Applications of Stevens [1,2]-Shifts of Cyclic Ammonium Ylides. A Route to Morpholin-2-ones[1]

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Received June 1, 1994[⊗]

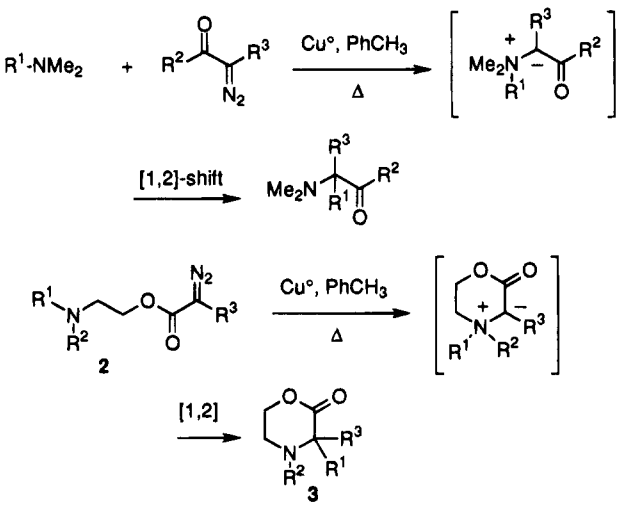
2-(*N,N*-Dialkylamino)ethyl diazoacetoacetates **2** were prepared in two steps from readily available ethanolamines **1**. When heated in the presence of catalytic Cu, the substrates cleanly formed morpholinones **3**, presumably via the intermediacy of copper carbenoids and cyclic ammonium ylides. In most cases involving benzylic or allylic migrating groups, ylide [1,2]-shift occurred in good yield (55–80%). In the case of benzhydryl containing substrate **2g**, only dimer **4** was isolated. Simple alkyl groups failed to undergo the rearrangement, with the exception of *tert*-butyl case **2i**, which furnished morpholinone **3i** in low yield. Substituted allylic case **2l** gave only [1,2]-shift product **3l**, with no evidence for competing [2,3]-shift to give **3l′**. Diazoacetates **2n–p** also underwent conversion to morpholinones **3n–p** in 19–64% yield with $Cu(acac)_2$ catalysis.

Introduction

The development of preparative routes to rare or unnatural α-amino acids and their derivatives is an important objective in synthesis, given the significance of these compounds in a variety of fields.[2] Several effective approaches to amino acid synthesis involving C–C bond formation to a glycine synthon in the key step have been reported.[3–6] While developing new synthetic methodology utilizing the Stevens [1,2]-shift of ammonium ylides, we have investigated its application to the synthesis of α-amino acid derivatives, since the products of rearrangement are typically α-substituted-α-aminocarbonyl compounds. Moreover, direct ylide formation from carbenoid precursors involves simple, readily available reactants and mild conditions.

Recently we reported a one-step synthesis of α-(*N,N*-dialkylamino) esters and ketones using simple tertiary amines and α-diazocarbonyl compounds.[7] The reaction proceeds via intermolecular carbenoid addition to amine

Scheme 1



and subsequent [1,2]-shift of one of the nitrogen substituents (Scheme 1). Potential drawbacks of this protocol include the requirement for more than 1 equiv of amine and the unsuitability of the resulting tertiary amines for subsequent transformations. These limitations, coupled with the high efficiency of [1,2]-shifts of cyclic ammonium ylides derived from *intramolecular* carbenoid–amine additions,[8] led us to investigate an alternative route to α-amino acid derivatives. Linkage of the carbenoid precursor and the nucleophilic amine via an ester would permit the intervention of cyclic ylides and obviate the need for excess amine. Furthermore, subsequent oxidative cleavage of the enthanolamine linker would lead to more synthetically versatile secondary amines. We report here the synthesis of cyclic α-amino acid derivatives, morphilin-2-ones **3**, via sequential carbenoid generation/ylide formation and Stevens [1,2]-shift of readily available diazo esters **2**.

Results and Discussion

Substrate Preparation. We envisioned the acyclic substrates as coming from diazo transfer to the corresponding acetoacetates, which should be accessible via

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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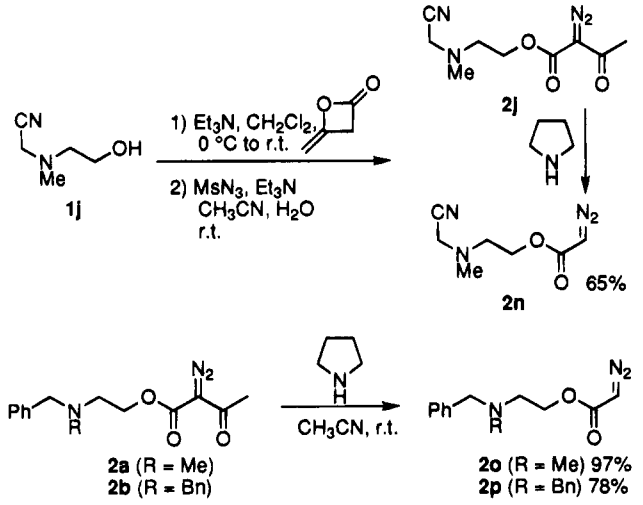
Table 1. Preparation of Diazo Esters 2[a]

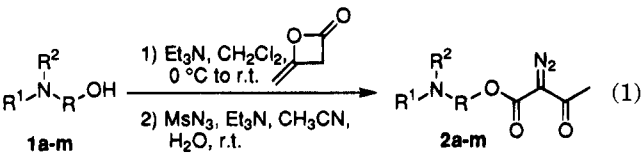
reactant	R	R^1	R^2	yield of **2** (%)[b]
1a	$(CH_2)_2$	$PhCH_2$	Me	80
1b	$(CH_2)_2$	$PhCH_2$	$PhCH_2$	78
1c	$(CH_2)_2$	$4\text{-}NO_2C_6H_4CH_2$	Me	73
1d	$(CH_2)_2$	$4\text{-}AcC_6H_4CH_2$	Me	51
1e	$(CH_2)_2$	$4\text{-}MeOC_6H_4CH_2$	Me	75
1f	$(CH_2)_2$	$4\text{-}Me_2NC_6H_4CH_2$	Me	73
1g	$(CH_2)_2$	Ph_2CH	Me	71
1h	$(CH_2)_2$	Me_2CH	Me	69
1i	$(CH_2)_2$	Me_3C	Me	74
1j	$(CH_2)_2$	$NCCH_2$	Me	*c*
1k	$(CH_2)_2$	$(CH_2{=}CHCH_2)_2$		54
1l	$(CH_2)_2$	$(CMe_2{=}CHCH_2)_2$		65
1m	*o*-C_6H_4	$PhCH_2$	Me	31

[a] See eq 1. [b] Isolated yields after chromatography. [c] An inseparable 1:1 mixture of **2j** and **2n** was obtained (see Scheme 2).

