# Photocyclization of NN-Disubstituted Benzoylacetamides and Acetoacetamides 

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$N N$-Dialkyl-benzoylacetamides ( $1 \mathrm{a}-\mathrm{e}$ and $\mathrm{j}-\mathrm{n}$ ) and -acetoacetamides ( $1 \mathrm{f}-\mathrm{i}$ ), and $N$-methylbenzoylacetanilide (1o) undergo photocyclization involving $\delta$-hydrogen abstraction by the ketone carbonyl group to give $N$-substituted 4-hydroxypyrrolidin-2-ones ( $2 \mathrm{a}-\mathrm{o}$ ) in high yields.

Although the photochemistry of $\beta$-diketones ${ }^{1-5}$ and $\beta$-oxo-esters ${ }^{5-7}$ has been studied extensively, that of $\beta$-oxo-amides has been paid little attention. ${ }^{8-10}$ Photocyclization involving intramolecular hydrogen abstraction by excited carbonyl oxygen is a well known reaction of carbonyl compounds; ${ }^{11}$ however, much less is known about the cyclization of $\beta$-dicarbonyl compounds. ${ }^{12}$ We report here the photocyclization of $\beta$-oxo-amides involving hydrogen abstraction by ketone carbonyl.
Irradiation of a solution of $N N$-dimethylbenzoylacetamide (la) in a Pyrex vessel under nitrogen with a highpressure mercury lamp gave 4 -hydroxy-1-methyl-4-phenylpyrrolidin-2-one (2a) in $88 \%$ yield. Similarly,
$\dagger$ The absolute configuration of the substituents is not still elucidated.

[^0]irradiation of the $\beta$-oxo-amides ( $1 \mathrm{~b}-\mathrm{k}$ ) gave the corresponding 4-hydroxypyrrolidin-2-ones ( $2 \mathrm{~b}-\mathrm{k}^{\prime}$ ) in high yields. In the cases of the oxo-amides ( $\mathrm{li}, \mathrm{j}$, and k ) stereoisomers ( 2 i and $\mathrm{i}^{\prime} ; \mathrm{j}$ and $\mathrm{j}^{\prime} ; \mathrm{k}$ and $\mathrm{k}^{\prime}$ ) were formed, whereas only one isomer was produced from the oxoamides ( $\mathrm{lb}-\mathrm{c}, \mathrm{e}$, and g ). The structures of the pyr-rolidin- 2 -ones ( $2 \mathrm{a}-\mathrm{k}^{\prime}$ ) were elucidated by i.r., n.m.r., and mass spectra, and by elemental analyses. The i.r. spectra showed characteristic hydroxy ( $c a .3300 \mathrm{~cm}^{-1}$ ), and five-membered lactam carbonyl absorptions (ca. $1660-1680 \mathrm{~cm}^{-1}$ ).

The configurations of the substituents in the pyrroli-din- 2 -ones were elucidated on the basis of the n.m.r. spectra. $\dagger$ The n.m.r. spectrum of (2d) showed peaks at

[^1]$\delta 0.77$ and 1.36 , attributable to the C- 5 methyl groups. The signal at $\delta 0.77$ can be assigned to methyl protons cis to the C-4 phenyl group. $\dagger$ Only one signal was observed for the C-5 methyl group in (2b), at $\delta$ 1.19, suggesting that one stereoisomer was produced exclusively and that the methyl group is trans to the C-4 phenyl

(2)

|  | $\mathrm{R}^{1}$ | $\mathrm{R}^{2}$ | $\mathrm{R}^{3}$ | $\mathrm{R}^{4}$ | $\mathrm{R}^{5}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (1) a ; | Ph | H | H | Me | Me |
| b; | Ph | H | H | Et | Et |
| c; | Ph | H | H | Pr ${ }^{\text {n }}$ | Pr ${ }^{\text {n }}$ |
| d; | Ph | H | H | $\mathrm{Pr}^{1}$ | Pri |
| e; | Ph | H | H | $\mathrm{CH}_{2} \mathrm{Ph}$ | $\mathrm{CH}_{2} \mathrm{Ph}$ |
| f; | Me | H | H | Me | Me |
| g; | Me | H | H | Et | Et |
| h; | Me | H | H | $\mathrm{Pr}^{\text {i }}$ | Pri |
| i; | Me | H | H | $\mathrm{CH}_{2} \mathrm{Ph}$ | $\mathrm{CH}_{2} \mathrm{Ph}$ |
| j; | Ph | Me | H | $\mathrm{CH}_{2} \mathrm{Ph}$ | $\mathrm{CH}_{2} \mathrm{Ph}$ |
| k; | Ph | Me | Me | $\mathrm{CH}_{2} \mathrm{Ph}$ | $\mathrm{CH}_{2} \mathrm{Ph}$ |
| 1; | Ph | H | H | $\left[\mathrm{CH}_{2}\right]$ | $\left.\mathrm{CH}_{2}\right]_{2}$ |
| m; | Ph | H | H |  |  |
| n; | Ph | $\stackrel{H}{H}$ | H |  |  |
| o; | Ph | H | H | Me | Ph |


