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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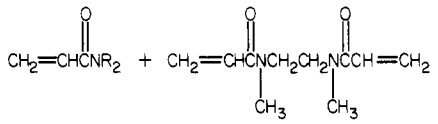
Table I. Poly(acrylamide)-Catalyzed Phenoxide Displacement[a]



R	cross-link density, mol %	PhO-*n*-C_7H_{15}, % yield[b]
CH_3	1	75
	5	53
	10	69 (16)[c]
C_2H_5	1	51
	5	52
	10	32
n-C_3H_7	1	16
	5	20
	10	15
n-C_4H_9	1	9
	5	13
	10	13
n-C_8H_{17}	10	10

[a] Reaction of 0.058 g (0.05 mmol) of sodium phenoxide in 2.0 mL of dry dioxane with 0.358 g (2.0 mmol) of 1-bromoheptane containing 0.02 g of *n*-dodecane as an internal standard catalyzed by 0.05 g of poly(acrylamide). [b] Yield (GLC) of phenyl *n*-heptyl ether relative to starting phenoxide after 5 h at 75 °C. [c] 0.019 g of polymer used is equivalent in moles of amide (0.19 mmol) to that present in 0.05 g of 10% cross-linked poly(*N,N*-di-*n*-octylacrylamide).

acting as *solid-phase cosolvents*.[4] By virtue of their insolubility, such materials would be particularly attractive since they could be recovered by filtration and would avoid the toxicity problems associated with many of the above solvents.[5] In this note we report the results of a survey of a series of poly(acrylamide) gels evaluated as cosolvent-type catalysts for nucleophilic displacement reactions under biphase and triphase conditions. Data presented herein establish the synthetic potential of these relatively simple polymer networks.

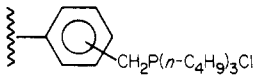
Attempted reaction of sodium phenoxide with excess 1-bromoheptane in dioxane (homogeneous reaction) afforded a 2% yield of phenyl *n*-heptyl ether after 17 h at 75 °C. In contrast, a similar reaction carried out in the presence of poly(*N,N*-dimethylacrylamide) cross-linked with 1 mol % *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) produced a 75% yield of the ether in 5 h. Results obtained by using related poly(acrylamide) gels are shown in Table I. In general, the apparent activity/gram of polymer showed little sensitivity to the cross-link density but was highly dependent on the length of the *N*-alkyl chain. The latter appears to be due to the change in amide concentration in the polymer; i.e., when *N,N*-dimethyl- and *N,N*-di-*n*-octylacrylamide (10% cross-linked) gels were compared on the basis of moles of amide used, similar activity was observed (Table I). In Table II we provide an operational comparison between HMPA, Me_2SO, DMF, DEA, *N,N*-dimethylacetamide, and 1% cross-linked poly(*N,N*-dimethylacrylamide) as cosolvents for promoting phenoxide displacement on 1-bromoheptane. While HMPA was clearly most efficient, the insoluble polymer proved superior to all other cosolvents.

Table II. Influence of Cosolvent on Phenoxide Displacement[a]

cosolvent[b]	time, h	PhO-*n*-C_7H_{15}, % yield[c]
HMPA	3	83
polyamide[d]	3	56
Me_2SO	3	50
DMF	3	33
N,N-dimethylacetamide	3	24
DEA	3	14
	17	2

[a] Reaction of 2 mL of 0.25 M sodium phenoxide in dioxane with 4 equiv of 1-bromoheptane at 75 °C. [b] Cosolvent concentration used was 0.25 M. [c] Yield (GLC) based on starting phenoxide. [d] 0.050 g (0.5 mmol of amide) of 1% cross-linked poly(*N,N*-dimethylacrylamide).

Two standard nucleophilic displacement reactions that have been used extensively for evaluating triphase catalytic activity are chloride displacement on *n*-decyl methanesulfonate and iodide displacement on *n*-octyl bromide.[6,7] Using these as a basis for judging the efficacy of each of the polymers listed in Table I, we have found that only the hydrophobic gel derived from *N,N*-di-*n*-octylacrylamide exhibited significant activity (see Experimental Section). This result parallels our earlier empirical observations made with ammonium-type catalysts, where high lipophilic character was required for high activity.[8] If this polyamide is compared to **1**, **2**, and **3** for catalyzing chloride displacement on *n*-decyl methanesulfonate, we find that, on a weight basis, it has approximately 0.14, 0.07, and 0.03 times as much activity, respectively.[9]



functionalized microporous polystyrene–1% divinylbenzene
1, percent ring substitution (prs) = 52; 20–50 mesh
2, prs = 52; 200–400 mesh
3, prs = 17; 200–400 mesh

