Table II. Rate Constants for Toluene (Tol) Bromination and for Pentamethylbenzene (PMB) Iodination at 25.0 °C

$10^3[Hg(OCOR)_2]_i$, M	$10^3[Br_2]_i$, M	$[Tol]_i$, M	10^3k, M^{-1} s^{-1}
	Propionic Acid Solvent		
48.1	9.60	0.309	20
12.0	4.80	0.309	14
24.0	4.80	0.154	15
48.1	9.60	0.155	21
48.1	9.60	0.0772	24
	Butyric Acid Solvent		
35.4	9.75	0.467	7.3
70.7	9.75	0.233	9.9
56.6	15.6	0.187	9.6
$10^3[Hg(OCOR)_2]_i$, M	$10^3[I_2]_i$, M	$[PMB]_i$, M	10^3k M^{-1} s^{-1}
	Propionic Acid Solvent		
1.26	1.10	0.0866	5.1
2.52	1.10	0.0578	5.4
2.10	1.83	0.0481	6.2
3.16	3.26	0.0490	4.7
	Butyric Acid Solvent		
12.1	1.05	0.0972	1.6
20.1	1.80	0.0540	1.5
10.1	1.80	0.0540	1.2

and all three constants are substantially greater than that for trifluoroacetyl hypoiodite[4] (0.111). All the values for K_{RCOOX} for the hypoiodites are significantly larger than those for the corresponding hypobromites, in reflection of the relative ease of positive polarization of bromine and iodine.

The rate constants (eq 3) for bromination of toluene in solutions of mercuric propionate and bromine in propionic acid and mercuric *n*-butyrate and bromine in *n*-butyric acid and the corresponding ones for iodination of pentamethylbenzene are given in Table II. Though benzene reacts with acetyl hypobromite (in mixtures of bromine and mercuric acetate) in acetic acid at 25.0 °C at a rate suitable for spectrophotometric investigation, the reaction of propionyl hypobromite and benzene in propionic acid at 25.0 °C is too slow for convenient kinetic study. One rate run on the propionyl hypobromite–benzene reaction was allowed to proceed at room temperature (about 22 °C) long enough to follow its progress to better than 50% completion. From the results a rough value of $k = 6 \times 10^{-5}$ M^{-1} s^{-1} for the reaction of benzene and propionyl hypobromite was obtained.

In Table III a summary of the rate constants is provided and the constants are compared with those reported in earlier work.[2,3] As observed previously for the reactions of the acetyl hypohalites the propionyl and *n*-butyryl hypobromites are considerably more reactive than the hypoiodites. The three hypobromites are reactive enough that they are consumed at easily measurable rates at room temperature by either benzene or toluene, hydrocarbons which are not highly susceptible to electrophilic halogenation.[7] The much more reactive hydrocarbon, pentamethylbenzene, reacts with all three hypoiodites at rates generally comparable to those for reactions of the corresponding hypobromites with benzene or toluene. Clearly the difference in electrophilicity of the hypobromites and hypoiodites is substantial.

Both for the hypobromites and hypoiodites (RCOOX) the reactivities fall off as R is changed in the order CH_3 > CH_3CH_2 > $CH_3CH_2CH_2$. The difference in reactivity

(7) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 4549.

Table III. Relative Reactivities of Acyl Hypohalites with Aromatic Hydrocarbons[a]

Ar substrate	halogenating agent	solv	k (25.0 °C), M^{-1} s^{-1}	$k_{AcOX}/k_{PrOX}/k_{BuOX}$
benzene	AcOBr[b]	AcOH	3.2×10^{-3}	~50/1.0/0
	PrOBr	PrOH	$\sim 6 \times 10^{-5}$	
toluene	AcOBr	AcOH	1.5[c]	172/2.2/1.0
	PrOBr	PrOH	19.0×10^{-3}	
	BuOBr	BuOH	8.7×10^{-3}	
pentamethylbenzene	AcOI	AcOH	78×10^{-3}	56/3.6/1.0
	PrOI	PrOH	5.1×10^{-3}	
	BuOI	BuOH	1.4×10^{-3}	

