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Studies on Acetylenic Compounds. LIX.[1] Reactions of Acetylene Sulfonium Ylids with α,β-Unsaturated Esters[2]

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Novel 2-ethynylcyclopropanecarboxylates were synthesized by the reaction of acetylene sulfonium ylids with α,β-unsaturated esters. An unequivocal synthesis and degradation were performed to determine the structure and stereochemistry.

The chemistry of sulfur-stabilized carbanions (sulfur ylids)[4] has recently been an interesting subject in organic syntheses. In our laboratories the nucleophilic reactions of acetylene sulfonium[5] and sulfone[6] ylids with benzaldehyde derivatives and cyclic ketones have been investigated.

While Julia's[7a] school and Martel's[7b] group have reported, independently,[7c] one-step syntheses of chrysanthemate by the base-treated reactions of 3,3-dimethyl-2-propenyl phenyl sulfone with senecioate derivatives. Trost and co-workers have reported the syntheses of vinyl cyclopropane derivatives by the reaction of vinyl sulfonium ylids with chalcone.[7d] On these backgrounds, we attempted an extension of the electrophiles to α,β-unsaturated esters in the nucleophilic reactions of acetylene sulfone ylids.

Contrary to our expectation, the reactions of 2-propynylsulfonyl ylids with methyl acrylate afforded the cyclohexanone derivatives[1] as a sole product. However the triple bond of the starting ylids remained intact in the products contrasting to all other reactions of acetylene sulfur ylids.[5,6] In this case no formation of cyclopropane ring would be due to the weak leaving ability of the phenylsulfonyl group which should leave as phenylsulfonyl anion. Accordingly, sulfonium ylid was considered to be more suitable for the formation of cyclopropane ring because the sulfide (neutral species) would be more effective leaving group than the phenylsulfonyl anion. In this paper we wish to describe the syntheses of novel acetylene cyclopropanes by the reaction of 2-propynylsulfonium ylids with α,β-unsaturated esters.[8]

In the preceding paper[1] we discussed the general reaction of acetylene sulfonyl ylids in view of the reaction sites initiating the first nucleophilic attack on electrophiles, comparing with the reaction of the acyl-stabilized sulfur ylids by Johnson and Amel.[9] In this study

1) Part LVIII: M. Yoshimoto, N. Ishida, and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **20**, 2137 (1972).
2) Preliminary Communication: M. Yoshimoto, N. Ishida, and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **19**, 863 (1971).
3) Location: *2-58, 1-chome, Hiromachi, Shinagawa-ku, Tokyo.*
4) A.W. Johnson, "Ylid Chemistry," Academic Press, New York and London, 1966, p. 304—366.
5) *a*) With benzaldehydes: A. Terada, and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **18**, 490, 497 (1970); *b*) With cyclic ketones: *idem, ibid.*, **18**, 991 (1970).
6) *a*) With benzaldehydes: M. Yoshimoto and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **18**, 2518, 2528 (1970); *b*) With cyclic ketones: M. Yoshimoto, N. Ishida, and Y. Kishida, *ibid.*, **19**, 1409 (1971).
7) *a*) M. Julia and A.G. Roualt, *Bull. Soc. Chim. France*, **1967**. 1411; *b*) J. Martel and C. Huynh, *ibid.*, **1967**, 985; J. Martel and G. Nomine, *Compt. Rend.* (*C*), **1969**, 2199; *c*) Recently this reaction has been applied to the synthesis of presqualene alcohol: R.V.M. Campbell, L. Crombie, and G. Pattenden, *Chem. Commun.*, **1971**, 218; *d*) R.W. LaRochelle, B.M. Trost, and L. Krepski, *J. Org. Chem.*, **36**, 1126 (1971).
8) The reactions of 2-propynylsulfonium ylids with α,β-unsaturated ketones and nitriles also afforded acetylene cyclopropanes: M. Yoshimoto, N. Ishida, and Y. Kishida, unpublished data.
9) A.W. Johnson and R.T. Amel, *Tetrahedron Letters*, **1966**, 819; *idem, J. Org. Chem.*, **34**, 1240 (1969).

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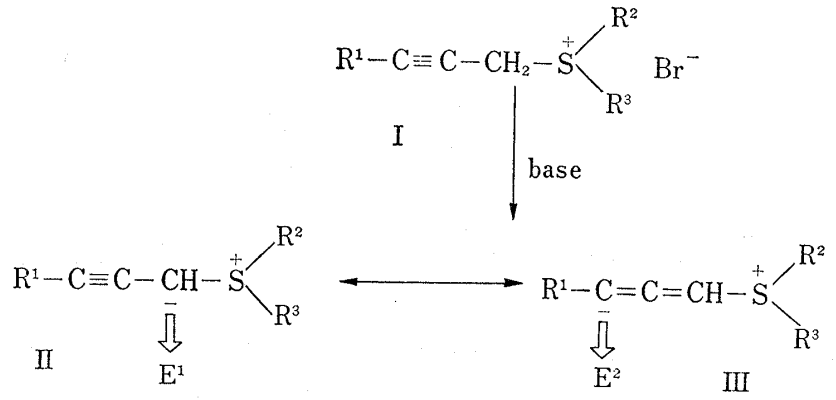
we will describe an example of E^1-type electrophiles. As shown in Chart 1 propargylsulfonium ylid (II) resonates with allenic sulfonium betaine (III) and the electrophiles are classified into E^1 and E^2 depending upon their choice of susceptibility of either II or III.



