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Synthesis of 2-Substituted-3-oxo-3-[(aryloxycarbonyl)amino]-propanoic Acids, Ethyl 3-{[(1E)-ethoxy(aryloxy)methylene]-amino}-2-substituted-3-oxopropanoate, (1Z, 2Z) [Chloro(aryloxy)methylene]hydrazine and Structurally Related Compounds from the Reactions of Alkyl or Aryl Malonyl Chloride with Aryl Cyanates

MOHAMMED A. SHEAT† and JASIM M. A. AL-RAWI*
Pharmacy Department, School of Health and Environment
La Trobe University, Bendigo VIC 3552, Australia
Fax: (61)354447476; Email: j.al-rawi@latrobe.edu.au

Treatment of the reaction mixture of alkyl or arylmalonyl chlorides and aryl cyanates with water give 2-substituted-3-oxo-3-[(phenoxycarbonyl)amino]propanoic acid (**1**); while with absolute ethanol ethyl 3-{[(1E)-ethoxy (aryloxy)methylene]amino}-2-substituted-3-oxopropanoate (**3**) is produced. Aryl 3-chloro-2-substituted-3-oxoprop-anoylcarbamate (**2**) was obtained from the reaction of alkyl or aryl malonyl chlorides with aryl carbamate. Compound **1** was also obtained from the reaction of compound **2** with water. A mechanism is suggested for the formation of compounds **1** and **3**. The (1Z, 2Z) [chloro(aryloxy)methylene]hydrazine (**5**) is isolated from the reaction of alkyl or aryl malonyl chloride (1 mol) with aryl cyanate (2 mol). Product **5** is also prepared from an equimolar reaction of acetyl or benzoyl chloride with aryl cyanates.

Key Words: Synthesis, Malonyl chloride, Aryl cyanate.

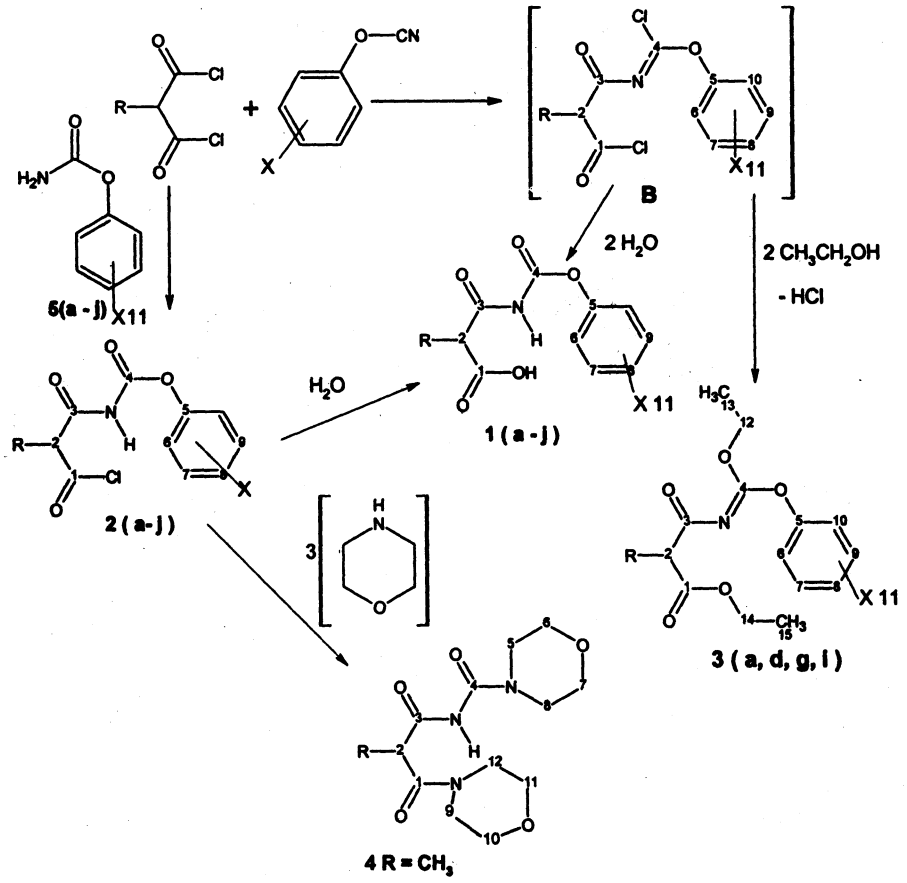
INTRODUCTION

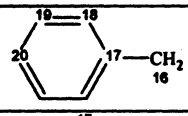
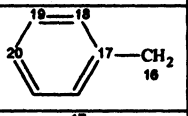
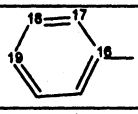
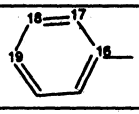
Alkyl or arylmalonyl chlorides were found to react with acrylonitriles and isocyanates producing substituted 1,3-oxazines[1], while with aryl or alkyl thio cyanate yielding 4,6-dichloropyramidines[2]. Furthermore, some of the 1,3-oxazines was previously prepared from the reaction of malonyl chloride and organic thiocyanate[3], which showed antimicrobial activity[4].

RESULTS AND DISCUSSION

The reaction of alkyl or aryl malonyl chlorides (1 mol) with aryl cyanates (1 mol) is expected to produce either 1,3-oxazine or pyrimidine analogues. However, many attempts (changing reaction temperature, molar ratio and solvent) to isolate a solid product from the reaction mixture failed and only oily products B (**Scheme-1**) were obtained. The addition of water (4 : 1 molratio) to the above

†Chemistry Department, College of Science, University of Mosul, Mosul, Iraq.



	R	X		R	X
a	CH_3 16	H	b	CH_3 16	*p*–CH_3
c	CH_3 16	*p*–CH_3O	d	CH_3 16	*m*–CH_3O
e	$H_3C–CH_2$ 17 16	H	f	$H_3C–CH_2$ 17 16	*p*–CH_3O
g		H	h		*p*-CH_3O
i		H	j		*p*–CH_3

Scheme-1

reaction mixture gave a solid product. This product was recrystallized from benzene and identified as 2-substituted-3-oxo-3-[(phenoxycarbonyl)-amino]propanoic acid **1(a–j)** (**Scheme-1** and Table-1). On the other hand, the reactions of alkyl or aryl malonyl chlorides (1 mol) with aryl carbamates **5(a–j)** (1 or 2 mol) gave aryl 3-chloro-2-substituted-3-oxopropanoylcarbamate **2(a–j)**. The structures of compounds **2(a–j)** were confirmed by their spectral data (Table-2). It is worth noting that the treatment of compounds **2** with water gave compounds **1**.

