added by syringe. The reaction mixture was then warmed to room temperature for 15 min and finally transferred to a dry NMR tube under Ar. Protonation of aliquots of the azaallylmetal reagents was accomplished by addition of anhydrous methanol by syringe. The azaallylmetal reagents were alkylated by the addition of 2 equiv of ethyl iodide or benzyl bromide using a syringe. The resulting solutions were then analyzed by gas chromatography using internal standard procedures to calculate yields.

Acknowledgment. The support of the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. 1, 1193-93-7; 2, 51072-12-9; 3, 100681-66-1; 4, 100655-84-3; 5, 100681-65-0; EtI, 75-03-6; $PhCH_2Br$, 100-39-0; $CH_2{=}CHN(C_6H_{11})CH_2CH_3$, 100655-85-4; $CH_2{=}CHN(C_6H_{11})$-CH_2Ph, 100655-86-5; acetaldehyde, 75-07-0; cyclohexylamine, 108-91-8.

Diethylaluminum Chloride–Amine Complex Mediated Aminolysis of Activated Cyclopropanes

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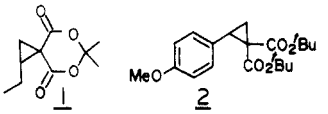
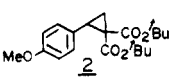
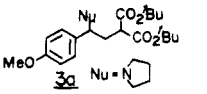
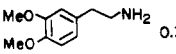
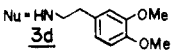
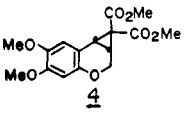
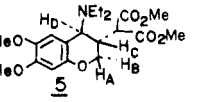
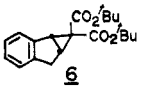
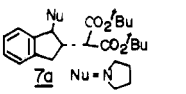
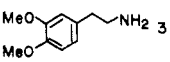
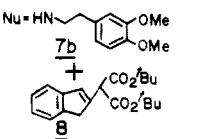
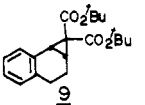
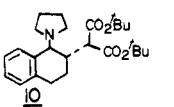
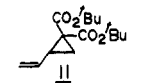
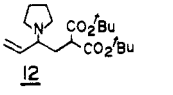
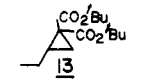
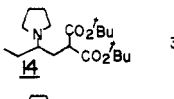
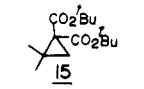
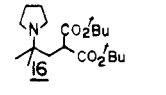
The ring opening of cyclopropane-1,1-dicarboxylic acid esters with amines represents a useful synthetic transformation but is limited in scope. Diethyl 1,1-cyclopropanedicarboxylate undergoes aminolysis with secondary amines, but with primary amines only amidation of the starting material is observed.[1] Introduction of an alkyl substituent on the cyclopropane ring seriously impedes ring opening, even with secondary amines, and complex mixtures of products are obtained.[2] An elegant solution to this problem is the spiroacylal approach developed by Danishefsky and Singh.[3] Spiroactivated cyclopropane 1 undergoes facile aminolysis with secondary amines at the more substituted carbon.[4] However, in the reaction with primary aliphatic amines acylation of the amine becomes competitive.[4]



1 2

Our interest in this area stemmed from the anticipation that opening of cyclopropane **2** with a variety of primary and secondary amines would provide entry to compounds possessing interesting central nervous system activity. We chose the di-*tert*-butyl esters to minimize amidation. Vigorous exposure of **2** to pyrrolidine and/or pyrrolidine hydrochloride ($PhCH_3$, 110 °C, 24 h) gave unchanged starting material. Drawing on our earlier success in opening related cyclopropanes with diethylaluminum cyanide,[5] we examined aluminum as a potential Lewis acid activator. Dialkylaluminum amides, known to effect aminolysis of epoxides,[6] proved ineffective, giving largely

Table I

	Cyclopropane	NuH	Time(h)[a]	Products[b]	Yield(%)
1	 2		3.5	 3a Nu = N	91
2	2	Et_2NH	2	3b Nu = NEt_2	89
3	2	$EtNH_2$	1.5	3c Nu = HNEt	72
4	2		0.3	 3d	83
5	2	NH_3	3.5[c]	3e Nu = NH_2	55
6	 4	Et_2NH	1.5	 5	59
7	 6		22	 7a Nu = N	47
8	6		3	 7b + 8	30 16
9	 9		20	 10	37
10	 11		12	 12	71
11	 13		12	 14	30
12	 15		4	 16	34

