

Synthesis of Amino Derivatives of 5-Aralkylidene-3-pyrrolin-2-ones

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Preparation of some derivatives of 5-aralkylidene-3-pyrrolin-2-ones is reported. Compounds with an amino group on the phenyl ring at the 3-position of the pyrrolinone ring showed suitable properties as potential UV-A filters. Some of the compounds were quaternarized to enhance their solubility in aqueous solvents.

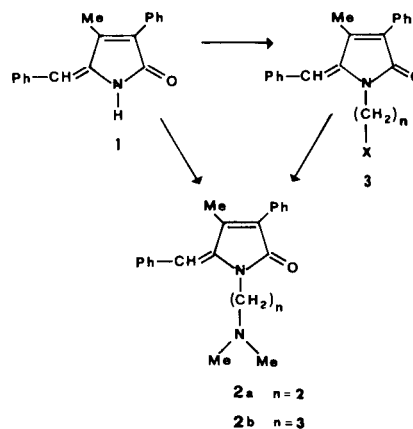
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Introduction.

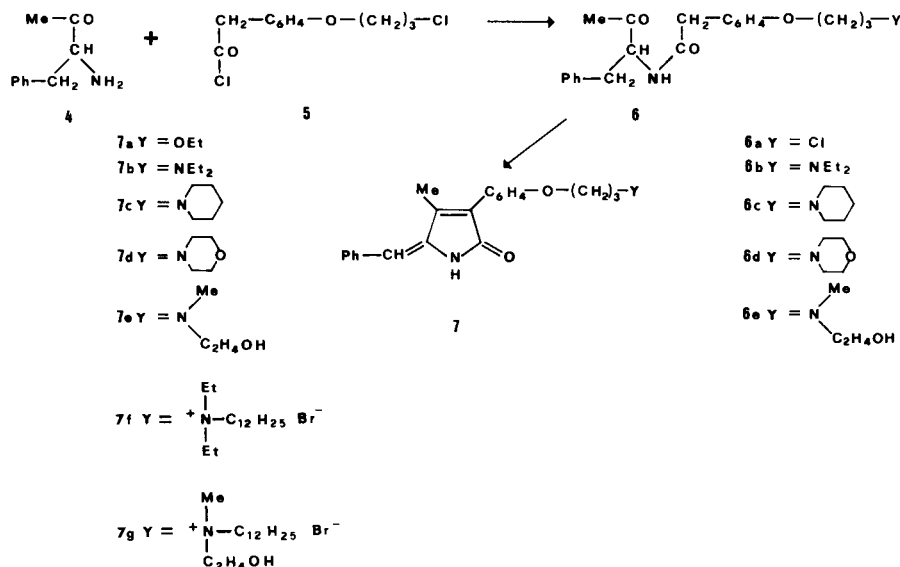
In an earlier paper we described the one-pot synthesis of a number of 3-aryl-4-methyl-5-alkylidene-3-pyrrolin-2-ones starting from *N*-acylaminoketones [1]. Of the two possible geometrical isomers only the *Z* forms were obtained. The resulting pyrrolinones are very stable and show uv maxima in the range 290-346 nm, which is the region where sun protecting compounds would have maximum absorbance of uv radiation [2]. Moreover, when irradiated, they gave exclusively the *E* isomers, without any trace of decomposition products. Therefore, they may act as potential uv filters: UV-B (280-320 nm) and UV-A (320-400 nm) sunscreens. One of the drawbacks to their use as uv sun-screening agents is their low solubility in the commonly used cosmetic solvents. Thus, we decided to suitably modify the substituents of the pyrrolinone ring to increase their solubility. Moreover, it was considered of interest to modify the structure by introducing a group suitable for im-

parting skin adhesive properties to the molecule in order to resist removal by bathing and perspiration, thus en-

Scheme 1



Scheme 2



hancing the protective efficacy. Much research [3] has been carried out on UV-B sunscreens whose properties of skin adhesivity or skin substantivity were obtained by introducing a sulphonium or a quaternary ammonium group, which can interact with negative sites of skin proteins [4]. Therefore, we planned to introduce a quaternary alkylamine chain into the pyrrolinone moiety.

