Reaction of Dianions of Acyclic β-Enamino Ketones with Electrophiles. 3.† Nitriles: Synthesis of Pyridine and Pyrimidine Derivatives

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A new method for the construction of pyridine and pyrimidine derivatives is described, based on the electrophilic attack of nitriles to dianions of β-(monoalkylamino)-α,β-unsaturated ketones and the subsequent cyclization of the addition product. The reaction proceeds in good to high yields with both α′- and γ-dianions which are regioselectively generated. The reaction of γ-dianions with nitriles is strongly influenced by temperature. The γ-addition products cyclize to 4-aminopyridines when the reaction is run below −50 °C. From reactions performed over 0 °C pyrimidines arising from addition of 2 mol of nitriles are isolated. Owing to the polar conditions employed, a side metalation reaction is observed with aliphatic nitriles. On the other hand, the α′-addition products can be isolated in neutral conditions but they cyclize to 4-pyridinones in strong acidic media.

The reaction of anions and dianions with nitriles has been widely employed for the synthesis of pyridine derivatives. The aim of these syntheses is generally the preparation of 1,5-diamino derivatives of 5-imino ketones. For example, the former intermediate is obtained from addition to nitriles of metalated α,β-unsaturated imines[1] or of 2-methyleneallyl dianion.[2] However, the utility of these reactions is restricted by the low yields in the first method and by the introduction of 12 mol of the nitrile in the second one, which allows only the synthesis of pyridines with two identical substituents in the 2- and 6-positions, respectively. 5-Imino ketones can be prepared by reaction of β-diketone dianions with nitriles in liquid ammonia,[3] but the reaction is limited to symmetrical ketones because of regioselectivity problems. Acetoacetonitrile dianion reacts with nitriles as well,[4] but this reaction works well only with a few nitriles. Another approach to the synthesis of pyridine derivatives involves metal-promoted addition of nitriles to the intercarbonylic methylene of β-dicarbonyls.[5]

We recently used dianions of the β-(monoalkylamino)-α,β-unsaturated ketones as versatile intermediates for the regioselective alkylation of the α′- and γ-positions of unsymmetrical acyclic 1,3-dicarbonylic derivatives.[6] The γ-dianions **2** and the α′-dianions **3** were generated by treatment with MeLi/TMEDA (γ-conditions) or LTMP (α′-conditions), respectively (Scheme I). Anilino derivatives were found to prevent competitive equilibration of the α′-dianion into the most stable γ-isomer.[6b].

These findings and the ready availability of the starting materials suggested the reaction of γ- and α′-dianions with nitriles to be a suitable route to the synthesis of 4-pyridinamines or 4-pyridinones, respectively.

In this paper, we report the results of the addition of nitriles at both the γ- and the α′-position of β-(monoalkylamino)-α,β-unsaturated ketones.

When a solution of a nitrile **4** is added to a solution of γ-dianion **2**[6] at −50 °C, followed by quenching with saturated ammonium chloride, 4-pyridinamines **7** are obtained in good to high yields (Scheme II, Table I).

It is noteworthy that a large variety of enaminones can be employed in this reaction. In fact, under the γ-conditions, detectable amounts of products arising from attack at the α′-position have never been found. The isopropylimino derivative of ethyl acetoacetate **1e** gives the interesting 4-amino-2-pyridinone system.

α,β-Unsaturated nitriles such as cinnamonitrile give mainly conjugate addition products. Tertiary nitriles such as pivalonitrile failed to yield pyridines, and reactants were

Scheme I

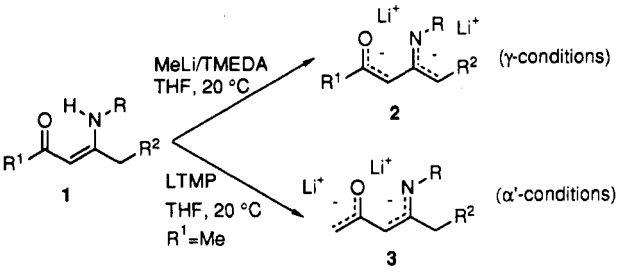

Table I. Reaction between γ-Dianions 2 and Nitriles 4 in THF at −50 °C for 15 min Followed by Quenching with Ammonium Chloride

dianion	nitrile	pyridine	yield (%)
2a	**4a**	**7aa**	70
2a	**4b**	**7ab**	84
2a	**4c**	**7ac**	90
2a	**4d**	**7ad**	83
2a	**4e**	**7ae**	57[a]
2a	**4f**	**7af**	51[b]
2a	**4g**	**7ag**	0[c]
2b	**4a**	**7ba**	84
2c	**4a**	**7ca = 7ab**	63
2d	**4a**	**7da**	95
2e	**4a**	**7ea**	80

[a] Based on 58% reacted enaminone. [b] Based on 34% reacted enaminone. [c] After 48 h starting materials were recovered.