Scheme 2



acylation of a variety of 2-(*N*,*N*-dialkylamino)ethanols **1** (eq 1). The requisite starting materials were prepared



from either ethanolamine or commercially available 2-(*N*-alkylamino)ethanols by direct alkylation with the corresponding halides or by reductive amination of aldehydes or ketones.[9] Aromatic substrate **1m** was prepared analogously from 2-aminophenol.

Acetoacetylation of alcohols **1a**–**m** could be easily effected by treatment with diketene and Et_3N (Table 1). Diazo transfer[10] ($MsN_3/Et_3N/H_2O/CH_3CN$) then furnished diazoacetoacetates **2a**–**l** in yields of 51–80% and the somewhat more labile **2m** in 31% yield. Nitrile-substituted substrate **2j** was formed as an inseparable 1:1 mixture with deacylated diazoacetate **2n**. This mixture was treated with pyrrolidine to afford pure **2n** in 65% yield (Scheme 2). Likewise, substrates **2a** and **2b** could be cleanly deacylated to furnish diazoacetates **2o**–**p** in 78–97% yield.

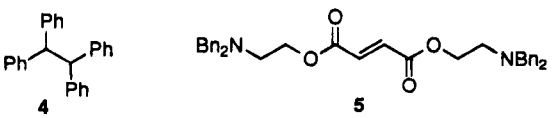
Ylide Generation and [1,2]-Shift. In order to establish the optimum procedure for effecting the [1,2]-shift, we examined various conditions using substrate **2a** (Table 2). In contrast to our previous work,[8] exposure of **2a** to catalytic $Rh_2(OAc)_4$ in CH_2Cl_2 at room temperature failed to produce the desired morpholinone product **3a**, instead giving intractable polar material, and heating at reflux was required for consumption of starting material. Slow addition of **2a** to $Rh_2(OAc)_4$ in refluxing toluene led to modest yields of **3a**. On the other hand, **2a** smoothly underwent ylide formation and [1,2]-shift to give **3a** (74%) when stirred in toluene at reflux with 15 mol % of Cu powder in toluene. Not surprisingly, lower concentrations reduced the amount of side products but required unacceptably long reaction times. However, heating the substrate with 50 mol % Cu powder in toluene (0.02 M) reproducibly gave **3a** in very good yield. The soluble catalysts copper(II) acetylacetonate, copper(II) trifluoroacetylacetonate, and copper(II) hexafluoroacetylacetonate also led to excellent yields of **3a**; however, copper powder was used in subsequent studies due to its low cost. More efficient ylide formation with copper-based catalysts may derive from their greater electrophilicity.[11] It has also been suggested that the energy difference between metal-bound ylides and transition states for rearrangement is lower when copper catalysts are employed.[12] The procedural simplicity of this transformation is notable, in that high dilution conditions or slow addition are unnecessary, and the cost of the catalyst is considerably lower than that of any of the commonly used Rh(II) catalysts.

Table 2. Catalytic Decomposition of 2a[a]

catalyst	conditions	yield of **3a** (%)[b]
$Rh_2(OAc)_4$	3 mol %/CH_2Cl_2/rt/0.01 M	0
$Rh_2(OAc)_4$	3 mol %/$PhCH_3$/110°C/0.01 M/1.5 h	34
Cu^0	15 mol %/$PhCH_3$/110 °C/0.05 M/3 h	74
Cu^0	15 mol %/$PhCH_3$/110 °C/0.02 M/4.5 h	76
Cu^0	50 mol %/$PhCH_3$/110 °C/0.01 M/6 h	80
Cu^0	50 mol %/$PhCH_3$/110 °C/0.02 M/2 h	79
$Cu(acac)_2$	5 mol %/$PhCH_3$/110 °C/0.01 M/1.5 h	86
$Cu(tfacac)_2$	5 mol %/$PhCH_3$/110 °C/0.01 M/1.5 h	86
$Cu(hfacac)_2$	5 mol %/$PhCH_3$/110 °C/0.01 M/1.5 h	72

[a] See Scheme 1 (R^1 = $PhCH_2$, R^2 = Me, R^3 = Ac). [b] Isolated yields after chromatography.

In most cases **2** could be converted to functionalized morpholinones **3** in good yields (Table 3). The failure to observe ylide-derived product in the case of *N*,*N*-dibenzyl substrate **2b** may be due to the hindered environment around the amine.[13] It is important to note that migration was not limited to benzylic groups (entries 9–11 and 14). A radical homodimer (**4**) was isolated in only one



case (entry 7), although their formation has been described in previous studies by us and others.[8,14] Most mechanistic evidence supports a radical pair mechanism

(9) Experimental details for the preparation of 2-(*N*,*N*-dialkylamino)-ethanols can be found in the supplementary material.

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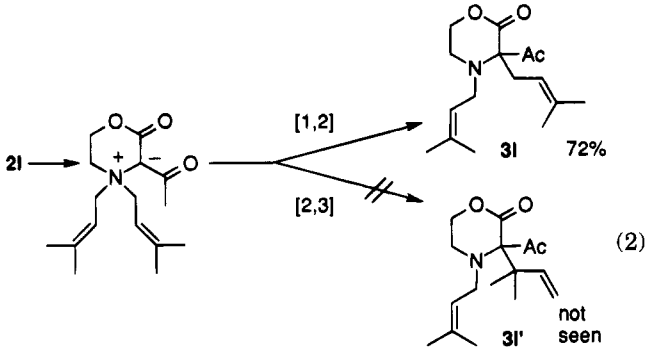
Table 3. Rearrangement of Diazo Esters 2 to Morpholinones 3[a]

