+118.46° (c 10, absolute EtOH).

The proton NMR spectrum ($CDCl_3$) showed resonances at δ 0.43 (3 H, s), 1.12 (3 H, s), 1.32 (3 H, s), 1.3–2.6 (7 H, overlapping m), 3.77 (3 H, s), 5.09 (1 H, br s), and 6.9–7.7 (4 H, overlapping m). Addition of D_2O to the sample resulted in the collapse of the broad singlet at δ 5.09. The C^{13}, completely decoupled NMR spectrum ($CDCl_3$) showed signals at δ 18.3 (q), 22.4 (q), 24.7 (t), 29.4 (q), 33.4 (t), 40.7 (t), 44.7 (s), 50.1 (d), 52.5 (s), 55.1 (q), 85.2 (s), 111.1 (d), 119.7 (d), 126.8 (d), 128.7 (d), 132.7 (s), 157.8 (s). The IR spectrum (CCl_4) had absorptions at 3545, 3070, 2970, 2935, 2880, 2840, 1460, 1435, 1380, 1360, 1305, 1290, 1225, 1180, 1130, 1110, 1070, 1050, 1030, and 922 cm^{-1}.

Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.46; H, 9.23. Found: C, 78.23; H, 9.23.

Attempted Chlorination of 1 with Anhydrous Hydrogen Chloride. Anhydrous hydrogen chloride was passed through a solution of 0.024 g (0.125 mmol) of **1** in $CDCl_3$ contained in a glass NMR tube at 25 °C for 0.5 h. Analysis of the reaction solution by VPC (column A, 170 °C, 40-mL/min flow rate) showed two major products and no starting material. The first product (**2**) had a retention time of 1.8 min (5%) and the second (**3**) one of 2.7 min (90%). The remaining 5% of the solution was comprised of three unknown components. The reaction mixture was then subjected to an additional hour of hydrogen chloride treatment. Analysis of this reaction mixture by VPC, under the same conditions, showed only one major product comprising 95% of the mixture and having a retention time of 2.7 min.

The reaction was rerun in chloroform at 0 °C. After 2 h, only **2** and **3** were present in a 2:1 ratio. After an additional 7 h reaction time, the product distribution had shifted to 45% **2** and 55% **3**. The experiment was performed again at ca. −60 °C. After 9 h, VPC analysis showed the presence of unreacted starting material and **2** and **3** in a 2:1 ratio.

Attempted Chlorination of 1 with Phosphorus Pentachloride. To a solution of 4.00 g (15.4 mmol) of **1** and 2.15 g (21.5 mmol) of calcium carbonate in 70 mL of chloroform at 9 °C contained in a dry, 250-mL round-bottomed flask fitted with a magnetic stirrer, reflux condenser, and gas inlet was added with stirring 4.17 g (20 mmol) of phosphorus pentachloride. The reaction was stirred under a nitrogen atmosphere for 1.5 h, at which time an excess of potassium carbonate was added, and the reaction mixture was then filtered. The filter cake was rinsed with chloroform, and the volatile solvents were removed by rotary evaporation. VPC analysis of the resulting yellow liquid (column A, 190 °C, 40-mL/min flow rate) showed two major components making up 95% of the mixture in a distribution of 52% and 48%. Coinjection of this mixture with the mixture resulting from HCl treatment of **1** indicated the two major components in each reaction to be the same (**2** and **3**).

The yellow liquid was introduced onto a silica gel (35–70 mesh) chromatography column (16.5 cm × 5 cm), and elution was followed by VPC analysis (column A, 190 °C, 40-mL/min flow rate). After component **2** was completely eluted from the column with pentane, the solvent was changed to diethyl ether and **3** was washed from the column. Removal of volatile solvents by rotary evaporation resulted in the formation of thick yellow liquids for both **2** and **3**.