† Part 2: ref 6b.
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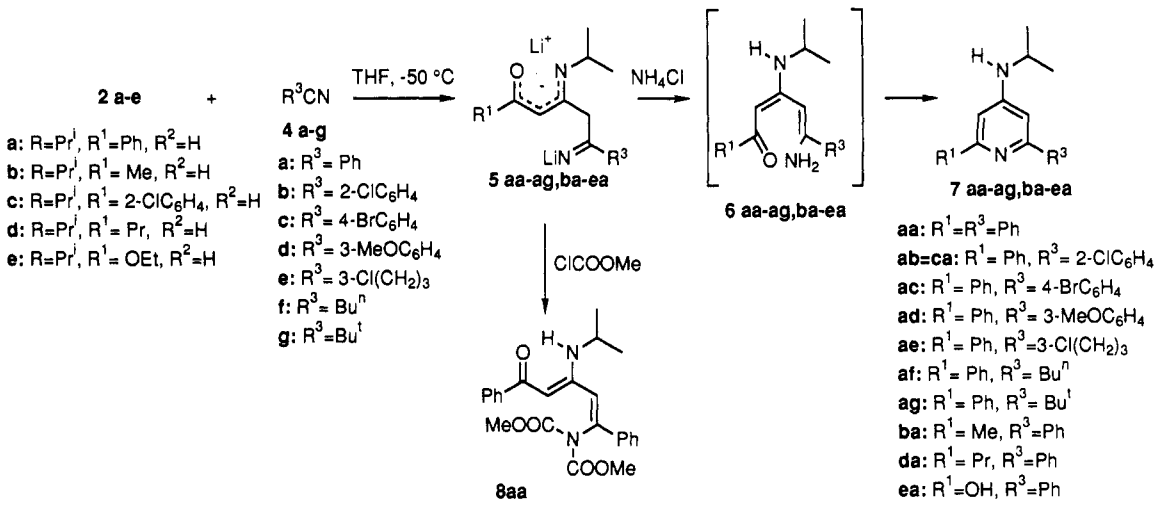
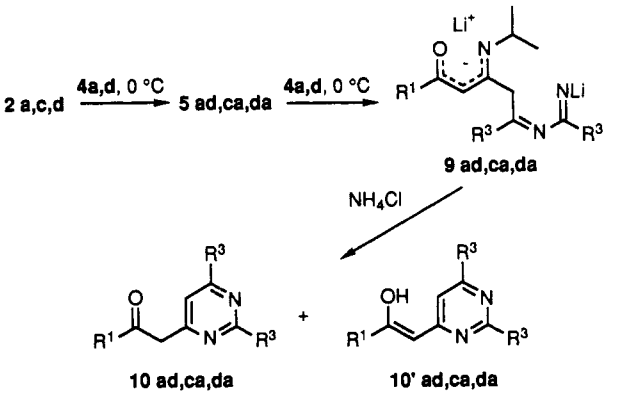
Scheme II



Scheme III



recovered unaltered after 48 h. Owing to the very polar conditions employed, aliphatic nitriles undergo competitive proton abstraction from the dianion leading to a mixture of starting materials and pyridine. The separation of the products can be easily accomplished, and the yields of recovered pyridine calculated with respect to reacted enaminone are good. Competitive transmetalation[1,2,4] and steric requirements[4] are common features of many syntheses of pyridines involving reactions of anions or dianions with nitriles.

The reaction seems to proceed as depicted in Scheme II. The cyclization step occurs only after quenching of the lithium salt **5** with ammonium chloride. In fact, the addition of methylchloroformate to the solution of **5aa** leads to the isolation of the linear derivative **8aa**.[7] The cyclization is faster than hydrolysis of the imino and enamino functions even when the mixture is quenched with 10% hydrochloric acid. In fact, pyridinamine **7aa** was recovered in 72% yield under these conditions.

Finally, the temperature drastically influences the reaction course. At 0 °C and higher, a completely different reaction pathway was observed. Quenching of the mixture and separation of the main product by chromatography allowed pyrimidines arising from incorporation of 2 mol of nitrile to be isolated in good yields (Scheme III).

The molar ratio between enaminone and nitrile does not influence the reaction course. In fact, over 0 °C a deficit of nitrile causes starting enaminone to be isolated together with pyrimidine, whereas below −50 °C the exclusive formation of pyridine was observed even with an excess of nitrile (Table II).

Very likely under the strongly polar conditions employed, the intermediate **5** is able to add to another mole of nitrile to give **9**. Subsequent cyclization and elimination of isopropylamine affords the products **10**. Pyrimidines such as **10** were previously prepared by Claisen-like condensation of esters with the anion of 4-methylpyrimidines.[8]

(7) Attempts to trap intermediate **5** with methyl iodide or acetic anhydride were unsuccessful.

Table II. Reaction between γ-Dianions 2a,c,d and Nitriles 4 in THF at 0 °C for 15 min Followed by Quenching with Ammonium Chloride

dianion	nitrile	molar ratio 4:2	yield (%) 10	yield (%) 7	enol vs keto ratio
2a	**4d**	2.5:1	84 (**ad**)		100:1
2a	**4d**	1.5:1[a]	51 (**ad**)		
2a	**4d**	2.5:1[b]		82 (**ad**)	
2c	**4a**	2.5:1	62 (**ca**)		100:1
2d	**4a**	2.5:1	70 (**da**)		1:2

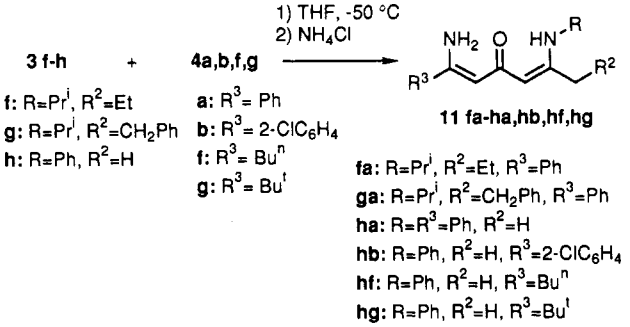
[a] 25% of starting enaminone is recovered. [b] Carried out at −50 °C.

Table III. Yields and Relevant Physical Data of Products from the Reaction between α′-Dianions 3 and Nitriles 4 in THF at −50 °C for 15 min Followed by Quenching with Ammonium Chloride

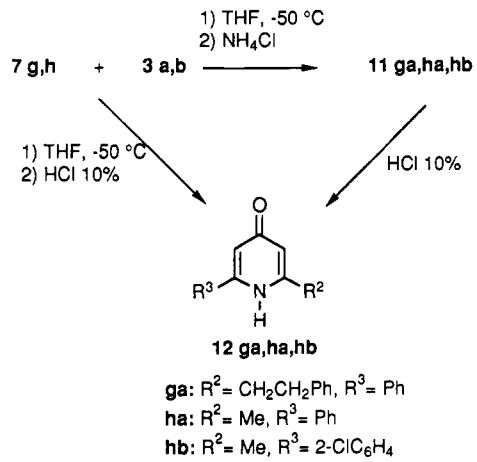
dianion	nitrile	product	yield (%)	$\delta_{H\alpha}$ and $\delta_{H\alpha'}$	δ_{NH}	$\delta_{C=O}$
3f	**4a**	**11fa**	87	4.85, 5.20	10.55	191.15
3g	**4a**	**11ga**	84	5.29, 5.29	10.59	190.86
3h	**4a**	**11ha**	61	5.12, 5.29	12.40	191.42
3h	**4b**	**11hb**	88	5.00, 5.04	12.43	191.46
3h	**4f**	**11hf**	83	6.14, 6.15	12.17	180.72
3h	**4g**	**11hg**	0[a]			

[a] After 48 h starting materials were recovered.