E^1, E^2 : electrophile

Chart 1

When a mixture of 3-phenyl-2-propynylsulfonium salts (Ia—c) and methyl acrylate (MA) was treated with sodium hydride in tetrahydrofuran (THF) in an inert atmosphere, two kinds of cyclopropane derivatives were obtained, each of which was composed of two stereoisomers. The major component of the first cyclopropane derivatives (bp: 110°/0.3 mmHg) was 1: 1 reaction product of I and MA, and assigned to methyl *trans*-2-phenethynylcyclopropanecarboxylate (IV_1 t) from the following data. The molecular formula was $C_{13}H_{12}O_2$ from the elemental analysis and mass spectrum (MS): m/e=200 (M^+). The ultraviolet (UV) spectrum exhibited λ_{max}^{EtOH}: 249 nm (log ε=4.31) suggesting the retention of the phenethynyl group and the infrared (IR) absorption maxima appeared at ν_{max}^{Film} cm^{-1}: 2235 (C≡C), 1733 (CO_2Me), 1600 (C_6H_5–). The nuclear magnetic resonance (NMR) spectrum showed the peaks of 1.35 ppm (2H, m), 2.05 (2H, m), 3.70 (3H, s), and aromatic protons (5H). The configuration of this compound was deduced to be *trans* from an analogy with the predominant *trans* formation in the reaction of carbonyl-stabilized sulfonium ylids with α,β-unsaturated esters[10] and by the degradation reactions described later. The minor component (IV_1c) exhibited the similar MS, UV, IR, and NMR spectrum to those of IV_1t, but showed a longer retention time than IV_1t in the gas–liquid partition chromatography (GLPC) analysis. This was in good agreement with the result obtained in carbethoxycyclopropane derivatives by Payne.[10b] The major component of the second cyclopropane derivatives was 1: 2 reaction product of I and MA, respectively, and assignable to methyl 2-phenethynyl-2-(2-carbomethoxyethyl)cyclopropanecarboxylate (V_1) from the following data. The molecular formula of $C_{17}H_{18}O_4$ was obtained by the elemental analysis and MS: m/e=286 (M^+). The UV exhibited λ_{max}^{EtOH}: 249 nm (log ε=4.30; C_6H_5-C≡C-) and the IR maxima at ν_{max}^{Film} cm^{-1}: 2230 (C≡C), 1740 (CO_2Me), 1734 (CO_2Me), and 1600 (C_6H_5-). The NMR spectrum exhibited the peaks of 1.0—2.9 ppm (7H, m), 3.67 (3H, s), 3.75 (3H, s), and aromatic protons (5H). The assignment of the protons on the cyclopropane ring of the major component, V_1, was based on the analysis using a shift reagent[11]: J_{ab}=4.5 Hz, J_{bc}=6.5, J_{ca}=8.3 (Chart 2). The minor component (V_2) exhibited the similar MS, UV, IR, and NMR spectrum to those of V_1, however it showed a longer retention time than V_1 in the GLPC.

10) *a*) J. Casanova and D.A. Rutolo, *Chem. Commun.*, **1967**, 1224; G.B. Payne and M.R. Johnson, *J. Org. Chem.*, **33**, 1285 (1968); H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, **22**, 2145 (1966); *b*) G.B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).

11) M. Yoshimoto, T. Hiraoka, H. Kuwano, and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **19**, 849 (1971).

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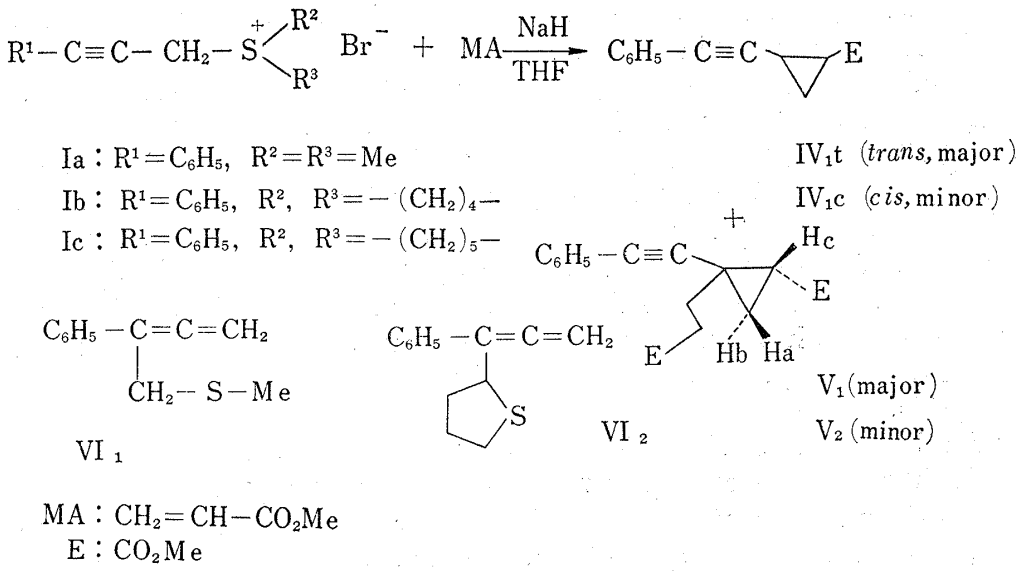

Chart 2

TABLE I. Influence of Various Sulfides Constituting the Sulfonium Bromides (I)

Run	Molar ratio of MA/I	Yield of IV_1[a] % (IV_1t: IV_1c)	Yield of V % (V_1: V_2)	Yield of VI %
1	2.4 (Ia)	36 (91: 9)	11 (3:2)	6
2	1.2 (Ib)	54 (90:10)	10 (3:2)	
3	2.0 (Ib)	50 (94: 6)	20 (3:2)	
4	5.0 (Ic)	54 (89:11)	22 (3:2)	
5	2.0 (Ic)	42 (91: 9)	23 (3:2)	

a) The water content was not investigated. During the preparatory process of the small scale experiments (I: 20 mmol, THF:[b] 100 ml), a small amount of water seemed to participate in the reaction.
b) purified through alumina column (Woelm grade super 1)

TABLE II. Role of Water Content in the Reaction of Ib with MA

Water content in THF (%)	Yield (%)[a] of IV_1	Water content in THF (%)	Yield (%)[a] of IV_1
0.2[b]	58	0.4[b]	45
0.3[b]	75	2.0[c]	34

a) Molar ratio of MA/Ib in every run was two *b*) distilled on KOH *c*) distilled on $LiAlH_4$

Acetylene sulfonium ylids are liable to produce allenic sulfides by the concerted, symmetry conserved, [2,3]-sigmatropic rearrangement.[12] In the present case we also isolated allenic sulfides (VI); thus the sulfide, VI_1 obtained from the reaction using Ia was identified with an authentic sample of VI_1.[12a] In order to avoid this rearrangement, 3-phenyl-2-propynylsulfonium salts derived from tetramethylene- or pentamethylene sulfide in place of dimethyl sulfide were chosen. In fact Ib and Ic afforded better results than Ia as shown in Table I. Moreover, in these reactions the water content of the solvent (THF) used played

12) *a*) J.E. Baldwin, R.E. Hackler, and D.P. Kelly, *Chem. Commun.*, **1968**, 1083; A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **17**, 966 (1969); *b*) The mechanistic and theoretical treatment of the [2,3]-sigmatropic rearrangements is described in the following paper and many references are cited therein: J.E. Baldwin and J.E. Patrick, *J. Am. Chem. Soc.*, **93**, 3556 (1971).