[a] The abbreviations Ac, Pr, and Bu represent $CH_3C{=}O$, $CH_3CH_2C{=}O$, and $CH_3CH_2CH_2C{=}O$, respectively. [b] From ref 2. [c] Based on the composition of products of reaction of known mixtures of benzene and toluene with AcOBr in HOAc (ref 2).

of the acetyl and propionyl hypohalites is much larger than that for propionyl and *n*-butyryl hypohalites. The differences in reactivity are probably to a considerable extent related to differences in medium effects of acetic, propionic, and *n*-butyric acids and largely the result of differences in medium dielectric constants. The dielectric constant of acetic acid is significantly larger than the constants for propionic and *n*-butyric acids, which are similar to each other.[9] Though the halogenation reactions may be subject to acid catalysis, the acidities of these acids are closely similar.[8] Decreases in reactivities of the hypohalites with changes in R groups may also to some degree be associated with the relative inductive effects of those groups.

Registry No. PMB, 700-12-9; $Hg[OC(O)CH_2CH_3]_2$, 26719-04-0; $Hg[OC(O)(CH_2)_2CH_3]_2$, 19348-32-4; Br_2, 7726-95-6; I_2, 7553-56-2; $CH_3CH_2C(O)OBr$, 82198-80-9; $CH_3(CH_2)_2C(O)OBr$, 100814-78-6; $CH_3CH_2(O)OI$, 100814-79-7; $CH_3(CH_2)_2C(O)OI$, 100814-80-0; PhMe, 108-88-3; benzene, 71-43-2.

(8) The K_A value for acetic acid at 25 °C is reported as 1.856×10^{-5}, while the corresponding values for propionic and *n*-butyric acids aare of the order of 1.4×10^{-5} and 1.5×10^{-5}, respectively (from: "Beilsteins Handbuch der Organischen Chemie"; Springer-Verlag: Berlin, 1920; Vol. II, pp 101, 236, 267).

(9) The dielectric constants for the three acids are 6.4 (20 °C) for acetic acid, 3.19 (19 °C) for propionic acid, and 2.85 (20°C) for *n*-butyric acid (from: "International Critical Tables"; McGraw-Hill: New York, 1929; Vol. VI, pp 84–87).

Dynamic Structures of Zinc, Magnesium, and Aluminum Azaallylmetal Reagents

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Azaallylmetal reagents are important and versatile reactive intermediates. Synthetically they are equivalent to metal enolates. These reagents are useful in electrophilic asymmetric synthesis in which electrophiles react with chiral 1-azaallylmetal reagents that have a homochiral group on nitrogen.[2] While lithium has been the most common metal used in azaallylmetal reagents, less electropositive metals are receiving more attention in this and

(1) Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.

(2) Bergbreiter, D. E.; Newcomb, M. In "Asymmetric Syntheses"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 9.

0022-3263/86/1951-1369$01.50/0

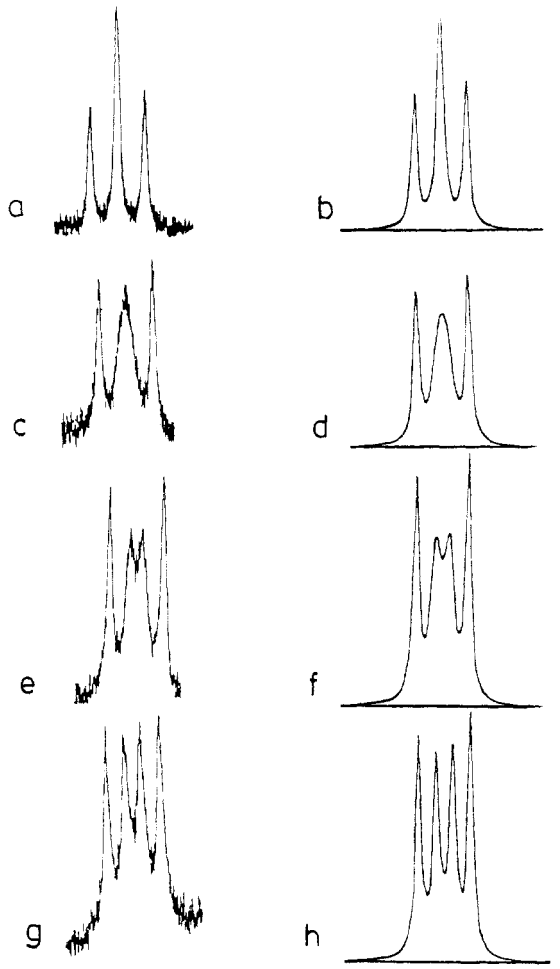
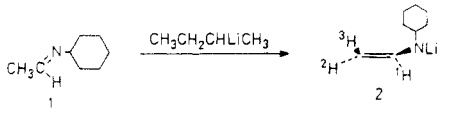


