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Treatment of heterocyclic *o*-aminonitriles and *o*-aminoesters **1a-5a** with dibromotriphenylphosphorane gives iminophosphoranes **1b-5b** which undergo a facile aza-Wittig reaction at room temperature with phenyl isocyanate to provide the carbodiimides **1c-5c**. Treatment of the latter intermediates with ammonia leads to intramolecular ring closure of the initially formed guanidines to provide the fused 4-aminopyrimidines and 4(3*H*)-pyrimidinones **1d-5d**.

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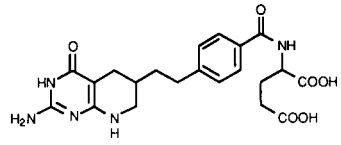
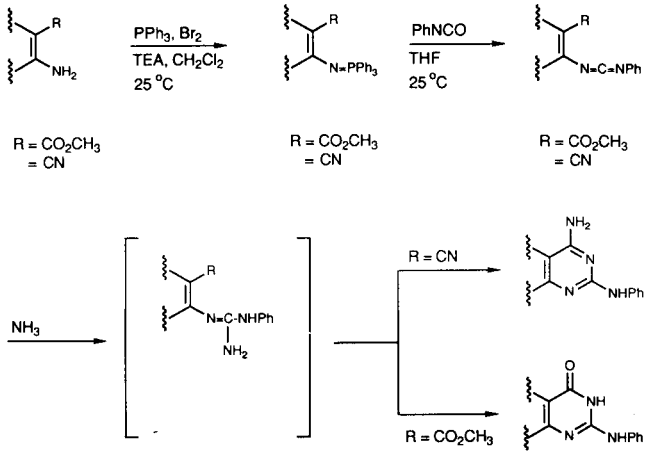
Fused pyrimidines are found in a broad variety of natural products [*e.g.*, purines, pyrrolopyrimidines, pteridines], pharmaceuticals, agrochemicals, and veterinary products [1]. Our current interest in this class of compounds stems from ongoing efforts directed towards the development of second generation folate antimetabolites. During the course of synthetic endeavors directed towards



DDATHF

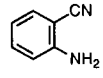
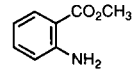
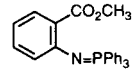
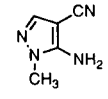
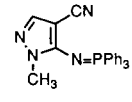
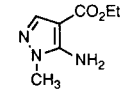
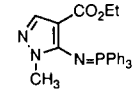
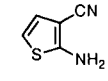
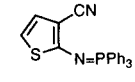
the preparation of 5,10-dideazatetrahydrofolic acid (DDATHF) and its analogs [2], we have developed a facile pyrimidine annulation process which takes place under mild conditions, and which appears to be general for *o*-aminonitriles and for *o*-aminoesters (Scheme I).

Scheme I



Recent literature has discussed in depth the synthetic utility of iminophosphoranes for the preparation of amines, amides and fused heterocyclic systems containing an endocyclic C=N bond [3,4]. Treatment of *o*-aminoesters and *o*-aminonitriles with dibromotriphenylphosphorane (generated *in situ* by slow addition of bromine to a cold solution of triphenylphosphine in methylene chloride) resulted in formation of the corresponding iminophosphoranes (Table I) [5]. It is well known that iminophosphoranes undergo aza Wittig reactions with isocyanates to give carbodiimides [6]. In the case of iminophosphoranes derived from *o*-aminoesters. Wamhoff and co-workers found that the initially formed carbodiimides underwent

Table I. The Preparation of Iminophosphoranes [a]

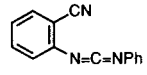
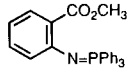
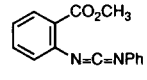
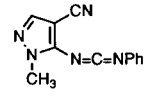
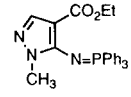
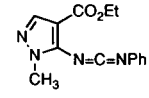
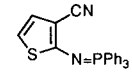
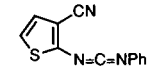
Entry	Substrate	Time	Product	Yield
1.	 **1a**	18 h	 **1b**	93 %
2.	 **2a**	4 h	 **2b**	85 %
3.	 **3a**	20 h	 **3b**	77 %
4.	 **4a**	16 h	 **4b**	48 %
5.	 **5a**	20 h	 **5b**	87 %