Kugelrohr distillation [60 °C (0.1 torr)] of **2** left it unchanged both in appearance and in its measured proton NMR spectrum. Purification of **2** by VPC (column B, 250 °C, 40 mL/min flow rate) resulted in the formation of a colorless liquid. The proton NMR spectrum ($CDCl_3$, 28 °C) remained identical with the non-VPC-purified **2** and showed resonances at δ 0.66–1.00 (6 H, br s), 1.1 (3 H, s), 1.11–2.22 (6 H, overlapping m), 3.64 (3 H, s), and 6.67–7.33 (4 H, overlapping m). The fully decoupled carbon-13 NMR spectrum showed at least six signals which were very broad (see Figure 1). The carbon-13 NMR spectrum at 0 °C showed that each of the signals was split into two signals, indicating the existence of a rotational barrier in the molecule. The coalescence temperature representing the activation energy for the rotational barrier was investigated by variable-temperature carbon-13 NMR and was found to be 45 °C. The proton NMR spectrum of **2** at 0 °C showed the signals corresponding to the three methyl groups [δ 0.66–1.00 (br s) and 1.1 (s)] to each be split into two signals. At 60 °C, the carbon-13 spectrum ($CDCl_3$) of **2** consisted of sharp signals at δ 15.3 (q), 22.1 (2 superimposed q), 26.3 (d), 29.8 (s), 32.9 (t), 38.6 (t), 43.4 (d), 48.4 (s), 55.1 (q), 84.9 (s), 111.0 (d), 120.5 (d), 126.6 (s), 128.1 (d), 135.1 (d), and 161.2 (s). The IR spectrum (between NaCl plates) showed major absorptions at 3100, 2900–3000, 1800–1950, 1500, 1460, 1360, 1380, 1000–1020 cm^{-1}.

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.25; H, 9.40.

Compound **3** was subjected to Kugelrohr distillation [60 °C (0.1 torr)] to afford 0.57 g of white crystals. The proton NMR spectrum ($CDCl_3$) for **3** showed resonances at δ 1.16 (3 H, s), 1.21 (3 H, s), 1.33 (3 H, s), 0.75–2.1 (7 H, overlapping m), and 6.63–6.2 (4 H, overlapping m). The carbon-13, completely decoupled spectrum ($CDCl_3$) showed signals at δ 17.8 (q), 19.6 (q), 22.0 (q), 22.9 (t), 33.8 (t), 42.2 (t), 49.3 (d), 50.7 (s), 56.0 (s), 97.8 (s), 109.3 (d), 120.0 (d), 124.0 (d), 128.4 (d), 134.2 (s), 159.1 (s). The IR spectrum showed major absorptions at 3100, 2950, 1600, 1380, 1390, 1240, 1090, and 755 cm^{-1}. The mass spectrum showed peaks at m/e 228 (M^+) and 213 (base peak, $M^+ - 15$).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.21; H, 8.77; O, 7.02. Found: C, 84.19; H, 8.86; O, 6.94.

Acknowledgment. We thank Drs. J. E. Gano and D. A. Horne for their help in obtaining and interpreting a number of NMR spectra and The University of Toledo Faculty Research Awards and Fellowships Program for support.

Registry No. **1**, 76833-22-2; **2**, 76847-44-4; **3**, 76833-23-3; *o*-bromoanisole, 578-57-4; (+)-fenchone, 7787-20-4.

Diels–Alder Reaction of Heterocyclic Azadienes. 1. Thermal Cycloaddition of 1,2,4-Triazine with Enamines: Simple Preparation of Substituted Pyridines

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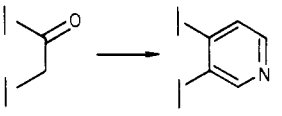
During the course of synthetic studies designed for the preparation of substituted pyridine derivatives[1] we have had the occasion to investigate methods for the construction or annelation of a pyridine ring onto a saturated precursor. Most useful for our purposes would be a direct and simple process for the annelation of a pyridine ring onto a preexisting ketone as illustrated in eq 1.[2] Though



(1)

multistep procedures are available for carrying out this transformation, the overall yields and effort involved discourage their general utility.[2]

