(965 mg, 4.0 mmol) in DMF (9.4 mL) was stirred under nitrogen at room temperature. After 18 h water was added and the product extracted with chloroform. The extract was washed with water, dried, evaporated, and chromatographed on silica TLC (chloroform–ethanol, 9:1) to give **5d** as a pale yellow oil (789 mg, 98%); NMR ($CDCl_3$) δ 1.22 (s overlapping J = 7 Hz, total 12 H), 1.8–2.6 (m, 4 H), 3.40 (s, 3 H), 4.15 (q, 4 H, J = 7 Hz), 6.21 (s, 2 H), and 7.8 (s, 1 H). Similar procedures were used to prepare **5c** (91% yield, mp 108–109 °C) and **5b** (100% yield, mp 69–71 °C).

The oily suspension of xanthine **5d** (760 mg, 1.93 mmol) in 2 N aqueous sodium hydroxide (54 mL) was refluxed under nitrogen for 2 h. The reaction mixture was cooled, acidified (pH 2–3) with 10% hydrochloric acid, and extracted with chloroform. The aqueous layer was evaporated to dryness and recrystallized from water to give the title compound, **6d**, as colorless crystals (210 mg, 43%): mp 220–222 °C; NMR (Me_2SO-d_6/$CDCl_3$) δ 1.7–2.3 (m, 4 H), 3.27 (s, 3 H), 4.10 (t, J = Hz, 2 H), 8.02 (s, 1 H).

Anal. Calcd for $C_{10}H_{12}N_4O_4 \cdot 0.5H_2O$: C, 45.97; H, 4.98; N, 21.45. Found: C, 46.09; H, 4.88; N, 21.72.

Hydrolysis of **5b** and **5c** in a similar fashion gave theophylline (1, 68% yield, mp >280 °C) and **6c** [76% yield, mp 200–201 °C (lit.[15] mp 199–201 °C)].

1-Methyl-3-(cyanoethyl)xanthine (6e). A mixture of 1-methyl-7-[(pivaloyloxy)methyl]xanthine (**5a**, 100 mg), sodium carbonate (44 mg), and acrylonitrile (38 mg) in DMF (1 mL) was heated at 100 °C under nitrogen. After 16 h water was added and the product extracted with chloroform. The organic layer was washed with water, dried, evaporated, and chromatographed on silica TLC (chloroform–ethanol, 9:1) to give **5e** as a heavy oil (109 mg) which after crystallization from methylene chloride–hexane gave white needles: mp 118–120 °C; NMR ($CDCl_3$) δ 1.18 (s, 9 H), 2.8 (t, J = 7 Hz, 2 H), 3.40 (s, 3 H), 4.20 (t, J = 7 Hz, 2 H), 6.20 (s, 2 H), and 7.85 (s, 1 H).

Hydrolysis of **5e** (100 mg) with 1 N sodium hydroxide (0.35 mL) at room temperature for 4 h gave 50 mg (70%) of 1-methyl-3-(cyanoethyl)xanthine (**6e**, mp 229–230 °C, crystallized from methylene chloride–hexane–ethanol); NMR (Me_2SO-d_6/$CDCl_3$) δ 2.85 (t, J = 7 Hz, 2 H), 3.34 (s, 3 H), 4.35 (t, J = 7 Hz, 2 H), and 7.81 (s, 1 H).

Anal. Calcd for $C_9H_9N_5O_2$: C, 49.31; H, 4.11; N, 31.99. Found: C, 48.76; H, 4.16; N, 31.44.

1,3-Dimethyl-7-[(carbethoxy)methyl]xanthine. To a partial solution of 1,3-dimethylxanthine (1, 3.6 g) in benzene (60 mL) was added under nitrogen triethylamine (2.78 mL) and trimethylchlorosilane (2.64 mL). The reaction mixture was stirred at room temperature for 16 h, filtered, and evaporated to give 1,3-dimethyl-7-(trimethylsilyl)xanthine (3.3 g, mp 158–161 °C); NMR (CCl_4) δ 0.5 (s, 9 H), 3.28 (s, 3 H), 3.50 (s, 3 H), 7.50 (s, 1 H).