[a] Substrates were heated in toluene at 110° with 2 equiv $Et_2AlCl{\cdot}HNR_2$. [b] Chromatographed, pure compounds. [c] Refluxed in $CHCl_3$ with 10 equiv $Et_2AlCl{\cdot}NH_3$.

monoamide and diamide derivatives of **2**.[7] However, treatment of **2** with 2 equiv of a 1:1 mixture of Et_2AlCl and pyrrolidine resulted in a 90% yield of desired amino malonate **3a** (Table I). Diethylamino malonate **3b** was obtained in comparable yield. The dimethyl ester **4** also underwent ring opening with diethylamine in good yield, although small amounts of amidation products were detected. Amino diester **5** was useful in confirming the trans stereochemistry of the ring-opened product. In the ^1H NMR spectrum (400 MHz) neither H_A (δ 4.4, dd, J_{AB} = 11.2, J_{AC} = 2.7 Hz) nor H_B (δ 4.29, ddd, J_{BA} = 11.2, J_{BC} = 5.7, J_{BD} = 1.1 Hz) exhibits a large diaxial coupling to H_C. Therefore, H_C is equatorial and the malonate moiety is axial. Long-range *W*-type coupling between H_B and H_D establishes the diequatorial relationship of these protons. Hence, the C-4 substituent must be trans diaxial to the malonate group.[8] The axial diethylamino group deshields the C-2 axial proton H_A and accounts for the unusual

(1) Stewart, J. M.; Westberg, H. H. *J. Org. Chem.* **1965**, *30*, 1951.
(2) Danishefsky, S.; Rovnyak, G. *J. Org. Chem.* **1975**, *40*, 114.
(3) Danishefsky, S.; Singh, R. K. *J. Org. Chem.* **1975**, *40*, 3807.
(4) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66.
(5) (a) Blanchard, L. A.; Schneider, J. A., unpublished results. (b) Gilbert, J. C.; Luo, T.; Patel, U. *J. Org. Chem.* **1981**, *46*, 4042.
(6) Overman, L. E.; Flippin, L. A. *Tetrahedron Lett.* **1981**, 195.
(7) Basha, A.; Lipton, M.; Weinreb, S. M. *Tetrahedron Lett.* **1977**, 4171.
(8) The dihedral angle between the pseudoequatorial protons (H_B, H_C, H_D) in this ring system is comparable to the axial–equatorial angle in cyclohexane; hence the relatively large (J_{BC} = 5.4 Hz, J_{CD} = 5.5 Hz) "diequatorial" coupling constants.

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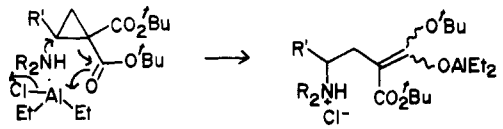
circumstance in which an equatorial proton appears upfield of the axial proton bonded to the same carbon in a six-membered ring.

The indene and dihydronaphthalene derived cyclopropanes **6** and **9** reacted less efficiently, yielding the pyrrolidinyl malonates **7a** and **10** in 47% and 37% yields, respectively.[9] Vinylcyclopropane **11** reacted well with pyrrolidine,[10] but the saturated anlogue **13** and the disubstituted cyclopropane **15** gave lower yields of product, although only one mode of ring cleavage was observed. It would appear that vinyl- and arylcyclopropanedicarboxylates are substrates of choice. We were gratified to find that ring opening with aliphatic primary amines proceeded in comparable yields and that functionalized amines may be employed (Table I, entries 3 and 8). Reaction of **6** with homoveratrylamine and Et_2AlCl produced indene **8** as a byproduct. The structure of **8** was confirmed by degradation (trifluoroacetic acid) to indene-2-acetic acid, which melted at 116–117 °C (lit.[11] mp 116–117 °C; lit.[12] mp 114–116 °C; indene-3-acetic acid, lit.[12] mp 93–94 °C). In the case of pyrrolidine <5% of **8** was formed, indicating that the extent of eliminative ring opening is amine dependent.[13] Finally, exposure of **2** to 10 equiv $Et_2AlCl{\cdot}NH_3$ in refluxing chloroform gave a surprisingly good yield (55%) of ammonolysis product **3e**. However, this process failed when applied to **11**.



