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Reaction of a 1-Azirine-3-methylacrylate and Derivatives with Diphenylketene. A Convenient Route to 5-Pyrrolin-2-ones.

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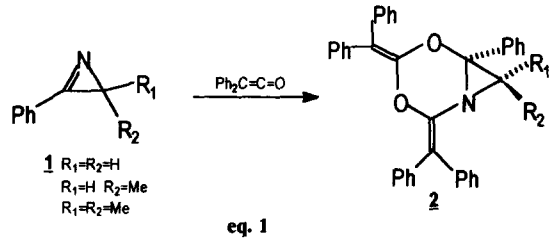
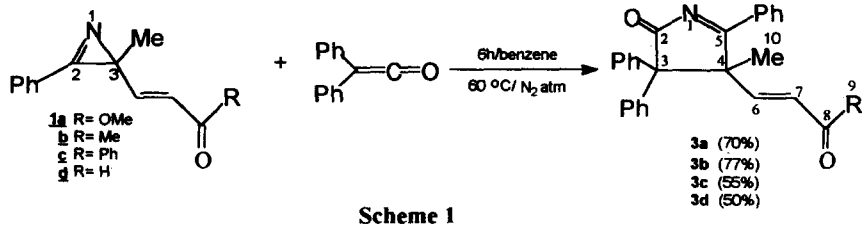
Abstract: Reaction of 1-azirines **1a-d** with diphenylketene afforded 1:1 adducts that were shown to be 5-pyrrolin-2-ones **3a-d**. Some transformations of **3** are described. © 1997 Elsevier Science Ltd.

Reaction of simple 1-azirines **1** with diphenylketene has been reported to afford bicyclic aziridines **2**, formed by way of addition of two equivalents of ketene to the imine moiety (eq. 1)[1]. Our interest in the effect of higher order functionality at the 3-position of the 1-azirine nucleus on the mode of ring opening[2] prompted us to investigate the above reaction utilizing more complex derivatives of **1**, with special emphasis on synthetic implications.



eq. 1

Thus, when 1-azirine-3-methylacrylate **1a** was submitted to the above reaction conditions (1,2-diphenyldiazoethanone employed as source of diphenylketene), a 1:1 adduct was obtained (70% yield) which was shown to be the 5-pyrrolin-2-one **3a** (**Scheme 1**). The data obtained from the long-range (^3J) carbon-proton correlation (COLOC) spectrum (**Table 1**) defines the regiochemistry of ketene addition at the N_1-C_3



Scheme 1

bond of **1a**. Only structure **3a** is consistent with this data. Although 2,3-diphenyl-1-azirine has been reported to produce a 5-pyrrolin-2-one under these same condtions[3], the low yield presented (percentage yield not cited) coupled with a mechanistic proposal requiring that C_3 accommodate positive charge as the N_1-C_3 bond breaks, makes the present observation an unexpected one.

Table 1 - ^{13}C and ^{1}H Shifts, and 2D NMR Data for 3a.

Position	^{13}C (ppm)	^{1}H (ppm)	COLOC [a]
2	190.2s	-	-
3	71.3s	-	1.33; 7.40
4	60.1s	-	1.33; 5.75
5	199.1s	-	1.33; 7.40; 8.20
6	131.0d	7.40d	5.75
7	123.0d	5.75d	7.40
8	165.8s	-	3.65; 5.75; 7.40
9	51.8q	3.65	-
10	25.2q	1.33	7.40
11	-	8.20	-

Position 11 - ortho protons of the phenyl group at C_5.

[a] Long-range carbon-proton correlation observed in the long-range COLOC spectrum.

Formation of the 5-pyrrolin-2-one nucleus appears to be quite general for 1-azirines containing an α,β-unsaturated carbonyl fragment at the 3-position, as may be seen from the results of the reactions of derivatives **1b-d**, wherein **3b-d** were obtained in good yields (**Scheme 1**). It should be mentioned that while **1d** reacted smoothly with diphenylketene, 2-phenyl-3-formyl-3-methyl-1-azirine was unreactive, thus demonstrating the importance of the α,β -unsaturation for the process.