In this study, we have demonstrated that simple poly(acrylamide) resins can function effectively as cosolvents. Based on their low cost and easy preparation, they should find immediate use in many practical syntheses requiring polar aprotic solvents.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and were used without further purification. Benzene, dioxane, and toluene were dried by distillation from sodium and benzophenone under a nitrogen atmosphere. Deionized water was distilled from $KMnO_4/Ba(OH)_2$. The temperature of the oil bath used for all reactions was controlled (±0.5 °C) with the aid of a Therm-O-Watch electronic controller Model L6-1000 (I^2R Co., Cheltenhan, PA) attached to a thermometer. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830A flame-ionization instrument (2

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ft × 0.125 in. UCW-982 on Chromosorb W column at 160 °C). All ^{1}H NMR and IR spectra were recorded by using Varian A-60 and Beckman Acculab 7 spectrometers, respectively. All *N,N*-dialkylacrylamides were prepared by condensation of acryloyl chloride with the appropriate secondary amine by using standard procedures and were distilled prior to use:[10] *N,N*-dimethyl, bp 37–38 °C (1.0 mm); *N,N*-diethyl, bp 65–67 °C (1.0 mm); *N,N*-di-*n*-propyl, bp 62–64 °C (2.0 mm); *N,N*-di-*n*-butyl, bp 80–81 °C (1.0 mm); *N,N*-di-*n*-octyl, bp 155–156 °C (1.0 mm). All acrylamides gave the expected IR and ^{1}H NMR spectra. Samples of *N,N*-dimethylacrylamide, *N,N*-diethylacrylamide, and *N,N*-di-*n*-butylacrylamide obtained commercially (Polysciences) gave identical results.

***N,N'*-Dimethyl-*N,N'*-ethylenebis(acrylamide).**[12] To a cooled solution (−30 °C) of acryloyl chloride (9.0 g, 0.10 mol) in $CHCl_3$ (75 mL) was added dropwise a mixture of *N,N'*-dimethylethylenediamine (4.4 g, 0.05 mol) and triethylamine (10.2 g, 0.1 mol). The mixture was then warmed to room temperature and stirred for an additional 2 h, and the solvent was evaporated under reduced pressure. Hexane (100 mL) was then added and the mixture filtered. Evaporation of the solvent from the filtrate followed by column chromatography of the residue on neutral alumina, using $CHCl_3$ as eluent, afforded 8.5 g (86%) of *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) as a colorless oil: ^{1}H NMR ($CDCl_3$) 6.0–6.9 (m, 4 H, CH=CH), 5.68 (m, 2 H, HCH=C), 3.62 (s, 4 H, CH_2N), 3.06 (s, 6 H, CH_3N); IR (neat) C=O 1635 (s, C=O), 1610 (m, C=C) cm^{-1}; exact mass calcd for $C_{10}H_{16}N_2O_2$ 196.2512, found 196.1227 (Midwest Center for Mass Spectroscopy, Lincoln, NE).

Polymerization Reactions. Procedures similar to that described below were used for preparing all of the polymers described in Table I. A mixture of *N,N*-diethylacrylamide (1.2 g, 10 mmol), *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) (0.019 g, 0.1 mmol), azobis(isobutyronitrile) (0.016 g, 0.1 mmol), and 2 mL of benzene was placed in a 50-mL culture tube and sealed with a Teflon-lined screw cap. The tube was heated for 3 h at 80 °C, and the resulting gel was isolated by filtration. Successive washing with two 10-mL portions of water, two 25-mL portions of distilled THF, and two 25-mL portions of toluene followed by drying [110 °C, 24 h (1.0 mm)] yielded 1.11 g of copolymer (90%). The resin was crushed with a mortar and pestle prior to use, yielding particles of ~20–40 mesh. When *N,N*-di-*n*-octylacrylamide was copolymerized with 1 or 5 mol % *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide), intractable and highly sticky polymers were formed. In all other cases, polymerization proceeded smoothly, affording resins which were convenient to handle.

Triphase Displacement. All triphase reactions were carried out in 50-mL culture tubes, using established procedures.[7] In all cases, vigorous stirring was employed (ca. 1000 rpm, using a Teflon-coated magnetic stirring bar ($0.5 \times {}^5/_{16}$ in. octagonal bar with pivot ring)). Reaction of 0.37 mmol of *n*-decyl methanesulfonate in 3 mL of toluene with 5 mL of a saturated aqueous sodium chloride solution catalyzed by 0.1 g of 10% cross-linked poly(*N,N*-di-*n*-octylacrylamide) at 90 °C afforded a 42% yield of *n*-chlorodecane after 24 h. By use of similar reaction conditions and catalyst, potassium iodide displacement on 1-bromooctane yielded 36% 1-iodooctane; all other poly(acrylamide) gels listed in Table I produced less than 4% yields of alkyl chloride or iodide.