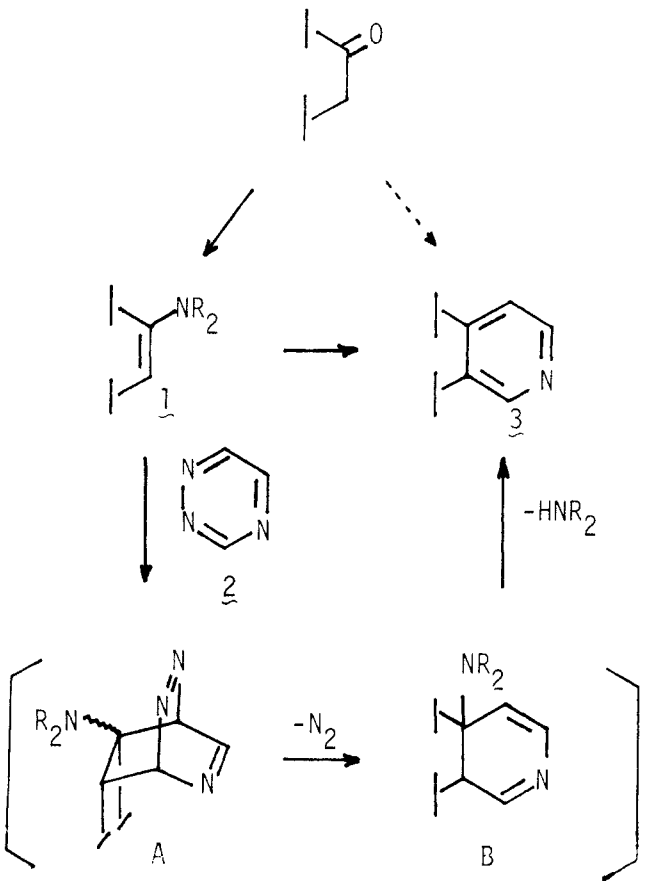
In the search for a more direct and convenient method, we were intrigued by the possible use of 1,2,4-triazine (**2**) as a dependable, azadiene component in a Diels–Alder route to substituted pyridines.[3,4] Previous studies have

(1) Typified by sesbanine, a cytotoxic constituent of *Sesbania drummondii*; see: Powell, R. G.; Smith, C. R., Jr.; Weisleder, D.; Muthard, D. A.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 2784.

(2) Weissberger, A.; Taylor, E. C. Eds. *Chem. Heterocycl. Comp.* **1974**, *14*, *Suppl., Part 2*; **1975**, *14*, *Suppl., Part 4*; **1960–1964**, *14*, *Parts 1–4*.

0022-3263/81/1946-2179$01.25/0

Scheme I



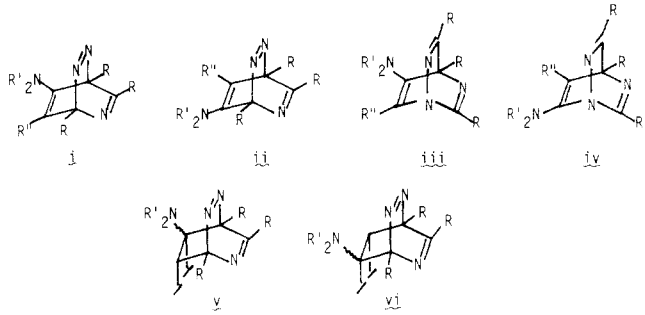
demonstrated the capability of substituted 1,2,4-triazines to react with *electron-rich* olefins,[3] though subject to dubious regiocontrol,[5] for the preparation of substituted pyridines. Pertinent to our interests was the potentially useful participation of an enamine[5] (electron-rich olefin prepared from a ketone) in an "inverse electron demand" Diels–Alder reaction[6] with 1,2,4-triazine (**2**; electron deficient heterocycle possessing a reactive azadiene). With the assumption of the expected regiocontrol, subsequent loss of nitrogen and aromatization (Scheme I, loss of R_2NH) would afford the desired annelated pyridine directly. This potential has led us to investigate the scope and limitations of the reaction of 1,2,4-triazine (**2**) with enamines **1** with the expectation that this process could serve as a simple and expedient method for pyridine annelation (eq 1, Scheme I).

Table I summarizes the important findings of this investigation. Clearly the pyrrolidine enamines are more reactive than morpholino enamines (compare **1c** and **1d**) and generally result in the clean, rapid, and efficient preparation of substituted pyridines. In no instance is there evidence of products resulting from alternative cycloadditions[5] or products arising from unexpected, but not unprecedented,[5] regiocontrol. Pyrrolidine enamine **1j** affords 4-cyclohexylpyridine (**3j**) exclusively,[7] pyrrolidine enamines **1a,b** afford **3a,b**, respectively, with no trace of isomeric pyridines,[8] and the substituted cyclohexyl en-