(a) All reactions were carried out in methylene chloride at room temperature

a pericyclic rearrangement in alcoholic solvents to give 2-alkoxy fused pyrimidines [7]. It seemed to us that this re-

arrangement was probably the consequence of the rather severe reaction conditions (80°, 4-8 hours) employed for the carbodiimide synthesis, and that the latter intermediates might be isolable under milder conditions. This supposition proved to be the case. The aza-Wittig reactions of iminophosphoranes **1b-5b** with phenyl isocyanate were carried out at room temperature, which permitted isolation in good yields of the corresponding carbodiimides (Table II) [8]. [In contrast, the use of aryl isothiocyanates under similar reaction conditions failed in every case to generate the desired carbodiimides]. Addition of ammonia to the resulting highly reactive carbodiimides **1c-5c** generated intermediate guanidino-substituted intermediates which underwent intramolecular cyclization across the *ortho*-situated electrophilic nitrile or ester functionalities to give the fused pyrimidines **1d-5d** (Schemes II-IV). In examples **2c** and **5c**, spontaneous closure *at room temperature* to **2d** and **5d** respectively occurred [9]. With carbodiimides **1c** and **3c**, the poor solubility of the derived guanidines in tetrahydrofuran reduced the rate of cyclization so that subsequent heating in methanol was required to effect cyclization. In the case of **4c**, cyclization was greatly facilitated by addition of sodium ethoxide. The intermediate guanidines derived from addition of ammonia to the carbodiimides **3c** and **4c** could be isolated and characterized, thus confirming the suggested reaction pathway [10].

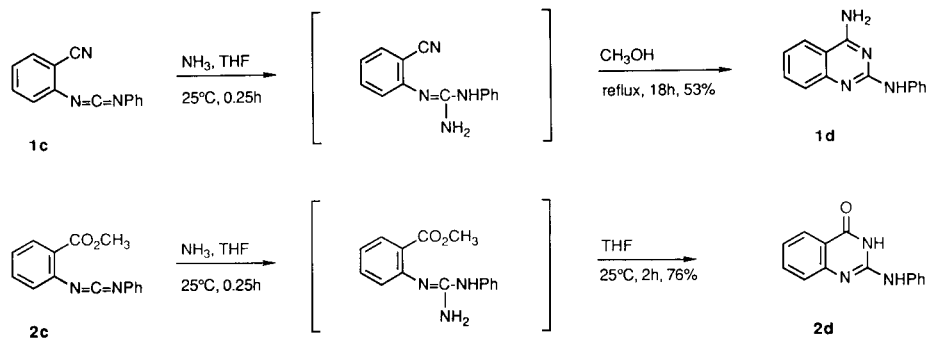
Table II. The Aza-Wittig Reaction: Preparation of Carbodiimides [a]

Entry	Substrate	Time	Product	Yield
1.	 **1b**	0.25 h	 **1c**	90 %
2.	 **2b**	1 h	 **2c**	64 %
3.	 **3b**	1 h	 **3c**	64 %
4.	 **4b**	1 h	 **4c**	81 %
5.	 **5b**	1 h	 **5c**	74 %

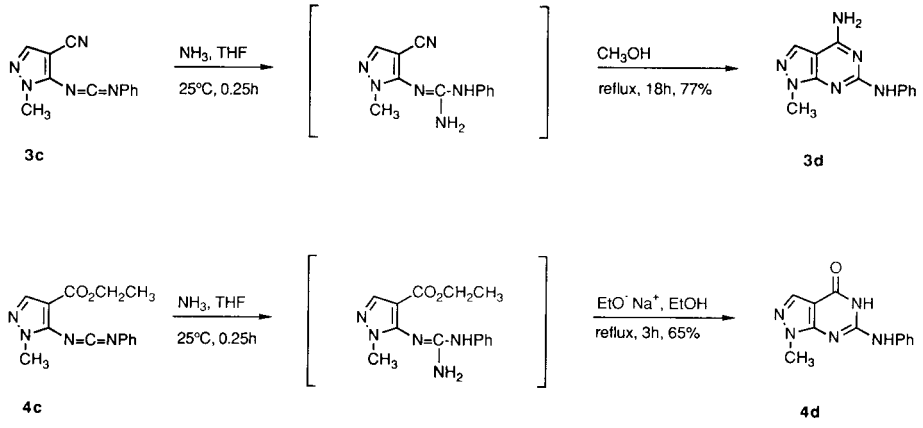
(a) All reactions were carried out in tetrahydrofuran at room temperature