TABLE-1
^{13}C NMR CHEMICAL SHIFTS (PPM RELATIVE TO INTERNAL TMS) OF 2-SUBSTITUTED-3-OXO-3-[(PHENOXYCARBONYL)AMINO]PROPANOIC ACID **1(a–j)**

Compd.	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j
C-1[a]	170.9	170.6	170.3	170.5	169.6	169.8	172.8	169.0	171.3	168.4
C-2	47.4	47.2	46.5	46.7	54.3	54.5	53.9	54.6	43.4	58.9
C-3[a]	171.8	171.4	171.3	171.5	170.4	170.7	172.8	169.7	171.3	169.4
C-4[b]	153.0	150.9	150.4	151.0	150.8	151.0	150.9	150.9	150.9	151.0
C-5[b]	151.4	148.6	143.2	150.0	150.6	144.2	150.8	144.1	150.6	144.1
C-6	122.4	121.8	122.6	107.9	122.1	123.0	122.2	122.9	122.2	122.9
C-7	130.3	130.3	114.5	160.3	129.9	115.0	129.8	114.8	129.9	129.9
C-8	126.8	136.0	157.1	111.9	126.4	158.1	128.9	158.1	126.4	158.1
C-9	130.3	130.3	114.5	130.0	129.9	115.0	12.8	114.8	129.9	129.9
C-10	122.4	121.8	122.6	113.8	122.1	123.0	122.2	122.9	122.2	122.9
C-11	—	20.7	55.3	55.3	—	55.9	—	55.7	—	55.7
C-16	13.7	13.6	13.2	13.3	22.7	22.9	38.7	34.9	135.0	134.2
C-17	—	—	—	—	12.2	12.3	141.6	139.2	128.8	128.8
C-18	—	—	—	—	—	—	129.8	129.5	130.0	130.2
C-19	—	—	—	—	—	—	128.8	128.8	127.3	128.3
C-20	—	—	—	—	—	—	126.3	126.9	—	—

[a] Assignments could be exchanged. [b] Assignments could be exchanged.

Solvent for NMR measurements, **1a, b** and **e–j** solvent acetone-d_6, **1c** and **d** solvent DMSO-d_6.

It was noticed that 1 mol of aryl carbamate reacted with the substituted malonyl chloride. This could be due to the deactivation effect of the aryl carbamate group on the carbonyl chloride group of compound **1**. Good support came from the fact that acetyl chloride or benzoyl chloride did not react with aryl carbamate under the above reaction conditions even after prolonged reaction time (3 days).

The reaction of phenyl 3-chloro-2-methyl-3-oxopropanoylcarbamate **2a** with dry morpholine resulted in a replacement of the chlorine atom and the phenoxy group with morpholine groups giving the carboxamide **4** (R=CH_3). The yield improved to 52 per cent when 3 mol of morpholine was used. IR, ^1H and ^{13}C NMR spectra were in agreement with the proposed structure for compound **4**.

TABLE-2
^{13}C NMR CHEMICAL SHIFTS (ppm RELATIVE TO INTERNAL TMS) OF ARYL 3-CHLORO-2-SUBSTITUTED-3-OXOPROPANOYLCARBAMATE **2(a–j)**

Compd.	**2a**	**2b**	2c	2d	**2e**	2f	2g	2h	2i	2j
C-1[a]	168.7	168.6	168.4	168.1	169.3	169.6	169.1	169.1	168.2	166.2
C-2	57.3	57.1	57.3	57.2	53.0	53.5	54.6	54.6	58.8	55.4
C-3[a]	171.1	174.2	170.7	170.6	173.3	172.5	169.8	169.6	169.0	168.6
C-4[b]	150.6	150.3	150.6	150.1	150.0	150.0	150.6	150.6	150.6	150.3
C-5[b]	149.9	147.1	143.2	150.1	149.4	142.8	150.3	144.0	150.6	142.7
C-6	121.4	120.6	121.9	107.2	121.0	121.8	121.9	122.9	122.0	121.8
C-7	129.8	129.8	114.3	160.2	129.2	114.4	129.8	114.8	128.8	114.3
C-8	126.8	136.1	157.4	112.2	126.1	157.5	126.4	158.0	126.4	157.3
C-9	129.8	129.8	114.3	129.7	129.2	114.4	129.8	114.8	128.8	114.3
C-10	121.4	120.6	121.9	113.1	121.0	121.8	121.9	122.9	122.0	121.8
C-11	—	20.8	55.5	55.4	—	55.5	—	55.7	—	—
C-16	13.7	13.4	13.7	13.6	22.8	22.8	34.8	34.8	134.0	132.0
C-17	—	—	—	—	11.9	11.9	139.0	139.1	128.7	128.6
—	—	—	—	—	—	—	128.7	128.8	130.1	130.0
C-19	—	—	—	—	—	—	129.4	129.4	128.2	127.9
C-20	—	—	—	—	—	—	126.8	126.9	—	—

[a]Assignments could be exchanged. [b]Assignments could be exchanged.
Solvent for NMR measurements, **2a–f** and **j** solvent $CDCl_3$, **2g–i,** solvent Acetone-d_6.

The treatment of the oily product B (**Scheme-1**) with absolute ethanol gave pale yellow oil after distillation under reduced pressure. The structures of these oily products were identified as 3-oxopropanoate **3(a, d, g** and **i)** (Table-3).

The suggested mechanism for the formation of compounds **1** involves the formation of 4-membered ring transition state (product A, **Scheme-2**) by analogy to the previously suggested transition state for the formation of dihydroxy pyridine[5], pyrimidone[6] and N-(6-chloro-4-hydroxy-2-oxo-2H-pyran-3-carbonyl)chloroformimid acid[7,8]. Therefore, the double bond configuration of B should be Z and not E, as it resulted from *syn* addition reaction.

Furthermore, the Z form of product B (**Scheme-2**) reacted with alcohol through an *anti* addition and *trans* elimination mechanism to yield compounds **3** in the E form (*ca.* 70 %) and Z form (*ca.* 30%). This is a result of the free rotation after the addition of the alcohol molecule (**Scheme-2**). The 70 : 30 ratio of E to Z is determined from the ^1H and shown in the ^{13}C NMR spectra of the product. The reaction of methylmalonyl chloride (1 mol) with aryl cyanate (2 mol) in dry CCl_4 at 50–60°C for 30–60 min gave solid products which recrystallized from dry CCl_4; they were identified as hydrazines **5(a–d)**. The proposed mechanism for the formation of product **5** is a *syn* addition of the cyanide group on the product B (**Scheme-2**).

