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An Unexpected Photoadduct of N-Carbomethoxymethylpyrrolidine with a Chiral Butenolide and Benzophenone: X-ray Structure and Synthetic Utility

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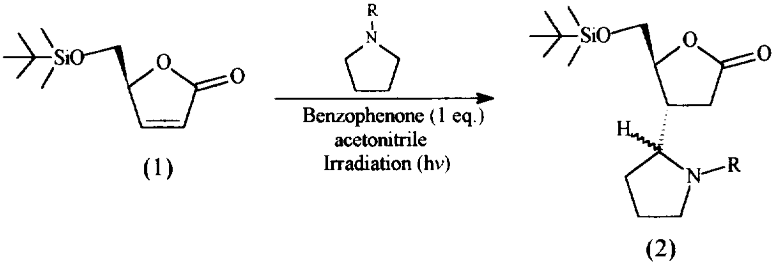
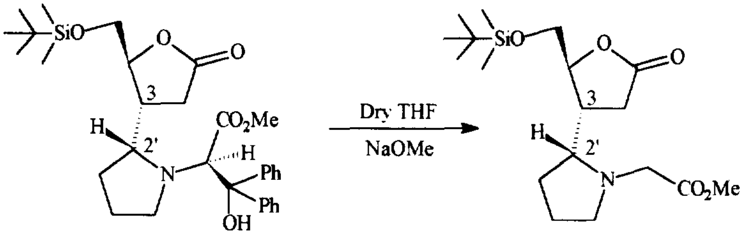
Abstract: The regio- and stereoselective photoinduced addition of N-carbomethoxymethylpyrrolidine to 5(S)-*tert*-butyldimethylsiloxymethyl-furan-2(5H)-one in the presence of benzophenone yields 3(R)-[N-(diphenylhydroxymethyl)carbo methoxymethylpyrrolidin-2'-yl]-4(S)-*tert*-butyldimethylsiloxymethyl)-butan-4-olides (epimeric at C-2'), and we report the X-ray structure of the major adduct together with its conversion into the 1-azabicyclo[4.3.0]-nonane ring system.

Our earlier work on the photoinduced addition of alcohols and acetals to butenolides like (**1**)[1] had encouraged us to explore the scope of similar reactions with cyclic amines. As described in our communication[2], the addition of both N-methylpyrrolidine and N-trimethylsilylpyrrolidine proceeded in good yield and high regio- and stereoselectivity to produce adducts (**2**).



Extension of these synthetic efforts to include more complex pyrrolidines commenced with N-carbomethoxymethyl-pyrrolidine in the presence of one equivalent of benzophenone (as photosensitiser). Irradiation resulted in formation of the expected photoadducts (**3**) in low yield and the unexpected photoadducts (**4**) together with around 40% recovery of starting butenolide (**1**). Repetition of the reaction with two equivalents of benzophenone led to complete consumption of butenolide and formation of photoadducts (**3**) (30%) and (**4**) (20%) as the major products. One of these, compound (**4a**) crystallised directly from the collection vials during column chromatography, while pure (**3a** and **b**) were obtained after chromatography. NMR studies were carried out on the pure crystalline isomer (**4a**) and on its isomer (**4b**) in the presence of (**4a**). All the signals for these diastereoisomers were assigned by 400 MHz ^{1}H NMR, HETCOR and COSY. The large ^{1}H shift difference between 5'-H$_a$ and 5'-H$_b$ in both isomers is explained by the deshielding of the proton 5'-H$_a$ by the nitrogen lone pair parallel to 5'-H$_b$. The ring current of the π electrons of the phenyl ring induced by the magnetic field shielded the protons 2-H$_a$ and 2-H$_b$ of (**4a**) and 5-H$_a$ and 5-H$_b$ of (**4b**) which are close to the middle of one of the rings. Of course, only a small number of the rapidly tumbling molecules have these conformations, but the overall average shift is affected by them. Only C-2 of (**4a**) was slightly shielded by the anisotropic effect viz. $\delta_C \sim 29$. All the other carbons of both isomers (**4a** and **4b**) had expected shifts. The stereochemistry α to the ester and at position 2' on (**4a**) could not be established by n.O.e. experiments.



