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Research Article

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Synthesis and characterization of bisazo derivatives of 4-acetyl resorcinol

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ABSTRACT

A new series of bisazo derivatives of 4-acetylresorcinol have been synthesized by diazotization of substituted aniline followed by coupling with 4-acetylresorcinol. All the synthesized compounds have been characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectral analysis.

Key words: bisazo, 4-acetylresorcinol, diazotization.

INTRODUCTION

Azo compounds are high-value chemicals widely used in many fields. Among them, aromatic azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly coloured and have been utilized as dyes, pigments and analytical reagents. They can also be used as indicators in chemical laboratories and as stains in the biological fields. Azo compounds are used as food additives and drugs for a long time[1-23]. In fact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts. Azo compounds are considered as class of organic colourants which consist of at least a conjugated chromophore azo (-N=N-) group in association with one or more aromatic or heterocyclic system[24]. They are capable of providing high intensity colour and have reasonably good technical properties, including light and weather fastness and resistance to solvents and water. The biological importance of azo compounds is well known due to their use as inflammatory [25,-26], anticancer [27,-28], antibacterial [29-32] and antifungal [33-35].

The synthesis of azo compounds is very simple, requires short time, involves very easy product separation and the raw materials are readily available and cheap. These lead to the manufacture of azo compounds at a larger scale. The reactions are generally carried out at lower temperature and the solvent mostly used is water which reduces the environmental impact. In the present work, the investigator has made an attempt to synthesis and characterize azo compounds of 4-acetylresorcinol (**I-V**). Compounds have been synthesized by diazotization of substituted anilines followed by coupling with 4-acetylresorcinol. All the synthesized compounds are characterized by elemental analyses, IR, ^{1}H NMR, ^{13}C NMR and mass spectral data.

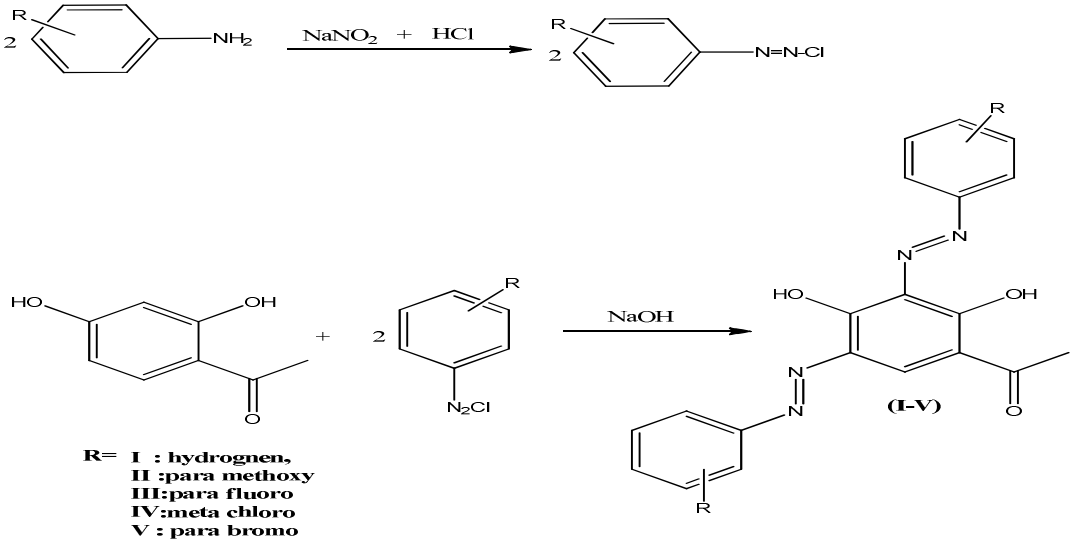
EXPERIMENTAL SECTION

The purity of the compounds was checked by TLC using silica gel-G plates and visualized in iodine vapours. Melting points were recorded in open capillary tubes in sulfuric acid bath and were uncorrected. FT-IR spectra were obtained on SHIMADZU FT-IR Affinity-I instrument using KBr pellets. ^{1}H NMR spectra were taken in BRUKER 400MHz instrument in $CDCl_3$ using TMS as internal standard. The chemical shift values are expressed in ppm.