Results.

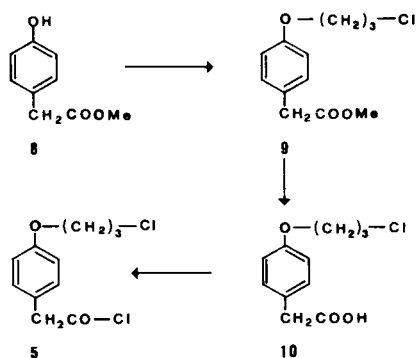
The introduction of a dialkylaminoalkyl chain on the nitrogen atom of the ring to yield compounds **2** can be performed directly by treatment of the pyrrolinone **1** with *N,N*-dimethyl-2-chloroethylamine in dimethylsulphoxide or by amination of the pyrrolinone **3** prepared from **1** with ω,ω' -dihaloalkane. However the presence of the alkyl chain attached to the ring nitrogen atom led to a hypsochromic shift ($\lambda_{\max} = 325 \text{ nm}$) with respect to the unsubstituted product; hence, the UV-A suncreening activity is greatly reduced. This effect can be ascribed to a minor conjugation of the phenyl ring at the 5-position, which is forced out of the plane of the exocyclic double bond. The corresponding Dreiding model shows clearly the steric hindrance between the phenyl group and the alkyl chain attached to the ring nitrogen and it is practically independent on the length of the chain.

We, therefore, decided to introduce the amino group on the phenyl group at the 3-position. The best approach proved to be the preparation of an acylaminoketone **6** which had the chain on the phenyl group of the acyl moiety.

Because the pyrrolinone ring closure is carried out with sodium ethoxide, it is more convenient to convert **6a** to the amino derivatives **6b-e**. Sodium ethoxide, besides affecting ring closure, also leads to the formation of the ethoxy derivative **7a**.

The acid chloride **5** was synthesized from methyl *p*-hydroxyphenylacetate by the following scheme:

Scheme 3



The acylaminoketones **6a-e** were cyclized to the corresponding pyrrolinones **7a-e** following the previously re-

ported [1].

The pyrrolinones **7b** and **7e** were quaternarized with dodecyl bromide to give the ammonium salts **7f** and **7g** respectively. Our previous research on UV-B filters [5] and literature data [4] have shown that quaternary ammonium salts containing *N*-alkyl chains of different length (C_2 to C_{20}) display the maximum activity in the case of compounds bearing C_{12} alkyl chains.

The presence of an aminoalkyl chain increased remarkably the solubility in 2-propanol and in water/2-propanol mixtures.

At present a study is in progress for determining the substantivity of the synthesized compounds.

A portion of this work appeared recently in an Italian patent application [6].

EXPERIMENTAL

Unless otherwise stated, the ir spectra were recorded on a Perkin-Elmer 782 spectrophotometer using samples in potassium bromide pellets or as a film. The pmr spectra were recorded for deuteriochloroform solutions with a Hitachi-Perkin-Elmer R-600 instrument, chemical shifts ($J = \text{Hz}$) are reported in ppm downfield from internal tetramethylsilane. The uv spectra were measured for solutions in methanol with a Perkin-Elmer 124 spectrophotometer. Silica gel plates (Merck F_{254}) and silica gel 60 (Merck 70-230 mesh) were used for analytical and preparative tlc and for column chromatography, respectively. Extracts were dried over sodium sulphate and solvents were evaporated *in vacuo*. Petroleum ether refers to the fraction of bp 30-50°.

1-[2-(*N,N*-Dimethylamino)ethyl]-3-phenyl-4-methyl-5-benzylidenepyrrolin-2-one (**2a**, $n = 2$).