Scheme IV



Scheme V



Direct cyclization of a suitable intermediate to pyrimidines of structure **10** has not been previously reported, and the present results are a novel approach to these compounds. When a solution of a nitrile is added to a solution of α'-dianion **2**[6] at −50 °C, followed by quenching with saturated ammonium chloride, the expected addition product is isolated in high yields (Scheme IV, Table III).

In contrast to γ-conditions and to the reaction of acetacetonitrile dianion,[4] no side metalation reaction is observed with aliphatic nitriles. Very likely, the absence of a strong complexing agent of the lithium ion makes the α'-dianion a better nucleophile than the γ-isomer. Moreover, the α'-position is less crowded than the γ. In fact, we demonstrated[6a] that under the γ-conditions the more stable conformation of the dianion **2** constrains both the alkyl group bound to the nitrogen atom and the α'-substituent to shield the γ-position.

On the other hand, under the α'-conditions only the hydrogen atom in the α-position hinders the reactive terminus of dianion **3** in its more stable conformation. Nevertheless, under these experimental conditions, the cyano group of pivalonitrile is too hindered to be attacked and no reaction occurs.

As expected on the basis of the previous findings,[6b] the *N*-phenyl substituent prevents the formation of pyridines arising from attack at the γ-position. Moreover, it should be noted that an alkyl chain except methyl in the γ-position delays equilibration of the kinetic α'-dianion into the more stable γ-isomer enough to avoid formation of γ-derivatives.

During chromatographic separation of products **11**, a partial decomposition on silica gel was observed, which required some care to be taken in the workup (see Experimental Section). After 48 h on silica gel, the almost quantitative conversion of **11** into a 4-pyridinone derivative **12** was observed. Otherwise, the cyclization of **11** to **12** was complete in about 45 min in a 10% methanolic hydrochloric acid solution (Scheme V). Pyridinones can be recovered as well in comparable overall yields in a one-pot procedure by quenching the mixture of enaminone dianion and nitrile with hydrochloric acid (Table IV).

Notwithstanding the presence of two different amino groups, cyclization proceeds always via conjugate addition of the unsubstituted amino function to the α,β-unsaturated ketone, followed by elimination of either aromatic or aliphatic primary amine bound to the β-carbon atom. In contrast, it is reported that in the acid-catalyzed cyclization of diketoenamines a different cyclization pathway is followed by aliphatic or aromatic amines,[9] leading to pyridinones or pyranones, respectively.

Table IV. Yields of 4-Pyridinones: Comparison between Method A and Method B

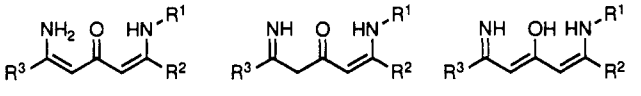
pyridinone	method A[a] overall yield[c] (%)	method B[b] yield[c] (%)
12ga	60	62
12ha	55	52
12hb	59	73

[a] Reaction carried out in two stages: preparation of the straight-chain derivative **11**, followed by isolation and cyclization in 10% hydrochloric acid in methanol. [b] Reaction carried out in a single stage, quenching the mixture from the reaction of nitrile and α'-dianion with 10% aqueous hydrochloric acid. [c] Calculated on starting enaminone **1**.

Characterization of Compounds. All compounds were identified essentially by their NMR spectra. However, some points should be outlined.

Pyrimidines like **10** are reported[8] to exist in the keto form. However, both ^{1}H- and ^{13}C-NMR of the prepared pyrimidines show that 4-phenacylpyrimidines are essentially present in solution in the enol form **10'ad,ca** rather than in the corresponding keto form **10**, very likely owing to a more extended conjugation which stabilizes the former tautomer. On the other hand, when R^1 is an alkyl chain as in **10da**, the keto tautomer accounts for 66% of the mixture (Table II).

Compounds **11** can exist as a combination of possible tautomers. It is reported[10] that related macrocycles assume a configuration with two enaminic functions. Moreover, the products arising from reaction of β-dicarbonyls and nitriles at the intercarbonyl methylene were found to exist as β-enaminodiones rather than ketoimines.[11] All these structures were supported by X-ray diffraction data.[10a,11b]



11A **11B** **11C**

In the ^{1}H-NMR spectra of compounds **11** (Table III), the presence of a peak near 11 ppm is characteristic of the enaminone system,[6] and therefore tautomers different from **11A-C** can be ruled out. Moreover, the presence of two peaks near 5 ppm each accounting for only one hydrogen atom rules out tautomer **11B**. Finally, the ^{13}C-NMR signal near 190 ppm assigns the configuration **11A** to these products, at least in solution.

To confirm this assignment a single-crystal X-ray analysis of compound **11ha** was performed. It is interesting to note that the asymmetric unit is formed by as many as three molecules of **11ha**. The C–C, C–N, and C–O bond lengths are similar in all three molecules and comparable with those of similar molecules[10a] (Table V). The sequence short–long–long–short in the pattern of C1–C5 lengths supported the configuration **11A** for the molecules.