entry	reactant	R^1	R^2	R^3	product	yield (%)[b]
1	**2a**	$C_6H_5CH_2$	CH_3	Ac	**3a**	79
2	**2b**	$C_6H_5CH_2$	$C_6H_5CH_2$	Ac	**3b**	0[c]
3	**2c**	4-$NO_2C_6H_4CH_2$	CH_3	Ac	**3c**	68
4	**2d**	4-$AcC_6H_4CH_2$	CH_3	Ac	**3d**	64
5	**2e**	4-$MeOC_6H_4CH_2$	CH_3	Ac	**3e**	76
6	**2f**	4-$Me_2NC_6H_4CH_2$	CH_3	Ac	**3f**	55
7	**2g**	$(C_6H_5)_2CH$	CH_3	Ac	**3g**	0[d]
8	**2h**	$(CH_3)_2CH$	CH_3	Ac	**3h**	0[c]
9	**2i**	$(CH_3)_3C$	CH_3	Ac	**3i**	10
10	**2k**	CH_2=$CHCH_2$	CH_2=$CHCH_2$	Ac	**3k**	70
11	**2l**	CMe_2=$CHCH_2$	CMe_2=$CHCH_2$	Ac	**3l**	72
12	**2m**	$C_6H_5CH_2$	CH_3	Ac	**3m**	80
13	**2n**	$NCCH_2$	CH_3	H	**3n**	0[c]
14	**2n**	$NCCH_2$	CH_3	H	**3n**	19[e]
15	**2o**	$C_6H_5CH_2$	CH_3	H	**3o**	30
16	**2o**	$C_6H_5CH_2$	CH_3	H	**3o**	64[e]
17	**2p**	$C_6H_5CH_2$	$C_6H_5CH_2$	H	**3p**	0[f]
18	**2p**	$C_6H_5CH_2$	$C_6H_5CH_2$	H	**3p**	64[e]

[a] See Scheme 1. Standard procedure described in Experimental Section. [b] Isolated yields after chromatography. [c] Only intractable polar material was obtained. [d] 1,1,2,2-Tetraphenylethane (**4**) was isolated in 19% yield. [e] $Cu(acac)_2$ (5 mol %) was used in place of Cu^0. [f] Carbenoid dimer **5** was isolated in 20% yield.

for the [1,2]-shift of ammonium ylides, and in this special case, the normal [1,2]-shift pathway may be compromised by the greater steric demand of the benzhydryl radical. Formation of **3i**, albeit in low yield, is especially significant in that the *tert*-butyl migrating group is completely devoid of any conjugatively stabilizing moieties. However, the product of isopropyl migration, **3h**, was not observed. Thus, it would appear that the minimum radical stability required for homolysis of the intermediate ylide falls somewhere between that of the isopropyl and *tert*-butyl radicals. The low yield of **3i** may derive from both inefficient homolysis and the extreme congestion encountered during recombination, in analogy to the benzhydryl case (entry 7).

Surprisingly, and in contrast to allylically substituted *oxonium* ylides,[15] substrate **2l** showed no evidence of competing [2,3]-sigmatropic rearrangement of the intermediate *N,N*-diprenyl ylide to give isomeric morpholinone **3l′** (eq 2). The concerted [2,3]-shift pathway is presumably disfavored by sterics, permitting the stepwise mechanism to dominate. The resulting radical pair is unlikely to recombine at the more substituted end for similar reasons. Finally, diazoacetates **2n−p** displayed a profound sensitivity to catalyst (entries 13−18), furnishing the desired morpholinones in substantially higher yield when $Cu(acac)_2$ was employed in place of Cu^0. Efficient rearrangement of *N,N*-dibenzyl substrate **2p** was especially gratifying, since reductive removal of the remaining *N*-benzyl group could provide access to primary amino acid derivatives. In contrast to **2b**, the less substituted metal carbenoid derived from **2p** is apparently able to approach the hindered amine and form the desired ylide. The explanation for the superior yields with the homogeneous catalyst $Cu(acac)_2$ remains elusive but is under current study.



(2)

Summary

In summary, we have demonstrated that the overall sequence of copper-catalyzed carbenoid generation/ammonium ylide formation/Stevens [1,2]-shift utilizing acyclic (*N,N*-dialkylamino)ethyl diazoacetoacetates can be applied to the synthesis of racemic morpholinones **3** in good yields. Starting materials are easily prepared in two steps from readily available 2-(*N,N*-dialkylamino)-ethanols **2**. The key step is exceedingly simple and does not require high-dilution or slow addition conditions. Morpholinones **3** should serve as precursors to a variety of amino acid derivatives, including α,α-dialkylamino acids,[16] via lactone opening followed by oxidative cleavage of the ethanolamine tether.[17] These applications and related studies will be reported elsewhere.

Experimental Section

General. Reactions were conducted in oven-dried glassware under a positive nitrogen atmosphere unless otherwise stated. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes or cannula. Solvents were distilled before use: dichloromethane from calcium hydride, diethyl ether and tetrahydrofuran from sodium/benzophenone. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F_{254} (Merck). Flash columns were packed with 230−400 mesh silica gel (Merck or Baxter). Melting points were obtained in open capillary tubes and are uncorrected. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded at 300 MHz and coupling constants (J) are reported in hertz (Hz). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 75 MHz and are reported (ppm) relative to the center line of a triplet at 77.0 ppm for deuteriochloroform.

Representative Acetoacetylation/Diazotransfer: Preparation of 2′-(*N*-Benzyl-*N*-methylamino)ethyl 2-Diazoacetoacetate (2a). Diketene (0.58 mL, 7.5 mmol) was added neat over a period of 5 min to a 0 °C solution of **1a** (0.83 g, 5.0 mmol) and Et_3N (0.7 mL, 5.0 mmol) in 20 mL of dry CH_2Cl_2. The reaction was stirred for 3 h at 0 °C and 1 h at rt. Solvent and excess diketene were removed under reduced pressure, and the resulting orange liquid was immediately dissolved in 20 mL of CH_3CN. To this solution were added Et_3N (0.70 mL, 5.0 mmol), H_2O (0.10 mL, 5.0 mmol), and MsN_3 (0.56 mL, 6.5 mmol), and the reaction was stirred at rt for 12 h. Most of the solvent was removed by rotary evaporation, and the resulting orange oil was dissolved in 100 mL of Et_2O and washed successively with 1 N NaOH (4 × 20 mL) and brine (25 mL), dried ($MgSO_4$), filtered, and concentrated to give a yellow oil. Flash chromatography (silica gel, 5 cm × 18 cm column, 3:7 and then 2:3 EtOAc/hexanes) gave 1.1 g (80%) of

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2a as a pale yellow oil: R_f 0.16 (3:7 EtOAc/hexanes); IR (neat) 2960, 2795, 2140, 1715, 1660, 1450, 1310 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31–7.25 (m, 5H), 4.33 (t, 2H, J = 5.7 Hz), 3.55 (s, 2H), 2.68 (t, 2H, J = 5.7 Hz), 2.46 (s, 3H), 2.30 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 190.0, 161.3, 138.6, 128.7, 128.2, 127.1, 76.3, 62.9, 62.5, 55.1, 42.7, 28.3. Anal. Calcd for $C_{14}H_{17}N_3O_3$: C, 61.08; H, 6.22; N, 15.26. Found: C, 60.94; H, 6.17; N, 15.39.

