BAZI p–(BENZOİLAMİNO) BENZOİK ASİT HİDRAZİDİ HİDRAZONLARININ SENTEZİ VE KARAKTERİSZASYONU

SYNTHESIS AND CHARACTERIZATION OF SOME ARYLHYDRAZONES OF p–(BENZOYLAMINO) BENZOIC ACID HYDRAZIDE

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SUMMARY

In this study, ten new p–(benzoylamino) benzoic acid arylmethylenehydrazide derivatives have been synthesized. The structure of the compounds have been elucidated by UV, IR, $^1$H–NMR and elementary analyses.

ÖZET

Bu çalışmada on yeni p–(benzoilamino) benzoik asit arilmetilen hidrazid türü bileşikin sentezi yapılmıştır. Bileşiklerin yapılan UV, IR, $^1$H–NMR ve elementler analiz yardımcı ile kanıtlanmıştır.

INTRODUCTION

The existence of hydrazone function is an important property for anticonvulsant and antimicrobial activities of some compounds (1 – 8). The present paper reports the synthesis and the structure elucidation of p–(benzoylamino) benzoic acid arylmethylene hydrazide derivatives. Furthermore, we have been using these compounds for the cyclization of some substituted 1,3,4-oxadiazoline derivatives. All of these compounds will be screened for their antimicrobial activities after interpretation of 1,3,4-oxadiazolines. These results will be reported in a later study.

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EXPERIMENTAL PART

All m.p.'s were taken on a Buchi 510 melting point apparatus and uncorrected. IR spectra were run on a Perkin Elmer 240 spectrophotometer. 1H–NMR spectra were taken on a AC Bruker 200L spectrometer. UV spectra were taken on a Schimadzu UV–2100S spectrophotometer. Elementar analyses were run on a Carlo Erba 1106.

Ethyl p-(benzoylamino) benzoate (1)

A solution of benzocaine (0.03 mol) in diethylether (30 ml) was added slowly, with stirring to a cooled (below 10°C) solution of benzoylchloride (3.6 ml) in the same solvent. The mixture was stirred for 1 hr and allowed to stand overnight at the room temperature.

The solid residue was collected by filtration and washed with water. The compound was recrystallized from ethanol, mp 140°C (9).

p-(Benzoylamino) benzoyl hydrazine (2)

A mixture of 1 (0.02 mol) and hydrazine hydrate (18 ml) was heated under reflux for 1 hr at 110°C – 130°C. The hot reaction mixture was setaside to cool to room temperature. The precipitate formed was filtered and washed with water. The crude product was purified by washing ethanol m.p 240°C. 2.40 gr (Yield % 85).

Analyses C₁₇H₁₃N₃O₂ N, 16.46. Calc. N, 16.97 Found Spectral Properties:

UV λ max. 202 (ε : 36844), 282 (ε : 26548) nm (1 mg/100 ml), IR (KBr) γ max. 3310 – 3275 (amid N–H); 3180 (hydrazine N–H); 1650 (C = O); 1610, 1590, 1575 (C = C); 1510 (N–H, C–N ); 840 (1,4–disubstitue benz); 705 and 690 (monosubstitute benz) cm⁻¹.

General Procedure for the synthesis of arylhydrazones of p-(benzoylamino) benzoic acid hydrazide (3a – 3j)

To a solution of 0.005 mol of substance 2 in 50 ml of ethanol, a solution of 0.005 mol of aldehyde compound dissolved in a minimum quantity of ethanol was added. The mixture was heated under reflux for 1.5 – 2 hr in a boiling water bath. The mixture was allowed to cool to room temperature. The precipitate and recrystallized from ethan

1H–NMR of compd. 3, hydrazone N–H); 10.43 (s, 8.02–7.36 (m, 14H, Ar–H) 3 hydrazone N–H); 10.46 (s, H); 8.45 (S 1H, = CH–); 8.09

RESULTS AND DISCUSSION

p–(Benzoylamino) benzoic aromatic aldehydes in e compounds 3a–j were obtained

\[
\begin{align*}
&\text{C–Cl + H}_2\text{N} \\
&\text{C–N} \\
&\text{C–N} \\
&\text{C–I}
\end{align*}
\]

The structure of the

1H–NMR (for compd 3a, 38 compounds were characteri
room temperature. The precipitate was filtered, washed with water, dried and recrystallized from ethanol.

