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Simple Generation of Ester-Stabilized Azomethine Ylides from 2-Amino Esters and Carbonyl Compounds. Stereochemistry of Their Cycloadditions

Otohiko Tsuge,* Shuji Kanemasa, Masayuki Ohe, Kiyotaka Yorozu, Shigeori Takenaka, and Kazunori Ueno

Institute of Advanced Material Study, and Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasugakoen, Kasuga 816

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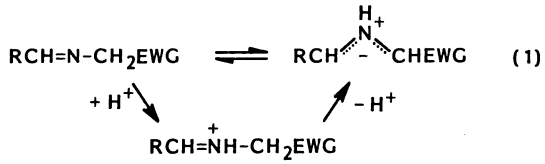
Condensation of 2-amino esters with carbonyl compounds leads to simple generation of ester-stabilized azomethine ylides which are trapped by olefinic dipolarophiles as cycloadducts. Anti ylides are exclusively involved in the cycloadditions when *N*-substituted 2-amino esters are employed for the ylide generation, while syn ylides from *N*-unsubstituted 2-amino esters. Relative stability among all possible ylide isomers has been inspected and the selective involvement of particular ylidic forms has been explained on the ground of 1,5-dipole interaction or hydrogen bonding stabilization. Endo- and exo-selectivity of the cycloadditions is also discussed.

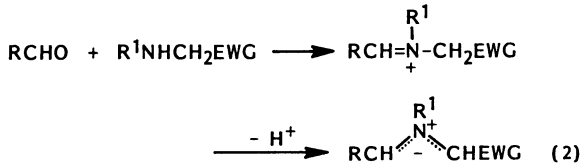
Cycloaddition of azomethine ylides with olefinic and acetylenic dipolarophiles affords pyrrolidines, pyrrolines, and pyrroles. The importance of azomethine ylide chemistry is being increased more than ever as a tool for constructing the nitrogen-containing five-membered heterocycles which are often central ring systems of numerous natural products. Its synthetic application was encouraged by the recent discovery of new generation methods of azomethine ylides, including wide range of stabilized to nonstabilized azomethine ylides. Two typical methods involve the desilylation route[1] discovered by Vedejs; the imine route[2] by Grigg, Joucla, and Tsuge, separatedly.

Griggs' method of generating azomethine ylides is based upon a thermal tautomerization of imine (Eq. 1). The acidic hydrogen adjacent to both the imine



(1)

nitrogen and ester moiety migrates onto the nitrogen (1,2-proton migration). This imine–azomethine ylide tautomerization is known to be catalyzed by an acid which facilitates the reaction by the rapid formation of an iminium intermediate.[3] It is therefore envisaged that the iminium compounds which will be produced from the condensation of *N*-substituted 2-amino esters with carbonyl compounds would allow ready deprotonation to lead to the generation of ester-stabilized azomethine ylides (Eq. 2). This process has been



(2)

recently realized by several groups,[4-6] while the reaction examples were quite limited so that no details of this promising azomethine ylide generation are known.

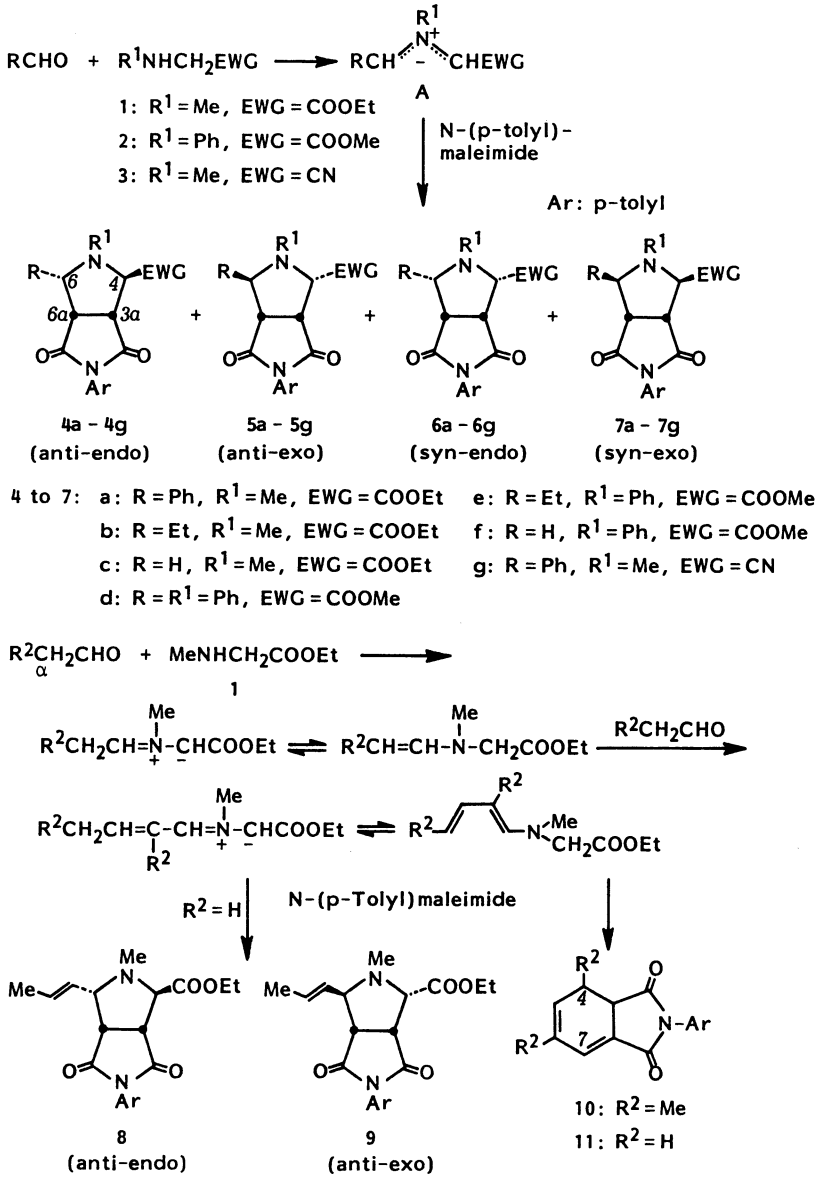
The present article describes full details of the 2-amino ester route as a simple and general generation method of ester-stabilized azomethine ylides. Stereochemical features of the cycloaddition of ester-stabilized azomethine ylides with olefins have been figured out. The origin of anti- and syn-selectivity with respect to the ylides as well as the endo-, exo, and regioselectivity of the cycloaddition is discussed.[7]

Results and Discussion

Generation and Cycloaddition of *N*-Substituted Azomethine Ylides of Ester-Stabilized Types. According to the Eq. 2, benzaldehyde and ethyl *N*-methylaminoacetate (**1**) were heated under reflux in toluene. The water eliminated was removed by the aid of a Dien–Stark trap and the azomethine ylide **A** (R=Ph, R^1=Me, EWG=COOEt) generated was captured by *N*-(*p*-tolyl)maleimide to give three stereoisomers of 1 : 1 cycloadducts **4a**, **5a**, and **6a** in 93% of total yield (Scheme 1 and Table 1).

Their structures are readily assigned as 3a,4-trans-6,6a-cis- (**4a**, 69%), 3a,4-cis-6,6a-trans- (**5a**, 20%), and 3a,4-cis-6,6a-cis-isomer (**6a**, 4%) on the basis of the vicinal coupling constants as well as other spectral and analytical data: **4a**: $J_{3a,4}$=0.8 and $J_{6,6a}$=9.4 Hz; **5a**: $J_{3a,4}$=8.8 and $J_{6,6a}$=5.7 Hz; **6a**: $J_{3,3a}$=8.8 and $J_{6,6a}$=7.0 Hz. Thus, **4a** and **5a** are cycloadducts to the anti form of ylide **A** and **6a** to the syn ylide.

Aliphatic aldehydes can be used as carbonyl compounds albeit low yield formation of the cycloadducts. The azomethine ylide **A** (R=Et, R^1=Me, EWG=COOEt) derived from propanal reacted with the maleimide to produce 48% yield of two stereoisomeric cycloadducts **4b** and **5b** to the anti



Scheme 1.

Table 1. Cycloaddition of *N*-(*p*-Tolyl)maleimide with Ester- or Cyano-Stabilized Azomethine Ylides **A** Generated from 2-Amino Esters **1**, **2** or Nitrile **3** and Aldehydes

Entry	Amine	Aldehyde	Product	R	R^1	R^2	EWG	Yield[a] %	Isomer ratio[b]	anti : syn	endo : exo
1	**1**	PhCHO	**4a**+**5a**+**6a**	Ph	Me	—	COOEt	93	69 : 20 : 4	96 : 4	78 : 22
2	**1**	EtCHO	**4b**+**5b**+**10**	Et	Me	Me	COOEt	66	37 : 11 : 18	anti only	77 : 23
3	**1**	MeCHO	**8**+**9**+**11**	—	—	H	—	87	58 : 18 : 11	anti only	76 : 24
4	**1**	$(CH_2O)_n$	**4c**+**5c**	H	Me	—	COOEt	93	58 : 35	—	62 : 38
5	**2**	PhCHO	**4d**+**5d**	Ph	Ph	—	COOMe	77	35 : 42	anti only	45 : 55
6	**2**	EtCHO	**4e**+**5e**	Et	Ph	—	COOMe	64	30 : 34	anti only	47 : 53
7	**2**	$(CH_2O)_n$	**4f**+**5f**	H	Ph	—	COOMe	78	1 : 1[c]	—	50 : 50
8	**3**	PhCHO	**4g**+**5g**+**6g**+**7g**	Ph	Me	—	CN	49	12 : 12 : 16 : 9	49 : 51	57 : 43

a) Total yield. b) Yield of separated products. c) Determined by ^{1}H NMR.

ylide together with the third product **10** which was assigned as 4,6-dimethyl-2-(*p*-tolyl)-1,3,3a,4-tetrahydro-2*H*-isoindole-1,3-dione. When ethanal was employed, no trace of the cycloadducts of methyl-substituted azomethine ylide **A** (R=Me) was even detected but two stereoisomeric cycloadducts **8**+**9** to 1-propenyl-substituted ylide were obtained. Isoindoledione **11** was again accompanied.