The three molecules are held together by weak hydrogen bonds. Other hydrogen bonds are found between neighboring molecules, and rows along which the compound

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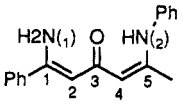
Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) for One of the Molecules $C_{18}H_{18}N_2O$ with esd's in Parentheses. Complete Data for All Three Molecules Are Available as Supplementary Material



bond lengths		bond angles	
O(1)–C(3)	1.276 (9)	C(5)–N(2)–C(13)	130.9 (6)
N(1)–C(1)	1.345 (9)	N(1)–C(1)–C(7)	116.0 (6)
N(2)–C(5)	1.341 (9)	N(1)–C(1)–C(2)	122.9 (6)
N(2)–C(13)	1.422 (8)	C(7)–C(1)–C(2)	121.1 (6)
C(7)–C(1)	1.501 (9)	C(1)–C(2)–C(3)	124.0 (6)
C(1)–C(2)	1.358 (10)	O(1)–C(3)–C(2)	121.4 (6)
C(2)–C(3)	1.447 (9)	O(1)–C(3)–C(4)	120.3 (6)
C(3)–C(4)	1.435 (10)	C(2)–C(3)–C(4)	118.3 (6)
C(4)–C(5)	1.353 (9)	C(3)–C(4)–C(5)	126.1 (6)
C(5)–C(6)	1.494 (10)	N(2)–C(5)–C(4)	120.3 (6)
		N(2)–C(5)–C(6)	118.6 (6)
		C(4)–C(5)–C(6)	121.1 (6)

grows may be identified. These rows are held together only by weak van der Waals interactions. On the contrary, a related macrocyclic structure[10a] shows intramolecular and no intermolecular hydrogen bonds. Conversely, from macrocycles in which the N1–C1–C2–C3–O1–C4–C5–N2 atoms lie in a plane, in **11ah** two plaines can be observed with a dihedral angle of 6–11° depending on the molecule. The phenyl rings, which are all practically planar, form different angles with respect to the central moiety in the three molecules (supplementary material).

In conclusion, the reaction of nitriles with dianions of β-(monoalkylamino)-α,β-unsaturated ketones can be employed to synthesize three different pharmaceutically important[12] six-membered azaheterocycles. The ready availability of the starting materials and the relatively mild reaction conditions employed make this method competitive with known ones.[13]

Experimental Section

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ solutions. J values are given in Hz. Melting points are uncorrected. THF was dried by refluxing over sodium wires until the blue color of benzophenone ketyl persisted and then distilled into a dry receiver under nitrogen atmosphere. LTMP was prepared by equimolecular amounts of butyllithium and amine in THF at 0 °C. Commercial methyllithium solutions (Aldrich) were employed under dry atmosphere and were titrated before use. Commercial compounds (Aldrich) were distilled and dried over molecular sieves before use. Isopropylacetonimine was synthesized according to the literature.[14]

1-Phenyl-3-(*N*-isopropylamino)but-2-en-1-one (**1a**), 4-(*N*-isopropylamino)pent-3-en-2-one (**1b**), and ethyl 3-(*N*-isopropylamino)but-2-enoate (**1e**) were synthesized according to Singh and Tandom's procedure.[15] 4-(*N*-Phenylamino)pent-3-en-2-one (**1h**) was synthesized according to Boatman and Hauser's procedure.[16] 2-(*N*-isopropylamino)hept-2-en-4-one (**1d**) and 1-(2-chlorophenyl)-3-(*N*-isopropylamino)but-2-en-1-one (**1c**) were prepared from metalated isopropylacetonimine and the appropriate esters according to our procedure.[17] 4-(*N*-Isopropylamino)hept-3-en-2-one (**1f**) and 6-phenyl-4-(*N*-isopropylamino)hex-3-en-2-one (**1g**) were prepared from the γ-dianion of **1b** and the appropriate bromide according to our procedure.[6a] γ- and α′-dianions were prepared as described.[6]

Reaction of the γ-Dianion with Nitriles. A. Synthesis of 4-Pyridinamines. A THF solution of the appropriate nitrile **4** (8 mmol) was added to a cooled (−50 °C) solution of the γ-dianion **2** (5 mmol), and the mixture was allowed to stir for 15 min under a nitrogen atmosphere. The solution was poured into saturated aqueous ammonium chloride and extracted with Et_2O. The organic layer was dried and evaporated under reduced pressure and the residue submitted to a chromatographic separation with silica gel (hexane:ether = 1:1 as eluant). The reaction mixture arising from dianion **2a** and nitrile **4a** was quenched with 10% HCl, neutralized with saturated $NaHCO_3$, and then treated as above. The pyridinamine **7aa** was recovered in 72% yield.

Yields are reported in Table I. Physical data follow.

2,6-Diphenyl-*N*-isopropyl-4-pyridinamine (**7aa**): mp 85–6 °C; IR (CCl_4) 3428 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 1.30 (d, J = 6.24, 6 H, Me), 3.86 (d, hept, 1 H, CH), 4.11 (d, J = 10, 1 H, NH), 6.83 (s, 2 H, H3, H5), 7.34–7.68 (m, 6 H, ArH) 8.00–8.30 (m, 4 H, ArH); MS m/z 288 (M^+, 63), 273 (100), 246 (8), 231 (4), 219 (4). Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.3; H, 7.0; N, 9.7. Found: C, 83.1; H, 7.1; N, 9.8.

2-(2-Chlorophenyl)-*N*-isopropyl-6-phenyl-4-pyridinamine (**7ab** = **7c**): oil; IR (CCl_4) 3429 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 1.24 (d, J = 6.32, 6 H, Me), 3.75 (d, hept, 1 H, CH), 4.22 (d, J = 10, 1 H, NH), 6.69 (d, J = 2, 1 H, H3 or H5), 6.81 (d, J = 2, 1 H, H5 or H3), 7.28–7.52 (m, 6 H, ArH), 7.67–7.75 (m, 1 H, ArH), 7.96–8.05 (m, 2 H, ArH); MS m/z 324 (M^+ + 2, 20), 322 (M^+, 59), 307 (100), 280 (15), 253 (4). Anal. Calcd for $C_{20}H_{19}ClN_2$: C, 74.4; H, 5.9; N, 8.7. Found: C, 74.2; H, 6.0; N, 8.8.

2-(4-Bromophenyl)-*N*-isopropyl-6-phenyl-4-pyridinamine (**7ac**): mp 96–97 °C; IR (CCl_4) 3429 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 1.27 (d, J = 6.3, 6 H, Me), 3.81 (m, 1 H, CH), 4.15 (bs, 1 H, NH), 6.76 (d, J = 1, 1 H, H3 or H5), 6.81 (d, J = 1, 1 H, H3 or H5), 7.33–7.53 (m, 3 H, Ph), 7.57 (d, J = 8.6, 2 H, 4-BrPh), 7.94 (d, J = 8.6, 2 H, 4-BrPh), 8.00–8.09 (m, 2 H, Ph); MS m/z 368 (M^+ + 2, 67), 366 (M^+, 67), 353 (100), 351 (99), 324 (11), 272 (4), 245 (3). Anal. Calcd for $C_{20}H_{19}BrN_2$: C, 65.4; H, 5.2; N, 7.6. Found: C, 65.2; H, 5.3; N, 7.4.

