Bicyclic Enamines V. Sigmatropic Rearrangement of Quaternary 2-Dehydroquinuclidine-3-carboxamides (1)

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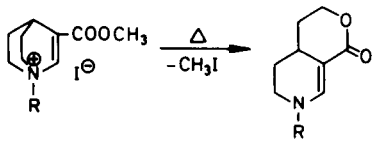
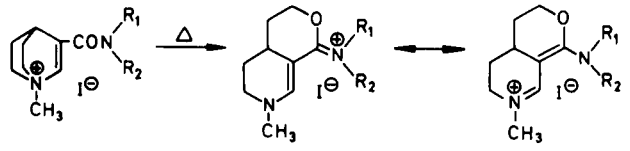
We have previously reported that the quaternary 2-dehydroquinuclidine-3-carboxylic acid ester **1**, when heated, is converted to the lactone **2** *via* two consecutive suprafacial 1,3-sigmatropic rearrangements (3). We now report, that the corresponding carboxamides **3-6** under similar conditions are converted to the iminolactones **7-10**.



1 **2**

The quaternary carboxamides **3-6** were prepared from the corresponding tertiary bases (4) by treatment with methyl iodide. These compounds were then heated to their melting points for 30 seconds. This afforded the iminolactones **7-10** in 60-80% yield. The starting materials and the products are presented in Scheme 1.

SCHEME 1



Compd no	R_1	R_2	Compd no
3	H	H	**7**
4	H	CH_3	**8**
5	H		**9**
6	CH_3		**10**

The structures of the iminolactones are based on chemical and spectral evidence. The nonprotonated forms of **7-9** are strong bases which rapidly absorb carbon dioxide from the atmosphere. By acid hydrolysis of **7-10**, the imino function was converted to a carbonyl group, thus forming the previously described lactone **2** ($R = CH_3$) (3). The spectral data are presented in detail in the experimental section. The uv spectra have maxima at 320-330 nm which is consistent with spectra of similarly conjugated imino compounds (5). The ir spectra have two characteristic bands in the carbonyl region appearing at 1625-1640 and 1540-1585 cm^{-1}, respectively, probably due to C=C and C=N absorptions. Two bands in the same region appear in the spectra of enaminolactones of type **2** (6). Compound **10** was obtained as an oil. The structure was confirmed by preparing it in an unambigous manner from the base of **8** by treatment with methyl iodide. The ir and uv spectra of the oil thus obtained were identical to those of the product formed by rearrangement of **6**.

By analogy with the mechanism for the conversion of **1** to **2** (3), we propose that the carboxamides **3-6**, upon heating, form the iminolactones **7-10** *via* two consecutive suprafacial 1,3-sigmatropic rearrangements.

EXPERIMENTAL

Ir spectra (potassium bromide) were recorded on a Perkin-Elmer 457 spectrophotometer and uv spectra were measured on a Zeiss PMQ II Spectrophotometer using ethanol as solvent. Microanalysis were performed in the laboratories of Dr. A. Bernhardt, Mulheim, Germany.

General Procedure for the Preparation of the Quaternary Carboxamides **3-6**.

The appropriate tertiary base, prepared as previously described (4) (0.01 mole) and methyl iodide (0.1 mole) in dry acetone (25 ml.) was left at room temperature over night, whereupon the solid product was filtered off and crystallized from ethanol-ether, yield 70-90%. The compounds had the following characteristics:

3: M.p. 152-154°; λ max: 218 nm (ϵ = 18,000); ν max: 3365s, 3185s, 1680s, 1660s, 1640s, 1610s.

Anal. Calcd. for $C_9H_{15}IN_2O$: C, 36.7; H, 5.14; N, 9.53. Found: C, 36.8; H, 4.91; N, 9.50.

4: M.p. 157-159°; λ max: 218 nm (ϵ = 17,700); ν max: 3270s, 1665s, 1630s, 1530s.

Anal. Calcd. for $C_{10}H_{17}IN_2O$: C, 39.0; H, 5.56; N, 9.09. Found: C, 38.9; H, 5.94; N, 8.86.

5: M.p. 184-185°; λ max: 215 nm (ϵ = 25,200); ν max: 3240s, 1885s, 1645w.

Anal. Calcd. for $C_{16}H_{20}ClIN_2O$: C, 45.9; H, 4.81; N, 6.69. Found: C, 45.8; H, 5.12; N, 6.49.

6: M.p. 140-142°; λ max: 219 nm (ε = 17,200); ν max: 1625s.

Anal. Calcd. for $C_{11}H_{19}IN_2O$: C, 41.0; H, 5.94; N, 8.70. Found: C, 40.8; H, 5.98; N, 8.66.

General Procedure for the Preparation of the Iminolactones **7-10**.

The quaternary carboxamides **3-6** were heated without solvent in a small flask to the melting points for 30 seconds. Acetone was then added, the mixture was filtered and the iminolactone precipitated by addition of ether to the filtrate. The products were recrystallized from ethanol-ether, yield 60-80%. The compounds had the following characteristics:

7: M.p. 175-177°; λ max: 323 nm (ε = 26,800); ν max: 3290s, 3185s, 3120s, 1640s, 1625s, 1540s.

Anal. Calcd. for $C_9H_{15}IN_2O$: C, 36.7; H, 5.14; N, 9.53. Found: C, 36.5; H, 5.32; N, 9.79.

8: M.p. 142-144°; λ max: 330 nm (ε = 24,900); ν max: 3240s, 3145s, 1635s, 1585s.

Anal. Calcd. for $C_{10}H_{17}IN_2O$: C, 39.0; H, 5.56; N, 9.09. Found: C, 39.0; H, 5.82; N, 8.89.

9: M.p. 218-219°; λ max: 324 nm (ε = 17,000); ν max: 3150s, 3080s, 1670m, 1630s, 1560s.

Anal. Calcd. for $C_{16}H_{20}ClIN_2O$: C, 45.9; H, 4.81; N, 6.69. Found: C, 45.8; H, 4.62; N, 6.89.

10: Oil; λ max: 326 nm (ε = 24,600); ν max: 1635s, 1575s.

Anal. Calcd. for $C_{11}H_{19}IN_2O$: C, 41.0; H, 5.94; N, 8.70. Found: C, 40.7; H, 5.91; N, 8.78.

Acid Hydrolysis of the Iminolactones.

The iminolactones **7-10** were all hydrolyzed as described for compound **7**. This compound (200 mg.) was dissolved in 20% aqueous hydrochloric acid (5 ml.). The solution was allowed to stand at room temperature over night. The acid solution was then extracted with benzene, the extract was dried (sodium sulfate) and evaporated *in vacuo*. This yielded 80 mg. (70%) of the lactone **2** (R = CH_3) (3) having identical m.p., ir and uv spectra as an authentic sample.

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