A mixture of the pyrrolinone **1** (1.044 g, 4 mmoles) and potassium hydroxide (0.536 g, 9.5 mmoles) in dimethylsulphoxide (10 ml) was stirred at room temperature for 1 hour. *N,N*-Dimethyl-1-chloroethylamine hydrochloride (0.576 g, 4 mmoles) was added and the solution was stirred for 12 hours. The solution was diluted with water and extracted with chloroform. The organic layer was dried and evaporated to dryness. The residue was separated by preparative layer chromatography with chloroform/methanol (in a ratio 9:1) as eluent. The faster running band was starting material (0.3 g), the slower running band yielded compound **2a** (0.5 g, 38%), mp 146-149° (from petroleum ether); ir: 1690 (CO), 1595 cm^{-1} (C=C); uv: ($\log \epsilon$) 205 (4.23), 220 (4.11) 315 (4.43) nm; pmr: δ 1.92 (6H, s, 2 \times Me-N), 2.06 (2H, t, CH_2 -N), 2.27 (3H, s, Me), 3.56 (2H, t, CH_2 -N), 6.42 (1H, s, CH), 6.87-7.57 (10H, m, 2 \times Ar).

Anal. Calcd. for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43. Found: C, 79.63; H, 7.12; N, 8.84.

1-(3-Chloropropyl)-3-phenyl-4-methyl-5-benzylidenepyrrolin-2-one (**3**).

A mixture of the pyrrolinone **1** (0.523 g, 2 mmoles) and potassium hydroxide (0.134 g, 2.3 mmoles) in anhydrous dimethylsulphoxide (4 ml) was stirred for 1 hour at room temperature. 1-Bromo-3-chloropropane (0.2 ml, 2 mmoles) was added and the solution was stirred at room temperature for 1 hour. The solution was diluted with water and extracted with chloroform. The organic layer was washed with water, dried and evaporated to dryness to give the pyrrolinone **3** (0.5 g, 75%), mp 112-113° (from petroleum ether); ir: 1680 (CO), 1600 cm^{-1} (C=C); pmr: δ 1.64 (2H, m, CH_2), 2.27 (1H, s, Me), 3.09 (2H, t, CH_2 -N), 3.66 (2H, t, CH_2 -Cl), 6.45 (1H, s, CH), 7.36-7.42 (10H, m, 2 \times Ar).

Anal. Calcd. for $C_{21}H_{20}ClNO$: C, 74.67; H, 5.92; Cl, 10.52; N, 4.15. Found: C, 74.36; H, 5.81; Cl, 10.25; N, 4.21.

1-(3-*N,N*-Dimethylpropyl)-3-phenyl-4-methyl-5-benzylidenepyrrolin-2-one (**2b**, *n* = 3).

A mixture of the pyrrolinone **3** (1.35 g, 4 mmoles), dimethylamine (1.8 g, 40 mmoles), potassium iodide (0.33 g, 2 mmoles) in anhydrous dimethylformamide (3 ml) was heated at 100° for 5 hours in a pressure vessel. After cooling, the solution was diluted with water, acidified, and extracted with ether to eliminate the unreacted products. The aqueous solution was then basified and extracted with chloroform. The organic layer was evaporated to dryness. The residue was purified by preparative layer chromatography with chloroform/methanol (95:5). Compound **2b** (*n* = 3) was obtained in 75% yield (1.05 g), mp 219-221° (from petroleum ether); ir: 1690 (CO), 1595 cm⁻¹ (C=C); uv: (log ϵ) 207 (4.25), 216 (4.10), 312 (4.21) nm; pmr: δ 1.82 (2H, m, CH₂), 2.03 (6H, s, 2 \times Me-N), 2.20 (5H, m, Me + CH₂-3), 3.56 (2H, t, CH₂-1), 6.38 (1H, s, CH), 6.90-7.52 (10H, m, 2 \times Ar).

Anal. Calcd. for C₂₅H₂₆N₂O: C, 79.77; H, 7.51; N, 8.09. Found: C, 79.68; H, 7.65; N, 7.95.

Methyl [4-(3-Chloropropoxy)phenyl]acetate (**9**) [7.8].

