Chart 2

The infrared spectrum of III-a showed absorptions at 1020 (-SO-) and 1667 cm^{-1} (α,β-unsaturated ester), and the ultraviolet spectrum showed absorption maxima at 230 (ε=8220), 270 (ε=6770) and 346 mμ (ε=15630). That the absorption maxima of III in the ultraviolet spectra unusually red-shifted indicates an existence of the resonance contribution between ylide and ylene structure as shown in Chart 3.

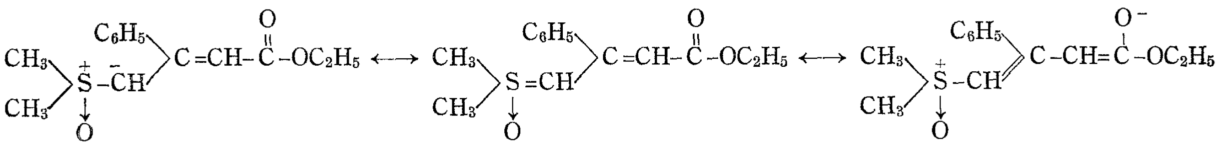


Chart 3

The nuclear magnetic resonance spectrum[24] consists of the signals at 1.25 (three protons, triplet) and 4.15 (two protons, quartet) due to the ethyl ester, 7.45 (five protons, multiplet) for phenyl group, 2.95 (six protons, singlet) for dimethylsulfoxonium group $\left(-\overset{\overset{O}{\uparrow}}{\underset{+}{S}}\langle{}^{CH_3}_{CH_3}\right)$, 4.77 (one

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[21] E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).

[22] E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

[23] The authors already reported in a preliminary form on these sulfoxonium ylides.[17]

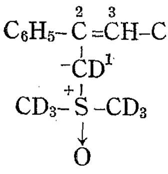
[24] The nuclear magnetic resonance spectra were measured using Varian A-60 spectrometer and the chemical shifts were expressed in ppm unit from the internal standard of tetramethylsilane in $CDCl_3$ solution.

proton, singlet) assigned to C–3 proton[25] and 6.29 ppm (one proton, slightly broader singlet) assigned to C–1 proton.

Addition of deuterium oxide to a solution of III in deuterochloroform causes remarkable decreases in the intensities at 6.29 and 2.95 ppm peaks with more broadening, whereas none of the change was observed at the signal located at 4.77 ppm. From these results, the signal located at 4.77 ppm was assigned to the vinylic proton, and that located at 6.29 ppm to ylide proton at C–1.

On the other hand, a reaction of ethyl phenylpropionate with dimethylsulfoxonium methylide in dimethylsulfoxide followed by treatment with deuterium oxide, instead of water, gave heptadeuterated dimethylsulfoxonium 3–ethoxycarbonyl–2–phenylallylide (IV). This compound possesses the deuterium atoms on the methyl groups on sulfoxonium ion and at C–1 position but the vinyl proton at C–3 position was not deuterated from the nuclear magnetic resonance spectrum.

This facts showed that on treatment of the reaction mixture with deuterium oxide, the C–3 position of the betaine type intermediate (V), initially formed by the addition of ethyl phenylpropiolate to dimethylsulfoxonium methylide in dimethylsulfoxide, was not deuterated but the C–3 position of V had been protonated before the treatment with deuterium oxide. Therefore, when the reaction mixture was treated with deuterium oxide, the protons on the ylide–carbanion and the two methyl groups on the sulfoxonium ion were only exchanged with deuterium ion.


