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Simple Generation of Nonstabilized Azomethine Ylides through Decarboxylative Condensation of α-Amino Acids with Carbonyl Compounds via 5-Oxazolidinone Intermediates

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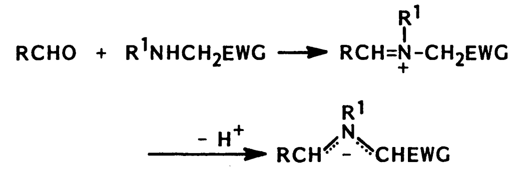
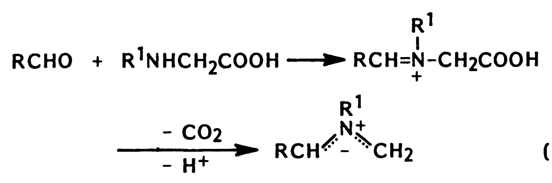
Heating α-amino acids with a variety of carbonyl compounds generates N-unsubstituted or N-substituted azomethine ylides of nonstabilized types through the elimination of water and carbon dioxide. The ylides are captured by olefinic, acetylenic, and carbonyl dipolarophiles producing pyrrolidines, pyrrolines, and oxazolidines. The reaction involves intermediary 5-oxazolidinones which can be sometimes isolated. Some synthetic equivalents of parent azomethine ylide, methaniminium methylide, are accessible by this route.

In the previous paper a simple generation method of ester- or cyano-stabilized azomethine ylides was reported.[1a] This method is a modification of imine-azomethine ylide tautomerism[2] and involves the condensation of α-amino esters or nitriles with aldehydes leading to iminium compounds, which spontaneously deprotonate at the position adjacent to the electron-withdrawing group (EWG) to generate the ylides (Eq. 1).



$$\mathrm{RCHO + R^1NHCH_2EWG \longrightarrow RCH{=}\overset{R^1}{\underset{+}{N}}{-}CH_2EWG \xrightarrow{-H^+} RCH\overset{\overset{R^1}{N}}{-}CHEWG} \qquad (1)$$

During this investigation we noticed that the condensation of α-amino acids with carbonyl compounds would afford a general route to azomethine ylides bearing no stabilizing substituent.[3] As shown in Eq. 2 the intermediates expected to be formed in this condensation are iminium acids which will then undergo ready decarboxylation leading to azomethine ylides.[4]

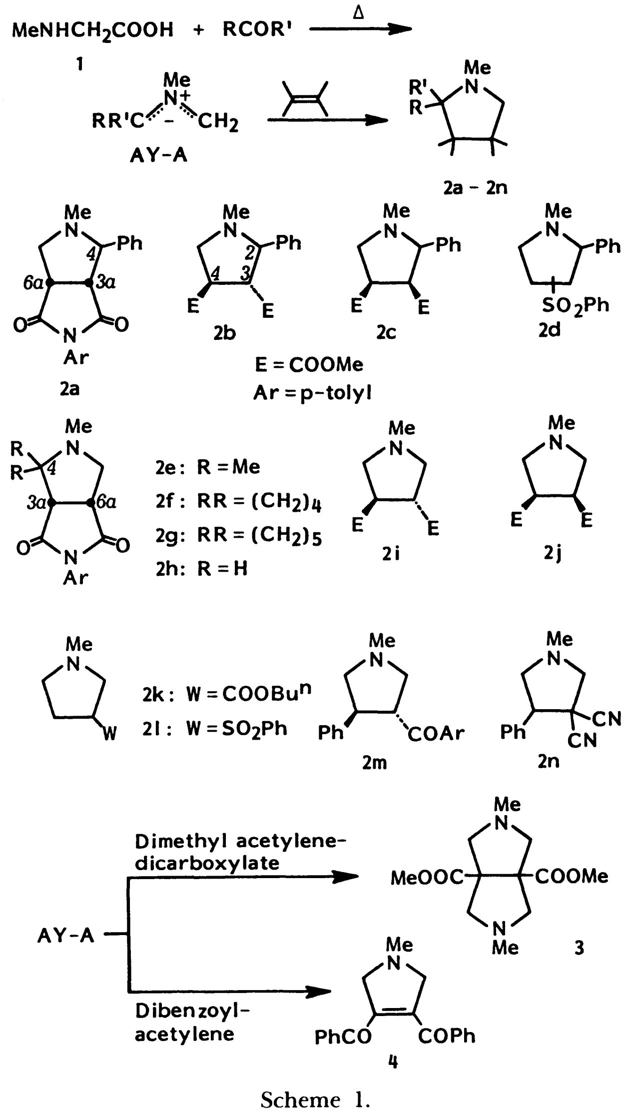


$$\mathrm{RCHO + R^1NHCH_2COOH \longrightarrow RCH{=}\overset{R^1}{\underset{+}{N}}{-}CH_2COOH \xrightarrow[-H^+]{-CO_2} RCH\overset{\overset{R^1}{N^+}}{-}CH_2} \qquad (2)$$

In the present article, we will present a general and practical generation method of nonstabilized azomethine ylides via the decarboxylative condensation route and the scope and limitation of the method will be discussed.[1b]

Results and Discussion

Benzaldehyde and a slightly excess of N-methylaminoacetic acid (sarcosine, **1**) were heated to reflux in toluene in the presence of electron-deficient olefins to give cycloadducts **2a**—**2d** (Scheme 1 and Table 1), indicating the formation of azomethine ylide **AY-A** (R=Ph, R′=H). poor endo- and exo-selectivity of these reactions is consistent with the reported results on the related ylides derived from N-benzylidene(trimethylsilyl)methylamine.[5,6] The reaction with dimethyl maleate gave two cycloadducts, 3,4-cis-adduct **2c** in a poorer yield (11%) and 3,4-trans-adduct



Scheme 1.

2b (71%) as a major product. Under the reaction conditions, the 3,4-cis-adduct **2c** does not epimerize into the 3,4-trans-adduct **2b**, and the isomerization of dimethyl maleate into fumarate does not proceed at an appreciable rate. Catalysis of benzaldehyde in the isomerization was not observed.

The poor stereospecificity is not due to the isomerization of dimethyl maleate into fumarate prior to its cycloaddition trapping, consequently.[7] A stepwise mechanism is responsible for the nonstereospecific cycloaddition of ylide **AY-A** (R=Ph, R′=H).

Azomethine ylides **AY-A** (R, R′=alkyl) with two substituents at the same carbon are available by similar reactions of **1** with ketones. The cycloadducts **2e**—**2g** to *N*-(*p*-tolyl)maleimide were obtained in high yields (Scheme 1 and Table 1).

Azomethine ylide **AY-A** (R=R′=H) carrying no *C*-substituent is also accessible by the condensation of **1** with paraformaldehyde under reflux in toluene. 2,5-Unsubstituted pyrrolidines **2h**—**2l** were produced by trapping ylide **AY-A** with a variety of olefinic dipolarophiles. Both the cycloadditions to dimethyl fumarate and maleate were exclusively stereospecific to give **2i** and **2j**, respectively. This high stereospecificity makes a striking contrast to the previous cycloadditions of **AY-A** (R=Ph, R′=H) leading to **2b** and **2c**. With dimethyl acetylenedicarboxylate two molecules of the ylide **AY-A** (R=R′=H) were incorporated in the reaction to give perhydropyrrolo[3,4-*c*]pyrrole-3a,6a-dicarboxylate **3**.

Azomethine ylides **AY-A** (R=R′=H) bearing no *C*-substituent have been previously generated by several routes, all of which have utilized *N*-silylmethyl amine reagents.[8] Our method has some advantages over these precedents: 1) Our ylide generation starts with readily available chemicals, paraformaldehyde and sarcosine (**1**). 2) Reaction can be performed by a simple operation under almost neutral conditions. 3) Cycloaddition takes place with a variety of dipolarophiles producing high yields of cycloadducts.

The above decarboxylative ylide generation utilizing paraformaldehyde was further applied to cyclic α-amino acids such as 2-pyrrolidinecarboxylic acid (proline, **5**) and 4-thiazolidinecarboxylic acid (**7**). Cyclic azomethine ylides **AY-B** and **AY-C** generated were captured with *N*-(*p*-tolyl)maleimide or dimethyl maleate to give **6**, **8**, and **9**, all as mixtures of stereoisomers (Scheme 2 and Table 2). Each two stereoisomers of the maleimide cycloadducts **6** and **8** could be separated through column chromatography, while **9** was a 5:4 mixture (GLC) of two inseparable stereoisomers.

It was surprising to know that 3-phenyl-5-oxazolidinone (**11**) was isolated in a quantitative yield in the reaction of *N*-phenylaminoacetic acid (**10**) with paraformaldehyde under reflux in toluene for 15 min. The azalactone **11** readily eliminated carbon dioxide by heating to generate azomethine ylide **AY-D**, which was in situ trapped with olefinic dipolarophiles to give **12a**—**12c** (Scheme 3 and Table 2).