|  | $\mathrm{R}^{1}$ | R ${ }^{2}$ | $\mathrm{R}^{3}$ | $\mathrm{R}^{4}$ | $\mathrm{R}^{5}$ | $\mathrm{R}^{6}$ | $\begin{aligned} & \text { Yield } \\ & (\%) \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (2) a; | Ph | H | H | H | H | Me | 88 |
| b; | Ph | H | H | H | Me | Et | 60 |
| c; | Ph | H | H | H | Et | $\mathrm{Pr}^{\text {n }}$ | 73 |
| d; | Ph | H | H | Me | Me | $\mathrm{Pr}^{\text {i }}$ | 90 |
| e; | Ph | H | H | H | Ph | $\mathrm{CH}_{2} \mathrm{Ph}$ | 80 |
| f; | Me | H | H | H | H | Me | 73 |
| g; | Me | H | H | H | Me | Et | 76 |
| h; | Me | H | H | Me | Me | $\mathrm{Pr}^{\text {i }}$ | 83 |
| i; | Me | H | H | H | Ph | $\mathrm{CH}_{2} \mathrm{Ph}$ | (51) ${ }^{*}$ |
| i'; | Me | H | H | Ph | H | $\mathrm{CH}_{2} \mathrm{Ph}$ | (9) * |
| j; | Ph | Me | H | H | Ph | $\mathrm{CH}_{2} \mathrm{Ph}$ | (63) * |
| j'; | Ph | Me | H | Ph | H | $\mathrm{CH}_{2} \mathrm{Ph}$ | (27) * |
| k; | Ph | Me | Me | H | Ph | $\mathrm{CH}_{2} \mathrm{Ph}$ | (43) * |
| $\mathrm{k}^{\prime}$; | Ph | Me | Me | Ph | H | $\mathrm{CH}_{2} \mathrm{Ph}$ | 22 |
| 1; | Ph | H | H | H | $\mathrm{CH}_{2}$ | $\left.\mathrm{H}_{2}\right]_{2}$ | 80 |
| m; | Ph | H | H | H |  |  | 73 |
| n; | Ph | H | $\stackrel{\mathrm{H}}{ }$ | H | ${ }^{+}$ |  | 81 |

* Isomers were not isolated. Yields were determined on the basis of n.m.r. spectra.
group. This configuration would be expected to be the more thermally stable.
In the n.m.r. spectrum of the 4 -methylpyrrolidin-2one ( 2 h ), methyl signals were observed at $\delta 1.25,1.33$, and 1.45, whereas the C-4 and C-5 methyl signals of ( 2 g ) appeared as a singlet at $\delta 1.39$ and a doublet at

[^2]$\delta 1.27$, respectively. These results indicate that one stereoisomer was formed exclusively in the photolysis of ( lg ), and that the methyl groups in $(2 \mathrm{~g})$ are trans to each other. In this case also the thermally stable isomer was formed exclusively.

The n.m.r. spectrum of $\left(2 i^{\prime}\right)$ showed a peak at $\delta 0.92$, which can be assigned to the C-4 methyl protons cis to the C-5 phenyl group and shielded by the anisotropic effect of the latter. On the other hand, the n.m.r. signal of the C-4 methyl protons in (2i) was observed at $\delta 1.28$, indicating their location trans to the C-5 phenyl group. In this case also the thermally stable isomer was produced predominantly. The predominant formation of the thermally stable isomers would be expected in the photolyses of ( lj and k). More bulky substituents at C-3 or C-5 will appear trans to a C-4 phenyl or methyl group.

