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ON THE SYNTHESIS OF METHYL (Z/E)-2-ACETAMIDO(OR BENZAMIDO)-3-ARYL 2-BUTENOATES

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Abstract.- The methyl Z-2-acetamido(or benzamido)-3-aryl-2-butenoates (Z-9a-e,Z-10a-e) were obtained by two alternative procedures: stereospecific opening of Z-2-methyl(or phenyl)-4-|α-arylethylidene|-5(4H)-oxazolones (Z-7a-e,Z-8a-e) and stereospecific homologation of methyl Z-2-acetamido(or benzamido)-3-aryl-2-propenoates (Z-3a-e,Z-4a-e). The methyl E-2-benzamido-3-aryl-2-butenoates (E-10a-e) were obtained by stereospecific opening of E-2-phenyl-4-|α-arylethylidene|-5(4H)-oxazolones (E-8a-e).

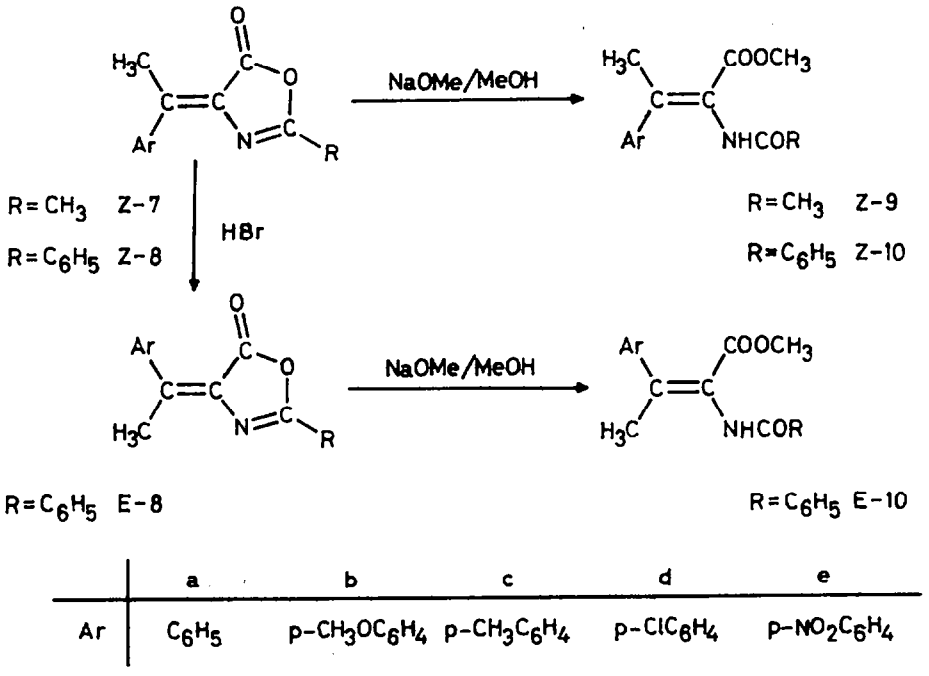
A considerable interest is at present being shown in the synthesis of 2,3-dehydroamino acid derivatives as they have been found in small peptides with antimicrobial activity[1]. Moreover, they are one of the best precursors of optically-active α-amino acid derivatives obtained by asymmetric hydrogenation[2]. We are therefore interested in the synthesis of new 2,3-dehydroamino acid derivatives which contain a methyl group at β-position precisely because this group leads to a new series of potencially active compounds.

As these compounds show geometric isomerism we are interested in the stereospecific synthesis of each one of the possible isomers Z or E, and so we only tested those procedures which had proved to be stereospecific on related compounds[3] or synthetic routes[4].

RESULTS AND DISCUSSION

(Z/E)-2-methyl(or phenyl)-4-|α-arylethylidene|-5(4H)-oxazolones (Z-7a-e, Z-8a-e and E-8a-e) gave stereospecific opening of the oxazolinone ring with sodium methylate/methanol to afford the corresponding methyl (Z/E)-2-acetamido(or benzamido)-3-aryl-2-butenoates (Z-9a-e, Z-10a-e and E-10a-e) in high yield, but when the aryl substituent was the p-nitrophenyl group, the initially-formed isomer immediately isomerized to afford a mixture of Z and E 2-acetamido(or benzamido)-3-(p-nitrophenyl)-2-butenoate (9e, 10e) with the E-isomer predominating (Scheme 1).