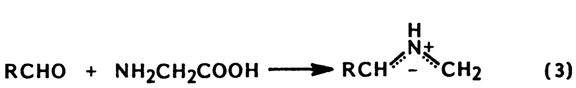
Table 1. Generation and Cycloaddition of Azomethine Ylides **AY-A** Generated from Sarcosine **1** and Carbonyl Compounds

Entry	Carbonyl compound	Type of ylide[a]	Dipolarophile	Condition[b]	Product (yield/%)[c]	Isomer ratio[d]
1	Benzaldehyde	A1	*N*-(*p*-Tolyl)maleimide	A, 1 h	**2a** (86)	5 : 2
2	Benzaldehyde	A1	Dimethyl fumarate	A, 1 h	**2b** (86)	1 : 1
3	Benzaldehyde	A1	Dimethyl maleate	A, 2 h	**2b** (71) + **2c** (11)	**2b**: 1 : 1 **2c**: 2 : 1
4	Benzaldehyde	A1	Phenyl vinyl sulfone	A, 2 h	**2d** (29)[e,f]	
5	Acetone	A2	*N*-(*p*-Tolyl)maleimide	A, 9 h	**2e** (85)	
6	Cyclopentanone	A3	*N*-(*p*-Tolyl)maleimide	A, 5 h	**2f** (79)	
7	Cyclohexanone	A4	*N*-(*p*-Tolyl)maleimide	A, 3 h	**2g** (91)	
8	Paraformaldehyde	A5	*N*-(*p*-Tolyl)maleimide	B, 15 min	**2h** (89)	
9	Paraformaldehyde	A5	Dimethyl fumarate	B, 15 min	**2i** (80)	
10	Paraformaldehyde	A5	Dimethyl maleate	B, 15 min	**2j** (84)	
11	Paraformaldehyde	A5	Butyl acrylate	B, 15 min	**2k** (79)	
12	Paraformaldehyde	A5	Phenyl vinyl sulfone	B, 15 min	**2l** (84)	
13	Paraformaldehyde	A5	2-Benzylidene-4′-methylacetophenone	A, 1 h	**2m** (93)	
14	Paraformaldehyde	A5	Benzylidenemalononitrile	A, 1 h	**2n** (94)	
15	Paraformaldehyde	A5	Dimethyl acetylene-dicarboxylate	B, 15 min	**3** (68)	
16	Paraformaldehyde	A5	Dibenzoylacetylene	B, 15 min	**4** (36)	

a) A1: R=Ph, R′=H, A2: R=R′=Me, A3: RR′=(CH$_2$)$_4$, A4: RR′=(CH$_2$)$_5$, A5: R=R′=H. b) A: Under reflux in toluene with *N*,*N*-diisopropylethylamine (1.5 equiv), B: Under reflux in toluene. c) Yield of isolated products. d) Mixture of stereoisomers whose ratio was based on ^{1}H NMR. e) 2-(Dimethylamino)ethyl phenyl sulfone was obtained in 55% yield. f) Mixture of two regioisomers.

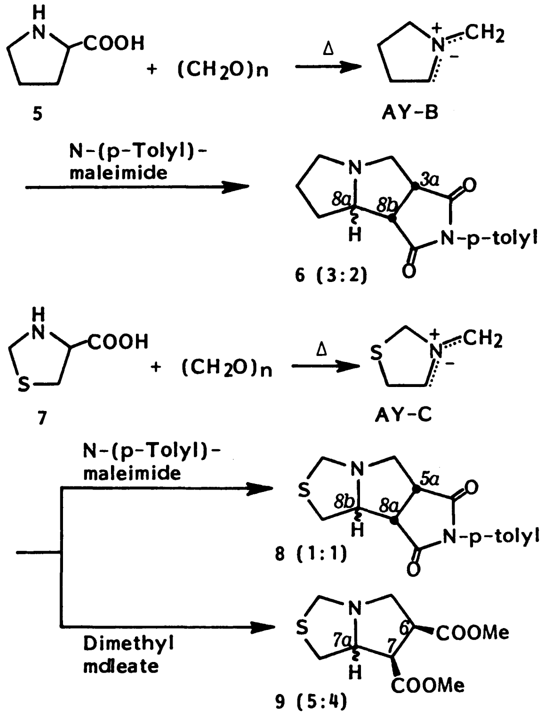
Successful isolation of the azomethine ylide precursor **11** enabled the use of some activated aldehydes as dipolarophiles. Thus heating **11** with *p*-nitrobenzaldehyde or phenylglyoxal gave the oxazolidine cycloadduct **13a** or **13b**, respectively. Pyruvaldehyde was incorporated into 5-oxazolidinone skeleton through an acetal-exchange reaction of **11**. The resulting acetyl-substituted 5-oxazolidinone **A** underwent the decarboxylative generation of azomethine ylide **AY-E**, which was captured by the same aldehyde to give cycloadduct **13c** (Scheme 3).

It is now apparent that the condensation of *N*-substituted α-amino acids with carbonyl compounds offers a simple and versatile generation route to a variety of nonstabilized azomethine ylides **AY-A** to **AY-D**, presumably via 5-oxazolidinone intermediates.[9] Extension of this method to the generation of *N*-unsubstituted azomethine ylides of nonstabilized types is worthy to be tested. This may be achieved by the reaction of *N*-unsubstituted α-amino acids with carbonyl compounds (Eq. 3).

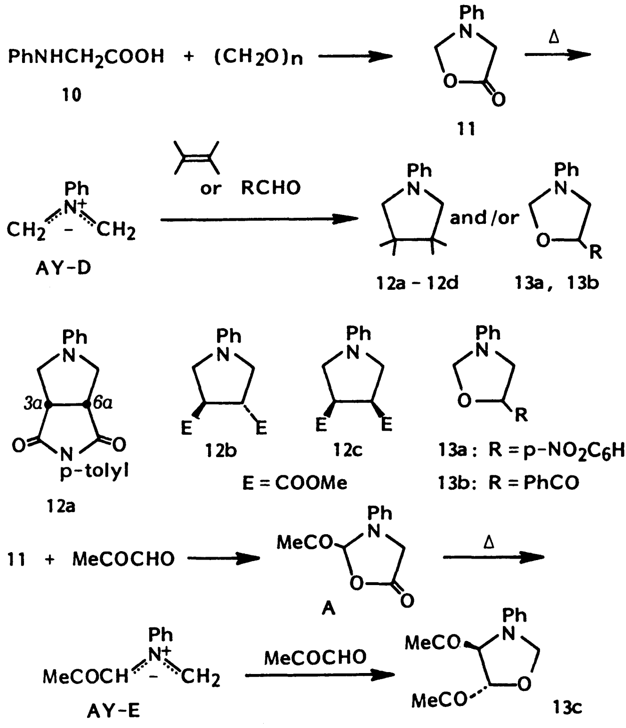


$$\mathrm{RCHO + NH_2CH_2COOH \longrightarrow RCH\overset{\overset{H}{N^{+}}}{-}CH_2} \qquad (3)$$

According to Eq. 3, glycine (**14**) was allowed to react with carbonyl compounds under reflux in toluene to



Scheme 2.



Scheme 3.

Table 2. Generation of Azomethine Ylides **AY-B** to **AY-E** from *N*-Substituted 2-Amino Acids and Carbonyl Compounds

Entry	2-Amino acid	Carbonyl compound	Type of ylide	Dipolarophile	Condition[a]	Product (yield/%)[b]	Isomer ratio[c]
1	**5**	Paraformaldehyde	B	*N*-(*p*-Tolyl)maleimide	A, 15 min	**6** (100)	3 : 2[d]
2	**7**	Paraformaldehyde	C	*N*-(*p*-Tolyl)maleimide	A, 30 min	**8** (81)	41%+40%[e]
3	**7**	Paraformaldehyde	C	Dimethyl maleate	A, 30 min	**9** (77)	5 : 4[f]
4	**10**	Paraformaldehyde	D	*N*-(*p*-Tolyl)maleimide	B, 8 h	**12a** (92)	
5	**10**	Paraformaldehyde	D	Dimethyl fumarate	B, 8 h	**12b** (97)	
6	**10**	Paraformaldehyde	D	Dimethyl maleate	B, 8 h	**12c** (65)	
7	**10**	Paraformaldehyde	D	*p*-Nitrobenzaldehyde	B, 4 h	**13a** (51)	
8	**10**	Paraformaldehyde	D	Phenylglyoxal	B, 8 h	**13b** (39)	
9	**10**	Paraformaldehyde	E	Pyruvaldehyde	B, 3 h	**13c** (26)	

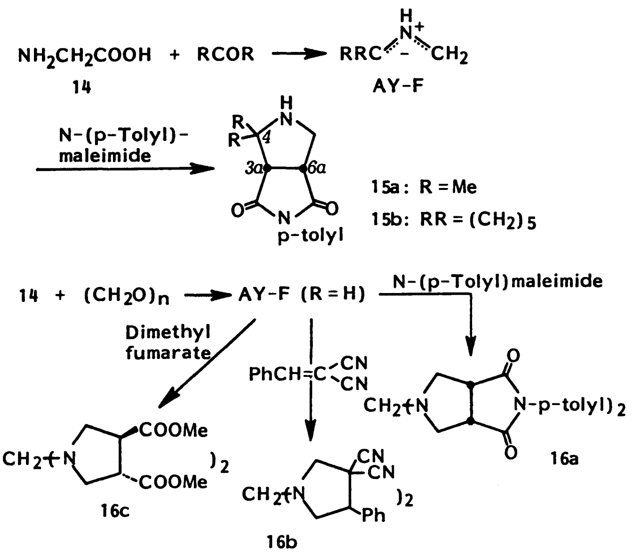
a) A: Under reflux in toluene, B: 3-Phenyl-1,3-oxazolidin-5-one (**11**) was first prepared by heating **10** with paraformaldehyde (0.5 h in toluene), and its decarboxylation was conducted in the presence of a dipolarophile under reflux in toluene. b) Yield of isolated products. c) Mixture of stereoisomers. d) Determined by ^{1}H NMR. e) Yield of isolated isomers. f) Determined by GLC.

generate *N*-unsubstituted azomethine ylides **AY-F**. The use of acetone and cyclopentanone as carbonyl compounds afforded the maleimide cycloadducts **15a** and **15b**, but the yields were unsatisfactory (Scheme 4 and Table 3).

The decarboxylative condensation of **14** with formaldehyde was expected to offer a direct generation method of parent azomethine ylide **AY-F** (R=H), methaniminium methylide, whose preparation is so far unknown. The ylide generation from **14** and paraformaldehyde under reflux in toluene was followed by the cycloaddition trapping with *N*-(*p*-tolyl)maleimide, benzylidenemalononitrile, or dimethyl fumarate. The cycloadducts obtained were not the expected 1,2,5-unsubstituted pyrrolidines but their *N*-methylene-bridged dimers **16a**—**16c**.[10] Use of less than one equivalent of paraformaldehyde was not effective, and the identical products **16** were only afforded in poorer yields.

Similar reactions of paraformaldehyde with 2-aminopropanoic acid (alanine) or 2-amino-3-hydroxypropanoic acid (serine) in the presence of *N*-(*p*-tolyl)maleimide under reflux in toluene led to the formation of complex mixture of products.

Two routes are possible for the formation of *N*-methylene-bridged pyrrolidines **16a**—**16c**: participation of either the parent azomethine ylide **AY-F** (R=H) or *N*,*N*′-methylenebis(azomethine ylide) **AY-**



Scheme 4.