The classical procedure which utilizes guanidine for the conversion of *o*-aminonitriles and *o*-aminoesters to fused pyrimidines probably involves initial acylation of the guanidine by the nitrile or ester functionality, followed by cyclization with loss of ammonia [11]. Since a more facile procedure for construction of an intermediate *o*-guanidino system might lead to cyclization under milder conditions, various procedures have been devised for the conversion of *o*-aminocarboxamides to fused 2-amino-4(3*H*)-pyrimidinones which involve, *inter alia*, treatment with (a) benzoyl isothiocyanate, followed by *S*-methylation and subsequent heating with ammonia [12,13], or (b) the carbodiimide formed from 1-(alkoxycarbonyl)-3-(benzyl)thioureas and phosgene/triethylamine, followed by reductive debenzylation, prolonged heating, and final removal of the ethoxycarbonyl protecting group with concentrated ammonium hydroxide/pyridine [14]. The present procedure generates under exceptionally mild conditions an *o*-guanidino functionality *which is not deactivated by electron-withdrawing protecting groups*, and which consequently cyclizes very readily to the fused pyrimidine. Extensions of

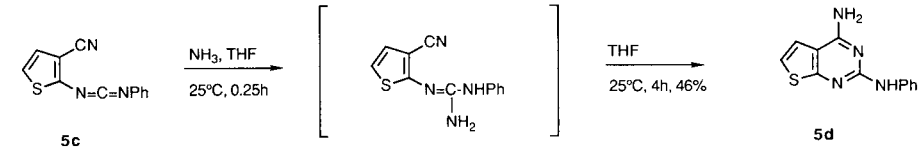
Scheme II



Scheme III



Scheme IV



this simple methodology utilizing appropriate isocyanates to the synthesis of DDATHF, its analogs and related fused pyrimidine systems will be reported in due course.

EXPERIMENTAL

General.

Melting points were determined in open capillary tubes using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on Nicolet 730 and 800 ftir spectrometers. The ^{1}H nmr spectra were recorded on a General Electric QE 300 MHz spectrometer. Mass spectral data were obtained on Kratos MS50TC and AEI MS-902 spectrometers. Column chromatography was performed by the procedure of Still *et al.* [15] using Merck silica gel 60 (240-400 mesh). Methyl anthranilate (**1a**) and anthranilonitrile (**2a**) were purchased from Aldrich Chemical Company.

General Procedure for the Preparation of Iminophosphoranes. 1-Methyl-4-cyano-5-[(triphenylphosphoranylidene)amino]pyrazole (**3b**) (Table I).

A solution of triphenylphosphine (7.37 g, 28.11 mmoles) in dichloromethane (120 ml) at 0° was treated with bromine (1.45 ml, 28.11 mmoles). The resulting reaction mixture was stirred at 0° for 5 minutes and then treated with triethylamine (7.82 ml, 56.22 mmoles) followed immediately by the addition of amine **3a** (3.43 g, 28.11 mmoles). The cooling bath was removed and the reaction mixture was allowed to stir at 25° for 20 hours. The reaction mixture was poured onto water (100 ml) and extracted with methylene chloride (3 x 100 ml). The combined extracts were dried over anhydrous sodium sulfate and concentrated *in vacuo*. Flash chromatography (silicon dioxide, 50% ether-hexanes eluant) gave 8.32 g (10.74 g theoretical, 77%) of **3b** as a pale yellow solid, mp 166-168°; ^{1}H nmr (deuteriochloroform, 300 MHz: δ 7.65-7.45 (m, 15 H), 7.38 (s, 1 H), 3.79 (s, 1 H); ir (potassium bromide): 2203, 1555, 1520, 1492, 1428, 1287, 1182, 1104, 1034, 991, 734, 689, 579, 548, 515 cm^{-1}; eims: m/z 382 (M$^+$, base), 313, 262, 183, 152, 108, 77; hrms: Calcd. for $C_{23}H_{19}N_4P$: 382.1347. Found: 382.1350.

2-[(Triphenylphosphoranylidene)amino]benzonitrile (**1b**) (Table I).