On the other hand, diazomethane reacted with methyl Z-2-acetamido(or benzamido)-3-aryl-2-propenoates (Z-3a-e, Z-4a-e) regio and stereospecifically to afford cis-4-aryl-3-acetamido(or benzamido)-3-carbomethoxy-Δ^1-pyrazolines (cis-5a-e, cis-6a-e) which when heated at about 200º C in 1,2-ethanediol extruded nitrogen to afford stereospecifically methyl Z-2-acetamido(or benzamido)-3-aryl-2-butenoates (Z-9a-e, Z-10a-d) in high yields (Scheme 2). However, in the case of methyl 2-benzamido-3-(p-nitrophenyl)-2-butenoate (10e) a mixture of isomers with the Z isomer predominating was obtained.

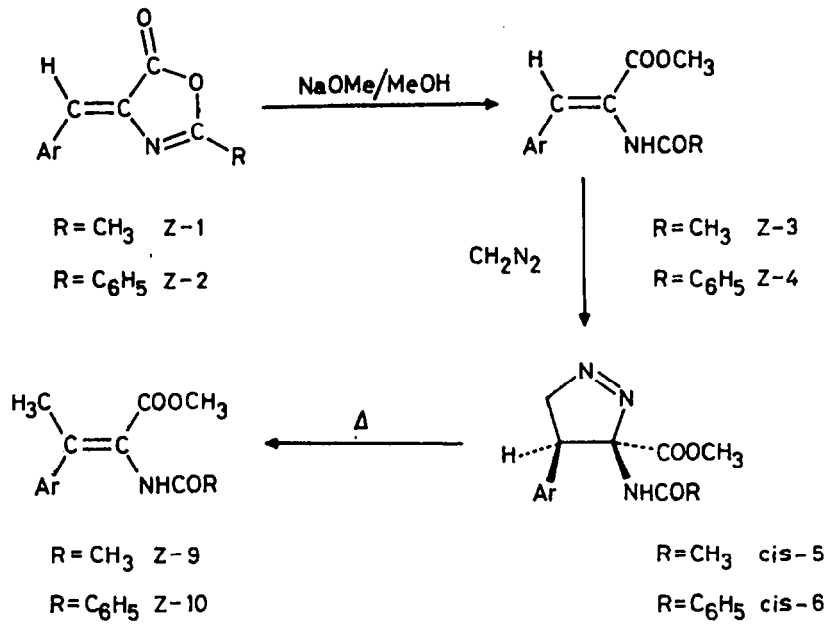


Scheme 1

Table 1. Preparation of methyl (Z/E)-2-acetamido(or benzamido)-3-aryl-2-butenoates.

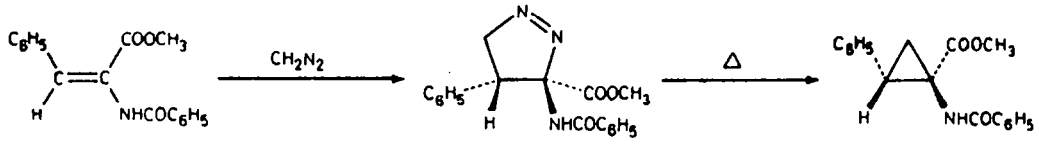
Compound	Yields (%)		m.p.	I.R. (nujol) (cm^{-1})		
	A	B	[°C]	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=O}$
Z-9a	87	80	141-2	3260	1735	1660
Z-9b	85	79	124-6	3340	1700	1680
Z-9c	90	80	123-5	3270	1730	1650
Z-9d	86	75	117-9	3270	1730	1650
Z-9e	--	70	137-8	3290	1730	1660
Z-10a	95	76	147-9	3250	1710	1635
Z-10b	93	77	107-9	3240	1725	1650
Z-10c	96	74	121-3	3240	1730	1635
Z-10d	95	76	140-2	3230	1730	1635
Z-10e	57[a]	--	137-9	3260	1730	1650
E-10a	83	--	203-5	3330	1730	1645
E-10b	85	--	160-2	3310	1720	1640
E-10c	87	--	190-1	3300	1730	1645
E-10d	95	--	178-9	3300	1730	1645
E-10e	95	--	184-5	3360	1740	1650

a) Methanolysis in acidic medium
A- Stereospecific opening
B- Stereospecific homologation