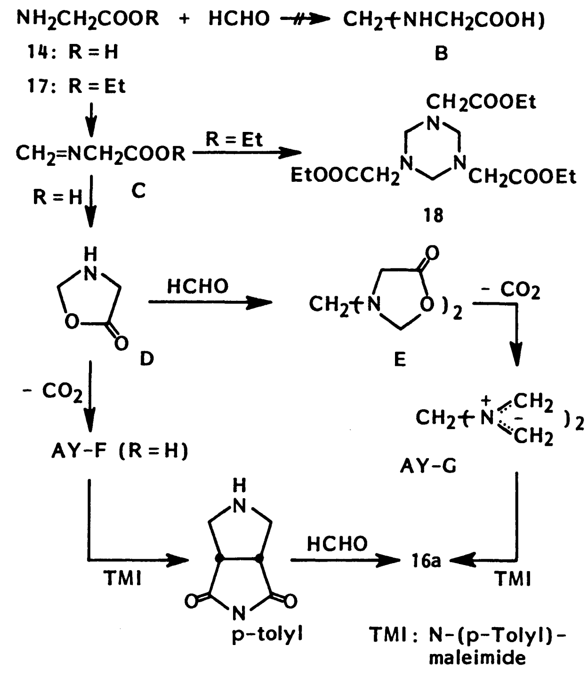


Fig. 1. Two possible routes to **16a**.

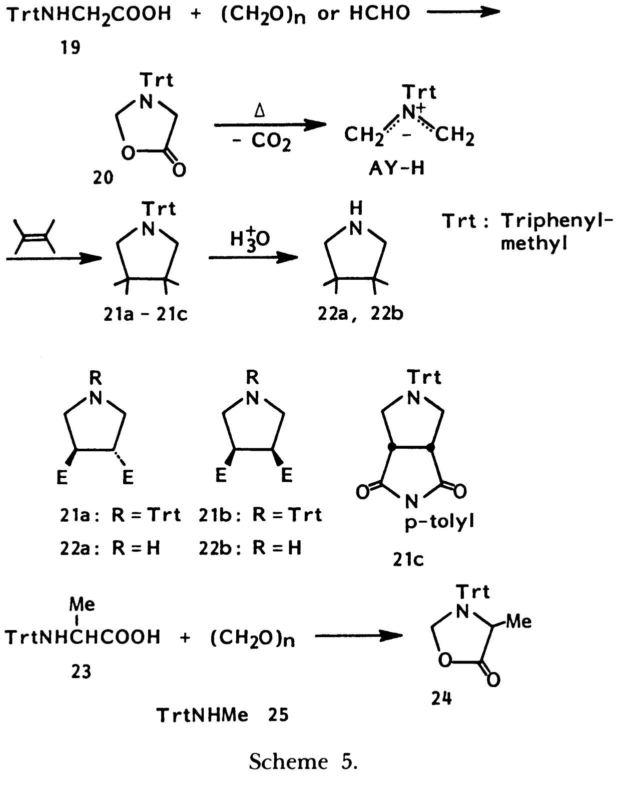
Table 3. Generation of Azomethine Ylides **AY-F**, **AY-H**, and **AY-I** from Aminoacetic Acid or Its Equivalents **20** and **26**

Entry	2-Amino acid	Carbonyl compound	Type of ylide[a]	Dipolarophile	Condition[b]	Product (yield/%)[c]
1	**14**	Acetone	F 1	*N*-(*p*-Tolyl)maleimide	A, 48 h	**15a** (29)
2	**14**	Cyclohexanone	F 2	*N*-(*p*-Tolyl)maleimide	A, 8 h	**15b** (30)
3	**14**	Paraformaldehyde	F 3	*N*-(*p*-Tolyl)maleimide	A, 1 h	**16a** (65)
4	**14**	Paraformaldehyde	F 3	*N*-(*p*-Tolyl)maleimide	B, 15 min	**16a** (74)
5	**14**	Paraformaldehyde	F 3	Benzylidenemalononitrile	C, 12 h	**16b** (71)
6	**14**	Paraformaldehyde	F 3	Dimethyl fumarate	A, 3 h	**16c** (52)
7	**20**		H	*N*-(*p*-Tolyl)maleimide	D, 48 h	**21a** (74)
8	**20**		H	Dimethyl fumarate	D, 48 h	**21b** (73)
9	**20**		H	Dimethyl maleate	D, 48 h	**21c** (63)
10	**26**	Paraformaldehyde	I	Dimethyl fumarate	A, 15 min	**27a** (100)
11	**26**	Paraformaldehyde	I	Dimethyl maleate	A, 15 min	**27b** (91)
12	**26**	Paraformaldehyde	I	*N*-(*p*-Tolyl)maleimide	A, 15 min	**27c** (93)
13	**26**	Paraformaldehyde	I	Butyl acrylate	A, 15 min	**27d** (38)

a) F1: **AY-F** (R=Me), F2: **AY-F** ($RR=(CH_2)_5$), F3: **AY-F** (R=H). b) A: Under reflux in toluene, B: Under reflux in DMF, C: Under reflux in toluene with potassium carbonate (excess), D: Under reflux in toluene using **20**. c) Yield of isolated product.

G. The initial methylene bridging of glycine (**14**) leading to methylenediamine-*N*,*N'*-diacetic acid (**B**) is unlikely to happen since the reaction of ethyl aminoacetate (**16**) with paraformaldehyde forms 1,3,5-tris(ethoxycarbonylmethyl)-1,3,5-triazine **18**, a trimer of ethyl *N*-methyleneaminoacetate **C** (R=Et) (Fig. 1). *N*-Methyleneaminoacetic acid **C** (R=H) cyclizes into labile 5-oxazolidinone (**D**).[11] This heterocycle **D** loses carbon dioxide generating the parent azomethine ylide **AY-F** (R=H) whose cycloaddition to *N*-(*p*-tolyl)maleimide and subsequent reaction with formaldehyde gives **16a**.[12] Another route to **16a** is the initial bridging of **D** forming *N*,*N'*-methylenebis(5-oxazolidinone) (**E**), elimination of carbon dioxide generating *N*,*N'*-methylenebis(azomethine ylide) **AY-G**, and the final cycloaddition. Discrimination of the both routes depends upon the stability of intermediary 5-oxazolidinone **D**.

One of the synthetic equivalents of the parent azomethine ylide **AY-F** (R=H) will be *N*-triphenylmethyl azomethine ylide **AY-H**. Reaction of *N*-(triphenylmethyl)aminoacetic acid (**19**) with aqueous formaldehyde in ethanol or with paraformaldehyde under reflux in toluene gave 3-(triphenylmethyl)-5-oxazolidinone (**20**) as a stable compound, both in quantitative yields (Scheme 5). When heated under reflux in toluene, **20** gradually eliminated carbon dioxide to generate the parent ylide equivalent **AY-H**, which was captured by *N*-(*p*-tolyl)maleimide, dimethyl fumarate, or maleate leading to cycloadducts **21a**—**21c** (Scheme 5 and Table 3). The triphenylmethyl moiety of **21a** and **21b** was readily removed on treatment with hydrochloric acid in dichloromethane at room temperature to give **22a**—**22c**.

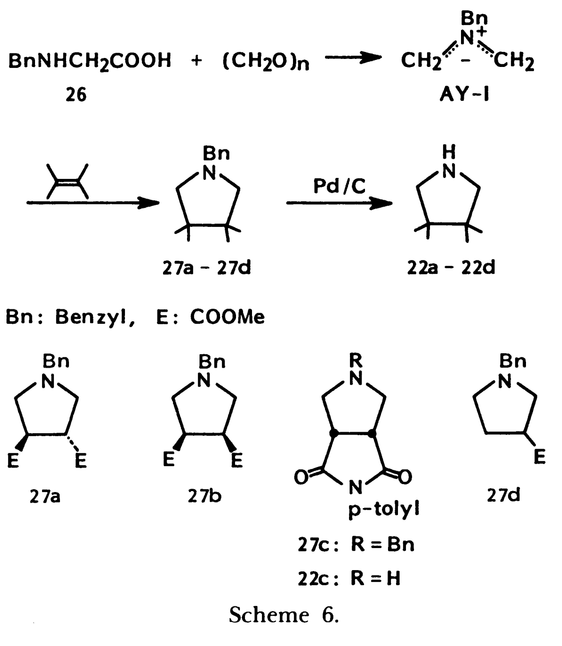


Scheme 5.

In contrast with the ready formation of 5-oxazolidinone **20** from **19** and paraformaldehyde, similar reactions of **19** with acetaldehyde or benzaldehyde all resulted in the quantitative recovery of **19**. The bulky triphenylmethyl group of **19** may have inhibited its attack to these aldehydes. On the other hand, 3-triphenylmethyl-4-methyl-5-oxazolidinone (**24**) was obtained in a high yield from *N*-(triphenylmethyl)-2-aminopropanoic acid (**23**) and paraformaldehyde. However heating **24** in the presence of a variety of dipolarophiles yielded no cycloadducts. *N*-(Methyl)triphenylmethylamine **25** was the only product.[13]

There are some problems in the employment of 3-(triphenylmethyl)-5-oxazolidinone **20** as a synthetic equivalent of parent azomethine ylide **AY-F** (R=H). Table 3 indicates that 1) the decarboxylative ylide generation takes many hours (48 h), 2) the yields of cycloadducts **21** remain to be improved (63—74%), and 3) removal of the triphenylmethyl moiety is not a high-yield reaction. Since the thermal stability of 5-oxazolidinones seems to decrease with the decreased steric size of the 3-substituent, a 5-oxazolidinone bearing a smaller 3-substituent, which should be readily removable after the cycloaddition, is needed.

We chose *N*-benzylaminoacetic acid (**26**) as the parent ylide equivalent. Although all attempts to isolate the corresponding 5-oxazolidinone failed, the reaction of **26** with paraformaldehyde was completed in 15 min under reflux in toluene. The azomethine ylide **AY-I** generated was captured by *N*-(*p*-tolyl)-maleimide, dimethyl maleate, fumarate, and butyl acrylate to give excellent yields of cycloadducts **27a**—



Scheme 6.