The polyfunctional nature of the 5-pyrrolin-2-ones **3** obtained in this study motivated us to examine the reactivity of this interesting system. Some preliminary findings in this direction are summarized in **Schemes 2** and **3**. Thus, alcohols added readily to the imine fragment in **3**, as illustrated for the reactions of methanol with **3a-c**, wherein methoxy pyrrolidinones **4a-c** were obtained as mixtures of diastereomers.

The anisotropic shielding effect of the C_5-phenyl on the cis C_4-methyl in **4**, observed in the ^{1}H-NMR spectrum, allows facile distinction of isomers. Under conditions of catalytic hydrogenation (H_2/Pd-C/MeOH/6h), diastereomeric mixtures of **4b-c** (**4a-a'** did not react under these conditions) suffered concomitant hydrogenolysis of the C_5 methoxy with intramolecular Michael addition to afford 2-

azabicyclo[3.1.0]hexanes **5a-b**, respectively. The stereochemistry presented is the result a NOE-difference experiment performed on **5a** (Figure 1).

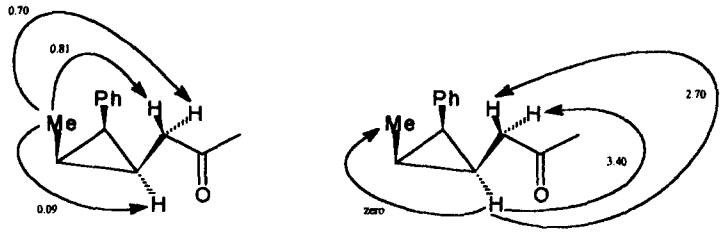
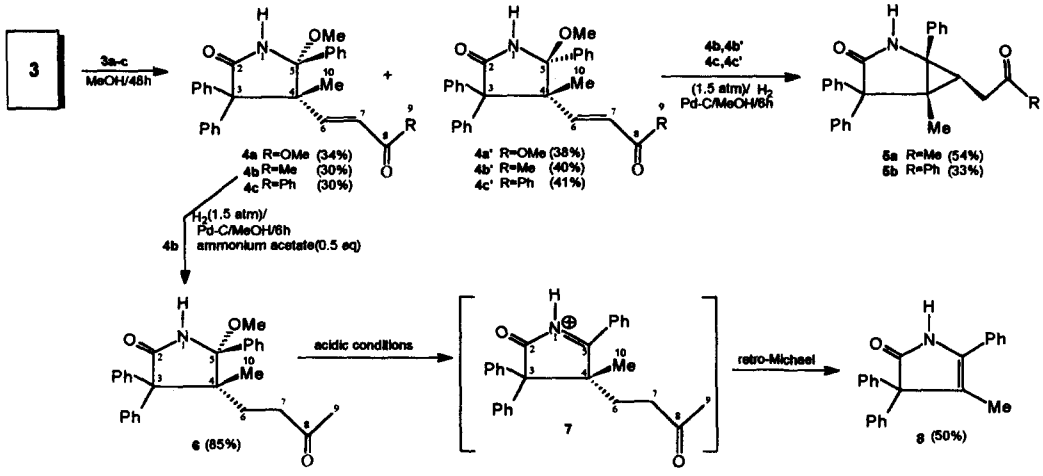