A mixture of methyl (*p*-hydroxyphenyl)acetate (**8**) (20 g, 0.12 moles), 1-bromo-3-chloropropane (19 g, 0.12 moles) and anhydrous potassium carbonate (24.8 g) in anhydrous acetone (70 ml) was refluxed for 40 hours. After cooling, the precipitate was filtered off and the solution was evaporated to dryness to give the phenylacetate **9**, as an oily semisolid (90% yield), which was purified by preparative layer chromatography with petroleum ether:ether (2:1) as eluent, (24.2 g, 83% yield); ir: 1740 (CO), 1245 (C-O-C), 1160 cm⁻¹ (C-O-C); pmr: δ 2.14 (2H, m, CH₂), 3.52 (2H, s, CH₂-Ar), 3.63 (3H, s, Me), 3.67 (2H, t, CH₂-Cl, J = 6.4), 4.04 (2H, t, CH₂-O, J = 5.9), 6.99 (4H, AB, Ar, J = 8.7).

Anal. Calcd. for C₁₂H₁₃ClO₂: C, 59.38; H, 6.18; Cl, 14.64. Found: C, 59.25; H, 6.11; Cl, 14.40.

4-(3-Chloropropoxy)phenylacetic Acid (**10**) [7.8].

A mixture of the phenylacetate **9** (30.5 g, 0.126 mole) and a solution of 1*N* sodium hydroxide (126 moles) was stirred at room temperature for 20 hours. After acidification the acid **10** separated as white crystals, mp 83-85° (from cyclohexane), 18.7 g, 65% yield; ir: 3300-2500 (OH), 1710 cm⁻¹ (CO); pmr: δ 2.21 (2H, m, CH₂), 3.58 (2H, s, CH₂-Ar), 3.73 (2H, t, CH₂-Cl, J = 6.4), 4.10 (2H, t, CH₂-O, J = 5.9), 6.04 (1H, vbs, OH), 7.02 (4H, AB, Ar, J = 8.8).

Anal. Calcd. for C₁₁H₁₃ClO₂: C, 57.78; H, 5.73; Cl, 15.50. Found: C, 57.90; H, 5.78; Cl, 15.22.

4-(3-Chloropropoxy)-*N*-[3-(4-phenyl-2-oxobutyl)]phenylacetamide (**6a**).

4-(3-Chloropropoxy)phenylacetic acid (**10**) (9.6 g, 42 mmoles) was refluxed with an excess of thionyl chloride for 6 hours. The mixture was evaporated under vacuum to eliminate the excess thionyl chloride. The acid chloride **5** was distilled at 170° at 0.7 mm (yield 7.8 g, 75%).

A solution of the acid chloride **5** (7.8 g, 32 mmoles) in chloroform (50 ml) was slowly added under stirring to a cold solution of 3-amino-4-phenyl-2-butanone hydrochloride (**4**) (5.6 g, 28 mmoles) in water (15 ml). Then a solution of sodium acetate (8.1 g, 98 mmoles) in water (30 ml) was added. The mixture was stirred overnight at room temperature. The organic layer was evaporated to dryness and the residue was crystallized from ether to give compound **6a**, mp 90-92° (8.7 g, 82% yield); ir: 3280 (NH), 1710 (CO), 1645 cm⁻¹ (CO-NH); pmr: δ 2.10 (3H, s, Me), 2.22 (2H, m, C-CH₂-C), 2.98 (2H, dd, CH₂-Ar), 3.46 (2H, s, CH₂CO), 3.75 (2H, t, CH₂-Cl), 4.11 (2H, t, CH₂-O), 4.78 (1H, m, CH), 5.90 (1H, bs, NH), 6.74-7.17 (9H, m, 2 \times Ar).

Anal. Calcd. for C₂₁H₂₄ClNO₂: C, 67.56; H, 6.43; Cl, 9.38; N, 3.75. Found: C, 67.50; H, 6.35; Cl, 9.08; N, 3.77.

General Procedure for 4-[3-(*N,N*-Alkylamino)propoxy]-*N*-[3-(4-phenyl-2-oxobutyl)]phenylacetamide **6b-e**.