(3) (a) For an excellent treatment of the chemistry of 1,2,4-triazine derivatives see: Neunhoeffer, H.; Wiley, P. F. *Chem. Heterocycl. Compd.* **1978**, *33*, 189. For previously reported Diels–Alder reactions of *substituted* 1,2,4-triazines see ref 3a, pp 226–228. (b) With ynamines and 1-ethoxy-*N,N*-dimethylvinylamine, see: Neunhoeffer, H.; Fruhauf, N.-W. *Tetrahedron Lett.* **1969**, 3151; **1970**, 3355; *Justus Liebigs Ann. Chem.* **1972**, *758*, 120, 125; Neunhoeffer, H.; Frey, G. *Ibid.* **1973**, 1963; Neunhoeffer, H.; Bernd, L. *Ibid.* **1977**, 1413, 1718; Steigel, A.; Sauer, J. *Tetrahedron Lett.* **1970**, 3357. (c) With an enamine and strained olefins, see: Dittmar, W.; Sauer, J.; Steigel, A. *Tetrahedron Lett.* **1969**, 5171. (d) With strained olefins, see: Elix, J. A.; Wilson, W. S.; Warrener, R. N. *Tetrahedron Lett.* **1970**, 1837; Elix, J. A.; Wilson, W. S.; Warrener, R. N.; Calder, I. C. *Aust. J. Chem.* **1972**, *25*, 865. (e) With cyclopropenes, see: Steigel, A.; Sauer, J.; Kleier, D. A.; Binsch, G. *J. Am. Chem. Soc.* **1972**, *94*, 2770; Gockel, U.; Hartmannsgruber, U.; Steigel, A.; Sauer, J. *Tetrahedron Lett.* **1980**, *21*, 595, 599; Oeser, O.; Neunhoeffer, H.; Fruhauf, H.-F. *Justus Liegibs Ann. Chem.* **1975**, 1445. (f) With benzocyclopropene, see: Maddox, M. L.; Martin, J. C.; Muchowski, J. M. *Tetrahedron Lett.* **1980**, 7. (g) With olefins, see: Barlow, M. G.; Haszeldine, R. N.; Simpkin, D. J. *J. Chem. Soc., Chem. Commun.* **1979**, 658.

(4) For recent and representative Diels–Alder routes to pyridines see the following. (a) The use of oxazoles: Karpeiskii, M. Y. Florent'ev, V. L. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 540; Kozikowski, A. P.; Isobe, K. *Heterocycles* **1978**, *9*, 1271; Kozikowski, A. P.; Hasan, N. M. *J. Org. Chem.* **1977**, *42*, 2039; Morisawa, Y.; Kataoka, M.; Watanabe, T. *Chem. Pharm. Bull.* **1976**, *24*, 1089; Szlompek, D. N.; Rudnicki, A.; Sikorska, T. *Przem. Chem.* **1975**, *54*, 298; *Chem. Abstr.* **1975**, *83*, 79046, Jaworski, T.; Rudnicki, A. *Rocz. Chem.* **1972**, *46*, 1679; Takagaki, H.; Yasuda, N.; Asaoka, M.; Takei, H. *Chem. Lett.* **1979**, 183; Firestone, R. A.; Harris, E. E.; Reuter, W. *Tetrahedron* **1967**, *23*, 943; Muhlradt, P. F.; Morino, Y.; Snell, E. E. *J. Med. Chem.* **1967**, *10*, 341. (b) The use of pyrimidines: Neunhoeffer, H.; Werner, G. *Justus Liebigs Ann. Chem.* **1974**, 1190; Neunhoeffer, H.; Lehmann, B. *Ibid.* **1975**, 1113. (c) The use of pyrazines: Neunhoeffer, H.; Werner, G. *Justus Liebigs Ann. Chem.* **1972**, 761, 39. (d) The use of 1,3-oxazin-6-ones: Steglich, W.; Buschmann, E.; Hollitzer, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 533. (e) The use of pyridazines: Neunhoeffer, H.; Werner, G. *Tetrahedron Lett.* **1972**, 1517. (f) The use of 6-oxopyrimidines: Davies, L. B.; Sammes, P. G.; Watt, R. A. *J. Chem. Soc., Chem. Commun.* **1977**, 663.

(5) Various substituted 1,2,4-triazines have been shown to react with ynamines and 1-ethoxy-*N,N*-dimethylvinylamine to give 3- *and* 4-amino-substituted pyridines and/or substituted pyrimidines (mixture of initial cycloadducts with mixed regiocontrol, e.g., i–iv); see ref 3a,b. One report[3c] demonstrated the potential capability of substituted 1,2,4-triazines to react with one enamine to afford substituted pyridines (cycloaddition across the azadiene). However, no information on the regiospecificity of this cycloaddition can be derived from the work (e.g., v vs. vi).