Formation of **8** to **11** was not surprising since we have already experienced a similar reaction pattern in the reaction of aminoacetonitrile with aliphatic aldehydes.[3b] As illustrated in Scheme 1, an aliphatic aldehyde undergoes condensation with ethyl *N*-methylaminoacetate **1** to generate the expected azomethine ylide which is in equilibrium with an enamine isomer. The enamine then adds to the second molecule of the aldehyde to form 1-alkenyl-substituted azomethine ylide which is also equilibrating with the dienamine. 1,3-Dipolar cycloaddition of the ylide leads to **8** and **9**, while Diels–Alder reaction of the latter gives **10** and **11** after the elimination of amino ester **1**.

The condensation of **1** with paraformaldehyde generated the azomethine ylide **A** (R=H, R^1=Me, EWG=COOEt) bearing an ester as the only *C*-substituent. It was captured by *N*-(*p*-tolyl)maleimide to give two stereoisomeric cycloadducts **4c** and **5c** in an excellent combined yield.

Reactions of methyl *N*-phenylaminoacetate (**2**) with benzaldehyde, propanal, and paraformaldehyde generated azomethine ylides **A** (R^1=Ph, EWG=COOMe) whose cycloadditions with *N*-(*p*-tolyl)maleimide afforded mixtures of endo- and exo-cycloadducts to the anti forms of ylides **A** (**4d**+**5d** to **4f**+**5f**, Scheme 1 and Table 1).

The exclusive involvement of the anti form of *N*-substituted azomethine ylides **A** (EWG=$COOR^2$) bearing a ylide-stabilizing ester in their cycloadditions

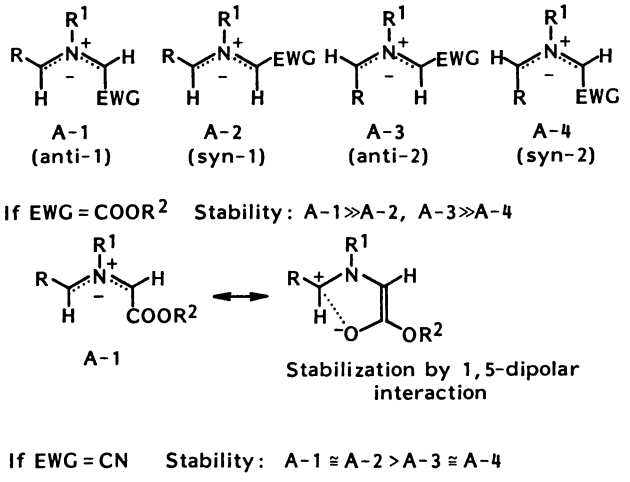


Fig. .1. Stable configuration of *N*-substituted azomethine ylides of ester- and cyano-stabilized types.

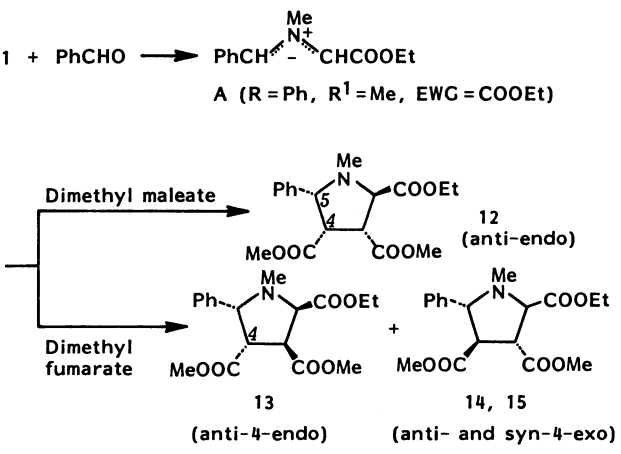
contrasts with the extremely poor selectivity of cyano-stabilized azomethine ylide **A** (EWG=CN), with respect to both the ylide configuration and cycloaddition approach. For instance, reaction of *N*-methylaminoacetonitrile (**3**) with benzaldehyde in the presence of *N*-(*p*-tolyl)maleimide gave a mixture of four stereoisomeric cycloadducts **4g**, **5g**, **6g**, and **7g**, all possible stereoisomers, in a comparable ratio (Table 1).

Each two anti (**A-1** and **A-3**) and syn configurations (**A-2** and **A-4**) are possible for the *N*-substituted azomethine ylide **A** with an ester or a cyano stabilizing substituent (Fig. 1). Their relative stability may be estimated on the ground of steric and electronic interactions among the substituents.

The U-shaped syn ylide **A-4** of ester-stabilized type is first discarded as the concerned species because it is too congested to exist as a stable form. Although the other three ylides seem equally stable from a sterical standpoint, only the S-shaped anti ylide **A-1** with the ester group opposite to the *N*-substituent R^1 has an additional stabilization by 1,5-dipole interaction.[8,9] In the end the relative stability of ester-stabilized ylides (EWG=$COOR^2$) becomes as follows: **A-1**≫**A-2**≅**A-3**≫**A-4**. Accordingly the anti ylide **A-1** must have been selectively involved in its cycloaddition.

On the other hand such stabilization by an extended dipole is impossible in the case of cyano-stabilized azomethine ylide **A** (EWG=CN). Cyano moiety is only slightly bulkier than hydrogen so that the difference of steric stability between **A-1** and **A-2**, and also **A-3** and **A-4**, is negligible. Thus the relative stability becomes in the following order: **A-1**≅**A-2**> **A-3**≅**A-4**. Poor stereoselectivity will be unavoidable in the cycloadditions of *N*-substituted azomethine ylides **A** of cyano-stabilized types.

Exclusively stereospecific cycloadditions of the azomethine ylide **A** (R=Ph, R^1=Me, EWG=COOEt) derived from **1** and benzaldehyde is shown in Scheme 2 and Table 2. Contrary to the poor stereoselectivity observed in the cycloaddition to *N*-(*p*-tolyl)maleimide



Scheme 2.

(Entry 1 of Table 1), the reaction with dimethyl maleate was highly endo-selective leading to **12**. With dimethyl fumarate, three stereoisomeric cycloadducts **13—15** were produced. Similar dramatic change of stereoselectivity has been recently reported by Joucla.[5] 4,5-Cis structure of **12** and **13** was assigned on the basis of the intense shielding of 4-ester moiety by the adjacent phenyl (5-Ph).

With unsymmetrically substituted olefins such as methyl acrylate and (*E*)-β-nitrostyrene, the above ylide **A** (R=Ph, R[1]=Me, EWG=COOEt) as well as its *N*-phenyl analog **A** (R=R[1]=Ph, EWG=COOMe) underwent highly endo- and regioselective cycloadditions giving 2,3-cis-3,4-trans-4,5-cis-cycloadducts **16a—16d** as single isomers (Scheme 3 and Table 2). As will be realized soon, these high regio- and stereoselectivities can not be achieved without the phenyl substituent.

The azomethine ylide bearing an ester moiety as the only *C*-substituent was previously generated by thermolysis of aziridine-2-carboxylates,[6a,b] deprotonation of *N*-(phenylthiomethyl)aminoacetates,[6c] or desilylation of *N*-(trimethylsilylmethyl)iminoacetates.[6d] This ylide **A** (R=H, R[1]=Me, EWG=COOEt) which was more simply generated from **1** and paraformaldehyde under reflux in toluene undergoes cycloadditions to unsymmetrically substituted olefins, but both the regio- and stereoselectivities are very poor like the precedents. Thus a mixture of two regioisomeric cycloadducts **17a** or **17b** was produced with methyl acrylate or phenyl vinyl sulfone, respectively (Scheme 3). It is noteworthy that this ylide showed high reactivity toward styrene as an aryl-substituted olefin to give the regioselective cycloadduct **17c**. This is the first example for the cycloaddition of ester-stabilized azomethine ylide to such an aryl-substituted olefin as styrene.[10,11]

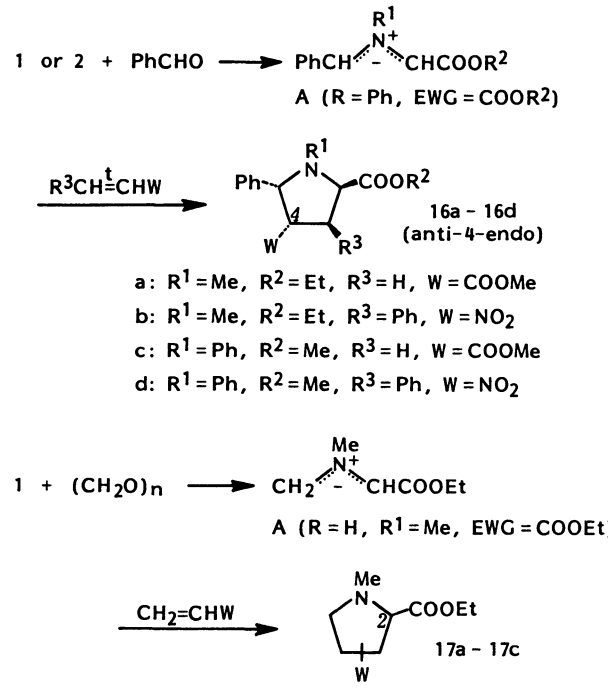
As some incorrect structural assignments are contained in the previous work,[13] our structural

Table 2. Cycloaddition of Ester-Stabilized Azomethine Ylides **A** and **B**

Entry	2-Amino ester	Aldehyde	Olefin	Condition[a]	Product (yield/%)[b]	Isomer ratio[c]	anti : syn	endo : exo
1	**1**	Benzaldehyde	Dimethyl maleate	A, 1 h	**12** (62)		anti only	endo only
2	**1**	Benzaldehyde	Dimethyl fumarate	A, 1 h	**13**+**14**+**15** (87)[d]	3 : 3 : 2		
3	**1**	Benzaldehyde	Methyl acrylate	A, 1 h	**16a** (73)		anti only	endo only
4	**1**	Benzaldehyde	β-Nitro-styrene	A, 1 h	**16b** (72)		anti only	endo only
5	**2**·HCl	Benzaldehyde	Methyl acrylate	B, 24 h	**16c** (31)		anti only	endo only
6	**2**·HCl	Benzaldehyde	β-Nitro-styrene	B, 24 h	**16d** (39)		anti only	endo only
7	**1**	Paraform-aldehyde	Methyl acrylate	C, 12 h	**17a** (100)[e]	6 : 5[f]	—	g)
8	**1**	Paraform-aldehyde	Phenyl vinyl sulfone	A, 1 h	**17b** (82)[e]	1 : 4[h]	—	g)
9	**1**	Paraform-aldehyde	Styrene	C, 12 h	**17c** (61)[i]	1 : 1[j]	—	50 : 50
10	**18**	Benzaldehyde	*N*-Methyl-maleimide	A, 24 h	**19a** (100)		syn only	endo only
11	**18**	Benzaldehyde	*N*-Methyl-maleimide	D, 13 h	**19a**+**20** (100)		67 : 33	endo only
12	**18**	Phenylglyoxal	*N*-Methyl-maleimide	E, 16 h	**19b** (100)		syn only	endo only
13	**18**	2-Methyl-propanal	*N*-Methyl-maleimide	A, 20 h	**19c** (58)		syn only	endo only
14	**18**	Cyclohexa-none	*N*-Methyl-maleimide	A, 19 h	**21** (85)		—	endo only