Scheme 2

When this procedure was tried out with methyl E-2-benzamido-3-phenyl-2-propenoate (E-4a) the stereospecifically-obtained trans-4-phenyl-3-benzamido-3-carbomethoxy-Δ^1-pyrazoline (trans-6a) heated at about 200° C in 1,2-ethanediol extruded nitrogen but methyl trans-2-phenyl-1-benzamido-cyclopropane-1-carboxylate (11) was obtained (Scheme 3).



Scheme 3

After establishing the different procedures by which the compounds dealt with in this paper can be stereospecifically obtained a comparison can be made and the following conclusions reached: Methyl Z-2-acetamido-3-aryl-2-butenoates (Z-9a-e) can be obtained by either of the two procedures described, but as Z-2-methyl-4-|α-arylethylidene|-5(4H)-oxazolones (Z-7a-e) cannot be obtained by standard procedures and the one we have recently described[5] (stereospecific homologation of Z-2-methyl-4-arylidene-5(4H)-oxazolones (Z-1a-e)) affords the desired compounds in low to moderate yields, homologation of methyl Z-2-acetamido-3-aryl-2-propenoates (Z-3a-e) is the better in this case.

Methyl Z-2-benzamido-3-aryl-2-butenoates (Z-10a-d) can also be obtained by the two procedures described but in this case the opening procedure proved more useful as Z-2-phenyl-4-|α-arylethylidene|-5(4H)-oxazolones (Z-8a-e) can be obtained by standard procedures[6]. When the aryl substituent was the p-nitrophenyl group, methanolysis of Z-2-phenyl-4-|α-(p-nitrophenyl)-ethylidene|-5(4H)-oxazolone (Z-8e) was carried out in acidic medium to avoid isomerization.

Methyl E-2-benzamido-3-aryl-2-butenoates (E-10a-e) can only be obtained by stereospecific opening of E-2-phenyl-4-|α-arylethylidene|-5(4H)-oxazolones (E-8a-e), which were synthesized by isomerization of the corresponding Z-isomers with HBr[6].

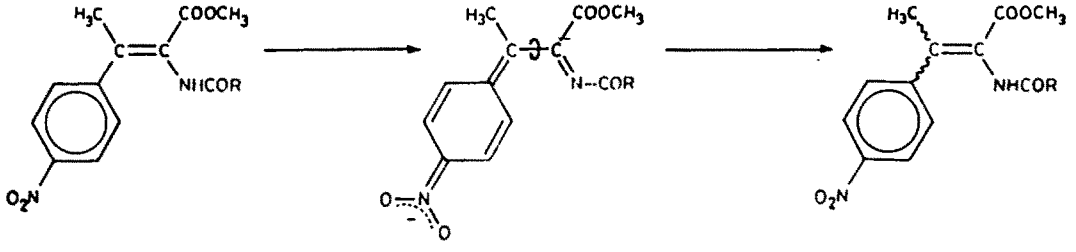
Table 2. ^{1}H RMN spectral parameters of Z-9a-e, Z-10a-e and E-10a-e.