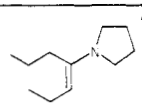
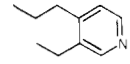
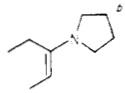
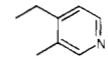
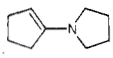
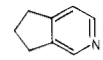
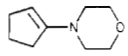
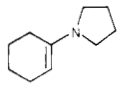
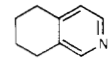
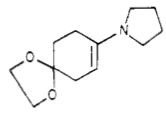
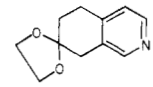
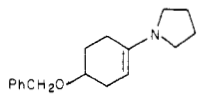
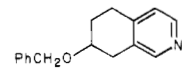
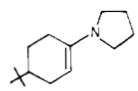
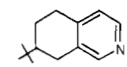
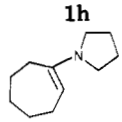
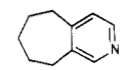
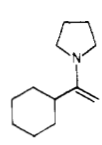
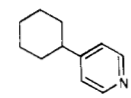


(6) (a) Since the concept of the "inverse electron demand" Diels–Alder reaction was first recognized (Bachmann, W. E.; Deno, N. C. *J. Am. Chem. Soc.* **1949**, *71*, 3062), first demonstrated (Carboni, R. A.; Lindsey, R. V., Jr. *Ibid.* **1959**, *81*, 4342), and confirmed (Sauer, J.; Wiest, H. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 269), a number of interesting cases have been investigated. For recent and related examples, see ref 3a–c, 4b–f, and the following. (b) With pyridazines: Neunhoeffer, H.; Werner, G. *Justus Liebigs Ann. Chem.* **1973**, *437*, 1955. (c) With 1,3,5-triazines: Neunhoeffer, H.; Bachmann, M. *Chem. Ber.* **1975**, *108*, 3877. (d) With 1,2,4,5-tetrazines: Roffey, R.; Verge, J. P. *J. Heterocycl. Chem.* **1969**, *6*, 497; Avram, M.; Dinulescu, I. G.; Marica, E.; Nenitzescu, C. D. *Chem. Ber.* **1962**, *95*, 2248; Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 26; **1966**, *5*, 211; Sauer, J.; Heinrichs, G. *Tetrahedron Lett.* **1966**, 4979; Sauer, J.; Mielert, A.; Lang, D.; Peter, D. *Chem. Ber.* **1965**, *98*, 1435; Deyrup, J. A.; Gingrich, H. L. *Tetrahedron Lett.* **1977**, 3115.

(7) No trace (<2%) of the isomeric 3-cyclohexylpyridine could be detected by chromatographic or spectroscopic (^1H or ^{13}C NMR) techniques.

(8) No trace (<2%) of the isomeric 3,4-disubstituted pyridines could be detected by chromatographic or spectroscopic (^1H or ^{13}C NMR) techniques. Comparison of commercially available (ICN K & K Laboratories) 3-ethyl-4-methyl pyridine [^1H NMR ($CDCl_3$) 8.18 (1 H, s, aromatic), 8.15 (1 H, d, J = 5 Hz, aromatic), 6.85 (1 H, d, J = 5 Hz, aromatic), 2.58 (2 H, q, CH_2), 2.27 (3 H, s, Ar CH_3), 1.16 ppm (3 H, t, J = 6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) 149.2 (C-2), 147.2 (C-6), 144.6 (C-4), 137.7 (C-3), 125.0 (C-5), 23.6 (CH_2), 18.2 (Ar CH_3), 14.3 ppm (CH_3); IR (film) ν_{max} 2960, 2830, 1584, 1442, 1395, 1165, 1040, 942, 808, 720 cm^{-1}] with **3b** allows the conclusive assignment of structure **3b**. GLC analysis (6 ft × $^1/_8$ in., 10% Apiezon L–2% KOH on Chromosorb W-AW 80-100, column temperature 80 °C isotherm, flow rate 30 mL/min) indicated the complete absence (less than <0.1%) of 3-ethyl-4-methyl pyridine (R_T = 5.06 min) in **3b** (R_T = 5.18 min).