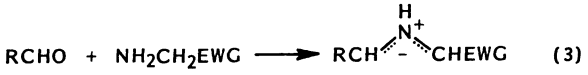
a) A: Under reflux in toluene, B: Uuder reflux in toluene together with *N*,*N*-diisopropylethylamine, C: At 180 °C in a sealed tube together with anhydrous potassium carbonate, D: At room temperature in acetonitrile in the presence of acetic acid (10 mol%), E: Under reflux in chloroform. b) Yield of isolated products. c) Determined by ^{1}H NMR. d) Only **15** was separated from the other two. e) Inseparable mixture of two regioisomers. f) 2,3-Isomer : 2,4-isomer=6 : 5 (^{1}H NMR). g) Stereostructure remains unsolved. h) 2,3-Isomer : 2,4-isomer=1 : 4 (^{1}H NMR). i) Inseparable mixture of two stereoisomers. j) Both 2,3-isomers.

analysis on **17a—17c** based upon the ^{13}C NMR is summarized in Table 3. Adjacent substitution with an ester brings about a downfield ^{13}C shift by 3—5 ppm, and with a phenyl by 7—10 ppm. Substitution with a sulfonyl makes no significant shift to the adjacent carbon. Thus **17a** and **17b** were assigned as mixtures of two regioisomers, while their stereostructures could not be determined. Also apparent is the 2,3-disubstituted structure of **17c**. A 6:5 ratio of 2,3- to 2,4-substitution of **17a** is opposite to the reported one (1:3),[6c] indicating that regioselectivity in the azomethine ylide cycloadditions strongly depends upon the generation method or reaction medium.



Scheme 3.

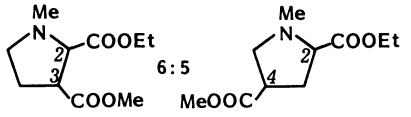
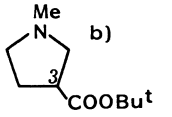
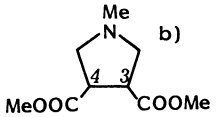
Generation and Cycloaddition of *N*-Unsubstituted (or *N*-Protonated) Azomethine Ylides of Ester-Stabilized Types. As shown with Eq. 1 *N*-(alkoxycarbonylmethyl)imines undergo a ready thermal tautomerization and this reaction is one of the most useful generation methods of *N*-unsubstituted azomethine ylides of ester-stabilized types.[2] This procedure may be simplified by omitting the isolation step of the imines and this modified method would be especially useful when imine esters as ylide precursors are labile.[3b] Our procedure consists of heating a mixture of 2-amino ester and carbonyl compound under continuous removal of water (Eq. 3).[14]

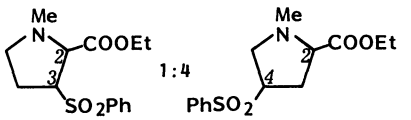
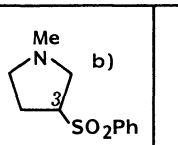
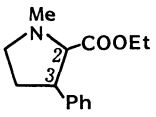


(3)

N-Unsubstituted azomethine ylides **B** of ester-stabilized types were directly generated by similar reactions of methyl aminoacetate (**18**) with carbonyl compounds and trapped with *N*-methylmaleimide to provide the exclusive formation of endo-cycloadducts **19a—19c** and **21** to the syn form of **B** (Scheme 4 and

Table 3. ^{13}C NMR Chemical Shifts for the Ring Carbons of **17a—17c**[a]

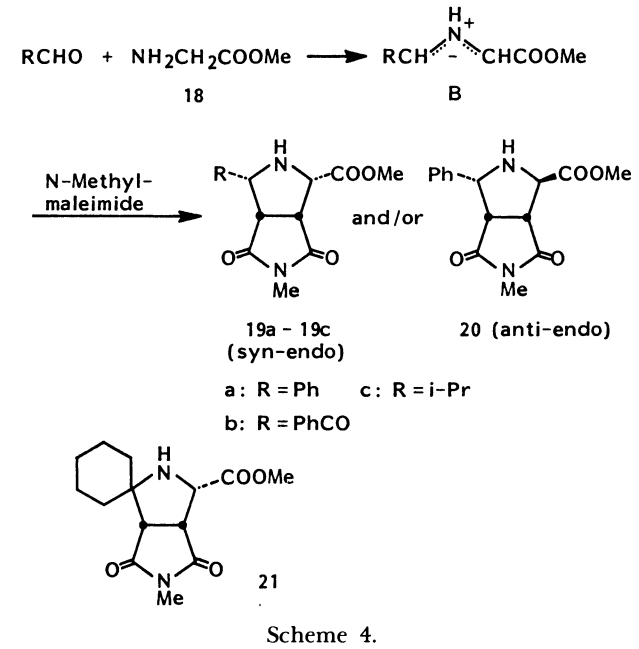
	 17a (2,3-isomer)	17a (2,4-isomer)		
	6:5			3,4-cis 3,4-trans
2-C	70.24 (d)	66.83 (d)	58.24 (t)	58.35 (t) 59.06 (t)
3-C	47.12 (d)	32.77 (t)	41.94 (d)	45.85 (d) 45.94 (d)
4-C	27.83 (t)	41.47 (d)	27.47 (t)	
5-C	55.77 (t)	58.83 (t)	55.30 (t)	

	 17b (2,3-isomer)	17b (2,4-isomer)		 17c (1:1 mixture)
	1:4			2,3-trans 2,3-cis
2-C	66.95 (d)	65.36 (d)	55.47 (t)	76.01 (d) 73.01 (d)
3-C	65.71 (d)	29.59 (t)	62.48 (d)	49.65 (d) 47.94 (d)
4-C	24.71 (t)	60.30 (d)	25.94 (t)	31.94, 32.71 (each t)
5-C	54.94 (t)	54.24 (t)	55.30 (t)	55.83, 56.12 (each t)

a) All recorded in $CDCl_3$. b) See Ref. 12.

Table 2). Benzaldehyde and cyclohexanone form relatively stable imines so that the thermal tautomerization method could be also applied to these imines. Although the imines of **18** with phenylglyoxal and 2-methylpropanal are too unstable to be isolated, our method worked well in both cases. However a serious limitation appeared when such aldehydes as propanal and cinnamaldehyde were employed. No corresponding azomethine ylides were trapped by a maleimide dipolarophile.

As shown above the imine derived from **18** and benzaldehyde tautomerized into a syn form of azomethine ylide **B** (R=Ph) on heating in toluene. To our surprise the stereoselectivity with respect to the ylide was extremely decreased when the same imine was heated in acetonitrile in the presence of acetic acid (10 mol%). Thus a 1:2 mixture of the syn and anti ylide cycloadducts **19a+20** was obtained. This will be discussed later.



Scheme 4.

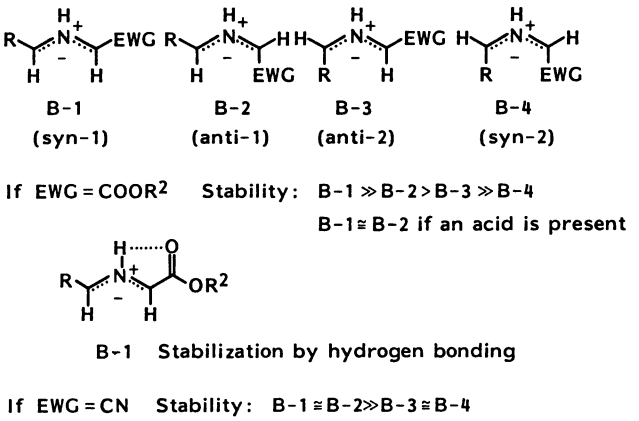


Fig. 2. Stable configuration of *N*-protonated azomethine ylides of ester- and cyano-stabilized types.

Four configurations including each two syn (**B-1** and **B-4**) and anti ylidic forms (**B-2** and **B-3**) are also possible for the *N*-unsubstituted azomethine ylide **B** of ester- or cyano-stabilized type (Fig. 2). In all the cycloaddition examples described in Scheme 4 with an exception the syn form of ester-stabilized ylide **B** (EWG=COOMe) was exclusively incorporated in the cycloadducts, indicating higher stability of the syn ylide. This makes a striking contrast to the case of *N*-substituted ylide **A** where anti form has predominated. It is quite easy to understand that ylide **B-1** is much more stabilized than the other syn ylide **B-4** on the basis of both steric consideration and the hydrogen bonding between the ester carbonyl and NH hydrogen. In a polar or protic solvent this hydrogen bonding becomes fragile, and the positively charged ylide nitrogen is stabilized through the coordination of the solvent molecules nearby. In this case syn configuration **B-1** is no longer the most stable.

In the case of *N*-protonated azomethine ylide **B** (EWG=CN) of cyano-stabilized type, syn ylide **B-1** and anti ylide **B-2** would have an identical stability. Poor stereoselectivity with respect to the ylidic carbon bearing a CN substituent has been previously demonstrated.[3b]

Stereochemical Aspects of Cycloaddition of Ester-Stabilized Azomethine Ylides. The predominant participation in cycloaddition of the anti ylide **A-1** of *N*-substituted azomethine ylide (Fig. 1) and of the syn ylide **B-1** of *N*-unsubstituted ylide has been discussed above (Fig. 2). Table 1 summarizes the endo–exo ratios of cycloadducts derived from *N*-substituted azomethine ylides **A** (EWG=COOEt or COOMe) bearing a variety of *C*-substituents and *N*-(*p*-tolyl)-maleimide, and Entries 10—14 of Table 2 show the exclusive formation of endo cycloadducts from *N*-unsubstituted azomethine ylides **B** and the maleimide. Apparently the endo–exo selectivity depends upon the *N*-substituents.