Figure 1. NOE experiment for **5a**

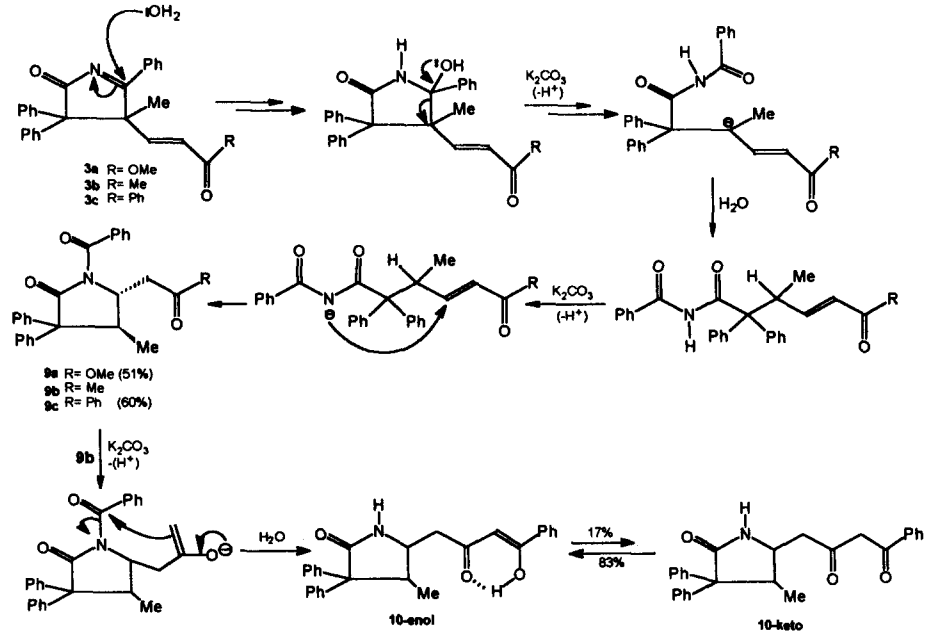
To the best our knowledge this reaction represents a new approach to cyclopropane ring formation. The addition of ammonium acetate (0.5 equiv.) to the Pd-C catalyst has recently been reported[4] to inhibit hydrogenolysis of benzyl ethers during reduction of isolated olefins.



Scheme 2

Interestingly, when diastereomer **4b** (that which contains C_4-Me cis to C_5-Ph) was submitted to this condition, a smooth reduction to **6** was observed without any indication of hydrogenolysis. It is noteworthy that diastereomer **4b'**, which contains the more hindered doubled bond, did not react under these conditions. Although **6** (under acidic conditions) would seem to be an excellent candidate for an intramolecular aldol process involving C_9 in acylimminium intermediate **7**, a competing retro-Michael pathway actually produced pyrrolinone **8** exclusively. Extensive substitution at C_4 and C_5 in **6** appears to be responsible for this observation, in as much as simpler analogues have been reported[5] to undergo intramolecular cyclization. Hydrolysis of the imine fragment in **3a-c** occurred smoothly under mild basic conditions (K_2CO_3/DMSO-H_2O) to afford the rearranged pyrrolidinones **9a,c** and **10** (59% yield). A mechanistic rational is presented in **Scheme 3**. Formation of **10** involves an interesting benzoyl migration in an enolate derivative of **9b**. The

stereochemistry presented in a **9** is supported by the NOE-difference experiment performed on **9a** (Figure 2).



Scheme 3

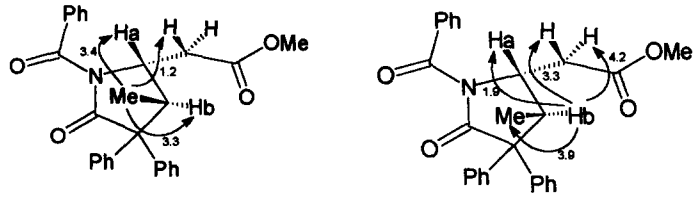


Figure 2. NOE experiment for **9a**

While the motive for the change in behavior of 1-azirines towards diphenylketene as a function of the nature of the substituent at the 3-position is at the present time unclear to us, it is apparent from the results of this study that modification of these substituents constitutes an excellent approach to diversity in ring-opening, thus providing access to an ever increasing number of new nitrogen-containing heterocycles.