The exact nature of the reagent is open to speculation. The lack of obvious reaction, such as gas evolution, on mixing amines with Et_2AlCl and the successful reaction of volatile amines such as NH_3 at elevated temperatures leads us to propose a diethylaluminum chloride–amine complex ($Et_2AlCl{\cdot}HNR_2$) as the active reagent. Indeed, an alternate preparation of the reagent is to add the amine hydrochloride to triethylaluminum (gas evolution occurs). Most likely HCl protonates an ethyl group to generate ethane and form Et_2AlCl, which complexes with the liberated free amine. Aluminum is presumed to facilitate ring cleavage by coordinating to an ester carbonyl to further activate the cyclopropane (eq 1). On nucleophilic opening by the amine an intermediate aluminum ester enolate is formed, which yields the organic product on protonation with acetic acid.

Experimental Section

Commercially available chemicals and solvents were reagent grade and used as received. Diethylaluminum chloride (25 wt % in toluene) was purchased from Aldrich Chemical Co. ^1H NMR spectra were recorded on a Perkin-Elmer R-12 or Varian XL-400 spectrometer, using tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 281B spectrophotometer. Mass spectra were obtained with a Hewlett-Packard 5985 GC/MS system. Melting points were determined with a Büchi melting point apparatus and are uncorrected.

Di-*tert*-butyl 2-(4-Methoxyphenyl)-1,1-cyclopropanedicarboxylate (2). A stirred solution of 5.0 g (37.3 mmol) of 4-vinylanisole and 1.3 g of $CuI{\cdot}P(OMe)_3$[14] was heated to 100 °C under nitrogen. A solution of 13.5 g (56 mmol) of di-*tert*-butyl diazomalonate[15] in 5 mL of toluene was added dropwise over 30 min. After 45 min the reaction mixture was cooled, concentrated, and flash chromatographed[16] with hexane–EtOAc (20:1) to yield 11.3 g (32.5 mmol, 87%) of pure **2**: mp 46–48 °C; IR (CH_2Cl_2) 1705, 1170, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (AB q, J = 8 Hz, 4 H), 3.74 (s, 3 H), 3.03 (t, J = 8 Hz, 1 H), 1.94 (dd, J = 5, 8 Hz, 1 H), 1.49 (m, 1 H), 1.49 (s, 9 H), 1.14 (s, 9 H). Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.12. Found: C, 68.94; H, 8.01.

***cis*-Dimethyl 1,1a,2,7b-Tetrahydro-5,6-dimethoxybenzo[*b*]cyclopropa[*d*]pyran-1,1-dicarboxylate (4).** Following the procedure for **2**, 1.0 g of 6,7-dimethoxy-2*H*-benzopyran[17] and 3.0 g of dimethyl diazomalonate[14] yielded 873 mg (2.7 mmol, 52%) of pure **4** after chromatography with hexane–EtOAc (7:3): mp 119–120 °C; IR (CH_2Cl_2) 1730, 1511, 1225, 1198 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.81 (s, 1 H), 6.36 (s, 1 H), 4.50 (br d, J = 12 Hz, 1 H), 3.90 (dd, J = 2, 12 Hz, 1 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 3.75 (s, 3 H), 3.57 (s, 3 H), 2.80 (d, J = 9 Hz, 1 H), 2.48 (br d, J = 9 Hz, 1 H). Anal. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63. Found: C, 60.00; H, 5.61.

***cis*-Di-*tert*-butyl 1,1a,6,6a-Tetrahydrocyclopropa[*a*]indene-1,1-dicarboxylate (6).** Following the procedure for **2**, 2.5 g (21.5 mmol) of indene gave 4.87 g (14.8 mmol, 69%) of pure **6**: mp 106–107 °C; IR (CH_2Cl_2) 1715, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.49–6.97 (m, 4 H), 3.41–3.05 (m, 3 H), 2.50 (dt, J = 2.8 Hz, 1 H), 1.49 (s, 9 H), 1.02 (s, 9 H). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.84; H, 7.77.