IV

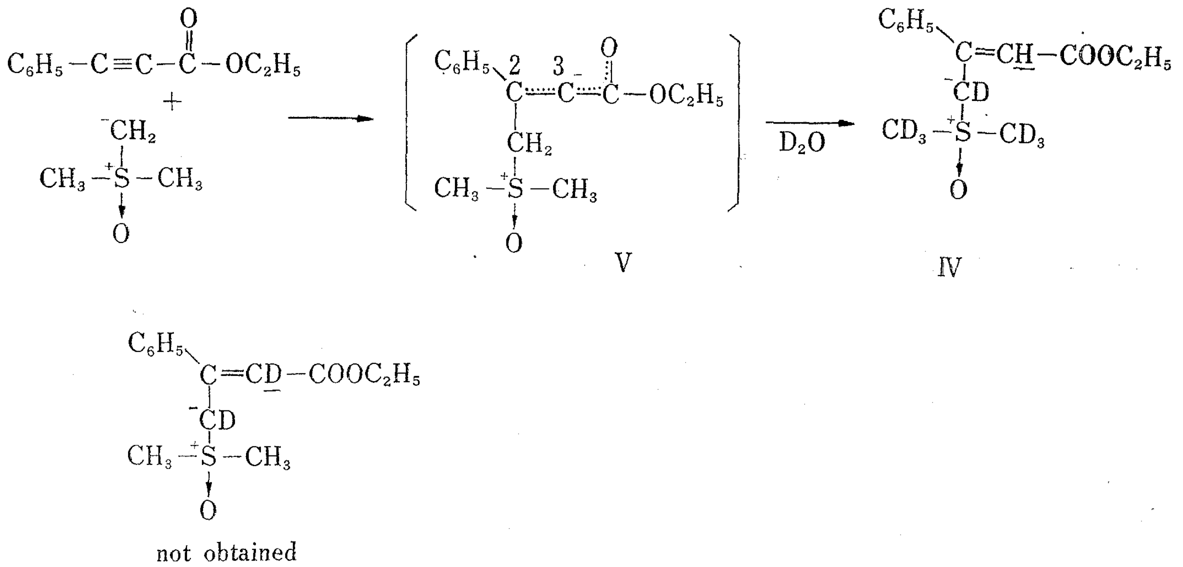


Chart 4

From these results, the proton at C–3 of IV must originate from the solvent, dimethylsulfoxide, or intermolecular or intramolecular proton transfer before treatment with deuterium oxide. The proton transfer from dimethylsulfoxide seems to be difficult from a comparison of the acidity of dimethylsulfoxide, which has a very weak acidity(pK_a 41),[26,27] with the basisity

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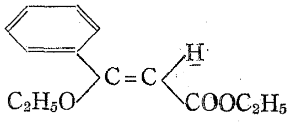
25) In the NMR spectrum of ethyl *trans*–*β*–ethoxycinnamate, the signal of the vinylic proton appeared at 5.19 ppm.



26) D.J. Cram, *Chem. Eng. News*, Aug. 19, p. 92 (1963).

27) H.O. House, "Modern Synthetic Reactions," W.A. Benjamin, Inc., New York, Amsterdam, 1965, p. 164.

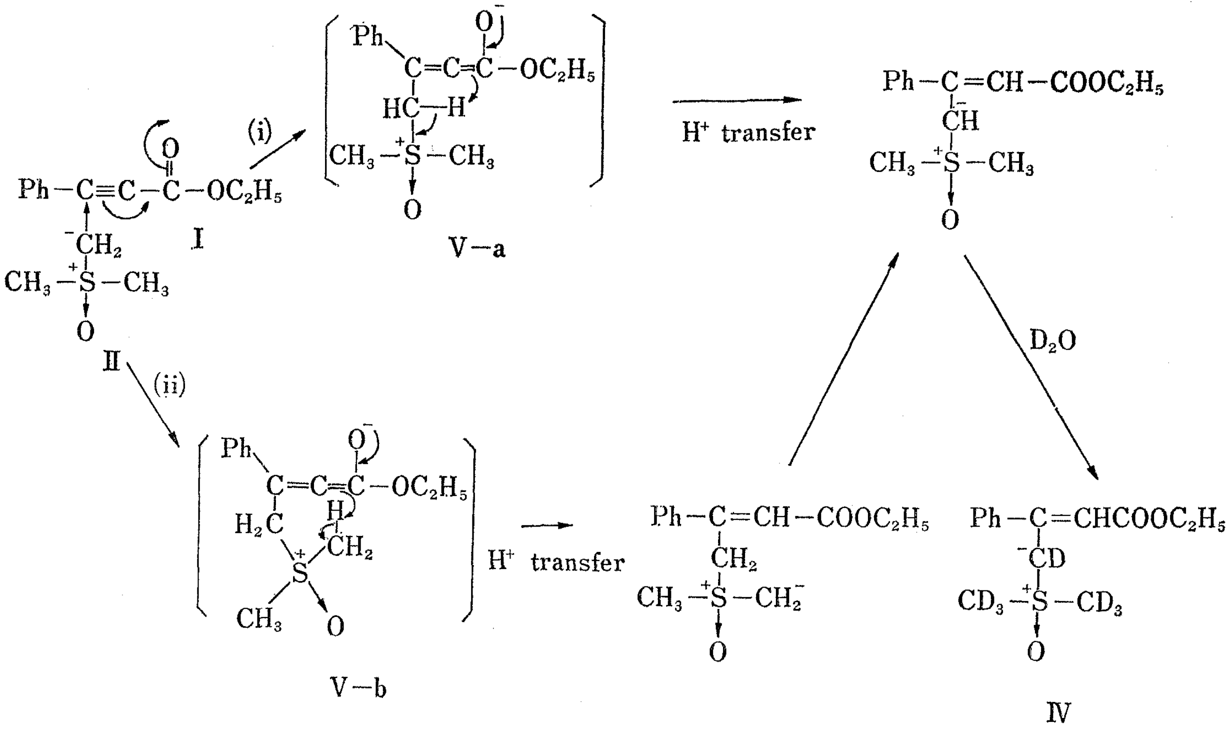
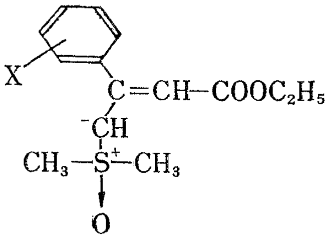