\(^1\)H–NMR of compd. 3a : DMSO–d\(_6\) / TMS, \(\delta\)(ppm) 11.68 (s, 1 H, hydrazone N – H) ; 10.43 (s, 1 H, amid N – H) ; 8.46 (s, 1H, = CH –); 8.02–7.36 (m, 14H, Ar–H) 3b : DMSO – d\(_6\) / TMS, \(\delta\)(ppm) 11.96 (s, 1H, hydrazone N – H) ; 10.46 (s, 1H, amid N – H) ; 8.66 (d, 2H, pyridine orto–H); 8.45 (S 1H, = CH–) ; 8.09 – 7.51 (m, 11H, Ar–H and pyridine–H).

RESULTS AND DISCUSSION

p–(Benzoylamino) benzoyl hydrazine was reacted with appropriate aromatic aldehydes in ethanolic medium and the corresponding compounds 3a–j were obtained according to scheme.

![Scheme](image)

The structure of the products were also confirmed by UV, IR and \(^1\)H–NMR (for compd 3a, 3b) spectroscopic methods. All the synthesized compounds were characterized by their elementary analyses.
<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
<th>Yield (%)</th>
<th>Molecular Formula (M.W.)</th>
<th>Elemental Analysis</th>
<th>UV Emax (cm⁻¹)</th>
<th>IR (cm⁻¹)</th>
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<td></td>
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<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
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<td>3a</td>
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<td>90</td>
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<td>4.85</td>
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<td>(344.34)</td>
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<td>(561.58)</td>
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<td>60.04</td>
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<td>9.98</td>
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The UV spectral data

The IR spectra of cor and 3229 – 3221 cm⁻¹ regi and amid groups. The hydrates were observed between 1660

In the 1H-NMR spectra, the methyl protons of the original aldehyde appeared as a singlet at 8.45 ppm (10) azomethine proton at 8.45 ppm. Change in the chemical shift during the formation of the TBDHP field shift.

The signals due to the hydrazone

The hydrazone signal at 11.68, 11.96 ppm. The hydrazone signal (11) and would be a doublet. This could not be bonded.

The signal of aromatization

REFERENCES

(Received December 27, 199.)
The UV spectral data for compounds 3n-j were given on the table.

The IR spectra of compounds 3n-j showed bands in the 3330–3300 and 3229 – 3221 cm\(^{-1}\) region indicating the presence of the hydrazone and amid groups. The hydrazide and amid C=O bands of compounds 3n-j were observed between 1660 – 1640 cm\(^{-1}\).

In the 1H–NMR spectra, the aldehyde signal of compounds 3a, 3b appeared as a singlet at 8.46, 8.45 ppm respectively. Compared to the protons of the original aldehyde which resonate at about 9.00 – 10.00 ppm (10) azomethine protons, –N = CH –, resonate at a higher field (8.46, 8.45 ppm). Change in the chemical environment of the concerned protons during the formation of the azomethine linkage could be accounted for this high field shift.

The signals due to the amid N–H were observed at 10.43 and 10.46 ppm.

The hydrazone signal of compounds 3a, 3b appeared as a singlet at 11.68, 11.96 ppm. The hydrazone N–H resonated at about 13.70–14.76 ppm (11) and would be observed at about 10.95 ppm (12) provided it hadn’t been bonded. This observation showed that the hydrazone N–H could not be bonded.

The signal of aromatic protons was also found in the expected field.

REFERENCES

(Received December 27, 1991)