Endo and exo approaches of maleimide to an azomethine ylide 1,3-dipole is illustrated in Fig. 3 with Approach I and II, respectively (either A or B is an ester moiety). In Approach II (exo) there exist four sets of near-eclipsed repulsion (H/CO, A/CO, R/H, B/H), and in Approach I (endo) steric repulsion

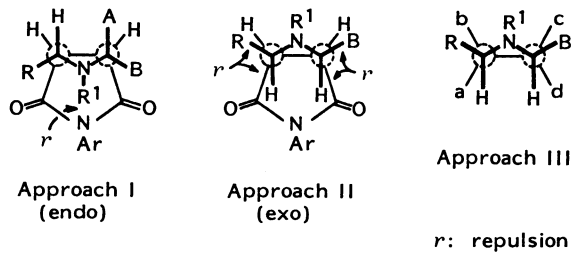


Fig. 3. Approaches between azomethine ylide $RCH{=}\overset{+}{N}(R^1)\text{-}\underline{C}AB$ and olefinic dipolarophiles.

between both the *N*-substituents (R^1 and Ar) is the only barrier. Accordingly it is readily understood that cycloaddition becomes highly endo-selective if the *N*-substituent R^1 is small in size, for instance a hydrogen. On the other hand this steric repulsion is critical when R^1 is bulky, the endo selectivity becoming lowered.

The small bond angle of CO–CH=CH and the planer geometry make maleimides a very special dipolarophile. The *N*-substituent repulsion of Approach I and the eclipsed repulsion of Approach II are both amplified compared with other acyclic dipolarophiles whose approach is illustrated with Approach III (Fig. 3). Now the substituents a and d are not bonded so that the steric repulsion toward the *N*-substituent R^1 is reduced. This may be the main reason why the cycloaddition of ylide **A** (R=Ph, R^1=Me, EWG=COOEt) to dimethyl maleate was absolutely endo-selective to lead to **12** (Entry 1 of Table 2). Attractive interaction working between the phenyl substituent and the ester group, each is on either the ylide or olefin, is also responsible for the high endo selection as shown with Entries 3—6 of Table 2.

The present generation method of ester-stabilized azomethine ylides is valuable because of 1) simple procedure using readily available 2-amino esters and carbonyl compounds, 2) high yield formation of a variety of ylides, 3) no need of the isolation of ylide precursors, 4) mild generation conditions. As the aziridine route leading to ester-stabilized azomethine ylides with no other ylide-stabilizing substituent requires the pyrolysis at an elevated temperature,[6a] the ylide trapping with olefins are not so effective as the present case.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-40 (90 MHz) or a JEOL FX-100 instrument (100 MHz) and ^{13}C NMR on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. High resolution mass spectra were also obtained on the same instrument. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck). Visualization was made with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

General Procedure for the Azomethine Ylide Generation from the Condensation of 1—3 with Carbonyl Compounds. An amine (**1**, **2**, or **3**) and an aldehyde were heated under reflux in dry toluene (5 ml for 1 mmol of the amine) in the presence of *N*-(*p*-tolyl)maleimide. The water formed was continuously removed by the aid of a Dean-Stark trap. Equimolar amounts of the amine and *N*-(*p*-tolyl)maleimide were used, while the aldehydes were employed in excess: Benzaldehyde and propanal: 1.5 equivalent. Acetaldehyde and paraformaldehyde: 5 equivalents. The reaction conditions as well as the results are all summarized in Table 1.

4a+5a+6a: This mixture was chromatographed over silica gel with hexane–ethyl acetate (10:1 vol/vol) to give **4a** (63%), **5a** (21%), and then **6a** (7%). **4a**: Colorless needles (benzene–hexane); mp 151—152 °C; IR (KBr) 1720 and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.35 (3H, t, COOEt), 2.28 2.32 (each 3H, s, NMe and *p*-Me), 3.47 (1H, dd, J=8.0 and 0.8 Hz, 3a-H), 3.75 (1H, dd, J=9.4 and 8.0 Hz, 6a-H), 4.25 (2H, q, COOEt), 4.40 (1H, br s, 4-H), 4.49 (1H, d, J=9.4 Hz, 6-H), and 6.8—7.4 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=14.47 (q, COOEt), 21.18 (q, *p*-Me), 35.56 (q, NMe), 48.65 (d, 3a-C), 50.42 (d, 6a-C), 61.00 (t, COOEt), 67.53 (d, 4-C), 69.06 (d, 6-C), 128.00 128.10, 128.54, 128.77, 129.83 (each d), 129.48, 137.19, 138.54 (each s), 171.01 (s, COOEt), 174.84, and 176.54 (each s, CON); MS *m/z* (rel intensity, %) 393 (M^+, 1), 320 (25), 319 (base peak), and 158 (42). Found: C, 70.42; H, 6.20; N, 7.03%. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.37; H, 6.17; N, 7.13%. **5a**: Pale yellow liquid; IR (neat) 1780 and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.27 (3H, t, COOEt), 2.16, 2.26 (each 3H, s, NMe and *p*-Me), 3.41 (1H, dd, J=9.7 and 5.7 Hz, 6a-H), 3.85 (1H, dd, J=9.7 and 8.8 Hz, 3a-H), 4.17 (2H, q, COOEt), 4.27 (1H, d, J=8.8 Hz, 4-H), 4.37 (1H, d, J=5.7 Hz, 6-H), and 7.0—7.4 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=14.30 (q, COOEt), 21.24 (q, *p*-Me), 35.06 (q, NMe), 46.94 (d, 3a-C), 53.47 (d, 6a-C), 61.29 (t, COOEt), 67.48 (d, 4-C), 69.12 (d, 6-C), 126.69, 127.90, 128.38, 129.01, 129.95 (each d), 129.60, 138.89, 139.89 (each s), 174.01, 175.59, and 176.36 (each s, COOEt and CON); MS *m/z* (rel intensity, %) 393 (M^+, 1), 320 (23), 319 (base peak), 158 (21), 143 (6), and 42 (5). Found: C, 70.57; H, 6.24; N, 7.12%. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 7.14%. **6a**: Colorless needles (benzene–hexane); mp 179—180.5 °C; IR (KBr) 1730 and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.34 (3H, t, COOEt), 2.25, 2.31 (each 3H, s, NMe and *p*-Me), 3.42 (1H, d, J=7.0 Hz, 4-H), 3.52 (1H, dd, J=8.8 and 7.5 Hz, 6a-H), 3.68 (1H, dd, J=7.5 and 7.0 Hz, 3a-H), 3.74 (1H, d, J=8.8 Hz, 6-H), 4.32 (2H, dq, COOEt), and 6.9—7.4 (9H, m, Ar); MS *m/z* (rel intensity, %) 393 (M^+, 1), 320 (25), 319 (base peak), 160 (6), 158 (23), 143 (7), and 42 (5). Found: C, 70.12; H, 6.16; N, 7.04%. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.37; H, 6.17; N, 7.13%.

4b+5b+10: This mixture was separated into **4b** (37%), **5b** (11%), and **10** (18%) through column chromatography over silica gel by using hexane–ethyl acetate (10:1 vol/vol). **4b**: Pale yellow liquid; IR (neat) 1780, 1730, and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.03 (3H, t, Et), 1.26 (3H, t, COOEt), 1.4—1.8 (2H, m, Et), 2.34 (6H, s, NMe and *p*-Me), 3.20 (1H,

m, 6-H), 3.38 (1H, dd, J=8.0 and 0.5 Hz, 3a-H), 3.42 (1H, dd, J=8.0 and 6.5 Hz, 6a-H), 3.99 (1H, d, J=0.5 Hz, 4-H), 4.15 (2H, q, COOEt), 7.04, and 7.25 (each 2H, d, J=8.0 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ=10.59 (q, Et), 14.41 (q, COOEt), 21.18 (q, p-Me), 22.18 (t, Et), 35.41 (q, NMe), 47.18, 47.36 (each d, 3a- and 6a-C), 60.89 (t, COOEt), 65.83 (d, 4-C), 68.30 (d, 6-C), 126.42, 129.90 (each d), 129.60, 138.77 (each s), 170.66 (s, COOEt), 176.01, and 177.01 (each s, CON); MS m/z (rel intensity, %) 344 (M^+, 5), 272 (20), and 271 (base peak). Found: C, 66.15; H, 6.95; N, 8.04%. Calcd for $C_{19}H_{24}N_2O_4$: C, 66.24; H, 7.04; N, 8.13%. **5b**: Pale yellow liquid; IR (neat) 1755 and 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.15 (3H, t, Et), 1.30 (3H, t, COOEt), 1.6—1.8 (2H, m, Et), 2.28, 2.32 (each 3H, s, NMe and p-Me), 3.1—3.6, 3.9—4.2 (3H+1H, m, 3a-, 4-, 6-, and 6a-H), 4.25 (2H, q, COOEt), and 7.0—7.3 (4H, m, Ar); MS m/z (rel intensity, %) 344 (M^+, 2) and 271 (base peak). HRMS Found: m/z 344.1721. Calcd for $C_{19}H_{24}N_2O_4$: M, 344.1734. **10**: Pale yellow grains (benzene-hexane) mp 109—110 °C; IR (KBr) 1763 and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, d, J=6.9 Hz, 7-Me), 1.91 (3H, s, 5-Me), 2.36 (3H, s, p-Me), 3.8—4.1 (1H, m, 7-H), 4.69 (1H, dd, J=8.7 and 3.0 Hz, 7a-H), 5.8—6.0 (1H, m, 6-H), 6.8—6.9 (1H, m, 4-H), and 7.1—7.3 (4H, m, Ar); MS m/z (rel intensity, %) 267 (M^+, base peak), 134 (77), 133 (26) 119 (59), 106 (36), and 91 (49). Found: C, 76.42; H, 6.43; N, 5.28%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24%.