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an important role. The influence of the water content to the yields of IV_1 was investigated and the results are summarized in Table II.[13]

For confirming the structure of IV_1 an independent synthesis was carried out. Phenylpropiolaldehyde was treated with triphenylphosphonium methylide to afford 1-phenyl-3-buten-1-yne (VII).[14] VII gave ethyl *trans*- (IV_8t) and *cis*-2-phenethynylcyclopropanecarboxylate (IV_8c) in 24% and 16% yield, respectively, when treated with ethyl diazoacetate at 125—130° in an argon atmosphere.[15] Also in this case the predominant product was deduced to possess *trans* configuration. Careful hydrolysis of IV_8t and IV_8c (5% KOH in 90% EtOH at 25° for 15 hr) afforded the *trans*- ($VIII_1t$: mp, 89—90°) and *cis*-carboxylic acid ($VIII_1c$: mp, 84—85°) which were treated with diazomethane to give pure methyl esters, IV_1t and IV_1c, respectively. Both IV_1t and IV_1c were identified with the products from the phenethynyl ylids.

Determination of the configuration of IV_1t was due to a usual degradation method. The partial hydrogenation[16] of IV_1t in methanol containing a trace of quinoline using 5% palladium on calcium carbonate gave IX ($M^+=202$, $\nu_{C=O}=1730\ cm^{-1}$, $\delta=6.42$ ppm: 1H, d, $J_1=11.5$ Hz, 5.07 ppm: 1H, dd, $J_1=11.5$ Hz, $J_2=9.0$), which was treated successively with osmium tetroxide and sodium metaperiodate. The reaction mixture, which comprised

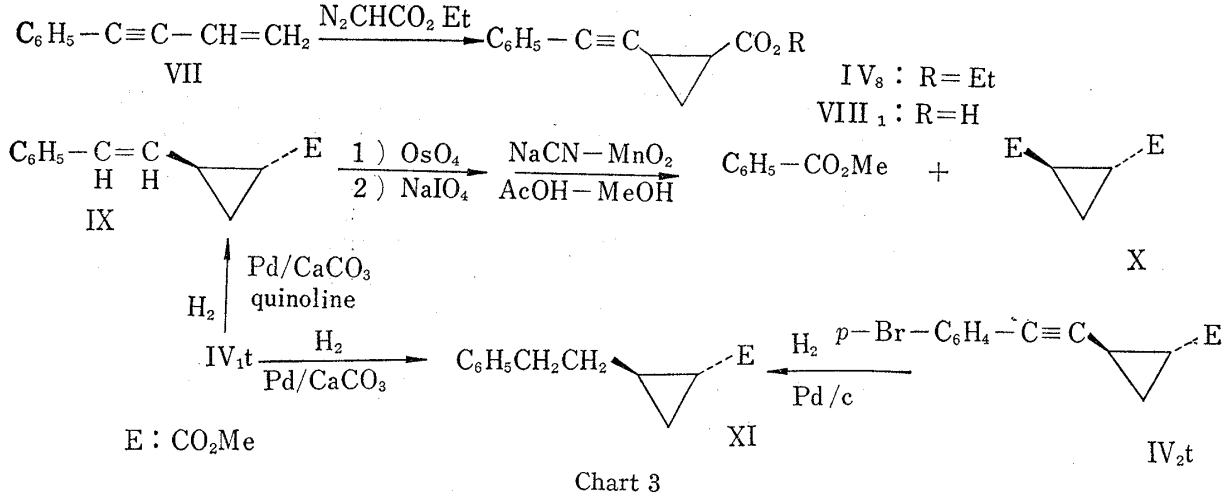

Chart 3

benzaldehyde and methyl *trans*-2-formylcyclopropanecarboxylate, was converted directly to two esters, methyl benzoate and dimethyl cyclopropane-*trans*-dicarboxylate (X) by treatment with manganese dioxide, acetic acid and sodium cyanide.[17] These two esters were identified with authentic samples by glpc analysis, respectively. Moreover, the hydrogenation of IV_1t by 5% palladium on calcium carbonate in methanol gave methyl *trans*-2-phenethylcyclopropanecarboxylate (XI) quantitatively, which was also given by the hydrogenation of the major isomer of methyl *p*-bromophenethynylcyclopropanecarboxylate (Compd. IV_2 in Table III).

The reaction mechanisms for the formations of IV and V were assumed as shown in Chart 4 depicting the reaction of Ib with methyl acryrate (MA). The first generated sulfonium ylid

13) The authors express their thanks to Dr. T. Hiraoka in our laboratories for his valuable suggestion on the role of water in this reaction.
14) A.A. Petrov and V.B. Lebedev, *Z. Obshch. Khim.*, 33, 3558 (1963).
15) Recently this type of 2-ethynylcyclopropanecarboxylate was synthesized by the diazoacetate method: R.N. Gmyzina, L.P. Danilkina, and I.A. Dyakonov, *Z. Org. Khim.*, **6**, 2168 (1970).
16) Lindlar's catalyst which has been used most frequently in the partial hydrogenation of the acetylenic linkage was not effective at all in this case.
17) E.J. Corey, A. Katzenellenbogen, N.W. Gilman, S.A. Roman, and B.W. Erickson, *J. Am. Chem. Soc.*, **90**, 5618 (1968).