Experimental Section

The melting points are uncorrected. The IR spectra (KBr was used for solid samples and film for liquid samples) were measured with a Perkin Elmer FTIR-1600 spectrophotometer, ^{1}H NMR spectra (in $CDCl_3$) with BRUCKER AW-80, VARIAN GEMINI-300 and BRUCKER AC 300/P instruments with Me_4Si as an internal standard, ^{13}C NMR spectra (in $CDCl_3$) with a VARIAN GEMINI-300 spectrometer. The elemental analyses were determined with a Perkin-Elmer 2400-CHN instrument.

The 1-azirines[6] and diphenyldiazoethanone[7] were prepared according to known procedures. Formylmethylenetriphenylphosphorane used in the preparation of **1d** was prepared as described in the literature[8]. Physical data of new **1b-d** (obtained as oils) are as follows:

1b. ^{1}H NMR (CCl_4) δ 1.55 (s,3H), 2.05 (s,3H), 6.05 (d, 1H, J=16Hz), 6.45 (d, 1H, J=16Hz), 7.50 (m, 5H). Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.51; H, 6.48; N, 7.20.

1c. ^{1}H NMR (CCl_4) δ 1.60 (s,3H), 6.83 (s, 2H), 7.50 (m, 10H). Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N,5.36. Found: C, 82.83; H, 5.90; N, 5.16.

1d. ^{1}H NMR (CCl_4) δ 1.59 (s,3H), 6.16 (dd, 1H, J=8 and 16Hz), 6.40 (d, 1H, J=16Hz), 7.60 (m, 5H), 9.43 (d, 1H, J=8Hz). Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.98; H, 5.85; N, 7.40.

General Procedure for Reactions of 1-azirines 1 with diphenylketene.

A solution of 1-azirine and 1,2-diphenyldiazoethanone (20% molar excess) in dry benzene (10 mL per mmol of 1-azirine) was heated (60°C) under nitrogen atmosphere for 6h after which time the solvent was removed by rotatory evaporation. The following **3** were obtained by recrystallization using CH_2Cl_2/petroleum ether (30-60 °C) as solvents:

3a. Obtained as a colorless solid (137.4 mg, 70% yield) from the reaction of 1-azirine **1a** (103.2 mg, 0.48 mmol): m.p. 160-161 °C; ^{1}H NMR δ 1.33 (s,3H), 3.65 (s,3H), 5.75 (d, 1H, J=16Hz), 7.40 (d, 1H, J=16Hz), 7.50 (m, 15H); ^{13}C NMR δ 25.2, 51.8, 60.1, 71.3, 123.0, 131.0, 113.0-150.0, 165.8, 190.2, 199.1; IR 1731, 1582 cm^{-1}. Anal. Calcd for $C_{27}H_{23}NO_3$: C, 79.22; H, 5.62; N, 3.42. Found: C, 79.32; H, 5.70; N, 3.26.

3b. Obtained as a colorless solid (230.7 mg, 77% yield) from the reaction of 1-azirine **1b** (157.7 mg, 0.76 mmol): m.p. 79-81 °C; ^{1}H NMR δ 1.49 (s,3H), 2.00 (s,3H), 6.04 (d, 1H, J=16Hz), 6.98 (d, 1H, J=16Hz), 7.50 (m, 15H); ^{13}C NMR δ 23.6, 27.2, 60.6, 71.0, 126.0-150.0, 190.2, 199.1, 197.4; IR 1748, 1680 cm^{-1}. Anal. Calcd for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56. Found: C, 52.59; H, 5.71; N, 3.71.