Synthesis of 4- Acetylresorcinol

The required starting material 4-Acetylresorcinol was prepared by the procedure reported in literature [36-38]

To a mixture of freshly fused and powdered $ZnCl_2$ (10g) in dry acetic acid (15ml) contained in a conical flask, dry resorcinol(10g) was added quickly while stirring. The mixture was gently heated on a flame to 142˚C for 20 minutes. The viscous red solution was allowed to cool to room temperature. 80 ml of HCl (1:1) was added to syrupy mass and stirred. After a few minutes an orange- red crystalline material separated out. The crude product was crystallized twice from methanol to give 4-acetylresorcinol as a colorless solid. Yield 90%, m.p. 145-150 ˚C



R= I : hydrognen,
II :para methoxy
III:para fluoro
IV:meta chloro
V : para bromo

Synthesis of 2, 6-bis-(substituted phenyl)azo-4-acetylresorcinol

Substituted aniline (0.002mol) was dissolved in 3ml HCl and to it was added 3ml of H_2O. The solution was cooled to 0-5˚C in an ice bath and maintained this temperature. Sodium nitrite (0.004mol) in water (3ml) was then added drop wise. Stirring was continued for 20 minutes to produce diazonium salt at the same temperature. To this mixture, 2-acetylresorcinol (0.001mol, 0.152g) dissolved in 10% NaOH was added drop wise with stirring at 0-5˚C. The mixture was stirred for 20 minutes. The precipitate was collected by filtration at vacuum and recrystallised from suitable solvent.

Table-1: Characterization data of compounds I-VI

Compd	Molecular Formula	Molecular Weight	Melting Point (˚C)	IR (KBr) (cm^{-1})		Purification Solvent
				C=O	N=N	
I	$C_{20}H_{16}N_4O_3$	360	160	1666	1582	Acetonitrile
II	$C_{22}H_{20}N_4O_5$	420	140	1665	1600	Ethyl acetate
III	$C_{20}H_{14}N_4O_3F_2$	396	180	1664	1594	Acetonitrile
IV	$C_{20}H_{14}N_4O_3Cl_2$	428	200	1667	1583	Ethyl acetate
V	$C_{20}H_{14}N_4O_3Br_2$	515	240	1671	1603	Acetonitrile

RESULTS AND DISCUSSION

As a representative case, the spectral identification of 2, 6-bis-(paramethoxyphenylazo)-4-acetylresorcinol has been discussed.

2, 6-bis-(4-methoxyphenyl)azo-4-acetylresorcinol (II)

It shows a weak absorption band at 3429cm^{-1} indicating the presence of O–H group. The absorption peaks at 3071 cm^{-1} and 2930 cm^{-1} are due to Ar–H and CH_3 stretching vibrations respectively. A strong absorption peak at 1665 cm^{-1} is assigned for C=O stretching vibration. This low absorption frequency for C=O is due to chelating effect[31-33] of C=O and –OH group. The presence of N=N group is evidenced by a stretching absorption peak at 1600 cm^{-1}. Aromatic C⋯⋯C stretching frequency appears at 1476cm^{-1}. Absorption peaks at 1394 cm^{-1} and 1252 $cm^{-1}$are due to C–N and C–O stretching vibrations respectively.

In ^{1}H NMR the chemical shift values at δ 2.6 and 3.8 as singlets are due to the presence of three protons of acetyl groups of resorcinol moiety and six protons of methoxy group of phenyl moiety. A triplet at δ 7.1 assigned to $C_{3',5'}$ and $C_{3'',5''}$- 4H of phenyl moiety. Two doublets at δ 7.8 and 7.9 are assigned to $C_{2',6'}$ and $C_{2'',6''}$- 4H of phenyl moiety. A singlet at δ 8.1 ppm corresponds to C5 hydrogen of resorcinol moiety.