TABLE-3
^{13}C NMR CHEMICAL SHIFTS (ppm RELATIVE TO INTERNAL TMS) OF ETHYL 3-{[(1E)-ETHOXY (ARYLOXY) METHYLENE] AMINO}-2-SUBSTITUTED-3-OXOPROPANOATE **3(a, d, g and i)**

Compd.	**3a**	**3d**	**3g**	**3i**
C-1	170.9[a]	170.6[a]	168.6	167.9
C-2	46.6	46.6	53.8	57.9
C-3	172.8[a]	172.8[a]	168.6	167.9
C-4	156.6	157.8	156.2	156.2
C-5	151.9	151.9	150.0	150.0
C-6	115.5	101.7	119.0	121.0
C-7	129.5	161.0	129.7	129.0
C-8	126.2	105.8	126.0	125.9
C-9	129.5	130.0	129.7	129.0
C-10	115.5	108.1	119.0	121.0
C-11	—	55.1	—	—
C-12	61.7	62.6	61.3	61.7
C-13	14.0	14.1	13.9	13.9
C-14	61.5	61.6	61.3	61.7
C-15	14.7	14.1	13.9	13.9
C-16	13.6	13.5	37.7	132.5
C-17	—	—	137.5	128.3
C-18	—	—	128.2	129.1
C-19	—	—	128.5	127.9
C-20	—	—	126.4	—

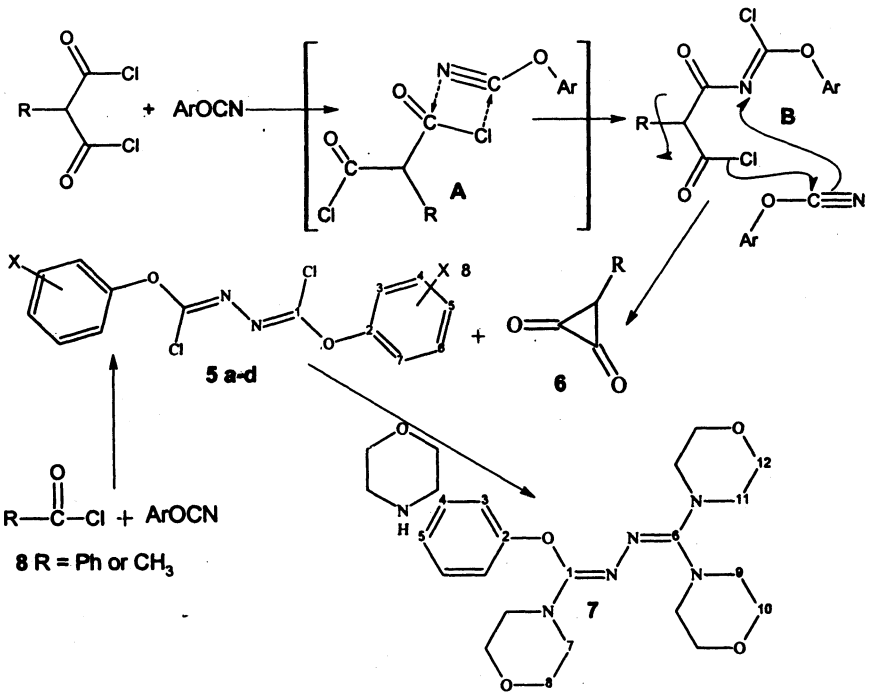
[a]Assignment could be exchanged.

When the mother liquors, from the above reactions were boiled with an excess of water (4 mol) for 30 min, solid products were obtained which recrystallized from benzene and identified as 2-substituted-3-oxo-3-[(phenoxycarbonyl) amino]propanoic acid , **1a**, 18%; **1b**, 20%; **1c**, 11% and **1d**, 26% respectively.

The formation of products **5(a–d)** from the reaction of aryl cyanate (2 mol) with acid chloride (the malonyl chloride role is the source of 2-chlorine) is a general reaction. So **5(a–d)** can be synthesized (in a similar yield) from the reaction of 2 mol of aryl cyanate with 1 mol of malonyl chloride, substituted malonyl chloride (ethyl, benzyl and phenyl) or 2 mol of acetyl or benzoyl chloride (**8a** or **8b**, **Scheme 2**) respectively.

The mechanism for the formation of **5a–d** involved the formation of a 4-membered ring transition state A (**Scheme-2**) which then gave product B. Compound B then reacted with another mole of aryl cyanate to yield products **5a–d** (**Scheme-2**).

Compound **5a** was allowed to react with 4 mol of morpholine in toluene at 110°C for 20 h and gave phenyl N-[bis-(morpholino)methylene] morpholine-4-carbohydrazonoate, **7**.



Scheme 2

Note: Structure numbering is for spectroscopic identification and not according to IUPAC nomenclature.

The ^{13}C chemical shift analysis of compounds: The reported ^{13}C chemical shifts[9] for methylmalonic acid were used to assign the chemical shift C-1, C-2 and C-16 in compounds **1a**, **1b**, **1c** and **1d**, while the reported carbon chemical shifts[9] for phenylmalonic acid were used to confirm the assignments of C-1, C-2, C-3, C-16, C-17, C-18 and C-19 in compounds **1i** and **1j**. Similarly, the reported carbon chemical shifts[9] for benzylmalonic acid were used to confirm the assignments of C-1, C-2, C-3, C-16, C-17, C-18, C-19 and C-20 in compounds **1g** and **1h**. The carbon chemical shifts C-4, C-5, C-6, C-7, C-8, C-9, C-10 and C-11 in compounds **1(a–j)** were confirmed using the previously reported[10] values for the aryl carbamate analogues **5(a–j)**. The same approach was used to confirm the analysis of the ^{13}C chemical shifts for compounds **2(a–j)** (Table-2) and **3a, d, g, i** (Table-3).

EXPERIMENTAL

IR (Nujol) spectra were measured with a Pye Unicam SP 2000 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker WH 90 DS, FT spectrometer. Microanalyses were done using an elemental analyzer MOD 1106 supplied by Carlo-Erba Strumentazion. All the starting materials, substituted

malonyl chlorides[11], aryl cyanates[12] and aryl carbamates[13] have been prepared by reported methods

Synthesis of substituted malonamic acids 1(a–j): Under anhydrous conditions with stirring, aryl cyanate (16.8 mmol) was added using a syringe through a serum cap to the substituted malonyl chloride (16.8 mmol) in dry CCl_4 (30 mL) at 0°C. Stirring was continued for 10 min and then the mixture was heated at 80°C for 30 min. Ice (2 g) was added and the mixture was heated again at 80°C for 30 min (15 min in case of benzyl and phenyl malonyl chloride). The mixture was allowed to cool to room temperature and stirred until a solid product was obtained, which was filtered and recrystallized from benzene (charcoal).