***cis*-Di-*tert*-butyl 1*H*-Cyclopropa[*a*]naphthalene-1,1-dicarboxylate (9).** Following the procedure for **2**, 2.0 g of 1,2-dihydronaphthalene yielded 4.66 g (13.5 mmol, 88%) of pure **9**: mp 88–93 °C; IR (CH_2Cl_2) 1715, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43–6.81 (m, 4 H), 2.84–1.95 (m, 6 H), 1.48 (s, 9 H), 1.14 (s, 9 H). Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.02; H, 8.27.

Di-*tert*-butyl 2-Vinylcyclopropane-1,1-dicarboxylate (11).[18] To a well stirred mixture of 4.2 g (12.5 mmol) of tetrabutylammonium hydrogen sulfate in 3 mL of 50% NaOH and 15 mL of CH_2Cl_2 was added a solution containing 2.0 g (12.5 mmol) of di-*tert*-butyl malonate and 1.56 g (12.5 mmol) of 1,4-dichloro-2-butene (85% trans) in 10 mL of CH_2Cl_2. After 3 h, 75 mL of hexane–ether (1:1) was added and the organic layer decanted and concentrated. The residue was partitioned between ether and water. The organic phase was washed two times with 15 mL of H_2O, dried over Na_2SO_4, filtered, concentrated, and flash chromatographed[16] with hexane–EtOAc (25:1) to give 1.97 g (7.3 mmol, 59%) of pure **11** as an oil: IR (CH_2Cl_2) 1720, 1175, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53–4.88 (m, 3 H), 2.43 (q, J = 7 Hz, 1 H), 1.40 (s, 18 H), 1.75–1.19 (m, 2 H); mass spectrum, m/z (relative intensity) 212 ($M^+ - C_4H_8$, 4), 156 (85), 57 (100).

Di-*tert*-butyl 2-Ethylcyclopropane-1,1-dicarboxylate (13). To 0.35 g (1.3 mmol) of **11** in 6 mL of MeOH was added 0.88 g (5.2 mmol) of dipotassium azodicarboxylate[19] followed by dropwise addition of 0.6 g of acetic acid in 1 mL of MeOH. After 2 h, 10 mL of H_2O and 25 mL of CH_2Cl_2 were added. The organic phase was separated and washed with saturated Na_2CO_3 solution and with 20 mL of H_2O. It was dried over Na_2SO_4, filtered, and concentrated to 0.35 g (1.3 mmol, 100%) of pure **13**:[17] mp 38–39 °C; IR (CH_2Cl_2) 1712, 1170, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03–0.85 (m, 8 H), 1.47 (s, 18 H). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 66.65; H, 9.42.

Di-*tert*-butyl 2,2-Dimethylcyclopropane-1,1-dicarboxylate (15). Prepared according to the procedure for the diethyl ester.[2] Thus, 5.2 g (22.8 mmol) of di-*tert*-butyl diazomalonate[15] yielded 1.55 g (5.7 mmol, 25%) of **15**: mp 41–51 °C; ^1H NMR ($CDCl_3$) δ 1.48 (s, 18 H), 1.18 (s, 8 H). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 66.64; H, 9.52.

General Procedure for Cyclopropane Aminolysis. To a stirred solution of 2 mmol of amine in 3 mL of toluene under N_2

(9) Stereochemistry assigned by analogy to **5**.
(10) (a) Danishevsky, S.; Rovnyak, G. *J. Chem. Soc., Chem. Commun.* **1972**, 820. (b) Stewart, J. M.; Pagenkopf, G. K. *J. Org. Chem.* **1969**, *34*, 7.
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(12) Jirkovsky, I.; Humber, L. G.; Noureldin, R. *Eur. J. Med. Chem.* **1976**, *11*, 571.
(13) Exposure of **7b** to aminolysis conditions did not generate **8**. Therefore **8** is formed directly from the starting cyclopropane **6**.
(14) Peace, B. W.; Carman, F.; Wulfman, D. S. *Synthesis* **1971**, 658.
(15) Ledon, H. J.; Hobbs, S. J.; Coates, R. M. *Org. Synth.* **1980**, *59*, 66.
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(17) Omokawa, H.; Yamashita, K. *Agric. Biol. Chem.* **1973**, *37*, 195.
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(19) Corey, E. J.; Mock, W. L.; Pasto, D. J. *Tetrahedron Lett.* **1961**, 347.