A mixture of the phenylacetamide **6a** (4 mmoles), the amine (20 mmoles), potassium iodide (2 mmoles) in anhydrous dimethylformamide (5 ml) was heated at 100° in a pressure vessel for 5 hours. The solution was acidified and extracted with ether to eliminate unreacted products;

then the solution was basified and extracted with ether. The solvent was evaporated to dryness to give compounds **6b-e**.

4-[3-(*N,N*-Diethylamino)propoxy]-*N*-[3-(4-phenyl-2-oxobutyl)]phenylacetamide (**6b**).

This compound was obtained in 72% yield, as white crystals, mp 60-62° (from cyclohexane); ir: 3310 (NH), 1710 (CO), 1655 cm⁻¹ (CONH); pmr: δ 1.04 (6H, t, 2 \times Me, J = 7.2), 1.97 (2H, m, C-CH₂-C), 2.10 (3H, s, Me), 2.55 (6H, m, 3 \times CH₂-N), 2.98 (2H, dd, CH₂-CH), 3.46 (2H, s, CH₂CO), 4.01 (2H, t, CH₂-O, J = 6.3), 4.78 (1H, q, CH), 6.70-7.01 (9H, m, 2 \times Ar).

Anal. Calcd. for C₂₇H₃₄N₂O₂: C, 73.14; H, 8.32; N, 6.82. Found: C, 73.44; H, 8.29; N, 6.84.

4-[3-(*N*-Piperidyl)propoxy]-*N*-[3-(4-phenyl-2-oxobutyl)]phenylacetamide (**6c**).

This compound was obtained in 79% yield, as white crystals mp 81-83° (from cyclohexane); ir: 3330 (NH), 1710 (CO), 1660 cm⁻¹ (CONH); pmr: δ 1.50 (6H, bs, 3 \times CH₂), 2.10 (5H, s + m, Me + C-CH₂-C), 2.39 (6h, bs, 3 \times CH₂-N), 2.98 (2H, dd, CH₂-CH, J = 6.2, J = 1.6), 3.45 (2H, s, CH₂CO), 4.01 (2H, t, CH₂-O, J = 6.3), 4.84 (1H, q, CH, J = 6.2), 5.93 (1H, m, NH), 6.70-7.17 (9H, m, 2 \times Ar).

Anal. Calcd. for C₂₆H₃₄N₂O₂: C, 73.90; H, 8.11; N, 6.63. Found: C 73.66; H, 8.43; N, 6.38.

4-[3-(*N*-Morpholinyl)propoxy]-*N*-[3-(4-phenyl-2-oxobutyl)]phenylacetamide (**6d**).

This compound was obtained in 60% yield, as white crystals, mp 86-89° (from ether); ir: 3300 (NH), 1715 (CO), 1650 cm⁻¹ (CONH); pmr: δ 1.96 (2H, m, C-CH₂-C), 2.10 (3H, s, Me), 2.55 (6H, m, 3 \times CH₂-N), 2.99 (2H, dd, CH₂-CH, J = 6.1, J = 1.2), 3.46 (2H, s, CH₂CO), 3.73 (4H, m, 2 \times CH₂-O), 4.02 (2h, t, CH₂-O, J = 6.4), 4.79 (1H, q, CH, J = 6.1), 5.97 (1H, bs, NH), 6.70-7.19 (9H, m, 2 \times Ar).

Anal. Calcd. for C₂₅H₃₃N₂O₄: C, 70.75; H, 7.50; N, 6.60; Found: C, 70.75; H, 7.48; N, 6.44.

4-[3-(*N*-Hydroxyethyl-*N*-methyl)propoxy]-*N*-[3-(4-phenyl-2-oxobutyl)]phenylacetamide (**6e**).

This compound was obtained in 76% yield as an oily semisolid; ir: 3400 (OH), 3300 (NH), 1720 (CO), 1640 cm⁻¹ (CONH); pmr: δ 1.96 (2H, m, C-CH₂-C), 2.08 (3H, s, Me), 2.28 (3H, s, Me), 2.54 (4H, m, 2 \times CH₂-N), 3.05 (3H, m, CH₂-N + OH), 3.43 (2H, s, CH₂CO), 3.58 (2H, t, CH₂-O, J = 5.9), 3.95 (2H, t, CH₂-O, J = 5.9), 4.75 (1H, q, CH, J = 7.1), 6.18 (1H, bds, 1, NH), 6.75-7.22 (9H, m, 2 \times Ar).