This compound was prepared in the same manner, and melted at 149-151°; ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.95 (m, 5 H), 7.65-7.45 (m, 11 H), 7.10 (t, 1 H, J = 8 Hz), 6.62 (t, 1 H, J = 8 Hz), 6.41 (d, 1 H, J = 8 Hz); ir (potassium bromide): 3041, 2210, 1576, 1471, 1435, 1344, 1273, 1146, 1104, 1034, 1006, 717, 576, 527, 492 cm^{-1}; eims: m/z 378 (M$^+$), 277 (base), 199, 183, 152, 133, 118, 91, 77; hrms: Calcd. for $C_{25}H_{19}N_2P$: 378.1286. Found: 378.1282.

Methyl 2-[(Triphenylphosphoranylidene)amino]benzoate (**2b**) (Table I).

This compound was prepared in the same manner and melted at 164-166°; ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.83-7.76 (m, 9 H), 7.65-7.52 (m, 1 H), 7.50-7.42 (m, 6 H), 6.90 (t, 1 H, J = 8 Hz), 6.65 (t, 1 H, J = 8 Hz), 6.51 (d, 1 H, J = 8 Hz), 3.88 (s, 3 H); ir (potassium bromide): 3048, 1710, 1583, 1471, 1365, 1287, 1217, 1091, 1034, 830, 766, 717, 696, 576, 534 cm^{-1}; eims: m/z 411 (M$^+$, base), 378, 352, 277, 201, 183, 78; hrms: Calcd. for $C_{26}H_{22}NO_2P$: 411.1388. Found: 411.1363.

Anal. Calcd. for $C_{26}H_{22}NO_2P$: C, 75.90; H, 5.39; N, 3.40; O, 7.78. Found: C, 75.74; H, 5.60; N, 3.62; O, 7.51.

1-Methyl-4-ethoxycarbonyl-5-[(triphenylphosphoranylidene)amino]pyrazole (**4b**) (Table I).

This compound was prepared in the same manner and melted at 148-150°; ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.8-7.40 (m, 16 H), 3.65 (q, 2 H, J = 7 Hz), 3.63 (s, 3 H), 0.95 (t, 3 H, J = 7 Hz); ir (potassium bromide): 2957, 1682, 1534, 1499, 1435, 1379, 1323, 1259, 1196, 1153, 1111, 1027, 998, 858, 822, 780, 766, 717, 689, 625, 562, 527, 470 cm^{-1}; eims: m/z 429 (M^+, base), 384, 356, 308, 262, 201, 183, 108, 77; hrms: Calcd. for $C_{25}H_{24}N_3O_2P$: 429.1606. Found: 429.1612.

2-[(Triphenylphosphoranylidene)amino]-3-cyanothiophene (**5b**) (Table I).

The compound was prepared in the same manner and melted at 184-186°; ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.90-7.45 (m, 15 H), 6.73 (d, 1 H, J = 6 Hz), 6.07 (d, 1 H, J = 6 Hz); ir (potassium bromide): 2196, 1499, 1456, 1295, 1217, 1175, 1098, 956, 922, 753, 724, 696, 623, 562, 527, 499 cm^{-1}; eims: m/z 384 (M^+), 277, 201, 149, 97, 83 (base); hrms: Calcd. for $C_{23}H_{17}N_2PS$: 384.0850. Found: 384.0838.

Anal. Calcd. for $C_{23}H_{17}N_2PS$: C, 71.86; H, 4.46; N, 7.29; S, 8.32. Found: C, 72.12; H, 4.28; N, 7.13; S, 8.32.

General Procedure for the Preparation of Carbodiimides. *N*-Phenyl-*N'*-[5-(1-methyl-4-cyanopyrazolo)]carbodiimide (**3c**) (Table II).

A solution of iminophosphorane **3b** (0.6 g, 1.57 mmoles) in THF (5 ml) at 25° was treated with phenyl isocyanate (0.17 ml, 1.57 mmoles) and the resulting reaction mixture was allowed to stir at 25° for 1 hour and then concentrated *in vacuo*. Flash chromatography (silicon dioxide, 50% ether-hexanes eluant) gave 0.223 g (0.350 g theoretical, 64%) of **3c** as a pale yellow solid, mp 68-70°; ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.60 (s, 1 H), 7.55-7.25 (m, 5 H), 3.76 (s, 3 H); ir (potassium bromide): 2224, 2175, 1583, 1520, 1492, 1442, 1393, 1358, 1273, 1203, 1168, 1062, 977, 900, 858, 759, 682, 583, 541 cm^{-1}; eims: m/z 223 (M^+), 194, 183, 152, 119, 84 (base), 77; hrms: Calcd for $C_{12}H_9N_5$: 223.0858. Found: 223.0858.