Compound	Chemical Shift, δ ppm
Z-9a	1.84(s,3H); 2.28(s,3H); 3.82(s,3H); 6.90(brs,1H); 7.30-7.50(m,5H)
Z-9b	1.89(s,3H); 2.27(s,3H); 3.81(s,6H); 6.63(brs,1H); 6.90(d,2H, J=8 Hz); 7.19 (d,2H, J=8 Hz)
Z-9c	1.85(s,3H); 2.26(s,3H); 2.36(s,3H); 3.80(s,3H); 7.20-7.40(m,5H)
Z-9d	1.84(s,3H); 2.27(s,3H); 3.82(s,3H); 7.10(brs,1H); 7.20-7.55(m,4H)
Z-9e	1.80(s,3H); 2.36(s,3H); 3.86(s,3H); 7.41(brs,1H); 7.52(d,2H, J=9 Hz); 8.26 (d,2H, J=9 Hz)
Z-10a	2.33(s,3H); 3.82(s,3H); 7.30-7.65(m,11H)
Z-10b	2.29(s,3H); 3.77(s,3H); 3.81(s,3H); 6.87(d,2H, J=8 Hz); 7.10-7.70(m,8H)
Z-10c	2.33(s,6H); 3.84(s,3H); 7.10-7.85(m,10H)
Z-10d	2.33(s,3H); 3.85(s,3H); 7.25-7.90(m,10H)
Z-10e	2.35(s,3H); 3.80(s,3H); 7.20-7.70(m,8H); 8.15(d,2H, J=9 Hz)
E-10a	2.20(s,3H); 3.48(s,3H); 7.33(s,5H); 7.50-7.70(m,4H); 7.80-8.10(m,2H)
E-10b	2.17(s,3H); 3.53(s,3H); 3.84(s,3H); 6.92(d,2H, J=9 Hz); 7.25(d,2H, J=9 Hz); 7.36(brs,1H); 7.45-7.70(m,3H); 7.90-8.20(m,2H)
E-10c	2.15(s,3H); 2.33(s,3H); 3.46(s,3H); 7.12(m,4H); 7.28(brs,1H); 7.30-7.55 (m,3H); 7.75-8.00(m,2H)
E-10d	2.15(s,3H); 3.50(s,3H); 7.20-7.65(m,8H); 7.85-8.05(m,2H)
E-10e	2.16(s,3H); 3.46(s,3H); 7.37(d,2H, J=9 Hz); 7.50-7.70(m,4H); 7.85-8.15 (m,2H); 8.36(d,2H, J=9 Hz)

All attempts to synthesize methyl E-2-acetamido-3-aryl-2-butenoates or their precursors E-2-methyl-|α-arylethylidene|-5(4H)-oxazolones were unsuccessful.

MECHANISTIC CONSIDERATIONS

Isomerization of 3-(p-nitrophenyl) derivatives occurs through a quinonoid intermediate which was detected by ^{1}H NMR spectroscopy. It can be assumed that in the reaction conditions the hydrogen in the acylamino group is sufficiently acidic to be removed and the quinonoid compound is formed. In this intermediate, rotation round the C-C bond is possible and when the 2,3-dehydrocompound is recovered isomerization has occured (Scheme 4).



R=CH_3 Z-9e R=CH_3 12e

R=C_6H_5 Z-10e R=C_6H_5 13e

Scheme 4

Mechanisms explaining pyrazoline decomposition to afford unsaturated or cyclopropanic compounds are discussed in a recent review by Engel[7].

STEREOCHEMICAL ASPECTS

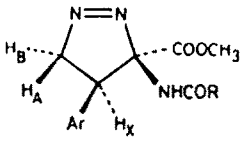
Stereochemistry of compounds Z-3a-e, Z-4a-e and E-4a has been established unambiguously by ^{13}C NMR couplings[8].

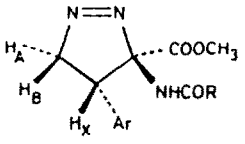
Table 3. ^{1}H NMR spectral parameters of cis-5a-e, cis-6a-e and trans-6a.