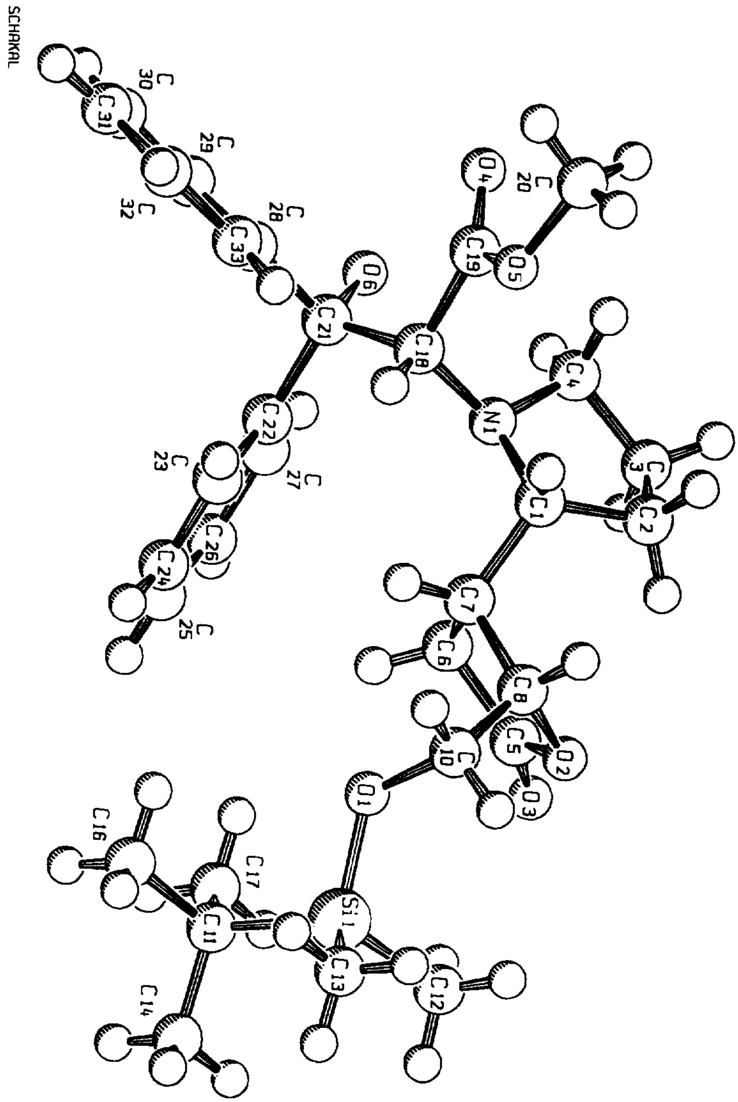
(**4a**)
(**4b**, epimer at C-2')

(**3b**)
(**3a**, epimer at C-2')

The formation of these interesting photoadducts (**4a** and **b**) probably proceeds via the pathway shown in (**fig 1**). The radical α to the nitrogen in the photo intermediate is most likely formed by intramolecular hydrogen transfer due to its close proximity to the carbon. The radical intermediate can also be neutralised by hydrogen transfer most likely from water dissolved in acetonitrile to form (**3a** and **b**). The radical intermediate then combines with either the benzhydrol radical or benzophenone to form the benzhydrol adduct (**4a** and **b**). The by-products benzhydrol and benzopinacol were also formed by either hydrogen abstraction or combination of the benzhydrol radical.

An X-ray structure determination was carried out on compound (**4a**) and was in complete agreement with the structure assigned (**fig 2**)[3]. It also confirmed the predicted position of one of the phenyl rings in space in relation to the protons 2-H$_a$ and 2-H$_b$.