A solution of the silylated product (252 mg) in benzene (2.5 mL) was treated at room temperature under nitrogen with dry sodium carbonate (211 mg) and ethyl bromoacetate (182 mg). The reaction mixture was stirred, quenched after 90 h with water, and extracted with chloroform to give 1,3-dimethyl-7-[(carbethoxy)-methyl]xanthine (mp 139–140 °C, 182 mg, 68%); NMR ($CDCl_3$) δ 1.33 (t, J = 7 Hz, 3 H), 3.4 (s, 3 H), 3.63 (s, 3 H), 4.3 (q, J = 7 Hz, 2 H), 5.13 (s, 2 H), 7.57 (s, 1 H). Anal. Calcd for $C_{11}H_{14}N_4O_4$: C, 49.62; H, 5.26; N, 21.05. Found: C, 49.31; H, 5.27; N, 21.08.

Registry No. 1, 58-55-9; 4, 43018-00-5; **5a**, 69150-36-3; **5b**, 64210-71-5; **5c**, 73018-01-6; **5d**, 69150-37-4; **5e**, 73018-02-7; **6a**, 6136-37-4; **6c**, 28822-58-4; **6d**, 73017-77-3; **6e**, 69150-39-6; 1,3-dimethyl-7-[(carboethoxy)methyl]xanthine, 7029-96-1; 1,3-dimethyl-7-(trimethylsilyl)xanthine, 62374-32-7; 1-methyl-7-[(carboethoxy)-methyl]xanthine, 73017-78-4; 1-methyl-3,7-bis[(carboethoxy)-methyl]xanthine, 73017-79-5; chloromethyl pivalate, 18997-19-8; ethyl 4-iodobutyrate, 7425-53+-8.

(14) Melting points are determined in capillary tubes with a Thomas–Hoover Uni-Melt apparatus and are uncorrected. Solutions in organic solvents were dried over anhydrous sodium sulfate. UV spectra were recorded on a Cary 15 spectrophotometer, while IR spectra were recorded on a Perkin-Elmer instrument. Unless specified otherwise, the NMR spectra were recorded on a Varian T-60 instrument and the values are given in parts per million downfield from tetramethylsilane as an internal standard.

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Use of Vinylogous Urethanes in Alkaloid Synthesis: Formal Synthesis of Ipalbidine

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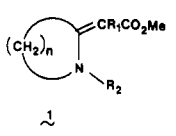
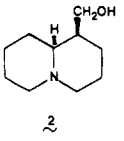
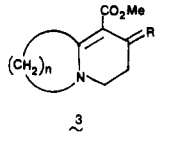
Fused five- and six-membered rings containing nitrogen at the bridgehead position are a common structural feature in a wide variety of alkaloidal systems. We are at present developing a reaction sequence which should be of general use in the synthesis of such systems. The key intermediates in this sequence are exocyclic vinylogous urethanes such as 1 (R_1 = H, R_2 = H or alkyl, n = 3 or 4), which are most conveniently prepared by means of the "sulfide contraction" procedure developed by Eschenmoser.[1] Vinylogous urethanes are stabilized enamines, and it is in this sense that we use them in intramolecular cyclizations to form bicyclic structures. Depending on the needs of the particular synthesis being carried out, the cyclization may be an alkylative one (as shown in our earlier synthesis of lupinine (**2**)[2]) or an acylative one (as in the present case). The bicyclic systems (**3**, R = O or 2H) produced in this way retain the vinylogous urethane grouping, and hence further annulation is possible.[2] The alkoxycarbonyl group, introduced initially to stabilize the exocyclic enamine, may readily be removed after the cyclization if this is desired, but in many cases it is correctly positioned for conversion to a functionality present in a particular alkaloid (e.g., lupinine, **2**).



