CONFORMATION OF cis-1-(S-α-PHENYLETHYL)DECAHYDROQUINOLIN-4-ONE

A. É. Aliev and G. V. Grishina

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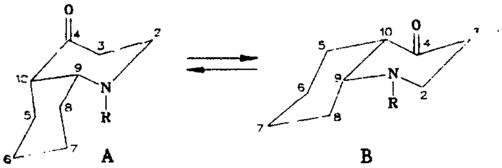
Additive calculations of the ^{13}C chemical shifts have shown [1] that of the two sets of calculated values for conformers A and B of cis-1-(S-α-phenylethyl)-decahydroquinolin-4-one (I), the best agreement with the experimental values of the ^{13}C chemical shifts is shown for form (IA).



I R=CH(CH$_3$)C$_6$H$_5$

In the same communication, the $^3J_{9,10}$ coupling constant was found to be 5.5 Hz, but was not used in discussing the conformation of (I), although according to data for substituted cyclohexanones [2] and γ-piperidones [3, 4] this value indicates preponderance of the conformer (IB). In order to resolve unambiguously the question of the conformation of the decahydroquinoline (I), we have again studied the ^1H and ^{13}C NMR spectra.

Combined analysis of the bivariate correlation spectra (^1H, ^1H)-COSY and (^1H, ^{13}C)-COSY has given the ^1H and ^{13}C chemical shifts for the ketone (I). Further, the $^2J_{HH}$, $^3J_{HH}$, $^4J_{HH}$, and $^1J_{CH}$ values have been found from the univariate ^1H and ^{13}C NMR spectra. The following results have been obtained, indicating the preponderance of the conformer (IB):

1) the shift of the 9-H proton (3.10 ppm), bearing in mind the shift of the 2-H proton in the cis- and trans-isomers of 1-benzyl-2,5-dimethylpiperidin-4-one [4], indicates that this proton is located equatorially in the piperidine ring.

2) the 9-H proton has a ^3J value of 11.3 Hz with 8a-H, i.e., the 9-H occupies the trans(a,a)-position relative to the 8a-H in the cyclohexane ring.

3) The measured remote coupling constants $^4H_{3a,10}$ = 1.2 Hz and $^4J_{2e,9}$ = 1.4 Hz, bearing in mind the $^4J_{HH}$ values for cyclohexanones [2] and γ-piperidones [4], indicate the interacting protons are cis-oriented.

4) The values of the direct coupling constants are $^1JC_{(9)},_{9}$-H = 137.1 and $^1JC_{(10)},_{10}$-H = 125.0 Hz. According to results obtained for trans-1-α-phenyl-ethyl-2,5-dimethylpipieridin-4-one, the axial and equatorial protons in the methylene groups loated in the α-position to the nitrogen atom (6-H) and to the carbonyl group (3-H) have different J_{CH} coupling constants:

$^1JC_{(6)},_{6a}$-H = 132.2 Hz; $^1HC_{(6)},_{6e}$-H = 137.5 Hz; $^1JC_{(3)},_{3a}$-H = 125.9 Hz; $^1JC_{(3)},_{3e}$-H = 131.1 Hz. Comparison of these values for those of $^1JC_{(9)},_{9}$-H and $^1JC_{(10)},_{10}$-H shows that the protons 9-H and 10-H in the piperidine ring have the equatorial and axial orientations respectively.

The ^1H and ^{13}C NMR spectra were obtained at room temperature on a Bruker WM-400 spectrometer, in C_6D_6.

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CONDENSATION OF 2-AMINOBENZIMIDAZOLES WITH o-SUBSTITUTED BENZOYL CHLORIDES

I. I. Popov, S. L. Boroshko, B. A. Tertov, and
E. V. Tyukavina

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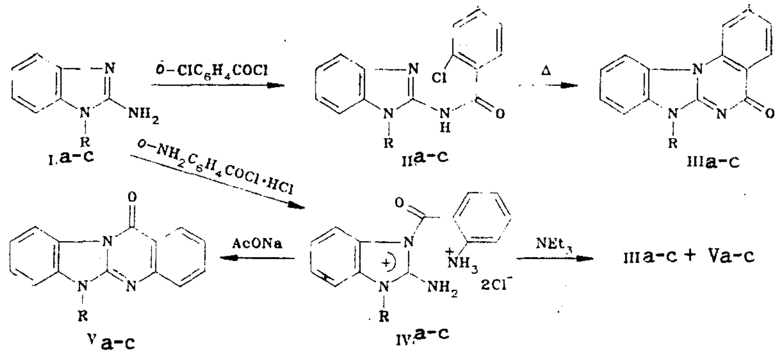
We have found novel routes for the synthesis of benzimidazoles, which include highly active immunodepressants [1].

It has been estabished that intramolecular thermal condensation of the o-chlorobenzamides (IIa-c) at 200-210°C affords derivatives of the novel heterocyclic system benzimidazo [2,1-c]quinazolin-5-one (IIIa-c).

The structures of (IIIa-c) were confirmed by their elemental analyses, and IR, PMR, and mass spectra.



I—V a $R=H$, b $R=CH_3$, c $R=C_2H_5$

Given are: compound, yield (%), mp (°C) (solvent for recrystallization): (IIIa), 53; 348-350 (DMF); (IIIb), 48; 254-256 (aqueous DMF); (IIIb), 45; 220-221 (ethanol).

The amides (IIa-c) were obtained by acylating the 2-aminobenzimidazoles (Ia-c) with o-chlorobenzoyl chloride in the presence of 10% sodium carbonate solution.

It has also been shown that the acylium salts (IVa-c), obtained by reacting the amines (Ia-c) with anthraniloyl chloride in acetone, on heating in the presence of triethylamine are converted into mixtures of (IIIa-c) and the benzimidazolo[2,1-b]quinazolin-12(6H)-ones (Va-c) in yields of 8-12 and 30-35% respectively. If the reaction is carried out in the presence of sodium acetate (Va-c) are formed exclusively in yields of 42-48%. The melting points and other constants of (Va-c) are in agreement with the literature values [2].

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