Figure 1. Experimental and calculated ^1H NMR spectra at 90 MHz for a 0.4 N tetrahydrofuran solution of **4** in the region δ 6.0–7.0 at various temperatures: (a) 25 °C; (b) k = 150 s^{-1}; (c) 0 °C; (d) k = 16 s^{-1}; (e) −5 °C; (f) k = 8.0 s^{-1}; (g) −15 °C; (h) k = 1.5 s^{-1}.

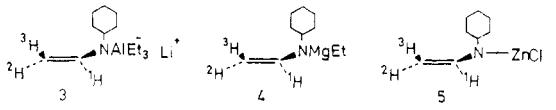
related chemistry.[3] Our objective in this study was to measure the effect of such metal substitution on the dynamic structures of these reagents.

The stereochemistry about the C–N and C–C bonds of azaallylmetal reagents is known to affect the stereoselectivity of electrophilic asymmetric syntheses involving these reagents.[2] If interconversion of the stereoisomers of an azaallylmetal reagent were facile and if such equilibria could be biased by the appropriate choice of a metal or an *N*-alkyl group, rational development of asymmetric electrophilic syntheses using these reagents with chiral directing groups would be easier. Our previous studies showed that the barrier to C–C bond rotation in the azaallyllithium reagent **2** is 17.7 kcal/mol at 40 °C[5] (eq1).



(1)

Azaallyllithum reagent **2** was well suited to ^1H DNMR studies because rapid rotation about the C_1 and C_2 bond in **2** changed the multiplicity of the formyl proton of **2**. The formyl proton in **2** is a doublet of doublets when bond rotation is slow on the ^1H NMR time scale and is a triplet when C–C bond rotation is rapid (cf. Figure 1). We expected that azaallylmetal reagents in which the metal atom was an alkaline-earth or group 12[20] metal would have a significantly lower barrier to C–C bond rotation than **2**. We have now prepared azaallylaluminum, azaallyllyzinc, and azaallylmagnesium reagents **3–5**, respectively, by transmetalation of **2** with triethylaluminum, zinc chloride, and ethylmagnesium bromide and have examined the barriers to C–C bond rotation in these compounds.



Aldimine **1** was prepared by the reaction of acetaldehyde and cyclohexylamine. Deprotonation of the aldimine with *sec*-butyllithium in tetrahydrofuran (THF) produced a solution of the azaallyllithium reagent **2** that was then analyzed by ^1H NMR spectroscopy. The proton H_1 appeared as a doublet of doublets (δ 6.90, J_{cis} = 7.7 Hz, J_{trans} = 14.5 Hz) at room temperature as previously reported.[5] Attempts to use *n*-butyllithium in place of *sec*-butyllithium were frustrated by addition of *n*-butyllithium across the C=N bond. The competitive reaction of *tert*-butyllithium with THF solvent to form the lithium enolate of acetaldehyde precluded its use. Lithium diisopropylamide or lithium diethylamide were used in place of *sec*-butyllithium to form **2**. However, the unavoidable presence of dialkylamines in solutions of **2** led to other complications.[6]

Reaction of **2** with triethylaluminum in hexane formed **3**. The ^1H NMR spectra of **3** showed the formyl proton H_1 was a doublet of doublets (δ 6.53, J_{cis} = 8.0 Hz, J_{trans} = 16.0 Hz) up to +50 °C. The lack of DNMR behavior indicates that C_1–C_2 bond rotation is slow for this azaallylmetal reagent ($\Delta G^{\ddagger}$ > 19 kcal/mol).