N-Phenyl-*N'*-(2-cyanophenyl)carbodiimide (**1c**) (Table II).

This compound, prepared by the general procedure above, showed the following spectral characteristics: ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.65 (d, 1 H, J = 8 Hz), 7.55 (t, 1 H, J = 8 Hz), 7.45-7.20 (m, 7 H); ir (neat): 3063, 2147, 1583, 1471, 1435, 1267, 1217, 1154, 1117, 1069, 1020, 949, 907, 816, 760, 675, 590 cm^{-1}; eims: m/z 219 (M^+, base), 192, 168, 143, 129, 111, 102, 91, 77; hrms: Calcd. for $C_{14}H_9N_3$: 219.0796. Found: 219.0796.

N-Phenyl-*N'*-(2-methoxycarbonylphenyl)carbodiimide (**2c**) (Table II).

This compound, prepared by the general procedure above, showed the following spectral characteristics: ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.89 (d, 1 H, J = 8 Hz), 7.46 (t, 1 H, J = 8 Hz), 7.39-7.16 (m, 7 H), 3.89 (s, 3 H); ir (neat): 3048, 2936, 2154, 1717, 1576, 1478, 1435, 1294, 1252, 1210, 1069, 957, 900, 837, 752, 682; eims: m/z 252 (M^+, base), 235, 221, 194, 166, 146, 132, 119, 91, 77; hrms: Calcd. for $C_{15}H_{12}N_2O_2$: 252.0898. Found: 252.0899.

N-Phenyl-*N'*-[5-(1-methyl-4-ethoxycarbonylpyrazolo)]carbodiimide (**4c**) (Table II).

This compound, prepared by the general procedure above, showed the following spectral characteristics: ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.79 (s, 1 H), 7.4-7.2 (m, 5 H), 4.22 (q, 2 H, J = 7 Hz), 3.77 (s, 3 H), 1.26 (t, 3 H, J = 7 Hz); ir (neat): 2978, 2133, 1696, 1576, 1527, 1485, 1400, 1280, 1245, 1189, 1168, 1055, 984, 900, 830, 745, 634 cm^{-1}; eims: m/z 270 (M^+), 242, 225, 198, 150 (base), 123, 103, 77; hrms: Calcd. for $C_{14}H_{14}N_4O_2$: 270.1117. Found: 270.1111.

N-Phenyl-*N'*-(2-cyanothieno)carbodiimide (**5c**) (Table II).

This compound, prepared by the general procedure above, showed the following spectral characteristics: ^{1}H nmr (deuteriochloroform, 300 MHz): δ 7.4-7.2 (m, 5 H), 6.98 (d, 1 H, J = 6 Hz), 6.92 (d, 1 H, J = 6 Hz); ir (neat): 3055, 2154, 1633, 1591, 1555, 1499, 1429, 1252, 1224, 1196, 1062, 1013, 949, 907, 724, 689, 633 cm^{-1}; eims: m/z 225 (M^+, base), 198, 151, 103, 91, 77; hrms: Calcd. for $C_{12}H_7N_3S$: 225.0361. Found: 225.0343.

4-Amino-2-anilinoquinazoline (**1d**).