Compounds (**4a**) and (**4b**) were converted into (**3a**) and (**3b**) through treatment with sodium methoxide in dry THF, via a retro-aldol reaction, in 95% yield. The absolute stereochemistry of (**3b**) was


SCHAKAL
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C2
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C7
C6
C8
C5
O2
O3
C10
O1
C16
C17
Si1
C11
C13
C12
C14

Figure 2

established by its synthesis from pure (**4a**). However, prolonged reaction of photoadducts (**4a** and **4b**) with potassium *tert*-butoxide in THF provided the unexpected tricyclic compound (**5**).

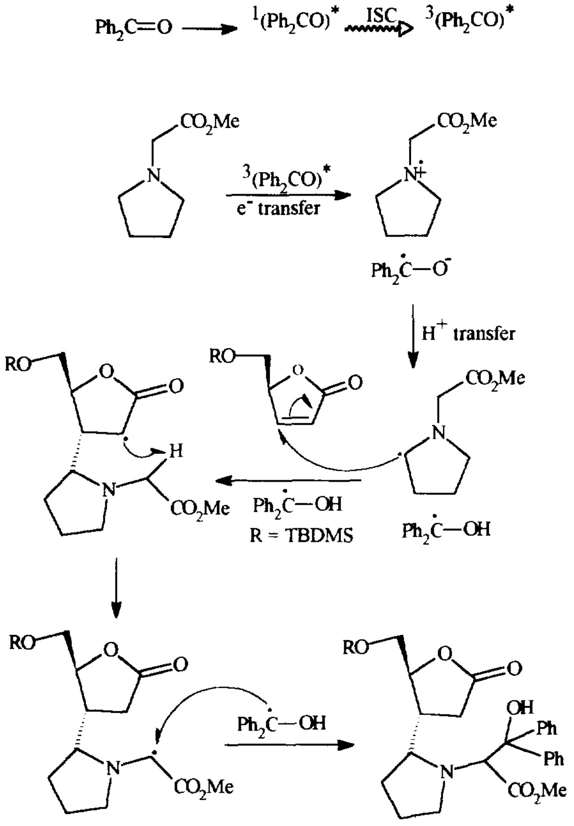
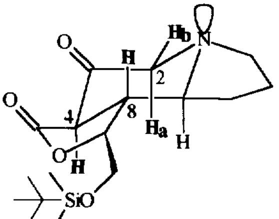


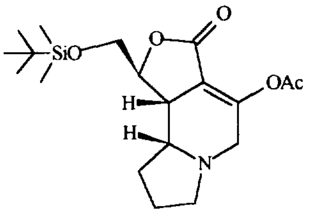
Figure 1

After work-up ^{1}H NMR showed the presence of the tricycle (**5**), unreacted (**3b**) and benzophenone. However, when the reaction was performed with pure isomer (**3a**), ^{1}H NMR showed the formation of pure 7-(*tert*-butyldimethylsiloxymethyl)-1-aza-6-oxa-tricyclo[7.3.0.$0^{4,8}$]dodeca-3,5-dione (**5**) which was isolated in 60% yield. The tricycle (**5**) was not formed by prolonged reaction of (**3b**) with potassium *tert*-butoxide. 7-(*tert*-Butyldimethylsiloxymethyl)-1-aza-6-oxa-tricyclo[7.3.0.$0^{4,8}$] dodeca-3,5-dione (**5**) was characterised by IR, NMR, and mass spectra. The thin film IR of (**5**) before work-up showed only one carbonyl band at ν/cm^{-1} 1693 but the IR spectrum after work-up showed two carbonyl bands at ν/cm^{-1} 1779 and 1711. In the former situation the potassium *tert*-butoxide abstracted the bridge-head proton yielding the enolate and in the latter situation the acidic work-up neutralised the base giving the keto-lactone tricycle (**5**).

The evidence for the relative stereochemistry of protons 4-H and 8-H is the J value of 10.1 Hz. A typical value of J axial-axial for a six membered ring is 8-10 Hz. The large ^{1}H shift difference between protons 2-H_a and 2-H_b viz. $\delta \sim 2.9$ and $\delta \sim 3.8$ respectively, is explained by the position of proton 2-H_b inside the equatorial deshielding cone and by the greater deshielding effect of the nitrogen lone pair.