Compound	chemical shift, δ ppm								coupling constants[a]		
	Ar	RCO	$COOCH_3$	other	H_{N-H}	H_A	H_B	H_X	J_{AB}	J_{AX}	J_{BX}
cis-5a	6.85-7.00(m,2H) 7.15-7.30(m,3H)	1.68	3.84	-	6.35	5.30	5.03	4.04	-17.95	3.50	8.10
cis-5b	6.80-6.85(m,4H)	1.72	3.84	3.78	6.55	5.23	4.99	4.00	-17.90	3.20	8.00
cis-5c	6.95(d,2H, J=8) 7.24(d,2H, J=8)	1.72	3.88	2.35	7.08	5.32	5.08	4.12	-18.00	3.90	8.10
cis-5d	6.82(d,2H, J=8) 7.20(d,2H, J=8)	1.70	3.81	-	7.10	5.25	5.05	4.12	-18.00	3.50	9.30
cis-5e	7.10(d,2H, J=8) 8.07(d,2H, J=8)	1.70	3.86	-	7.29	5.30	5.14	4.25	-18.00	3.80	8.90
cis-6a	6.90-7.05(m,2H) 7.15-7.30(m,3H)	7.35	3.86	-	7.16	5.38	5.08	4.15	-18.10	3.20	8.05
cis-6b	6.81(d,2H, J=9) 7.04(d,2H, J=9)	7.44	3.83	3.71	7.57	5.35	5.10	4.19	-18.40	3.05	8.95
cis-6c	6.88(d,2H, J=8) 6.95(d,2H, J=8)	7.25	3.78	2.19	7.07	5.27	5.01	4.10	-18.00	4.60	7.40
cis-6d	6.88(d,2H, J=8) 7.10(d,2H, J=8)	7.28	3.74	-	7.74	5.29	5.09	4.27	-18.00	2.15	8.25
cis-6e	7.13(d,2H, J=8) 7.95(d,2H, J=8)	7.32	3.82	-	7.66	5.39	5.19	4.41	-18.00	2.00	8.00
trans-6a[b]	7.50-7.65(m,3H) 7.85-8.00(m,2H)	7.25	3.26	-	9.29	4.73	5.12	3.84	-17.80	7.30	8.30

a Theoretical ^{1}H NMR spectral data were generated by using the Panic Program (Bruker Instrument Corp.) which applies the LAOCOON III algorithm, coupling constants are given in hertz.
b In DMSO d_6.

Stereospecificity of the diazomethane cycloaddition to afford Δ^1-pyrazolines has been verified by NOE by irradiation of the hydrogen in the acylamino group which causes greater NOE enhancements of the signals of the groups cis to it (Figure 1).





R = CH_3 cis-5
R = C_6H_5 cis-6

R = C_6H_5 trans-6

	a	b	c	d	e
Ar	C_6H_5	p-$CH_3OC_6H_4$	p-$CH_3C_6H_4$	p-ClC_6H_4	p-$NO_2C_6H_4$

Figure 1

^{1}H NMR spectral data of pyrazolines (cis-5a-e, cis-6a-e and trans-6a) are given in Table 3. Geminal protons of the pyrazoline ring appear as the AB part of ABX systems and show little chemical shift difference. Each one can be identified by vicinal coupling constants as in 5-membered rings in general J^{trans} is less than J^{cis} [9] (Figure 1).

Stereochemistry of compounds Z-10a-e and E-10a-e can be established on the basis of the methyl ^{1}H NMR chemical shifts as this group gives rise to a signal further downfield in Z-isomers than in E isomers as it is cisoid with respect to the carbonyl group[10]. Moreover, the carbomethoxy group also

gives rise to a signal further downfield in Z-isomers than in E-isomers[11].

For acetamido derivatives (Z-9a-e), the configuration can be established by comparing their ^{1}H NMR chemical shifts with those of Z-benzamido derivatives since the carbomethoxy group gives rise to a signal in the same frequency range.

EXPERIMENTAL

All melting points were taken on a Büchi 510 capillary melting point apparatus and are uncorrected. Ir were performed on a Perkin Elmer 283 spectrometer. Data are recorded in cm^{-1}. Routine ^{1}H NMR spectra were recorded for solutions in $CDCl_3$ on a Perkin Elmer R-12 60 MHz spectrometer. Fourier transform ^{1}H NMR spectra were recorded at 80 MHz on a Bruker WP-80-SY spectrometer, under ASPECT-2000 computer control. All chemical shifts are expressed in δ values from Me_4Si as internal standard, and coupling constants are given in hertz. Overhauser enhancement factors were determined for undegassed 50 mM solutions of the pyrazoline by using the NOE difference technique, by gated irradiation of the amide NH proton (saturation time 10 s, decoupling power 45 dB below 0.2 W, decoupler bandwidth $^{Y}B_2$=2.5 Hz). NOE signal enhancements of approximately 3-15% were observed. Elemental analyses were measured on a Perkin-Elmer 240-B analyzer.