(a) Using the above general procedure, the reaction of phenyl cyanate (2.0 g, 16.8 mmol) with methyl malonyl chloride (2.6 g, 16.8 mmol) gave fine white crystals of 2-methyl-3-oxo-3-[(phenoxycarbonyl)amino]propanoic acid (**1a**), (1.5 g, 38%, m.p. 120-122°C); [found: C, 55.53; H, 4.43; N, 5.77; $C_{11}H_{11}NO_5$ required: C, 55.69; H, 4.64; N, 5.91]; IR (λ_{max}, cm^{-1}) (Nujol) 1800s ν(4-C=O), 1700s ν(1-C=O), 1710m ν(3-C=O); δ ^1H (acetone-d_6) 1.4 (3H, d, J 7.4 Hz, CH_3), 4.15 (1H, q, J 7.4 Hz, CH), 6.1 (1H, b, NH), 7.0–7.6 (5H, m, Ph) and 10.1 (1H, b, OH).

(b) The reaction of methyl malonyl chloride (2.6 g, 16.8 mmol) with *p*-methyl phenyl cyanate (1.97 g, 16.8 mmol) gave fine white crystals of 2-methyl-3-oxo-3-[(*p*-methylphenoxycarbonyl)amino]propanoic acid (**1b**), (1.4 g, 31%, m.p. 134-136°C); [found: C, 57.17; H, 4.98; N, 5.52; $C_{12}H_{13}NO_5$ required: C, 57.37; H, 5.18; N, 5.58]; IR (λ_{max}, cm^{-1}) (Nujol) 1760s ν(4-C=O), 1730s ν(1-C=O), 1700sh ν(3-C=O); δ ^1H (acetone-d_6) 1.32 (3H, d, J 7.0 Hz, CH_3), 2.28 (3H, s, *p*-CH_3), 4.1 (1H, q, J 7.0 Hz, CH), 6.46 (1H, b, NH), 6.9 and 7.1 (total 4H, AB q, J 9.6 Hz, C_6H_4) and 9.8 (1H, b, OH) ppm.

(c) The reaction of methyl malonyl chloride (2.6 g, 16.8 mmol) with *p*-methoxy phenyl cyanate (2.23 g, 16.8 mmol) gave fine white crystals of 2-methyl-3-oxo-3-[(*p*-methoxy phenoxycarbonyl)amino]propanoic acid (**1c**), (yield 1.46g, 31%, m.p. 121–123°C); [found: C, 60.42; H, 4.78; N, 4.99; $C_{12}H_{13}NO_6$ required: C, 60.76; H, 4.87; N, 5.24]; IR (λ_{max}, cm^{-1}) (Nujol) 1780s ν(4-C=O), 1710sb ν(1- and 3-C=O); δ ^1H (acetone-d) 1.4 (3H, d, J 7.4 Hz, CH_3), 3.8 (3H, s, *p*-CH_3O), 4.1 (1H, q, J 7.4 Hz, CH), 6.4 (1H, b, NH), 6.92 and 7.08 (total 4H, AB q, J 10 Hz, C_6H_4) and 10.0 (1H, b, OH) ppm.

(d) Using the above general procedure, the reaction of methyl malonyl chloride (2.6 g, 16.8 mmol) with *m*-methoxy phenyl cyanate (2.23 g, 16.8 mmol) gave fine white crystals of 2-methyl-3-oxo-3-[(*m*-methoxy phenoxycarbonyl)-amino]propanoic acid (**1d**), (yield 2.4 g, 54%, m.p. 100–102°C); [found: C, 60.58; H, 4.77; N, 5.02; $C_{12}H_{13}NO_6$ required: C, 60.76; H, 4.87; N, 5.24]; IR (λ_{max}, cm^{-1}) (Nujol) 1780s ν(4-C=O), 1740s ν(1-C=O), 1710s ν(3-C=O); δ ^1H (acetone-d_6) 1.4 (3H, d, J 7.0 Hz, CH_3), 3.8 (3H, s, *m*-CH_3O), 4.2 (1H, q, J 7.0 Hz, CH), 6.2 (1H, b, NH), 6.5–6.8 and 7.0–7.34 total, 4H, m, C_6H_4) and 9.8 (1H, b, OH) ppm.

(e) The reaction of ethyl malonyl chloride (2.84 g, 16.8 mmol) with phenyl cyanate (2.0 g, 16.8 mmol) gave fine white crystals of 2-ethyl-3-oxo-3-[(phenoxycarbonyl)amino]propanoic acid (**1e**); (1.2 g, 29%, m.p. 118–120°C);

[found: C, 57.13; H, 4.99; N, 5.45; $C_{12}H_{13}NO_5$ required: C, 57.37; H, 5.18; N, 5.58]; IR (λ_{max}, cm^{-1}) (Nujol) 1780m ν(4-C=O), 1735m ν(1-C=O), 1710sh ν(3-C=O); δ ^1H (acetone-d_6), 1.0 (3H, t, J 7.0 Hz, CH_3), 2.0 (2H, m, CH_2), 3.96 (1H, t. J 7.0 Hz, CH), 5.9 (1H, b, NH), 6.8–7.3 (5H, m, Ph) and 9.9 (1H, b, OH) ppm.

(f) The reaction of ethyl malonyl chloride (2.84 g, 16.8 mmol) with *p*-methoxyphenyl cyanate (2.23 g, 16.8 mmol) gave fine white crystals of 2-ethyl-3-oxo-3-[(*p*-methoxy phenoxycarbonyl)amino]propanoic acid (**1f**); (1.0 g, 22%, m.p. 117–119°C); [found: C, 55.33; H, 5.23; N, 5.00; $C_{13}H_{15}NO_6$ required: C, 55.52; H, 5.34; N, 4.98]; IR (λ_{max}, cm^{-1}) (Nujol) 1770s ν(4-C=O), 1760m ν(1-C=O), 1720m ν(3-C=O); δ ^1H (Acetone-d_6), 1.0 (3H, t, J 7.2 Hz, CH_3), 2.0 (2H, m, CH_2), 3.8 (3H, s, *p*-CH_3O), 3.9 (1H, t, J 7.2 Hz, CH), 5.8 (1H, b, NH), 6.91 and 7.09 (total 4H, AB q, J 10 Hz, C_6H_4) and 10.1 (1H, b, OH) ppm.

(g) The reaction of benzyl malonyl chloride (3.88 g, 16.8 mmol) with phenyl cyanate (2.0 g, 16.8 mmol) gave fine white crystals of 2-benzyl-3-oxo-3-[(phenoxycarbonyl)amino]propanoic acid (**1g**), (1.5 g, 29%, m.p. 104–107°C); [found: C, 6493; H, 4.67; N, 4.28; $C_{17}H_{15}NO_5$ required: C, 65.17; H, 4.79; N. 4.47]; IR (λ_{max}, cm^{-1}) (Nujol) 1795s ν(4-C=O), 1710w ν(1- and 3-C=O); δ ^1H (acetone-d_6), 2.9 (2H, d, J 7.0 Hz, CH_2), 3.7 (1H, J 7.0 Hz, CH), 6.5 (1H, b, NH), 7.0–7.40 (10H; m, 2 Ph) and 9.6 (1H, b, OH) ppm.