Anal. Calcd. for C₂₄H₃₂N₂O₄: C, 69.90; H, 7.77; N, 6.80. Found: C, 69.75; H, 7.80; N, 6.69.

General Procedure for Cyclization of the Phenylacetamides **7a-e**.

The phenylacetamides **6a-e** (1 mmole) were refluxed with sodium ethoxide (3 mmoles) in ethanol (10 ml) for 16 hours. A stream of oxygen was bubbled into the solution for 8 hours. After cooling, the resulting solid pyrrolinones **7a-e** were filtered off, washed with water and crystallized. Evaporation of the ethanolic solution gave another crop of the pyrrolinones **7**.

3-[4-(3-Ethoxypropoxy)phenyl]-4-methyl-5-benzylidenepyrrolin-2-one (**7a**).

This compound was obtained from compound **6a** in 71% yield, as yellow crystals, mp 158-160° (from ethanol); ir: 3240 (NH), 1675 (CO), 1600 cm⁻¹ (C=C); uv: (log ϵ) 228 (4.24), 343 (4.59) nm; pmr: δ 1.21 (3H, t, Me, J = 7.0), 2.06 (2H, m, C-CH₂-C), 2.29 (3H, s, Me), 3.50 (2H, q, CH₂, J = 7.0), 3.61 (2H, t, CH₂-O, J = 6.3), 4.11 (2H, t, CH₂-O, J = 6.3), 6.22 (1H, s, CH), 7.40 (9H, m, 2 \times Ar), 8.20 (1H, bs, NH).

Anal. Calcd. for C₂₃H₂₅NO₂: C, 76.01; H, 6.93; N, 3.85. Found: C, 75.76; H, 6.81; N, 4.03.

3-[4-(*N,N*-Diethylaminopropoxy)phenyl]-4-methyl-5-benzylidenepyrrolin-2-one (**7b**).

This compound was obtained from compound **10b** in 68% yield, as

yellow needles, mp 130-132° (from aqueous ethanol); ir: 3190 (NH) 1700 (CO), 1600 cm^{-1} (C=C); uv: (log ϵ) 224 (4.24), 354 (4.66) nm; pmr: δ 1.02 (6H, t, 2 \times Me, J = 7.0), 1.75 (2H, m, C-CH₂-C), 2.29 (3H, s, Me), 2.53 (6H, q, 3 \times CH₂N, J = 7.0), 4.05 (2H, t, CH₂, J = 6.3), 6.21 (1H, s, CH), 6.85-7.50 (9H, m, 2 \times Ar), 7.92 (1H, bs, NH).

Anal. Calcd. for C₂₂H₃₀N₂O₂: C, 76.86; H, 7.74; N, 7.17. Found: C, 76.54; H, 7.66; N, 7.21.

3-[4-[3-(*N*-Piperidinyloxy)propoxy]phenyl]-4-methyl-5-benzylidenepyrrolin-2-one (7c).

This compound was obtained from compound 6c in 87% yield, as yellow crystals, mp 177-179° (from cyclohexane); ir: = 3230 (NH), 1670 (CO), 1600 cm^{-1} (C=C); uv: (log ϵ) 225 (4.23), 340 (4.52) nm; pmr: δ 1.30 (6H, m, 3 \times CH₂), 1.82 (2H, m, CH₂), 2.30 (3H, s, Me), 2.34 (6H, m, 3 \times CH₂N), 4.05 (2H, t, CH₂-O), 6.23 (1H, s, CH), 6.70-7.36 (9H, m, 2 \times Ar).

Anal. Calcd. for C₂₆H₃₀N₂O₂: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.26; H, 7.54; N, 6.90.