Ammonia was bubbled into a solution of carbodiimide **1c** (0.58 g, 2.65 mmoles) in tetrahydrofuran (2 ml) at 25° to saturate the reaction mixture. The reaction mixture was stirred at 25° for 2 hours and then concentrated *in vacuo*. Methanol (2 ml) was added to the residue and the reaction mixture was stirred at reflux for 18 hours and then concentrated *in vacuo*. Flash chromatography (silicon dioxide, ether eluant) gave 0.33 g, (0.625 g theoretical, 53%) of **1d** as a pale yellow foam. Recrystallization from ethyl acetate/hexane gave a pale yellow solid, mp 155-157°; ^{1}H nmr (deuteriodimethyl sulfoxide, 300 MHz): δ 9.0 (br s, 1 H), 8.15 (d, 1 H, J = 8 Hz), 7.95 (d, 2 H, J = 8 Hz), 7.6 (t, 1 H, J = 8 Hz), 7.55 (br s, 2 H), 7.4 (d, 1 H, J = 8 Hz), 7.25 (t, 2 H, J = 8 Hz), 7.15 (t, 1 H, J = 8 Hz), 6.85 (t, 1 H, J = 8 Hz); ir (potassium bromide): 3393, 1604, 1569, 1527, 1492, 1436, 1408, 1337, 1280, 1168, 1097, 1020, 858, 752, 675, 583 cm^{-1}; eims: m/z 236 (M^+), 235 (base), 212, 163, 143, 118, 83; hrms: Calcd. for $C_{14}H_{12}N_4$: 236.1062. Found: 236.1054.

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.14; H, 5.27; N, 23.55.

2-Anilino-4(3*H*)-quinazolinone (**2d**).

Ammonia was bubbled into a solution of carbodiimide **2c** (0.532 g, 2.11 mmoles) in tetrahydrofuran (2 ml) at 25° to saturate the reaction mixture. The reaction mixture was stirred at 25° for 2 hours and then concentrated *in vacuo*. The residue was washed with ether and dried *in vacuo* to give 0.382 g (0.5 g theoretical, 76%) of **2d** as a white solid, mp 258-260°; ^{1}H nmr (deuteriodimethyl sulfoxide): δ 10.78 (br s, 1 H), 8.63 (br s, 1 H), 7.93 (d, 1 H, J = 7 Hz), 7.70 (d, 2 H, J = 7 Hz), 7.62 (t, 1 H, J = 7 Hz), 7.39-7.25 (m, 3 H), 7.19 (t, 1 H, J = 7 Hz), 7.02 (t, 1 H, J = 7 Hz); ir (potassium bromide): 3394, 2908, 1682, 1618, 1570, 1492, 1442, 1407, 1330, 1252, 1140, 1027, 893, 752, 689, 534 cm^{-1}; eims: m/z 237 (M^+), 236 (base), 170, 151, 141, 137, 120, 111, 97, 92; hrms: Calcd. for $C_{14}H_{11}N_3O$: 237.0902. Found: 237.0896.

Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71; O, 6.74. Found: C, 71.14; H, 4.75; N, 17.59; O, 6.81.

4-Amino-1-methyl-6-anilinopyrazolo[3,4-*d*]pyrimidine (**3d**).

Ammonia was bubbled into a solution of carbodiimide **3c** (0.14 g, 0.63 mmole) in tetrahydrofuran (2 ml) at 25° to saturate the reaction mixture. The reaction mixture was stirred at 25° for 1 hour and then concentrated *in vacuo*. Methanol (2 ml) was added to the residue and the reaction mixture was stirred at reflux for 18 hours. The reaction mixture was concentrated *in vacuo*. Flash chromatography (silicon dioxide, ether eluant) gave 0.117 g

(0.151 g theoretical, 77%) of **3d** as a white solid, mp 196-198° (from ethyl acetate/hexane); nmr (deuteriodimethyl sulfoxide, 300 MHz): δ 9.1 (br s, 1 H), 7.95 (m, 3 H), 7.3 (br s, 2 H), 7.25 (t, 2 H, J = 8 Hz), 6.85 (t, 1 H, J = 8 Hz), 3.95 (s, 3 H); ir (potassium bromide): 3443, 3330, 3162, 1661, 1590, 1527, 1471, 1428, 1316, 1232, 1182, 1069, 970, 844, 781, 745, 682, 632 cm^{-1}; eims: m/z 240 (M^+, base), 148, 123, 103, 93, 77; hrms: Calcd. for $C_{12}H_{12}N_6$: 240.1123. Found: 240.1126.

Anal. Calcd. for $C_{12}H_{12}N_6$: C, 59.99; H, 5.03; N, 34.98. Found: C, 59.75; H, 5.03; N, 34.86.

1-Methyl-6-anilinopyrazolo[3,4-*d*]pyrimid-4(3*H*)-one (**4d**).