Chart 5

TABLE I.



IIIa−f

Substituent (X)		mp (°C)	Yield (%)	UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε)
III-a	H	130—131	91	230 (8220) 270 (6770) 346 (15630)
III-b	*p*-CH_3	120—121	86	237 (7930) 255 (7590) 346 (15690)
III-c	*p*-CH_3O	123—124	62	247 (7400) 269 (8020) 341 (18500)
III-d	*o*-Cl	130—131	71	344 (23650)
III-e	*m*-Cl	112—113	100	234 (8050) (shoulder) 272 (6040) 347 (17000)
III-f	*p*-Cl	133—134	87	240 (9980) 277 (9510) (shoulder) 347 (17830)

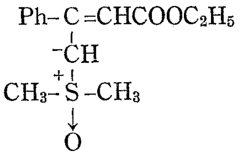
of the betaine intermediate (V–a) or (V–b). The intramolecular proton transfer would be more favorable in taking into account of facile deuterium exchange. In this case, there would be considered two path ways; (i) involving *via* four–membered ring transition state in which the hydrogen at C–1 position transferred into C–3 position, (ii) involving *via* six–membered ring transition state in which the hydrogen on sulfoxonium methyl groups transferred into C–3 position.

The latter, *via* six–membered ring transition state (V–b), seems to be more favored energetically than the former, *via* four–membered ring transition state. On the other hand, proton transfer in intermolecular way of the betaine intermediate (V–a) or (V–b) would be more difficult energetically than intramolecular proton transfer. Consequently a favorable addition reaction of dimethylsulfoxonium methylide to ethyl phenylpropionate would proceed *via* the six–membered ring transition state (V–b).

In the similar manner, sulfoxonium ylides bearing various substituents in the phenyl group were synthesized and the results are summarized in Table I.

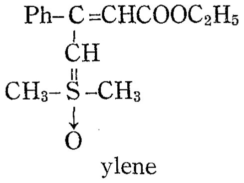
The reactions of ethyl propionate, dimethyl acetylenedicarboxylate, *p*–tolylsulfonylphenylacetylene, and 1,4–diphenyl–1,3–butadiyne with dimethyloxosulfonium methylide (II) occurred with heat evolution, but none of the corresponding stable ylides were obtained. Whereas, in the case of phenylpropiolamide, diphenylacetylene and phenylacetylene, no reaction occurred with II.