27d (Scheme 6 and Table 3). Debenzylation of **27c** by Pd/C proceeded smoothly under reflux in xylene to produce a quantitative yield of **22c**. However, similar debenzylation of ester-substituted pyrrolidines **27a**—**27b** and **27d** led to a complex mixture of many products. In these cases also the debenzylation was completed, but subsequent condensation of the resulting secondary amine moiety with the esters would be a main reason for the complex results.

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 as well as high resolution mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. 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) or of aluminum oxide 60 F-254 type-E (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). 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 Generation of Azomethine Ylide AY-A from Sarcosine (1) and Carbonyl Compounds, and Subsequent Ylide Trapping with Olefins Leading to 2—4. A mixture of sarcosine **1**, carbonyl compound, and olefin was heated under reflux in toluene (10—15 ml for 1 mmol of the dipolarophile). A mixture of sarcosine hydrochloride and *N,N*-diisopropylethylamine (1.5 equiv of the hydrochloride) may be employed instead of **1**. The water formed was removed by the aid of a Dean-Stark trap. The reaction conditions are listed in Table 1. The molar equivalents of **1** and carbonyl compounds are based on dipolarophiles as follows: **1** (2 equiv)+benzaldehyde (1.5 equiv); **1** (2 equiv)+acetone (10 equiv); **1** (2 equiv)+cycloalkanones (1.5 equiv); **1** (2 equiv)+paraformaldehyde (5 equiv). After the completion of reaction the solvent was evaporated in vacuo. The residue was chromatographed over silica gel by using hexane–ethyl acetate (3:1 to 1:1 vol/vol) to give **2**—**4**. All the results are summarized in Table 1 in which yields are based on the dipolarophiles.

2a: This cycloadduct **2a** consists of two stereoisomers (3a,4-trans:3a,4-cis=2:5 (^{1}H NMR)). The 3a,4-trans isomer could be separated from the 3a,4-cis isomer by washing the mixture with diethyl ether (3a,4-trans isomer is less soluble) and through column chromatography over silica gel (hexane–diethyl ether=3:1 vol/vol). 3a,4-*trans*-**2a**: Colorless prisms (diethyl ether); mp 153—154 °C; IR (KBr) 1765 and 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.15 (3H, s, *p*-Me), 2.36 (3H, s, NMe), 2.70 (1H, ddd, *J*=9.6, 8.2, and 5.8 Hz, 6a-H), 3.3—3.8 (2H, m, 3a-H and 6-H), and 7.0-7.4 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=21.00 (q, *p*-Me), 38.53 (q, NMe), 44.06 (d, 6a-C), 53.42 (d, 3a-C), 57.18 (t, 6-C), 72.42 (d, 4-C), 126.24, 127.83, 127.95, 128.65, 129.30, 129.66 (each d), 138.42, 139.07 (each s), 176.54, and 177.12 (each s, CON); MS *m/z* (rel intensity, %) 320 (M$^+$, 21), 158 (28), 132 (100), 118 (26), 115 (28), 91 (46), 82 (62), 77 (35), and 43 (28). Found: C, 74.70; H, 6.30; N, 8.62%. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29; N, 8.74%. 3a,4-*cis*-**2a**: Colorless needles (benzene–hexane); mp 121—122.5 °C; IR (KBr) 1765 and 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.18 (3H, s, *p*-Me), 2.33 (3H, s, NMe), 2.62 (1H, dd, *J*=9.4 and 6.5 Hz, 6a-H), 3.2—3.8 (4H, m, 3a-H, 4-H, and 6-H), and 7.0—7.4 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=21.12 (q, *p*-Me), 39.71 (q, NMe), 44.53 (d, 6a-C), 50.59 (d, 3a-C), 58.24 (t, 6-C), 73.30 (d, 4-C), 126.13, 128.07, 128.18, 128.54, 128.77, 129.71 (each d), 137.01, 138.36 (each s), 175.07, and 178.54 (each s, CON) MS *m/z* (rel intensity, %) 320 (M$^+$, 22), 158 (22), 133 (39), 132 (base peak), 118 (25), 91 (44), 82 (37), and 77 (24). Found: C, 75.24; H, 6.40; N, 8.64%. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29; N, 8.74%.

2b: (An inseparable mixture of 2,3-cis and 2,3-trans isomers (1:1)): Colorless liquid; IR (neat) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.08, 2.17 (each 1/2×3H, s, NMe), 2.50, 2.67 (each 1H, dd, *J*=9.4 and 8.2 Hz, 5-H), 3.06, 3.60, 3.68, 3.74 (each 1/2×3H, s, COOMe), 3.2—3.7 (3H, m, 3-, 4-, and 5-H), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=39.26, 39.60 (each q, NMe), 43.99, 44.73 (each d, 4-C), 50.93, 51.66, 51.95, 52.44 (each q, COOMe), 54.69 (d, 3-C), 58.30, 58.50 (each t, 5-C), 72.75, 74.46 (each d, 2-C), 127.59, 127.78, 127.88, 128.12, 128.32 (each d), 138.37, 140.33 (each s), 171.97, 173.09, 173.29, and 173.63 (each s, COOMe); MS *m/z* (rel intensity, %) 277 (M$^+$, 14), 262 (42), 216 (33), 202 (25), 184 (33), 158 (base peak), 143 (35), 140 (40), 118 (42), 117 (20), 116 (31), 115 (95), 91 (73), 82 (40), 81 (23), 77 (51), 59 (68), 52 (23), 45 (23), and 43 (64). HRMS Found: *m/z* 277.1318. Calcd for $C_{15}H_{19}NO_4$: M, 277.1318.

2c: (An inseparable mixture of 2,3-cis and 2,3-trans isomers (1:2)): Colorless liquid; IR (neat) 1745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.18 (2/3×3H, s, NMe), 2.23 (1/3×3H, s, NMe), 2.5—4.1 (5H, m, 2-, 3-, 4-, and 5-H), 3.20, 3.65 (each 1/3×3H, s, COOMe of 2,3-cis isomer), 3.60, 3.67 (each 2/3×3H, s, COOMe of 2,3-trans isomer), and 7.2—7.4 (5H, m, Ph); MS *m/z* (rel intensity, %) 277 (M$^+$, 30), 262 (44), 246 (21), 218 (21), 158 (37), 133 (31), 132 (95), 115 (base peak), 91 (22), 82 (28), and 42 (23). HRMS Found: *m/z* 277.1329. Calcd for $C_{15}H_{19}NO_4$: M, 277.1313.

2d: (An inseparable mixture of two regioisomers): Colorless liquid; IR (neat) 1295 and 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, s, NMe), 2.3—2.9 (3H, 3- and 4-H), 3.1—3.8 (3H, m, 2- and 5-H), and 7.0—7.8 (10H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=25.88 (t, 4-C of 2,3-isomer), 36.00 (t, 3-C of 2,4-isomer), 39.77 (q, NMe), 55.53, 56.24 (each t, 5-C), 61.00 (d, 4-C of 2,4-isomer), 70.24 (d, 3-C of 2,3-isomer), 70.83 (each d, 2-C), 127.36, 127.54, 127.89, 128.07, 128.48, 128.65, 128.95, 129.24, 129.36, 129.53 (each d), 133.71, 134.01, 140.60, and 141.01 (each s); MS *m/z* (rel intensity, %) 301 (M$^+$, 3), 159 (base peak), 158 (32), and 91 (22). HRMS Found: *m/z* 301.1136. Calcd for $C_{17}H_{19}NO_2S$: M, 301.1142.

This compound **2d** was accompanied by 2-(dimethylamino)ethyl phenyl sulfone: Pale yellow liquid; IR (neat) 1319, 1306, and 1149 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.16 (6H, s, NMe$_2$), 2.5—2.8 (2H, m, NCH$_2$), 3.1—3.4 (2H, m, CH$_2$), 7.4—7.7 (3H, m, Ph), and 7.8—8.0 (2H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=44.89 (q, NMe$_2$), 52.24, 53.83 (each t, CH$_2$), 128.01, 129.36, 133.83 (each d), and 139.66 (s); MS *m/z* (rel intensity, %) 213 (M$^+$, 4), 77 (64), 71 (98), 58 (base peak), 56 (28), 51 (29), and 42 (55). Found: C, 56.50; H, 7.05; N, 6.57%. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.10; N, 6.57%.

2e: Colorless needles (benzene–hexane); mp 153—154 °C; IR (KBr) 1770 and 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.06, 1.24 (each 3H, s, 4-Me), 2.20 (3H, s, *p*-Me), 2.35 (3H, s, NMe), 2.90 (1H, dd, *J*=9.9 and 8.0 Hz, one of 6-H (exo)), 2.94 (1H, d, *J*=7.3 Hz, 3a-H), 3.26 (1H, ddd, *J*=8.0, 7.3, and 1.7 Hz, 6a-H), 3.30 (1H, dd, *J*=9.9 and 1.7 Hz, the other of 6-H (endo)), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=18.77, 20.65 (each q, 4-Me), 22.41 (*p*-Me), 32.77 (q, NMe), 42.77 (d, 6a-C), 54.42 (d, 3a-C), 54.42 (t, 6-C), 62.30 (s, 4-C), 126.01, 129.24 (each d), 129.42, 137.89 (each s), 176.01, and 178.42 (each s, CON); MS *m/z* (rel intensity, %) 272 (M$^+$, 2), 257 (33), and 96 (base peak). Found: C, 70.53; H, 7.33; N, 9.96%. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29%.

2f: Colorless needles (diethyl ether); mp 145.5—147 °C; IR (KBr) 1770 and 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.2—2.2 (8H, m, *c*-Pen), 2.22 (3H, s, *p*-Me), 2.35 (3H, s, NMe), 2.75 (1H, dd, *J*=10.2 and 8.2 Hz, one of 6-H (exo)), 2.97 (1H, d, *J*=7.9 Hz, 3a-H), 3.25 (1H, ddd, *J*=8.2, 7.9, and 1.2 Hz, 6a-H), 3.28 (1H, dd, *J*=10.2 and 1.2 Hz, the other of 6-H (endo)), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=20.82 (q, *p*-Me), 23.12, 23.35, 27.24, 29.83 (each t, *c*-Pen), 33.30 (q, NMe), 42.89 (d, 6a-C), 53.47 (d, 3a-C), 56.00 (t, 6-C), 74.71 (s, 4-C), 126.13, 129.30 (each d), 129.66, 137.95 (each s), 176.42, and 178.66 (each s, CON); MS m/z (rel intensity, %) 298 (M$^+$, 14), 269 (70), 256 (base peak), 108 (31), and 94 (29). Found: C, 72.54; H, 7.46; N, 9.08%. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.45; H, 7.43; N, 9.39%.