(5)



(6)

This tricyclic compound was relatively unstable but could be easily converted into its crystalline enol acetate (**6**) (20%).

It is noteworthy that compounds (**3a**) and (**3b**) have three contiguous stereogenic centres whilst the starting material (**1**) has only one such centre: an interesting and potentially useful example of 'chiral multiplication'. In addition, the tricyclic compounds (**5**) and (**6**) possess the basic skeleton of the indolizidine alkaloids with defined stereochemistry at three centres. Efforts to optimise these transformations and to provide a route to indolizidine alkaloids and their analogues are in progress.

EXPERIMENTAL

Reagents and solvents were purified when necessary according to the usual procedures described in the literature[4]. Flash column chromatography was performed using Crosfield Sorbil C60 (32-63 μm). R_f's were determined by Analytical Thin Layer Chromatography on a 0.25 mm film of silica gel containing fluorescent indicator UV_{254} supported on a plastic sheet (Camlab plc.). The melting points were determined on a Electrothermal digital apparatus without correction. Infrared Spectra were recorded on a Perkin Elmer 881 grating spectrometer, scanning from 625 to 4000 cm^{-1}. The samples were diluted in chloroform or dichloromethane and run against a reference cell with the same solvent. Mass Spectra were recorded on a MICROMASS 7070F. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 (400 and 100.53 MHz). Alternatively they were recorded in $CDCl_3$ and tetramethylsilane was used as the internal standard. All the NMR analysis was supported by NOE, DEPT, COSY and HETCOR spectral data. Compound (**1**) was prepared according to the literature procedures[5].

Methyl pyrrolidineacetate

A solution of pyrrolidine (10 cm^3, 8.52 g, 0.12 mol) in toluene (50 cm^3) was added dropwise to a two-necked round-bottomed flask containing toluene (50 cm^3) with synchronous addition of methyl bromoacetate (10 cm^3, 16.16 g, 0.11 mol) in toluene (50 cm^3). The reaction mixture was stirred for 30 min. then toluene was evaporated using a rotary evaporator with the temperature below 30 °C. To the yellow oil was added DCM (200 cm^3) and the mixture was shaken with saturated aqueous sodium bicarbonate (2 x 10 cm^3). The water layer was extracted twice with DCM (10 cm^3) and the combined organic layers was dried ($MgSO_4$). The DCM was evaporated and the yellow oil purified by flash column chromatography (ethyl acetate) to give methyl pyrrolidineacetate as an yellow oil (6.50 g, MW 143, 38 %). **R_f** 0.17 (ethyl acetate); **(found**: M$^+$, 143.0943. $C_7H_{13}NO_2$ **requires,** M$^+$, 143.0947); **ν(thin film)/cm^{-1}** 2958 (CH_2), 2792 (OCH_3 and NCH_2) and 1755 (C=O); **δ_H(60 MHz; $CDCl_3$; J/Hz)** 1.70-2.00 (m, 4 H, 2 x CH_2), 2.50-2.80 (m, 4 H, NCH_2), 3.30 (s, 2 H, CH_2CO_2), 3.70 (s, 3 H, CH_3).

3-(N-Carbomethoxymethylpyrrolidin-2'-yl)-4-(*tert*-butyldimethylsiloxymethyl)-butan-4-olide (3a) and (3b) and 3-[N-(diphenylhydroxymethyl)carbomethoxymethylpyrrolidin-2'-yl]-4-(*tert*-butyldimethylsiloxymethyl)-butan-4-olide (4a and b)