The compounds (III–a—f) seem to possess the ylide–like structure rather than the ylene–like structure from the facile proton exchange with deuterium ion at the ylide–carbanion as described before. Therefore, the ylide–carbanion in III may be estimated to be an appreciably strong base so as to be able to react with α,β–unsaturated carbonyl compounds in a Michael type addtion or with various acylating reagents.



$$\begin{array}{c}\mathrm{Ph\text{-}C{=}CHCOOC_2H_5}\\ |\\ \mathrm{{}^{-}CH}\\ {}^{+}|\\ \mathrm{CH_3\text{-}\overset{+}{S}\text{-}CH_3}\\ \downarrow\\ \mathrm{O}\end{array}$$

ylide



$$\begin{array}{c}\mathrm{Ph\text{-}C{=}CHCOOC_2H_5}\\ |\\ \mathrm{CH}\\ \|\\ \mathrm{CH_3\text{-}S\text{-}CH_3}\\ \downarrow\\ \mathrm{O}\end{array}$$

ylene

When III–a was treated with dimethyl acetylenedicarboxylate (VI) in tetrahydrofuran at 3—5°, a new stable ylide, dimethylsulfoxonium 1,2–dimethoxycarbonyl–5–ethoxycarbonyl–4–phenyl–1,4–pentadien–3–ylide (VII), mp 114—115° was obtained in 63% yield. The ultraviolet spectra of VII showed the absorption maxima at 277 (plateau) (ε=6700), 352 (ε=9690) and 388 mμ (ε=9690), and the nuclear magnetic resonance spectrum showed the triplet at 1.17 and the quartet at 4.08 due to the ethyl ester, singlet of six protons due to the two methyl groups on sulfoxonium ion at 2.91, two singlets at 3.50, 3.70 assignable to two methyl esters, a sharp singlet of one proton at 5.33 and a slightly broader singlet of one proton at 6.65 and the

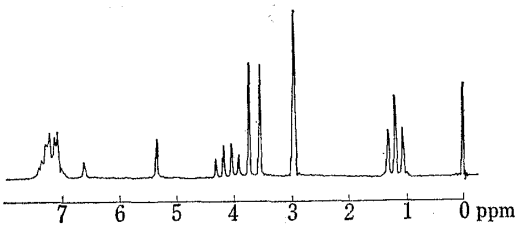


Fig. 1–a. Nuclear Magnetic Resonance Spectra (60 Mc) of Dimethylsulfoxonium 1,2–Dimethoxycarbonyl–5–ethoxycarbonyl–4–phenyl–1,4–pentadien–3–ylide in $CDCl_3$ using Tetramethylsilane as Internal Standard

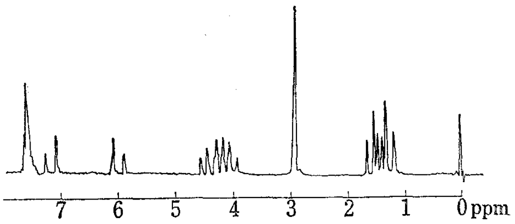


Fig. 1–b. Nuclear Magnetic Resonance Spectra (60 Mc) of Dimethylsulfoxonium 1,5–diethoxycarbonyl–4–phenyl–1,4–pentadien–3–ylide in $CDCl_3$ using Tetramethylsilane as Internal Standard

multiplet at about 7.39 ppm due to the five protons of aromatic ring. The two peaks at 5.33 and 6.65 ppm are assignable to vinyl protons adjacent to ester group, but which is which could not be assigned. The same reaction when it was carried out in acetonitrile, gave no product.

Similarly, treatment of III-a with ethyl propiolate at 16—17° in dimethylsulfoxide gave a stable ylide compound, dimethylsulfoxonium 1,5-diethoxycarbonyl-4-phenyl-1,4-pentadien-3-ylid (VIII), mp 144—145° in 35% yield. Its ultraviolet spectrum showed absorption maxima at 238 (plateau) (ε=5990), 318 (ε=11190) and 396 mμ (ε=13390). The nuclear magnetic resonance spectrum of VIII showed the signals at 1.12 (three protons, triplet) and 1.29 (three protons, triplet) due to the methyl groups of ethyl esters, 4.01 (two proton, quartet) and 4.24 (two protons, quartet) due to the two methylene groups of the ethyl esters, 2.91 (six protons, two methyl groups on sulfoxonium ion), 5.92 and 7.13 (two protons, AB type pattern, J_{AB}=16.0 cps) assignable to the two vinyl protons with *trans* configuration,[28] 6.48 (one proton, singlet) due to the vinyl proton adjacent to ethoxycarbonyl group and 7.43 ppm (five protons, broader singlet) for aromatic ring.