2-(*N*,*N*-Dibenzylamino)ethyl 2-Diazoacetoacetate (2b). Compound **1b** (1.21 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 1:19 EtOAc/hexanes) provided 1.37 g (78%) of **2b** as a pale yellow oil: R_f 0.20 (1:9 EtOAc/hexanes); IR (neat) 3028, 2801, 2139, 1720, 1659, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34–7.22 (m, 10H), 4.29 (t, 2H, J = 5.6 Hz), 3.62 (s, 4H), 2.75 (t, 2H, J = 5.6 Hz), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 190.1, 161.1, 139.1, 128.6, 128.2, 127.0, 76.2, 62.6, 58.8, 52.0, 28.2. Anal. Calcd for $C_{20}H_{21}N_3O_3$: C, 68.36; H, 6.02; N, 11.96. Found: C, 68.28; H, 6.08; N, 11.96.

2-[*N*-(4-Nitrobenzyl)-*N*-methylamino]ethyl 2-Diazoacetoacetate (2c). Compound **1c** (1.05 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 3:7 and then 2:3 EtOAc/hexanes) provided 1.17 g (73%) of **2c** as a yellow oil: R_f 0.18 (1:1 EtOAc/hexanes); IR (neat) 2955, 2141, 1721, 1659, 1605, 1520, 1346 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.17 (d, 2H, J = 8.7 Hz), 7.50 (d, 2H, J = 8.8 Hz), 4.37 (t, 2H, J = 5.8 Hz), 3.67 (s, 2H), 2.74 (t, 2H, J = 5.7 Hz), 2.48 (s, 3H), 2.31 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 189.8, 161.1, 147.0, 146.7, 129.0, 123.4, 76.1, 62.5, 61.6, 55.5, 42.5, 28.2. Anal. Calcd for $C_{14}H_{16}N_4O_5$: C, 52.50; H, 5.04; N, 17.49. Found: C, 52.51; H, 5.09; N, 17.53.

2-[*N*-(4-Acetylbenzyl)-*N*-methylamino]ethyl 2-Diazoacetoacetate (2d). Compound **1d** (1.04 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 3:7 and then 2:3 EtOAc/hexanes) provided 0.81 g (51%) of **2d** as a yellow oil: R_f 0.16 (1:1 EtOAc/hexanes); IR (neat) 2957, 2141, 1719, 1684, 1659, 1607, 1314, 1082 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.91 (d, 2H, J = 8.3 Hz), 7.40 (d, 2H, J = 8.1 Hz), 4.35 (t, 2H, J = 5.7 Hz), 3.61 (s, 2H), 2.70 (t, 2H, J = 5.7 Hz), 2.60 (s, 3H), 2.47 (s, 3H), 2.31 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 197.6, 189.9, 161.2, 144.4, 136.1, 128.6, 128.3, 76.2, 62.7, 62.1, 55.3, 42.6, 28.2, 26.6. Anal. Calcd for $C_{16}H_{19}N_3O_4$: C, 60.56; H, 6.03; N, 13.24. Found: C, 60.66; H, 5.99; N, 13.29.

2-[*N*-(4-Methoxybenzyl)-*N*-methylamino]ethyl 2-Diazoacetoacetate (2e). Compound **1e** (0.98 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 3:7 and then 2:3 EtOAc/hexanes) provided 1.15 g (75%) of **2e** as a yellow oil: R_f 0.17 (1:1 EtOAc/hexanes); IR (neat) 2955, 2139, 1719, 1659, 1613, 1512, 1248 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.19 (d, 2H, J = 8.4 Hz), 6.84 (d, 2H, J = 8.4 Hz), 4.32 (t, 2H, J = 5.7 Hz), 3.79 (s, 3H), 3.48 (s, 2H), 2.65 (t, 2H, J = 5.7 Hz), 2.46 (s, 3H), 2.28 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 190.0 161.2, 158.6, 130.5, 129.8, 113.5, 76.2, 62.9, 61.8, 55.1, 54.8, 42.5, 28.2. Anal. Calcd for $C_{15}H_{19}N_3O_4$: C, 59.01; H, 6.27; N, 13.76. Found: C, 58.93; H, 6.28; N, 13.73.

2-[*N*-(4-(*N*,*N*-Dimethylamino)benzyl)-*N*-methylamino]-ethyl 2-Diazoacetoacetate (2f). Compound **1f** (1.04 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 1:1 then 3:2 EtOAc/hexanes) provided 1.16 g (73%) of **2f** as a yellow oil: R_f 0.13 (1:1 EtOAc/hexanes); IR (neat) 2949, 2139, 1715, 1659, 1615, 1524, 1163 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.13 (d, 2H, J = 8.5 Hz), 6.67 (d, 2H, J = 8.8 Hz), 4.31 (t, 2H, J = 5.7 Hz), 3.44 (s, 2H), 2.92 (s, 6H), 2.64 (t, 2H, J = 5.7 Hz), 2.45 (s, 3H), 2.28 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 190.0, 161.2, 149.7, 129.7, 126.1, 112.2, 76.3, 63.0, 62.0, 54.6, 42.6, 40.6, 28.2. Anal. Calcd for $C_{16}H_{22}N_4O_3$: C, 60.36; H, 6.96; N, 17.60. Found: C, 60.26; H, 6.97; N, 17.62.

2-(*N*-(Diphenylmethyl)-*N*-methylamino)ethyl 2-Diazoacetoacetate (2g). Compound **1g** (1.21 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 1:9 and then 1:4 EtOAc/hexanes) provided 1.23 g (71%) of **2g** as a pale yellow oil: R_f 0.39 (3:7 EtOAc/hexanes); IR (neat) 3027, 2797, 2139, 1719, 1659, 1311 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.15 (m, 10H), 4.40 (s, 1H), 4.34 (t, 2H, J = 5.7 Hz), 2.67 (t, 2H, J = 5.7 Hz), 2.48 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 190.1, 161.3, 142.5, 128.4, 127.8, 127.0, 76.2, 75.8, 62.9, 53.5, 40.9, 28.3. Anal. Calcd for $C_{20}H_{21}N_3O_3$: C, 68.36; H, 6.02; N, 11.96. Found: C, 68.29; H, 6.07; N, 11.91.