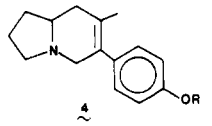
1



2



3



4

Ipalbidine (**4**, R = H), the aglycon of the alkaloid ipalbine (**4**, R = β-D-glucosyl), isolated from *Ipomoea alba L.*[3] has been synthesized by several groups of workers.[4-7] In two of these syntheses[5,6] the bicyclic ketone (**12**) was prepared and converted to ipalbidine; our synthesis of compound (**12**), outlined in Scheme I, thus constitutes a formal synthesis of ipalbidine.

The key feature of our sequence is the acylative ring closure (**7**) to (**9**). In principle, it should be possible to attach the appropriate substituent for the annulation step to the nitrogen atom of the vinylogous urethane system (1, R_1 = R_2 = H, n = 3), but in practice, we have not found

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(2) G. C. Gerrans, A. S. Howard, and B. S. Orlek, *Tetrahedron Lett.*, 4171 (1975).

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(5) T. R. Govindachari, A. R. Sidhaye, and N. Viswanathan, *Tetrahedron*, **26**, 3829 (1970).

(6) R. V. Stevens and Y. Luh, *Tetrahedron Lett.*, 979 (1977).

(7) S. H. Hedges and R. B. Herbert, *J. Chem. Res. (S)*, 1 (1979).

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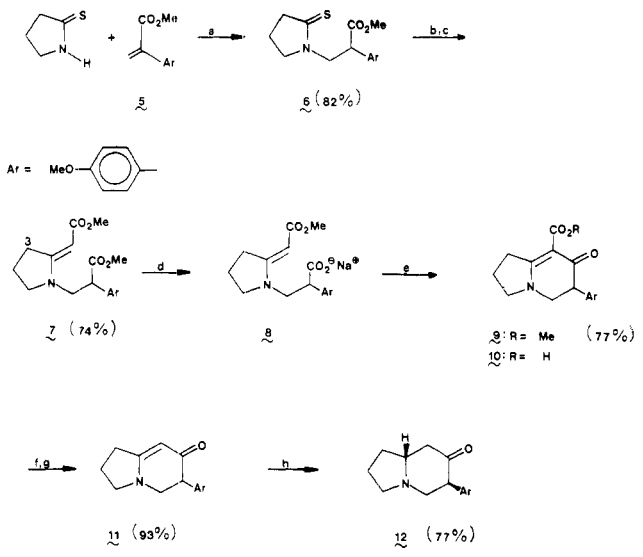
Scheme I[a]



[a] (a) NaOH (catalyst), THF; (b) $BrCH_2CO_2Me$, THF; (c) PPh_3, NEt_3, CH_3CN; (d) NaOH, H_2O; (e) Bu_4NI (catalyst), $ClCO_2Me$, THF; (f) KOH, H_2O, N_2; (g) HCl, H_2O; (h) $LiAlH_4$, THF.

reaction conditions under which this can reliably be achieved.[8] However, N-alkylation of thiolactams, themselves ambident nucleophiles, may be achieved in high yields by means of the Michael reaction. In this case, pyrrolidine-2-thione[9] was treated with methyl 2-(4-methoxyphenyl)propenoate (**5**), prepared according to the method of Ames and Davey,[10] by using a catalytic amount of base, to produce the N-substituted thiolactam (**6**) in 82% yield.