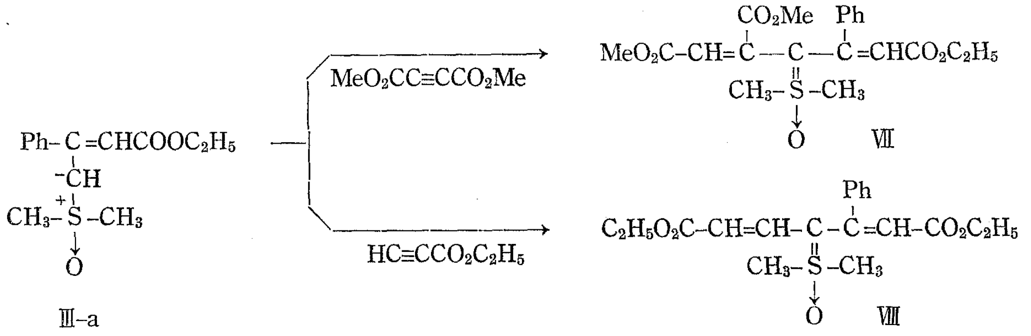


Chart 6

In addition to acetylenic carboxylic esters, other strong electrophiles also react with the ylide (III-a) to afford stable ylides. Then the ylide (III-a) was treated with benzoyl chloride in the presence of triethylamine in tetrahydrofuran at 7—10° to give dimethylsulfoxonium 1-benzoyl-3-ethoxycarbonyl-2-phenylallylylide, mp 165—167° (IX) in 55% yield. Its ultraviolet spectra showed the absorption maxima at 281 (ε=15280) and 360 mμ (ε=5220) and the nuclear magnetic resonance spectrum showed the peaks 1.22 (three protons, triplet) and 4.12 (two protons, quartet) due to the ethyl ester, 3.71 (six protons, singlet) for two methyl groups on sulfoxonium ion, 6.10 (one proton, sharp singlet) assigned to vinyl proton adjacent to the ethoxycarbonyl, and at about 7.3 ppm (five protons, multiplet) for aromatic ring.

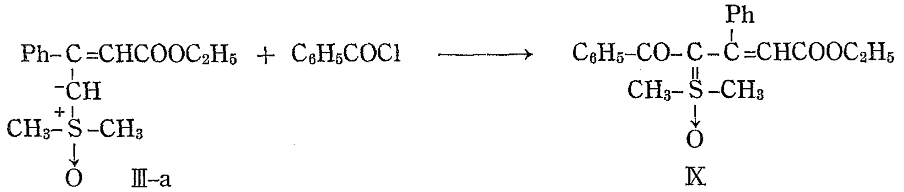


Chart 7

Likewise, several phenylisocyanates reacted with the ylide (III) and its derivatives at 7—10° in dimethylsulfoxide or tetrahydrofuran to afford a novel series of stable sulfoxonium ylide derivatives (X) in high yields and the results are summarized in Table II.

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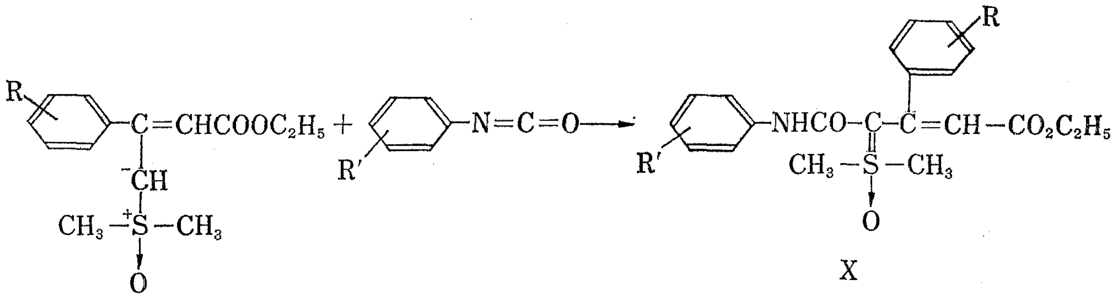
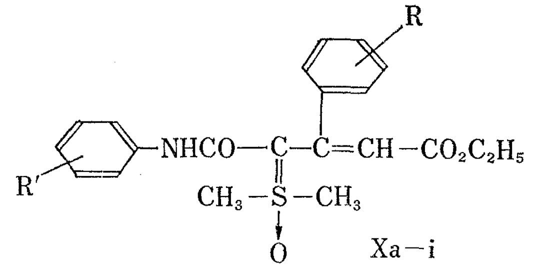
28) L.M. Jackman, "Application Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 85.



