Table I. Molar Ratios of Monoamine Adducts vs 3

	ratio		ratio
4a:3	76:24	**4e:3**	81:19
4b:3	81:19	**4f:3**	90:10
4c:3	62:38	**4g:3**	77:23
4d:3	35:65	**4h:3**	22:78

stirred at room temperature until the solution became homogeneous, usually for 3–4 days. The reaction mixture was poured into 400 mL of water and extracted with ether. The ether layer was separated and washed with a 10% HCl aqueous solution. After separation of the aqueous from the ether layer, the hydrochloride salt of **4a–g** (1:1) gradually precipitated out from the aqueous solution. The crude salt was collected by filtration and dried in a vacuum oven overnight. The dry salt was then suspended in chloroform and extracted with a saturated aqueous sodium bicarbonate solution. The chloroform layer was separated, dried ($MgSO_4$), and concentrated in vacuo to give the free amine adduct **4a–g**. The diol **3** was isolated after drying ($MgSO_4$) and concentration of the ether layer in vacuo.

4a·HCl: mp 165–172 °C. **4a**: 51% yield; mp 120–122 °C (ethanol–water); IR (KBr) 3420, 1605, 1470, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 9 H), 2.3 (s, 6 H), 3.6 (s, 2 H), 6.9–7.2 (m, 4 H); exact mass calcd for $C_{18}H_{23}NO_2$ 285.1729, obsd 285.1725.

4b·HCl: mp 235–237 °C. **4b**: 46% yield; mp 144–146 °C (ethanol–water); IR (KBr) 3460, 2940, 1605, 1470, 1202, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5 (m, 6 H), 2.2 (s, 9 H), 2.5 (m, 4 H), 3.6 (s, 2 H), 6.9–7.3 (m, 4 H); exact mass calcd for $C_{21}H_{27}NO_2$ 325.2042, obsd 325.2062.

4c·HCl: mp 205–207 °C. **4c**: 43% yield; mp 162–163 °C (ethanol–water); IR (KBr) 3410, 2920, 1605, 1470, 1200, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9 (m, 4 H), 2.3 (s, 9 H), 2.6 (m, 4 H), 3.8 (s, 2 H), 6.9–7.3 (m, 4 H), 7.5 (br s, 2 H); exact mass calcd for $C_{20}H_{25}NO_2$ 311.1885, obsd 311.1885.

4d·HCl: mp 233–235 °C. **4d**: 30% yield; mp 117–118 °C (ethanol–water); IR (KBr) 3440, 2920, 1605, 1478, 1230, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3 (s, 9 H), 2.6 (m, 4 H), 3.7 (m, 6 H), 6.9–7.3 (m, 4 H); exact mass calcd for $C_{20}H_{25}NO_3$ 327.1834, obsd 327.1840.

4e·HCl: mp 175–178 °C. **4e**: 55% yield; mp 78–79 °C (purified through flash column chromatography using ether as the eluent); IR (KBr) 3400, 2930, 1600, 1470, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (m, 6 H), 1.0–1.8 (br m, 8 H), 2.1 (s, 3 H), 2.3 (s, 6 H), 2.5 (t, 4 H), 3.8 (s, 2 H), 6.9–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 15.4, 16.0, 20.6, 28.4, 53.1, 58.3, 121.6, 123.3, 124.3, 124.9, 126.8, 128, 131.6, 133.5, 151.2, 155.3; exact mass calcd for $C_{24}H_{35}NO_2$ 369.2668, obsd 369.2661.

4f·HCl: mp 258 °C dec. **4f**: 66% yield; mp 56–58 °C (flash column chromatography, ethyl acetate–methanol, 10:1); IR (KBr) 3430, 2885, 1605, 1475, 1200, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s, 9 H), 2.3 (s, 9 H), 3.95 (s, 2 H), 5.3 (br, 3 H), 7.0–7.3 (m, 4 H); exact mass calcd for $C_{20}H_{27}NO_2$ 313.2042, obsd 313.2053.

4g·HCl: mp 198–199 °C. **4g**: 45% yield; mp 98–99 °C (ethanol–water); IR (KBr) 3400, 2970, 1608, 1470, 1207, 1087 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, 6 H), 2.20 (s, 9 H), 2.54 (q, 4 H), 3.69 (s, 2 H), 6.89–7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 15.8, 16.1, 46.2, 57.1, 121.3, 124.3, 125.0, 126.8, 128.0, 131.5, 133.5, 151.5, 155.5; exact mass calcd for $C_{20}H_{27}NO_2$ 313.2042, obsd 313.2046; UV ($CHCl_3$) 275 (ϵ 20 100), 247 nm (18 100).