Formation of the pyrrolidin-2-ones from the $\beta$-oxoamides can be explained in terms of photocyclization involving $\delta$-hydrogen transfer to ketone carbonyl oxygen. ${ }^{3}$ The favoured trans-configurations can be explained in terms of relief of steric compression between substituents in the reorganization step [ 1,5 -diradical intermediate (3) to pyrrolidin-2-one (2)].


Irradiation of the $\beta$-oxo-amides ( $11-\mathrm{n}$ ) and the $\beta$ -oxo-anilide (lo) gave the corresponding bicyclic pyr-rolidin-2-ones (21-n) or 1-phenylpyrrolidin-2-one (20), respectively, identified on the basis of i.r. and n.m.r, spectra and elemental analyses.

## EXPERIMENTAL

I.r. spectra were recorded with a Hitachi EPI-2 spectrometer, n.m.r. spectra with a Hitachi R-20 spectrometer (tetramethylsilane as internal standard), and mass spectra with a Shimazu LKB- 9000 spectrometer. A Ushio 450 W high-pressure mercury lamp was used as radiation source.

[^3]The $\beta$-oxo-amides and $\beta$-oxo-anilide were prepared according to previously described methods. ${ }^{14-19}$

General Procedure for Photoreactions of $\beta$-Oxo-amides.A solution of the $\beta$-oxo-amide (1) in benzene was irradiated in a Pyrex vessel under nitrogen with a high-pressure mercury lamp for $\mathbf{1 - 5 0}$ ( $\mathbf{l a}$-e and j-o) or $160-200 \mathrm{~h}$ ( $\mathrm{lf}-\mathrm{i}$ ). The solvent was removed and the residue chromatographed on silica gel. Elution with benzene-ethyl acetate afforded the pyrrolidin-2-one (2).
(i) 4-Hydroxy-4-phenylpyrrolidin-2-one (2a) had m.p. $139-140{ }^{\circ} \mathrm{C}$; $\nu_{\text {max }}(\mathrm{KBr}) 3275$ and $1660 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right)$ $2.80\left(2 \mathrm{H}, \mathrm{ABq}, J 17.3 \mathrm{~Hz}, 3-\mathrm{H}_{2}\right), 2.87\left(3 \mathrm{H}, \mathrm{s}, \mathrm{NCH}_{3}\right)$, $3.53\left(2 \mathrm{H}, \mathrm{ABq}, J 10.5 \mathrm{~Hz}, 5-\mathrm{H}_{2}\right), 3.77 \mathrm{br}(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}$, $\mathrm{D}_{2} \mathrm{O}$-exchangeable), and $7.2-7.5(5 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 69.3; H, 6.8; N, 7.1. $\mathrm{C}_{11} \mathrm{H}_{13} \mathrm{NO}_{2}$ requires C, 69.1 ; H, 6.85 ; N, 7.35\%).
(ii) 1-Ethyl-4-hydroxy-5-methyl-4-phenylpyrrolidin-2-one (2b) had m.p. $148-149^{\circ} \mathrm{C}$; $\nu_{\text {max. }}(\mathrm{KBr}) 3220$ and 1670 $\mathrm{cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 1.00\left(3 \mathrm{H}, \mathrm{t}, J 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{3}\right)$, 1.11 $\left(3 \mathrm{H}, \mathrm{d}, J 5.8 \mathrm{~Hz}, 5-\mathrm{CH}_{3}\right), 2.74(2 \mathrm{H}, \mathrm{ABq}, J 18.0 \mathrm{~Hz}$, $\left.3-\mathrm{H}_{2}\right), 3.05(1 \mathrm{H}, \mathrm{q}, J 5.8 \mathrm{~Hz}, 5-\mathrm{H}), 3.65(2 \mathrm{H}, \mathrm{q}, J 7.2 \mathrm{~Hz}$, $\left.\mathrm{NCH}_{2} \cdot \mathrm{CH}_{3}\right), 3.80(1 \mathrm{H}, \mathrm{s}, \mathrm{OH})$, and $7.1-7.6(5 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, $71.15 ; \mathrm{H}, 7.8 ; \mathrm{N}, 6.2 . \mathrm{C}_{13} \mathrm{H}_{17} \mathrm{NO}_{2}$ requires $\mathrm{C}, 71.2 ; \mathrm{H}, 7.8 ; \mathrm{N}, 6.4 \%$ ).