2g: Colorless grains (benzene–hexane); mp 119—120 °C; IR (KBr) 1770 and 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.1—1.9 (10H, m, *c*-Hex), 2.24 (3H, s, *p*-Me), 2.35 (3H, s, NMe), 2.8—3.4 (4H, m, 3a-, 6-, and 6a-H), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=21.12 (q, *p*-Me), 23.30, 23.71, 25.30, 26.00, 32.36 (each t, *c*-Hex), 33.12 (q, NMe), 43.00 (d, 6a-C), 50.42 (d, 3a-C), 54.77 (t, 6-C), 66.83 (s, 4-C), 126.48, 129.71 (each d), 129.83, 138.42 (each s), 176.72, and 179.07 (each s, CON); MS *m/z* (rel intensity, %) 312 (M$^+$, 34), 270 (22), 269 (base peak), and 256 (28). Found: C, 73.12; H, 7.69; N, 8.89%. Calcd for $C_{19}H_{24}N_2O_2$: C, 73.04; H, 7.74; N, 8.97%.

2h: Colorless prisms (benzene–hexane); mp 138—139 °C; IR (KBr) 1770 and 1708 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.24 (3H, s, *p*-Me), 2.35 (3H, s, NMe), 2.2—2.4, 3.1—3.4 (2H+4H, m, 3a-, 4-, 6-, and 6a-H), 7.04 (2H, d, Ar), and 7.26 (2H, d, Ar); ^{13}C NMR (CDCl$_3$) δ=21.00 (q, *p*-Me), 40.71 (q, NMe), 44.94 (d, 3a- and 6a-C), 58.83 (t, 4- and 6-C), 126.36, 129.66 (each d), 129.83, 138.36 (each s), and 178.66 (CON); MS *m/z* (rel intensity, %) 244 (M$^+$, 40), 82 (55), 57 (base peak), and 41 (24). Found: C, 68.93; H, 6.61; N, 11.33%. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47%.

2i: Colorless liquid; IR (neat) 1736 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.31 (3H, s, NMe), 2.6—3.0, 3.3—3.6 (4H+2H, m, 2-, 3-, 4-, and 5-H), and 3.70 (6H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=41.53 (q, NMe), 45.94 (d, 3- and 4-C), 59.06 (t, 2- and 5-C), 52.24 (q, COOMe), and 174.01 (s, COOMe); MS *m/z* (rel intensity, %) 201 (M$^+$, 7), 142 (13), 140 (27), 82 (base peak), 59 (21), 58 (33), and 42 (57). HRMS Found: *m/z* 201.0991. Calcd for $C_9H_{15}NO_4$: M, 201.1000.

2j: Colorless liquid; IR (neat) 1741 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.37 (3H, s, NMe), 2.6—2.8, 2.9—3.2, 3.2—3.4 (each 2H, m, 2-, 3-, 4-, and 5-H), and 3.65 (6H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=41.85 (q, NMe), 45.85 (d, 3- and 4-C), 51.81 (q, COOMe), 58.35 (d, 2- and 5-C), and 172.99 (s, COOMe); MS *m/z* (rel intensity, %) 201 (M$^+$, 7), 81 (base peak), 59 (25), 57 (27), and 41 (54); HRMS Found: *m/z* 201.1003. Calcd for $C_9H_{15}NO_4$: M, 201.1000.

2k: Colorless liquid; IR (neat) 2960, 2939, 2875 2779, and 1736 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.93 (3H, t, *n*-Bu), 1.2—1.8 (4H, m, *n*-Bu), 2.0—3.2 (7H, m, 2-, 3-, 4-, and 5-H), 2.35 (3H, s, NMe), and 4.08 (2H, t, *n*-Bu); ^{13}C NMR (CDCl$_3$) δ=12.94 (q, *n*-Bu), 18.41, 30.06 (each t, *n*-Bu), 27.47 (t, 4-C), 41.06 (q, NMe), 41.94 (d, 3-C), 55.30 (t, 5-C), 58.24 (t, 2-C), 63.65 (t, *n*-Bu), and 174.19 (s, COOBu-*n*); MS *m/z* (rel intensity, %) 185 (M$^+$, 7), 128 (56), 84 (24), 83 (28), 82 (57), 58 (42), 43 (base peak), 42 (67), and 40 (30). HRMS Found: *m/z* 185.1455. Calcd for $C_{10}H_{19}NO_2$: M, 185.1415.

2l: Pale yellow liquid; IR (neat) 1308 and 1147 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.0—2.9 (6H, m, 2-, 4-, and 5-H), 2.31 (3H, s, NMe), 3.5—3.9 (1H, m, 3-H), 7.4—7.7 (3H, m, Ph) and 7.8—8.0 (2H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=25.94 (t, 4-C), 41.30 (q, NMe), 55.30, 55.47 (each t, 2- and 5-C), 62.48 (d, 3-C), 128.13, 129.13 (each d), 133.60, and 138.36 (each s); MS *m/z* (rel intensity, %) 225 (M$^+$, 3), 83 (base peak), 82 (45), and 41 (37). Found: C, 58.36; H, 6.76; N, 6.21%. Calcd for $C_{11}H_{15}NO_2S$: C, 58.63; H, 6.72; N, 6.22%.

2m: Colorless liquid; IR (neat) 1675 and 1605 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.34, 2.40 (each 3H, s, NMe and *p*-Me), 2.6—3.2, 3.7—4.1 (4H+2H, m, 2-, 3-, 4-, and 5-H), 7.12 (2H, d, COPh), 7.25 (5H, s, Ph), and 7.66 (2H, d, COPh); ^{13}C NMR (CDCl$_3$) δ=21.47 (q, *p*-Me), 42.00 (q, NMe), 46.65 (d, 4-C), 55.30 (d, 3-C), 60.36 (t, 2-C), 64.36 (t, 5-C), 126.60, 127.71, 128.72, 128.89. 129.30 (each d), 134.07, 143.83, 144.60 (each d), and 199.13 (s, CO); MS *m/z* (rel intensity, %) 279 (M$^+$, 42), 175 (51), 174 (base peak), 133 (59), 119 (20), 117 (26), 91 (28), 58 (32), 44 (22), and 43 (23). Found: C, 81.58; H, 7.58; N, 5.15%. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01%.

2n: Colorless needles (hexane); mp 78—80 °C; IR (KBr) 2250 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.49 (3H, s, NMe), 3.13 (2H, d, *J*=8.0 Hz, 5-H), 3.35 (2H, s, 2-H), 3.97 (1H, t, *J*=8.0 Hz, 4-H), and 7.37 (5H, s, Ph); ^{13}C NMR (CDCl$_3$) δ=40.48 (q, NMe), 40.67 (s, 3-C), 54.35 (d, 4-C), 58.79 (t, 2-C), 64.89 (t, 5-C), 113.87, 115.62 (each s, CN), 128.17, 128.76 (each d), and 135.01 (s); MS *m/z* (rel intensity, %) 211 (M$^+$, 3), 57 (88), and 41 (base peak). Found: C, 73.66; H, 6.20; N, 19.64%. Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89%.

3: Colorless prisms (benzene–hexane); mp 72—74 °C; IR (KBr) 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.34 (6H, s, NMe), 2.71, 3.04 (each 4H, d, *J*=9.5 Hz, 2-, 3-, 5-, and 6-H), and 3.65 (6H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=41.75 (q, NMe), 52.29 (q, COOMe), 63.87 (s, 3a- and 6a-C), 65.62 (t, 1-, 3-, 4-, and 6-C), and 173.92 (s, COOMe); MS *m/z* (rel intensity, %) 256 (M$^+$, 32), 180 (34), 94 (22), 58 (base peak), and 43 (25). Found: C, 56.30; H, 7.76; N, 10.70%. Calcd for $C_{12}H_{20}N_2O_4$: C, 56.23; H, 7.87; N, 10.93%.

4: Pale yellow grains (benzene–hexane); mp 157—158 °C; IR (KBr) 1640 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.55 (3H, s, NMe), 4.03 (4H, s, 2- and 5-H), and 7.0—7.5 (10H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=42.30 (q, NMe), 64.48 (t, 2- and 5-C), 128.24, 128.54, 128.65 (each d), 133.24 (d), 137.66 (s), 143.95

(s, 3- and 4-C), and 193.12 (s, CO); MS *m/z* (rel intensity, %) 291 (M^+, 5), 105 (52), 77 (base peak), and 51 (25). HRMS Found: *m/z* 291.1204. Calcd for $C_{19}H_{17}NO_2$: M, 291.1258.

Generation of Azomethine Ylide AY-B or AY-C by the Reaction of Proline (5) or 4-Thiazolidinecarboxylic Acid (7) with Paraformaldehyde and Subsequent Ylide Trapping with Olefins Leading to 6, 8, and 9. As a typical procedure, the reaction of **5** with paraformaldehyde in the presence of a maleimide is described: A mixture of **5** (0.3 g, 2.61 mmol), paraformaldehyde (0.2 g, 6.7 mmol), and *N*-(*p*-tolyl)maleimide (0.25 g, 1.32 mmol) was heated under reflux in toluene (15 ml) for 15 min. The water formed was removed by an azeotropic distillation. The mixture was evaporated in vacuo and the residue (0.36 g, 100%, 3:2 by ^{1}H NMR) was chromatographed over silica gel by using hexane–ethyl acetate (1:1 vol/vol) to give two stereoisomers of **6**. The results are summarized in Table 2.