3c. Obtained as a yellow oil (108.1 mg, 55% yield) from the reaction of 1-azirine **1c** (112.8 mg, 0.43 mmol): ^{1}H NMR δ 1.50 (s,3H), 6.75 (d, 1H, J=16Hz), 7.65 (d, 1H, J=16Hz), 7.80 (m, 20H); ^{13}C NMR δ 25.2, 60.8, 71.6, 126.0-150.0, 190.4, 190.8, 199.9; IR 1741, 1670 cm^{-1}. Anal. Calcd for $C_{32}H_{25}NO_2$: C, 84.37; H, 5.53; N, 3.07. Found: C, 84.23; H, 5.41; N, 3.21.

3d. Obtained as a colorless solid (123.7 mg, 50% yield) from the reaction of 1-azirine **1d** (120.8 mg, 0.31 mmol): m.p. 98-100 °C; ^{1}H NMR δ 1.47 (s,3H), 6.17 (m,1H), 7.80 (m, 16H), 9.40 (d, 1H, J=8Hz); ^{13}C NMR δ 24.7, 60.9, 71.4, 126.0-138.0, 190.3, 193.0, 198.9; IR 1742, 1693 cm^{-1}. Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.46; H, 5.73; N,3.56.

Reaction of 5-pyrrolin-2-ones 3a-c with methanol. The residues of the reactions of 1-azirines **1** with 1,2-diphenyldiazoethanone were dissolved in methanol (200mg/10 mL) and allowed to stand for 48h after which time the solvent was removed by rotatory evaporation. The residues were treated as follows:

Separation of 4 and 4'. Chromatography of the residues on Florisil afforded **4** as a colorless solid [35% petroleum ether (30-60 °C)-benzene as eluant] and **4'** as a colorless solid [10% ethyl ether (30-60 °C)-benzene as eluant]. The following **4** and **4'** were isolated:

4a. Obtained as a colorless solid (97.3 mg, 30% yield from **1a**) from the reaction of 1-azirine **1a** (152.8 mg, 0.71 mmol): m.p. 169-171 °C; ^{1}H NMR δ 1.54 (s,3H), 3.00 (s,3H), 3.48 (s,3H), 5.19 (d, 1H, J=16Hz), 6.67 (d, 1H, J=16Hz), 7.50 (m, 15H); ^{13}C NMR δ 14.9, 49.4, 51.4, 59.0, 64.2, 94.4, 119.0-154.0, 166.3, 179.1; IR 3166, 1691 cm^{-1}. Anal. Calcd for $C_{28}H_{27}NO_4$: C, 76.17; H, 6.16; N, 3.17. Found: C, 76.41; H, 6.31; N, 3.06.

4a'. Obtained as a colorless solid (129.7 mg, 40% yield from **1a**) from the reaction of 1-azirine **1a** (152.8 mg, 0.71 mmol): m.p. 167-169 °C; ^{1}H NMR δ 0.60 (s,3H), 2.87 (s,3H), 3.80 (s,3H), 5.67 (d, 1H, J=16Hz), 7.50 (m, 15H) , 8.07 (d, 1H, J=16Hz); ^{13}C NMR δ 24.6, 49.4, 51.9, 57.3, 66.5, 95.3, 126.0-153.0, 167.1, 179.0; IR 3192, 1698 cm^{-1}. Anal. Calcd for $C_{28}H_{27}NO_4$: C, 76.17; H, 6.16; N, 3.17. Found: C, 76.35; H, 6.09; N, 3.10.

4b. Obtained as a colorless solid (84.0 mg, 34% yield from **1b**) from the reaction of 1-azirine **1b** (115.7 mg, 0.58 mmol): m.p. 190-191 °C; ^{1}H NMR δ 1.54 (s,3H), 1.64 (s,3H), 3.03 (s,3H), 5.33 (d, 1H, J=16Hz), 6.26 (d, 1H, J=16Hz), 7.40 (m, 15H); ^{13}C NMR δ 14.8, 25.8, 49.6, 58.6, 64.8, 94.2, 126.0-153.0, 179.2, 198.1; IR 3211, 1693 cm^{-1}. Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29. Found: C, 76.32; H, 6.59; N, 3.21.