3-[4-[3-(*N*-Morpholinyl)propoxy]phenyl]-4-methyl-5-benzylidenepyrrolin-2-one (7d).

This compound was obtained from compound 6d in 83% yield, as yellow crystals, mp 183-185° (from cyclohexane); ir: 3200 (NH), 1690 (CO), 1600 cm^{-1} (C=C); uv: (log ϵ) 228 (4.16), 343 (4.52) nm; pmr: δ 1.97 (2H, m, CH₂), 2.30 (3H, s, Me), 2.44 (6H, m, 3 \times CH₂N), 3.73 (4H, m, 2 \times CH₂-O), 4.07 (2H, t, CH₂-O, J = 5.9), 6.24 (1H, s, CH).

Anal. Calcd. for C₂₂H₂₈N₂O₃: C, 74.26; H, 6.93; N, 6.93. Found: C, 74.35; H, 6.82; N, 6.75.

3-[4-[3-(*N*-Hydroxyethyl-*N*-methyl)aminopropoxy]phenyl]-4-methyl-5-benzylidenepyrrolin-2-one (7e).

This compound was obtained from 10c in 85% yield, as yellow crystals, mp 135-138° (from ethyl acetate); ir: 3210 (NH), 1700 (CO), 1610 cm^{-1} (C=C); uv: (log ϵ) 227 (4.15), 344 (4.5) nm; pmr: δ 1.98 (3H, m, CH₂ + OH), 2.29 (6H, s, 2 \times Me), 2.65 (4H, m, 2 \times CH₂-N), 3.61 (2H, t, CH₂-O), 4.06 (2H, t, CH₂-O), 6.23 (1H, s, CH), 7.04 (9H, m, 2 \times Ar).

Anal. Calcd. for C₂₄H₂₈N₂O₃: C, 73.10; H, 7.61; N, 7.11. Found: C, 72.96; H, 7.48; N, 7.22.

Dodecyl Quaternary Salts of Compounds 7b and 7e.

A mixture of the pyrrolinone 7b or 7e (0.5 g) and dodecyl bromide (0.3 ml) were heated at 100° for 8 hours. After cooling, the solid was washed

with ether and crystallized from 2-propanol.

The dodecyl ammonium salt 7f was obtained in 62% yield, mp 185-186°; ir: 3210 (NH), 1680 cm^{-1} (CO); uv: (log ϵ) 344 (4.52) nm; pmr: δ 0.87 (3H, s, Me), 1.26 (26H, bs, 10 \times CH₂ + 2 \times Me), 1.98 (2H, m, CH₂), 2.28 (3H, s, Me), 2.76 (2H, m, CH₂), 3.40 (8H, m, 4 \times CH₂-N), 4.12 (2H, m, CH₂-O), 6.24 (1H, s, CH), 6.88-7.57 (9H, m, 2 \times Ar), 7.83 (1H, bs, NH).

Anal. Calcd. for C₃₇H₅₅BrN₂O₂: C, 69.48; H, 8.61; Br, 12.52; N, 4.38. Found: C, 69.55; H, 8.49; Br, 12.25; N, 4.37.

The dodecyl ammonium salt 7g was obtained in 52% yield, mp 173-175°; ir: 3210 (NH), 1680 cm^{-1} (CO); uv: (log ϵ) 345 (4.52) nm; pmr: δ 0.87 (3H, m, Me), 1.26 (20H, m, 10 \times CH₂), 1.91 (2H, m, CH₂), 2.26 (3H, s, Me), 2.76 (2H, m, CH₂), 3.28 (3H, s, Me), 3.67 (6H, m, 3 \times CH₂-N), 3.91 (2H, m, CH₂-OH), 4.13 (2H, m, CH₂-O), 6.23 (1H, s, CH), 6.90-7.40 (9H, m, 2 \times Ar), 7.91 (1H, bs, NH).

Anal. Calcd. for C₃₆H₅₃BrN₂O₃: C, 67.39; H, 8.27; Br, 12.48; N, 4.37. Found: C, 67.25; H, 8.29; Br, 12.30; N, 4.45.

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