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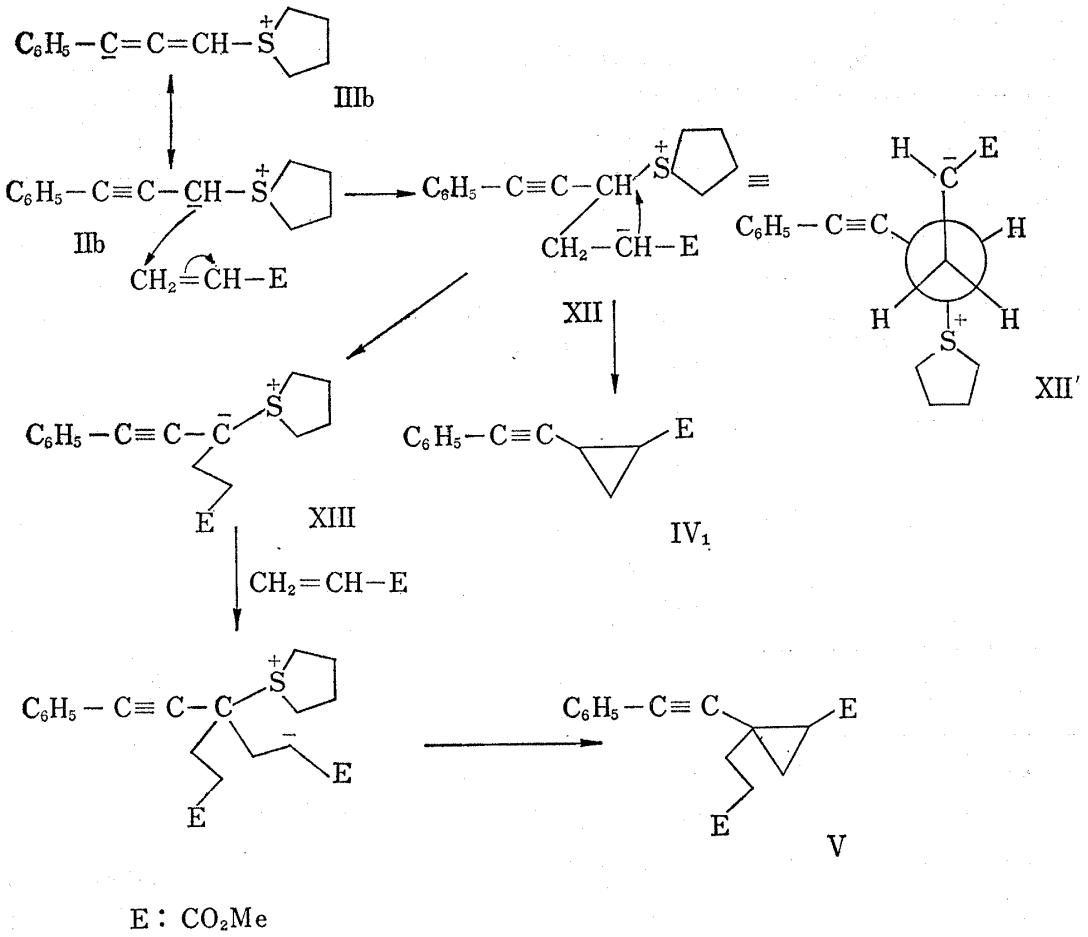
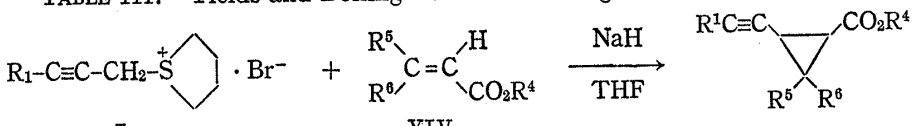


Chart 4

TABLE III. Yields and Boiling Points or Melting Points of IV and VIII



Compd.[a]	R^1	XIV[b]	R^5	R^6	R^4	Yield[c] %	bp (mmHg) or (mp) °C	mp of R^4=H °C	Compd.
IV_1	C_6H_5	MA	H	H	Me	75	110 (0.3)	90: *trans* 85: *cis*	$VIII_1$
IV_2	*p*-Br-C_6H_4	MA	H	H	Me	56	[59]: *trans*	124: *trans*	$VIII_2$
IV_3	C_6H_5	MC	Me	H	Me	11	115 (0.2)		
IV_4	Me	MA	H	H	Me	57	110 (50)	88	$VIII_3$
IV_5	Me	MC	Me	H	Me	33	108 (30)	56	$VIII_4$
IV_6	H	MA	H	H	Me	6			
IV_7	*p*-Me-C_6H_4	MA	H	H	Me	43	113 (0.01)	106	$VIII_5$
IV_8	C_6H_5	EA	H	H	Et	55	107 (0.1)		
IV_{10}	C_6H_5	MF	CO_2Me	H	Me	19	155 (0.01)	207: *trans* (R^2=CO_2H)	$VIII_6$
IV_{10}	C_6H_5	MM	H	CO_2Me	Me	25	155 (0.01)	207: *trans* (R^3=CO_2H)	$VIII_6$
IV_{11}	*p*-Br-C_6H_4	MCi	C_6H_5	H	Me	5			
IV_{12}	C_6H_5	ES	Me	Me	Et	*trace*			

a) All compounds described are mainly composed of *trans* isomers.
b) MA: methyl acrylate; MC: methyl crotonate; EA: ethyl acrylate; MF: methyl fumarate; MM: methyl maleate; MCi: methyl cinnamate; ES: ethyl senecioate
c) Except IV_1 the efforts for improving the yield and the experiments in various conditions were not carried out.

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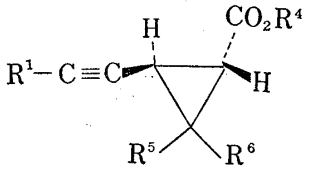
(IIb), which was derived from the base treatment of Ib and stabilized by resonating with an allene carbanion (IIIb), would react with MA. In the resulting betaine intermediate, XII, the anion would attack the propargylic carbon, with concomitant departure of the sulfide, to afford the cyclopropane derivative (IV_1). The preferred rotamer (XII′) in the Newman projection of XII would explain the predominant formation of the *trans* isomer (IV_1t) by a *trans*-elimination of the sulfide. This is in good accordance with the results in the reactions of carbonylstabilized ylids with α,β-unsaturated esters and ketones.[10] On the other hand the proton abstraction from the propargylic carbon by the anion in XII would again lead to a formation of another ylid species (XIII) which would react with the second MA with the elimination of tetramethylene sulfide yielding V.

TABLE IV. Spectroscopic Data of 2-Ethynylcyclopropanecarboxylate (IV, VIII)