Preparation of 4h. In a round-bottom flask, ϵ-caprolactam (11.31 g, 0.1 mol), **2** (5.0 g, 0.021 mol), and NMP (100 mL) were heated at 120 °C for 1 day. The reaction mixture was poured into water and then extracted with ether. The organic layer was separated, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified through flash column chromatography using ether as the eluent. The first compound eluted was **3**, and the second one was **4h**: mp 224–225 °C; IR (KBr) 3440, 2930, 1610, 1590, 1480, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (br m, 6 H), 2.25 (s, 9 H), 2.50 (br m, 2 H), 3.45 (m, 2 H), 4.40 (s, 2 H), 7.1–7.2 (m, 4 H); exact mass calcd for $C_{22}H_{27}NO_3$ 353.1991, obsd 353.1987.

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A Simple Regiospecific Synthesis of Substituted Pyridines from 2-Aza 1,3-Dienes

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2-Aza 1,3-dienes have been used widely as synthons in the building of nitrogen six-membered rings, most of them through [4 + 2]-cycloaddition processes.[1] The ability of these systems to undergo reactions through their nitrogen atom is also well known. Thus, the formation of *N*-vinyl iminium salts[2] and the preparation of *N*-trimethylsilyldivinylamines[3] are processes described, in this context, in the literature.

In previous papers,[4] we have indicated the participation of unactivated 2-aza 1,3-dienes of the type **1** in Diels-Alder reactions with different heterodienophiles. Thus, for example, compounds **1** react with aldehydes **2** (X = O) by heating and/or in the presence of a Lewis acid to yield 1,3-oxazine derivatives **3**[4a] (see Scheme I). Surprisingly, when the reaction is carried out with aromatic aldehydes and trifluoroacetic acid, compounds identified as pentasubstituted pyridines were isolated as the only reaction products. The lack of general methods of synthesis of this type of pyridines[5,6] along with our own interest in the reactivity of 2-aza dienes **1** induced us to study this reaction more thoroughly.

In this paper, we report a new, simple, and regiospecific synthesis of substituted pyridines **4** by reacting 2-aza dienes **1** (R^1 = cyclohexyl, aryl; R^2 = alkyl) with aldehydes and aldimines **2** (X = O, NR^4) in the presence of catalytic amounts of trifluoroacetic acid. The reaction of 2-aza 1,3-dienes **1** (20 mmol), **2** (20 mmol), and trifluoroacetic acid (2 mmol) for 24 h in THF under reflux affords a crude residue, which consists exclusively of pentasubstituted pyridines **4**α or **4**β in high yields (see Scheme I and Table I).

The nature of the pyridine **4**α or **4**β (Scheme I) obtained is strongly dependent on the nature of X in **2**. Thus, symmetrical pyridines **4**α were the only products obtained when aldimines **2**[6] (X = NR^4) were used as starting material. The path to **4**α is most likely a direct condensation reaction between the aldimine and **1**, giving rise to the aza triene **5**. This can undergo an electrocyclic closure and loss of hydrogen to form **4**α.[7,8]

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(6) For aldimines similar results were obtained when trifluoroacetic acid was substituted by a Lewis acid (e.g. BF_3·Et_2O) as the catalyst. For aldehydes see ref 4a.