N-Isopropyl-2-(3-methoxyphenyl)-6-phenyl-4-pyridinamine (**7ad**): mp 85–86 °C; IR (CCl_4) 3429 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 1.27 (d, J = 6.4, 6 H, Me), 3.87 (d hept, 1 H, CH), 3.89 (s, 3 H, OMe), 4.17 (d, J = 7.6, 1 H, NH), 6.79–6.82 (AB, 2 H, H3, H5), 6.98 (dd, J = 8, 1.5, 1 H, ArH), 7.34–7.74 (m, 6 H, ArH), 8.05–8.15 (m, 2 H, ArH); MS m/z 318 (M^+, 100), 317 (100), 303 (54), 288 (21). Anal. Calcd for $C_{21}H_{22}N_2O$: C, 79.2; H, 7.0; N, 8.8. Found: C, 79.0; H, 7.0; N, 8.9.

6-(3-Chloropropyl)-*N*-isopropyl-2-phenyl-4-pyridinamine (**7ae**): mp 100–101 °C; IR (CCl_4) 3428 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 0.85–0.96 (m, 2 H, $CH_2CH_2CH_2$), 1.04–1.14 (m, 2 H, $ClCH_2CH_2CH_2$) 1.22 (d, J = 6.22, 6 H, Me), 1.88–2.04 (m, 2 H, $ClCH_2CH_2CH_2$), 3.74 (d hept, 1 H, CH), 3.97 (d, J = 10, 1 H, NH), 6.22 (d, J = 2, 1 H, H3 or H5) 6.63 (d, J = 2, 1 H, H5 or H3), 7.32–7.47 (m, 3 H, ArH) 7.88–7.98 (m, 2 H, ArH); MS m/z 252 (M^+ − HCl, 100), 237 (28), 209 (13), 195 (6). Anal. Calcd for $C_{17}H_{21}ClN_2$: C, 70.7; H, 7.3; N, 9.7. Found: C, 70.9; H, 7.2; N, 9.7.

2-Butyl-*N*-isopropyl-6-phenyl-4-pyridinamine (**7af**): oil; IR (CCl_4) 3411 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 0.91 (t, J = 6, 3H, $Me(CH_2)_3$), 1.05–1.76 (m, 4 H, $Me(CH_2)_2CH_2$), 1.30 (d, J = 6.3, 6 H, Me), 2.72 (t, J = 7.2, 2 H, $Me(CH_2)_2CH_2$), 3.22–3.89 (m, 2 H, CH + NH), 6.25 (bs, 1 H, H3 or H5), 6.63 (bs, 1 H, H5 or H3), 7.35–7.41 (m, 3 H, ArH), 7.80–7.83 (m, 2 H, ArH); MS m/z 268 (M^+, 4), 253 (8), 239 (12), 226 (100), 211 (6), 184 (5). Anal. Calcd for $C_{18}H_{24}N_2$: C, 80.6; H, 9.0; N, 10.4. Found: C, 80.8; H, 8.9; N, 10.3.

N-Isopropyl-6-methyl-2-phenyl-4-pyridinamine (**7ba**): mp 90–91 °C; IR (CCl_4) 3450 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 1.25 (d, J = 6.28, 6 H, Me), 2.49 (s, 3 H, 6-Me), 3.80 (hept, J = 6.28, 1 H, CH), 4.02 (s, 1 H, NH), 6.27 (d, J = 1.9, 1 H, H3 or H5) 6.64

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(d, J = 1.9, 1 H, H5 or H3), 7.5–7.6 (m, 3 H, ArH) 7.85–7.90 (m, 2 H, ArH); MS m/z 226 (M^+, 46), 211 (100). Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.6; H, 8.0; N, 12.4. Found: C, 79.8; H, 7.9; N, 12.3.

N-Isopropyl-2-phenyl-6-propyl-4-pyridinamine (**7da**): oil, IR (CCl_4) 3428 cm^{-1} (NH); ^{1}H-NMR (200 MHz) δ 0.97 (t, J = 7.3, 3 H, $Me(CH_2)_2$), 1.19 (d, J = 6.4, 6 H, Me), 1.50–1.70 (m, 2 H, $MeCH_2CH_2$), 2.67 (t, J = 7.7, 2 H, $MeCH_2CH_2$), 3.22–3.89 (m, 1 H, CH), 4.28 (bs, 1 H, NH), 6.22 (bs, 1 H, H3 or H5), 6.61 (bs, 1 H, H5 or H3), 7.32–7.40 (m, 3 H, ArH), 7.81–7.91 (m, 2 H, ArH); MS m/z 254 (M^+, 10), 253 (8), 239 (20), 226 (100), 211 (5). Anal. Calcd for $C_{17}H_{22}N_2$: C, 80.3; H, 8.7; N, 11.0. Found: C, 80.4; H, 8.7; N, 10.9.

4-(*N*-Isopropylamino)-6-phenylpyrid-2-one (**7ea**): mp 237–238 °C; IR (CCl_4) 3438 (NH) 1638 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz) δ 1.20 (d, J = 6.4, 6 H, Me), 3.60 (d hept, 1 H, CH), 4.70 (d, J = 8, 1 H, Me_2CHNH), 5.44 (d, J = 1.1, 1 H, H3 or H5), 5.77 (d, J = 1.1, 1 H, H5 or H3), 7.38–7.60 (m, 6 H, ArH + NH); MS m/z 228.1259 (M^+ $C_{14}H_{16}N_2O$ requires 228.1263, 71), 213 (100), 186 (13), 170 (20).