(h) The reaction of benzyl malonyl chloride (3.88 g, 16.8 mmol) with *p*-methoxyphenyl cyanate (2.23 g, 16.8 mmol) gave fine white crystals of 2-benzyl-3-oxo-3-[(*p*-methoxy phenoxycarbonyl)amino]propanoic acid (**1h**), (2.0 g, 35%, m.p. 122–124°C); [found: C, 62.53; H, 4.88; N, 4.01, $C_{18}H_{17}NO_6$ required: C, 62.97; H, 4.95; N, 4.08]; IR (λ_{max}, cm^{-1}) (Nujol) 1780s ν(4-C=O), 1760m ν(1-C=O), 1740sh ν(3C==O); δ ^1H (acetone-d_6), 3.1 (2H, d, J 7.0 Hz, CH_2), 3.7 (3H, s, *p*-CH_3O), 4.3 (1H, t, J 7.0 Hz, CH), 6.4 (1H, b, NH), 6.78 and 6.94 (total 4H, AB q, J 10.8 Hz, C_6H_4), 7.0–7.2 (5H, m, Ph) and 9.8 (1H, b, OH) ppm.

(i) The reaction of phenyl malonyl chloride (3.65 g, 16.8 mmol) with phenyl cyanate (2.0 g, 16.8 mmol) gave fine white crystals of 2-phenyl-3-oxo-3-[(phenoxycarbonyl)amino]propanoic acid (**1i**) (2.4 g, 48%, m.p. 137–140°C); [found: C, 64.20; H; 4.16; N, 4.53; $C_{16}H_{13}NO_5$ required: C, 64.21; H, 4.35; N, 4.68]; IR (λ_{max}, cm^{-1}) (Nujol) 1775s ν(4-C=O), 1700s ν(1- and 3-C=O); δ (acetone-d_6) 4.7 (1H, s, CH), 6.2 (1H, b, NH), 6.8–7.4 (10H, m, 2Ph) and 9.7 (1H, b, CH) ppm.

(j) The reaction of phenyl malonyl chloride (3.65 g, 16.8 mmol) with *p*-methoxyphenyl cyanate (2.49 g, 16.8 mmol) gave fine white crystals of 2-phenyl-3-oxo-3-[(*p*-methoxy phenoxycarbonyl)amino]propanoic acid (**1j**), (1.66 g, 30%, m.p. 102–104°C); [found: C, 62.20; H, 4.46; N, 4.33; $C_{17}H_{15}NO_6$ required: 62.01; H, 4.56; N, 4.26]; IR (λ_{max}, cm^{-1}) (Nujol) 1760m ν(4-C=O), 1700s ν(1- and 3-C=O); δ ^1H (acetone-d_6) 3.7 (3H, s, *p*-CH_3), 5.3 (1H, s, CH), 6.2 (1H, b, NH), 6.81 and 7.03 (total 4H, AB q, J 12.0 Hz, C_6H_4), 7.1–7.4 (5H, m, Ph) and 10.1 (1H, b, OH) ppm.

Synthesis of Aryl 3-chloro-2-substituted-3-oxopropanoylcarbamate 2(a–j): A mixture of aryl carbamate (8.4 mmol) and substituted malonyl chloride (8.4 mmol) in dry *n*-hexane (30 mL) was heated with stirring at 70°C for 2.3 h. After cooling, decantation of the solvent and trituration of the product with dry *n*-hexane (30 mL) gave a white powder, recrystallized from dry chloroform or dry ether-petroleum ether (40–60°C).

(a) Using the above general procedure, the reaction of phenyl carbamate (1.15 g, 8.4 mmol) and methyl malonyl chloride (1.37 g, 8.4 mmol) gave a white powder of phenyl 3-chloro-2-methyl-3-oxopropanoylcarbamate (**2a**), (1.4 g, 65%, m.p. 120–123°C; [found: C, 51.66; H, 3.87; N, 5.31; $C_{11}H_{10}ClNO_4$ required: C, 51.66; H, 3.91; N, 5.48], IR (λ_{max}, cm^{-1}) (Nujol) 1800s ν(1-C=O), 1775s ν(4-C=O), 1710m ν(3-C=O); δ ^1H ($CDCl_3$), 1.6 (3H, d, J 7.3 Hz, CH_3), 4.8 (1H, q, J 7.3 Hz, CH), 7.0–7.6 (5H, m, Ph) and 8.3 (1H, b, NH) ppm.

(b) The reaction of methyl malonyl chloride (1.33 g, 8.4 mmol) and *p*-methyl phenyl carbamate (1.27 g, 8.4 mmol) gave white powder of *p*-methyl phenyl 3-chloro-2-methyl-3-oxopropanoylcarbamate (**2b**), (2.0 g, 88%, m.p. 119–122°C); [found: C, 53.11; H, 4.26; N, 5.09; $C_{12}H_{12}ClNO_4$ required: C, 53.43; H, 4.45; N, 5.19]; IR (λ_{max}, cm^{-1}) (Nujol) 1800s ν(1-C=O), 1770s ν(4-C=O), 1710w ν(3-C=O); δ ^1H ($CDCl_3$): 1.6 (3H, d, J 7.0 Hz, CH_3), 2.36 (3H, s, *p*-CH_3), 4.7 (1H; q, J 7.0 Hz, CH), 6.78 and 6.98 (total 4H, AB q, J 9.6 Hz, C_6H_4) and 8.2 (1H, b, NH) ppm.

(c) The reaction of methyl malonyl chloride (1.33 g, 8.4 mmol) with *p*-methoxyphenyl carbamate (8.4 mmol) gave white powder of *p*-methoxyphenyl 3-chloro-2-methyl-3-oxopropanoylcarbamate (**2c**), (2.0 g, 84%; m.p. 112–114°C); [found: C, 50.12; H, 4.12; N, 4.81; $Cl_2H_{12}ClNO_5$ required: C, 50.44; H, 4.20; N, 4.90]; IR (λ_{max}, cm^{-1}) (Nujol) 1810s ν(1-C=O), 1780m ν(4-C=O), 1710m ν(3-C=O); δ ^1H ($CDCl_3$) 1.6 (3H, d, J 7.0 Hz, CH_3), 3.8 (3H, s, *p*-CH_3O), 4.7 (1H, q, J 7.0 Hz, CH), 6.73 and 6.85 (total 4H, AB q, J 10.2 Hz, C_6H_4) and 8.6 (1H, b, NH) ppm.