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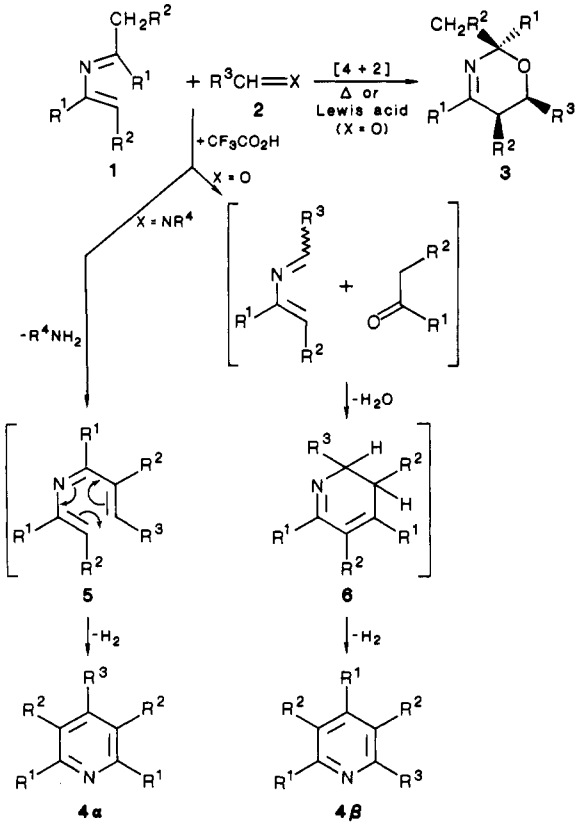
Table I. Pyridines 4 from 2-Aza 1,3-Dienes 1 and 2

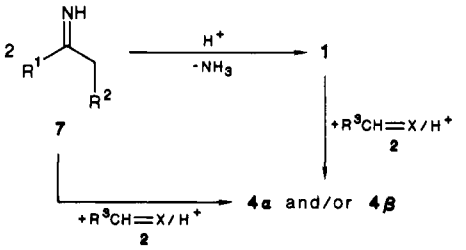
entry	compd[a]	R^1	R^2	R^3	X	yield, %	mp, °C
1	**4a**	Ph	Me	Ph	O	88	154–6[b]
2					NPh	75	154–6[b]
3	**4bβ**	Ph	Me	*p*-Me-C_6H_4	O	80	136–8
4	**4bα**				NPh	89	164–6
5	**4cβ**	Ph	Me	*p*-Cl-C_6H_4	O	88	170–2
6	**4cα**				NPh	91	200–2
7	**4dβ**	Ph	Me	*p*-MeO-C_6H_4	O	72	131–3
8	**4dα**				NPh	95	208–10
9	**4eβ**	*p*-Me-C_6H_4	Me	Ph	O	87	135–7
10	**4f**	*p*-Me-C_6H_4	Me	*p*-Me-C_6H_4	O	67	178–80
11	**4g**	Ph	Et	Ph	O	87	161–3
12	**4hβ**	*c*-C_6H_{11}	Me	*p*-Me-C_6H_4	O	72	114–6
13	**4iα**	Ph	Me	H	NCO_2Et	47[c]	133–5[d]

[a] All new compounds reported here gave satisfactor elemental analyses. [b] Lit.[7a] mp 155–6 °C. [c] Compound **9** (Scheme IV) was also obtained in a 40% yield (see ref 4b and the Experimental Section). [d] Lit.[7b] mp 136–7 °C.

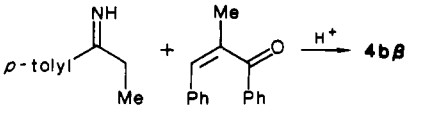
Scheme I



Scheme II



Scheme III



On the other hand, the reaction of **1** with aldehydes **2** (X = O) is, also, regiospecific, giving rise to the unsymmetrical regioisomer 4β. The formation of the unsymmetrically pyridine 4β can probably be explained as the result of a rapid ketimine-to-aldimine exchange and the subsequent condensation of the new aza diene and the displaced ketone. Pyridines 4β are obtained through the corresponding dihydropyridines **6** upon dehydrogenation.

Since 2-aza 1,3-dienes **1** are obtained from two molecules of imine,[4a] a further possibility for the synthesis of pyridines **4** (α or β) would be to circumvent the isolation of **1** by allowing **2** mol of imine **7** to react directly with 1 mol of **2** (Scheme II).

We have studied the above mentioned process, and we have found that the reaction of **7** (40 mmol), **2** (20 mmol), and trifluoroacetic acid (2 mmol) in THF at 80 °C for 30 h leads to the corresponding pyridines **4** in good yields (see the Experimental Section). However, if $R^1 \neq R^3$ (e.g. R^1 = Ph, R^3 = *p*-tolyl), a ~1.5:1 mixture of pyridines 4α and 4β is obtained, in all cases, regardless of the nature of X (Scheme II).

These facts indicate that the processes **1** + **2** → **4** and **2**(**7**) + **2** → **4** must proceed by different routes.