2-(*N*-Isopropyl-*N*-methylamino)ethyl 2-Diazoacetoacetate (2h). Compound **1h** (0.586 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 2:3 and then 1:1 and 3:1 EtOAc/hexanes) provided 0.784 g (69%) of **2h** as a pale yellow oil: R_f 0.10 (1:1 EtOAc/hexanes); IR (neat) 2969, 2139, 1721, 1661, 1312 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.29 (t, 2H, J = 6.0 Hz), 2.83 (septet, 1H, J = 6.6 Hz), 2.67 (t, 2H, J = 6.0 Hz), 2.48 (s, 3H), 2.28 (s, 3H), 1.00 (d, 6H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 190.0, 161.3, 76.2, 63.8, 54.0, 51.0, 38.2, 28.2, 17.9. Anal. Calcd for $C_{10}H_{17}N_3O_3$: C, 52.85; H, 7.54; N, 18.49. Found: C, 53.01; H, 7.60; N, 18.41.

2-(*N*-*tert*-Butyl-*N*-methylamino)ethyl 2-Diazoacetoacetate (2i). Compound **1i** (0.656 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 3:7 and then 2:3 and 1:1 EtOAc/hexanes) provided 0.893 g (74%) of **2i** as a yellow oil: R_f 0.10 (3:7 EtOAc/hexanes); IR (neat) 2972, 2139, 1721, 1661, 1312 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.25 (t, 2H, J = 6.1 Hz), 2.66 (t, 2H, J = 6.1 Hz), 2.40 (s, 3H), 2.27 (s, 3H), 1.05 (s, 9H); ^{13}C ($CDCl_3$, 75 MHz) δ 190.1, 161.4, 76.3, 64.6, 54.1, 49.7, 36.2, 28.2, 26.0. Anal. Calcd for $C_{11}H_{19}N_3O_3$: C, 54.76; H, 7.94; N, 17.41. Found: C, 54.66; H, 7.96; N, 17.35.

2-(*N*,*N*-Diallylamino)ethyl 2-Diazoacetoacetate (2k). Compound **1k** (0.71 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 1:4 EtOAc/hexanes) provided 0.68 g (54%) of **2k** as a yellow oil: R_f 0.11 (2:8 EtOAc/hexanes); IR (neat) 2978, 2139, 1721, 1661, 1314 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.88–5.75 (m, 2H), 5.22–5.13 (m, 4H), 4.29 (t, 2H, J = 6.0 Hz), 3.14 (d, 4H, J = 6.4 Hz), 2.75 (t, 2H, J = 6.0 Hz), 2.48 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 189.9, 161.2, 135.2, 117.6, 76.2, 63.2, 57.4, 51.2, 28.2. Anal. Calcd for $C_{12}H_{17}N_3O_3$: C, 57.36; H, 6.82; N, 16.72. Found: C, 57.46; H, 6.86; N, 16.73.

2-[*N*,*N*-Bis(3,3-dimethylallyl)amino]ethyl 2-Diazoacetoacetate (2l). Compound **1l** (0.99 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 1:4 EtOAc/hexanes) provided 1.00 g (65%) of **2l** as a yellow oil: R_f 0.17 (2:8 EtOAc/hexanes); IR (neat) 2970, 2139, 1721, 1663, 1312 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.17 (m, 2H), 4.29 (t, 2H, J = 6.0 Hz), 3.07 (d, 4H, J = 6.8 Hz), 2.70 (t, 2H, J = 6.0 Hz), 2.48 (s, 3H), 1.73 (s, 6H), 1.63 (s, 6H); ^{13}C ($CDCl_3$, 75 MHz) δ 190.1, 161.3, 135.0, 121.4, 76.4, 63.6, 52.0, 51.5, 28.3, 25.9, 18.0. Anal. Calcd for $C_{16}H_{25}N_3O_3$: C, 62.52; H, 8.20; N, 13.67. Found: C, 62.64; H, 8.21; N, 13.56.

2-(*N*-Benzyl-*N*-methylamino)phenyl 2-Diazoacetoacetate (2m). Compound **1m** (1.07 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 3:97 and then 1:19 and 1:9 EtOAc/hexanes) provided 0.502 g (31%) of **2m** as a yellow oil: R_f 0.20 (1:9 EtOAc/hexanes); IR (neat) 2783, 2120, 1740, 1650, 1600, 1010 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.29–7.00 (m, 9H), 4.18 (s, 2H), 2.72 (s, 3H), 2.46 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 189.6, 159.8, 145.5, 142.1, 138.3, 128.3, 127.2, 127.1, 127.0, 123.5, 122.2, 119.9, 76.2, 60.0, 39.8, 28.2. Anal. Calcd for $C_{18}H_{17}N_3O_3$: C, 66.86; H, 5.30; N, 13.00. Found: C, 66.77; H, 5.31; N, 12.91.

2-(*N*-(Cyanomethyl)-*N*-methylamino)ethyl Diazoacetate (2n). Compound **1j** (0.571 g, 5.0 mmol) was treated according to the general procedure, and flash chromatography (silica gel, 5 cm × 18 cm column, 2:3 EtOAc/hexanes) provided 0.787 g of an inseparable 1:1 mixture of **2j** and **2n** as a pale yellow oil: R_f 0.17 (1:1, EtOAc/hexanes). This mixture was redissolved in dry CH_3CN (5 mL), pyrrolidine (0.17 mL, 2.0 mmol) was added, and the reaction was stirred for 24 h at rt. Most of the solvent was removed by rotary evaporation, and the resulting orange residue was taken up into 20 mL of 1 N

NaOH and extracted with EtOAc (4 × 20 mL). The combined EtOAc extracts were washed with brine (25 mL), dried ($MgSO_4$), and concentrated to give a yellow oil. Flash chromatography (silica gel, 5 cm × 18 cm column, 1:1 and then 3:1 EtOAc/hexanes) provided 0.592 g (65%) of **2n** as a yellow oil: R_f 0.17 (1:1 EtOAc/hexanes); IR (neat) 3113, 2958, 2114, 1692, 1352, 1186 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.81 (s, 1H), 4.27 (t, 2H, J = 5.4 Hz), 3.60 (s, 2H), 2.76 (t, 2H, J = 5.4 Hz), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.4, 114.4, 61.7, 54.3, 46.2, 45.3, 42.3. Anal. Calcd for $C_7H_{10}N_4O_2$: C, 46.15; H, 5.53; N, 30.75. Found: C, 46.04; H, 5.57; N, 30.65.