X

Chart 8

Table II.



Xa−i

X	Substituent R	Substituent R′	Solvent	mp (°C)	Yield (%)	UV λ_{max}^{EtOH} mμ (ε)
X-a	H	H	DMSO THF	134—135 134—135	69 90	271(32860) 376(5240)
X-b	*p*-CH_3	H	THF	129—130	97	273(32730) 376(4580)
X-c	*p*-OCH_3	H	THF	139—140	91	274(30040) 304(14090)(shoulder) 374(4560)
X-d	*o*-Cl	H	DMSO	117—118	71	270(24310) 374(5190)
X-e	*p*-Cl	H	DMSO	131—132	85	271(33690) 381(4590)
X-f	H	*m*-CH_3	THF	74— 77	69	271(32200) 379(4700)
X-g	H	*p*-Br	THF	118—119	76	276(34400) 376(4400)
X-h	H	*p*-Cl	THF	117—119	65	275(35000) 375(4730)
X-i	H	*m*-Cl	THF	121—123	90	274(28000) 372(4150)

Experimental[29]

General Procedure of Dimethylsulfoxonium 3-Ethoxycarbonyl-2-phenylallylide Derivatives (III-a—f)—— To a solution of dimethylsulfoxonium methylide, which was prepared from 1.2 mole of trimethylsulfoxonium iodide and 1.0 mole of sodium hydride in 500 ml of anhyd. dimethylsulfoxide in nitrogen under ice-water cooling, was added slowly dropwise a solution of 1.0 mole of ethyl substituted-phenylpropiolate in 200 ml of anhyd. dimethylsulfoxide at 10—12° under stirring in nitrogen. After addition was completed, the

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[29] All melting points were uncorrected. Dimethylsulfoxide was used by vacuum-distillation after dried over calcium hydride.

reaction mixture was stirred for 2 hr at 12—14° and then poured slowly into 2 liter of crushed ice–water with vigorous stirring. The precipitate was collected, washed with water twice, and then with cold ethanol–*n*–hexane (1:1). The crude sulfoxonium ylide was obtained in 60—100% yield. Pure sample was obtained by recrystallization from ethanol.

Dimethyloxosulfonium 3-Ethoxycrabonyl-2-phenylallylide (III-a)——To a solution of dimethylsulfoxonium methylide, which was prepared from 42 g (1.9 mole) of trimethylsulfoxonium iodide and 8.4 g (1.75 mole of 50% oily mixture) of sodium hydride in 200 ml of anhyd. dimethylsufoxide, was added dropwise a solution of 28.4 g (1.75 mole) of ethyl phenylpropiolate in 70 ml of anhyd. dimethylsulfoxide at 12—14° in nitrogen under stirring. After the addition was completed, the reaction mixture was stirred for 2 hr and then poured into 1000 ml of crushed ice with vigorous stirring. The precipitate was collected and washed with cold water and then with cold ethanol–*n*–hexane (1:1) to give 42.3 g of almost pure dimethylsulfoxonium 3–ethoxycarbonyl–2ν–phenylallylide (91% yield). Recrystallization from ethanol give colorless needles, mp 130—131°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1020 (–SO–), 1670 (–COOEt). *Anal.* Calcd. for $C_{14}H_{18}O_3S$: C, 63.12; H, 6.81; S, 12.01. Found: C, 63.05; H, 6.71; S, 12.12.