The magnesium reagent **4** was prepared from **2** by the addition of 1 equiv of ethylmagnesium bromide to a solution of **2**.[7] The ^1H NMR spectrum of **4** so formed contained a signal for the formyl proton that appeared as a triplet (δ 6.50, J = 11.25 Hz) at room temperature. After the solution of **4** was cooled, a reversible change in the multiplicity of H_1 was observed. At −30 °C the H_1 signal appeared as a doublet of doublets (δ 6.50, J_{cis} = 7.3 Hz, J_{trans} = 14.6 Hz). These spectral changes are most readily explained by facile C–C bond rotation on the NMR time scale at room temperature. Simulated spectra using the line-shape analysis program DNMR3H[8,9] provided an estimate for the free energy of rotation of 14.5 ± 0.3 kcal/mol at 0 °C for **4**.

(3) Among the azaallylmetal reagents that have been described in recent years are azaallylpotassium reagents,[4a] azaallylmagnesium reagents,[4b] azaallylboron reagents,[4c] azaallylzinc reagents,[4d] azaallylcopper reagents,[4e] and azaallyltin[4f] reagents.

(4) (a) Gawley, R. E.; Termine, E. J.; Aube, J. *Tetrahedron Lett.* **1980**, *21*, 3115–3118. (b) Koga, K. *ACS Symp. Ser.* **1982**, *No. 185*, 73–81. (c) Meyers, A. I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1981**, *103*, 4278–4279. (d) Saigo, K.; Kasahara, A.; Ogawa, S.; Nohira, H. *Tetrahedron Lett.* **1983**, *24*, 511–512. (e) Yamamoto, K.; Iijima, M.; Ogimura, Y. *Tetrahedron Lett.* **1982**, *23*, 3711–3714. (f) De Jeso, B.; Pommier, J. C. *Tetrahedron Lett.* **1980**, *21*, 4511–4514.

(5) Lee, J. Y.; Lynch, T. J.; Mao, D. T.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1981**, *103*, 6215–6217.

(6) The use of lithium dialkylamide bases in these studies unavoidably generated dialkylamines. Subsequent addition of a zinc, magnesium, or aluminum Lewis acid resulted in both transmetalation of **2** and reaction with these amines. As a result, mixtures of the starting aldimine, the desired azaallylmetal reagent, and condensation products formed.

(7) Direct formation of azaallylmagnesium reagents by deprotonation of aldimines with alkylmagnesium halides has been described. Cf.: Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178–2180.

(8) (a) Stempfle, W.; Klein, J.; Hoffmann, E. G. *QCPE* **1982**, *10*, program 450. (b) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411–428.

(9) The effective transverse relaxation time (T_2) was calculated to be 0.11 s from the width at half-height of the formyl proton signal in the slow-exchange spectrum of **4**.[8b]

The azaallylzinc reagent **5** was prepared by transmetalation of **2** with anhydrous zinc chloride in THF at −78 °C. After this solution was warmed to room temperature, NMR analysis showed that **5** had temperature-dependent ^{1}H NMR spectra similar to those seen for **4**. The formyl proton H_1 of **5** appeared as a triplet at room temperature (δ 7.7, J = 8.6 Hz). At −20 °C a doublet of doublets was observed (δ 7.7, J_{cis} = 5.6 Hz, J_{trans} = 11.2 Hz). The free energy of activation for rotation for the zinc reagent **5** was estimated to be 14.2 ± 0.8 kcal/mol[10] by the use of the DNMR3H program.