The obtention of **4** through the sequence **2**(**7**) + **2** → **4** can be easily explained by an initial aldol type condensation followed by elimination with formation of the not isolated α,β-unsaturated iminic compound, which then reacts with a second molecule of **7**. This reaction mechanism is supported by the following facts: (a) when **7** (R^1 = Ph, R^2 = Me), and **2** (X = O, R^3 = *p*-tolyl) are mixed in a 1:5 molar ratio, the reaction leads, after hydrolysis, to the corresponding α,β-unsaturated ketone (80%) as well as a small amount (12%) of a mixture of pyridines **4** (α and β); (b) the reaction of the α,β-unsaturated ketone, 2-methyl-1-phenyl-3-*p*-tolylprop-2-en-1-one,[9] and ethyl phenyl ketimine leads at the same results as those obtained through the sequence **2**(**7**) + **2** → **4** (see the Experimental Section).

The structure of pyridines **4** has been elucidated by elemental analyses and spectral characterization (see the Experimental Section). A further characterization was made by comparison of **4bβ** (Table I, entry 3) with a sample prepared by reacting 1,3-diphenyl-2-methylprop-2-en-1-one (10 mmol)[9] and ethyl *p*-tolyl ketimine (**7**, R^1 = *p*-tolyl, R^2 = Me) (10 mmol)[10] in the presence of CF_3CO_2H (5 mmol) (yield 70%)[11] (Scheme III).

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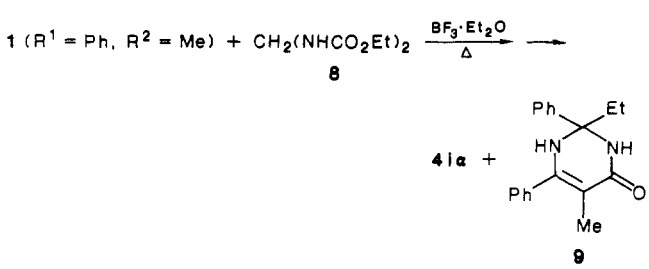
(11) In this case, only the pyridine **4bβ** was obtained with independence of whether the reaction proceeded by initial attack of the enaminic N or D atom. Frank, R. L.; Seven, R. P. *J. Am. Chem. Soc.* **1949**, *71*, 2629.

Scheme IV



The different behaviour of 1 in condensation and/or [4 + 2]-cycloaddition reactions can be illustrated in the reaction of 1 (e.g. R^1 = Ph, R^2 = Me), methylenebis(urethane) (8) and BF_3·Et_2O (ratio of 1:8:catalyst of 1:1:0.6). This reaction led to a readily separated 1:1 mixture of pyridine **4iα** (see Table I, entry 13) (a condensation process through the transient intermediate CH_2=NCO_2Et[12] and 1,2-dihydropyrimidin-4(3*H*)-one **9**,[4b] the adduct resulting from a [4 + 2]-cycloaddition between 1 and the isocyanic acid formed in situ from 8 (Scheme IV).

In conclusion, we describe a general, new, and simple method for the regiospecific synthesis of tetra- and pentasubstituted pyridines. In addition, the versatility and potentiality of 2-aza dienes 1 in organic synthesis is shown, not only in [4 + 2]-cycloaddition reactions,[4] but also in condensation processes.

Experimental Section

General Methods. Melting points are uncorrected. Infrared spectra were recorded with a Pye-Unicam SP-1000 spectrophotometer. The ^{1}H NMR spectra were determined on a Varian FT-80A with internal tetramethylsilane as the reference. The ^{13}C NMR were determined on a Varian FT-80A. Mass spectra were taken on a Hewlett-Packard 5930A spectrometer. Microanalysis were performed on a Perkin-Elmer Model 240 instrument.

Materials. 2-Aza 1,3-dienes 1 and imines 7 were prepared according to literature methods.[4a,10] All reactions were run under argon. All organic extracts were dried over anhydrous sodium sulfate. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under argon prior to use.[13] All other reagents were commercially available and were used as received.