IV: ester
VIII: carboxylic aidc

Compd.[a]	R^1	R^5	R^6	R^4	UV: λ_{max}^{EtOH} nm (log ε)	IR: ν_{max} cm^{-1} C≡C C=O (OH)	NMR: δ ppm (in $CDCl_3$) H_a, H_b	R^1	R^5, R^6	R^4
IV_1t	C_6H_5	H	H	Me	249(4.31)	2235 1733	1.9—2.2 (2H, m)	7.3 (5H, m)	1.1—1.6 (2H, m)	3.72 (3H, s)
IV_2t	Br- 	H	H	Me	257(4.45)	2250 1737	1.9—2.2 (2H, m)	7.18, 7.45 (4H, ABq)	1.2—1.6 (2H, m)	3.73 (3H, s)
IV_3t	C_6H_5	Me	H	Me	250(4.32)	2240 1735	1.6—2.3 (2H, m)	7.3 (5H, m)	1.30 (3H, d, J=4.6) 1.2 (1H, m)	3.70 (3H, s)
IV_4t	Me	H	H	Me		1735	1.6—2.1 (2H, m)	1.75 (3H, d, J=10)	0.9—1.6 (2H, m)	3.68 (3H, s)
IV_5t	Me	Me	H	Me		1732	1.4—2.2 (2H, m)	1.78 (3H, d, J=10)	1.21 (3H,d, J=4.6) 1.0—1.5 (1H, m)	3.67 (3H, s)
IV_6t	H	H	H	Me		2100 1735	1.6—2.1 (2H, m)	1.89 (1H, d, J=2.0)	1.0—1.6 (2H, m)	3.72 (3H, s)
IV_7t	Me-  -H		H	Me	250(4.34)	1735	1.9—2.2 (2H, m)	2.33 (3H, s) 7.10—7.28 (4H, ABq)	1.1—1.7 (2H, m)	3.55 (3H, s)
IV_8t	C_6H_5	H	H	Et	249(4.31)	2240 1732	1.9—2.2 (2H, m)	7.2—7.4 (5H, m)	1.1—1.6 (2H, m)	1.27, 4.17 (3H, t)(2H, q)
IV_9t	C_6H_5	H	H	$C_6H_5CH_2$	249(4.30)	2230 1730	1.6—2.1 (2H, m)	7.30 (5H, m)	1.1—1.6 (2H, m)	5.17, 7.40 (2H, s)(5H, m)
$IV_{10}t$	C_6H_5	CO_2Me	H	Me	250(4.19)	1735	2.4—2.8 (2H, m)	7.33 (5H, m)	3.75, 0.7—1.3 (3H, s)(1H, m)	3.77 (3H, s)
$IV_{11}t$	Br- 	C_6H_5	H	Me		2220 1735	2.3 (2H, m)	7.18, 7.45 (4H, ABq)	7.3, 2.8 (5H, m)(1H, m)	3.75 (3H, s)
$IV_{12}t$	C_6H_5	Me	Me	Et		2225 1737	2.0 (2H)	7.25 (5H, m)	1.3, 1.3 (3H, s)(3H, s)	1.25, 4.15 (3H, t)(2H, q)
$VIII_1t$	C_6H_5	H	H	H	249(4.30)	2225 1690 (2550—2780)	1.9—2.3 (2H, m)	7.3 (5H, m)	1.2—1.7 (2H, m)	12.0 (1H, s)
$VIII_2t$	Br- 	H	H	H	258(4.43)	2230 1710 (2550—2780)	1.9—2.3 (2H, m)	7.3, 7.5 (4H, ABq)	1.2—1.7 (2H, m)	11.2 (1H, s)
$VIII_3t$	Me	H	H	H		1720 (1550—2800)	1.6—2.1 (2H, m)	1.74 (3H, d, J=1.0)	1.0—1.6 (2H, m)	11.5 (1H, s)
$VIII_4t$	Me	Me	H	H		1695 (2550—2800)	1.4—2.2 (2H, m)	1.76 (3H, d, J=2.0)	1.20 (3H,d, J=4.5) 1.0—1.4 (1H, m)	8.53 (1H, s)
$VIII_5t$	Me-  -H		H	H	250(4.33)	1720 (2400—2800)	1.8—2.3 (2H, m)	2.32 (3H, s) 7.06, 7.30 (4H, ABq)	1.2—1.7 (2H, m)	9.15 (1H, s)

a) The *trans* configurations were deduced from the analogies with IV_1t and IV_2t.

The scope and limitation of this reaction are summarized in Table III. Substituents of alkyl, phenyl, and carbomethoxy on the olefin carbon (*i.e.*, R^5 and R^6 in XIV) lowered markedly the yield of cyclopropanes. The spectral and analytical or mass spectral data are presented in Table IV and Table V, respectively. The products of the type of V were found in only three cases (see Experimental) and not rigorously sought in other cases.

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Experimental

General Procedure for the Preparation of 2-Propynylsulfonium Salts (I)——The preparations of dimethyl 2-propynylsulfonium bromides were reported by Terada and Kishida.[18] Here the preparations of the cyclic sulfonium bromides are described. A mixture of each 2-propynyl bromide (1 eq.), cyclic sulfide (1.5—2.0 eq.) and an appropriate amount of benzene[18] was allowed to stand at room temperature(r.t.) for several hours to a few days. The precipitated salts were collected by filtration in high yields and recrystallization from EtOH gave pure colorless crystals.

Table V. Elemental Analysis and MS of IV and VIII

Compd.[a]	Formula	Analysis (%) Calcd. C	H	Br	Found C	H	Br
IV_1t	$C_{13}H_{12}O_2$	77.95	6.04		77.44	6.16	
IV_2t	$C_{13}H_{11}O_2Br$	55.93	3.97	28.63	55.99	3.94	28.34
IV_3t	$C_{14}H_{14}O_2$	Mass Spectrum: m/e=214 (M^+), 183 (M-OMe), 155 (M-CO_2Me)					
IV_4t	$C_8H_{10}O_2$	69.54	7.30		70.01	7.68	
IV_5t	$C_9H_{12}O_2$	71.11	7.96		71.10	8.29	
IV_6t	$C_7H_8O_3$	Mass Spectrum: m/e=124 (M^+), 87 (M-C_3H), 65 (M-CO_2Me)					
IV_7t	$C_{14}H_{14}O_2$	78.48	6.59		78.28	6.69	
IV_8t	$C_{14}H_{14}O_2$	78.48	6.59		78.43	6.53	
IV_9t	$C_{19}H_{16}O_2$	82.58	5.84		82.54	5.92	
$IV_{10}t$	$C_{15}H_{14}O_4$	69.75	5.46		68.91	5.51	
$IV_{11}t$	$C_{19}H_{15}O_2Br$	Mass Spectrum: m/e=355 (M^+), 324 (M-OMe), 296 (M-CO_2Me)					
$VIII_1t$	$C_{12}H_{10}O_2$	77.40	5.41		77.62	5.51	
$VIII_2t$	$C_{12}H_9O_2Br$	54.36	3.48	30.61	54.35	3.07	29.98
$VIII_3t$	$C_7H_{10}O_2$	67.73	6.50		67.84	6.56	
$VIII_4t$	$C_8H_{10}O_2$	69.54	7.30		69.22	7.21	
$VIII_5t$	$C_{13}H_{12}O_2$	77.95	6.04		77.98	6.07	

a) The *trans* configurations were deduced from the analogies with IV_1t and IV_2t.