4b'. Obtained as a colorless solid (93.9 mg, 38% yield from **1b**) from the reaction of 1-azirine **1b** (115.7 mg, 0.58 mmol): m.p. 192-194 °C; ^{1}H NMR δ 0.67 (s,3H), 2.32 (s,3H), 2.89 (s,3H), 5.93 (d, 1H, J=16Hz), 7.60 (m, 15H) , 7.77 (d, 1H, J=16Hz); ^{13}C NMR δ 23.8, 27.1, 49.5, 57.4, 66.0, 95.5, 126.0-148.0, 179.2, 199.1; IR 3211, 1698 cm^{-1}. Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29. Found: C, 79.32; H, 6.59; N, 3.21.

4c. Obtained as a colorless solid (82.3 mg, 30% yield from **1c**) from the reaction of 1-azirine **1c** (147.0 mg, 0.56 mmol): m.p. 132-133 °C; ^{1}H NMR δ 1.64 (s,3H), 3.02 (s,3H), 6.05 (d, 1H, J=16Hz), 6.51 (d, 1H, J=16Hz), 7.40 (m, 15H); ^{13}C NMR δ 15.3, 49.4, 59.3, 64.3, 94.3, 125.0-153.0, 178.8, 191.2; IR 1700, 1670cm^{-1}. Anal. Calcd for $C_{33}H_{29}NO_3$: C, 81.29; H, 5.99; N, 2.87. Found: C, 81.08; H, 6.18; N, 2.74.

4c'. Obtained as a colorless solid (112.4 mg, 41% yield from **1c**) from the reaction of 1-azirine **1c** (147.0 mg, 0.56 mmol): m.p. 131-133 °C; ^{1}H NMR δ 0.68 (s,3H), 2.88 (s,3H), 6.68 (d, 1H, J=16Hz), 7.50 (m, 15H) , 8.20 (d, 1H, J=16Hz); ^{13}C NMR δ 24.5, 49.6, 53.0, 66.5, 95.0, 126.0-150.0, 179.6, 190.5; IR 3177, 1701, 1671 cm^{-1}. Anal. Calcd for $C_{33}H_{29}NO_3$: C, 81.29; H, 5.99; N, 2.87. Found: C, 81.17; H, 5.82; N, 2.69.

Hydrogenolysis of pyrrolidinones 4b,c.

In a typical reaction, a solution of **3** (0.25 mmol) in methanol (10 mL) was treated with a catalytic amount of 10%-Pd/C. The system was purged several times with hydrogen. The mixture was stirred at room temperature under hydrogen (1.5 atm) for 6h (**5a**) and 18h (**5b**). The catalyst was removed by filtration and washed with methanol. The solvent was removed by rotatory evaporation. The following **5** were obtained:

5a. Reaction of **4b,b'** (110.4 mg, 0.28 mmol) afforded a residue that was pure by ^{1}H NMR. Recrystallization from methylene chloride/petroleum ether (30-60°C) gave **5a** as a colorless solid (59.9 mg, 54% yield) m.p. 206-208 °C; ^{1}H NMR δ 0.96 (s, 3Hz), 1.92 (dd,1H, J= 3 and 10 Hz), 2.77 (dd, 1H, J= 10 and 18 Hz), 3.42 (dd, 1H, J= 3 and 18 Hz), 7.60 (m,20H); ^{13}C NMR δ 14.0, 33.0, 35.4, 36.8, 49.4, 64.0, 127.0-144.0, 176.5, 198.4; IR 3182, 1694 cm^{-1}. Anal. Calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 82.22; H, 6.24; N, 3.37.

