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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 arylmenthylenehydrazide derivatives have been synthesized. The structure of the compounds have been elucidated by UV, IR, ^{1}H–HMR and elementary analyses.

ÖZET

Bu çalışmada on yeni p–(benzoilamino) benzoik asit arilmetilen hidrazid türevi bileşiğin sentezi yapılmıştır. Bileşiklerin yapılan UV, IR, ^{1}H–HMR ve elementler analiz yardımı 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 cylization 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. ^{1}H–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) benzoat (1)

A solution of benzocaine (0.03 mol) in diethylether (30 ml) was added slowly, with stirring to a cooled (below 10°) solution of benzoylchloride (3.6 ml) in the same solvent. The mixture was stirred for 1hr 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° (9).

p – (Benzoylamino) benzoyl hydrazine (2)

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

Analyses $C_{14}H_{13}N_3O_2$ N, 16.46. Calc. N, 16.97 Found Spectral Properties :

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

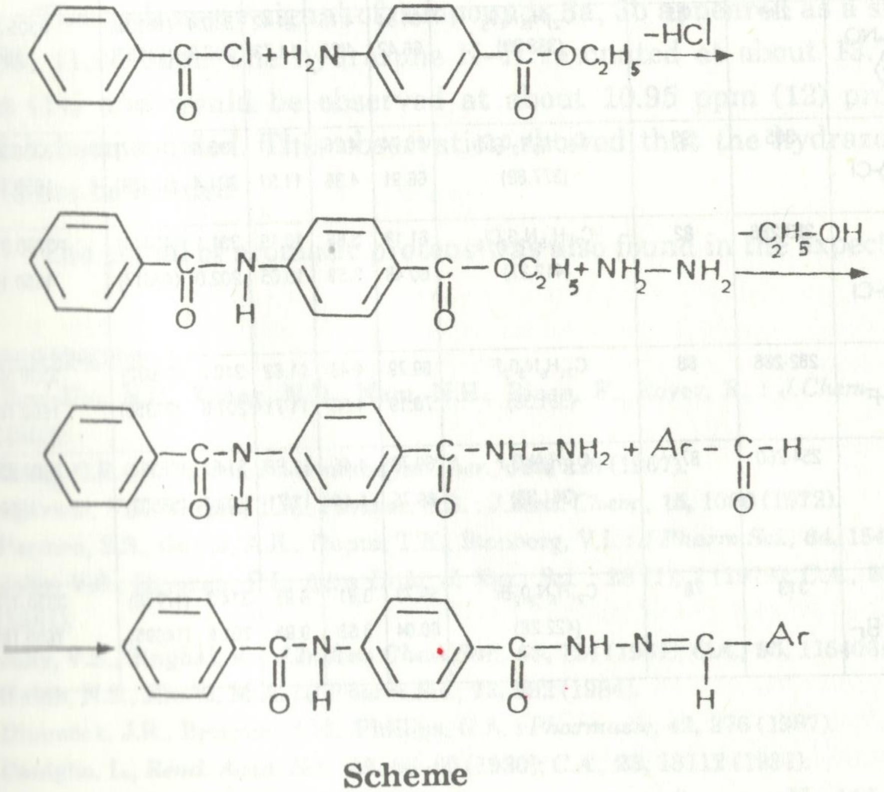
General Procedure for the synthesis of arylhydrazones of p–(benzoylamino) benzoic acid hydrazide (3a – 3j)

To a solution of 0.005 mol of subtance 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 was filtred, washed with water, dried and recrystallized from ethanol.

^{1}H–NMR of compd. 3a : DMSO–d_6 / TMS, δ(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, δ(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

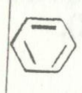
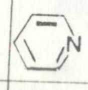
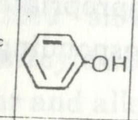
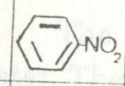
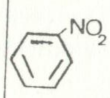
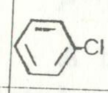
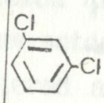
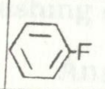
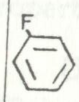
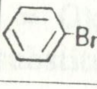
p–(Benzoylamino) benzoyl hydrazine was reacted with appropriate aromatic aldlehydes in ethanolic medium and the corresponding compounds 3_{a-j} were obtained according to scheme.



Scheme

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 – Physical Data for Compounds 3a – j

Compound	Ar	m.p.(°C)	Yield (%)	Molecular Formula (M.W.)	Elemental Analysis Calc/Found			UV EtOH λmax (ε)	IR (KBr) (cm⁻¹) (N-Hger, C = Oger)
					C	H	N		
3a		218-225	90	$C_{21}H_{17}N_30_2$ (343.4)	73.45 73.15	4.99 5.02	12.13 12.4	309.2 (50995) 219.2 (27747) 202.3 (42238)	3330.3260 1640.1660
3b		300	72	$C_{20}H_{16}N_40_2$ (344.38)	69.76 70.88	4.68 4.8	16.26 16.76	312.7 (48833) 202.5 (39397)	3330.3270 1650.1655
3c		292-295	82	$C_{21}H_{17}N_30_3.1/2\ H_20$ (359.40)	68.4 68.75	4.61 4.97	11.4 11.74	321.6 (51358) 220.2 (30729) 202.3 (48052)	3300.3260 1655
3d		316	95	$C_{21}H_{16}N_40_4$ (388.39)	64.94 64.22	4.15 4.12	14.42 14.26	334.6 (36936) 202.1 (43228)	3320.3230 1640
3e		298	85	$C_{21}H_{16}N_40_5$ (388.39)	64.94 66.42	4.15 4.23	14.42 14.73	310.4 (18138) 202.3 (14953)	3305.3220 1640
3f		305	93	$C_{21}H_{16}N_30_2Cl$ (377.88)	66.74 66.91	4.26 4.36	11.11 11.31	313.4 (14397) 201.4 (10429)	3330.3290 1650.1660
3g		283-286	82	$C_{21}H_{15}N_30_2Cl_2$ (412.27)	61.18 60.48	3.66 3.59	10.19 10.05	301.1 (40444) 202.0 (47617)	3280.3210 1650.1655
3h		282-286	88	$C_{21}H_6N_30_2F$ (361.38)	69.79 70.19	4.46 4.53	11.62 11.71	310.0 (24032) 201.6 (21358)	3330.3290 1660.1650
3i		254-260	87	$C_{21}H_6N_30_2F$ (361.38)	69.79 69.76	4.46 4.44	11.62 11.71	314.1 (77588) 203.3 (58562)	3300.3210 1650
3j		313	78	$C_{21}H_6N_30_2Br$ (422.28)	59.73 60.04	3.81 3.83	9.95 9.98	314.3 (17778) 201.6 (14695)	3330.3280 1650.1655

The UV spectral data for compounds 3_{a-j} were given on the table.

The IR spectra of compounds 3_{a-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 3_{a-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.

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