A further reason for alkylating at nitrogen at this early stage is that we have found[8] that the sulfide contraction proceeds under very much milder conditions and in better yields for tertiary thiolactams rather than for the secondary thiolactams investigated by Eschenmoser.[1] Here, reaction of (**6**) with methyl bromoacetate yielded the S-alkylated iminium salt which, without purification, was stirred at room temperature with triethylamine and triphenylphosphine to effect extrusion of sulfur. The stereochemistry of the product, the vinylogous urethane (**7**), was assigned as shown on the basis of the ultraviolet spectrum[11] and the anisotropic deshielding experienced by the protons at C-3 in the pyrrolidine ring of **7**. These protons appear as a triplet at δ 3.09, whereas vinylogous urethanes having the opposite geometry about the double bond (as in **1** when R_2 = H and n = 3) typically give a signal around δ 2.50 for the C-3 protons.[1,8,12]

Since our previous attempts to bring about acylative ring closure by the intramolecular reaction of vinylogous urethanes with ester groups had proved unsuccessful,[13] compound **7** was hydrolyzed to the salt **8**. On treatment with methyl chloroformate in the presence of a catalytic quantity of tetrabutylammonium iodide, **8** was converted to a mixed anhydride which, without isolation, was irreversibly cyclized to **9** on stirring in tetrahydrofuran under nitrogen at room temperature. In the absence of nitrogen, a highly fluorescent impurity was formed which proved difficult to remove.

Removal of the methoxycarbonyl group was expected to be straightforward in view of the results reported by Eschenmoser[14] with compound **1** (R_1 = CN, R_2 = H, n = 3), and this was indeed the case. The hydrolyzed but not decarboxylated compound **10** could be isolated if treatment with acid was omitted, though normal base hydrolysis followed by acidic workup gave the vinylogous amide **11** in 93% yield. Selective reduction of the carbon–carbon double bond in vinylogous amides is known to be difficult to achieve,[15] but careful reduction with lithium aluminium hydride yielded the target product **12** in 77% yield. The infrared spectrum of this compound was identical with that of an authentic sample.[16]

The recently published[17] use of a vinylogous urethane in the synthesis of a pyrrolizidine alkaloid, the above synthesis of an indolizidine, and our previous synthesis of a quinolizidine[2] suggest that vinylogous urethanes should serve as useful precursors for more complex alkaloids with nitrogen at bridgehead positions.

Experimental Section

Spectroscopic data were obtained by using the following instruments: ^{1}H NMR, Varian HA-100; IR, Perkin-Elmer 521; UV, Unicam SP-1800; mass spectra, Varian CH-5 or AEI MS-9. Unless otherwise specified the ^{1}H NMR spectra were measured in $CDCl_3$ solution and the chemical shifts are reported on the δ scale relative to Me_4Si as internal standard; the IR spectra were measured as KBr dispersions; the UV spectra were obtained for solutions in ethanol and are reported as λ_{max} (ϵ_{max}); the mass spectra were measured at 70 eV by using a direct insertion probe and are reported in m/e values (relative abundance), with all peaks of relative abundance greater than 10% given. Melting points were obtained by using a micro hotstage apparatus and are uncorrected.

Methyl 2-(4-Methoxyphenyl)propenoate (5). The procedure followed is a modification of that of Ames and Davey.[10] Sodium hydride (4.2 g, 0.14 mol, 80% dispersion in oil), washed free of oil with dry THF, was suspended in dry benzene (100 mL) in which was dissolved dimethyl oxalate (10.5 g, 89 mmol). A solution of methyl (4-methoxyphenyl)acetate (15.75 g, 87.5 mmol) in dry benzene (100 mL) was added dropwise to the vigorously stirred suspension (room temperature, 1 h). After 4.5 days, the thick yellow solid which had formed was filtered and washed thoroughly with ether. The solid cake was dissolved in 2 M HCl (100 mL) and the solution was extracted with ether (3 × 50 mL). The combined extracts were dried (Na_2SO_4) and evaporated to an oil (20.6 g, 88.5%); IR (liquid film) 1750, 1660, 1615, 1520 cm^{-1}.