(d) The reaction of methyl malonyl chloride (1.33 g, 8.4 mmol) with *m*-methoxyphenyl carbamate (1.44 g, 8.4 mmol) gave white powder of *m*-methoxyphenyl 3-chloro-2-methyl-3-oxopropanoylcarbamate (**2d**), (1.51 g, 63%, m.p. 91–94°C); [found; C, 50.22; H, 4.30; N, 4.79; $C_{12}H_{12}ClNO_5$ required: C, 50.44; H, 4.20; N, 4.90]; IR (λ_{max}, cm^{-1}) (Nujol) 1805m ν(1-C=O), 1775m ν(4-C=O), 1710w ν(3-C=O); δ ^1H ($CDCl_3$), 1.6 (3H, d, J 7.0 Hz, CH_3), 3.8 (3H, s, *m*-CH_3O), 4.8 (1H, q, J 7.0 Hz, CH), 6.6–7.0 and 7.1–7.5 (total 4H, m, C_6H_4) and 8.4 (1H, b, NH) ppm.

(e) The reaction of ethyl malonyl chloride (1.45 g, 8.4 mmol) with phenyl carbamate (8.4 mmol) gave white powder of phenyl 3-chloro-2-ethyl-3-oxopropanoylcarbamate (**2e**), (1.25 g, 54%, m.p. 87–90°C); [found: C, 53.33; H, 4.15; N, 5.22; $C_{12}H_{12}ClNO_5$ required: C, 53.43; H, 4.05; N, 5.19]; IR (λ_{max}, cm^{-1}) (Nujol) 1800sh ν(1-C=O), 1775s ν(4-C=O), 1710w ν(3-C=O); δ ^1H ($CDCl_3$), 1.0 (3H, t, J 7.0 Hz, CH_3), 2.1 (2H, m, CH_2), 4.8 (1H, t, J 7.0 Hz, CH), 7.0–7.7 (5H, m, Ph) and 8.6 (1H, b, NH) ppm.

(f) The reaction of ethy' malonyl chloride (1.45 g, 8.4 mmol) with *p*-methoxyphenyl carbamate (1.44 g, 8.4 mmol gave white powder of *p*-

methoxyphenyl 3-chloro-2-ethyl-3-oxopropanoylcarbamate (**2f**), (1.30 g, 50%, m.p. 102–105°C); [found: C, 51.33; H, 5.25; N, 4.52; $C_{13}H_{16}ClNO_5$ required: C, 51.74; H, 5.31; N, 4.64]; IR (λ_{max}, cm^{-1}) (Nujol) 1810sh ν(1-C=O), 1775s ν(4-C=O), 1715w ν(3-C=O); δ ^1H ($CDCl_3$) 1.1 (3H, t, J 7.2 Hz, CH_3), 2.1 (2H, m, CH_2), 3.8 (3H, s, *p*-CH_3O), 4.8 (1H, t, J 7.2 Hz, CH), 6.9 and 7.07 (total 4H, AB q, J 10.0 Hz, C_6H_4) and 8.6 (1H, b, NH) ppm.

(g) The reaction of benzyl malonyl chloride (1.99 g, 8.4 mmol) with phenyl carbamate (1.15 g, 8.4 mmol) gave white powder of phenyl 3-chloro-2-benzyl-3-oxopropanoylcarbamate (**2g**) (1.28 g, 45%, m.p. 100–103°C); [found: C, 61.31; H, 4.12; N, 4.13; $C_{17}H_{14}ClNO_4$ required: C, 61.53; H, 4.22; N, 4.22]; IR (λ_{max}, cm^{-1}) (Nujol) 1800s ν(1-C=O); 1760m ν(4-C=O), 1715sh ν(3-C=O); δ ^1H ($CDCl_3$) 3.3 (2H, d, J 7.0 Hz, CH_2), 4,6 (1H, t, J 7.0 Hz, CH), 6.8–7.4 (10H, m, 2 Ph) and 8.4 (1H, b, NH) ppm.

(h) The reaction of benzyl malonyl chloride (1.99 g, 8.4 mmol) with *p*-methoxyphenyl carbamate (1.30 g, 8.4 mmol) gave white powder of *p*-methoxyphenyl 3-chloro-2-benzyl-3-oxopropanoylcarbamate (**2h**), (1.59 g, 51% m.p. 50–53°C); [found: C, 59.86; H, 4.32; N, 3.90; $C_{18}H_{16}ClNO_5$ required: C, 59.75; H, 4.43; N, 3.87]; IR (λ_{max}, cm^{-1}) (Nujol) 1800m ν(1-C=O), 1780m ν(4-C=O), 1720m ν(3-C=O); δ ^1H (Acetone-d_6) 3.3 (2H, d, J 7.2 Hz, CH_2), 3.8 (3H, s, *p*-CH_3O), 4.5 (1H, t, J 7.2 Hz, CH), 5.2 (1H, b, NH), 6.9 and 7.1 (total 4H, AB q, J 10.5 Hz, C_6H_4) and 7.2–7.5 (5H, m, Ph) ppm.

(i) The reaction of phenyl malonyl chloride (1.87 g, 8.4 mmol) with phenyl carbamate (1.15 g, 8.4 mmol) gave yellow-orange powder of phenyl 3-chloro-2-phenyl-3-oxopropanoylcarbamate (**2i**), (2.43 g, 89%, m.p. 72–75°C); [found: C, 60.18; H, 3.67; N, 4.28; $C_{16}H_{12}ClNO_4$ required: C, 60.47; H, 3.78; N, 4.41]; IR (λ_{max}, cm^{-1}) (Nujol) 1805m ν(1-C=O), 1785mν (4-C=O), 1710m ν(3-C=O); δ ^1H ($CDCl_3$) 6.0 (1H, s, CH), 6.8–7.5 (10H, m, 2Ph) and 8.0 (1H, b, NH) ppm.

(j) The reaction of phenyl malonyl chloride (1.87 g, 8.4 mmol) with *p*-methoxyphenyl carbamate (1.15 g, 8.4 mmol) gave yellow-orange powder of *p*-methoxyphenyl 3-chloro-2-phenyl-3-oxopropanoylcarbamate chloride (**2j**), (2.40 g, 80%, m.p. 98–100°C); [found: C, 58.35; H, 4.25; N, 4.13; $C_{17}H_{15}ClNO_5$ required: C, 58.54; H, 4.30; N, 4.02]; IR (λ_{max}, cm^{-1}) (Nujol) 1800s ν(4- and 1-C=O), 1715m ν(3-C=O) cm^{-1}; δ ^1H ($CDCl_3$) 3.8 (3H, s, *p*-CH_3O—), 6.1 (1H, s, CH), 6.99 and 7.07 (total 4H, AB q, J 11.0 Hz, C_6H_4), 7.2–7.6 (5H, m, Ph) and 8.4 (1H, b, NH) ppm.