8a,8b-*trans*-6: Colorless prisms (benzene–hexane); mp 150—152 °C; IR (KBr) 1775 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.5—2.2 (4H, m, 7- and 8-H), 2.36 (3H, s, *p*-Me), 2.7—3.1, 3.2—3.8 (3H+4H, m, 3a-, 4-, 6-, 8a-, and 8b-H), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=21.12 (q, *p*-Me), 23.59 (t, 7-C), 29.65 (t, 8-C), 45.94 (d, 3a-C), 50.06 (d, 8b-C), 51.95 (t, 6-C), 55.00 (t, 4-C), 69.12 (d, 8a-C), 126.48, 129.77 (each d), 129.77, 138.60 (each s), 177.83, and 178.37 (each s, CON); MS *m/z* (rel intensity, %) 270 (M^+, 15), 133 (31), 132 (28), 108 (27), 104 (26), 83 (base peak), 82 (23), 81 (59), 80 (54), 78 (21), and 77 (31). Found: C, 71.15; H, 6.72; N, 10.22%. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36%. **8a,8b-*cis*-6:** Colorless solid; mp 138—140 °C; IR (KBr) 1770 and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.6—3.9 (11H, m, CH_2 and CH), 2.16 (3H, s, *p*-Me), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=21.06 (q, *p*-Me), 24.83 (t, 7-C), 25.18 (t, 8-C), 48.24 (d, 3a-C), 48.42 (d, 8b-C), 52.95 (t, 6-C), 54.65 (t, 4-C), 68.42 (d, 8a-C), 125.95, 129.66 (each d), 129.83 (s), 177.12, and 179.01 (each s, CON); MS *m/z* (rel intensity, %) 270 (M^+, 13), 108 (21), 83 (base peak), 81 (39), 80 (35), 77 (21), 68 (21), 56 (49), 42 (23), and 40 (24). Anal. Found: C, 70.65; H, 6.75; N, 10.18%. Calcd for $C_{16}H_{18}N_2O_2$: C, 71. 09; H, 6.71; N, 10.36%.

8: A similar procedure employing **7** (0.2 g, 1.5 mmol), paraformaldehyde (0.2 g, 6.7 mmol), and *N*-(*p*-tolyl)maleimide (0.25 g, 1.32 mmol) in toluene (18 ml) followed by silica-gel chromatography gave **8a,8b-*trans*-8** (0.156 g, 41%, from the elution with hexane–ethyl acetate (2:1 vol/vol)) and **8a,8b-*cis*-8** (0.153 g, 40%, from the elution with ethyl acetate). **8a,8b-*trans*-8:** Colorless needles (benzene-hexane); mp 213-215 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.34 (3H, s, *p*-Me), 2.62 (1H, t, *J*=10.0 Hz, one of 1-H (exo)), 2.8—3.5 (5H, m), 3.78 (1H, dd, *J*=10.0 and 7.5 Hz, 8b-H), 4.10, 4.26 (each d, *J*=9.8 Hz, 3-H), and 7.0—7.3 (4H, m, Ar); MS *m/z* (rel intensity, %) 288 (M^+, 53), 242 (74), 101 (26), 81 (base peak), and 80 (24). Found: C, 62.53; H, 5.62; N, 9.53%. Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; N, 9.71%. **8a,8b-*cis*-8:** Colorless prisms (benzene–hexane); mp 162—164 °C; IR (KBr) 1775 and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.34 (3H, s, *p*-Me), 2.5—3.9 (7H, m), 4.04, 4.20 (each 1H, d, *J*=9.8 Hz, 3-H), 7.07 (2H, d, Ar), and 7.23 (2H, d, Ar); ^{13}C NMR ($CDCl_3$) δ=21.18 (q, *p*-Me), 30.71 (t, 1-C), 46.12 (d, 5a-C), 47.89 (d, 8a-C), 52.06 (t, 5-C), 57.18 (t, 3-C), 70.48 (d, 8b-C), 126.36, 129.19 (each d), 130.01, 139.07 (each s), 175.36, and 177.07 (each s, CON); MS *m/z* (rel intensity, %) 288 (M^+, 73), 242 (53), 101 (22), 100 (46), 81 (base peak), 80 (23), and 55 (22). Found: C, 62.72; H, 5.63; N, 9.70%. Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; N, 9.71%.

9: A similar procedure using **7** (0.2 g, 1.5 mmol), paraformaldehyde (0.2 g, 6.7 mmol), and dimethyl maleate (0.2 g, 1.39 mmol) in toluene (15 ml) followed by silica-gel chromatography gave **9** as a mixture of **7,7a-*trans*-9** and **7,7a-*cis*-9** (5:4 by GLC, 0.207 g, 77%, eluent: hexane–ethyl acetate (5:1 vol/vol)). The separation of either isomer was unsuccessful. **9:** Colorless liquid; IR (neat) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.6—4.3 (9H, m), 3.65, and 3.68 (each 3H, s, COOMe); ^{13}C NMR ($CDCl_3$) δ=32.65, 39.71 (each t, 4:5, 1-C), 44.71, 45.83 (each d, 4:5, 6-C), 48.60, 51.36 (each d, 4:5, 7-C), 51.89, 52.06, 52.18 (each q, COOMe), 53.30, .56.18 (each t, 4:5, 5-C), 58.00, 61.42 (each t, 4:5, 3-C), 68.48, 70.65 (each d, 5:4, 7a-C), 171.01, 171.66, 172.96, and 173.36 (each s, COOMe); MS *m/z* (rel intensity, %) 245 (M^+, 57), 214 (38), 212 (25), 199 (38), 140 (base peak), 101 (26), 81 (25), 80 (46), 59 (26), 55 (27), 41 (40), and 40 (24). HRMS Found: *m/z* 245.0731. Calcd for $C_{10}H_{15}NO_4S$: M, 245.0721.

General Procedure for the Generation of Azomethine Ylide AY-D by Thermolysis of 5-Oxazolidinone 11 and Subsequent Ylide Trapping with Olefins or Aldehydes Leading to 12 or 13. A mixture of *N*-phenylglycine (**10**, 0.2 g, 1.32 mmol) and paraformaldehyde (0.207 g, 6.9 mmol) was heated under reflux in toluene (10 ml). The water formed was removed by the aid of Dean-Stark trap. After 20 min the toluene was evaporated to dryness in vacuo to give almost pure **11** (0.215 g, 100%) as a labile solid: ^{1}H NMR ($CDCl_3$) δ=3.83 (2H, s, 4-H), 5.24 (2H, s, 2-H), 6.3—6.5 (2H, m, Ph), 6.7—6.9 (1H, m, Ph), and 7.0—7.3 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=46.18 (t, 4-C), 81.54 (t, 2-C), 112.60, 119.89, 129.42 (each d), 144.07 (s), and 171.42 (s, COO). The generation of ylide **AY-D** was conducted without isolation of the precursor **11** as follows: A mixture of **10** (0.2 g, 1.32 mmol) and paraformaldehyde (0.207 g, 6.9 mmol) was heated under reflux in toluene (10 ml) for 30 min under continuous removal of the water formed and then an olefin or an aldehyde (1.32 mmol) was added. The resulting mixture was heated under reflux. The residue obtained by evaporation of the solvent in vacuo was chromatographed over silica gel by using hexane–ethyl acetate to give **12** or **13**. The reaction conditions as well as the results are all summarized in Table 2.

12a: Colorless needles (ethyl acetate-hexane); mp 214—216 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s, *p*-Me), 3.1—3.4, 3.4—3.7 (each 2H, m), 4.07 (2H, d, *J*=8.9 Hz, 4- and 6-H), 6.6—6.9 (3H, m, Ar), and 7.0—7.4 (6H, m, Ar); MS *m/z* (rel intensity, %) 306 (M^+, base peak), 144 (74), 119 (37), 105 (26), 104 (36), 91 (62), and 77 (46). Found: C, 74.61; H, 5.89; N, 8.90%. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14%.

12b: Colorless needles (hexane); mp 104—106 °C; IR (KBr) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.4—3.7 (6H, m, 2-, 3-, 4-, and 5-H), 3.72 (6H, s, COOMe), 6.4—6.8 (3H, m, Ph), and 7.1—7.3 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=45.53 (d, 3- and 4-C), 50.30 (t, 2- and 5-C), 52.36 (q, COOMe), 112.42, 117.12, 129.36 (each d), 147.31 (s), and 172.83 (s, COOMe); MS *m/z* (rel intensity, %) 263 (M^+, base peak), 202 (31), 145 (37), 144 (74), 119 (21), 104 (32), 91 (42), and 77 (41). Found: C, 64.17; H, 6.60; N, 5.39%. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32%.

12c: Colorless needles (hexane); mp 78—80 °C; IR (KBr) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.2—3.7 (6H, m, 2-, 3-, 4-, and 5-H), H), 3.65 (6H, s, COOMe), 6.4—6.8 (3H, m, Ph), and 7.0—7.3 (2H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=45.06 (d, 3- and 4-C), 49.06 (t, 2- and 5-C), 52.12 (q, COOMe), 111.95, 116.65, 129.36 (each d), 147.24 (s), and 172.31 (s, COOMe); MS *m/z* (rel intensity, %) 263 (M$^+$, 77), 204 (21), 145 (56), 144 (base peak), 104 (32), 91 (38), and 77 (49). Found: C, 63.94; H, 6.50; N, 5.58%. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32%.

13a: Yellow prisms (benzene–hexane); mp 118—120 °C; IR (KBr) 1595 and 1345 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.27 (1H, dd, *J*=8.6 and 7.5 Hz, one of 4-H), 3.86 (1H, dd, *J*=8.6 and 6.5 Hz, the other of 4-H), 5.05, 5.17 (each 1H, d, *J*=2.3 Hz, 2-H), 5.33 (1H, dd, *J*=7.5 and 6.5 Hz, 5-H), 6.4—6.6 (2H, m, Ph), 6.7—6.9 (1H, m, Ph), 7.1—7.3 (2H, m, Ph), 7.55 (1H, d, *J*=8.8 Hz, Ar), and 8.20 (1H, d, *J*=8.8 Hz, Ar); ^{13}C NMR (CDCl$_3$) δ=53.59 (t, 4-C), 78.88 (d, 5-C), 82.18 (t, 2-C), 113.07, 118.54, 123.95, 126.89, 129.60 (each d), 145.48, 147.31, and 147.89 (each s); MS *m/z* (rel intensity, %) 270 (M$^+$, 32), 119 (92), 91 (base peak), and 77 (35). Found: C, 67.00; H, 5.30; N, 10.17%. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36%.