The reaction of cinnamonitrile with dianion **2a** was carried out and worked up as described above. 1,5-Diphenyl-3-(*N*-isopropylamino)-6-cyanohex-2-en-1-one was isolated in 74% yield as an oil: IR (CCl_4) 2251 cm^{-1} (CN); ^{1}H-NMR (200 MHz) δ 1.15 (d, J = 6.2, 3 H, Me); 1.21 (d, J = 6.2, 3 H, Me), 2.70–2.90 (m, 4 H, CH_2CHCH_2), 3.16–3.32 (m, 1 H, CH_2CHCH_2), 3.65 (d hept, 1 H, CH), 5.55 (s, 1 H, CH=), 7.10–7.80 (m, 10 H, ArH), 11.38 (d, J = 8.8, 1 H, NH); MS m/z 332 (M^+, 20), 292 (18), 227 (11), 202 (100), 105 (85), 98 (21), 77 (20). Anal. Calcd for $C_{22}H_{24}N_2O$: C, 79.5; H, 7.3; N, 8.4. Found: C, 79.3; H, 7.4; N, 8.4.

Methyl chloroformate (20 mmol) was added to the cooled reaction mixture arising from enaminone **1a** and nitrile **4a**. The temperature was allowed to rise, and the mixture was then quenched with ammonium chloride. Workup and chromatographic separation with silica gel (hexane/ethyl acetate (1:1)) afforded 1,5-diphenyl-5-[*N*,*N*-bis(dimethoxycarbonyl)amino]-3-(*N*-isopropylamino)penta-2,4-dien-1-one (**8aa**) in 46% yield: mp 131–133 °C; IR (CCl_4) 1767, 1578 cm^{-1} (C=O); ^{1}H-NMR (200 MHz) δ 1.24 (d, 6 H, J = 6.2, Me), 3.71 (s, 6 H, OMe), 3.73 (d hept, 1 H, CH), 5.75 (s, 1 H, CH=), 6.61 (s, 1 H, CH=), 7.26–7.52 and 7.72–7.88 (m, 10 H, ArH), 11.10 (d, 1 H, J = 8.7, Pr^iNH); MS m/z 422.1864 (M^+, $C_{24}H_{26}N_2O_5$ requires 422.1842, 9), 379 (44); 317 (31); 290 (21); 274 (67); 105 (100); 77 (50).

B. Synthesis of Pyrimidines. A THF solution of the appropriate nitrile **4** (12.5 mmol) was added to a solution of the γ-dianion **2** (5 mmol) cooled in an ice bath, and the mixture was allowed to stir for 15 min under a nitrogen atmosphere. The mixture was worked up as described for pyridinamines to isolate pyrimidines **10** (hexane:Et_2O = 7:3 as eluant). When the reaction of dianion **2a** (5 mmol) and nitrile **4d** (12 mmol) was carried out at −50 °C, after workup, pyridinamine **7ad** was recovered in 82% yield and recognized by comparison with a sample synthesized as described above. No formation of the corresponding pyrimidine was detected by GC–MS or TLC analyses. When the reaction of dianion **2a** (5 mmol) and nitrile **4d** (8 mmol) was carried out at 0 °C, after workup, pyrimidine **10ad** was recovered in 51% yield together with 25% of enaminone **1a**. No formation of the corresponding pyridinamine was detected by GC–MS or TLC analyses.

Compounds **10ad** and **10ca** showed NMR spectra in agreement with the enol tautomer **10′**, while NMR spectra of pyrimidine **10da** showed the coexistence of both tautomers.

Yields are reported in Table II. Physical data follow.

2,6-Bis(3-methoxyphenyl)-4-(1-hydroxystyr-2-yl)pyrimidine (**10′ad**): mp 124–125 °C; ^{1}H-NMR (200 MHz) δ 3.92 (s, 3 H, MeO), 3.94 (s, 3 H, MeO), 6.18 (s, 1 H, CH=), 7.27 (s, 1 H, H5), 7.34–8.09 (m, 14 H, ArH + OH); relevant ^{13}C-NMR (200 MHz) δ 55.70 (q), 93.65 (d), 110.98 (d) 160.53 (s), 163.14 (s), 164.33 (s), 170.10 (s); MS m/z 410.1626 (M^+ $C_{26}H_{22}N_2O_3$ requires 410.1630, 99), 382 (34), 381 (28), 333 (10), 105 (100), 77 (49).

2,6-Diphenyl-4-(1-hydroxy-*o*-chlorostyr-2-yl)pyrimidine (**17ca**): mp 118–120 °C; ^{1}H-NMR (200 MHz) δ 5.99 (s, 1 H, CH=), 7.22 (s, 1 H, H5), 7.30–7.73 (m, 11 H, ArH + OH), 8.12–8.25 (m, 2 H, ArH), 8.40–8.55 (m, 2 H, ArH); relevant ^{13}C-NMR (200 MHz) δ 98.35 (d), 110.69 (d), 163.23 (s), 163.57 (s), 172.25 (s); MS m/z 386 (M^+, +2, 22), 384.1023 (M^+ $C_{24}H_{17}ClN_2O$ requires 384.1029, 56), 358 (16), 356 (42), 321 (92), 273 (31), 139 (100), 111 (30), 77 (49).

2,6-Diphenyl-4-(2-oxopent-1-yl)pyrimidine (**17da**): This compound exists as an equilibrium mixture of keto and enol tautomers in a 2:1 ratio, which gave a single spot by TLC analysis.

Mixture: mp 85–86 °C; MS m/z 316.15668 (M + $C_{21}H_{20}N_2O$ requires 316.15756; 39), 301 (11), 273 (18), 246 (100).

Keto tautomer: IR (CCl_4) 1718 cm^{-1} (CO); ^{1}H-NMR (200 MHz) δ 0.94 (t, J = 7.4, 3 H, $Me(CH_2)_2$), 1.68 (m, J = 7.4, 2 H, $MeCH_2CH_2$), 2.64 (t, J = 7.4, 2 H, $MeCH_2CH_2$), 3.99 (s, 2 H, CH_2), 7.12 (s, 1 H, H5), 7.45–7.76 (m, 10 H, ArH); relevant ^{13}C-NMR (200 MHz) δ 13.69 (q), 17.11 (t), 45.21 (t), 52.20 (t), 114.89 (d), 206.87 (s).

