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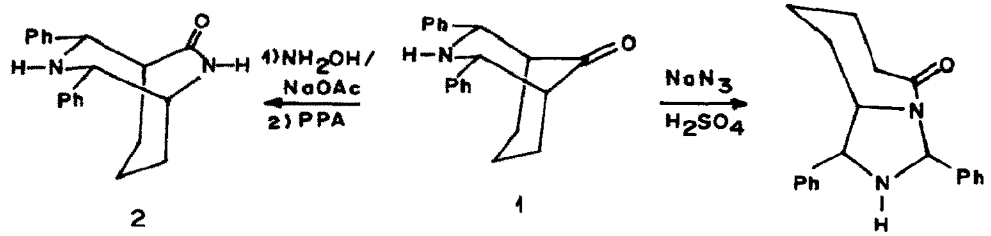
A New Rearrangement of 2,4-Diphenyl-3-azabicyclo[3.3.1]nonan-9-one leading to 8,10-Diphenyl-1,9-diazabicyclo[5.3.0]decan-2-one

Ramasubbu Jeyaraman* and Udayampalayam P. Senthilkumar
Department of Chemistry, Bharathidasan University
Tiruchirappalli-620 024, India

Abstract: Treatment of 2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one (1) with hydrazoic acid in $CHCl_3$-H_2SO_4 mixture resulted in a new rearrangement leading to 8,10-diphenyl-1,9-diazabicyclo[5.3.0]decan-2-one (3).

In connection with our investiations[1,2] on the chemistry of *N*-nitroso compounds, we required 2,4-diphenyl-3,9-diazabicyclo[3.3.2]decan-10-one (2). The lactam **2** was prepared by the conversion of ketone **1** into its oxime, followed by Beckmann rearrangement in polyphosphoric acid (**Scheme I**).[3] However, since the Beckmann rearrangement of the oxime has been found to be sensitive to the reaction time and temperature, and generally afforded the lactam **2** in low yields[3] we attempted an alternative route involving Schmidt rearrangement[4] of the ketone **1**. Instead of the lactam **2** a new product **3** was obtained.

Powdered and dried azabicyclononane **1** (12.44 mmol) was added, in portions, to a mixture of chloroform (50 mL) and conc. H_2SO_4 (25 mL). The reaction mixture was stirred with a magnetic stirrer. When all the ketone dissolved, sodium azide (15.0 mmol) was added slowly to the solution. After the addition was over, stirring was continued for 1 h. The reaction mixture was poured into crushed ice and neutralized with cold solution of sodium hydroxide. The chloroform layer was separated, washed with water and dried. Evaporation of chloroform, followed by recrystallization from ethanol afforded colorless crystals of the new product (mp 174 °C).



2

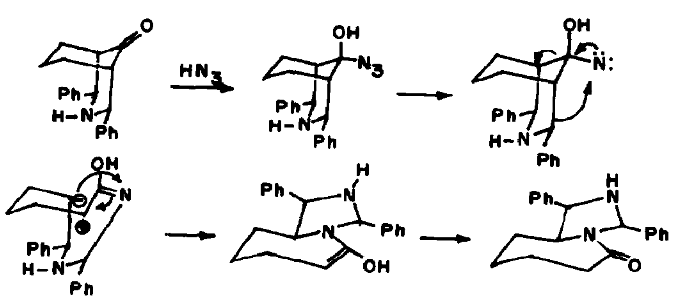
1

Scheme I

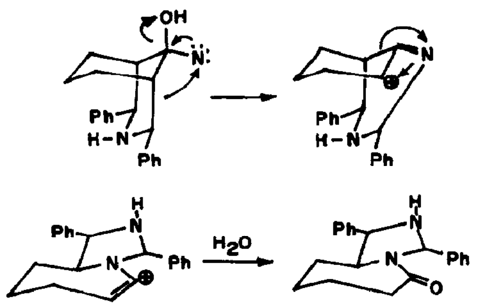
3

Analysis of the product exploying IR, ^1H and ^{13}C NMR spectral data, mass spectrum and elemental analysis indicated that it was not the expected secondary amide **2** but a new compound **3**. IR: 3300, 1630 cm^{-1}). ^1H NMR: 6.28 (s, 1H), 3.90 (d, 1H), 3.68 (dd, 1H), 1.4-2.8 (m, 9H), 7.2-7.6 (m, 10H); ^{13}C NMR: 73.7 (CH), 66.4 (CH), 64.9 (CH), 37.1 (CH_2), 30.6 (CH_2), 28.1 (CH_2), 22.0 (CH_2), 172.6 (CO) ppm. MS: m/z 306, 249, 194 and 91. Anal. Calcd. for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.69; H, 7.03; N, 9.13.

Possible pathways. The possible pathways for the product **3** under the conditions of the Schmidt reaction are shown in **Scheme II.**



Mechanism I



Mechanism II

Scheme II

In the normal Schmidt rearrangements,[4] the ketone interacts with hydrazoic acid to form a nitrene followed by migration of an *alpha* C-C bond to nitrogen generating a carbenium ion which rearranges to the amide **2**.

The compound **3** is formed by the migration of alternate *alpha-* and *beta-* bonds in the heterocyclic wing. In order to check if the lactam **2** is a possible intermediate it was treated with conc.$H_2SO_4/CHCl_3$ under the same conditions (except using NaN_3). The new compound **3** was not formed. Hence **3** is formed by one of the two possible routes as shown in **Scheme II.**

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