SYNTHETIC REACTION USING N,N'-DIBENZYLIDENETOLUENE-α,α-DIAMINES (7) HETEROCYCLES BY CYCLIZATION WITH KETONE (CH_3-CO-$CR^1R^2R^3$)

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Recently, we found the reaction that affords tetrahydropyrimido[1,2-c][1,3]benzoxazines and tetrahydropyrimido[3,4-c][1,3]benzoxazines from N,N'-bis[2-hydroxybenzylidene]-2-hydroxy-α,α-tolyldiamine and methyl alkyl ketone such as shown in the title. At this time, we wish moreover to submit a novel heterocyclization that affords 3,7-diazabicyclo[3.3.1]nonan-9-ones, heptahydropyrido[4,3-d]pyrimidines and 1,3,7-triazabicyclo[3.3.1]non-3-enes from other N,N'-dibenzylidenetoluene-α,α-diamines and methyl alkyl ketones in high yield. For these heterocycles, acetic acid facilitates the synthesis of 3,7-diazabicyclo[3.3.1]nonan-9-ones, while inhibits the synthesis of the latter, of which the unsaturated ring systems have hitherto not been described.

By the treatment with N,N'-dibenzylidenetoluene-α,α-diamine, acetone afforded 2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one (m.p. 247-249 °C) in 79 % yield, methyl ethyl ketone afforded 1-methyl-2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one (m.p. 240.5-242 °C) in 64 % yield and 2,4,5,7-tetraphenyl-8-methyl-2,3,4,5,6,7,8-heptahydro-4aH-pyrido[4,3-d]pyrimidine (m.p. 183-184 °C) in 84 % yield, methyl isopropyl ketone afforded 2,4,5,7-tetraphenyl-8,8-dimethyl-2,3,4,5,6,7,8-heptahydro-4aH-pyrido[4,3-d]pyrimidine (m.p. 189-190 °C) in 80 % yield, and methyl tert-butyl ketone afforded 2,6,8,9-tetraphenyl-4-tert-butyl-1,3,7-triazabicyclo[3.3.1]non-3-ene (m.p. 181-183 °C) in 97 % yield.

The initial step of these reactions is the Michael addition of the ketone to the azomethine group of the Schiff bases, followed by elimination of aldehydes from the adducts. The resultant intermediates are then cyclized to three heterocycles described above.

We have tried to determine the most favorable conformations of the novel heterocyclic compounds thus obtained with the clue based on the long-range coupling constants over five bonds and vicinal coupling constants in the system H-C-C=N-C-H, H-C-N-H, H-C-C-H, chemical shifts, observed for P.M.R. spectra of them.