Z-2-Methyl-4-arylidene-5(4H)-oxazolones (Z-1a-e) and Z-2-phenyl-4-arylidene-5(4H)-oxazolones (Z-2a-e) were prepared by condensation of N-acetylglycine or N-benzoylglycine with the corresponding benzaldehyde by a general procedure[12].

E-2-Phenyl-4-arylidene-5(4H)-oxazolones (E-2a-e) were prepared by isomerization of the corresponding Z-isomer with HBr by a general procedure[12].

Methyl Z-2-acetamido-3-aryl-2-propenoates (Z-3a-e), methyl Z-2-benzamido-3-aryl-2-propenoates (Z-4a-e) and methyl E-2-benzamido-3-phenyl-2-propenoate (E-4a) were prepared by stereospecific opening of the corresponding 5(4H)-oxazolones by a general procedure[11].

cis-4-Aryl-3-acetamido-3-carbomethoxy-Δ^1-pyrazolines (cis-5a-e). A total of 4.5 mmol of the corresponding methyl Z-2-acetamido-3-aryl-2-propenoate (Z-3a-e) dissolved in 20 ml of chloroform were treated with an ethereal solution of diazomethane (from 2 g of N-methyl-N-nitrosourea in 20 ml of ether) in a stoppered and protected from light flask at room temperature for about 3 days until completion (TLC). The solution was treated with anhydrous $CaCl_2$ to get rid of excess diazomethane, filtered, and concentrated in vacuo. The resultant solid was dried over P_2O_5 to give quantitative yield of pure samples of the corresponding cis-5a-e.

cis-4-Aryl-3-benzamido-3-carbomethoxy-Δ^1-pyrazolines (cis-6a-e). A total of 3.6 mmol of the corresponding methyl Z-2-benzamido-3-aryl-2-propenoate (Z-4a-e) underwent diazomethane cycloaddition under exactly tha same conditions used in the preparation of cis-5a-e to give quantitative yield of pure samples of the corresponding cis-6a-e.

trans-4-Phenyl-3-benzamido-3-carbomethoxy-Δ^1-pyrazoline (trans-6a). A total of 1 g (3.6 mmol) of methyl E-2-benzamido-3-phenyl-2-propenoate (E-4a) underwent diazomethane cycloaddition under exactly the same conditions used in the preparation of cis-5a-e to give quantitative yield of pure trans-6a as a white solid.

Z-2-Methyl-4-|α-arylethylidene|-5(4H)-oxazolones (Z-7a-e) were obtained by diazomethane cycloaddition from the corresponding Z-1a-e by a recently described procedure[5].

Z-2-Phenyl-4-|α-arylethylidene|-5(4H)-oxazolones (Z-8a-e) were prepared by condensation of N-benzoylglycine with the corresponding acetophenone by a general procedure[6].

E-2-Phenyl-4-|α-arylethylidene|-5(4H)-oxazolones (E-8a-e) were prepared by isomerization of the corresponding Z-isomer with HBr by a general procedure[6].

Methyl Z-2-acetamido-3-aryl-2-butenoates (Z-9a-e).
Method A. A total of 3.8 mmol of the corresponding Z-7a-e were stirred at room temperature with sodium methylate (0.01 g) in absolute methanol (20 ml) until the solid went into solution. The solution was concentrated and water was added. Filtration and washing of the solid furnished pure samples of the corresponding Z-9a-e in good to very good yields (see Table 1).
Method B. A total of 3.8 mmol of the corresponding cis-5a-e dissolved in 10 ml of 1,2-ethanediol were heated at about 200° C for 10 min. The solution was cooled and water added until the solution became cloudy; crystalization at room temperature afforded pure samples of the corresponding Z-9a-e in good yields (see Table 1).