was added at 0 °C 2 mmol of Et_2AlCl (25 wt % in toluene). After the mixture was stirred 5 min, 1 mmol of cyclopropane in 2 mL of toluene was added and the solution heated at 110 °C until no starting material was visible by TLC (0.3–22 h). Acetic acid (1 mL) was added to the cooled reaction mixture followed by 20 mL of H_2O. The reaction mixture was extracted with 25 mL of EtOAc and with three 20-mL portions of CH_2Cl_2. The EtOAc and CH_2Cl_2 extracts were washed separately with 20 mL of saturated aqueous Na_2CO_3 and 10 mL of H_2O. The two organic phases were then combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography[16] using hexane–EtOAc (4:1 to 1:4, depending on the polarity of the products).

Di-*tert*-butyl 2-[2-pyrrolidinyl-2-(4-methoxyphenyl)-ethyl]propanedioate (3a): yield, 91%; mp (fumarate) 70–80 °C; IR (free base, CH_2Cl_2) 1720, 1610, 1240, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.02 (AB q, J = 9 Hz, 4 H), 3.77 (s, 3 H), 3.07 (dd, J = 4.5, 11.5 Hz, 1 H), 2.96–2.30 (m, 7 H), 1.90–1.55 (m, 4 H), 1.48 (s, 9 H), 1.37 (s, 9 H). Anal. Calcd for $C_{24}H_{37}NO_5$: C, 68.70; H, 8.89; N, 3.34. Found: C, 68.62; H, 8.66; N, 3.38.

Di-*tert*-butyl 2-[2-(diethylamino)-2-(4-methoxyphenyl)-ethyl]propanedioate (3b): yield, 89%; mp (citrate) 70–85 °C dec; IR (citrate, CH_2Cl_2) 1720, 1140 cm^{-1}; ^1H NMR (free base, $CDCl_3$) δ 7.02 (AB q, J = 8 Hz, 4 H), 3.78 (s, 3 H), 3.66 (t, J = 7 Hz, 1 H), 3.28 (t, J = 7 Hz, 1 H), 2.95–1.91 (m, 6 H), 1.48 (s, 9 H), 1.44 (s, 9 H), 0.92 (t, J = 7 Hz, 6 H). Anal. Calcd for $C_{30}H_{47}NO_{12}$ (citrate): C, 58.71; H, 7.72; N, 2.28. Found: C, 58.35; H, 8.41; N, 1.97.

Di-*tert*-butyl 2-[2-(ethylamino)-2-(4-methoxyphenyl)-ethyl]propanedioate (3c): yield, 72%; mp (hydrochloride) 193 °C dec; IR (free base, CH_2Cl_2) 3400, 1724, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00 (AB q, J = 8 Hz, 4 H), 3.78 (s, 3 H), 3.56 (t, J = 7 Hz, 1 H), 3.11 (t, J = 7 Hz, 1 H), 2.63–1.82 (m, 5 H), 1.46 (s, 9 H), 1.42 (s, 9 H), 1.01 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{22}H_{36}ClNO_5$ (hydrochloride): C, 61.45; H, 8.44; N, 3.26. Found: C, 61.51; H, 8.15; N, 3.06.

Di-*tert*-butyl 2-[2-[(2-(3,4-dimethoxyphenyl)ethyl)-amino]-2-(4-methoxyphenyl)ethyl]propanedioate (3d): yield, 83%; oil; IR (CH_2Cl_2) 3440, 1730, 1250, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30–6.62 (m, 7 H), 3.82 (s, 6 H), 3.77 (s, 3 H), 3.55 (br t, J = 7 Hz, 1 H), 3.08 (t, J = 7 Hz, 1 H), 2.65 (s, 4 H), 2.26–1.88 (m, 2 H), 1.50 (s, 1 H), 1.46 (s, 9 H), 1.42 (s, 9 H). Anal. Calcd for $C_{30}H_{43}NO_7$: C, 68.03; H, 8.18; N, 2.65. Found: C, 68.30; H, 8.20; N, 2.67.