General Preparation Method of 2-Ethynylcyclopropanecarboxylates (IV) from 2-Propynylsulfonium Bromides (I) and α,β-Unsaturated Carboxylic Esters (XIV)——To a mixture of sulfonium bromide (10.0 mmole), α β-unsaturated ester (20.0 mmole), dry THF (50 ml, distilled on lithium aluminum hydride) and H_2O (0.15 ml) was added a 50% NaH-oil (0.48 g, 10 mmole) in a nitrogen atmosphere under vigorous stirring at 0—5° in ice–bath. Stirring was continued at 0—5° for 30 min and at 20—25° for 3 hr. The resulting mixture was poured into 200 ml of H_2O and extracted with AcOEt. The combined extracts were dried over anhyd. Na_2SO_4 and concentrated to dryness. The residual oil was purified by dry column chromatography method[6b,19] (300 g of silica gel, developed with benzene). When the solvent reached the bottom of the column, the development was completed and the column tube was cut into seven equal length portions. The extracts of the third and fourth segments from the bottom with AcOEt were evaporated to dryness. The residue was submitted to distillation or recrystallization from an appropriate solvent [7th run of IV_2 (see Table III): MeOH] afforded alkyl 2-ethynylcyclopropanecarboxylate (IV). Likewise, the extract of the sixth segment from the bottom with AcOEt gave 2-ethynyl-2-(2-carbalkokyethyl)cyclopropanecarboxylic esters (*vide post*). The ratio of *cis* and *trans* stereoisomers of IV was determined by glpc.

Reaction of Dimethyl 3-Phenyl-2-propynylsulfonium Bromide (Ia) with Methyl Acrylate (MA)——According to the preceding general method the reaction and work up were carried out. The extract of the first segment from the bottom of the dry column chromatogram with AcOEt, worked up as before, afforded 4-methylmercapto-3-phenyl-1,2-butadiene (VI_1), which was identified with the authentic sample[12] by TLC, IR and NMR.

18) A. Terada and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **17**, 966 (1969).
19) B. Loev and K.M. Snader, *Chem. Ind.* (London), **1965**, 15; B. Loev and M.M. Goodman, *ibid.*, **1967**, 2026.

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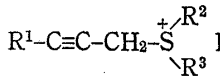
TABLE VI. Spectroscopic Data of 2-Propynylsulfonium Bromides (I)



I

Compd.[a]	R^1	R^2, R^3	UV λ_{max}^{EtOH} nm(log ε)	IR ν_{max}^{Nujol} cm^{-1}	NMR δ ppm (J_{Hz}) R-C≡C-CH_2-S	$(CH_2)_n$ CH_2 CH_2 S	$(CH_2)_n$ CH_2 CH_2 S [b]
Ib	C_6H_5	$-(CH_2)_4-$	284 (4.24)	2210 (C≡C)	7.63[c] (5H, s)	4.62 (2H, s)	3.6—4.0 (4H, m)	2.3—2.6 (4H, m)
Ic	C_6H_5	$-(CH_2)_5-$	247 (4.16)	2210 (C≡C)	7.3—7.7[d] (5H, m)	4.62 (2H, s)	3.4—3.8 (4H, m)	1.6—2.6 (6H, m)
Id	Me- 	$-(CH_2)_4-$	254 (4.26)	2225 (C≡C)	2.30[c] (3H, s) 7.20, 7.42 (4H, ABq, J=9.0)	4.47 (2H, s)	3.5—3.9 (4H, m)	2.2—2.5 (4H. m)
Ie	Br- 	$-(CH_2)_4-$	259 (4.35)	2220 (C≡C)	7.47, 7.57[d] (4H, ABq, J=8.0)	4.63 (2H, s)	3.5—3.9 (4H, m)	2.2—2.6 (4H, m)
If	Me	$-(CH_2)_4-$		2235 (C≡C)	2.10[c] (3H, t, J=2.6)	4.37 (2H, q, J=2.6)	3.6—4.0 (4H, m)	2.3—2.7 (4H, m)
Ig	H	$-(CH_2)_4-$		2120, 3170 (C≡CH)	3.25[c] (1H, m)	4.38 (2H, s)	3.6—4.0 (4H, m)	2.3—2.7 (4H, m)

a) Ia was reported in the literature.[18] *b*) Ib, Id, Ie, If and Ig: n=2, Ic: n=3 *c*) Solvt: D_2O *d*) Solvt.: CD_3OD

TABLE VII. Melting Points, Yields and Analyses of 2-Propynylsulfonium Bromides (I)

Compd.[a]	mp (°C)	yield (%)	Formula	Analysis (%) Calcd. C	H	S	Br	Found C	H	S	Br
Ib	128	94	$C_{13}H_{15}SBr$	55.12	5.34	11.32	28.22	54.95	5.29	11.18	28.15
Ic	128	93	$C_{14}H_{17}SBr$	56.55	5.77	10.79	26.89	55.97	5.46	10.69	27.10
Id	112	80	$C_{14}H_{17}SBr$	56.55	5.77	10.79	26.89	56.45	5.88	10.66	26.78
Ie	131	85	$C_{13}H_{14}SBr_2$	43.12	3.90	8.86	44.13	43.16	4.13	8.87	44.23
If	130	80	$C_8H_{13}SBr$	43.44	5.92	14.50	36.14	43.20	6.08	14.42	36.35
Ig	83	23	$C_7H_{11}SBr$	*b*)							

a) Compounds abbreviated are the same as those in Table VI.

b) hygroscopic. Mass Spectrum: m/e=207 (M^+), 126 (M-HBr), 119 ($HC{\equiv}C\text{-}CH_2Br^+$), 88  , 39 ($HC{\equiv}C\text{-}CH_2^+$)

Formation of 2-(1-Phenyl)propadienyltetrahydrothiophene (VI_2)——Reaction of 3-phenyl-2-propynyl tetrahydrothiophenium bromide (Ib) and ethyl senecioate was conducted by the general method. After the usual work up, the first segment from the bottom of the dry column chromatogram finally gave the title compound. IR ν_{max}^{Film} cm^{-1}: 1945 (C=C=C), 850 (=CH_2) NMR δ ppm in CCl_4: 1.9—2.3 (4H, m), 2.7—3.0 (2H, m), 4.1—4.4 (1H, m), 5.17 (2H, d, J=3 Hz) and 7.1—7.4 (5H, m).

Synthesis of 1-Phenyl-3-buten-1-yne (VII)——Methylsulfinyl carbanion prepared from a 50% NaH-oil (0.48 g, 0.10 mole) and 100 ml of DMSO at 75° in an Ar atmosphere was cooled to r.t. To this solution was added dropwise a mixture of methyl triphenylphosphonium bromide (35.7 g, 0.10 mole) and DMSO (130 ml) at 15—20° under stirring. After the completion of the addition, stirring was continued for 0.5 hr at r.t. and phenylpropiolaldehyde (13 g, 0.10 mole) was added. After stirring for 3 hr at r.t., the reaction mixture was poured into 1.5 liter of ice-water and extracted with n-hexane. The combined extracts were dried over anhyd. Na_2SO_4 and condensed. The residue was submitted to distillation and the fraction distilled at 60° (3 mmHg) was collected. Yield, 1.0 g. UV λ_{max}^{EtOH} nm: 255, 268, 284. Mass Spectrum m/e: 128 (M^+), 102 ($C_6H_5\text{-}C{\equiv}CH^+$), 101 ($C_6H_5\text{-}C{\equiv}C^+$), 77 ($C_6H_5^+$). IR ν_{max}^{Film} cm^{-1}: 3060 (olefinic C-H), 2220 (C≡C). NMR, δ ppm in $CDCl_3$: 7.2—7.6 (5H, m), 5.4—6.2 (3H, m, characteristic pattern of -HC=CH_2).