(iii) 5-Ethyl-4-hydroxy-4-phenyl-1-n-propylpyrrolidin-2-one (2c) had m.p. $91-91.5^{\circ} \mathrm{C}$; $\nu_{\text {max }}(\mathrm{KBr}) 3350$ and $1680 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 0.78\left(3 \mathrm{H}, \mathrm{t}, J 6.5 \mathrm{~Hz}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{3}\right), 0.89(3 \mathrm{H}$, $\left.\mathrm{t}, J 6.5 \mathrm{~Hz}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{3}\right), \mathrm{I} .2-2.0\left(4 \mathrm{H}, \mathrm{m}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{3}\right.$ and $\left.\mathrm{CH}_{2} \cdot \mathrm{CH}_{3}\right), 2.80\left(2 \mathrm{H}, \mathrm{ABq}, J 17.1 \mathrm{~Hz}, 3-\mathrm{H}_{2}\right), 2.91(1 \mathrm{H}, \mathrm{t}, J$ $6.8 \mathrm{~Hz}, 5-\mathrm{H}), 3.13 \mathrm{br}(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}), 3.72(2 \mathrm{H}, \mathrm{t}, J 6.9 \mathrm{~Hz}$, $\mathrm{NCH}_{2}$ ), and $7.2-7.6$ ( $5 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 72.8 ; $\mathrm{H}, 8.4 ; \mathrm{N}, 5.5 . \quad \mathrm{C}_{15} \mathrm{H}_{21} \mathrm{NO}_{2}$ requires $\mathrm{C}, 72.85 ; \mathrm{H}, 8.55 ; \mathrm{N}$, $5.65 \%$ ).
(iv) 4-Hydroxy-1-isopropyl-5,5-dimethyl-4-phenylpyrroli-din-2-one (2d) had m.p. 193-194 ${ }^{\circ} \mathrm{C}$; $v_{\text {max. }}$ (KBr) 3200 and $1675 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 0.77\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right.$ cis to $\left.4-\mathrm{Ph}\right), 1.36$ ( $3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}$ trans to $4-\mathrm{Ph}$ ), $1.42\left(6 \mathrm{H}, \mathrm{d}, J 7.5 \mathrm{~Hz}, \mathrm{CH} M e_{2}\right)$, $2.83\left(2 \mathrm{H}, \mathrm{ABq}, J 15.1 \mathrm{~Hz}, 3-\mathrm{H}_{2}\right), 3.05 \mathrm{br}(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}$, $\mathrm{D}_{2} \mathrm{O}$-exchangeable), $3.36\left(1 \mathrm{H}\right.$, septet, $J 7.5 \mathrm{~Hz}, \mathrm{CHMe} \mathrm{C}_{2}$ ), and 7.2-7.6 ( $5 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 73.0; H, 8.75; $\mathrm{N}, 5.65 . \quad \mathrm{C}_{15} \mathrm{H}_{21} \mathrm{NO}_{2}$ requires $\left.\mathrm{C}, 72.85 ; \mathrm{H}, 8.55 ; \mathrm{N}, 5.65 \%\right)$.
(v) 1-Benzyl-4-hydroxy-4,5-diphenylpyrrolidin-2-one (2e) had m.p. $137-138{ }^{\circ} \mathrm{C}$; $\nu_{\text {max. }}(\mathrm{KBr}) 3300$ and $1675 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 3.00\left(2 \mathrm{H}, \mathrm{ABq}, J 15.6 \mathrm{~Hz}, 3-\mathrm{H}_{2}\right), 3.08 \mathrm{br}(1 \mathrm{H}$, $\mathrm{s}, \mathrm{OH}, \mathrm{D}_{2} \mathrm{O}$-exchangeable), $3.57\left(\mathrm{I} \mathrm{H}, \mathrm{d}, \mathrm{J} 15.0 \mathrm{~Hz}, \mathrm{NCH}_{2}\right.$ $\mathrm{Ph}), 4.53(1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}), 5.24\left(1 \mathrm{H}, \mathrm{d}, J 15.0 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{Ph}\right)$, and 6.5-7.25 ( $15 \mathrm{H}, \mathrm{m}$, aromatic) ; $m / e 343\left(M^{+}\right)$(Found: $\mathrm{C}, 80.35 ; \mathrm{H}, 6.15 ; \mathrm{N}, 4.05 . \mathrm{C}_{23} \mathrm{H}_{21} \mathrm{NO}_{2}$ requires $\mathrm{C}, 80.45$ H, 6.15 ; N, $4.1 \%$ ).