In general intra molecular and inter molecular hydrogen bonds have a very significant effect on ^{1}H chemical shift of OH protons which cover a region[34] from 4.5 to 19ppm and ^{1}H NMR of phenol –OH groups display broad signals at room temperature due to hydrogen bond. In **compound II** the –OH proton which involves in azo – hydrazone tautomerism of resorcinol moiety appears as a broad peak at δ 15.2 The other -OH of resorcinol moiety which may involve in intermolecular hydrogen bond with -OH of other molecules or the acidic impurities present in $CDCl_3$ solvent used in NMR study resulting from solvent decomposition. So the peak of this –OH would be extremely broad at room temperature. Hence it cannot be distinguished from the base line. Absence of a peak at δ 6.2 and 6.3 of C_2 , C_6 - hydrogen of parent compound 2-acetylresorcinol shows that bis diazo group is attached at C_2 - C_6 carbon of 4-acetylresorcinol and further confirms the product formation.

2, 6-bis-(phenyl)-azo-4-acetylresorcinol (I)
IR (cm^{-1}) : 3430 (O-H), 3065(Ar-H), 2924 (CH_3), 1666 (C=O), 1582 (N=N), 1454 (C⎓C), 1352 (C–N), 1232 (C–O) **^{1}H NMR (δ) :** 2.5 (s,3H, -CH_3) 7.2-8 (m,10H, Ar-H), 8.1 (s,1H,C_5-H), 15.2(hump, –OH) **^{13}C NMR (δ) :**31,116,122,130,145,196. **Mass:** m/e 360**,** $C_{20}H_{16}N_4O_3$.

2, 6-bis-(4-fluorophenyl)-azo-4-acetylresorcinol (III)
IR (cm^{-1}) : 3455 (O-H), 3041(Ar-H), 2996 (CH_3), 1664 (C=O), 1594 (N=N), 1474 (C⎓C), 1349 (C–N), 1224 (C–O) **^{1}H NMR (δ) :** 2.5 (s,3H, -CH_3) 7.3-7.9 (m,8H, Ar-H), 8.1 (s,1H,C_5-H), 15.2 (hump, –OH) **^{13}C NMR (δ) :**31,116,120,148,176,196. **Mass:** m/e 396**,** $C_{20}H_{14}N_4O_3F_2$

2, 6-bis-(3-chlorophenyl)-azo-4-acetylresorcinol (IV)
IR (cm^{-1}) : 3426 (O-H), 3026(Ar-H), 2925 (CH_3), 1667 (C=O), 1583 (N=N), 1474 (C⎓C), 1353 (C–N), 1275 (C–O) **^{1}H NMR (δ)** 2.6 (s,3H, -CH_3) 7.3-7.6 (m,6H, Ar-H), 8.1 (s,1H,C_5-H), 8.2 (s,2H,$C_{2',2''}$-2H), 15.9 (hump, –OH) **^{13}C NMR (δ) :**31,117,128,130,142,196. **Mass:** m/e 428**,** $C_{20}H_{14}N_4O_3Cl_2$

2, 6-bis-(4-bromophenyl)-azo-4-acetylresorcinol (V)
IR (cm^{-1}) : 3426 (O-H), 3123(Ar-H), 2927 (CH_3), 1671 (C=O), 1603 (N=N), 1476 (C⎓C), 1360 (C–N), 1281 (C–O) **^{1}H NMR (δ) :** 2.6 (s,3H, -CH_3) 7.2-7.8 (m,8H, Ar-H), 8.0 (s,1H,C_5-H), 15.3(hump, –OH) **^{13}C NMR (δ) :**31,118,130,145, 160,197. **Mass:** m/e 515**,** $C_{20}H_{14}N_4O_3Br_2$

CONCLUSION

A new series of bisazo derivatives of 4-acetylresorcinol have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectral analysis.

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