8+9+11: This mixture was separated into **8** (58%), **9** (18%), and **11** (11%) through column chromatography over silica gel with hexane-ethyl acetate (10:1 vol/vol). **8**: Pale yellow liquid; IR (neat)1780, 1732, and 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.26 (3H, t, COOEt), 1.70 (3H, d, 1-propenyl), 2.24, 2.35 (each 3H, s, NMe and p-Me), 3.3—3.6, 3.6—3.9 (2H+1H, m, 3a-, 6-, and 6a-H), 4.03 (1H, s, 4-H), 4.16 (2H, q, COOEt), 4.9—5.3, 5.6—5.9 (each 1H, m, 1-propenyl), 7.04, and 7.26 (each 2H, d, Ar); ^{13}C NMR ($CDCl_3$) δ=13.94 (q, COOEt), 17.30 (q, 1-propenyl), 20.65 (q, p-Me), 34.59 (q, NMe), 47.53, 48.42 (each d, 3a- and 6a-C), 60.24 (t, COOEt), 66.42, 67.01 (each d, 4- and 6-C), 125.94, 128.07, 129.30, 130.54 (each d), 129.30, 137.95 (each s), 170.13 (s, COOEt), 174.83, and 176.25 (each s, CON); MS m/z (rel intensity, %) 356 (M^+, 11), 284 (20), 283 (base peak), and 122 (47). HRMS Found: m/z 356.1743. Calcd for $C_{20}H_{24}N_2O_4$: M, 356.1735. **9**: Pale yellow liquid; IR (neat) 1780, 1740, and 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, t, COOEt), 1.74 (3H, d, 1-propenyl), 2.23, 2.32 (each 3H, s, NMe and p-Me), 3.1—4.0 (4H, m, 3a-, 4-, 6-, and 6a-H), 4.16 (2H, q, COOEt), 5.2—5.6, 5.6—6.0 (each 1H, m, 1-propenyl), and 7.1—7.3 (4H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=14.18 (q, COOEt), 17.82 (q, 1-propenyl), 21.18 (q, p-Me), 35.00 (q, NMe), 46.89, 50.71 (each d, 3a- and 6a-C), 61.18 (t, COOEt), 67.01, 67.89 (each d, 4-and 6-C), 126.48, 126.60, 128.48, 129.83 (each d), 129.60, 138.66 (each s), 170.48 (s, COOEt), 175.71, and 176.48 (each s, CON); MS m/z (rel intensity, %) 356 (M^+, 6), 284 (20), 283 (base peak), and 122 (26). HRMS Found: m/z 356.1733. Calcd for $C_{20}H_{24}N_2O_4$: M, 356.1734. **11**: Colorless prisms (benzene-hexane); mp 158—160 °C; IR (KBr) 1765 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.36 (3H, s, p-Me), 2.2—2.6, 2.6—3.1, 3.4—3.8 (each 1H, m, 7- and 7a-H), 6.2—6.4, 6.9—7.1 (2H+1H, m, 4-, 5-, and 6-H), and 7.22 (4H, m, Ar); MS m/z (rel intensity, %) 239 (M^+, 19), 132 (22), 106 (77), 105 (95), 78 (base peak), 77 (74), 52 (30), and 51 (35). HRMS Found: m/z 239.0951. Calcd for $C_{15}H_{13}NO_2$: M, 239.0946.

4c+5c: This mixture was separated into **4c** (58%) and **5c** (35%) through column chromatography over silica gel with hexane-ethyl acetate (5:1 vol/vol). **4c**: Colorless needles (benzene-hexane); mp 120—121 °C; IR (KBr) 1724 and 1711 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.29 (3H, t, COOEt), 2.35, 2.39 (each 3H, s, NMe and p-Me), 3.1—3.3, 3.4—3.6 (each 2H, m, 3a-, 6-, and 6a-H), 3.97 (1H, s, 4-H), 4.20 (2H, q, COOEt), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=14.35 (q, COOEt), 21.06 (q, p-Me), 36.89 (q, NMe), 44.71 (d, 6a-C), 49.00 (d, 3a-C), 55.65 (t, 6-C), 60.83 (t, COOEt), 67.77 (d, 4-C), 126.36, 129.77 (each d), 129.77, 138.60 (each s), 170.19 (s, COOEt), 176.83, and 178.30 (each s, CON); MS m/z (rel intensity, %) 316 (M^+, 3), 243 (base peak), and 82 (43). Found: C, 64.54; H, 6.46; N, 8.76%. Calcd for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86%. **5c**: Colorless needles (benzene-hexane); mp 106—108 °C; IR (KBr) 1776, 1747, and 1707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, COOEt), 2.34 (6H, s, NMe and p-Me), 2.58 (1H, dd, J=9.5 and 7.5 Hz, one of 6-H), 3.21 (1H, d, J=8.0 Hz, 4-H), 3.33 (1H, ddd, J=8.0, 7.5, and 1.0 Hz, 6a-H), 3.54 (1H, dd, J=9.5 and 1.0 Hz, the other of 6-H), 3.61 (1H, t, J=8.0 Hz, 3a-H), 4.24 (2H, q, COOEt), and 7.1—7.3 (4H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=14.06 (q, COOEt), 21.06 (q, p-Me), 39.83 (q, NMe), 43.83 (d, 6a-C), 47.83 (d, 3a-C), 57.83 (t, 6-C), 61.24 (t, COOEt), 70.18 (d, 4-C), 126.54, 129.60 (each d), 129.71, 138.66 (each s), 169.42 (s, COOEt), 175.48, and 177.66 (each s, CON); MS m/z (rel intensity, %) 316 (M^+, 2), 243 (base peak), and 82 (59). Found: C, 64.39; H, 6.43; N, 8.78%. Calcd for $C_{17}H_{24}N_2O_4$: C, 64.54; H, 6.37; N, 8.86%.

4d+5d: This mixture was chromatographed over silica gel with hexane-ethyl acetate (5:1 vol/vol) to afford **4d** (35%) and then **5d** (42%). **4d**: Colorless prisms (benzene-hexane); mp 203—205 °C; IR (KBr) 1780, 1730, and 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.28 (3H, s, p-Me), 3.61 (1H, dd, J=8.1 and 0.8 Hz, 3a-H), 3.68 (3H, s, COOMe), 4.04 (1H, dd, J=10.0 and 8.1 Hz, 6a-H), 5.43 (1H, d, J=0.8 Hz, 4-H), 5.48 (1H, d, J=10.0 Hz, 6-H), 6.5—6.8 (5H, m, Ar), and 7.0—7.3 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=20.53 (q, p-Me), 49.42 (d, 3a- and 6a-C), 52.24 (q, COOMe), 63.18 (d, 4-C), 64.48 (d, 6-C), 116.08, 118.82, 126.06, 127.78, 128.60, 128.87, 129.23 (each d), 137.91, 138.17, 145.02 (each s), 172.03 (s, COOMe), 173.47, and 175.71 (each s, CON); MS m/z (rel intensity, %) 440 (M^+, 28), 382 (27), 381 (base peak), and 220 (31). Found: C, 73.87; H, 5.64; N, 6.29%. Calcd for $C_{27}H_{24}N_2O_4$: C, 73.62, H, 5.49; N, 6.36%. **5d**: Colorless needles (benzene-hexane); mp 189—190 °C; IR (KBr) 1730 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.36 (3H, s, p-Me), 3.54 (1H, dd, J=9.9 and 3.7 Hz, 6a-H), 3.56 (3H, s, COOMe), 4.06 (1H, t, J=9.9 Hz, 3a-H), 5.26 (1H, d, J=9.9 Hz, 4-H), 5.53 (1H, d, J=3.7 Hz, 6-H), 6.5—6.8, and 7.0—7.4 (14H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=20.71 (q, p-Me), 46.30 (d, 3a-C), 52.12 (q, COOMe), 54.53 (d, 6a-C), 64.36 (d, 4- and 6-C), 116.01, 118.89, 126.48, 126.65, 127.60, 129.01, 129.66 (each d), 138.36, 142.36, 144.77 (each s), 171.95 (s, COOMe), 174.77, and 176.42 (each d, CON); MS m/z (rel intensity, %) 440 (M^+, 22), 382 (29), 381 (base peak), and 220 (28). Found: C, 73.39; H, 5.61; N, 6.31%. Calcd for $C_{27}H_{24}N_2O_4$: C, 73.62; H, 5.49; N, 6.36%.

4e+5e: This mixture was separated into **4e** (30%) and **5e** (34%) through column chromatography over silica gel by using hexane-ethyl acetate (10:1 vol/vol). **4e**: Colorless needles (benzene-hexane); mp 150—152 °C; IR (KBr) 1790, 1741, and 1713 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (3H, t, 6-Et), 1.2—1.5, 1.7—2.1 (each 1H, m, 6-Et), 2.36 (3H, s, p-Me), 3.50 (3H, s, COOMe), 3.52 (1H, dd, J=8.2 and 0.9 Hz, 3a-H), 3.79

(1H, dd, J=9.1 and 8.2 Hz, 6a-H), 4.26 (1H, dt, J=9.1, 9.1, and 1.7 Hz, 6-H), 4.96 (1H, d, J=0.9 Hz, 4-H), and 6.8—7.4 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=10.29 (q, 6-Et), 21.24 (q, p-Me), 22.53 (t, 6-Et), 47.12, 48.47 (each d, 3a- and 6a-C), 51.83 (q, COOMe), 61.77 (d, 4-C), 67.48 (d, 6-C), 121.12, 122.60, 126.36, 129.19, 130.01 (each d), 128.54, 139.01, 145.24 (each s), 171.48 (s, COOMe), 175.54, and 176.13 (each s, CON); MS m/z (rel intensity, %) 392 (M^+, 24), 334 (24), 333 (base peak), and 172 (26). Found: C, 70.47; H, 6.14; N, 7.12%. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 7.14%. **5e**: Colorless prisms (benzene–hexane); mp 161.5—162.5 °C; IR (KBr) 1778, 1743, and 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.95 (3H, t, 6-Et), 1.2—1.9 (2H, m, 6-Et), 2.36 (3H, s, p-Me), 3.37 (1H, dd, J=8.8 and 1.9 Hz, 6a-H), 3.61 (3H, s, COOMe), 3.88 (1H, dd, J=9.5 and 8.8 Hz, 3a-H), 4.56 (1H, ddd, J=9.0, 3.0, and 1.9 Hz, 6-H), 4.69 (1H, d, J=9.5 Hz, 4-H), and 6.6—7.3 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=9.79 (q, 6-Et), 21.12 (q, p-Me), 23.30 (t, 6-Et), 46.89, 49.24 (each d, 3a- and 6a-C), 52.47 (q, COOMe), 63.83, 63.95 (each d, 4- and 6-C), 117.01, 120.07, 126.60, 129.48, 129.95 (each d), 138.89, 145.07 (each s), 171.07 (s, COOMe), 175.54, and 177.07 (each s, CON); MS m/z (rel intensity, %) 392 (M^+, 16), 334 (25), 333 (base peak), 172 (56), 144 (21), 143 (22), and 76 (22). Found: C, 70.31; H, 6.22; N, 7.00%. Calcd for $C_{20}H_{24}N_2O_4$: C, 70.39; H, 6.10; N, 7.14%.