A solution of butenolide (**1**) (5.00 g, 0.0219 mol), methyl pyrrolidineacetate (6.27 g, 2 eq) and benzophenone (8.00 g, 2 eq.) in acetonitrile (750 cm^3) was degassed with nitrogen for 1 hour. Nitrogen was passed through the mixture during the subsequent irradiation while the light was shined (medium pressure mercury lamp, 125 watts, 24 hours). The reaction mixture was evaporated to dryness and the yellow syrup purified by flash column chromatography (gradient elution starting with light petroleum-diethyl ether 10% until benzophenone stopped eluting and then with diethyl ether). While the fractions were collected, one pure diastereoisomer of 3-[N-(diphenylhydroxymethyl)carbomethoxy methylpyrrolidin-2'-yl]-4-(*tert*-butyldimethylsiloxymethyl)-butan-4-olide (**4a**) crystallised out in the vials. After the chromatography the isomers (**4a** and **b**) (2.50 g, 21 %) were recrystallized in hexane (plus drops of DCM) to give an amourphous white solid. One of the isomers of 3-(N-Carbomethoxymethylpyrrolidin-2'-yl)-4-(*tert*-butyldimethylsiloxymethyl)-butan-4-olide (**4b**) was obtained as an amorphous white solid when very pure (3.20 g, 29%).

(Compound **4a**)

m.p. 153.4-154.0 °C; **(found:** C, 67.24; H, 7.83; N, 2.53. $C_{31}H_{43}NO_6Si$ **requires,** C, 67.18; H, 7.83; N, 2.56); **R_f** 0.26 (hexane-diethyl ether 3:2); **ν(solution in DCM)/cm^{-1}** 3507 (OH), 2955, 2931, 2857

(SiCH), 1773 (C=O, lactone), and 1713 (C=O, ester); **δ_H(400 MHz; CD$_2$Cl$_2$; J/Hz)** 0.11 and 0.14 (s, 6 H, SiMe$_2$), 0.97 [s, 9 H, C(CH$_3$)$_3$], 1.25-1.32 (m, 1 H, 3'-H$_b$), 1.30-1.38 (dd, 1 H, $J_{2a,3}$9.6, J_{gem}18.8, 2-H$_a$), 1.46-1.52 (dd, 1 H, $J_{2b,3}$4.4, 2-H$_b$), 1.60-1.71 (m, 3 H, 3'-H$_a$, 4'-H), 2.28-2.34 (m, 1 H, 3-H), 2.69-2.76 (m, 1 H, 5'-H$_b$), 3.19-3.24 (m, 1 H, 2'-H), 3.49-3.54 (m, 1 H, 5'-H$_a$), 3.54-3.58 (dd, 1 H, J_{gem}11.1, $J_{4,5a}$2.8, 5-H$_a$), 3.67-3.71 (dd, 1 H, $J_{4,5b}$3.6, 5-H$_b$), 3.71 (3, 3 H, OMe), 3.96-3.99 (m, 1 H, 4-H), 4.33 (s, 1 H, HCCO$_2$), 4.63 (s, 1 H, OH) and 7.20-7.50 (m, 10 H, Ar); **δ_C(400 MHz; CD$_2$Cl$_2$)** -5.65 (SiMe), -5.61 (SiMe), 18.3 [$\underline{C}$(CH$_3$)$_3$], 24.8 (C-4'), 25.1 (C-3'), 25.8 [C($\underline{C}$H$_3$)$_3$], 28.8 (C-2), 38.1 (C-3), 50.2 (C-5'), 51.7 (OMe), 64.3 (C-2'), 64.6 (C-5), 66.9 (CHCO$_2$), 80.3 (COH), 82.3 (C-4), 125.7 (CH, Ar), 126.3 (CH, Ar), 126.8 (CH, Ar), 127.4 (CH, Ar), 127.9 (CH, Ar), 128.6 (CH, Ar), 144.7 (C, Ar), 147.2 (C, Ar), 172.5 (C=O, ester) and 177.5 (C=O, lactone).