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Ethyl 2-Phenethynylcyclopropanecarboxylate (IV_8) from VII——A mixture of 1-phenyl-3-buten-1-yn (VIII) (0.80 g, 6.3 mmole) and ethyl diazoacetate (0.90 g, 7.9 mmole) was dropped into a flask heated at 125—135° in an Ar atmosphere. After the evolution of N_2 ceased (3 hr later), the resulted mixture was purified by dry column chromatography. Two kinds of stereoisomeric cyclopropane derivatives were isolated. Major component (*trans*; IV_8t in Table IV): Yield, 0.35 g (26%). Mass Spectrum *m/e*: 214 (M^+), 169 (M-OEt), 141 (M-CO_2Et). UV λ_{max}^{EtOH} nm (log ε): 249 (4.31). IR ν_{max}^{Film} cm^{-1}: 2240 (C≡C), 1732 (C=O), 1600, 750, 690 (C_6H_5-), 1190, 1180 (C-O-C). NMR (see Table IV). Minor component (*cis*; IV_8c): Yield, 0.19 g (14%). Mass Spectrum *m/e*: 214 (M^+), 169 (M-OEt), 141 (M-CO_2Et). UV λ_{max}^{EtOH} nm (log ε): 249 (4.30). IR ν_{max}^{Film} cm^{-1}: 2220 (C≡C), 1735 (C=O), 1603, 755, 690 (C_6H_5-), 1185 (C-O-C).

General Preparation Method of 2-Ethynylcyclopropanecarboxylic Acid (VIII)——A mixture of the corresponding cyclopropanecarboxylic ester and 5% KOH solution in 90% MeOH was allowed to stand at r.t. for several hours to 1 day. The resulted mixture was acidified with conc. HCl and extracted with ether. The combined extracts were washed with aq. NaCl solution, dried over anhyd. Na_2SO_4 and evaporated to dryness. Recrystallization from an appropriate solvent (*n*-hexane or *n*-heptane) or distillation afforded pure products. Yield, 80—90%. The physical data are given in Table III, IV, and V.

Methyl trans-2-(*cis*-Phenethenyl)cyclopropanecarboxylate (IX) from IV_1t——A mixture of methyl *trans*-2-phenethynylcyclopropanecarboxylate (IV_1t) (0.20 g, 1.0 mmole), 10 ml of MeOH, 5% Pd/$CaCO_3$ (40 mg) and quinoline (0.5 ml) was shaken in H_2 at 1 atm. at r.t. After 3 hr, 21 ml of H_2 was uptaken and the catalyst was filtered off. Evaporation of the solvent gave the title compound. Yield, 0.20 g (bp 110—113°/0.08 mmHg). Mass Spectrum *m/e*: 202 (M^+), 143 (M-CO_2Me), 142 (C_6H_5-CH=$\overset{+}{C}$H). UV λ_{max}^{EtOH}: 250 nm. IR ν_{max}^{Film} cm^{-1}: 1734 (C=O), 1644 (C=C), 1605 (C_6H_5-). NMR δ ppm in CCl_4: 0.8—2.1 (4H, m, protons on the cyclopropane ring), 3.67 (3H, s, OMe), 5.07 (1H, dd, J_1=11.5 Hz, J_2=9.0, *cis*-C_6H_5-CH=C<u>H</u>-), 6.42 (1H, d, J_1=11.5, *cis*-C_6H_5-C<u>H</u>=CH-), 7.2—7.4 (5H, m, C_6H_5). Hydrolysis of IX in 5% KOH in 90% MeOH afforded the corresponding carboxylic acid, mp 68—69° (from *n*-heptane). Yield, 75%. *Anal.* Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.44. Found: C, 76.25; H, 6.44. IR ν_{max}^{Nujol} cm^{-1}: 1695 (C=O), 1230 (C-O-). NMR δ ppm in $CDCl_3$: 0.9—1.9 (3H, m), 2.2—2.4 (1H, m), 5.10 (1H, dd, J_1=11.5 Hz, J_2=9.0), 6.50 (1H, d, J_1=11.5), 7.37 (5H, s), 11.93 (1H, s).

Methyl *trans*-2-(2-Phenyl-1,2-dihydroxyethyl)cyclopropanecarboxylate——A mixture of methyl *trans*-2-(*cis*-phenethenyl)cyclopropanecarboxylate (IX) (152 mg, 0.75 mmole), OsO_4 (191 mg, 0.75 mmole) and 6 ml of pyridine was stirred at 25° for 72 hr. To the mixture was added a mixture of $NaHSO_3$ (400 mg), H_2O (5 ml) and pyridine (3 ml) under stirring. The mixture was extracted with $CHCl_3$ and the combined extracts were dried over anhyd. Na_2SO_4 and evaporated to dryness. Yield, 177 mg. UV λ_{max}^{EtOH} nm: 251, 257 and 263. IR ν_{max}^{Film} cm^{-1}: 3500 (OH), 1730 (C=O), 1595, 750, 710 (C_6H_5-), 1210, 1180 (C-O-Me).

Conversion of Methyl *trans*-2-(2-Phenyl-1,2-dihydroxyethyl)cyclopropanecarboxylate to Methyl Benzoate and Dimethyl *trans*-Cyclopropanedicarboxylate (X)——To a mixture of the above diol (174 mg, 0.74 mmole), H_2O (5 ml) and MeOH (6 ml) was added a solution of $NaIO_4$ (161 mg) in 5 ml of H_2O and the resulted mixture was stirred for 47 hr at r.t. The completion of the reaction was checked by TLC and the reaction mixture was extracted with a mixture of ether and AcOEt (1:1). The combined extracts were dried over anhyd. Na_2SO_4 and concentrated to dryness to give an oily residue. The oil was dissolved in MeOH (60 ml) and NaCN (410 mg), AcOH (156 mg) and MnO_2 (3.0 g) were added under stirring. Work up was done according to Corey's method[17] to give an oil (21 mg). The presence and identity of methyl benzoate and dimethyl *trans*-cyclopropanedicarboxylate (X) in this oil were done by glpc (polyethyleneglycol succinate column).