Synthesis of N- (2-metyl-3-morpholin-4-yl-3-oxopropanoyl) morpholine-4-carboxamide (**4**): Dry morpholine (1.04 g, 12.0 mmol) was added to a suspension of compound **2a** (1.02 g, 4.0 mmol) in dry n-hexane (30 mL) with cooling and stirring. The mixture was heated at 70–75°C for 30 min. After cooling and decantation of the solvent, the product was recrystallized from dry acetone-petroleum ether (60–80°C) (charcoal) and gave a pale yellow powder of compound 4, (1.88 g, 52%, m.p. 140–142°C); [found: C, 59.45; H, 6.00; N, 8.00; $C_{15}H_{18}N_2O_5$ required: C, 59.60; H, 5.96; N, 7.95]; IR (λ_{max}, cm^{-1}) (Nujol) 1730m ν(1-C=O), 1690m ν(4-C=O), 1630m ν(3-C=O); δ ^1H (Acetone-d_6) 1.3 (3H, d, J 7.2 Hz, CH_3), 3.2 (1H, b, NH), 3.4–3.8 (16H, m, 2 morpholino groups) and 4.4 (1H, q, J 7.2 Hz, CH) ppm; δ ^{13}C ($CDCl_3$) 171.57, 170.2 (C-1 and 3), 46.5

(C-2), 46.4, 44.8, 43.9, 42.3 (C-5, 8, 9 and 12), 66.3 (C-6, 7, 10 and 11) and 15.1 (CH_3) ppm.

Synthesis of ethyl 3-{[(1E)-ethoxy(aryloxy)methylene]amino}-2-substituted-3-oxopropanoate [3(a, d, g and i)]: Aryl cyanate (16.8 mmol) was added using a syringe through a serum cap to substituted malonyl chloride (16.8 mmol) in dry CCl_4 (30 mL) at 0°C with stirring. The stirring was continued for 10 min and then the mixture was heated at 80°C for 30 min. Absolute ethanol (3.0 g) was added and the mixture was heated again at 80°C for 1 h. The product was isolated after the evaporation of the solvent and distillation under reduced pressure.

(a) Using the above general procedure, the reaction of phenyl cyanate (2.0 g, 16.8 mmol) with methyl malonyl chloride (2.60 g, 16.8 mmol) followed by addition of absolute ethanol (3.0 g) gave a pale yellow oil of ethyl 3-{[(1E)-ethoxy (phenoxy) methylene] amino}-2-methyl-3-oxopropanoate (**3a**), (1.23 g, 25%, b.p. 155°C/0.25 mmHg); [found: C, 61.06; H, 6.35; N, 4.65; $C_{15}H_{19}NO_5$ required: C, 61.14; H, 6.48; N, 4.78]; IR (λ_{max}, cm^{-1}) (Nujol) 1750s ν(1-C=O), 1730m ν(3-C=O), 1600m ν(C=N); δ ^1H ($CDCl_3$) 1.–1.7 (9H, m, $3CH_3$), 3.4 (1H, q, J 7.3 Hz, CH), 4.2 (4H, q, J 7.3 Hz, 2-CH_2) and 7.0-7.6 (5H, m, Ph) ppm.

(d) The reaction of *m*-methoxyphenyl cyanate (2.50 g, 16.8 mmol) with methyl malonyl chloride (2.6 g, 16.8 mmol) followed by addition of absolute ethanol (3.0 g) gave a pale yellow oil of ethyl 3-{[(1E)-ethoxy(*m*-methoxy phenoxy)methylene]amino-2-methyl-3-oxopropanoate (**3d**), (2.33g, 43%, b.p. 130°C/ 0.1 mm Hg); [found: C, 59.35; H, 6.35; N, 3.90; $C_{15}H_{19}NO_5$ required: C, 59.44; H, 6.50; N, 3.79]; IR (λ_{max}, cm^{-1}) (Nujol) 1750s ν(1-C=O), 1720sh ν(3-C=O), 1605s ν(C=N); δ ^1H ($CDCl_3$) 1.0–1.6 (9H, m, $3CH_3$), 3.4 (1H, q, J 7.5 Hz, CH), 3.8 (3H, s, m-CH_3O), 4.2 (4H, q, J 7.5 Hz, 2-CH_2), 6.4–6.6 and 7.0–7.3 (total 4H, m, C_6H_4) ppm.

(g) The reaction of phenyl cyanate (2.0 g, 16.8 mmol) with benzyl malonyl chloride (3.99 g, 16.8 mmol) followed by addition of absolute ethanol (3.0 g) gave a pale yellow oil of ethyl 3-{[(1E)-ethoxy(phenoxy) methylene]amino}-2-benxyl-3-oxopropanoate (**3g**), (2.23 g, 36%, b.p. 145°C/0.35 mm Hg); [found: C, 68.15; H, 6.27; N, 3.90; $C_{21}H_{23}NO_5$ required: C, 68.29; H, 6.23; N, 3.79];IR (λ_{max}, cm^{-1}) (Nujol) 1750s ν(1-C=O), 1720sh ν(3-C=O), 1600m ν(C=N), δ ^1H ($CDCl_3$) 1.2 (6H, t, J 7.0 Hz, $2CH_3$), 3.2 (2H, d, J 7.0 Hz, CH_2), 3.6 (1H, t, J 7.0 Hz, CH), 4.1 (4H, q, J 7.0 Hz, $2CH_2$) and 7.0–7.5 (10H, m, 2Ph) ppm.

(i) The reaction of phenyl cyanate (2.0 g, 16.8 mmol) with phenyl malonyl chloride (3.65 g, 16.8 mmol) followed by addition of absolute ethanol (3.0 g) gave a pale yellow oil of ethyl 3-{[(1E)-ethoxy(phenoxy)methylene] amino}-2-phenyl-3-oxopropanoate (**3i**), (1.91 g, 32%, b.p. 130°C/0.4 mm Hg); [found: C, 67.42; H, 5.83; N, 3.86; $C_{20}H_{21}NO_5$ required: C, 67.61; H, 5.92; N, 3.94]; IR (λ_{max}, cm^{-1}) (Nujol) 1750s ν(1-C=O), 1720sh ν(3-C=O), 1600m ν(C=N); δ ^1H ($CDCl_3$) 1.2 (6H, t, J 7.0 Hz, $2CH_3$), 4.2 (4H, q, J 7.0 Hz, $2CH_2$), 4.6 (1H, s, CH) and 7.0–7.7 (10H, m, 2 Ph) ppm.

Synthesis of (1Z, 2Z)*bis*[chloro(aryloxy)methylene]hydrazines 5(a-d): Phenyl cyanate (3.36 mmol) was added dropwise using a syringe through a serum

cap to methyl malonyl chloride (2.6 g, 1.68 mmol) in dry CCl_4 (30 mL) at 0°C with stirring. The mixture was stirred for 10min then heated at 60°C for 1 h under anhydrous conditions. The residue was filtered and washed with 20 mL of dry petroleum ether (40–60°C) and then recrystallized from dry CCl_4 (charcoal).