(Compound **4b**)

m.p.154.2-155.1 ^{o}C; **(found:** C, 67.24; H, 7.83; N, 2.53. C$_{31}$H$_{43}$NO$_6$Si **requires,** C, 67.18; H, 7.83; N, 2.56); **R$_f$** 0.26 (hexane-diethyl ether 3:2); **δ_H(400 MHz; CD$_2$Cl$_2$; J/Hz)** 0.00 and 0.02 (s, 6 H, SiMe$_2$), 0.86 [s, 9 H, C(CH$_3$)$_3$], 1.36-1.41 (m, 1 H, 3'-H), 1.62-1.72 (m, 3 H, 3'-H, 4'-H), 1.87-1.93 (dd, 1 H, $J_{2b,3}$3.50, J_{gem}17.7, 2-H$_b$), 2.23-2.28 (m, 1 H, 3-H), 2.38-2.42 (dd, 1 H, $J_{4,5a}$2.0, J_{gem}11.6, 5-H$_a$) 2.53-2.60 (dd, 1 H, $J_{2a,3}$9.5, 2-H$_a$), 2.90-2.97 (m, 1 H, 5'-H$_b$), 3.12-3.17 (m, 1 H, 2'-H), 3.30-3.34 (dd, 1 H, $J_{4,5b}$2.6, 5-H$_b$), 3.54-3.58 (m, 1 H, 5'-H$_a$), 3.65 (s, 3 H, OMe), 3.76-3.78 (m, 1 H, 4-H), 4.22 (s, 1 H, HCCO$_2$), 4.58 (s, 1 H, OH) and 7.16-7.50 (m, 10 H, Ar); **δ_C(400 MHz; CD$_2$Cl$_2$)** -5.5 (SiMe$_2$), 18.2 [$\underline{C}$(CH$_3$)$_3$], 24.5 (C-4'), 25.8 [C($\underline{C}$H$_3$)$_3$], 26.0 (C-3'), 32.9 (C-2), 38.9 (C-3), 50.4 (C-5'), 51.6 (OMe), 65.0 (C-2'), 65.0 (C-5), 67.4 (CHCO$_2$), 80.2 (COH), 80.6 (C-4), 125.5 (CH,Ar), 126.1 (CH,Ar), 126.9 (CH,Ar), 127.1 (CH,Ar), 127.3 (CH,Ar), 127.6 (CH,Ar), 143.8(C,Ar), 146.2 (C,Ar), 171.8 (C=O, ester) and 177.4 (C=O, lactone).

(Compound **3a**)

R$_f$ 0.36 (hexane-diethyl ether 1:1); **ν(thin film)/cm^{-1}** 2954, 2931,2884, 2857 (SiCH), 1777 (C=O, lactone) and 1736 (C=O, ester); **δ_H(400 MHz; CDCl$_3$; J/Hz)** 0.06 (s, 6 H, SiMe$_2$), 0.88 [s, 9 H, C(CH$_3$)$_3$], 1.50-1.58 (m, 1 H, 3'-H), 1.71-1.83 (m, 2 H, 4'-H), 1.86-1.95 (m, 1 H, 3'-H), 2.19-2.24 (dd, 1 H, $J_{2,3}$ 8.80, J_{gem}16.49, 2-H), 2.51-2.57 (m, 1 H, 5'-H), 2.70-2.78 (M, 2 H, 2-H, 3-H), 2.84-2.89 (m, 1 H, 2'-H), 3.17-3.21 (m, 1 H, 5'-H), 3.21-3.26 (d, 1 H, J_{gem}16.48, H$_c$), 3.50-3.55 (d, 1 H, H$_d$), 3.62-3.65 (dd, 1 H, $J_{4,5b}$2.57, J_{gem}11.36, 5-H$_b$), 3.71 (s, 3 H, OMe), 3.88-3.91 (dd, 1 H, $J_{4,5a}$2.93, 5-H$_a$) and 4.50-4.52 (m, 1 H, 4-H).