General Preparative Procedure for Pyridines 4 from 1. To a solution of 2-aza 1,3-diene 1 (20 mmol) in THF (15 mL) were added compound 2 (X = O or NPh) (20 mmol) dissolved in 15 mL of THF and trifluoroacetic acid (5 mmol) at room temperature. When both additions were finished, the mixture was refluxed for 48 h, hydrolyzed with ice-cooled 3 N KOH, and extracted with ether. The organic layer was dried, filtered, and evaporated under reduced pressure (0.1 Torr) to afford an oily residue, which by washing with *n*-hexane or, in other cases, high-vacuum distillation (10^{-4} Torr), yields the pyridines 4 as white solids. Recrystallization from a hot mixture *n*-hexane–chloroform (6:1) produces pure pyridines 4α or 4β as crystalline white solids. Reactions yields and melting points are listed in Table I.

3,5-Dimethyl-2,4,6-triphenylpyridine (4a): IR (Nujol) 1550, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 6 H), 7.1–7.7 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 155.9, 151.4, 141.1, 139.4, 130.1–127.0, 17.9; MS, *m/e* 335 (M^+). Anal. Calcd for $C_{25}H_{21}N$: C, 89.55; H, 6.27; N, 4.18. Found: C, 89.43; H, 6.22; H, 4.16.

3,5-Dimethyl-2,4-diphenyl-6-*p*-tolylpyridine (4bβ): IR (Nujol) 1550, 760, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 6 H), 2.3 (s, 3 H), 7.0–7.7 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 156.0, 151.5, 141.3, 139.7, 138.4, 137.0, 129.2–126.8, 21.0, 18.0; MS, *m/e* 349 (M^+). Anal. Calcd for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01. Found: C, 89.40; H, 6.52; N, 4.12.

3,5-Dimethyl-2,6-diphenyl-4-*p*-tolylpyridine (4bα): IR (Nujol) 1550, 750, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 6 H), 2.4 (s, 3 H), 6.8–8.0 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 156.0, 151.7, 141.4, 136.8, 136.6, 129.4–127.3, 21.1, 18.0; MS, *m/e* 349 (M^+). Anal. Calcd for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01. Found: C, 89.43; H, 6.50; N, 4.07.

2,4-Dicyclohexyl-3,5-dimethyl-6-*p*-tolylpyridine (4hβ): ^{1}H NMR ($CDCl_3$) δ 0.8–3.6 (m, 31 H), 6.9–7.5 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 160.4, 155.4, 151.0, 139.2, 135.7, 128.8, 127.6, 125.3, 124.5, 41.3, 31.3, 29.1, 26.8, 26.2, 25.5, 20.4, 17.4, 14.7; MS, *m/e* 361 (M^+). Anal. Calcd for $C_{26}H_{35}N$: C, 86.42; H, 9.69; N, 3.88. Found: C, 86.35; H, 9.60; N, 3.84.

Spectral data for compounds **4cβ**, **4cα**, **4dβ**, **4dα**, **4eβ**, **4f**, and **4g** are included as supplementary material.

General Preparative Procedure for Pyridines 4 from Imines 7. To a solution of imine 7[10] (40 mmol) in THF (15 mL) were added compound 2 (20 mmol) dissolved in 15 mL of THF and trifluoroacetic acid (2 mmol) at room temperature. When both additions were finished, the mixture was refluxed for 48 h, treated with ice-cooled 3 N KOH, and extracted with ether. The organic layer was dried, filtered, and evaporated under reduced pressure (0.1 Torr) to afford an oily residue, which by washing with *n*-hexane yields pyridines 4.

Reaction of Ethyl Phenyl Ketimine and *p*-Methylbenzaldehyde or *p*-Methylbenzalaniline. By reaction of ethyl phenyl ketimine and compound 2 (R^3 = *p*-tolyl, X = O or NPh) a 65:35 mixture of pyridines **4bα** and **4bβ** (yield 70%) was obtained. Both regioisomers were separated by fractional recrystallization in *n*-hexane. For spectra data, see above.

Reaction of Ethyl Phenyl Ketimine and *p*-Anisaldehyde or *p*-Methoxybenzalaniline. By reaction of ethyl phenyl ketimine and compound 2 (R^3 = *p*-MeO-C_6H_4, X = O or NPh) a 62:38 mixture of pyridines **4dα** and **4dβ** (yield 75%) was obtained. Both regioisomers were separated by fractional recrystallization in *n*-hexane. For spectral data, see above.

Alternative Procedure for the Preparation of Pyridine 4bβ. Compound **4bβ** (70%) was obtained from ethyl *p*-tolyl ketimine (20 mmol), 2-methyl-1,3-diphenylprop-2-en-1-one[9] (20 mmol), and trifluoroacetic acid (10 mmol) by following the same procedure described in the preceding cases. For spectral date, see above.