Heptadeuterated Dimethylsulfoxonium 3-Ethoxycarbonyl-2-phenylallylide (IV)——To a solution of dimethylsulfoxonium methylide prepared from 6.0 g (27.3 mmole) and 1.2 g (25 mmole of 50% oily mixture) of sodium hydride in 20 ml of dimethylsulfoxide by the procedure as described above, was added dropwise a solution of 4.21 g (26 mmole) of ethyl phenylpropiolate in 15 ml of anhyd. dimethylsulfoxide at 12—14° in nitrogen under stirring. After the addition was completed, the reaction mixture was stirred for 2 hr and then poured into 50 ml of cold D_2O under vigorous stirring in dry nitogen gas. The precipitate was filtered and washed with D_2O to give 5.6 g of almost pure IV. This sample was submitted to the measurement of NMR spectrum. The spectroscopic data of IR and UV were identical with those of nondeuterated ylide (III–a). The recrystallization of IV from ethanol gave nondeuterated ylide (III–a).

Dimethylsulfoxonium 1,2-Dimethoxycarbonyl-5-ethoxycarbonyl-4-phenyl-1,4-pentadien-3-ylide (VII)——To a suspension of 5.3 g (0.02 mole) of dimethylsulfoxonium 3–ethoxycarbonyl–2–phenylallylide (III–a) in 30 ml of anhyd. tetrahydrofuran was added slowly a solution of 2.8 g (0.02 mole) of dimethyl acetylenedicarboxylate in 8 ml of anhyd. tetrahydrofuran keeping the inner temperature at 7 to 8° under stirring. The color of the reaction mixture began to develop when about three fourth of a solution of dimethyl acetylenedicarboxylate in tetrahydrofuran had been added, the reaction mixture turned into transparent and after more five minutes precipitation began to occur. After the addition was completed, the reaction mixture was stirred for additional 40 min at 10°. The precipitate was collected and washed with cold solution of *n*–hexane–tetrahydrofuran (1:1) to give 5.1 g of a yellow solid (63% yield). Recrystallization from EtOH, or tetrahydrofuran gave yellow needles, mp 114.5—115.5°. *Anal.* Calcd. for $C_{20}H_{24}O_7S$: C, 58.81; H, 5.92; S, 7.85. Found: C, 58.80; H, 5.90; S, 7.73.

Dimethylsulfoxonium 1,5-Diethoxycarbonyl-4-phenyl-1,4-pentadien-3-ylide (VIII)——To a solution of 13.3 g (0.05 mole) of dimethylsulfoxonium 3–ethoxycarbonyl–2–phenylallylide (III–a) in 50 ml of anhyd. dimethylsulfoxide was added slowly a solution of 4.9 g (0.05 mole) of ethyl propiolate in 10 ml of anhyd. dimethylsulfoxide keeping the inner temperature at 13 to 14° during the addition. After the addition was completed, stirring was continued for 30 min at 13 to 14°. The reaction mixture was poured into 200 ml of crushed ice–water with vigorous stirring and extracted with CH_2Cl_2 six times. The combined extracts were washed with sat. NaCl solution twice and dried over Na_2SO_4. The evaporation of the solvent under diminished pressure gave a brown viscous oily product, to which a small portion of ethanol (about 3 ml) was added to afford a yellow solid. The solid was filtered and recrystallized from ethanol to furnish yellow neeldes 6.5 g (34% yield), mp 143.5—145°. *Anal.* Calcd. for $C_{19}H_{24}O_5S$: C, 62.61; H, 6.61; S, 8.79. Found: C, 62.85; H, 6.60; S, 8.44.

Dimethylsulfoxonium 1-Benzoyl-3-carboethoxy-2-phenylallylide (IX)——To a solution of 12.0 g (0.045 mole) of dimethylsulfoxonium 3–ethoxycarbonyl–2–phenylallylide (III–a) and 3.24 g (0.0495 mole) of triethylamine in 60 ml of anhyd. tetrahydrofuran was added slowly and dropwise a solution of 6.33 g (0.045 mole) of benzoyl chloride in 5 ml of anhyd. tetrahydrofuran keeping the inner temperature at 8—9° with stirring. When about one half of benzoyl chloride solution was added, precipitation began to occur. After the addition was completed, the stirring was continued for additional 3 hr at 15 to 17°. The precipitate was filtered and washed with tetrahydrofuran. The combined solution was evaporated under diminished pressure and trituation with 5 ml of *n*–hexane–ethanol (1:1) furnished 9.08 g of crude (IX) (54.4% yield). Recrystallization of the crude product from benzene afforded yellow prisms, mp 155—157°. *Anal.* Calcd. for $C_{21}H_{22}O_4S$: C, 67.99; H, 5.98; S, 8.65. Found: C, 68.37; H, 5.93; S, 8.33.