4f+5f: (a 1:1 mixture (^{1}H NMR)): Chromatographic separation of this mixture (silica gel, hexane–ethyl acetate (5:1 vol/vol)) was unsuccessful. **4f+5f**: Colorless solid; IR (KBr) 1780, 1741, and 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s, p-Me), 3.64, 3.68 (each 1/2×3H, s, COOMe), 3.7—4.2 (4H, m, 3a-, 6-, and 6a-H), 4.74 (1/2H, d, J=9.0 Hz, 4-H), 5.00 (1/2H, s, 4-H), and 6.6—7.4 (18H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=21.18 (q, p-Me), 43.47, 44.24 (d, 6a-C), 47.77, 49.12 (d, 3a-C), 50.65, 50.83 (each t, 6-C), 52.53, 52.36 (each q, COOMe), 62.95, 63.36 (each d, 4-C), 114.48, 119.54, 119.66, 126.30, 126.48, 129.19, 129.30, 129.56, 129.95 (each d), 139.13, 145.78, 146.07 (each s), 171.60, 175.01, 176.01, 176.83, and 177.60 (each s, COOMe and CON); MS m/z (rel intensity, %) 364 (M^+, 18), 306 (18), 305 (80), 144 (base peak), and 77 (26). Only **5f** was separated by crystallization from benzene–hexane. **5f**: Colorless needles (benzene–hexane); mp 170—172 °C; IR (KBr) 1785, 1738, and 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.36 (3H, s, p-Me), 3.64 (3H, s, COOMe), 3.7—4.2 (4H, m, 3a-, 6-, and 6a-H), 4.74 (1H, d, J=9.0 Hz, 4-H), and 6.6—7.4 (9H, m, Ar); MS m/z (rel intensity, %) 364 (M^+, 25), 306 (21), 305 (base peak), 144 (44), 85 (24), 83 (32), and 43 (26). Found: C, 68.97; H, 5.55; N, 7.68%. Calcd for $C_{21}H_{20}N_2O_4$: C, 69.21; H, 5.53; N, 7.69%.

4g+5g+6g+7g: This mixture was chromatographed over silica gel with hexane–ethyl acetate whose ratio was gradually changed from 10:1 vol/vol to 1:1 to afford **4g** (12%), **5g** (12%), **6g** (16%), and then **7g** (9%). **4g**: Colorless needles (benzene–hexane); mp 194—195 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.31, 2.32 (each 3H, s, NMe and p-Me), 3.4—3.6, 4.0—4.1 (2H+1H, 3a-, 6-, and 6a-H), 4.60 (1H, s, 4-H), and (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=21.18 (q, p-Me), 36.24 (q, NMe), 48.83, 49.08 (each d, 3a- and 6a-C), 57.83 (d, 4-C), 69.95 (d, 6-C), 115.12 (s, CN), 125.20, 127.95, 128.95, 129.94 (each d), 135.07, 138.89 (each s), 173.43, and 174.71 (each s, CON); MS m/z (rel intensity, %) 345 (M^+, 63), 158 (83), 157 (base peak), and 118 (22). Found: C, 72.95; H, 5.56; N, 12.20%. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.02; H, 5.56; N, 12.17%. **5g**: Pale yellow liquid; IR (neat) 1780 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.30, 2.36 (each 3H, NMe and p-Me), 3.41 (1H, dd, J=9.4 and 6.7 Hz, 6a-H), 3.85 (1H, dd, J=6.7 and 1.0 Hz, 6-H), 3.88 (1H, dd, J=9.4 and 8.3 Hz, 3a-H), 4.58 (1H, dd, J=8.3 and 1.0 Hz, 4-H), and 7.0—7.4 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=21.17 (q, p-Me), 35.94 (q, NMe), 47.00 (d, 3a-C), 53.06 (d, 6a-C), 58.06 (d, 4-C), 69.78 (d, 6-C), 114.00 (s, CN), 126.65, 127.72, 128.73, 129.19, 130.07 (each d), 128.89, 138.48, 139.24 (each s), 173.25, and 175.13 (each s, CON); MS m/z (rel intensity, %) 345 (M^+, 84), 160 (76), 158 (91), 157 (base peak), and 107 (48). Found: C, 72.80; H, 5.96; N, 11.29%. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.02; H, 5.56; N, 12.17%. **6g**: Colorless needles (benzene–hexane); mp 189—190 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.32, 2.37 (each 3H, s, NMe and p-Me), 3.4—3.8 (4H, m, 3a-, 4-, 6-, and 6a-H), and 7.0—7.4 (9H, m, Ar); MS m/z (rel intensity, %) 345 (M^+, 68), 158 (base peak), and 157 (90). Found: C, 72.79; H, 5.56; N, 12.14%. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.02; H, 5.56; N, 12.17%. **7g**: Colorless needles (benzene–hexane); mp 195—196.5 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.33, 2.38 (each 3H, s, NMe and p-Me), 3.47 (1H, dd, J=9.0 and 6.9 Hz, 6a-H), 3.68 (1H, d, J=6.9 Hz, 6-H), 3.70 (1H, d, J=6.2 Hz, 4-H), 3.90 (1H, dd, J=9.0 and 6.2 Hz, 3a-H), and 7.0—7.4 (9H, m, Ar); MS m/z (rel intensity, %) 345 (M^+, 30), 158 (52), 157 (base peak), 116 (53), 115 (60), and 107 (88). Found: C, 73.26; H, 5.61; N, 12.03%. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.02; H, 5.56; N, 12.17%.

Generation of Azomethine Ylide A (R=Ph, R^1=Me, EWG=COOEt) from 1 and Benzaldehyde, and Ylide Trapping with Dimethyl Maleate or Fumarate Leading to 12—15. A mixture of **1** (0.22 g, 1.66 mmol), benzaldehyde (0.24 g, 2.26 mmol), and dimethyl maleate or fumarate (0.24 g, 1.66 mmol) in dry toluene (15 ml) was heated under reflux under the reaction conditions listed in Table 2. The water formed was removed by the aid of a Dean-Stark trap. The solvent was evaporated in vacuo and the residue was chromatographed over silica gel. Elution of the maleate mixture with hexane–ethyl acetate (10:1 vol/vol) afforded **12** (0.368 g, 62%). Elution of the fumarate mixture (**13**:**14**:**15**= 3:3:2 (^{1}H NMR)) with hexane–ethyl acetate (20:1 vol/vol) gave **15** (0.194 g, 33%) and then **13+14** (0.323 g, 54%, **13**:**14**=1:1 (^{1}H NMR)).

12: Colorless needles (benzene–hexane); mp 93—94 °C; IR (KBr) 1740 and 1722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (3H, t, COOEt), 2.20 (3H, s, NMe), 3.17 (3H, s, 4-COOMe), 3.64 (3H, s, 3-COOMe), 3.5—3.7, 4.1—4.5 (2H+3H, m, 2-, 3-, 4-H, and COOEt), 4.60 (1H, d, J=6.5 Hz, 5-H), and 7.24 (5H, s, Ph); ^{13}C NMR ($CDCl_3$) δ=14.35 (q, COOEt), 34.53 (q, NMe), 48.77 (d, 3-C), 51.24, 53.18 (each q, COOMe), 52.12 (d, 4-C), 61.00 (t, COOEt), 65.71 (d, 2-C), 70.83 (d, 5-C), 127.83, 128.18, 128.42, 128.72 (each d), 137.71 (s), 171.31, and 173.43 (each s, COOMe and COOEt); MS m/z (rel intensity, %) 349 (M^+, 11) and 276 (base peak). Found: C, 61.81; H, 6.63; N, 4.13%. Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01%.

13+14: Colorless viscous liquid; IR (neat) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30, 1.31 (each 1/2×3H, t, COOEt), 2.16, 2.20 (each 1/2×3H, s, NMe), 3.03 (1/2×3H, s, 4-COOMe of **13**), 3.4—3.7 (1H, m, CH), 3.65 (3H, s, COOMe), 3.77 (1/2×3H, s, COOMe), 3.9—4.4 (3H, m, CH), 4.24, 4.25 (each 1/2×2H, COOEt), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=14.41 (q, COOEt), 34.88, 35.71 (each q, NMe), 47.77, 48.77 (each d, 3-C), 51.18, 51.47, 52.24, 52.77 (each q, COOMe), 54.65 (d, 4-C), 60.65, 60.89 (each t, COOEt), 67.65, 68.42 (each d, 2-C), 69.18, 70.01 (each d, 5-C), 128.18, 128.72

(each d), 141.24 (s), 171.48, 171.78, 172.36, and 172.95 (each s, COOMe and COOEt); MS *m/z* (rel intensity, %) 349 (M^+, 16), 276 (base peak), 244 (63), 216 (54), and 184 (22). HRMS Found: *m/z* 349.1593. Calcd for $C_{18}H_{23}NO_6$: M, 349.1524.

