REACTION OF 1-PHENYL-4-HYDRAZINO-4,5-DIHYDRO-6H-FURO-[2,3-d][1]BENZAZEPINE-5-CARBOXYLIC ACID HYDRAZIDE WITH AROMATIC ALDEHYDES\(^1\)

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1-Phenyl-4-hydrazino-4,5-dihydro-6H-furo[2,3-d][1]-benzazepine-5-carboxylic acid hydrazide (2) reacts with aromatic aldehydes in ethanol to give saturated monoarylylidene compounds (3a-c) and unsaturated monoarylylidene compounds (5a-c), respectively.

The reaction of \(\alpha,\beta\)-unsaturated esters with hydrazine hydrate has been reported by Godtfredsen et al.\(^2\). We applied this reaction to the synthesis of 1-phenyl-4-hydrazino-4,5-dihydro-6H-furo-[2,3-d][1]benzazepine-5-carboxylic acid hydrazide (2) from ethyl 1-phenyl-6H-furo[2,3-d][1]benzazepine-5-carboxylate (1)\(^3\) having a \(\alpha,\beta\)-unsaturated \(\alpha\)-amino ester moiety in the molecule. Next 2 was allowed to condense with aromatic aldehydes to afford saturated monoarylylidene compounds (3a-c) and unsaturated monoarylylidene compounds (5a-c). However in this case diarylylidene compounds (4) were not obtained.

2 was prepared in 60-70% yield by heating the mixture of 1 and hydrazine hydrate at 90-100\(^\circ\) for 10 min or refluxing of ethanolic solution of 1 and hydrazine hydrate in the presence of sodium hydroxide. In the nmr spectrum of 2, doublets (\(J=16\ Hz\)) observed at \(\delta 3.97\) and 3.76 were assigned to \(C_4\)-H and \(C_5\)-H of trans configu-
2 reacted with excess of aromatic aldehydes in ethanol at room temperature for 1-1.5 hr to give the corresponding monoarylylidene compounds (3a-c) in good yields. In the case of the reaction of 2 with excess of aromatic aldehydes in ethanol under reflux for 10 hr, unsaturated monoarylylidene compounds (5a-c) were obtained quantitatively. However, diarylylidene compounds (4) were not formed. Similarly, 5a-c were synthesized from 3a-c. 5a-c were completely identical with the compounds prepared from 5 (via 3 steps from 1) by mixed melting point tests and comparison of their ir spectra.

Ar: a=2-furyl, b=phenyl, c=p-chlorophenyl
Furthermore, 2 reacts with four equivalents of furfural in ethanol containing a small amount of acetic acid at room temperature for 7 hr to give a new product 7 (44%), along with 3a (12%) and 5a (22%), respectively. The formation of 7 seems to be due to the 1,2-hydride shift to carbonium ion resulting from the elimination of 4-hydrazino group and consequent transfer of nitrogen lone pair. 7 was also isomerized to 5a by heating in ethanol containing acetic acid or furfural. The structures of these compounds synthesized here were supported by their elemental analyses and spectral data.

\[
\begin{align*}
& \text{furfural} \quad \xrightarrow{\text{H}, \text{EtOH}, \text{room temp.}} \quad 3a \\
& \text{H}^+ \\
& \text{EtOH, reflux} \quad \xrightarrow{\text{H}^+ \text{ or furfural}} \quad 5a
\end{align*}
\]

References


4) Elemental analyses (EA) and spectral data of \( \mathcal{Z} \), \( 3a \), \( 5a \), \( 5b \), \( 6 \) and \( \mathcal{Z} \).

\( \mathcal{Z} \) [mp 158-159°, colorless scales (EtOH)]

EA Found

\[ \begin{align*}
C; & \quad 65.41, \ H; \quad 5.42, \ N; \quad 20.23\%.
\end{align*} \]

Calcd. for \( \text{C}_{19}\text{H}_{19}\text{N}_{5}\text{O}_{2} \)

\[ \begin{align*}
C; & \quad 65.31, \ H; \quad 5.48, \ N; \quad 20.05\%.
\end{align*} \]

IR (KBr, cm\(^{-1}\)) 3495, 3455, 3390, 3340, 3240, 1668, 1634.

NMR (\( \delta \) in CDC\(_3\)) 7.95 (1H, bs, NH), 7.67 (1H, s, \( \text{C}_2\)-H), 7.24 (5H, s, phenyl-H), 7.22-6.71 (4H, m, \( \text{C}_7\)-10-H), 5.96 (2H, bs, NH x 2), 3.77 (4H, b, NH\(_2\) x 2), 3.97 and 3.76 (2H, d x 2, J=16 Hz, \( \text{C}_4\),5\)-H).