General Procedure of Dimethylsulfoxonium 1-Phenylcarbamoyl-3-ethoxycarbonyl-2-phenylallylide Derivatives, using Anhyd. Tetrahydrofuran as a Solvent——To a solution of dimethylsulfoxonium 3–ethoxycarbonyl–2–phenylallylide derivative (0.005 mole) in 10 ml of anhyd. tetrahydrofuran was added dropwise a solution of phenylisocyanate derivative (0.005 mole) in 3 ml of anhyd. tetrahydrofuran keeping the inner temperature at 5—6°. The yellow color of the reaction mixture developed during addition. After the addition was completed, the reaction mixture was stirred for additional 15 to 30 min. at 18°. The solvent was evaporated under reduced pressure and trituation with a small amount of ethanol (about 1 ml) to give a solid. The solid was collected to give a yellow one (80—95% yield) and recrystallized from ethanol.

Dimethylsulfoxonium 1-Phenylcarbamoyl-3-ethoxycarbonyl-2-phenylallylide (X-a) using Anhyd. Tetrahydrofuran as a Solvent——To a solution of 3.99 g (0.015 mole) of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (III-a) in 30 ml of anhyd. tetrahydrofuran was added dropwise a soltuion of 1.787 g (0.015 mole) of phenylisocyanate in 10 ml of anhyd. tetrahydrofuran keeping the inner temperature at 5° yellow color of the reaction mixture developed during the addition. After the addition was completed, the sitrring was continued for additional 30 min at 18°. The solvent was evaporated under reduced pressure. The residual gummy substance was trituated with *ca.* 3 ml of ethanol to solidify. The solid, collected, weighed 5.2 g of a yellow substance (90.2% yield). Recrystallization from ethanol afforded yellow prisms, mp 134—135°. *Anal.* Calcd. for $C_{21}H_{23}O_4NS$: C, 65.43; H, 6.01; N, 3.63; S, 8.32. Found: C, 65.23; H, 6.17; N, 3.77; S, 8.59.

General Procedure of Dimethylsulfoxonium 1-Phenylcarbamoyl-3-ethoxycarbonyl-2-phenylallylide Derivatives using Anhyd. Dimethylsulfoxide as a Solvent——To a solution of 0.005 mole of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (III) in 15 ml of anhyd. dimethylsulfoxide was added dropwsie a solution of 0.005 mole of phenylisocyanate keeping the inner temperature at 20—22°. After the addition was completed, the stirring was continued for additional 1 hr at room temperature. The reaction mixture was poured into 100 ml of a crashed ice-water with vigorous stirring and extracted with CH_2Cl_2 four times. The combined extracts were washed with sat. NaCl solution and dried over Na_2SO_4. After evaporating the solvent under diminished pressure, a gummy substance was remained, which was trituated with a small portion of ethanol-*n*-hexane (1:1) to solidify. The solid was filtered and recrystallized from EtOH (69—85% yield).

Dimethylsulfoxonium 1-Phenylcarbamoyl-3-ethoxycarbonyl-2-phenylallylide (X-a) in Dimethylsulfoxide——To a solution of 1.3 g (0.005 mole) of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (III-a) in 15 ml of anhyd. dimethylsulfoxide was added slowly a solution of 600 mg (0.005 mole) of phenylisocyanate in 3 ml of anhyd. dimethylsulfoxide keeping the inner temperature at 20—22°. After the addition was completed, the stirring was continued for additional 1 hr at room temperature. The reaction mixture was poured into 100 ml of crashed ice-water with vigorous stirring and extracted with CH_2Cl_2 four times. The combined extracts were washed with sat. NaCl solution and dried over Na_2SO_4. After evaporating the solvent under reduced pressure, a gummy substance was remained, which was scratched on adding 2 ml of ethanol-*n*-hexane (1:1) to solidify. The solid was filtered and recrystallized from EtOH to give 1.2 g of yellow prisms (69% yield), mp 134—135°. Its spectroscopic data were identical with those of X-a prepared in tetrahydrofuran.

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