13b: Pale yellow liquid; IR (neat) 1690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.6—3.8 (2H, m, 4-H), 5.01, 5.04 (each 1H, d, *J*=2.1 Hz, 2-H), 5.50 (1H, dd, *J*=6.8 and 6.1 Hz, 5-H), 6.4—6.6 (2H, m, Ph), 6.7—6.9 (1H, m, Ph), 7.1—7.3 (2H, m, Ph), 7.3—7.6 (3H, m, PhCO), and 7.9—8.1 (2H, m, PhCO); ^{13}C NMR (CDCl$_3$) δ=48.36 (t, 4-C), 79.24 (d, 5-C), 82.06 (t, 2-C), 113.30, 118.42, 128.83, 128.95, 129.42 (each d), 133.83, 134.72, 145.42 (each s), 196.31 (s, CO); MS *m/z* (rel intensity, %) 253 (M$^+$, 39), 222 (23), 149 (30), 122 (49), 121 (56), 120 (34), 106 (40), 105 (base peak), 93 (26), 91 (29), 77 (77), 58 (29), 51 (25), and 43 (76). HRMS Found: *m/z* 253.1099. Calcd for $C_{16}H_{15}NO_2$: M, 253.1102.

13c: Pale yellow liquid; IR (neat) 1715 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.20, 2.23, (each 3H, s, COMe), 4.40 (1H, d, *J*=3.2 Hz, 4-H), 4.61 (1H, d, *J*=3.2 Hz, 5-H), 5.07, 5.18 (each 1H, d, *J*=2.5 Hz, 2-H), 6.4—6.5 (2H, m, Ph), 6.7—6.9 (1H, m, Ph), and 7.1—7.3 (2H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=25.94, 26.41 (each q, COMe), 67.36 (d, 4-C), 82.71 (t, 2-C), 84.77 (d, 5-C), 113.19, 119.60, 129.89 (each d), 144.19 (s), 206.25, and 208.72 (each s, COMe); MS *m/z* (rel intensity, %) 233 (M$^+$, 21), 190 (base peak), 162 (25), 149 (50), 146 (32), 91 (22), 77 (25), and 43 (40). HRMS Found: *m/z* 233.1055. Calcd for $C_{13}H_{15}NO_3$: M, 233.1051.

General Procedure for the Generation of Azomethine Ylides AY-F from Glycine (14) and Carbonyl Compounds and Subsequent Ylide Trapping with Olefins Leading to 15 and 16. A mixture of **14** (0.2 g, 2.66 mmol), paraformaldehyde (0.2 g, 6.67 mmol), and an olefin (1.32 mmol) was heated under reflux in toluene or DMF (15 ml). The solvent as well as the reaction conditions is listed in Table 3 (Entries 1—6). After the completion of reaction the solvent was evaporated in vacuo and the residue was chromatographed over silica gel with ethyl acetate as an eluent to give **15** or **16**. The results are summarized in Table 3. Elemental analyses for **16a—16c** were not available because of the absence of parent ion peaks in their mass spectra.

15a: Colorless grains (benzene–hexane); mp 159—161 °C; IR (KBr) 3330 and 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.31, 1.36 (each 3H, s, Me), 1.99 (1H, br s, NH), 2.35 (3H, s, *p*-Me), 2.9—3.1, 3.3—3.6 (1H+3H, m, 3a-, 6-, and 6a-H), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=21.12 (q, *p*-Me), 25.12, 28.83 (each q, Me), 47.94 (t, 6-C), 48.47 (d, 6a-C), 54.89 (d, 3a-C), 63.12 (s, 4-C), 126.30, 129.48 (each d), 129.83, 138.66 (each s), 176.36, and 178.66 (each s, CON); MS *m/z* (rel intensity, %) 258 (M$^+$, 2), 82 (base peak), and 67 (19). Found: C, 69.56; H, 7.03; N, 10.53%. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.73; H, 7.04; N, 10.85%.

15b: Colorless grains (benzene–hexane); mp 148—150 °C; IR (KBr) 3300 and 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.2—2.0 (10H, m, *c*-Hex), 2.35 (3H, s, *p*-Me), 2.96 (1H, br, NH), 3.1—3.6 (4H, m, 3a-, 6-, and 6a-H), and 7.0—7.3 (4H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=22.71, 23.24, 25.59, 34.71, 36.36 (each t, *c*-Hex), 21.24 (q, *p*-Me), 47.53 (d, 6a-C), 47.83 (t, 6-C), 54.65 (d, 3a-C), 126.42, 129.54, 129.95 (each d), 138.77 (s), 176.36, and 179.01 (each s, CON); MS *m/z* (rel intensity, %) 258 (M$^+$, 2), 82 (base peak), and 67 (19). Found: C, 69.56; H, 7.03; N, 10.53%. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.73; H, 7.04; N, 10.85%.

16a: Colorless needles (benzene–hexane); mp 102—104 °C; IR (KBr) 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.32 (6H, s, *p*-Me), 2.3—2.6 (4H, m, CH), 3.1—3.5 (10H, m, CH$_2$), and 7.0—7.3 (8H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=21.18 (q, *p*-Me), 44.24 (d, CH), 55.24 (t, CH$_2$), 72.01 (t, NCH$_2$N), 126.42, 129.95 (each d), 138.77 (s), and 178.66 (s, CON); MS *m/z* (rel intensity, %) 244 (M$^+$—228, 18), 243 (base peak) 96 (24), 81 (43), 80 (20), 68 (88), 55 (37), 43 (42), 42 (29), and 41 (25).

16b: Pale yellow liquid; IR (neat) 2250 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.2—4.1 (12H, m, CH$_2$ and CH) and 7.40 (10H, s, Ph); ^{13}C NMR (CDCl$_3$) δ=40.59 (s, q-C), 53.95 (d, CH), 54.89, 61.42 (each t, CH$_2$), 73.18 (t, NCH$_2$N), 114.01, 115.42 (each s, CN), 128.42, 129.30 (each d), and 134.36 (s); MS *m/z* (rel intensity, %) 211 (M$^+$—195, 17), 210 (base peak), 132 (36), 105 (32), 103 (23), 91 (34), and 42 (77).

16c: Colorless liquid; IR (neat) 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.8—3.7 (14H, m, CH$_2$ and CH) and 3.68 (12H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=45.24 (d, CH), 52.24 (q, COOMe), 55.06 (t, CH$_2$), 74.36 (t, NCH$_2$N), and 174.07 (s, COOMe); MS *m/z* (rel intensity, %) 343 (M$^+$—43, 12), 312 (15), 200 (93), 140 (33), 82 (27), 68 (21), 59 (base peak), 41 (27), and 33 (44).

Triethyl Perhydro-1,3,5-triazine-1,3,5-triacetate (18): To a solution of aqueous formaldehyde (37%, 0.39 g, 4.85 mmol) in ethanol (0.5 ml) was added at 0 °C ethyl aminoacetate (**17**) (0.35 g, 3.39 mmol). The mixture was stirred at 0 °C for 10 h, diluted with dichloromethane (30 ml), and then dried over magnesium sulfate. The residue obtained by evaporating the solvent in vacuo was chromatographed over silica gel with hexane–ethyl acetate (1 : 1 vol/vol) to give **18** (0.208 g, 53%): Colorless liquid; IR (neat) 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.24 (9H, t, COOEt), 3.39 (6H, NCH$_2$), 3.67 (6H, NCH$_2$N), and 4.13 (6H, q, COOEt); ^{13}C NMR (CDCl$_3$) δ=14.24 (q, COOEt), 54.06 (t, NCH$_2$), 60.71 (t, NCH$_2$N), 73.18 (t, COOEt), and 170.84 (s, COOEt).

3-(Triphenylmethyl)-5-oxazolidinone (20). This compound was prepared according to either of the following two methods: (1) A mixture of *N*-(triphenylmethyl)aminoacetic acid (**19**) (0.203 g, 0.64 mmol) and paraformaldehyde (0.1 g, 3.3 mmol) was heated under reflux in toluene (10 ml) for 15 min during which time the water formed was removed by the aid of a Dean-Stark trap. The residue, obtained by evaporation of the solvent, was dissolved in dichloromethane (30 ml). The dichloromethane was washed with water, dried over magnesium sulfate, and evaporated in vacuo to give colorless solid of **20** (0.189 g, 90%). (2) To a solution of **19** (0.205 g, 0.65 mmol) in ethanol (15 ml) was added at room temperature aqueous formaldehyde (37%, 0.3 ml). The mixture was stirred at room temperature for 2 h and evaporated in vacuo. The residue was dissolved in dichloromethane (30 ml). This solution was dried over magnesium sulfate and evaporated in vacuo to give **20** (0.211 g, 99%). **20**: Colorless needles (benzene–hexane); mp 153—155 °C; IR (KBr) 1775 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.55 (2H, s, 4-H), 5.09 (2H, s, 2-H), and 7.0—7.5 (15H, m, Trt); ^{13}C NMR (CDCl$_3$) δ=48.77 (t, 4-C), 76.01 (s, Trt), 83.54 (t, 2-C), 127.42, 128.48, 128.89 (each d), and 142.66 (s); MS *m/z* (rel intensity, %) 244 (M$^+$−86, 24), 243 (base peak), and 165 (27). Found: C, 80.01; H, 5.87; N, 4.40%. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25%.

Generation of Azomethine Ylide AY-H by Thermolysis of 20 and Subsequent Ylide Trapping with Olefins Leading to 21. A mixture of **20** (0.396 g, 1.2 mmol) and an olefin (1 mmol) in dry toluene (20 ml) was heated under reflux for the period shown in Table 3 (Entries 7—9). The mixture was evaporated in vacuo and the residue was chromatographed over silica gel by using hexane–ethyl acetate (1:1 vol/vol) to give **21**. The results are listed in Table 3.