2-(*N*-Benzyl-*N*-methylamino)ethyl Diazoacetate (2o). To a solution of **2a** (1.72 g, 5.0 mmol) in CH_3CN (20 mL) was added pyrrolidine (1.28 mL, 15.0 mmol), and the reaction was stirred for 24 h at rt. The reaction mixture was concentrated and taken up into 75 mL of diethyl ether and washed successively with 1 N NaOH (3 × 20 mL), water (20 mL), and brine (20 mL). The organic layer was dried ($MgSO_4$) and concentrated to give a yellow oil. Flash chromatography (silica gel, 5 cm × 18 cm column, 3:7 and then 2:3 EtOAc/hexanes) provided 1.13 g (97%) of **2o** as a pale yellow oil: R_f 0.10 (3:7 EtOAc/hexanes); IR (neat) 3109, 2791, 2110, 1694, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31–7.22 (m, 5H), 4.75 (s, 1H), 4.27 (t, 2H, J = 5.8 Hz), 3.55 (s, 2H), 2.66 (t, 2H, J = 5.9 Hz), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.6, 138.6, 128.7, 128.1, 127.0, 62.5, 62.4, 55.3, 46.2, 42.5. Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.68; H, 6.51; N, 17.91.

2-(*N*,*N*-Dibenzylamino)ethyl Diazoacetate (2p). Reaction of **2b** (1.05 g, 3.0 mmol) with pyrrolidine (0.76 mL, 9.0 mmol) in CH_3CN (10 mL) according to the procedure for **2o** and flash chromatography (silica gel, 5 cm × 18 cm column, 1:9 EtOAc/hexanes) provided 0.727 g (78%) of **2p** as a yellow oil: R_f 0.18 (1:9 EtOAc/hexanes); IR (neat) 2799, 2110, 1696, 1372, 1188 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36–7.15 (m, 10H), 4.67 (s, 1H), 4.23 (t, 2H, J = 5.9 Hz), 3.62 (s, 4H), 2.71-(t, 2H, J = 5.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.4, 139.2, 128.6, 128.1, 126.9, 62.5, 58.6, 51.8, 46.1. Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58. Found: C, 69.70; H, 6.20; N, 13.44.

Representative Cu^0-Catalyzed Diazoacetoacetate Decomposition: Preparation of 3-Acetyl-3-benzyl-4-methylmorpholin-2-one (3a). To a solution of **2a** (0.275 g, 1.0 mmol) in 50 mL of dry toluene was added copper powder (32 mg, 50 mol %), and the solution was stirred at reflux for 2 h. The reaction mixture was filtered through a plug of silica gel and concentrated to give a viscous yellow oil. Flash chromatography (silica gel, 3.5 cm × 16 cm column, 2:3 EtOAc/hexanes) gave 0.196 g (79%) of [1,2]-shift product **3a** as a pale yellow solid: mp 68–70 °C; R_f 0.23 (3:7 EtOAc/hexanes); IR (KBr) 2957, 2812, 1726, 1605, 1182 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30–7.17 (m, 5H), 4.10 (ddd, 1H, J = 10.7, 4.3, 3.1 Hz), 3.52 (ddd, 1H, J = 10.7, 9.0, 3.0 Hz), 3.27 (d, 1H, J = 13.9 Hz), 3.21 (d, 1H, J = 13.9 Hz), 3.08 (ddd, 1H, J = 12.7, 9.2, 3.3 Hz), 2.67 (ddd, 1H, J = 12.9, 4.3, 3.0 Hz), 2.49 (s, 3H), 2.22 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 201.2, 168.7, 136.0, 130.6, 128.0, 126.8, 77.4, 68.0, 46.4, 37.8, 37.2, 28.3. Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.01; H, 6.97; N, 5.60.

3-Acetyl-3-(4-nitrobenzyl)-4-methylmorpholin-2-one (3c). Compound **2c** (0.320 g, 1.0 mmol) was treated according to the general procedure to give 0.201 g (68%) of **2c** as a yellow solid: mp 143–45 °C; R_f 0.14 (3:7 EtOAc/hexanes); IR (KBr) 2818, 1721, 1603, 1510, 1190 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.13 (d, 2H, J = 8.7 Hz), 7.37 (d, 2H, J = 8.7 Hz), 4.19 (dt, 1H, J = 10.8, 3.4 Hz), 3.60 (ddd, 1H, J = 10.9, 9.4, 3.0 Hz), 3.37 (d, 1H, J = 13.7 Hz), 3.30 (d, 1H, J = 13.7 Hz), 3.20 (ddd, 1H, J = 12.9, 9.6, 3.3 Hz), 2.77 (dt, 1H, J = 13.1, 3.4 Hz), 2.51 (s, 3H), 2.25 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 200.4, 167.9, 146.8, 144.1, 131.5, 123.0, 77.4, 68.1, 46.3, 37.4, 37.3, 28.6. Anal. Calcd for $C_{14}H_{16}N_2O_5$: C, 57.53; H, 5.52; N, 9.58. Found: C, 57.61; H, 5.55; N, 9.54.

3-Acetyl-3-(4-acetylbenzyl)-4-methylmorpholin-2-one (3d). Compound **2d** (0.317 g, 1.0 mmol) was treated according to the general procedure to give 0.185 g (64%) of **3d** as a white solid: mp 94–96 °C; R_f 0.21 (1:1 EtOAc/hexanes); IR (KBr) 2973, 2822, 1725, 1680, 1607, 1194 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.87 (d, 2H, J = 8.3 Hz), 7.29 (d, 2H, J = 8.3 Hz), 4.13 (ddd, 1H, J = 10.7, 4.0, 3.1 Hz), 3.56 (ddd, 1H, J = 10.8, 9.1, 3.0 Hz), 3.32 (d, 1H, J = 13.7 Hz), 3.27 (d, 1H, J = 13.7 Hz), 3.13 (ddd, 1H, J = 12.8, 9.3, 3.3 Hz), 2.70 (ddd, 1H, J = 13.0, 4.0, 3.1 Hz), 2.60 (s, 3H), 2.50 (s, 3H), 2.24 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 200.7, 197.7, 168.2, 141.9, 135.7, 130.8, 128.0, 77.4, 68.1, 46.4, 37.6, 37.3, 28.4, 26.6. Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.50; H, 6.67; N, 4.83.