15: Colorless liquid; IR (neat) 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (3H, t, COOEt), 2.24 (3H, s, NMe), 3.3—4.0 (4H, m, 2-, 3-, 4-, and 5-H), 3.59, 3.66 (each 3H, s, COOMe), 4.20 (2H, q, COOEt), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=14.24 (q, COOEt), 39.36 (q, NMe), 48.53 (d, 3-C), 52.18, 52.18 (each q, COOMe), 54.12 (d, 4-C), 61.12 (t, COOEt), 68.71 (d, 2-C), 74.01 (d, 5-C), 128.01, 128.36, 128.72 (each d), 139.83 (s), 171.01, 171.36, and 172.95 (each s, COOEt and COOMe); MS *m/z* (rel intensity, %) 349 (M^+, 9), 276 (base peak), 244 (65), 216 (73), 184 (30), and 158 (25). HRMS Found: *m/z* 349.1519. Calcd for $C_{18}H_{23}NO_6$: M, 349.1524.

Capture of the Ester-Stabilized Azomethine Ylides A (R=Ph, EWG=COOR²) with Methyl Acrylate or (*E*)-β-Nitrostyrene Leading to 16. An identical procedure was applied to a mixture of **1** or **2** (0.93 mmol), benzaldehyde (1.32 mmol, 1.5 equiv), and methyl acrylate (4.67 mmol, 5 equiv) in dry toluene (10 ml) or a mixture of **1** or **2** (0.94 mmol), benzaldehyde (0.94 mmol), and (*E*)-β-nitrostyrene (0.87 mmol) in toluene (8 ml). When **2**·HCl was used, and equimolar amount of *N,N*-diisopropylethylamine was added to the mixture. The reaction conditions as well as the results are summarized in Table 2. Products were purified through column chromatography over silica gel with hexane–ethyl acetate (10:1 vol/vol).

16a: Colorless liquid; IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (3H, t, COOEt), 2.04 (1H, ddd, *J*=13.1, 8.7, and 1.7 Hz, one of 3-H), 2.26 (3H, s, NMe), 2.72 (1H, ddd, *J*=13.1, 9.0, and 8.0 Hz, the other of 3-H), 3.04 (3H, s, COOMe), 3.62 (1H, ddd, *J*=10.0, 9.0, and 8.7 Hz, 4-H), 3.97 (1H, dd, *J*=8.0 and 1.7 Hz, 2-H), 4.18 (2H, q, COOEt), 4.38 (1H, d, *J*=10.0 Hz, 5-H), and 7.22 (5H, s, Ph); ^{13}C NMR ($CDCl_3$) δ=14.47 (q, COOEt), 30.59 (t, 3-C), 35.47 (q, NMe), 48.89 (d, 4-C), 51.06 (q, COOMe), 60.30 (t, COOEt), 65.77 (d, 2-C), 69.36 (d, 5-C), 127.66, 128.01, 128.54 (each d), 139.89 (s), 173.01, and 173.71 (each s, COOEt and COOMe); MS *m/z* (rel intensity, %) 291 (M^+, 5), 219 (15), 218 (base peak), and 158 (15). Found: C, 66.16; H, 7.26; N, 4.96%. Calcd for $C_{16}H_{21}NO_4$: C. 65.94; H, 7.28; N, 4.81%.

16b: Colorless viscous liquid; IR (neat) 1720, 1540, and 1365 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (3H, t, COOEt), 2.30 (3H, s, NMe), 3.92 (2H, q, COOEt), 4.30 (1H, d, *J*=7.3 Hz, 2-H), 4.70 (1H, dd, *J*=10.0 and 7.3 Hz, 3-H), 4.88 (1H, d, *J*=10.0 Hz, 5-H), 6.03 (1H, t, *J*=10.0 Hz, 4-H), and 7.2—7.4 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=13.88 (q, COOEt), 35.77 (q, NMe), 49.53 (d, 2-C), 60.48 (t, COOEt), 69.95 (d, 3-C), 70.95 (d, 5-C), 91.95 (d, 4-C), 127.66, 128.06, 128.36, 128.65, 128.89 (each d), 134.36, 139.89 (s), 171.31 (s, COOEt); MS *m/z* (rel intensity, %) 354 (M^+, 1), 308 (14), 281 (38), 235 (22), 234 (base peak), 115 (17), and 91 (20). Found: C, 67.89; H, 6.30; N, 7.98%. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.27; N, 7.91%.

16c: Colorless needles (benzene–hexane); mp 174—176 °C; IR (KBr) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.16 (1H, ddd, *J*=13.5, 6.8, and 0.8 Hz, one of 3-H), 2.88 (1H, dt, *J*=13.5, 13.5, and 9.0 Hz, the other of 3-H), 3.36 (3H, s, 4-COOMe), 3.72 (3H, s, 2-COOMe), 3.90 (1H, ddd, *J*=13.5, 9.0, and 6.8 Hz, 4-H), 4.73 (1H, dd, *J*=9.0 and 0.8 Hz, 2-H), 5.26 (1H, d, *J*=9.0 Hz, 5-H), and 6.3—7.2 (10H, m, Ph); MS *m/z* (rel intensity, %) 339 (M^+, 28), 281 (17), 280 (base peak), 220 (16), and 77 (15). Found: C, 70.77; H, 6.26; N, 4.29%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

16d: Colorless needles (benzene–hexane); mp 205—207 °C; IR (KBr) 1730, 1550, and 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.33 (3H, s, COOMe), 4.70 (1H, dd, *J*=11.8 and 8.6 Hz, 3-H), 5.04 (1H, d, *J*=8.6 Hz, 2-H), 5.64 (1H, d, *J*=9.2 Hz, 5-H), 6.28 (1H, dd, *J*=11.8 and 9.2 Hz, 4-H), and 6.4—7.3 (15H, m, Ph); MS *m/z* (rel intensity, %) 402 (M^+, 44), 356 (23), 343 (29), 297 (25), 296 (base peak), 115 (15), 104 (21), and 77 (23). Found: C, 71.52; H, 5.60; N, 7.06%. Calcd for $C_{24}H_{22}N_2O_4$: C, 71.62; H, 5.51; N, 6.96%.

Capture of the Ester-Stabilized Azomethine Ylide A (R=H, R¹=Me, EWG=COOEt) with Unsymmetrically Substituted Olefins Leading to 17. A similar procedure employing **1** (2 mmol), paraformaldehyde (10 mmol, 5 equiv), and an olefin (methyl acrylate and styrene: 3 mmol, 1.5 equiv phenyl vinyl sulfone: 2 mmol, 1 equiv) afforded **17**. The reaction conditions and results are listed in Table 2. Purification of the products was carried out through column chromatography over silica gel with the following eluents: **17a** and **17c**: hexane–ethyl acetate (10:1 vol/vol), **17b**: hexane–ethyl acetate (1:1 vol/vol).

17a (a 6:5 mixture of 2,3- and 2,4-diesters (^1H NMR)): Pale yellow liquid; IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (3H, t, COOEt), 2.40 (5/11×3H, s, NMe), 2.42 (6/11×3H, s, NMe), 2.0—2.7, 3.0—3.5 (each 3H, m, CH_2 and CH), 3.68, 3.70 (3H, each s, COOMe), 4.20, and 4.22 (2H, each, q, COOEt); ^{13}C NMR ($CDCl_3$) 2,3-isomer: δ=14.30 (q, COOEt), 27.83 (t, 4-C), 40.36 (q, NMe), 47.12 (d, 3-C), 51.88 (q, COOMe), 55.77 (t, 5-C), 60.65 (t, COOEt), 70.24 (d, 2-C), 172.07, and 174.19 (each s, COOEt and COOMe). 2,4-isomer: δ=14.30 (q, COOEt), 32.77 (t, 3-C), 40.71 (q, NMe), 41.47 (d, 4-C), 52.06 (q, COOMe), 58.83 (t, 5-C), 60.89 (t, COOEt), 66.83 (d, 2-C), 172.65, and 174.37 (each s, COOEt and COOMe); MS *m/z* (rel intensity, %) 215 (M^+, 4), 156 (11), 142 (base peak), 83 (13), and 82 (42). HRMS Found: *m/z* 215.1146. Calcd for $C_{10}H_{17}NO_4$: M, 215.1157.

17b (a 1:4 mixture of 2,3- and 2,4-isomers (^1H NMR)): Pale yellow liquid; IR (neat) 1741, 1308, and 1149 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (3H, t, COOEt), 2.39 (3H, s, NMe), 2.0—3.5, 3.6—4.1 (5H+1H, m, CH_2 and CH), 4.16 (2H, q, COOEt), 7.4—7.7, and 7.8—8.0 (3H+2H, m, Ph); ^{13}C NMR ($CDCl_3$) 2,3-isomer: δ=13.29 (q, COOEt), 24.71 (t, 4-C), 38.94 (q, NMe), 54.94 (t, 5-C), 59.89 (t, COOEt), 65.71 (d, 3-C), 66.95 (d, 2-C), 127.89, 128.72, 133.24 (each d), 137.36 (s), and 169.66 (s, COOEt). 2,4-isomer: δ=13.29 (q, COOEt), 29.59 (t, 3-C), 38.94 (q, NMe), 54.24 (t, 5-C), 59.89 (t, COOEt), 60.30 (d, 4-C), 65.36 (d, 2-C), 127.60, 128.72, 133.24 (each d), 137.66 (s), and 170.84 (s, COOEt). MS *m/z* (rel intensity, %) 297 (M^+, 3), 224 (84), 82 (41), and 81 (base peak). HRMS Found: *m/z* 297.1034. Calcd for $C_{14}H_{19}NO_4S$: M, 297.1034.

17c (a 1:1 mixture of 2,3-cis and 2,3-trans isomers (GLC)): Pale yellow liquid; IR (neat) 1745 and 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.78 (3H, t, COOEt), 2.40 (3H, s, NMe), 2.0—2.7, 3.1—4.2 (2H+5H, m, CH_2 and CH), and 7.15 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=13.65, 14.24 (each q, COOEt), 31.94, 32.71 (each t, 4-C), 40.71, 40.83 (each q, NMe), 47.94, 49.65 (each d, 3-C (cis, trans)), 56.12, 55.83 (each t, 5-C), 60.24, 60.77 (each t, COOEt), 73.01, 76.01 (each d, 2-C (cis, trans)), 126.65, 126.95, 127.66, 128.25, 128.65 (each d), 141.48, 143.13 (each s), 171.13, and 172.72 (each s, COOEt); MS *m/z* (rel intensity, %) 233 (M^+, 2), 161 (12), 160 (base peak), and 43

(12). HRMS Found: *m/z* 233.1395. Calcd for $C_{14}H_{19}NO_2$: M, 233.1415.