The oil was suspended in water (75 mL) and an aqueous solution of formaldehyde (35–40%, 10 mL) was added. This was followed by the dropwise addition (room temperature, 0.75 h) of a solution of potassium carbonate (9.0 g) in water (50 mL) to the stirred solution. After a further 7.5 h, the resulting mixture was extracted with ether (3 × 50 mL). The combined ether extracts were dried (Na_2SO_4) and evaporated to yield the desired product (13.22 g). Distillation at 124 °C (0.15 mmHg) gave the product as a clear oil (10.42 g, 62% overall): ^{1}H NMR δ 3.72 (6 H, s), 5.70 (1 H, d, J = 1.5 Hz), 6.14 (1 H, d, J = 1.5 Hz), 6.75 (2 H, d, J = 8 Hz), 7.25 (2 H, d, J = 8 Hz); IR (liquid film) 1713, 1601, 1505 cm^{-1}; mass spectrum, m/e 192 (50, M$^+$), 135 (13), 134 (100), 122 (52); molecular ion calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0784.

Methyl 2-(4-Methoxyphenyl)-3-(2-thionopyrrolidin-1-yl)propionate (6). Pyrrolidine-2-thione[9] (0.800 g, 7.9 mmol) and **5** (1.554 g, 8.1 mmol) were dissolved in dry THF (20 mL), and sodium hydroxide (ca. 0.05 g) was added. The mixture was stirred

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(16) We should like to extend our thanks to Dr. N. Viswanathan of Ciba-Geigy Research Centre, Bombay, for providing us with a copy of the infrared spectrum of the amino ketone **12**.
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(room temperature, 13 h; 55 °C, 3.5 h), then poured into a saturated brine solution (20 mL), and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried (Na_2SO_4) and filtered and the volatiles removed under vacuum to yield the crude product (2.478 g). This was chromatographed (silica gel, 60 g; benzene, then benzene–ethyl acetate mixtures) to yield chromatographically pure samples of the starting ester (0.165 g, 11%), **6** (1.909 g, 82%), and pyrrolidine-2-thione (0.126 g, 16%). Attempted distillation of **6** under high vacuum (5×10^{-5} mmHg) resulted in extensive decomposition via the retro-Michael reaction, but it could be crystallized from petroleum ether/ethyl acetate: mp 58.5–60 °C; ^1H NMR δ 1.68–2.04 (2 H, m), 2.93 (2 H, t, J = 8 Hz), 3.10–3.34 (1 H, m), 3.50–4.58 (4 H, m), 3.65 (3 H, s), 3.73 (3 H, s), 6.83 (2 H, d, J = 8 Hz), 7.22 (2 H, d, J = 8 Hz); IR 1738, 1612, 1513 cm^{-1}; UV 229 (11 800), 270 (15 500) nm; mass spectrum, m/e 293 (34, M^+), 193 (16), 192 (100), 133 (36), 114 (17), 85 (16); molecular ion calcd for $C_{15}H_{19}NO_3S$ 293.1086, found 293.1057. Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.20; H, 6.46; N, 4.89.

Methyl 2-(4-Methoxyphenyl)-3-[2-[(methoxycarbonyl)-methylene]pyrrolidin-1-yl]propionate (7). Methyl bromoacetate (5.15 g, 33.3 mmol) was added to a solution of **6** (7.25 g, 24.7 mmol) in dry THF (50 mL) and stirred at room temperature (16 h). The volatiles were removed under vacuum, the residue was dissolved in acetonitrile (100 mL), and triphenylphosphine (6.6 g, 25 mmol) and triethylamine (4 mL, 29 mmol) were added at room temperature. An exothermic reaction occurred immediately. The solution was stirred (30 min), the volatiles were removed under vacuum, and the residue was chromatographed (silica gel, 250 g, petroleum ether (60–80 °C)/ether 9:1). The product so obtained was contaminated with a small amount of triphenylphosphine sulfide and was purified by extraction into 2 M HCl, basification with concentrated NH_3 and extraction back into CH_2Cl_2. After the solution was dried (Na_2SO_4), the solvent was removed to yield a crystalline product (6.053 g, 74%), mp 85–88 °C. Recrystallization from petroleum ether (60–80 °C)/ethyl acetate gave an analytical sample: mp 86.5–88 °C; ^1H NMR δ 1.60–1.94 (2 H, m), 3.09 (2 H, t, J = 8 Hz), 2.76–4.10 (5 H, m), 3.62, 3.65, 3.78 (each 3 H, s), 4.57 (1 H, br s), 6.84 (2 H, d, J = 8 Hz), 7.18 (2 H, d, J = 8 Hz); IR 1732, 1688, 1580, 1508 cm^{-1}; UV 229 (12 200), 280 (29 300) nm and after addition of acid 228 (11 200), 277 (6500), 282 (6600) nm; mass spectrum, m/e 333 (16, M^+), 192 (46), 154 (100), 122 (13), 45 (35), 43 (17); molecular ion calcd for $C_{18}H_{23}NO_5$: 333.1576, found 333.1608. Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.96; N, 4.21. Found: C, 64.62; H, 7.08; N, 4.30.