(vi) 4-Hydroxy-1,4-dimethylpyrrolidin-2-one (2f) had b.p. $125{ }^{\circ} \mathrm{C}$ at $2 \mathrm{mmHg} ; v_{\max }$ (film) 3400 and $1670 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 1.42\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 2.44\left(2 \mathrm{H}, \mathrm{s}, 3-\mathrm{H}_{2}\right), 2.81(3 \mathrm{H}$, $\left.\mathrm{s}, \mathrm{NCH}_{3}\right), 3.33\left(2 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}_{2}\right)$, and $3.65\left(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}, \mathrm{D}_{2} \mathrm{O}-\right.$ exchangeable); m/e $129\left(M^{+}\right)$(Found: C, $55.3 ; \mathrm{H}, 8.5$; $\mathrm{N}, 10.65 . \quad \mathrm{C}_{6} \mathrm{H}_{11} \mathrm{NO}_{2}$ requires $\left.\mathrm{C}, 55.8 ; \mathrm{H}, 8.6 ; \mathrm{N}, 10.85 \%\right) . \dagger$
(vii) 1-Ethyl-4-hydroxy-4,5-dimethylpyrrolidin-2-one (2g) had b.p. $155{ }^{\circ} \mathrm{C}$ at 4 mmHg ; $\nu_{\max }$ (film) 3350 and 1670
$\dagger$ The analyses are poor because these pyrrolidin-2-ones are so hygroscopic and volatile.
${ }^{14}$ H. Aoyama, T. Hasegawa, T. Nishio, and Y. Omote, Bull. Chem. Soc. Japan, 1975, 48, 1671.
${ }_{15}$ H. Bredereck, R. Gompper, K. Klem, and B. Föhlish, Chem. Ber., 1961, 94, 3119.
${ }_{16}$ G. E. Utzinger, Helv. Chim. Acta, 1952, 35, 1359.
$\mathrm{cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 1.17\left(3 \mathrm{H}, \mathrm{t}, J 5.9 \mathrm{~Hz}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{3}\right), 1.27(3 \mathrm{H}$, d, $\left.J 7.5 \mathrm{~Hz}, 5-\mathrm{CH}_{3}\right), 1.39\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 2.46(2 \mathrm{H}, \mathrm{s}, 3-$ $\mathrm{H}_{2}$ ), $2.64\left(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}, \mathrm{D}_{2} \mathrm{O}\right.$-exchangeable), $2.96(\mathrm{l} \mathrm{H}, \mathrm{q}$, $J 7.5 \mathrm{~Hz}, 5-\mathrm{H})$, and $3.57\left(2 \mathrm{H}, \mathrm{q}, J 5.9 \mathrm{~Hz}, \mathrm{NCH}_{2} \cdot \mathrm{CH}_{3}\right)$ (Found: C, 60.45; H, 9.4; N, 8.7. $\mathrm{C}_{8} \mathrm{H}_{15} \mathrm{NO}_{2}$ requires C , 61.1 ; H, 9.6 ; N, $8.9 \%$ ). $\dagger$
(viii) 4-Hydroxy-1-isopropyl-4,5,5-trimethylpyrrolidin-2one $(2 \mathrm{~h})$ had m.p. $72.5-73{ }^{\circ} \mathrm{C}$; $\nu_{\text {max }}(\mathrm{KBr}) 3300$ and 1665 $\mathrm{cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 1.17\left(6 \mathrm{H}, \mathrm{d}, J 6.4 \mathrm{~Hz}, \mathrm{CHMe} e_{2}\right), 1.25(3 \mathrm{H}$, $\left.\mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.33\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 1.45\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 2.37$ $\left(2 \mathrm{H}, \mathrm{s}, 3-\mathrm{H}_{2}\right), 3.45\left(1 \mathrm{H}\right.$, septet, $J 6.4 \mathrm{~Hz}, \mathrm{C} H \mathrm{Me}_{2}$ ), and 3.49 ( $1 \mathrm{H}, \mathrm{s}, \mathrm{OH}, \mathrm{D}_{2} \mathrm{O}$-exchangeable) (Found: C , 65.1; $\mathrm{H}, 10.2 ; \mathrm{N}, 7.45 . \quad \mathrm{C}_{10} \mathrm{H}_{19} \mathrm{NO}_{2}$ requires $\mathrm{C}, 64.85 ; \mathrm{H}, 10.35$; N, 7.6\%).