Reaction of Compound 1 (R^1 = Ph, R^2 = Me) with Methylenebis(urethane) (8) and BF_3·Et_2O. BF_3·Et_2O (4 mmol) was added to a stirred solution of methylenebis(urethane) 8 (7 mmol) in 20 mL of dry toluene under argon. This mixture was stirred at 110 °C for 5 min, and then 1 (6 mmol) in 10 mL of dry toluene was added. The reaction mixture was stirred at 110 °C overnight, and a red solution was obtained. Then, the reaction mixture was washed twice with saturated $NaHCO_3$ and H_2O and dried. When the solvents were removed under reduced pressure (0.1 Torr), a yellow oil was obtained. Treatment of this oil with *n*-hexane–chloroform (5:1) afforded 2-ethyl-5-methyl-2,6-diphenyl-1,2-dihydropyrimidin-4(3*H*)-one **9** as a light yellow solid. By cooling the mother liquors, colorless crystals of 3,5-dimethyl-2,6-diphenylpyridine **4iα** were obtained.

2-Ethyl-2,6-diphenyl-5-methyl-1,2-dihydropyrimidin-4-(3*H*)-one (9): mp 193–5 °C; IR (KBr) 3360, 3330 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.7 (s, 3 H), 2.0 (m, 2 H), 4.7 (br s, NH exchangeable with D_2O), 6.6 (br s, NH exchangeable with D_2O), 7.2–7.7 (m, 10 H); ^{13}C NMR (DMSO-d_6) δ 168.6, 151.0, 148.9, 136.5, 133.5, 133.0–125.0, 96.2, 73.0, 34.1, 11.0, 8.5; MS, *m/e* 292 (M^+). Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.04; H, 6.91; N, 9.58. Found: C, 78.02; H, 6.85; N, 9.50.

3,5-Dimethyl-2,6-diphenylpyridine (4iα): ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 6 H), 7.4–7.8 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 155.7, 141.0, 129.2, 127.9, 127.6, 19.4; MS, *m/e* 259 (M^+). Anal. Calcd for $C_{19}H_{17}N$: C, 88.03; H, 6.59; N, 5.40. Found: C, 87.97; H, 6.52; N, 5.36.

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Registry No. **1e**, 106553-03-1; **1g**, 106553-02-0; **1h**, 117096-12-5; **1i**, 41860-07-5; **2a** (X = NPh), 538-51-2; **2a**, 100-52-7; **2bα**, 2362-77-8; **2bβ**, 104-87-0; **2cα**, 780-21-2; **2cβ**, 104-88-1; **2dα**, 836-

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41-9; **2dβ**, 123-11-5; **4a**, 78018-66-3; **4bα**, 117096-03-4; **4bβ**, 117096-02-3; **4cα**, 117096-05-6; **4cβ**, 117096-04-5; **4dα**, 117096-07-8; **4dβ**, 117096-06-7; **4eβ**, 117096-08-9; **4f**, 117096-09-0; **4g**, 117096-10-3; **4hβ**, 117096-11-4; **4iα**, 14435-89-3; **7** (R^1 = Ph, R^2 = Me), 29076-84-4; **7** (R^1 = *p*-tolyl, R^2 = Me), 94115-03-4; **8**, 3693-53-6; **9**, 116916-17-7; 2-methyl-1-phenyl-3-*p*-tolylprop-2-en-1-one, 78451-39-5; 1,3-diphenyl-2-methylprop-2-en-1-one, 4258-37-1.

Supplementary Material Available: Spectral data for **4cβ**, **4cα**, **4dβ**, **4dα**, **4eβ**, **4f**, and **4g** (2 pages). Ordering information is given on any current masthead page.