Table I. Diels-Alder Reaction of 1,2,4-Triazine with Enamines

enamine	reaction conditions	product	yield,[a] %
 1a	$CHCl_3$, 45 °C, 20 h	 3a	71
 1b	$CHCl_3$, 45 °C, 23 h	 3b	68
 1c	$CHCl_3$, 25 °C, 1.5 h; 45 °C, 35 h	 3c	74
 1d	$CHCl_3$, 45 °C, 39 h		<30[c]
 1e	$CHCl_3$, 45 °C, 23 h CCl_4, 45 °C, 6 h dioxane, 25 °C, 30 min; 85 °C, 9 h	 3e	40 *d* *d*
 1f	$CDCl_3$, 45 °C, 28 h dioxane, 45 °C, 24 h $ClCH_2CH_2Cl$, 45 °C, 24 h	 3f	22 *d* *e*
 1g	$CHCl_3$, 45 °C, 27 h	 3g	23
 1h	$CHCl_3$, 45 °C, 27 h	 3h	35
 1i	$CHCl_3$, 45 °C, 16 h	 3i	78
 1j	$CHCl_3$, 45 °C, 20 h	 3j	64

[a] Yield of purified product isolated by column chromatography (SiO_2) unless indicated otherwise. All products exhibited the reported or expected ^1H NMR, IR, and mass spectrum characteristics. New compounds gave satisfactory C, H, and N analysis (±0.40%). [b] Prepared using 4-Å molecular sieves. See: Taguchi, K.; Westheimer, F. H. *J. Org. Chem.* **1971**, *36*, 1570. [c] Yield determined by ^1H NMR integration vs. an internal standard. [d] Little or no pyridine product detected by spectroscopic or chromatographic methods. [e] Slow with a small amount of product formation. [f] Prepared with the use of $TiCl_4$. See: White, W. A.; Weingarten, H. *J. Org. Chem.* **1967**, *32*, 213.

amines **1f–h** afford the 7-substituted 5,6,7,8-tetrahydroisoquinolines **3f–h** as the sole cycloaddition products.[9] The halogenated solvents chloroform and methylene chloride are superior to other solvents, and the order of solvent preference can be roughly estimated as $CHCl_3$, $CH_2Cl_2 \gg$ dioxane, $ClCH_2CH_2Cl >$ benzene, ether, CCl_4. Although the initial reaction of 1,2,4-triazine (**2**) with a pyrrolidine enamine usually is exothermic and is accompanied by an immediate evolution of nitrogen (**1** + **2** → A → B), complete conversion to the annelated pyridine (B → **3**) often requires extended reaction times (15–30 h, ca. 45 °C), indicating that aromatization is the slow and occasionally problematic step. The pyrrolidine enamines of aliphatic ketones (**1a,b,j**), cyclopentanones (**1c**), and cycloheptanones (**1i**) routinely afford annelated pyridines in yields ranging from 64 to 78%, whereas cyclohexanone derivatives **1e–h** result in lower overall yields (22–40%). Although the lower yields appear to result from problems in the ultimate conversion of B → **3**, all attempts to increase the rate and yield of this aromatization step have failed.[10]

Less nucleophilic olefins, for example, β-enamino ketones,[11] β-alkoxy enones,[11] trimethylsilyl enol ethers,[11]

(9) No trace of isomeric pyridines could be detected by chromatographic or spectroscopic methods; cf. ref 7 and 8.

(10) Higher reaction temperatures (either initially or after 1–4 h) or addition of acid catalysts (BF_3·OEt_2, HOAc; either initially or after 1–4 h) lead to diminished yields of pyridine product with enamine **1d**.

(11) 4-Pyrrolidinopent-3-en-2-one, 4-methoxy-but-3-en-2-one, and the trimethylsilyl and tri-*n*-butylstannyl enol ethers of 4-heptanone did not react with 1,2,4-triazine under a wide variety of conditions (25–200 °C).

tri-*n*-butylstannyl enol ethers,[11] are not sufficiently reactive to participate in a Diels–Alder reaction with 1,2,4-triazine (**2**).

Clearly, the use of 1,2,4-triazine (**2**) as an annelative reagent in the inverse electron demand Diels–Alder reaction with pyrrolidine enamines serves as a useful, efficient, and convenient process for pyridine annelation. Studies on related heterocyclic azadienes and their application to the synthesis of alkaloids of synthetic and medicinal interest currently are in progress and will be reported separately.