(ix) The 1-benzyl-4-hydroxy-4-methyl-5-phenylpyrroli-din-2-ones ( 2 i and $\mathrm{i}^{\prime}$ ) could not be separated because of difficulties in crystallization and distillation. The 6:1 mixture had $v_{\text {max. }}$ (film) 3375 and $1670 \mathrm{~cm}^{-1}$. The isomer (2i) showed $\delta\left(\mathrm{CDCl}_{3}\right) 1.28\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 2.1 \mathrm{br}(1 \mathrm{H}, \mathrm{s}$, $\mathrm{OH}), 2.54\left(2 \mathrm{H}, \mathrm{ABq}, J 16.2 \mathrm{~Hz}, 3-\mathrm{H}_{2}\right), 3.50(1 \mathrm{H}, \mathrm{d}, J 15.0$ $\left.\mathrm{Hz}, \mathrm{NCH}_{2} \mathrm{Ph}\right), 4.14(1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}), 5.16(1 \mathrm{H}, \mathrm{d}, J 15.0 \mathrm{~Hz}$, $\left.\mathrm{NCH}_{2} \mathrm{Ph}\right)$, and $6.9-7.5\left(10 \mathrm{H}, \mathrm{m}\right.$, aromatic) ; the isomer ( $2 \mathrm{i}^{\prime}$ ) showed $\delta\left(\mathrm{CDCl}_{3}\right) 0.92\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 2.1 \mathrm{br}(1 \mathrm{H}, \mathrm{s}, \mathrm{OH})$, $2.54\left(2 \mathrm{H}, \mathrm{ABq}, J 16.2 \mathrm{~Hz}, 3-\mathrm{H}_{2}\right), 3.50(1 \mathrm{H}, \mathrm{d}, J 15.0 \mathrm{~Hz}$, $\left.\mathrm{NCH} \mathrm{N}_{2} \mathrm{Ph}\right), 4.31(1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}), 5.16(1 \mathrm{H}, \mathrm{d}, J 15.0 \mathrm{~Hz}$, $\left.\mathrm{NCH}_{2} \mathrm{Ph}\right)$, and $6.9-7.5(10 \mathrm{H}, \mathrm{m}$, aromatic).
(x) The 1-benzyl-4-hydroxy-3-methyl-4,5-diphenylpyr-rolidin-2-ones ( 2 j and $\mathrm{j}^{\prime}$ ) could not be separated. The 7 : 3 mixture had m.p. $135-151^{\circ} \mathrm{C}$; $\nu_{\max }(\mathrm{KBr}) 3330$ and $1670 \mathrm{~cm}^{-1}$. The isomer (2j) showed $\delta\left(\mathrm{CDCl}_{3}\right) 1.21(3 \mathrm{H}, \mathrm{d}$, $\left.J 7.0 \mathrm{~Hz}, 3-\mathrm{CH}_{3}\right), 2.43\left(\mathrm{I} \mathrm{H}, \mathrm{s}, \mathrm{OH}, \mathrm{D}_{2} \mathrm{O}\right.$-exchangeable), $3.35(1 \mathrm{H}, \mathrm{q}, J 7.0 \mathrm{~Hz}, 3-\mathrm{H}), 3.62\left(1 \mathrm{H}, \mathrm{d}, J 14.0 \mathrm{~Hz}, \mathrm{NCH}_{2^{-}}\right.$ $\mathrm{Ph}), 4.45(1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}), 5.28\left(1 \mathrm{H}, \mathrm{d}, J 14.0 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{Ph}\right)$, and 6.6-7.4 ( $15 \mathrm{H}, \mathrm{m}$, aromatic). The isomer ( $2 \mathrm{j}^{\prime}$ ) showed $\delta\left(\mathrm{CDCl}_{3}\right) 1.17\left(3 \mathrm{H}, \mathrm{d}, J 7.0 \mathrm{~Hz}, 3-\mathrm{CH}_{3}\right), 2.43(\mathrm{l} \mathrm{H}, \mathrm{s}, \mathrm{OH}$, $\mathrm{D}_{2} \mathrm{O}$-exchangeable), $3,35(1 \mathrm{H}, \mathrm{q}, J 7.0 \mathrm{~Hz}, 3-\mathrm{H}), 3.65(1 \mathrm{H}$, d, $J 14.0 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{Ph}$ ), $4.65(1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}), 5.25(1 \mathrm{H}, \mathrm{d}$, $J 14.0 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{Ph}$ ), and $6.6-7.4(15 \mathrm{H}, \mathrm{m}$, aromatic). [Found (for mixture): C, 80.25; H, 6.5; N, 3.75. Calc. for $\mathrm{C}_{24} \mathrm{H}_{23} \mathrm{NO}_{2}$ : C, $80.65 ; \mathrm{H}, 6.5 ; \mathrm{N}, 3.9 \%$ ].
(xi) The 1-benzyl-4-hydroxy-3,3-dimethyl-4,5-diphenyl-pyrrolidin-2-ones ( 2 k and $\mathrm{k}^{\prime}$ ) were obtained in $65 \%$ yield (ratio 2:1). The pyrrolidin-2-one ( $2 \mathrm{k}^{\prime}$ ) was isolated by fractional recrystallization, but complete purification of (2k) was not achieved; the latter showed $\delta\left(\mathrm{CDCl}_{3}\right) 0.73$ $\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right.$ cis to $\left.4-\mathrm{Ph}\right), 1.27\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right.$ trans to $4-$ $\mathrm{Ph}), 1.7 \mathrm{br}(\mathrm{IH}, \mathrm{s}, \mathrm{OH}), 3.62\left(1 \mathrm{H}, \mathrm{d}, \mathrm{J} 14.1 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{Ph}\right)$, $5.10(1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}), 5.35\left(1 \mathrm{H}, \mathrm{d}, J 14.1 \mathrm{~Hz}, \mathrm{NCH} \mathrm{H}_{2} \mathrm{Ph}\right)$, and 6.8-7.5 ( $15 \mathrm{H}, \mathrm{m}$, aromatic). The isomer ( $2 \mathrm{k}^{\prime}$ ) had m.p. $176-177{ }^{\circ} \mathrm{C}$; $\nu_{\text {max }}(\mathrm{KBr}) 3450$ and $1665 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right)$ $1.11\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right.$ cis to $\left.4-\mathrm{Ph}\right), 1.23\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right.$ trans to 4 - Ph ), $2.5 \mathrm{br}(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}), 3.67\left(1 \mathrm{H}, \mathrm{d}, \mathrm{J} 14.1 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{Ph}\right)$, $4.50(1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}), 5.32\left(1 \mathrm{H}, \mathrm{d}, J 14.1 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{Ph}\right)$, and $6.6-7.3$ ( $15 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 81.05 ; H, 6.85 ; $\mathrm{N}, 3.75 . \quad \mathrm{C}_{25} \mathrm{H}_{25} \mathrm{NO}_{2}$ requires $\left.\mathrm{C}, 80.85 ; \mathrm{H}, 6.8 ; \mathrm{N}, 3.75 \%\right)$.
(xii) 7-Hydroxy-7-phenyl-4-oxa-1-azabicyclo[4.3.0]nonan9 -one (21) had m.p. $165-166{ }^{\circ} \mathrm{C}$; $\nu_{\text {max. }}(\mathrm{KBr}) 3250$ and $1680 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 2.80\left(2 \mathrm{H}, \mathrm{ABq}, J 17.3 \mathrm{~Hz}, \mathrm{CO} \cdot \mathrm{CH}_{2}\right)$, $3.4\left(1 \mathrm{H}, \mathrm{m}\right.$, methine), $3.79\left(5 \mathrm{H}, \mathrm{m}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{2}+\mathrm{NCH}_{2}\right), 4.0$