3-Acetyl-3-(4-methoxybenzyl)-4-methylmorpholin-2-one (3e). Compound **2e** (0.305 g, 1.0 mmol) was treated according to the general procedure to give 0.211 g (76%) of **3e** as a white solid: mp 88–89 °C; R_f 0.22 (3:7 EtOAc/hexanes); IR (KBr) 2958, 2824, 1725, 1709, 1610, 1512, 1246 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.10 (d, 2H, J = 8.8 Hz), 6.81 (d, 2H, J = 8.8 Hz), 4.12 (ddd, 1H, J = 7.5, 4.3, 3.1 Hz), 3.78 (s, 3H), 3.59 (ddd, 1H, J = 10.7, 8.9, 3.0 Hz), 3.21 (d, 1H, J = 14.0 Hz), 3.15 (d, 1H, J = 14.0 Hz), 3.08 (ddd, 1H, J = 12.9, 9.0, 3.1 Hz), 2.70 (ddd, 1H, J = 12.9, 4.3, 3.0 Hz), 2.48 (s, 3H), 2.21 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 201.4, 168.7, 158.4, 131.5, 127.8, 113.4, 77.4, 68.1, 55.1, 46.4, 37.2, 36.9, 28.4. Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 65.00; H, 6.88; N, 5.10.

3-Acetyl-3-(4-(*N*,*N*-dimethylamino)benzyl)-4-methylmorpholin-2-one (3f). Compound **2f** (0.318 g, 1.0 mmol) was treated according to the general procedure to give 0.160 g (55%) of **3f** as a purple solid: mp 105–107 °C; R_f 0.12 (3:7 EtOAc/hexanes); IR (KBr) 2949, 2857, 1732, 1707, 1620, 1531, 1169 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.05 (d, 2H, J = 8.6 Hz), 6.64 (d, 2H, J = 8.8 Hz), 4.13 (ddd, 1H, J = 10.6, 4.7, 3.2 Hz), 3.65 (ddd, 1H, J = 10.6, 8.4, 3.0 Hz), 3.20 (d, 1H, J = 14.1 Hz), 3.13 (d, 1H, J = 14.2 Hz), 3.03 (ddd, 1H, J = 12.8, 8.5, 3.2 Hz), 2.92 (s, 6H), 2.70 (ddd, 1H, J = 12.8, 4.7, 3.0 Hz), 2.48 (s, 3H), 2.21 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 201.7, 169.0, 149.5, 131.1, 123.5, 112.3, 77.4, 68.2, 46.5, 40.6, 37.3, 36.8, 28.2. Anal. Calcd for $C_{16}H_{22}N_2O_3$: C, 66.18; H, 7.64; N, 9.65. Found: C, 66.14; H, 7.67; N, 9.63.

1,1,2,2-Tetraphenylethane (4). Compound **2g** (0.351 g, 1.0 mmol) was treated according to the general procedure to give a yellow oil. Flash chromatography (silica gel, 3.5 cm × 16 cm column, 1:19 and then 1:9 and 1:4 EtOAc/hexanes) gave 0.064 g (19%) of **4** as a white solid: mp 109–110 °C (lit.[18] 110–111 °C); R_f 0.20 (1:9 EtOAc/hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.23–6.97 (m, 20H), 4.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.4, 128.4, 128.1, 125.8, 56.3.

3-Acetyl-3-*tert*-butyl-4-methylmorpholin-2-one (3i). Compound **2i** (0.241 g, 1.0 mmol) was treated according to the general procedure to give 0.022 g (10%) of **3i** as a white solid: mp 130–33 °C; R_f 0.17 (2:8 EtOAc/hexanes); IR (KBr) 2978, 2818, 1715, 1192, 1065 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.60 (ddd, 1H, J = 11.8, 11.2, 2.8 Hz), 4.36 (ddd, 1H, J = 11.2, 3.2, 1.6 Hz), 3.21 (ddd, 1H, J = 12.9, 11.9, 3.2 Hz), 3.03 (ddd, 1H, J = 13.0, 2.7, 1.6 Hz), 2.47 (s, 3H), 2.04 (s, 3H), 1.14 (s, 9H); ^{13}C ($CDCl_3$, 75 MHz) δ 198.8, 168.3, 80.3, 67.0, 49.3, 41.9, 40.5, 31.3, 26.8. Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98; N, 6.57. Found: C, 62.04; H, 8.97; N, 6.53.

3-Acetyl-3,4-diallylmorpholin-2-one (3k). Compound **2k** (0.251 g, 1.0 mmol) was treated according to the general procedure to give 0.156 g (70%) of **3k** as a yellow oil: R_f 0.21 (2:8 EtOAc/hexanes); IR (neat) 3081, 2982, 2845, 1730, 1642, 1304, 1175, 922 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.93–5.79 (m, 1H), 5.74–5.61 (m, 1H), 5.26–5.12 (m, 4H), 4.45 (t, 2H, J = 5.0 Hz), 3.20 (qt, 1H, J = 14.5, 6.2, 1.3 Hz), 3.10–3.01 (m, 3H), 2.85 (qt, 1H, J = 14.4, 7.0, 1.3 Hz), 2.74 (qt, 1H, J = 14.4, 7.8, 1.3 Hz), 2.26 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 201.4, 167.8, 134.4, 132.9, 119.2, 118.0, 76.8, 69.2, 52.1, 42.2, 36.7, 27.2. Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.56; H, 7.67; N, 6.27. Found: C, 64.63; H, 7.70; N, 6.19.

3-Acetyl-3,4-bis(3,3-dimethylallyl)morpholin-2-one (3l). Compound **2l** (0.307 g, 1.0 mmol) was treated according to the general procedure to give 0.201 g (72%) of **3l** as a pale yellow oil: R_f 0.14 (3:7 EtOAc/hexanes); IR (neat) 2971, 2859, 1730,

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1698, 1450, 1306, 1169, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.23–5.16 (m, 1H), 5.08–5.02 (m, 1H), 4.49–4.38 (m, 2H), 3.16–2.89 (m, 4H), 2.76 (ddd, 2H, J = 28.0, 15.0, 7.6 Hz), 2.25 (s, 3H), 1.73 (d, 3H, J = 1.2 Hz), 1.72 (d, 3H, J = 1.2 Hz), 1.65 (s, 3H), 1.63 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 202.0, 168.6, 136.3, 134.7, 120.8, 118.5, 76.8, 69.4, 46.7, 42.2, 31.1, 27.2, 26.0, 25.8, 18.0, 17.9. Anal. Calcd for $C_{16}H_{25}NO_3$: C, 68.79; H, 9.02; N, 5.01. Found: C, 68.70; H, 9.05; N, 5.00.