Generation of Azomethine Ylides B from Methyl Aminoacetate (18) and Carbonyl Compounds, and Ylide Trapping with *N*-Methylmaleimide Leading to 19—21. A mixture of methyl aminoacetate (**18**) (0.178 g, 2 mmol), *N*-methylmaleimide (0.222 g, 2 mmol), and a carbonyl compound (benzaldehyde, cyclohexanone: 2 mmol in toluene (20 ml); phenylglyoxal: 2 mmol in chloroform (20 ml); 2-methylpropanal: 6 mmol in toluene (20 ml)) was heated under reflux. The reaction time is summarized in Table 2. The solvent was evaporated in vacuo. The residue was chromatographed over silica gel with diethyl ether to give **19—21**.

19a: Colorless prisms (benzene–hexane); mp 215—216 °C; IR (KBr) 3300, 1740, and 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.41 (1H, br t, NH), 2.85 (3H, s, NMe), 3.40 (1H, dd, *J*=8.0 and 7.5 Hz, 6a-H), 3.66 (1H, dd, *J*=7.5 and 6.8 Hz, 3a-H), 3.85 (3H, s, COOMe), 4.04 (1H, dd, *J*=6.8 and 5.5 Hz, 4-H), 4.47 (1H, dd, *J*=8.0 and 5.5 Hz, 6-H), 7.30 (5H, br s, Ph); MS *m/z* (rel intensity, %) 288 (M^+, 23), 229 (86), 177 (79), 144 (59), 117 (base peak), and 115 (21). Found: C, 62.37; H, 5.53; N, 9.54%. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72%.

19b: Colorless prisms (acetonitrile); mp 228—230 °C; IR (KBr) 3310, 1775, 1740, and 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.67 (3H, s, NMe), 2.92 (1H, t, *J*=11.0 Hz, NH), 3.68 (1H, dd, *J*=8.1 and 7.7 Hz, 3a-H), 3.70 (3H, s, COOMe), 3.91 (1H, t, *J*=7.7 Hz, 6a-H), 4.04 (1H, dd, *J*=11.0 and 8.1 Hz, 4-H), 4.98 (1H, dd, *J*=11.0 and 7.7 Hz, 6-H), 7.4—7.8 (3H, m, Ph), and 7.9—8.1 (2H, m, Ph); MS *m/z* (rel intensity, %) 257 (M^+−59, 8), 211 (base peak), 179 (32), 151 (56), 105 (36), 97 (15), 95 (18), 94 (94), 91 (31), and 76 (50). Found: C, 60.82; H, 5.09; N, 8.87. Calcd for $C_{16}H_{16}N_2O_5$: C, 60.75; H, 5.10; N, 8.86%.

19c: Colorless needles (benzene–hexane); mp 166—167 °C; IR (KBr) 3360, 1750, and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03, 1.20 (each 3H, d, *J*=6.9 Hz, *i*-Pr), 1.6—2.2 (2H, m, NH and *i*-Pr), 2.80 (1H, dd, *J*=10.1 and 7.2 Hz, 6a-H), 2.94 (3H, s, NMe), 3.29 (1H, t, *J*=7.2 Hz, 3a-H), 3.50 (1H, t, *J*=7.2 Hz, 6-H), 3.81 (3H, s, COOMe), and 3.88 (1H, d, *J*=7.2 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ=20.94, 21.06 (each q, *i*-Pr), 25.12 (q, NMe), 29.36 (d, *i*-Pr), 47.47, 49.18 (each d, 3a- and 6a-C), 52.42 (q, COOMe), 62.59 (d, 6-C), 69.18 (d, 4-C), 170.71 (s, COOMe), 175.78, and 176.13 (each s, CON); MS *m/z* (rel intensity, %) 254 (M^+, 3), 211 (base peak), 195 (45), 179 (32), 151 (55), 110 (31), 94 (60), 68 (32), 67 (36), 40 (36), and 38 (28). Found: C, 56.65; H, 7.07; N, 10.87%. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.02%.

20: A mixture of **18** (0.178 g, 2 mmol) and benzaldehyde (0.212 g, 2 mmol) in dry dichloromethane (20 ml) was heated under reflux for 2 h. The dichloromethane was dried over magnesium sulfate and evaporated in vacuo. The residue was dissolved in acetonitrile (10 ml) containing acetic acid (0.024 g, 10 mol%). After *N*-methylmaleimide (0.222 g, 2 mmol) was added the mixture was stirred at room temperature for 13 h. A similar separation procedure gave **19a** and **20**. **20**: Colorless prisms (benzene–hexane); mp 141—142 °C; IR (KBr) 3300, 1740, and 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.59 (1H, br, NH), 2.88 (3H, s, NMe), 3.35 (1H, dd, *J*=8.5 and 7.8 Hz, 6a-H), 3.66 (1H, d, *J*=7.8 Hz, 3a-H), 3.78 (3H, s, COOMe), 4.39 (1H, s, 4-H), 4.59 (1H, dd, *J*=8.5 and 4.0 Hz, 6-H), and 7.30 (5H, br s, Ph); MS *m/z* (rel intensity, %) 288 (M^+, 21), 229 (96), 228 (21), 144 (base peak), 143 (28), 117 (76), and 115 (30). Found: C, 62.64; H, 5.62; N, 9.58%. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72%.

21: Colorless prisms (benzene–hexane); mp 120.5—121 °C; IR (KBr) 3400, 2990, 1755, 1725, and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.1—2.2 (10H, m, *c*-Hex), 1.96 (1H, br, NH), 2.91 (3H, s, NMe), 2.96 (1H, d, *J*=7.8 Hz, 6a-H), 3.52 (1H, t, *J*=7.8 Hz, 3a-H), 3.80 (3H, s, COOMe), and 4.02 (1H, d, *J*=7.8 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ=22.41, 23.18, 25.94, 34.93, 37.12 (each t, *c*-Hex), 24.94 (q, NMe), 50.53 (d, 6a-C), 52.42 (q, COOMe), 55.18 (d, 3a-C), 60.42 (d, 4-C), 65.36 (s, 6-C), 171.24 (s, COOMe), 176.13, and 176.42 (each s, CON); MS *m/z* (rel intensity, %) 280 (M^+, 20), 237 (66), 221 (54), 177 (72), 165 (25), 136 (40), 93 (22), 80 (base peak), 79 (21), 53 (26), 41 (33), and 39 (21). Found: C, 59.79; H, 7.15; H, 9.75%. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.99; H, 7.19; N, 9.99%.

References

1) E. Vedejs and G. R. Martinez, *J. Am. Chem. Soc.*, **101**, 6452 (1979); Reviews: N, Imai, Y. Terao, and K. Achiwa, *Yuki Gosei Kagaku Kyokai Shi*, **43**, 862 (1985); E. Vedejs and F. G. West, *Chem. Rev.*, **86**, 941 (1986) and references cited therein.

2) R. Grigg, J. Kemp, G. Sheldrick, and J. Trotter, *J. Chem. Soc., Chem. Commun.*, **1978**, 109; M. Joucla and J. Hamelin, *Tetrahedron Lett.*, **1978**, 2885; O. Tsuge, K. Ueno, and K. Oe, *Chem. Lett.*, **1979**, 1407; Review: R. Grigg, *Bull. Soc. Chim. Belg.*, **93**, 593 (1984) and references cited therein.

3) a) R. Grigg and H. Q. N. Gunaratne, *J. Chem. Soc., Chem. Commun.*, **1982**, 384 (1982); b) O. Tsuge, K. Ueno, S. Kanemasa, and K. Yorozu, *Bull. Chem. Soc. Jpn.*, **59**, 1809 (1986).

4) P. N. Confalone and E. M. Huie, *J. Org. Chem.*, **48**, 2994 (1983); *J. Am. Chem. Soc.*, **106**, 7175 (1984).

5) M. Joucla, J. Mortier, and J. Hamelin, *Tetrahedron Lett.*, **26**, 2775 (1985).

6) Other methods to ester-stabilized azomethine ylides: a) P. Deshong, D. A. Kell, and D. R. Sidler, *J. Org. Chem.*, **50**, 2309 (1985); b) P. Deshong, D. R. Sidler, D. A. Kell, and N. N. Aronson Jr., *Tetrahedron Lett.*, **26**, 3747 (1985); c) N. Imai, Y. Terao, K. Achiwa, and M. Sekiya, *ibid.*, **25**, 1579 (1984); d) N. Imai, Y. Terao, and K. Achiwa, *Heterocycles*, **23**, 1107 (1985).

7) Part of the present work has been presented as a communication letter (O. Tsuge, S. Kanemasa, M. Ohe, K. Yorozu, S. Takenaka, and K. Ueno, *Chem. Lett.*, **1986**, 1271).

8) O. Tsuge, S. Kanemasa, and S. Takenaka, *Heterocycles*, **20**, 1907 (1983); *Chem. Lett.*, **1985**, 355; *Bull. Chem. Soc. Jpn.*, **58**, 3137, 3320 (1985).

9) H. Ardill, R. Grigg, V. Sridharan, S. Surendrakumar, S. Thianpatanagul, and S. Kanajun, *J. Chem. Soc., Chem. Commun.*, **1986**, 602.

10) The ester-stabilized azomethine ylides derived from pyrolysis of aziridinecarboxylates failed to react with styrene (Ref. 6a).

11) It is known that azomethine ylides generated by dehydration of trialkylamine *N*-oxides are highly reactive to nonactivated alkenes as well as aryl-substituted olefins (R. Beugelmans, G. Negron, and G. Roussi, *J. Chem. Soc., Chem. Commun.*, **1983**, 31; L. B.-Iguertsira, J. Chastanet, G. Negron, and G. Roussi, *Can. J. Chem.*, **63**, 725 (1985); J. Chastanet and G. Roussi, *J. Org. Chem.*, **50**, 2910 (1985)).

12) Our unpublished data which will be published as a following article in this journal.

13) It has been reported that the reactions of A (R=H, R^1=*p*-$MeOC_6H_4$ or $PhCH_2$, EWG=COOMe) with *t*-butyl acrylate or phenyl vinyl sulfone lead to a mixture of stereoisomers of 2,4-substituted pyrrolidines (Ref. 6a).

14) It is not clear whether the *N*-protonated azomethine ylide is formed directly by the 1,3-elimination of an intermediary hemiacetal (or iminium salt) or via an imine.