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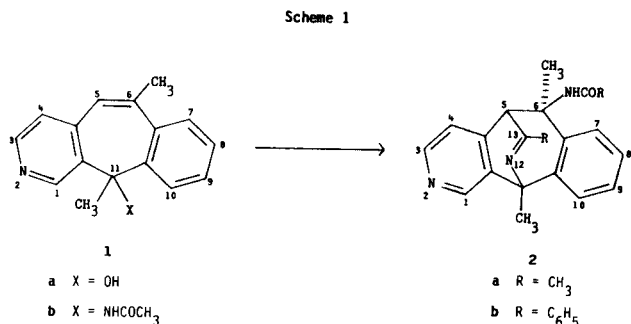
Received December 27, 1985

An attempt to generate a tertiary carbinamine from **1**, through use of the Ritter reaction, resulted in the formation of the new bridged system **2**. This product apparently resulted from an intramolecular cyclization of the 5,6 olefin to the C-11 nitrilium ion of **4**, followed by a second Ritter reaction at C-6.

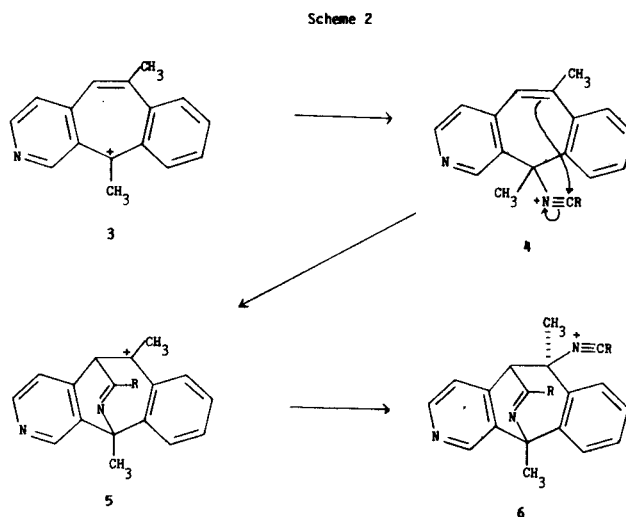
J. Heterocyclic Chem., **23**, 961 (1986).

In our earlier publications, we have established procedures for regiospecific syntheses of several imino-bridged benzocycloheptapyridines [3-5]. All of these preparations involved the generation of an amino function for cyclization into an internal or external olefin. To incorporate bridgehead alkyl functions into such products, it was necessary to place amino substituents at tertiary carbon atoms. Although this was accomplished readily through an extension of sulfenimine chemistry [5,6], we also examined the well known Ritter reaction [7] for the preparation of the desired tertiary carbinamines.

Treatment of the carbinol **1a** with concentrated sulfuric acid in the presence of acetonitrile produced a solid with a ¹H nmr spectrum inconsistent with the desired structure **1b**. The mass spectrum (*m/e* = 319) indicated an odd number of nitrogen atoms and suggested the incorporation of two acetonitrile moieties. The ¹H spectrum supported this, showing four methyl singlets and seven aromatic protons. Further examination of spectral and analytical data indicated the bridged structure **2a**. The stereochemistry of **2a** was determined using NOE difference spectroscopy [9] as outlined below.



Each of the four methyl groups was irradiated in order to define the spatial relationships throughout the molecule. The singlet at $\delta = 2.27$ ppm was assigned to the



11-CH₃ based on its NOE to the easily assigned 1-H and 10-H. Irradiation of the singlet at $\delta = 2.04$ ppm showed NOE to the -NH- defining the former as the *N*-acetyl. Irradiation of the methyl singlet at $\delta = 2.21$ ppm showed NOE to the 5-H singlet at 5.04 ppm while the methyl at 1.69 showed NOE enhancements to protons 4, 5, and 7. This latter methyl can thus be assigned as an α -CH₃ at the 6 position. Drieding models were used, in conjunction with this data, to confirm the stereochemistry as shown in **2a**.

The use of benzonitrile with **1a** and sulfuric acid produced the analogous bridged structure **2b**. NOE difference experiments gave results similar to those for **2a**, in particular, irradiation of the 6-CH₃ produced NOE's to hydrogens 4, 5, and 7. Reversing the stereochemistry at carbon 6 would be inconsistent with the NOE data outlined above.