A solution of carbodiimide **4c** (0.27 g, 1 mmole) in tetrahydrofuran (2 ml) at 25° was saturated with ammonia. The reaction mixture was stirred at 25° for 2 hours and then concentrated *in vacuo*. The residue was taken up in ethanol (2 ml) and treated with sodium ethoxide in ethanol (1.1 mmoles, 0.36 ml of a 3.09 *M* solution) and the resulting reaction mixture was allowed to stir at reflux for 3 hours; it was then concentrated *in vacuo*. Flash chromatography (silicon dioxide, 10% ethanol-ether eluant) gave 0.156 g (0.241 g theoretical, 65%) of **4d** as a clear foam; ^1H nmr (deuteriochloroform, 300 MHz): δ 10.75 (br s, 1 H), 8.70 (br s, 1 H), 7.90 (s, 1 H), 7.68 (d, 2 H, J = 8 Hz), 7.41 (t, 2 H, J = 8 Hz), 7.17 (t, 1 H, J = 8 Hz), 3.90 (s, 3 H); ir (neat): 2106, 1681, 1588, 1489, 1332, 1128, 778, 610 cm^{-1}; eims: m/z 241 (M^+), 225, 149, 137, 124, 111, 97, 83, 69 (base); hrms: Calcd. for $C_{12}H_{11}N_5O$: 241.0963. Found: 241.0972. Because of its physical characteristics (foam or gel, depending upon solvent), correct microanalytical data could not be obtained.

4-Amino-2-anilinothieno[2,3-*d*]pyrimidine (**5d**).

Ammonia was bubbled into a solution of carbodiimide **5c** (0.097 g, 0.43 mmole) in tetrahydrofuran (1 ml) at 25° to saturate the reaction mixture. The reaction mixture was stirred at 25° for 4 hours and then concentrated *in vacuo*. Flash chromatography (silicon dioxide, 5% ethanol-ether eluant) gave 0.048 g (0.104 g theoretical, 46%) of **5d** as a pale yellow foam; ^1H nmr (deuteriodimethyl sulfoxide, 300 MHz): δ 8.50 (br s, 1 H), 7.55-7.15 (m, 5 H), 6.85 (app t, 2 H, J = 6 Hz), 5.82 (br s, 2 H); lrfabms: m/z 243 (MH^+), 217, 177, 161, 155, 137, 119 (base); hrfabms: Calcd. for $C_{12}H_{11}N_4S$ (MH^+): 243.0704. Found: 243.0714. Because of its physical characteristics (foam), correct microanalytical data could not be obtained.

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[9] The ease of the cyclization of **5c** to **5d** stands in marked contrast to a recent report that 2-guanidino-3-cyanothiophene (from 2-amino-3-cyanothiophene and chloroformamidinium chloride) fails to cyclize under neutral, acid or basic reaction conditions [H. Link, *Helv. Chim. Acta*, **73**, 797 (1990)]. We feel that this latter reaction deserves reinvestigation.

[10] Substituted guanidine generated from **3c**, mp 188-190°; ^1H nmr (deuteriodimethyl sulfoxide, 300 MHz): δ 8.65 (s, 1 H), 7.70 (s, 1 H), 7.50 (d, 2 H, J = 8 Hz), 7.25 (t, 2 H, J = 8 Hz), 6.95 (t, 1 H, J = 8 Hz), 6.15 (br s, 2 H), 3.55 (s, 3 H); ir (potassium bromide): 2934, 2852, 2196, 1622, 1540, 1428, 1376 cm^{-1}; eims: m/z 240, 239 (M^+, base), 224, 148, 123, 93, 77; hrms: Calcd. for $C_{12}H_{12}N_6$: 240.1123. Found: 240.1115. Substituted guanidine generated from **4c**, mp 167-169°; ^1H nmr (deuteriochloroform, 300 MHz): δ 7.80 (s, 1 H), 7.4-7.2 (m, 4 H), 7.05 (t, 1 H, J = 8 Hz), 5.00 (br s, 2 H), 4.20 (q, 2 H, J = 7 Hz), 3.65 (s, 3 H), 1.30 (t, 3 H, J = 7 Hz); ir (potassium bromide): 3422, 2986, 1682, 1640, 1534, 1442, 1203, 1041, 977, 823, 753, 689, 555 cm^{-1}; eims: m/z 287 (M^+), 270, 241, 225, 169, 149, 123, 93 (base); hrms: Calcd. for $C_{14}H_{17}N_5O_2$: 287.1382. Found: 287.1394.

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