Cross-linked *N,N*-di-*n*-octylacrylamide used to convert *n*-decyl methanesulfonate to *n*-decyl chloride was recovered by filtration, washed with two 10-mL portions of water and two 10-mL portions of toluene, and dried [110 °C, 6 h (1 mm)]; the yield of recovered catalyst was 98%. Two successive reuses gave identical results. A small preparative-scale synthesis of *n*-decyl chloride was also performed, using 4.0 g (17 mmol) of *n*-decyl methanesulfonate, 4.0 g of polymer, 80 mL of toluene, and 50 mL of saturated aqueous sodium chloride. After 24 h at 90 °C, a quantitative conversion was obtained (GLC). Distillation of the organic phase yielded 2.24 g (75%) of *n*-decyl chloride (bp 62–63 °C (1.0 mm)) which was spectroscopically identical with an authentic sample.

Biphase Displacement. A 50-mL culture tube containing a Teflon-coated magnetic stirring bar was charged with 2 mL of dry dioxane, 0.058 g (0.5 mmol) of sodium phenoxide, 0.358 g (2.0 mmol) of 1-bromoheptane, 0.02 g (0.118 mmol) of *n*-dodecane (internal standard), and 0.050 g of poly(acrylamide). The tube was sealed with a Teflon-lined screw cap, placed in an oil bath maintained at 75 °C, and monitored (GLC) by withdrawing 1-μL aliquots from the liquid phase.

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Registry No. *N,N*-Dimethylacrylamide, 2680-03-7; *N,N*-diethylacrylamide, 2675-94-7; *N,N*-di-*n*-propylacrylamide, 68404-19-3; *N,N*-di-*n*-butylacrylamide, 2274-13-7; *N,N*-di-*n*-octylacrylamide, 7773-87-7; acryloyl chloride, 814-68-6; *N,N'*-dimethylethylenediamine, 110-70-3; *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide), 60134-80-7; *n*-decyl methanesulfonate, 41233-29-8; *n*-chlorodecane, 1002-69-3; 1-bromooctane, 111-83-1; 1-iodooctane, 629-27-6; sodium phenoxide, 139-02-6; 1-bromoheptane, 629-04-9; phenyl *n*-heptyl ether, 32395-96-3; *N,N*-dimethylacrylamide *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) copolymer, 76832-62-7; *N,N*-diethylacrylamide *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) copolymer, 76832-63-8; *N,N*-di-*n*-propylacrylamide *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) copolymer, 76832-64-9; *N,N*-di-*n*-butylacrylamide *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) copolymer, 76832-65-0; *N,N*-di-*n*-octylacrylamide *N,N'*-dimethyl-*N,N'*-ethylenebis(acrylamide) copolymer, 76832-66-1.

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Selective Electrochemical Reductive Acetylation of Aromatic Nitrosulfones[1]

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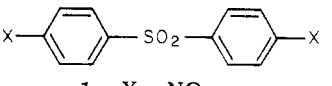
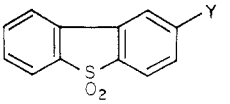
Loev et al. reported good prophylactic activity of 4,4'-bis(*N,O*-diacetylhydroxylamino)diphenyl sulfone (**1c**) vs. the malarial parasite *Plasmodium berghei*.[2] However, their synthesis of **1c** by successive steps of chemical reduction of nitro sulfone **1a** to the unstable hydroxylamino sulfone **1b** and subsequent acetylation thereof (31% overall yield) was fraught with experimental difficulties of reproducibility, side reactions, and purification. Also, an attempt to convert **1a** to **1b** by catalytic hydrogenation was abandoned because of the formation of complex mixtures.[2] We now report the successful, convenient one-step electrochemical reductive acetylation of **1a** to **1c** in 74–80% yield and the extension of this methodology to produce **2b** directly from **2a** (83%).



1a, X = NO_2
b, X = NHOH
c, X = NOAc
Ac
d, X = H



2a, Y = NO_2
b, Y = NOAc
Ac
c, Y = H

(1) (a) Paper 5 in the series on Reductive Acetylation of Nitro Compounds. For Paper 4 see: Klemm, L. H.; Barnish, I. T.; McCoy, D. R. *J. Heterocycl. Chem.* **1977**, *14*, 299. (b) Experiments conducted at the University of Melbourne.
(2) Loev, B.; Dowalo, F.; Theodorides, V. J.; Vogh, B. P. *J. Med. Chem.* **1973**, *16*, 161.

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