The interaction of the metal with the azaallyl ligand may be described as either a η^3, η^1-N, or a η^1-C interaction. Precedent for a π-type interaction is found in the reported solid-state structure of an azaallyllithium reagent derived from a ketone dialkylhydrazone.[11] An η^3-azaallyl ligand was also recently characterized in an azaallylmolybdenum complex.[12] Coordination of an azaallyl ligand in an η^1-N or a η^1-C fashion has less precedent. However, similar coordination has recently been reported for a rhodium enolate and some main-group metal enolates.[13-15]

The observed rotation could involve a mechanism like that previously described for allyllithium reagents[16] or could involve equilibration among the possible tautomeric structures having different M–C and M–N interactions. Our results do not preclude a concentration dependence for this rotational barrier. Comparison of spectra of 0.2–0.6 N solutions did not exhibit much difference in dynamic phenomena. Significantly higher concentrations were unattainable because of solubility considerations. Significantly lower concentrations led to spectra of inferior quality. Regardless of the mechanism for equilibration, it is evident that selection of the metal and its ligands controls the facility of stereoisomerization of azaallylmetal reagents. This will be important in stereoselective syntheses using azaallylmetal reagents. On the basis of our studies of **3–5** and our previous work with **2**, one concludes that it will be possible to use stereoisomeric azaallyllithium or lithium trialkyl(azaallyl)aluminate reagents whose stereochemistry is determined by kinetic factors since these reagents have relatively high barriers to C–C isomerization. Alternatively, control of stereochemistry by thermodynamic equilibration could readily be achieved by the use of azaallylmagnesium or azaallylzinc reagents whose rotational barriers are substantially lower. Control of azaallylmetal reagent stereochemistry has been exploited previously in asymmetric synthesis with chiral azaallyllithium reagents.[17] The use of an azaallylmagnesium reagent or catalytic amounts of an alkylmagnesium halide would be useful as a means of avoiding the rigorous conditions that had to be used to effect equilibration in this example.

We also briefly compared the reactivity of azaallyllithium azaallylaluminum, azaallylmagnesium, and azaallylzinc reagents **2–5**. Yields of alkylated products in reaction of each of these reagents with ethyl iodide and benzyl bromide at −78 °C were 99% and 100% (Li), 62% and 84% (Al), 94% and 98% (Mg), and 3% and 7% (Zn). All of these azaallylmetal reagents were protonated by treatment with methanol at −78 °C in high yield to re-form the starting aldimine.

Experimental Section

^{1}H NMR spectra were recorded on a Varian EM390 (90-MHz) or a T-60 (60-MHz) spectrometer using benzene as an internal standard. Moisture-sensitive samples were transferred by cannula from the reaction vessel into septa-sealed, oven-dried tubes that had been well flushed with argon. Variable-temperature NMR studies were carried out on the Varian EM390 using a Joule–Thompson effect cooled probe. Probe temperatures were measured from spectra of an ultrapure methanol sample. Line-shape analysis was performed by using the program DNMR3H. Gas chromatography was done on either a HP 5790 or Varian 2440 gas chromatograph using either decane or nonane as an internal standard. GC/MS studies were performed on a HP5790A gas chromatograph equipped with a 5970A mass selective detector. All reactions involving air- and/or moisture-sensitive samples were performed in flame-dried septa-sealed 40-mL centrifuge tubes under a positive pressure of Ar. Tetrahydrofuran (THF) was dried over potassium–benzophenone ketyl before use. Other reagents used were reagent grade and not purified further before use. The alkyllithium and alkylaluminum reagents were obtained from Aldrich Chemical Co. as hydrocarbon solutions. The alkyllithium reagents were periodically titrated with 2-butanol in xylene using 1,10-phenanthroline as an indicator while the alkylaluminum reagents were titrated by measuring the ethane gas evolution upon quenching with 20% H_2SO_4/1-butanol.[18,19]

Ethylidene-*N*-cyclohexylamine was prepared by the dropwise addition of acetaldehyde cooled to 0 °C (7 mL, 0.2 mol) to a 0 °C 100-mL flask containing cyclohexylamine (23 mL, 0.2 mol) over a period of 30 min. The mixture was stirred for a further 2 h after which time 2 g of KOH pellets was added. The brown solution was allowed to stand until two layers formed (15 min), and the organic layer was separated and stored overnight at 5 °C over 2 g of crushed KOH. The product was then purified by vacuum distillation from a few fresh KOH pellets to yield 16.3 g (57 %) of product: bp 46–48 °C (18 torr); ^{1}H NMR ($CDCl_3$) δ 7.4–7.7 (q, 1 H), 2.6–2.9 (m, 1 H), 1.7–1.9 (d, 3 H), 0.8–1.9 (m, 10 H). The imine was stored under argon at −10 °C.