Methyl Z-2-benzamido-3-aryl-2-butenoates (Z-10a-d).
Method A. A total of 3.1 mmol of the corresponding Z-8a-d were stirred at room temparature with sodium methylate (0.01 g) in absolute methanol (20 ml) until the solid went into solution. The solution was concentrated and water was added. Filtration and washing of the solid furnished pure samples of the corresponding Z-10a-d in good to very good yields (see Table 1).
Method B. A total of 3.1 mmol of the corresponding cis-6a-d dissolved in 10 ml of 1,2-ethanediol were heated at about 200° C for 10 min. The solution was cooled and water added until the solution became cloudy; crystallization at room temperature afforded pure samples of the corresponding Z-10a-d in good yields (see Table 1).

Methyl Z-2-benzamido-3-(p-nitrophenyl)-2-butenoate (Z-10e).
A total of 1 g (3.2 mmol) of Z-8e in absolute methanol (15 ml) and sulfuric acid (0.1 ml) were heated at about 100º C for 12 h. The solution was concentrated in vacuo and the solid deposited was filtered and recrystallized to afford Z-10e in 57% yield.

Methyl E-2-benzamido-3-aryl-2-butenoates (E-10a-e).
A total of 3.1 mmol of the corresponding E-8a-e were stirred at room temperature with sodium methylate (0.01 g) in absolute methanol (20 ml) until the solid went into solution. The solution was concentrated and water was added. Filtration and washing of the solid furnished pure samples of the corresponding E-10a-e in good to very good yields (see Table 1).

Methyl trans-2-phenyl-1-benzamidocyclopropane-1-carboxylate (11).
A total of 1 g (3.1 mmol) of trans-6a dissolved in 1,2-ethanediol were heated at about 200º C for 10 min. The solution was cooled and water added until the solution became cloudy; crystallization at room temperature afforded 11 in 82% yield. mp 194-195º C (lit.[13] mp 193-195º C); NMR($CDCl_3$) 1.71 (dd,1H, J=-5.3 Hz, J=10 Hz); 2.33 (dd,1H, J=-5.3 Hz, J=8.5 Hz); 3.04(dd,1H, J=8.5 Hz, J=10Hz); 3.40 (s,3H); 6.85(bra,1H); 7.30-7.60(m,8H), 7.90-8.10(m,2H).

Compound	Analysis % Calc/Found			Compound	Analysis % Calc/Found		
	C	H	N		C	H	N
cis-5a	59.77	5.74	16.09	Z-9a	66.95	6.43	6.00
	59.69	5.60	15.97		67.23	6.30	5.87
cis-5b	57.73	5.84	14.43	Z-9b	63.87	6.46	5.32
	57.58	6.03	14.36		63.68	6.54	5.19
cis-5c	61.09	6.18	15.27	Z-9c	68.01	6.88	5.66
	60.89	6.23	15.34		67.88	6.69	5.76
cis-5d	52.79	4.73	14.21	Z-9d	58.31	5.23	5.23
	52.92	4.81	14.19		58.10	5.00	5.05
cis-5e	50.98	4.57	18.30	Z-9e	56.11	5.03	10.06
	51.12	4.68	18.23		55.98	5.20	10.11
cis-6a	66.87	5,26	13.00	Z-10a	73.22	5.76	4.74
	66.92	5.12	12.96		73.01	5.58	4.92
cis-6b	64.58	5.38	11.89	Z-10b	70.15	5.84	4.30
	64.49	5.21	12.03		70.28	5.72	4.16
cis-6c	67.65	5.63	12.46	Z-10c	73.78	6.14	4.53
	67.49	5.72	12.37		73.69	6.22	4.69
cis-6d	60.41	4.47	11.74	Z-10d	65.55	4.85	4.24
	60.47	4.62	11.86		65.71	4.74	4.39
cis-6e	58.69	4.34	15.21	Z-10e	63.52	4.70	8.23
	58.54	4.57	15.41		63.69	4.56	8.35
trans-6a	66.87	5.26	13.00	E-10a	73.22	5.76	4.74
	67.02	5.09	13.21		72.97	5.71	4.87
				E-10b	70.15	5.84	4.30
					70,00	5.67	4.17
				E-10c	73.78	6.14	4.53
					73.96	6.19	4.38
				E-10d	65.55	4.85	4.24
					65.71	4.69	4.03
				E-10e	63.52	4.70	8.23
					63.64	4.51	8.19

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