(Compound **3b**)

R$_f$ 0.28 (hexane-diethyl ether 1:1); **ν(thin film)/cm^{-1}** 2954, 2931,2884, 2857 (SiCH), 1777 (C=O, lactone) and 1736 (C=O, ester); **δ_H(400 MHz; CDCl$_3$; J/Hz)** 0.06 and 0.07 (s, 6 H, SiMe$_2$), 0.89 [C(CH$_3$)$_3$], 1.43-1.54 (m, 1 H, 3'-H), 1.73-1.82 (m, 2 H, 4'-H), 1.86-1.95 (m, 1 H, 3'-H), 2.39-2.63 (m, 4 H, 5'-H, 2-H, 3-

H), 2.84-2.90 (m, 1 H, 2'-H), 3.13-3.18 (m, 1 H, 5'-H), 3.27-3.32 (d, 1 H, J_{gem}16.85, H_c), 3.46-3.51 (d, 1 H, H_d), 3.67-3.70 (dd, 1 H, $J_{4,5b}$2.57, J_{gem}11.00, 5-H_b), 3.70 (s, 3 H, OMe), 3.82-3.87 (dd, 1 H, $J_{4,5a}$ 3.30, 5-H_a) and 4.28-4.31 (m, 1 H, 4-H).

3-(N-Carbomethoxymethylpyrrolidin-2'-yl)-4-(*tert*-butyldimethylsiloxymethyl)-butan-4-olide (3a and b)

The diastereoisomers 3-[N-(diphenylhydroxymethyl)carbomethoxymethyl pyrrolidin-2'-y]-4-(*tert*-butyldimethylsiloxymethyl)-butan-4-olide (**4a and b**) (0.50 g, 9.04 x 10^{-4} mol) were dissolved in dried THF (50 cm^3) and treated with sodium methoxide (0.06 g, 1.11 x 10^{-3} mol). The mixture was stirred for 30 min. under nitrogen and the reaction was quenched by addition of saturated aqueous ammonium chloride. The solvent was evaporated, the residue diluted with DCM (100 cm^3), washed with distilled water (2 x 10 cm^3), dried over magnesium sulphate and purified by flash column chromatography (light petroleum-diethyl ether 3:2) to give the desired adduct as an yellow oil (0.32 g, MW 371, 95%).

7-(*tert*-Butyldimethylsiloxymethyl)-1-aza-6-oxa-tricyclo[7.3.0.0^{4,8}]dodeca-3,5-dione (5)

To a solution of potassium *tert*-butoxide (0.07 g, 6.24 x 10^{-4} mol) in dry THF (50 cm^3) under nitrogen was added a solution of 3-(N-carbomethoxymethylpyrrolidin-2'-yl]-4-(*tert*-butyldimethylsiloxymethyl)-butan-4-olide **3a** (0.20 g, 5.38 x 10^{-4} mol) in dry THF (10 cm^3) via syringe and the mixture was stirred for 4 hours. The reaction mixture was quenched with 10% aqueous citric acid (20 cm^3), the THF was evaporated and the aqueous mixture was extracted with ethyl acetate (3 x 20 cm^3). The combined organic solution was poured in a separating funnel, washed with deionised water (2 x 5 cm^3) and brine (1 x 5) and dried ($MgSO_4$). The ethyl acetate was evaporated giving the title compound (0.11 g , 60%).

R_f 0.12 (hexane-ethyl acetate 1:1); **ν(thin film)/cm^{-1}** 2954, 2929 and 2857 ($SiCH_3$), 1775 (C=O, lactone), 1724 (C=O, ketone), 1254 ($SiCH_3$), 1179 and 1126 (SiOaliphatic), 839 and 780 ($SiCH_3$) **δ_H(400 MHz; $CDCl_3$; J/Hz)** 0.05 (6, s, $SiMe_2$), 0.86 [9, s, $C(CH_3)_3$], 1.58-1.64 (1, m, CH_2), 1.80-1.99 (3, m, CH_2, NCH_2), 2.11-2.16 (1, m, CH_2), 2.60-2.65 (1, m, NCH_2), 2.85-2.90 (1, d, J_{gem}18.4, 2-H_a), 2.93-2.98 (1, dt, $J_{7,8,9}$3.7, $J_{4,8}$10.1, 8-H), 3.08-3.12 (1, m, 9-H), 3.56-3.59 (1, d, 4-H), 3.62-3.66 (1, dd, $J_{7,d}$2.5, J_{gem}11.2, H_d), 3.76-3.82 (1, d, 2-H_b), 3.87-3.91 (1, dd, $J_{7,e}$3.0, H_e) and 4.61-4.64 (1, m, 7-H); **δ_C(100 MHz; $CDCl_3$)** -5.6 ($SiMe_2$), 18.1 [$\underline{C}(CH_3)_3$], 24.5 (CH_2), 25.6 (CH_2), 25.7 [$C(\underline{C}H_3)_3$], 39.7 (CH), 54.1 (O=C$\underline{C}$H), 54.8 (NCH_2), 61.7 (NCH_2), 63.5 (OCH_2), 64.7 (NCH), 80.3 (OCH), 170.9 (C=O, lactone) and 201.1 (C=O, ketone). This compound was relatively unstable and was converted into the enol acetate **(6)** for further characterisation.