Experimental Section

General Procedure for the Diels–Alder Reaction of 1,2,4-Triazine with Enamines: 3-Ethyl-4-*n*-propylpyridine (3a). A solution of 4-pyrrolidinohept-3-ene (**1a**; 132 mg, 0.8 mmol) in chloroform (0.5 mL) was added to a stirred solution of 1,2,4-triazine[12] (95 mg, 1.2 mmol, 1.50 equiv) in chloroform (0.5 mL) under nitrogen (25 °C). The resulting dark orange solution was warmed at 45 °C for 20 h. Chromatography (SiO_2, 50% ether–hexane eluant) afforded 92 mg (130 mg theoretical, 71%) of pure **3a** as a light yellow oil:[8] ^1H NMR ($CDCl_3$) 8.20 (1 H, s, aromatic), 8.15 (1 H, d, J = 5 Hz, aromatic), 6.90 (1 H, d, J = 5 Hz, aromatic), 2.50 (4 H, m, CH_2Ar), 1.90–1.25 (2 H, m, CH_2), 1.17 (3 H, t, CH_3), 1.0 ppm (3 H, t, CH_3); IR (film) ν_{max} 2945, 2847, 1580, 1440, 1390, 795 cm^{-1}; mass spectrum, m/e (relative intensity) 149 (M^+, 57), 148 (9), 135 (6), 134 (71), 121 (10), 120 (50), 119 (8), 118 (10), 117 (7), 106 (base), 92 (14), 91 (9), 85 (8), 83 (4), 65 (11). Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.10; H, 10.48; N, 9.42.

4-Ethyl-3-methylpyridine (3b):[8,13] yield 68% (see Table I); picrate mp 142.5–143.5 °C (lit.[13a] mp 144–145 °C); ^1H NMR ($CDCl_3$) 8.33 (1 H, d, J = 5 Hz, aromatic), 8.31 (1 H, s, aromatic), 7.05 (1 H, d, J = 5 Hz, aromatic), 2.61 (2 H, q, J = 6 Hz, CH_2), 2.26 (3 H, s, Ar CH_3), 1.21 ppm (3 H, t, J = 6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) 150.2 (C-4), 150.1 (C-2), 147.5 (C-6), 131.2 (C-3), 122.5 (C-5), 25.5 (CH_2), 15.9 (Ar CH_3), 13.2 ppm (CH_3); IR (film) ν_{max} 3048, 2950, 2865, 1582, 1440, 1387, 1347, 887, 810, 705 cm^{-1}; mass spectrum, m/e (relative intensity) 121 (M^+, base), 120 (76), 106 (51), 94 (7), 93 (21), 92 (21), 89 (11), 80 (7), 79 (22), 78 (10), 77 (25), 65 (14), 53 (8), 51 (9).

3,4-Cyclopentenopyridine (3c):[14] yield 74% (see Table I); ^1H NMR ($CDCl_3$) 8.20 (1 H, s, aromatic), 8.12 (1 H, d, J = 5 Hz, aromatic), 6.95 (1 H, d, J = 5 Hz, aromatic), 2.84 (4 H, m, CH_2Ar), 2.30–1.84 ppm (2 H, m, CH_2).

5,6,7,8-Tetrahydroisoquinoline (3e):[15] yield 40% (see Table I); ^1H NMR ($CDCl_3$) 8.18 (1 H, s, aromatic), 8.11 (1 H, d, J = 5 Hz, aromatic), 6.93 (1 H, d, J = 5 Hz, aromatic), 3.05–2.34 (4 H, m, CH_2Ar), 2.12–1.74 ppm (4 H, m, CH_2CH_2).

7,7(8*H*)-(Ethylenedioxy)-5,6-dihydroisoquinolinone (3f): yield 22% (see Table I); mp 67–69 °C (ether–hexane); ^1H NMR ($CDCl_3$) 7.95 (1 H, d, J = 5 Hz, aromatic), 7.93 (1 H, s, aromatic), 6.70 (1 H, d, J = 5 Hz, aromatic), 3.85 (4 H, s, OCH_2CH_2O), 2.80 (4 H, m, CH_2Ar), 2.05–1.65 ppm (2 H, m, CH_2); IR (film) ν_{max} 3043, 3010, 2958, 2880, 1772, 1660, 1595, 1410, 1356, 1260, 1095, 935, 824 cm^{-1}; mass spectrum, m/e (relative intensity) 191 (M^+, 0.3), 99 (1), 84 (1), 40 (7), 34 (2), 31 (base). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.75; H, 6.70; N, 7.10.