Di-*tert*-butyl 2-[2-amino-2-(4-methoxyphenyl)ethyl]-propanedioate (3e): yield, 55%; oil; IR (CH_2Cl_2) 3380, 1720, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.07 (AB q, J = 8 Hz, 4 H), 4.20–3.85 (m, 1 H), 3.79 (s, 3 H), 3.17 (t, J = 7 Hz, 1 H), 2.12 (t, J = 7 Hz, 2 H), 1.55 (s, 9 H), 1.53 (s, 9 H). Anal. Calcd for $C_{20}H_{31}NO_5$: C, 65.73; H, 8.55; N, 3.85. Found: C, 65.58; H, 8.50; N, 3.88.

***trans*-Dimethyl 2-(3,4-dihydro-6,7-dimethoxy-4-(diethylamino)-2*H*-benzopyran-3-yl)propanedioate (5)**: yield, 59%; oil; IR (CH_2Cl_2) 1748, 1733, 1230, 1170, 1130 cm^{-1}; ^1H NMR (C_6D_6) δ 6.68 (s, 1 H), 6.39 (s, 1 H), 4.44 (dd, J = 2.7, 11.2 Hz, 1 H), 4.29 (ddd, J = 1.1, 5.7, 11.2 Hz, 1 H), 3.95 (d, J = 7.9 Hz, 1 H), 3.81 (br d, J = 5.4 Hz, 1 H), 3.40 (s, 3 H), 3.19 (s, 3 H), 3.17 (s, 3 H), 3.15 (s, 3 H), 2.88 (m, 1 H), 2.52 (m, 4 H), 0.86 (t, J = 7.5 Hz, 6 H). Anal. Calcd for $C_{20}H_{29}NO_7$: C, 60.74; H, 7.39; N, 3.54. Found: C, 60.60; H, 7.30; N, 3.60.

***trans*-Di-*tert*-butyl 2-[2,3-dihydro-1-(1-pyrrolidinyl)-1*H*-inden-2-yl]propanedioate (7a)**: yield, 47%; oil; IR (CH_2Cl_2) 1720, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.00 (m, 4 H), 3.97 (d, J = 2 Hz, 1 H), 3.55–2.35 (m, 8 H), 1.87–1.50 (m, 4 H), 1.75 (s, 9 H), 1.35 (s, 9 H). Anal. Calcd for $C_{24}H_{35}NO_4$: C, 71.79; H, 8.79; N, 3.49. Found: C, 71.60; H, 8.66; N, 3.40.

***trans*-Di-*tert*-butyl 2-[2,3-dihydro-1-((2-(3,4-dimethoxyphenyl)ethyl)amino)-1*H*-inden-2-yl]propanedioate (7b)**: yield, 30%; oil; IR (CH_2Cl_2) 3600, 1720, 1260, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (s, 4 H), 6.75 (s, 3 H), 4.30–4.05 (m, 2 H), 3.86 (s, 6 H), 3.64–2.38 (m, 7 H), 1.63 (br s, 1 H), 1.46 (s, 18 H). Anal. Calcd for $C_{30}H_{41}NO_6$: C, 70.42; H, 8.08; N, 2.74. Found: C, 70.26; H, 8.22; N, 2.85.

Di-*tert*-butyl 2-(1*H*-inden-2-yl)propanedioate (8): yield, 16%; mp 68–70 °C; IR (CH_2Cl_2) 1725, 1140 cm^{-1}; ^1H NMR 7.55–7.05 (m, 4 H), 6.82 (br s, 1 H), 4.43 (s, 1 H), 3.70–3.45 (m, 2 H), 1.48 (s, 18 H); mass spectrum, m/z 330 (M^+, 1), 229 (11.2), 57 (100). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.75; H, 7.70.

***trans*-Di-*tert*-butyl 2-[1,2,3,4-tetrahydro-1-(1-pyrrolidinyl)-2-naphthalenyl]propanedioate (10)**: yield, 37%; oil; IR (CH_2Cl_2) 1740, 1725, 1170, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.11 (s, 4 H), 3.26 (d, J = 3 Hz, 1 H), 3.03–1.95 (m, 10 H), 1.88–1.55 (m, 4 H), 1.45 (s, 18 H). Anal. Calcd for $C_{25}H_{37}NO_4$: C, 72.25; H, 8.98; N, 3.37. Found: C, 71.93; H, 8.68; N, 3.19.