Dimethyl *trans*-Cyclopropanedicarboxylate (X)——S-Carbomethoxymethyltetrahydrothiophenium bromide was prepared from a mixture of methyl bromoacetate: (50 g, 0.35 mole), and tetramethylene sulfide (37 g, 0.42 mole) in AcOEt (200 ml); deliquescent crystals; mp 40—42°. The bromide (4.32 g, 20 mmole) and methyl acrylate (3.44 g, 40 mmole) were dissolved in anhyd. THF (100 ml). To the mixture was added a 50% NaH-oil (0.96 g, 20 mmole) under stirring in an Ar atmosphere at 0—5° and the resulting mixture was stirred at 0—5° for 0.5 hr and then at r.t. for 2 hr. The mixture was poured into 500 ml of ice–water and extracted with AcOEt. The combined extracts were washed with aq. NaCl solution, dried over anhyd. Na_2SO_4. Evaporation of the solvent gave an oil, which was proved to be mostly composed of *trans* isomer by glpc, bp 120—125° (24 mmHg, bath temp.) (lit.,[20] bp 103—104°/24 mmHg). Yield, 2.8 g (90%). IR ν_{max}^{Film} cm^{-1}: 1740 (C=O), 1200, 1170 (C-OMe). NMR δ ppm in $CDCl_3$: 3.70 (6H, s), 2.00—2.33 (2H, m), 1.25—1.58 (2H, m).

Methyl *trans*-2-Phenethylcyclopropanecarboxylate (XI) from IV_1t——A mixture of methyl *trans*-2-phenethynylcyclopropanecarboxylate (IV_1t: 200 mg, 1.0 mmole), 5% Pd/C (50 mg) and MeOH (10 ml) was stirred in H_2 at 1 atm. and 25° for 3 hr. The reaction was completed when 44 ml of H_2 was uptaken. The catalyst was filtered off and the filtrate was concentrated to give an oily residue (200 mg). Distillation gave a pure sample as an oil, bp 115—117° (0.1 mmHg, bath temp.). Yield, 170 mg (85%). Mass Spectrum *m/e*: 204 (M^+). UV λ_{max}^{EtOH} 248, 254, 261, 268. IR ν_{max}^{Film} cm^{-1}: 1733, 1200, 1170 (COOMe), 1603, 745,

20) G. Bonavent, M. Causee, M. Guitard, and R.F.-Jullien, *Bull. Soc. Chim. France*, **1964**, 2462.

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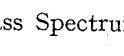
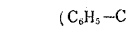
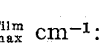
698 (benzene ring). NMR δppm in CCl_4: 7.15 (5H, s, C_6H_5), 3.60 (3H, s, CH_3), 2.70 (2H, t, $C_6H_5C\underline{H}_2$), 0.40—1.80 (6H, m). Hydrolysis of this ester was conducted according to the general preparation method of 2-ethynylcyclopropanecarboxylic acid. Yield, 80% (bp 135—140°/0.005 mmHg). *Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.47; H, 7.43. IR ν_{max}^{Film} cm^{-1}: 1735 (C=O), 1170, 1200 (-C-O-). NMR δ ppm in CCl_4: 0.85—1.80 (6H, m), 2.68 (2H, t, J=7.5 Hz), 3.60 (3H, s, OMe), 7.15 (5H, s).

Methyl *trans*-2-Phenethylcyclopropanecarboxylate (XI) from IV_2t——A mixture of methyl *trans*-2-*p*-bromophenethynylcyclopropanecarboxylate (IV_2t: 120 mg, 0.43 mmole), 5% Pd/C (50 mg), AcONa (35 mg, 0.43 mmole) and MeOH (10 ml) was stirred in H_2 at 1 atm. and 25° for 2 hr. The reaction finished after uptake of 20 ml of H_2. The insoluble substance was filtered off and the filtrate was diluted with Et_2O, washed with H_2O, dried over anhyd. Na_2SO_4 and concentrated to dryness. Distillation of the resulting oil gave a pure fraction of bp 135—140°/0.005 mmHg, which was identified with the sample of the above experimental by TLC, glpc and IR. Yield, 70 mg (80%).

Physical Properties of Methyl 2-Phenethynyl-2-(2-carbomethoxyethyl)cyclopropane (V_1c)——Preparation and isolation were described in the general procedure. The yield was 20% when the molar ratio of MA to the sulfonium salts (Ib or Ic) was two. *Anal.* Calcd. for $C_{17}H_{18}O_4$: C, 71.29; H, 6.33. Found: C, 71.49; H, 6.58. Mass Spectrum m/e=286 (M^+), 255 (M-OMe), 227 (M-CO_2Me), 195  , 139  . UV λ_{max}^{EtOH} nm (log ε): 249 (4.30). IR ν_{max}^{Film} cm^{-1}: 2230 (C≡C), 1740, 1734 (C=O), 1600, 753, 690 (benzene ring), 1195, 1170 (C-O-Me).

Physical Properties of Methyl 2-*p*-Bromophenethynyl-2-(2-carbomethoxyethyl)cyclopropanecarboxylate (A Mixture of Two Stereoisomers)——Yield, 20% by the general procedure. *Anal.* Calcd. for $C_{17}H_{17}O_4Br$: C, 55.91; H, 4.69; Br, 21.89. Found: C, 55.47; H, 4.78; Br, 22.01. Mass Spectrum m/e: 365 (M^+), 334 (M-OMe), 306 (M-CO_2Me), 292 (M-CH_2CO_2Me), 247 (M-2CO_2Me), 219  . UV λ_{max}^{EtOH} nm (log ε): 258 (4.42). IR ν_{max}^{Film} cm^{-1}: 2210 (C≡C), 1740 (C=O), 1590 (benzene ring), 1200, 1170 (C-O-Me). NMR δ ppm in $CDCl_3$: 1.1—2.8 (7H, m), 3.65, 3.68, 3.72, 3.73 (6H, each peak is singlet, OMe), 7.18, 7.45 (ABq, J=9.0 Hz).

Physical Properties of Methyl Ethynyl-2-(2-carbomethoxyethyl)cyclopropanecarboxylate——Yield, 6.2% by the general procedure. Mass Spectrum m/e: 210 (M^+), 179 (M-OMe), 151 (M-CO_2Me), 137 (M-CH_2CO_2Me), 91  . IR ν_{max}^{Film} cm^{-1}: 3300 (HC≡C), 2120 (C≡C), 1740 (C=O). NMR δ ppm in $CDCl_3$: 1.2—2.7 (8H, m), 3.68 (3H, s, OMe), 3.73 (3H, s, OMe).

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