A One-Step Route to (*E*)-1,2-Bis(9-anthryl)ethene

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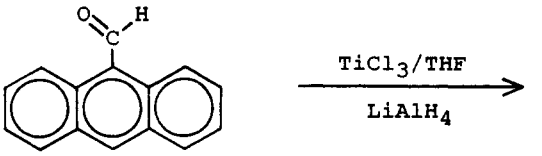
Recently there have been several groups interested in the structure and properties of sterically crowded alkenes.[1,2] Among these are the 1,2-bis(9-anthryl)ethenes, which are apparently not planar due to the steric interactions between the vinyl and the anthryl 1 and 1′ hydrogens.[2] The McMurry titanium coupling reaction[3] has shown remarkable utility for the synthesis of such compounds, having been used successfully for many of the compounds of interest.[1] However, in spite of the several routes noted in the literature for the preparation of 1,2-bis(9-anthryl)ethene,[4] the titanium coupling reaction has not been among them. We report here a simple one-step route to this compound from commercially available 9-anthraldehyde, thereby avoiding any prior preparation of difficult starting materials.

The low valent titanium coupling reaction has been described by McMurry[3] and others. The reaction is known to work well for a variety of ketones and aldehydes, even for the preparations of some of these crowded alkenes.[1] However, Geise[5] and Olah,[1d] for example, have noted some failure of the reaction for ketones where the carbonyl is excessively crowded sterically in its approach to the titanium surface. In these examples coupling either failed completely[1d,5] or led to a coupled symmetrical alkane,[5] where deoxygenation of the intermediate pinacol had occurred, but not to form the desired alkene. Lenoir[1a] made the only mention of a similar problem for an aldehyde, finding steric crowding for trimethylacetaldehyde. In this example the intermediate pinacol formed but was never deoxygenated to form the desired alkene or an alkane.

The primary goal of our research is the synthesis of electroactive polymers. We wished to apply the titanium coupling reaction to aromatic carbonyl compounds for the preparation of extended π-network systems. The 9-anthraldehyde (1) was chosen as a model compound. We felt that the steric requirements for 9-anthraldehyde would make it feasible to try this reaction as a quick route to the desired 1,2-bis(9-anthryl)ethene (2).

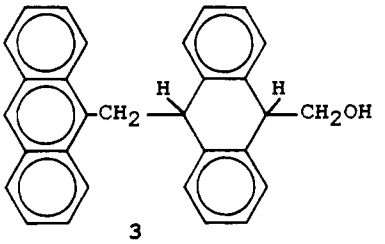


1

9-An-CH=CH-9-An

2

Interestingly, one other possible side reaction must be considered. It has been reported in the literature[6,7] that 9-anthraldehyde reacts with lithium aluminum hydride in THF to form an alcohol, but not the expected 9-(hydroxymethyl)anthracene (which is observed when the reaction is run in diethyl ether).[6] Instead a type of dimer forms, found to be 9-(hydroxymethyl)-10-(9-anthrylmethyl)-9,10-dihydroanthracene[7] (**3**), later proven by X-ray diffraction.[8] The earlier literature reports of 1,2-bis(9-anthryl)ethanol[6] were apparently in error.[7] In any event, our use of $LiAlH_4$ in THF for the coupling reaction meant a careful search for this other type of dimer must be made.



3

The experiment was run in the manner described by Geise.[5] One equivalent of $LiAlH_4$ (0.006 mol, 0.23 g) was added in small portions to 2 equiv of $TiCl_3$ (0.011 mol, 1.70 g) prechilled to 0 °C in 100 mL of THF (distilled from $LiAlH_4$ and stored over Na). This mixture was stirred for 30 min cold and then was raised to reflux for another 30 min. The 9-anthraldehyde (2 equiv, 0.006 mol, 1.24 g, Aldrich) dissolved in 50 mL of THF was added dropwise, and refluxing was continued for 20 h (a) or for 211 h (b).[9] After the reaction mixture was quenched with 40 mL of 2 N HCl, the product began precipitating and was collected by vacuum filtration.

The yields of 1,2-bis(9-anthryl)ethene from reactions a and b were modest, 28% and 53%, respectively. In view of the known twist of the anthracenes out of the plane of the ethylene[2] this is a fairly sterically crowded olefin. It was therefore noteworthy to achieve even these modest yields, if one considers the failure of this reaction to form the olefin from trimethylacetaldehyde, as reported by Lenoir[1a] to stop at the diol. The other sterically crowded olefin syntheses typically have low yields, cf. the yield observed by Olah[7] for the tetraneopentylethylene of 38%. Without further purification our 1,2-bis(9-anthryl)ethene had a melting point of 335–340 °C (lit. mp 350,[4c] 338,[4a] and

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(9) Authors' note: results from a similar molecule indicated that no significant improvements in yield could be seen prior to at least 5 days of reaction time.

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