MS (m/e) 349 (M\(^+\)).

\( 3a \) [mp 207-208°, colorless needles (EtOH-CHCl\(_3\))] 

EA Found

\[ \begin{align*}
C; \quad 67.51, \ H; \quad 4.89, \ N; \quad 16.31\%.
\end{align*} \]

Calcd. for \( \text{C}_{24}\text{H}_{21}\text{N}_{5}\text{O}_{3} \)

\[ \begin{align*}
C; \quad 67.43, \ H; \quad 4.95, \ N; \quad 16.39\%.
\end{align*} \]

IR (KBr, cm\(^{-1}\)) 3463, 3360, 3238, 3255, 3195, 1668, 1615.

NMR (\( \delta \) in DMSO-d\(_6\)) 11.21 (1H, bs, NH), 8.35 (1H, s, N=CH), 7.94 (1H, s, \( \text{C}_2\)-H), 7.82, 6.85 and 6.62 (3H, d, d and m, furyl-H), 7.43 (2H, bs, NH x 2), 7.23 (5H, s, phenyl-H), 7.22-6.51 (4H, m, \( \text{C}_7\)-10-H), 4.92 (2H, bs, NH\(_2\)), 3.81 and 3.62 (2H, d x 2, J=16 Hz, \( \text{C}_4\),5\)-H).

MS (m/e) 427 (M\(^+\)).

\( 5a \) [mp 151-152°, reddish needles (EtOH-CHCl\(_3\))] 

EA Found

\[ \begin{align*}
C; \quad 70.69, \ H; \quad 5.20, \ N; \quad 9.32\%.
\end{align*} \]

Calcd. for \( \text{C}_{24}\text{H}_{17}\text{N}_{3}\text{O}_{3}\text{EtOH} \)

\[ \begin{align*}
C; \quad 70.73, \ H; \quad 5.25, \ N; \quad 9.52\%.
\end{align*} \]

IR (KBr, cm\(^{-1}\)) 3315, 3190, 1625.

NMR (\( \delta \) in DMSO-d\(_6\)) 11.76 (1H, bs, NH), 8.35 (1H, s, N=CH), 7.91 (2H, s, ring-H), 7.41 (5H, s, phenyl-H), 7.18-6.45 (8H, m, ring-H and NH), 4.37 (1H, t, OH), 3.52 and 1.11 (5H, \( \text{C}_2\text{H}_5\)).

MS (m/e) 395 (M\(^+\)).
§b [mp 224-226°, reddish needles (EtOH-CHCl₃)]
EA Found
  C; 69.31, H; 4.86, N; 8.47%.
  Calcd. for C₂₆H₁₈N₃O₂₇EtOH C; 69.20, H; 4.98, N; 8.65%.
IR (KBr, cm⁻¹) 3310, 3185, 1620.
NMR (δ in DMSO-d₆) 11.67 (1H, b, NH), 8.31 (1H, s, N=CH), 7.77 (1H, s, C₂-H), 7.66 and 7.43 (4H, d × 2, p-chlorophenyl-H), 7.28 (5H, s, phenyl-H), 7.07-6.35 (6H, m, C₄-H, NH and C₇-10-H).
MS (m/e) 439 (M⁺).

§c [mp 212-213°, orange needles (EtOH)]
EA Found
  C; 71.99, H; 4.67, N; 13.04%.
  Calcd. for C₁₉H₁₅N₃O₂ C; 71.91, H; 4.76, N; 13.24%.
IR (KBr, cm⁻¹) 3295, 3235, 3190, 3130, 1653, 1630.
NMR (δ in DMSO-d₆) 9.73 (1H, b, NH), 7.81 (1H, s, C₂-H), 7.36 (5H, s, phenyl-H), 7.12-6.35 (6H, m, C₄-H, NH and C₇-10-H), 4.48 (2H, b, NH₂).
MS (m/e) 317 (M⁺).

§d [mp 162-163°, pale yellow prisms (EtOH)]
EA Found
  C; 73.00, H; 4.21, N; 10.37%.
  Calcd. for C₂₄H₁₇N₃O₃ C; 72.90, H; 4.33, N; 10.63%.
IR (KBr, cm⁻¹) 3260, 1662.
NMR (δ in CDCl₃) 10.52 (1H, bs, NH), 8.38 (1H, s, N=CH), 7.52, 6.84 and 6.47 (3H, d, d and m, furyl-H), 7.45 (1H, s, C₂-H), 7.32 (5H, s, phenyl-H), 7.17 (4H, m, C₇-10-H), 3.84 (2H, s, C₄-H).
MS (m/e) 395 (M⁺).

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