[^4]( $2 \mathrm{H}, \mathrm{m}, \mathrm{NCH}_{2}+\mathrm{OH}$; one $\mathrm{D}_{2} \mathrm{O}$-exchangeable), and $7.2-$ $7.6(5 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 66.4; H, 6.4; N, 5.7. $\mathrm{C}_{13} \mathrm{H}_{15} \mathrm{NO}_{3}$ requires $\left.\mathrm{C}, 66.95 ; \mathrm{H}, 6.5 ; \mathrm{N}, 6.0 \%\right)$.
(xiii) 4-Hydroxy-4-phenyl-1-azabicyclo[3.3.0]octan-2-one ( 2 m ) had m.p. $175-176{ }^{\circ} \mathrm{C}$; $v_{\text {max }}(\mathrm{KBr}) 3300$ and 1670 $\mathrm{cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 2.0\left(4 \mathrm{H}, \mathrm{m}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{2}\right), 2.8(2 \mathrm{H}, \mathrm{m}$, methine +OH ; one $\mathrm{D}_{2} \mathrm{O}$-exchangeable), $3.02(2 \mathrm{H}, \mathrm{ABq}, J$ $\left.16.2 \mathrm{~Hz}, \mathrm{CO} \cdot \mathrm{CH}_{2}\right), 3.6\left(1 \mathrm{H}, \mathrm{m}, \mathrm{NCH}_{2}\right), 4.22\left(\mathrm{IH}, \mathrm{m}, \mathrm{NCH}_{2}\right)$, and $7.2-7.55$ ( $5 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 71.75; H, 6.9 ; $\mathrm{N}, 6.15$. $\mathrm{C}_{13} \mathrm{H}_{15} \mathrm{NO}_{2}$ requires $\mathrm{C}, 71.85 ; \mathrm{H}, 6.95$; $\mathrm{N}, 6.45 \%$ ).
(xiv) 4-Hydroxy-4-phenyl-1-azabicyclo[4.3.0]nonan-2-one (2n) had m.p. $157-158^{\circ} \mathrm{C}$; $\nu_{\text {max. }}(\mathrm{KBr}) 3400$ and $\mathrm{I} 680 \mathrm{~cm}^{-1}$;
$\delta\left(\mathrm{CDCl}_{3}\right) 1.5\left(6 \mathrm{H}, \mathrm{m}, \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{2}\right), 2.7(1 \mathrm{H}, \mathrm{m}$, methine $)$, $2.80\left(2 \mathrm{H}, \mathrm{ABq}, J 16.2 \mathrm{~Hz}, \mathrm{CO} \cdot \mathrm{CH}_{2}\right), 3.4\left(1 \mathrm{H}, \mathrm{m}, \mathrm{NCH}_{2}\right)$, $3.68\left(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}, \mathrm{D}_{2} \mathrm{O}\right.$-exchangeable), $4.1\left(1 \mathrm{H}, \mathrm{m}, \mathrm{NCH}_{2}\right)$, and 7.1-7.5 ( $5 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 72.45; H, 7.35; $\mathrm{N}, 5.9 . \quad \mathrm{C}_{14} \mathrm{H}_{17} \mathrm{NO}_{2}$ requires $\left.\mathrm{C}, 72.7 ; \mathrm{H}, 7.4 ; \mathrm{N}, 6.05 \%\right)$.
(xv) 4-Hydroxy-1,4-diphenylpyrrolidin-2-one (20) had m.p. $178-179{ }^{\circ} \mathrm{C}$; $v_{\text {max }}(\mathrm{KBr}) 3300$ and $1670 \mathrm{~cm}^{-1}$; $\delta\left[\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right] 2.96\left(2 \mathrm{H}, \mathrm{ABq}, J 17 \mathrm{~Hz}, 5-\mathrm{H}_{2}\right), 4.08(2 \mathrm{H}$, $\left.\mathrm{ABq}, J 9.5 \mathrm{~Hz}, 3-\mathrm{H}_{2}\right), 5.93\left(1 \mathrm{H}, \mathrm{s}, \mathrm{OH}, \mathrm{D}_{2} \mathrm{O}\right.$-exchangeable), and $7.1-7.9$ ( $10 \mathrm{H}, \mathrm{m}$, aromatic) (Found: C, 75.5 ; H, $5.95 ; \mathrm{N}, 5.3 . \mathrm{C}_{16} \mathrm{H}_{15} \mathrm{NO}_{2}$ requires $\mathrm{C}, 75.85 ; \mathrm{H}, 5.95$; $\mathrm{N}, 5.55 \%)$.
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[^2]:    $\dagger$ A shift reagent study was attempted in order to assign methyl group cis or trans to the C-4 phenyl group in (2d). After addition of $\mathrm{Eu}(\mathrm{dpm})_{3}$, however, only small changes in the chemical shifts of both methyl groups were observed. The shift reagent did not bond to the hydroxy but to the carbonyl oxygen.

[^3]:    ${ }^{13}$ Further details of this reaction mechanism will be published soon, together with results of a mechanistic study.

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