These products apparently arose from trapping of the initially formed nitrilium ion **4** by the C-5, 6 olefinic linkage, leading to a second tertiary carbonium ion **5**. Ad-

dition of a nitrile would form the nitrilium ion **6**, and water would convert this to the observed products **2**.

Incorporation of an olefinic bond in an intramolecular cyclization reaction has been reported in Ritter reactions [7,8] but this is the first such report to produce this new class of heterocycle **2** [10].

EXPERIMENTAL

Melting points were taken on a Thomas Hoover melting point apparatus in open capillaries and are uncorrected values. Nmr spectra were obtained on a Bruker WM-250 spectrometer with 0.391 Hz/pt digital resolution using internal tetramethylsilane ($\delta = 0.0$) as reference. NOE difference experiments were run with a 2 second irradiation time. Solutions were not degassed. Microanalyses were performed under the direction of Dr. W. C. Randall.

N-[5,11-Dihydro-6 α ,11 α ,13-trimethyl-11,5-(nitrilomethano)-6*H*-benzo[5,6]cyclohepta[1,2-*c*]pyridin-6 β -yl]acetamide (**2a**).

Concentrated sulfuric acid (20 ml) was added to acetonitrile (80 ml) with cooling (0-5°). The carbinol **1a** [1] (4 g) was added gradually while maintaining the temperature at 0-5°. After allowing the reaction mixture to come to room temperature overnight, the mixture was poured over ice (400 g), and made alkaline by the addition of 20% sodium hydroxide solution. Some insoluble material was removed, and the filtrate was extracted with methylene chloride (3 x 400 ml). The combined extracts were washed with saturated sodium chloride solution and dried (sodium sulfate). The crude solid, 3.0 g, mp 246-250°, from evaporation of the solvent was recrystallized from ethyl acetate to give 2.25 g, mp 270-272°. ¹H nmr (deuteriochloroform): δ 1.69 (s, 6-CH₃, 3H), 2.04 (s, CH₃C=O, 3H), 2.21 (s, 13-CH₃, 3H), 2.27 (s, 11-CH₃, 3H), 5.10 (s, H-5, 1H), 6.40 (s, NH, 1H), 7.05-7.2 (m, H-8, H-9, 2H), 7.29 (d of d, J = 7.8, 1.6 Hz, H-7, 1H), 7.32 (d, J = 4.7 Hz, H-4, 1H), 7.52 (d of d, J = 7.8, 1.6 Hz, H-10, 1H), 8.38 (d, J = 4.7 Hz, H-3, 1H), 8.44 (s, H-1, 1H).

Anal. Calcd. for C₂₀H₂₁N₃O (319.39): C, 75.21; H, 6.63; N, 13.16. Found: C, 75.42; H, 6.79; N, 13.13.

N-[5,11-Dihydro-6 α -11 α -dimethyl-11,5-(nitrilometheno)-13-phenyl-6*H*-benzo[5,6]cyclohepta[1,2-*c*]pyridin-6 β -yl]benzamide (**2b**).

The procedure described above was followed using sulfuric acid (3.6 ml), benzonitrile (17.2 ml) and **1a** (1g). The solid that precipitated after basification was filtered, washed with water and air-dried, 1.7 g. Recrystallization from ethyl acetate gave 0.45 g of white crystals, mp 267-268°. Another 0.87 g was obtained from evaporation of the filtrate. ¹H nmr (deuteriochloroform): δ 1.89 (s, 6-CH₃, 3H), 2.42 (s, 11-CH₃, 3H), 5.94 (s, H-5, 1H), 6.09 (s, NH, 1H), selected aromatics: 7.38 (m, H-7, 1H), 7.54 (d, J = 4.7 Hz, H-4, 1H), 7.68 (m, H-10, 1H), 7.9 (m, ortho to imine, 2H), 8.48 (d, J = 4.7 Hz, H-3, 1H), 8.62 (s, H-1, 1H).

Anal. Calcd. for C₃₀H₂₅N₃O (443.52): C, 81.24; H, 5.68; N, 9.48. Found: C, 81.04; H, 5.75; N, 9.30.

REFERENCES AND NOTES

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