Sodium 2-(4-Methoxyphenyl)-3-[2-[(methoxycarbonyl)-methylene]pyrrolidin-1-yl]propionate (8). **7** (5.5 g, 16.5 mmol) was suspended in water (40 mL), and NaOH (0.680 g, 17 mmol) was added. The suspension was refluxed until the mixture became homogeneous (2.5 h). The water was removed under vacuum, the last traces were azeotroped off with benzene, and the resulting solid (5.66 g) was dried (room temperature, 0.1 mmHg). This salt was used without any further purification.

Methyl 1-Aza-3-(methoxyphenyl)-4-oxobicyclo[4.3.0]-5-nonene-5-carboxylate (9). **8** (0.844 g, 2.5 mmol) was suspended in dry THF (25 mL) under a N_2 atmosphere, and a catalytic amount (0.020 g) of tetrabutylammonium iodide was added. Methyl chloroformate (0.20 mL, 2.6 mmol) was added, and the solution was stirred at room temperature (8 h). The volatiles were removed and the dried residue was chromatographed (silica gel, 25 g; benzene–acetone 7:3, then increasing amounts of acetone up to pure acetone) to yield chromatographically pure samples of **7** (0.093 g, 11%) and **9** (0.572 g, 77%). An analytical sample was obtained by recrystallization from methanol–benzene (1:1): mp 126–127 °C; ^1H NMR δ 1.90–2.26 (2 H, m), 3.30 (2 H, t, J = 8 Hz), 3.40–3.85 (5 H, m), 3.70 (3 H, s), 3.74 (3 H, s), 6.80 (2 H, d, J = 8 Hz), 7.10 (2 H, d, J = 8 Hz); IR 3400, 1660, 1617, 1580, 1518 cm^{-1}; UV 226 (10 200), 246 (13 700), 285 sh (6800), 304 (11 700) nm and after addition of acid 226 (14 900), 244 sh (5700), 303 (8200) nm; mass spectrum, m/e 301 (40, M^+), 135 (24), 134 (100), 119 (18), 91 (14), 44 (20); molecular ion calcd for $C_{17}H_{19}NO_4$ 301.1314, found 301.1300. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.75; H, 6.36; N, 4.65. Found: C, 67.76; H, 6.20; N, 4.93.

1-Aza-3-(4-methoxyphenyl)bicyclo[4.3.0]-5-nonen-4-one (11). An aqueous solution of KOH (1 M, 25 mL) was deaerated by bubbling N_2 through it overnight. **9** (0.471 g, 1.56 mmol) was then added and the solution was refluxed (1 h). It was then cooled, acidified (concentrated HCl), stirred at room temperature (30 min), basified (concentrated NH_3), and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and filtered, and the solvent was removed under vacuum to yield chromatographically pure **11** (0.352 g, 93%). The aqueous layer was reacidified (concentrated HCl) and extracted with CH_2Cl_2 (3 × 10 mL) to yield, after drying and removal of the solvent, **10** (0.032 g, 7%). On some occasions greater proportions of **10** were obtained; it could, however, be converted to **11** simply by warming with 2 M HCl. **10** was recrystallized from nitromethane; mp 186–188 °C; IR 3430, 2650, 1705, 1565, 1495 cm^{-1}; UV 232 (15 600), 241 (17 100), 285 sh (6900), 307 (12 200) nm, and essentially no change on addition of acid, but on addition of base 226 (16 000), 241 sh (8300), 284 sh (3600), 322 (13 100) nm; mass spectrum, m/e 287 (25, M^+), 135 (32), 134 (100), 119 (40), 91 (35), 69 (30), 65 (18); molecular ion calcd for $C_{16}H_{17}NO_4$ 287.1158, found 287.1179. Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.71; H, 6.05; N, 5.42.