***tert*-Butyl 4-(1-pyrrolidinyl)-2-carbo-*tert*-butoxyhex-5-enoate (12)**:[20] yield, 71%; oil; IR (CH_2Cl_2) 1720, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.02–4.91 (m, 3 H), 3.23 (dd, J = 5.9 Hz, 1 H), 2.87–1.56 (m, 11 H), 1.48 (s, 18 H). Anal. Calcd for $C_{19}H_{33}NO_4$: C, 67.22; H, 9.80; N, 4.13. Found: C, 68.02; H, 9.70; N, 4.11.

***tert*-Butyl 4-(1-pyrrolidinyl)-2-carbo-*tert*-butoxyhexanoate (14)**: yield, 29%; oil; IR (CH_2Cl_2) 1720, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.38 (t, J = 7 Hz, 1 H), 2.75–1.57 (m, 13 H), 1.48 (s, 18 H), 0.92 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{19}H_{35}NO_4$: C, 66.82; H, 10.33; N, 4.10. Found: C, 66.77; H, 10.09; N, 4.19.

***tert*-Butyl 4-(1-pyrrolidinyl)-2-carbo-*tert*-butoxy-4-methylpentanoate (16)**: yield, 34%; oil; IR (CH_2Cl_2) 1720, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.04 (t, J = 6 Hz, 1 H), 2.80–2.30 (m, 4 H), 2.00 (d, J = 6 Hz, 2 H), 1.85–1.55 (m, 4 H), 1.46 (s, 18 H), 0.97 (s, 6 H). Anal. Calcd for $C_{19}H_{35}NO_4$: C, 66.83; H, 10.33; N, 4.10. Found: C, 66.19; H, 9.87; N, 3.97.

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Registry No. **2**, 100839-16-5; **3a**, 100839-20-1; **3a**·fumarate, 100839-21-2; **3b**, 100839-22-3; **3b**·citrate, 100839-23-4; **3c**, 100839-35-8; **3c**·HCl, 100839-24-5; **3d**, 100839-25-6; **3e**, 100839-26-7; **4**, 100839-17-6; **5**, 100839-27-8; **6**, 100857-92-9; **7a**, 100839-28-9; **7b**, 100839-29-0; **8**, 100839-30-3; **9**, 100839-18-7; **10**, 100839-31-4; **11**, 88326-58-3; **12**, 100839-32-5; **13**, 97935-31-4; **14**, 100839-33-6; **15**, 100839-19-8; **16**, 100839-34-7; 6,7-dimethoxy-2*H*-benzopyran, 41361-61-9; 4-vinylanisole, 637-69-4; di-*tert*-butyl diazomalonate, 35207-75-1; dimethyl diazomalonate, 6773-29-1; indene, 95-13-6; 1,2-dihydronaphalene, 447-53-0; di-*tert*-butyl malonate, 541-16-2; *trans*-1,4-dichloro-2-butene, 110-57-6; pyrrolidine, 123-75-1; diethylamine, 109-89-7; ethylamine, 75-04-7; 3,4-dimethoxyphenethylamine, 120-20-7; NH_3, 14798-03-9.

(20) Diethyl ester: see ref 2.

Vinyl Isocyanates as Aza Diene Equivalents. A Method for the Synthesis of Functionalized 4-Hydroxy-2(1*H*)-pyridones

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We wish to report a general and efficient preparation of functionalized 4-hydroxy-2(1*H*)-pyridones from the reaction of readily available α,β-unsaturated isocyanates with various ester enolates. This two-step protocol is illustrated in eq 1. Addition of an appropriate ester enolate to the electrophilic carbonyl carbon of the isocyanate at 0 °C provided in good yield an adduct which when heated for a short period (4–10 min) at 230–240 °C underwent smooth cyclization to furnish the corresponding six-membered heterocycle.[1]

The enolates of diethyl malonate and ethyl acetoacetate were found to react cleanly with 1-isocyanato-1-cyclo-

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