3-Acetyl-3-benzyl-4-methyl-5,6-benzomorpholin-2-one (3m). Compound **2m** (0.323 g, 1.0 mmol) was treated according to the general procedure to give 0.236 g (80%) of **3m** as a yellow oil: R_f 0.17 (1:9 EtOAc/hexanes); IR (neat) 2926, 1753, 1616, 1505, 1271 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.03–6.82 (m, 6H), 6.65–6.55 (m, 3H), 3.44 (d, 1H, J = 14.4 Hz), 3.20 (d, 1H, J = 14.4 Hz), 2.82 (s, 3H), 2.32 (s, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 199.0, 164.0, 139.0, 134.0, 132.5, 130.0, 128.1, 127.0, 125.5, 119.0, 115.9, 111.3, 75.8, 36.8, 32.4, 25.8. Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.21; H, 5.80; N, 4.74. Found: C, 73.30; H, 5.85; N, 4.71.

3-(Cyanomethyl)-4-methylmorpholin-2-one (3n). A solution of **2n** (0.720 g, 3.95 mmol) in dry $PhCH_3$ (80 mL) was added dropwise to a refluxing solution of $Cu(acac)_2$ (51.7 mg, 5 mol %) in 280 mL of dry toluene over a period of 50 min. The addition flask was rinsed with 10 mL of dry toluene, which was added to the reaction mixture. After 30 min, the reaction mixture was cooled and concentrated to give a brown liquid. Flash chromatography (silica gel, 5 cm × 16 cm column, 3:7, 2:3, 1:1, 3:2, and 7:3 EtOAc/hexanes) gave 0.116 g (19%) of **3n** as a viscous yellow liquid: R_f 0.16 (3:2 EtOAc/hexanes); IR (neat) 2962, 2251, 1732, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.56 (td, 1H, J = 11.1, 3.1 Hz), 4.39 (ddd, 1H, J = 11.0, 3.2, 2.2 Hz), 3.23 (dd, 1H, J = 5.1, 3.7 Hz), 3.13 (dd, 1H, J = 7.1, 3.5 Hz), 2.99 (dt, 1H, J = 13.0, 2.6 Hz), 2.91 (dd, 1H, J = 17.1, 5.1 Hz), 2.77 (ddd, 1H, J = 13.0, 11.1, 3.3 Hz), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.3, 116.6, 67.9, 63.1, 50.6, 43.1, 20.3; HRMS calcd for $C_7H_{10}N_2O_2$ m/e 154.0742, found m/e 154.0737.

3-Benzyl-4-methylmorpholin-2-one (3o). Compound **2o** (0.233 g, 1.0 mmol) was treated according to the procedure for **3n**, and flash chromatography (silica gel, 3.5 cm × 16 cm column, 3:7 and then 35:65 EtOAc/hexanes) gave 0.205 g (64%) of **3o** as a yellow oil: R_f 0.15 (3:7 EtOAc/hexanes); IR (neat) 2955, 1736, 1605, 1454, 1182 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.26–7.20 (m, 5H), 4.11 (dt, 1H, J = 10.8, 2.7 Hz), 3.93 (td, 1H, J = 10.8, 2.8 Hz), 3.36 (t, 1H, J = 4.4 Hz), 3.24 (dd, 1H, J = 14.1, 4.1 Hz), 3.11 (dd, 1H, J = 14.1, 4.8 Hz), 2.80 (dt, 1H, J = 12.7, 2.6 Hz), 2.60 (ddd, 1H, J = 13.3, 10.9, 3.1 Hz), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.0, 137.3, 129.8, 127.9, 126.5, 68.0, 67.4, 50.6, 43.1, 36.4. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.05; H, 7.46; N, 6.72.

3,4-Dibenzylmorpholin-2-one (3p). Compound **2p** (0.309 g, 1.0 mmol) was treated according to the procedure for **3n**, and flash chromatography (silica gel, 3.5 cm × 16 cm column, 1:9 and then 2:8 and 3:7 EtOAc/hexanes) gave 0.180 g (64%) of **2p** as a viscous yellow liquid: R_f 0.13 (15:85 EtOAc/hexanes); IR (neat) 3030, 1736, 1603, 1454, 1061 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.33–7.22 (m, 10H), 4.09 (dt, 1H, J = 10.9, 3.3 Hz), 4.03 (d, 1H, J = 13.4 Hz), 3.82 (td, 1H, J = 10.5, 2.7 Hz), 3.68 (t, 1H, J = 4.6 Hz), 3.38 (d, 1H, J = 13.4 Hz), 3.30 (dd, 1H, J = 13.9, 4.6 Hz), 3.18 (dd, 1H, J = 14.0, 4.7 Hz), 2.79 (dt, 1H, J = 12.9, 2.9 Hz), 2.45 (ddd, 1H, J = 12.9, 10.1, 3.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.4, 137.3, 136.9, 130.0, 128.7, 128.4, 128.1, 127.4, 126.6, 67.3, 66.0, 59.0, 46.4, 37.4; HRMS calcd for $C_{18}H_{19}NO_2$ m/e 281.1416, found m/e 281.1415.

(*E*)-Bis(2-(*N*,*N*-dibenzylamino)ethyl) Fumarate (5). Compound **2p** (0.309 g, 1.0 mmol) was treated according to the general procedure given for **3a**, and flash chromatography (silica gel, 3.5 cm × 16 cm column, 1:9 and then 1:4 EtOAc/hexanes) gave 0.056 g (20%) of **5** as a viscous yellow liquid: R_f 0.10 (1:9 EtOAc/hexanes); IR (neat) 3028, 2799, 1723, 1645, 1602, 1296, 1155 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36–7.17 (m, 20H), 6.78 (s, 2H), 4.28 (t, 4H, J = 5.8 Hz), 3.64 (s, 8H), 2.77 (t, 4H, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 139.1, 133.5, 128.6, 128.2, 127.0, 63.1, 58.7, 51.7; HRMS calcd for $C_{36}H_{38}N_2O_4$ (m + 1) m/e 217.1467, found m/e 217.1447.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the National Institutes of Health (BRSG Grant No. S07 RR07092) for partial support of this work, the American Cancer Society for a Junior Faculty Research Award (F.G.W.), and Eli Lilly and Company for a Granteeship (F.G.W.).

Supplementary Material Available: Experimental procedures and physical data for **1a–m** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.