11: Recrystallization from a variety of solvents did not yield material having a sharp melting point. A sample recrystallized finally from benzene, mp 125–138 °C, gave acceptable analytical results and was used for spectral characterization: ^1H NMR δ 1.86–2.24 (2 H, m), 2.70 (2 H, t, J = 8 Hz), 3.26–3.70 (5 H, m), 3.74 (3 H, s), 5.08 (1 H, s), 6.80 (2 H, d, J = 8 Hz), 7.14 (2 H, d, J = 8 Hz); IR 1633, 1616, 1585, 1520 cm^{-1}; UV 224 (11 600), 278 sh (3300), 285 sh (4200), 318 (15 200) nm and after addition of acid 224 (11 400), 276 sh (5200), 284 sh (6800), 307 (10 000) nm; mass spectrum, m/e 243 (36, M^+), 135 (19), 134 (100), 119 (22), 91 (22). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.14; H, 7.04; N, 5.76. Found: C, 74,47; H, 7.06; N, 5.87.

1-Aza-3-(4-methoxyphenyl)bicyclo[4.3.0]nonan-4-one (12). Vinylogous amide **11** (0.173 g, 0.71 mmol) was dissolved in dry THF (10 mL), $LiAlH_4$ (0.007 g, 0.18 mmol) was added, and the solution was stirred at room temperature. After 20 min, TLC (benzene–acetone 1:1) showed that approximately equal amounts of starting material and product were present, so more $LiAlH_4$ (0.007 g) was added. Stirring was continued for 10 min, and then water (0.2 mL) and CH_2Cl_2 (10 mL) were added. The solution was dried (Na_2SO_4), and the volatiles were removed under vacuum to leave an oily residue (0.205 g) which was crystallized from an acetone–petroleum ether (40–60 °C) mixture (0.134 g, 77%, mp 105–108 °C). Further recrystallizations from acetone raised the melting point to 109–110 °C (lit. 105–106 °C,[5] 105.5–106 °C [6]): ^1H NMR δ 1.4–3.9 (series of m), 3.77 (3 H, s), 6.84 (2 H, d, J = 8 Hz), 7.04 (2 H, d, J = 8 Hz); IR (5% solution in CH_2Cl_2) 2950, 2800, 1715, 1618, 1518 cm^{-1}; mass spectrum, m/e 245 (28, M^+), 134 (100), 133 (26), 131 (17), 119 (22), 97 (16), 96 (16), 91 (15), 69 (73); molecular ion calcd for $C_{15}H_{19}NO_2$ 245.1416, found 245.1405.

Registry No. **5**, 50415-68-4; **6**, 73048-93-8; **7**, 73048-94-9; **8**, 73048-95-0; **9**, 73048-96-1; **10**, 73048-97-2; **11**, 73048-98-3; **12**, 73048-99-4; pyrrolidine-2-thione, 2295-35-4; dimethyl oxalate, 553-90-2; methyl (4-methoxyphenyl)acetate, 23786-14-3.

Migration of the Acyl Group in Substituted *o*-Aminophenols: Acetyl–Chloroacetyl Derivatives

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Smith and Elrod have recently reported that the diacyl-*o*-aminophenols **1a**, **1b**, and **1c** predominate over their isomers **2a**, **2b**, and **2c** in the equilibrium mixtures formed

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