Enol tautomer: IR (CCl_4) 3420 cm^{-1} (OH); ^{1}H-NMR (200 MHz) δ 1.02 (t, J = 7.4, 3 H, $Me(CH_2)_2$), 1.69–1.80 (m, 2 H, $MeCH_2CH_2$), 2.36 (t, J = 7.2, 2 H, $MeCH_2CH_2$), 5.48 (s, 1 H, CH=), 7.26 (s, 1 H, H5), 7.45–7.76 (m, 11 H, ArH + OH); relevant ^{13}C-NMR (200 MHz) δ 13.85 (q), 20.17 (t), 39.07 (t), 95.06 (d), 109.75 (d), 178.08 (s).

Reaction of the α'-Dianion with Nitriles. A. Synthesis of Linear Products. A THF solution of the appropriate nitrile **4** (8 mmol) was added to a cooled (−50 °C) solution of the α'-dianion **3** (5 mmol), and the mixture was allowed to stir for 15 min under a nitrogen atmosphere. The solution was treated as described for pyridinamines (hexane/Et_2O (3:2) as eluant) to isolate compounds **11**. When the crude product was adsorbed on the silica gel before chromatography a loss of product and the formation of a new product was observed. If the crude product was allowed to stand for 48 h on silica only the new product was then separated. It was recognized as a 4-pyridinone derivative **12**. On the other hand, no formation of **12** was observed when the crude of reaction was submitted to the chromatographic purification without previous adsorption.

Yields and physical data for isolated compounds **11** follow.

1-Amino-5-(*N*-isopropylamino)-1-phenylocta-1,4-dien-3-one (**11fa**): 87%; mp 82.5–83.5 °C; IR (CCl_4) 3486, 3233 (NH_2) 1593 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz) δ 1.00 (t, J = 73.3 H, $Me(CH_2)_2$), 1.25 (d, J = 6.5, 6 H, Me), 1.60 (m, 2 H, $MeCH_2CH_2$), 2.19 (t, J = 7.3, 2 H, $MeCH_2CH_2$), 3.74 (d hept, 1 H, CH), 4.85 (s, 1 H, CH=), 5.20 (s, 1 H, CH=), 7.32–7.63 (m, 7 H, ArH + NH_2), 10.55 (d, J = 8.8, 1 H, ^{i}PrNH); ^{13}C-NMR (200 MHz) δ 14.21 (q), 22.33 (t), 24.59 (q), 34.42 (t), 44.38 (d), 95.86 (d), 97.96 (d), 126.59 (d), 129.12 (d), 129.87 (d), 139.52 (s), 156.79 (s), 164.00 (s), 191.15 (s); MS m/z 272 (M^+, 60), 229 (26), 214 (67), 185 (100), 146 (34), 126 (29). Anal. Calcd for $C_{17}H_{24}N_2O$: C, 75.0; H, 8.9; N, 10.3. Found: C, 75.2; H, 8.8; N, 10.3.

1-Amino-1,7-diphenyl-5-(*N*-isopropylamino)hepta-1,4-dien-3-one (**11ga**): 84%; oil; IR (CCl_4) 3486, 3234 (NH_2) 1584 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz) δ 1.25 (d, J = 6.2, 6 H, Me), 2.4–3.0 (m, 4 H, CH_2CH_2), 3.74 (d hept, 1 H, CH), 5.29 (s, 2 H, CH=), 7.2–7.7 (m, 12 H, ArH + NH_2), 10.59 (d, J = 9, 1 H, ^{i}PrNH); ^{13}C-NMR (200 MHz) δ 24.57 (q), 34.19 (t), 35.50 (t), 44.49 (d), 95.88 (d), 97.82 (d), 126.63 (d), 126.76 (d), 128.31 (d), 128.66 (d), 128.98 (d), 129.22 (d), 129.99 (s), 130.19 (s), 157.10 (s), 163.11 (s), 190.86 (s); MS m/z 334 (M^+, 46), 275 (66), 258 (24), 229 (28), 198 (87), 146 (55), 91 (39), 44 (100). Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.0; H, 7.8; N, 8.4. Found: C, 79.2; H, 7.9; N, 8.3.

1-Amino-5-(*N*-phenylamino)-1-phenylhexa-1,4-dien-3-one (**11ha**): 61%; mp 121–122 °C; IR (CCl_4) 3488, 3243 (NH_2) 1582 (CO) cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.07 (s, 3 H, Me), 5.12 (s, 1 H, CH=), 5.29 (s, 1 H, CH=), 7.10–7.70 (m, 12 H, ArH + NH_2), 12.40 (s, 1 H, NHPh); ^{13}C-NMR (200 MHz) δ 20.47 (q), 97.38 (d), 100.10 (d), 124.46 (d), 124.82 (d), 126.69 (d), 129.26 (d), 129.47 (d), 130.30 (d), 139.04 (s), 140.36 (s), 157.39 (s), 158.48 (s), 191.42 (s); MS m/z 278 (M^+, 21), 185 (100), 93 (74). Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.7; H, 6.5; N, 10.1. Found: C, 77.5; H, 6.5; N, 10.3.

1-Amino-1-(2-chlorophenyl)-5-(*N*-phenylamino)hexa-1,4-dien-3-one (**11hb**): 88%; mp 63.6–64.3 °C; IR (CCl_4) 3497, 3244 (NH_2) 1572 (CO) cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.03 (s, 3 H, Me), 5.00 (s, 1 H, CH=), 5.04 (s, 1 H, CH=), 7.02–7.57 (m, 11 H, ArH + NH_2), 12.43 (s, 1 H, NH); ^{13}C-NMR (200 MHz) δ 20.41 (q), 99.59 (d), 99.81 (d), 124.54 (d), 124.93 (d), 127.40 (d), 129.51 (d), 130.53 (d), 130.64 (d), 132.20 (s), 138.10 (s), 140.28 (s), 156.58 (s), 157.76 (s), 191.46 (s); MS m/z 314 (M^+ + 2, 11), 312 (M^+, 31), 220 (100), 184 (54), 118 (25), 93 (57), 77 (24). Anal. Calcd for $C_{18}HH_{17}ClN_2O$: C, 69.1; H, 5.5; N, 9.0. Found: C, 69.0; H, 5.5; N, 9.1.