General Procedure for Imine Deprotonation. To a flame-dried, septum-sealed 40-mL centrifuge tube was added 10 mL of dry THF followed by 4.7 mL of 1.45 N *sec*-butyllithium. The yellow solution was warmed to room temperature for 10 min and recooled to −78 °C, and 1 mL of ethylidene-*N*-cyclohexylamine was added drowpise over a period of 3 min. The pale yellow solution was then warmed to room temperature for 10 min to complete formation of the azaallyllithium reagent **2**.

General Procedure for Transmetalation. Azaallyllithium reagents were converted into other azaallylmetal reagents by transmetalation. This involved the addition of 1 equiv (with respect to lithium) of the appropriate alkylmetal reagent to an aliquot of the stock solution of the azaallyllithium reagent prepared as above. In a typical procedure, 5 mL of a stock solution was added to a flame-dried centrifuge tube that was cooled to −78 °C, and 1 equiv of triethylaluminum (1.0 M in hexane) was

(10) The spectra for **5** were broader than those for **4**. Other dynamic processes occur in NMR spectra of azaallylmetal reagents below −20 °C. While various explanations of these other dynamic phenomena have been advanced, exchange of azaallyl groups among azaallylmetal aggregates could be occurring and could be responsible for the broadening observed in the slow-exchange spectra of **5**.

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(12) Green, M.; Mercer, R. J.; Morton, C. E.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 422–424.

(13) Ellman, J. A.; Feldman, K.; Tulip, T. H. "Abstracts of Papers", 189th National Meeting of the American Chemical Society, Miami, FL, Apr 1985; American Chemical Society: Washington, DC, 1985; INOR 21.

(14) Dekker, J.; Boersma, J.; van der Kerk, G. J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 553–555.

(15) Lithium enolates have been the subject of numerous studies. Cf.: Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 3345–3346 and references therein.

(16) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459–5464.

(17) Meyers, A. I. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 3, Chapter 3.

(18) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(19) Crompton, T. R.; Reid, V. W. *Analyst* **1963**, *88*, 713–720.

(20) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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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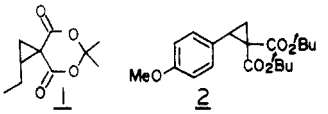
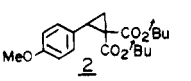
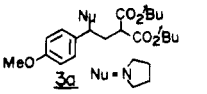
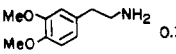
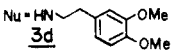
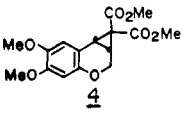
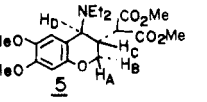
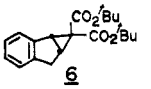
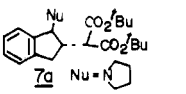
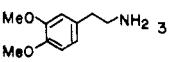
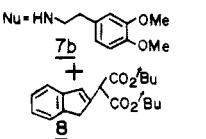
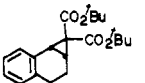
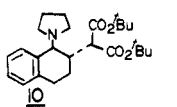
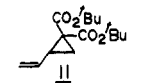
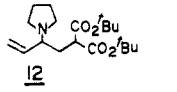
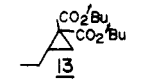
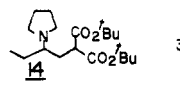
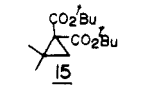
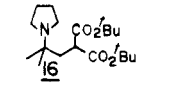
The ring opening of cyclopropane-1,1-dicarboxylic acid esters with amines represents a useful synthetic transformation but is limited in scope. Diethyl 1,1-cyclopropanedicarboxylate undergoes aminolysis with secondary amines, but with primary amines only amidation of the starting material is observed.[1] 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

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(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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