7-(Benzyloxy)-5,6,7,8-tetrahydroisoquinoline (3g): yield 23% (see Table I); ^1H NMR ($CDCl_3$) 8.18 (1 H, s, aromatic), 8.12 (1 H, d, J = 5 Hz, aromatic), 7.20 (5 H, s, C_6H_5), 6.89 (1 H, d, J = 5 Hz, aromatic), 4.45 (2 H, s, OCH_2Ph), 4.10–3.62 (1 H, m, CHO), 3.02–2.55 (4 H, m, CH_2Ar), 2.10–1.67 ppm (2 H, m); IR (film) ν_{max} 3045, 3020, 2920, 2860, 1589, 1440, 1403, 1350, 1072, 1050, 810, 710, 675 cm^{-1}; mass spectrum, m/e (relative intensity) 239 (M^+, 10), 211 (19), 210 (21), 148 (10), 132 (2), 130 (5), 120 (8), 117 (6), 91 (13), 90 (base), 71 (8), 65 (10), 57 (13), 55 (8), 43 (10), 41 (9), 40 (6), 32 (50). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.84. Found: C, 79.96; H, 7.10; N, 5.85.

7-*tert*-Butyl-5,6,7,8-tetrahydroisoquinoline (3h): yield 35% (see Table I); ^1H NMR ($CDCl_3$) 8.10 (1 H, s, aromatic), 8.02 (1 H, d, J = 5 Hz, aromatic), 6.80 (1 H, d, J = 5 Hz, aromatic), 2.95–2.27 (4 H, m, CH_2Ar), 1.93 (1 H, m, CH), 1.52–1.20 (2 H, m, CH_2), 0.90 ppm (9 H, s, $C(CH_3)_3$); IR (film) ν_{max} 3045, 2960, 2870, 1588, 1460, 1400, 1362, 1252, 900, 800, 710 cm^{-1}; mass spectrum, m/e (relative intensity) 189 (M^+, 50), 134 (12), 133 (90), 132 (base), 117 (40), 116 (20), 57 (90), 47 (40). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.34: H, 10.12; N, 7.48.

3,4-Cycloheptenopyridine (3i):[16] yield 78% (see Table I); picrate mp 140–141 °C (lit.[16] mp 141–142 °C, picrate); ^1H NMR 8.00 (2 H, m, aromatic), 6.75 (1 H, d, J = 5 Hz, aromatic), 2.85–2.40 (4 H, m, CH_2Ar), 1.75–1.33 ppm (6 H, m, $CH_2CH_2CH_2$); IR (film) ν_{max} 3060, 3025, 2920, 2850, 1585, 1440, 1400, 1350, 1295, 1180, 800, 712 cm^{-1}; mass spectrum, m/e (relative intensity) 147 (M^+, 8), 146 (30), 145 (17), 132 (13), 118 (20), 104 (17), 84 (15), 31 (base).

4-Cyclohexylpyridine (3j):[17] yield 64% (see Table I); picrate mp 152–153 °C (lit.[17] mp 154–155 °C); ^1H NMR ($CDCl_3$) 8.17 (2 H, d, J = 5 Hz, aromatic), 6.83 (2 H, d, J = 5 Hz, aromatic), 2.75–2.15 (1 H, m, CHAr), 1.97–0.68 (10 H, m, CH_2's); ^{13}C NMR ($CDCl_3$) 156.67 (C-4), 149.77 (C-2), 122.34 (C-3), 43.81 (C-1'), 33.49 (C-2'), 26.52 and 25.97 ppm (C-3', C-4'); IR (film) ν_{max} 3060, 3005, 2910, 2837, 1584, 1540, 1437, 1393, 970, 790 cm^{-1}.

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Registry No. **1a**, 23516-90-7; **1b**, 13750-57-7; **1c**, 7148-07-4; **1d**, 936-52-7; **1e**, 1125-99-1; **1f**, 57440-57-0; **1g**, 76833-13-1; **1h**, 4147-00-6; **1i**, 14092-11-6; **1j**, 76833-14-2; **2**, 290-38-0; **3a**, 76833-15-3; **3b** picrate, 76833-16-4; **3c**, 533-35-7; **3e**, 36556-06-6; **3f**, 76847-43-3; **3g**, 76833-17-5; **3h**, 76833-18-6; **3i** picrate, 76833-19-7; **3j** picrate, 13742-76-2.

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Poly(acrylamide)-Based Solid-Phase Cosolvents[1]

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Hexamethylphosphoric triamide (HMPA), dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO) are effective polar aprotic solvents for promoting nucleophilic displacement reactions.[2] Recently, it has been reported that *N*,*N*-diethylacetamide (DEA) and *N*-ethylpyrrolidone (NEP) have similar properties.[3] On the basis of this disclosure, it occurred to us that cross-linked polyamide analogues of DEA might exhibit useful "catalytic" features,

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