6-Amino-2-(*N*-phenylamino)deca-2,5-dien-4-one (**11hf**): 83%; oil; IR (CCl_4) 3496, 3239 (NH_2) 1572 (CO) cm^{-1}; ^{1}H-NMR (200 MHz) δ 0.87 (t, J = 7.3, 3 H, $Me(CH_2)_3$, 1.2–1.7 (m, 4 H, $Me(CH_2)_2CH_2$), 2.31 (s, 3 H, Me), 2.55 (t, J = 7.6, 2 H, $Me(CH_2)_2CH_2$), 6.14 (s, 1 H, CH=), 6.15 (s, 1 H, CH=), 6.6–6.8 and 7.0–7.2 (m, 7 H, ArH + NH_2), 12.17 (br s, 1 H, NH); ^{13}C-NMR (200 MHz) δ 13.87 (q), 19.16 (q), 22.35 (t), 31.24 (t), 33.02 (t), 114.07 (d), 115.04 (d), 115.53 (d), 118.74 (d), 129.46 (s), 129.69 (d), 149.69 (s), 154.04 (s), 180.72 (s); MS m/z 258 (M^+, 48), 201 (19), 166 (100), 160 (86), 126 (61). Anal. Calcd for $C_{16}H_{22}N_2O$: C, 74.4; H, 8.6; N, 10.8. Found: C, 74.5; H, 8.7; N, 10.7.

B. Synthesis of 4-Pyridinones. Method A. Products **11ga, ha, hb** (2 mmol) were dissolved in 10 mL of 10% hydrochloric acid in methanol. The solution was stirred at room temperature for 45 min, evaporated, neutralized with aqueous $NaHCO_3$, extracted with ether, washed with water, dried, and evaporated under reduced pressure, and the residue submitted to a chromatographic separation with silica gel (hexane:ether:methanol = 2:2:1 as eluant).

Method B. A THF solution of the appropriate nitrile 4 (8 mmol) was added to a cooled (−50 °C) solution of the α'-dianion (5 mmol), and the mixture was allowed to stir for 15 min under a nitrogen atmosphere. The solution was poured into 10% aqueous HCl and then treated as described above.

Yields of compounds **12** are reported in Table IV. Physical data for isolated compounds **12** follow.

2-Methyl-6-phenyl-4(1*H*)-pyridinone (**12ha**) and 2-phenyl-6-(2-phenylethyl)-4(1*H*)-pyridinone (**12ga**) were recognized by comparison with data of literature.[3]

2-Methyl-6-(2-chlorophenyl)-4(1*H*)-pyridinone (**12hb**): mp 83–86 °C; IR (CCl_4) 3420 (NH) 1623 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.33 (s, 3 H, Me), 5.98 (d, J = 1.9, 1 H, H3 or H5), 6.05 (d, J = 1.9, 1 H, H5 or H3), 7.20–7.42 (m, 5 H, ArH + NH); MS m/z 221 (16), 219 (M^+, 47), 184 (100). Anal. Calcd for $C_{12}H_{10}NOCl$: C, 65.6; H, 4.6; N, 6.4. Found: C, 65.5; H, 4.7; N, 6.4.

X-ray Data Collection and Structure Refinement. Diffraction data were collected on a Siemens R3m/V automatic four-circle diffractometer, using a graphite-monochromated MoKa radiation. A 0.12 × 0.36 × 0.51 mm crystal was used for intensity data collection. Lattice parameters were obtained from least-squares refinement of the setting angles of 25 reflections in the $15 \leq 2\theta \leq 30°$ range. Lorentz-polarization corrections were applied to the intensity data.

The structures were solved by standard direct methods and subsequently completed by Fourier recycling. The full-matrix least-squares refinement was based on $|F_o|$. The non-hydrogen atoms, except C atoms of the phenyl groups, were refined anisotropically. All hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. The final R values were 0.069, R' = 0.079. The weighting scheme used in the last refinement cycles was $w = 1.0000/s^2(F_o) + 0.006000(F_o)^2$.

Solutions and refinements were performed with the SHELXL-PLUS system (1989).[18] The final geometrical calculations were performed with the PARST[19] program. Additional material is available from the Cambridge Crystallographic Data Centre.

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Supplementary Material Available: Conditions of crystallographic data collection and structure refinement, tables of atom coordinates, thermal parameters, relevant least-squares planes, possible H-bonds, and bond lengths and angles, and an ORTEP drawing and view of the cell (13 pages). This material is contained in many 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.

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Epoxidation of 5-(Tosylamido)-3-hexen-2-ol Derivatives. Stereochemical Assignment of Product Configuration by NMR and Molecular Mechanics Studies

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Epoxidation of *syn*- and *anti*-5-(tosylamido)-3-hexen-2-ol derivatives was studied using three different epoxidation reagents: (i) *m*-CPBA, (ii) *t*-BuOOH/VO(acac)$_2$, and (iii) *t*-BuOOH/Ti(O-*i*-Pr)$_4$. A method for the stereochemical assignment of the 3,4-epoxy-5-(tosylamido)-3-hexen-2-ol derivatives obtained was developed by the use of NMR spectroscopy.

Palladium-catalyzed 1,4-oxidations of conjugated dienes offer unique opportunities to obtain 1,4-stereocontrol in both cyclic and acyclic systems.[1-3] In particular, 1,4-chloroacetates and 1,4-diacetates obtained from such oxidations have proved useful in this respect, and recently their use for obtaining a *dual* 1,4-stereocontrol in acyclic systems was demonstrated.[4,5] In one application *syn*- and *anti*-amido alcohols **1** were transformed into cis 2,5- and trans 2,5-disubstituted pyrrolidines **2**, respectively, via hydrogenation and ring closure (Scheme I). The synthetic utility of this methodology would be further enhanced by stereoselective mono or dihydroxylation of the double bond prior to cyclization.[6] In this way stereodefined pyrrolidine

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