7-(*tert*-Butyldimethylsiloxymethyl)-3-acetoxy-1-aza-6-oxa-tricyclo [7.3.0.0^{4,8}]dodeca-5-one-3-ene (6)

The tricyclo compound (**5**) (0.11 g, 3.24 x 10^{-4} mol) was dissolved in DCM (25 cm^3) and treated with triethyl amine (0.5 cm^3, 3.59 x 10^{-3} mol) and acetic anhydride (0.3 cm^3, 3.18 x 10^{-3} mol). The reaction mixture was stirred for 3 hours then washed with saturated sodium bicarbonate (2 x 5 cm^3) and brine (2 x 5 cm^3). The solvent was evaporated and the residue purified by column chromatography (petrol-diethyl ether 1:1) to give the enol acetate (**6**) (0.03 g, 24%). The crystals of the acetylated product were obtained by crystallisation from the minimum amount of diethyl ether with addition of heptane (or hexane).

m.p. 97.5-98.0 °C; (**found:** C, 60.08; H, 8.23; N, 3.61. $C_{19}H_{31}NO_5Si^-$ **requires**, C, 59.81; H, 8.19; N, 3.67); **R$_f$** 0.37 (diethyl ether); **ν(solution in CDCl$_3$)/cm^{-1}** 2927 and 2825 (SiCH$_3$), 1762 (C=O, lactone) and 1703 (C=O); **δ$_H$(400 MHz; CDCl$_3$; J/Hz)** 0.08 and 0.09 [6, 2 x s, Si(CH$_3$)$_2$], 0.89 [9, s, Si(C(CH$_3$)$_3$], 1.49-1.59 (1, m, 10-H$_b$), 1.79-1.87 (1, m, 11-H$_b$), 1.89-2.02 (2, m, 10-H$_a$, 11-H$_a$), 2.23-2.34 (5, m, s, 12-H$_b$, Ac, 9-H), 2.98-3.08 (2, m, dd, J 4.39, 2-H$_b$, 8-H), 3.17-3.22 (1, m, 12-H$_a$), 3.64-3.69 (1, dd, J 2.7, J 17.4, 2-H$_a$), 3.74-3.79 (1, dd, J 4.0, J 11.7, H$_e$), 3.94-3.98 (1, dd, J 3.0, H$_d$), 4.16-4.20 (1, m, 7-H); **δ$_C$(100 MHz; CDCl$_3$)** -5.4 and -5.3 [Si(CH$_3$)$_2$], 18.4 [9, s, Si$\underline{C}$(CH$_3$)$_3$], 20.7 ($\underline{C}$H$_3$CO$_2$), 22.2 (C-11), 25.8 [SiC($\underline{C}$H$_3$)$_3$], 28.4 (C-10), 43.8 (C-8), 52.7 (C-12), 52.9 (C-2), 62.5 (C-9), 63.1 (C$_{de}$), 82.0 (C-7), 115.5 (C-4), 152.2 (C-3), 166.0 (C=O) and 167.7 (C=O).

Acknowledgements: E.S.A. thanks the Brazilian Research Council (CNPq), for a studentship.

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R-factor for the 1711 reflections with I > 2σ(I) was 0.0865. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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