21a: Colorless prisms (benzene–hexane); mp 137—138.5 °C; IR (KBr) 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.4—2.8, 3.2—3.4 (4H+2H, m, 2-, 3-, 4-, and 5-H), 3.65 (6H, s, COOMe), and 7.0—7.5 (15H, m, Trt); ^{13}C NMR (CDCl$_3$) δ=44.07 (d, 3- and 4-C), 49.83 (t, 2- and 5-C), 52.12 (q, COOMe), 73.95 (s, Trt), 126.48, 127.71, 129.30 (each d), 142.13 (s), 174.24 (s, COOMe); MS (at 40 eV) *m/z* (rel intensity, %) 429 (M$^+$, 1), 244 (21), 243 (base peak), and 165 (37). Found: C, 75.31; H, 6.43; N, 3.49%. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26%.

21b: Colorless needles (benzene–hexane); mp 140—141 °C; IR (KBr) 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.5—2.8, 2.9—3.1 (2H+4H, m, 2-, 3-, 4-, and 5-H), 3.60 (6H, s, COOMe), and 7.0—7.6 (15H, m, Trt); ^{13}C NMR (CDCl$_3$) δ=44.18 (d, 3- and 4-C), 48.94 (t, 2- and 5-C), 51.71 (q, COOMe), 74.48 (s, Trt), 126.42, 127.66, 129.36 (each d), 142.42 (s), and 173.07 (s, COOMe); MS *m/z* (rel intensity, %) 429 (M$^+$, 1), 244 (33), 243 (base peak), and 165 (23). Found: C, 75.52; H, 6.43; N, 3.50%. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26%.

21c: Colorless prisms (benzene–hexane); mp 276—279 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.7—2.0 (2H, m, 3a- and 6a-H), 2.41 (3H, s, *p*-Me), 3.0—3.2, 3.5—3.7 (each 2H, m, 4- and 6-H), and 7.1—7.4 (19H, m, Ar); MS *m/z* (rel intensity, %) 473 (M$^+$, 1), 243 (base peak), 244 (22), and 165 (39). HRMS Found: *m/z* 472.2144. Calcd for $C_{32}H_{28}N_2O_2$: M, 472.2149.

General Procedure for the Elimination of Trityl Group of 21 Leading to 22. To a solution of **21a** or **21b** (0.1 g, 0.232 mmol) in dichloromethane (1 ml) was added concd HCl (0.05 ml). The mixture was stirred at room temperature for 0.5 h. Another portion of dichloromethane (30 ml) and then saturated aqueous sodium carbonate (30 ml) were added. The dichloromethane was dried over magnesium sulfate and evaporated in vacuo to give **22a** (0.023 g, 53%) or **22b** (0.022 g, 50%).

22a: Colorless liquid; IR (neat) 3330 and 1725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.17 (1H, s, NH, D$_2$O exchangeable), 3.0—3.5 (6H, m, 2-, 3-, 4-, and 5-H), and 3.67 (6H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=48.18 (d, 3- and 4-C), 52.12 (t, 2- and 5-C), 52.30 (q, COOMe), and 174.54 (s, COOMe); MS *m/z* (rel intensity, %) 187 (M$^+$, 3), 68 (base peak), 59 (21), 43 (44), 42 (22), 41 (35), and 39 (31). HRMS Found: *m/z* 187.0861. Calcd for $C_8H_{13}NO_4$: M, 187.0844.

22b: Colorless liquid; IR (neat) 3300 and 1725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.47 (1H, s, NH, D$_2$O exchangeable), 3.1—3.4 (6H, m, 2-, 3-, 4-, and 5-H), and 3.63 (6H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=47.71 (d, 3- and 4-C), 50.65 (t, 2- and 5-C), 52.00 (q, COOMe), and 173.54 (s, COOMe); MS *m/z* (rel intensity, %) 187 (M$^+$, 2), 68 (base peak), 59 (25), 43 (27), 42 (22), 41 (39), and 39 (33). HRMS Found: *m/z* 187.0843. Calcd for $C_8H_{13}NO_4$: M, 187.0844.

4-Methyl-3-triphenylmethyl-5-oxazolidinone (24): A mixture of *N*-triphenylmethyl-2-aminopropanoic acid (**23**) (1.12 g, 3.37 mmol) and paraformaldehyde (0.5 g, 16.7 mmol) was heated in toluene (30 ml) for 0.5 h. The water formed was removed by the aid of a Dean-Stark trap. The toluene was removed by evaporation in vacuo, the residue was dissolved in dichloromethane (30 ml). The dichloromethane was washed with water, dried over magnesium sulfate, and then evaporated to give **24** (1.01 g, 91%): Colorless needles (benzene–hexane); mp 174—177 °C; IR (KBr) 1775 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.52 (3H, d, *J*=7.2 Hz, 4-Me), 3.72 (q, 1H, *J*=7.2 Hz, 4-H), 5.15, 5.32 (each 1H, d, *J*=8.0 Hz, 2-H), and 7.1—7.5. (15H, m, Trt); ^{13}C NMR (CDCl$_3$) δ=15.41 (q, 4-Me), 55.42 (d, 4-C), 77.24 (s, Trt), 82.36 (t, 2-C), 127.24, 128.42, 128.77 (each d), 143.31 (s), and 177.01 (5-C); Ms *m/z* (rel intensity, %) 343 (M$^+$, 1), 266 (3), 244 (27), 243 (base peak), 241 (5), 239 (5), 166 (base peak), 165 (32), 91 (3), 78 (4), and 77 (4). Found: C, 80.43; H, 6.18; N, 4.20%. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08%.

***N*-(Triphenylmethyl)methylamine (25):** Colorless liquid; IR (neat) 3330, 1598, 1485, 1450, 900, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.5—1.7 (1H, br, NH), 2.03 (3H, s, NMe), and 7.0—7.5 (15H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=30.59 (q, NMe), 71.42 (s, q-C), 126.36, 127.89 128.91 (each d), and 146.01 (s); MS *m/z* (rel intensity, %) 273 (M$^+$, 13), 243 (33), 196 (base peak), 165 (28), and 77 (22). HRMS Found: *m/z* 273.1515. Calcd for $C_{20}H_{19}N$: M, 273.1517.

Generation of Azomethine Ylide AY-I and Ylide Trapping with Olefins Leading to 27. A mixture of *N*-benzylaminoacetic acid (**26**) (0.33 g, 2 mmol), paraformaldehyde (0.18 g, 6 mmol), and an olefin (1 mmol) in dry toluene (10 ml) was refluxed for 15 min. The water formed was continuously removed. The toluene was evaporated in vacuo and the residue was chromatographed over silica gel with hexane–ethyl acetate (3:1 to 1:1 vl/vol) to give **27a**—**27d**. The results are summarized in Table 3. Cycloadducts **27a** and **27b** are known and their structures were confirmed by comparison of the spectral data with the reported ones.[8]

27c: Colorless plates (benzene–hexane); mp 129—130 °C; IR (KBr) 1770 and 1695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2—2.5 (2H, m, 3a- and 6a-H), 2.31 (3H, s, *p*-Me), 3.0—3.4 (4H, m, 4- and 6-H), 3.51 (2H, s, PhCH$_2$), and 7.0—7.2 (9H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=21.12 (q, *p*-Me), 44.24 (d, 3a- and 6a-C), 56.47 (t, 4- and 6-C), 58.12 (t, PhCH$_2$), 126.36, 127.24, 128.30, 128.48, 129.83 (each d), 138.01, 138.60 (each s), and 178.66 (s, CON); MS *m/z* (rel intensity, %) 320 (M$^+$, 80), 319 (25), 243 (23), 229 (73), 133 (22), 92 (28), 91 (base peak), 42 (30), and 32 (28). Found: C, 74.95; H, 6.29; N, 8.75%. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74%.

27d: Colorless liquid; IR (neat) 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.92 (3H, t, *n*-Bu), 1.2—1.8, 1.9—2.2, 2.3—3.1 (4H+2H+5H, m, *n*-Bu and CH$_2$), 3.60 (2H, s, PhCH$_2$), 4.06 (2H, t, *n*-Bu), and 7.1—7.4 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=13.71 (q, *n*-Bu), 19.12, 27.71, 30.71 (each t, *n*-Bu and 4-C), 42.24 (d, 3-C), 53.77, 56.77, 60.12, 64.48 (each t, *n*-Bu, 2-, and

5-C), 127.07, 128.36, 128.83 each d), 139.13 (s), and 175.19 (s, COOBu-*n*); MS *m/z* (rel intensity, %) 261 (M^+, 6), 170 (30), 91 (base peak), 72 (30), and 42 (39). HRMS Found: *m/z* 261.1751. Calcd for $C_{16}H_{23}NO_2$: M, 261.1728.

Debenzylation of 27c by Pd/C Leading to 22c. A mixture of **27c** (0.16 g, 0.5 mmol) and palladium on charcoal (5%, 0.15 g) in dry xylene (1.5 ml) was refluxed under an atmosphere of hydrogen (ca. 1 atm) for 3 h. The catalyst was filtered off and washed with dichloromethane (5 ml). The filtrate and washing were combined and evaporated in vacuo to give **22c** (0.11g, 96%): Colorless viscous liquid; IR (neat) 3300, 1770, and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.7—2.0 (1H, m, D_2O exchangeable, NH), 2.38 (3H, s, *p*-Me), 2.9—3.7 (4H, m, 3a-, 4-, 6, and 6a-H), and 7.0—7.4 (4H, m, Ar); MS *m/z* (rel intensity, %) 230 (M^+, 70), 188 (24), 107 (18), 96 (31), 91 (19), 68 (base peak), and 43 (78). HRMS Found: *m/z* 230.1050. Calcd for $C_{13}H_{14}N_2O_2$: M, 230.1054.

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10) In the previous communication incorrect structures have been presented to **16a** and **16b** (See Ref. 1). They are correctly reassigned in this article.

11) 5-Oxazolidinone **D** is unknown. Thermal stability of its 3-substituted derivatives seems to depend upon the size of 3-substituent (See compounds **11** and **20**), indicating the thermal instability of the parent 5-oxazolidinone **D**.

12) In fact the reaction of *N*-unsubstituted cycloadduct **22c** with paraformaldehyde under reflux in toluene for 0.5 h led to a quantitative formation of **16a**.

13) *N*-(Methyl)triphenylmethylamine corresponds to the product derived through the hydrolysis of the expected azomethine ylide.