5b. Reaction of **4c,4c'** (88.6 mg, 0.19 mmol) afforded a residue that was pure based on ^{1}H NMR. Recrystallization from methylene chloride/petroleum ether (30-60 °C) gave **5b** as a colorless solid (29.4 mg, 33% yield) m.p. 208-210 °C; ^{1}H NMR δ 0.88 (s, 3Hz), 1.52 (dd,1H, J= 3 and 10 Hz), 2.16 (s, 3H), 2.35 (dd, 1H, J= 10 and 18 Hz), 2.85 (dd, 1H, J= 3 and 18 Hz), 7.25 (m,15H); ^{13}C NMR δ 13.9, 30.2, 34.9 (two signals), 41.8, 49.3, 64.1, 126.0-142.0, 176.6, 207.2; IR 3189, 1692 cm^{-1}. Anal. Calcd for $C_{32}H_{27}NO_2$: C, 84.00; H, 5.95; N, 3.06. Found: C, 83.87; H, 5.76; N, 3.11.

Obtention of 6 by catalytic hydrogenation of 4b using ammonium acetate as inhibitor of hydrogenolysis.

A solution of **4b** (45.2 mg, 0.11 mmol) in methanol (9 mL) was treated with a catalytic amount of 10%-Pd/C and ammonium acetate (4.4 mg, 0.05 mmol). The system was purged several times with hydrogen. The mixture was stirred at room temperature under hydrogen (1.5 atm) for 6h. The catalyst was removed by filtration and washed with methanol. The solvent was removed by rotatory evaporation to afford a residue that was pure based on ^{1}H NMR. Recrystallization from methylene chloride/petroleum ether (30-60 °C) gave **6** as a colorless solid (38.6 mg, 85% yield) m.p. 177-179 °C; ^{1}H NMR δ 0.29 (s, 3Hz), 2.04 (s, 3H), 2.2-2.7 (m, 4H), 2.98 (s, 3H), 7.60 (m,15H); ^{13}C NMR δ 25.9, 26.9, 30.0, 39.3, 49.7, 54.7, 67.2, 95.1, 126.0-142.0, 179.1, 208.5; IR 3206, 1692 cm^{-1}. Anal. Calcd for $C_{28}H_{29}NO_3$: C, 78.66; H, 6.84; N, 3.28. Found: C, 78.75; H, 6.98; N, 3.19.

Formation of 8 from 6 under acidic conditions.

To a solution of **6** (34.8 mg, 0.09 mmol) in dry benzene (4 mL), a catalytic amount of p-toluene sulfonic acid was added. The mixture was heated under reflux for 24h after which time water (15 mL) was added. The mixture was extracted with methylene chloride (3 X 5 mL) and the combined extracts were dried ($MgSO_4$) and the solvent was removed by evaporation. Recrystallization from methylene chloride/petroleum ether (30-60 °C) gave **8** as a colorless solid (14.3 mg, 50% yield) m.p. 230-232 °C; ^{1}H NMR δ 2.60 (s, 3Hz), 7.30 (m,15H), 10.20 (NH); ^{13}C NMR δ 14.2, 67.0, 116.8, 126.0-140.0, 130.5, 180.1; IR 3182, 1693 cm^{-1}. Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30. Found: C, 85.01; H, 5.70; N, 4.14.

Hydrolysis of 5-pyrrolin-2-ones 3a-c.

A mixture of 5-pyrrolin-2-one **3** and of K_2CO_3 (100% molar excess) was dissolved in DMSO-1% H_2O (20 mL per mmol of **3**). The resulting solution was stirred for 24h after which time water (30 mL) was added. The mixture was extracted with methylene chloride (6 X 15 mL) and the combined extracts were dried ($MgSO_4$) and the solvent was removed by evaporation. The following **9** were obtained:

9a. Obtained as a colorless solid (13.7 mg, 51% yield) from the reaction of 5-pyrrolin-2-one **3a** (25.8 mg, 0.063 mmol): m.p. 108-110 °C; ^{1}H NMR δ 0.97 (d,3H, J= 7Hz), 2.75 (dd,1H, J= 3 and 16 Hz), 3.13 (dd, 1H, J= 5 and 16 Hz), 3.45 (m, 1H), 3.65 (s, 3H) , 4.15 (m, 1H), 7.20 (m,15H); ^{13}C NMR δ 13.4, 33.9, 37.9, 51.8, 57.3, 61.5, 126.0-142.0, 170.8, 171.6, 175.9; IR 1742, 1734, 1675 cm^{-1}. Anal. Calcd for $C_{27}H_{25}NO_4$: C, 75.86; H, 5.89; N, 3.28. Found: C, 75.74; H, 5.79; N, 3.41.

9b. Obtained as a colorless solid (24.7 mg, 60% yield) from the reaction of 5-pyrrolin-2-one **3c** (39.7 mg, 0.09 mmol): m.p. 161-163 °C; ^{1}H NMR δ 0.95 (d,3H, J= 7Hz), 3.52 (m,3H), 4.45 (m, 1H), 7.50 (m,20H); ^{13}C NMR δ 15.2, 38.4, 38.9, 57.8, 61.9, 126.0-142.0, 171.7, 175.9, 197.7; IR 1722, 1680, 1678 cm^{-1}. Anal. Calcd for $C_{32}H_{27}NO_3$: C, 81.16; H, 5.75; N, 2.96. Found: C, 80.98; H, 5.61; N, 3.14.

10. Obtained as a colorless solid (31.5 mg, 59% yield) from the reaction of 5-pyrrolin-2-one **3b** (51.1 mg, 0.13 mmol): m.p. 184-186 °C; ^{1}H NMR δ 0.89 (s, 3Hz, J= 7Hz), 2.53 (dd,1H, J= 10 and 16 Hz), 2.95 (m, 2H), 3.50 (m, 1H), 6.20 (s, 1H), 7.70 (m,15H), 15.80 (OH); ^{13}C NMR δ 12.9, 43.4, 44.0, 54.1, 60.4, 96.7, 126.0-142.0, 177.5, 182.6, 194.7; IR 3189, 1702, 1600 cm^{-1}. Anal. Calcd for $C_{27}H_{25}NO_3$: C, 78.81; H, 6.12; N, 3.40. Found: C, 78.92; H, 6.31; N, 3.26.

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References

1. a) Hassner, A., Miller, A.S., Haddadin, M.J., *Tetrahedron Lett.*, **1972**, 1353.
   b) Woerner, F.R., Reimlinger, H., Merenyi,R., *Chem. Ber.*, **1971**, *104*, 2786.
2. Kascheres, A., Sá, M.M., *J. Org. Chem.*, **1996**, *61*, 3749.
3. Hassner, A., Haddadin, M.J., Levy, A.B., *Tetrahedron Lett.*, **1973**, 1015.
4. Sajiki, H., *Tetrahedron Lett.*, **1995**, *36*, 3465.
5. Speckamp W.N. , Wijnberg, W., Oostveen, A.R.C., *Tetrahedron*, **1982**, *38*, 209.
6. a) Padwa, A., Smolanoff, J. and Tremper, A., *J. Am. Chem. Soc.*, **1971**, *97*, 4682.
   b) Alper, H., Prickett, J. E. and Wollowitz, S., *J. Am. Chem. Soc.*, **1977**, *99*, 4330.
   c) Kascheres, A., Oliveira, C. M. A., Azevedo, M. B. M. and Nobre, C. M. S., *J. Org. Chem.*,**1991**, *56*, 7.
7. Nenitzescu, C.D., Solomonica, E., *Org. Syn. Coll.*, **1948**, *2*, 496.
8. a) Trippett, S., Wacker, D.M., *J. Chem. Soc.*, **1961**, 1266.
   b) Whitesides, G.M., *J. Org. Chem.*, **1988**, 53, 3457.

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