(a) Using the above general procedure, the reaction of phenyl cyanate (4.0 g, 3.36 mmol) with methyl malonyl chloride (2.6 g, 1.68 mmol) gave hair-like white crystals of (1Z, 2Z)*bis*[chloro(phenoxy)methylene]hydrazines (**5a**), (1.4 g, 27% m.p. 235°C); [found: C, 54.28; H, 3.14; N, 8.99; $C_{14}H_{10}Cl_2N_2O_2$ required: C, 54.36; H, 3.23; N, 9.06]; IR (λ_{max}, cm^{-1}) (Nujol) 1610m ν(C=N), 1580m and 1500sh ν(aromatic C=C); δ ^1H ($CDCl_3$) 6.9–7.5 (m, 10H, 2Ph) ppm: δ ^{13}C ($CDCl_3$) 173.8 (C-1), 151.8 (C-2), 129.5 (C-4), 126.0 (C-5), and 121.5 (C-3) ppm.

(b) The reaction of *p*-methyl phenyl cyanate (4.50 g, 3.36 mmol) with methyl malonyl chloride (2.60 g, 1.68 mmol) gave hair-like white crystals of (1Z, 2Z)*bis*[chloro(*p*-methylphenoxy)methylene]hydrazines (**5b**), (1.02 g, 18%, m.p. 215°C); [found: C, 49.76; H, 4.01; N, 8.11; $C_{16}H_{14}Cl_2N_2O_2$ required: C, 49.85; H, 4.15; N, 8.31%]; IR (λ_{max}, cm^{-1}) (Nujol) 1620m ν(C=N), 1600sh, 1585s and 1515m ν(aromatic C=C); δ ^1H ($CDCl_3$) 2.3 (s, $2CH_3$); 6.98 and 7.08 (AB q, J 9.6 Hz, 8H, $2C_6H_4$) ppm; δ ^{13}C ($CDCl_3$) 173.9 (C-1), 149.5 (C-2), 135.5 (C-5), 129.9 (C-4), 121.1 (C-3) and 20.8 (C-8) ppm.

(c) Using the above general procedure, the reaction of *p*-methoxy phenyl cyanate (5.00 g, 3.36 mmol) with methyl malonyl chloride (2.60 g, 1.68 mmol) gave hair-like white crystals of (1Z, 2Z)*bis*[chloro(*p*-methoxy phenoxy)methylene]hydrazines (**5c**), (1.43 g, 23%, m.p. 197°C); [found: C, 51.94; H, 3.69; N, 7.51; $C_{16}H_{14}N_2O_4Cl_2$ required: C, 52.03; H, 3.79; N, 7.59 %]; λ_{max} (cm^{-1}) (Nujol) 1620m (C=N), 1600sh, 1590s and 1515 (aromatic C=C); δ ^1H ($CDCl_3$) 13.8 (s, 2 CH_3O) 6.89 and 7.09 (AB q, J 10.2 Hz, 4H; δ ^{13}C ($CDCl_3$) 174.0 (C-1), 157.4 (C-5), 145.3 (C-2), 122.2 (C-3), 114.5 (C-4) and 55.6 (C-8) ppm.

(d) The reaction of *m*-methoxy phenyl (5.0 g, 3.36 mmol) with methyl malonyl chloride (2.60 g, 1.68 mmol) gave hair-like white crystals of (1Z, 2Z)*bis*[chloro(*m*-methoxy phenoxy)methylene]hydrazines (**5d**), (1.98 g, 32% m.p. 143°C); [found: C, 51.94; H, 3.69; N, 7.51; $C_{16}H_{14}Cl_2N_2O_4$ required: C, 52.03; H, 3.79; N, 7.59%]; IR (λ_{max}, Nujol) 1620m ν(C=N), 1600sh, 1580s and 1490 ν(aromatic C=C); δ ^1H ($CDCl_3$) 3.8 s, 6H, $2CH_3O$) and 6.5–7.0 and 7.1–7.5 (m, 2 Ph) ppm; δ ^{13}C ($CDCl_3$) 173.7 (C-1), 160.5 (C-4), 152.5 (C-2), 129.9 (C-6), 113.6 (C-7), 112.0 (C-5), 107.6 (C-3) and 55.5 (C-8) ppm.

The filtrates from reactions **5a**, **5b**, **5c** and **5d** were treated with ice (2.0 g) and the mixture was heated at 80°C for 30 min. In each case the mixture was allowed to cool to room temperature and stirred until a solid product was obtained. The solid was filtered and recrystallised from benzene (charcoal) giving compounds **1a** (0.76 g, 18%), **1b** (0.84 g, 20%), **1c** (0.49 g, 11%) and **1d** (1.17 g, 26%) respectively.

Synthesis of (1Z, 2Z)*bis*[chloro(aryloxy)methylene]hydrazines 5(a and c) using acetyl or benzoyl chloride: An equimolar mixture of acetyl chloride (1.32 g, 16.8 mmol) and phenyl cyanate (2.0 g, 16.8 mmol) or *p*-methoxyphenyl cyanate (2.50 g, 16.8 mmol) in dry CCl_4 (30 mL) was stirred at room temperature for 2 days and gave **5a** (0.52 g, 20%) and **5c** (0.77 g, 25%). Similarly, an

equimolar mixture of benzoyl chloride (2.28 g, 16.8 mmol) with phenyl cyanate (2.00g, 16.8mmol) or *p*-methoxyphenyl cyanate (2.50 g, 16.8 mmol) in dry CCl_4 (30 mL) was heated at 75–80°C for 2 d giving compounds **5a** (0.60 g, 23%) and **5c** (0.65 g, 21%).

Reaction of (1Z, 2Z)*bis*[chloro(phenoxy methylene]hydrazines 5a with 4 mol of morpholine: To a suspension of **5a** (0.5 g 1.6 mmol), in dry toluene (20 mL), morpholine (0.55 g, 6.4 mmol) was added and heated at 110°C for 20 h. The mixture was filtered, washed with water, and dried with anhydrous calcium chloride. After evaporation of the solvent the product was recrystallized from ethanol and gave pale yellow crystals of phenyl N-[*bis*(morpholino)methylene]morpholine-4-carbohydrazonoate (**7**), (0.2 g, 31%, m.p. 179°C); [found: C, 59.74; H, 7.12; N, 17.50; $C_{20}H_{29}N_5O_4$ required: C, 59.55; H, 7.20; N, 17.37%]; *IR* (λ_{max} (cm^{-1}) (Nujol) 1590s ν(C=N), 1580sh, and 1500sh ν(aromatic C=C); δ ^1H ($CDCl_3$) 3.6–3.9 (m, 24H of morpholine) and 7.1–7.5 (m, 5H, C_6H_5) ppm;δä ^{13}C ($CDCl_3$) 165.7 (C-1), 164.5 (C-6), 152.1 (C-2), 128.5 (C-4), 124.5 (C-5), 121.6 (C-3), 66.5 (C-9, 10, 11, and 12), and 43.7 (C-7 and C-8) ppm.

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