WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 5.990
Volume 4, Issue 6, 1694-1701. Research Article ISSN 2277– 7105

SYNTHESIS AND CHARACTERISATION OF 2-(SUBSTITUTED PHENYL)AZO-4,6-DIPROPIONYLRESORCINOL DERIVATIVES

K. Loganathan*, K. Sithick Ali, M. Purushothaman, S. Silambarasan, A. Jamal Abdul Nasser

PG and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli, India – 620 020.

Article Received on
02 April 2015,

Revised on 24 April 2015,
Accepted on 18 May 2015

***Correspondence for Author**
K. Loganathan

PG and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli, India – 620 020.

ABSTRACT

A series of 2-(substituted phenyl)azo-4,6-dipropionylresorcinol derivatives (**I-VI)** have been synthesized by keeping in mind the eco friendly, low cost and high yield reaction. 2-(substituted phenyl)azo-4,6-dipropionylresorcinols have been synthesized by diazotization of substituted aniline followed by coupling with 4,6-dipropionylresorcinol. All the synthesized compounds have been characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectral analysis. In general azo compounds can exist in azo hydrazone tautomeric forms. But in our study, all the spectral data show that 2-(substituted phenyl)azo-4,6-dipropionylresorcinol derivatives (I-VI) exist in the azo form.

KEYWORDS: azo, coupling, diazotization, dipropionyl, resorcinol, tautomerism.

INTRODUCTION

Azo compounds are organic molecules containing one or more azo groups of which the nitrogen atoms are sp^2 hybridised. The azo groups form links or bridges between organic residues of which one is usually an aromatic nucleus. The formation of diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions and azo coupling is carried out at low temperature in the presence of nucleophilic coupling components. They exist in the trans form with a bond angle of 120°.[1] The range of shades that could be obtained from azo dyes includes yellows, reds, oranges, violets, navy blues and blacks but green shades are limited.

Azo compounds 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,[2,3] anticancer,[4,5] antibacterial,[6-8] and antifungal.[9-14] Azo compounds have received much attention due to their versatile use in many practical applications such as coloring fiber.[15-17] Azo dyes show better stability than natural dyes in the whole pH range of foods, are heat stable and do not fade when exposed to light or oxygen. Because of low toxicity, less allergic reactions and no hyperactivity effect, azo dyes are used in food stuffs.

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. The reactions are generally carried out at lower temperature and the solvent mostly used is water which reduces the environmental impact. All these factors contribute to the cheap production of azo dyes. In the present work, the investigator has made an attempt to synthesise and characterize azo compounds of 4,6-dipropionylresorcinol (**I-VI**).

MATERIALS AND METHODS

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.

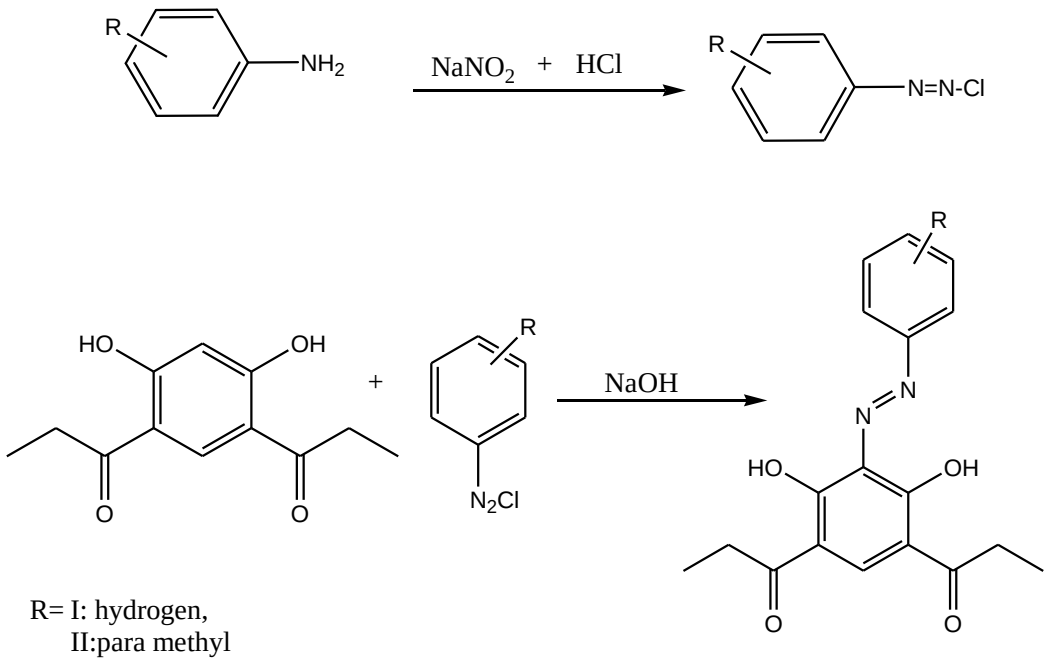
4, 6-dipropionylresorcinol

The required starting material 4,6-dipropionylresorcinol was prepared by the procedure reported in literature.[18]

To a mixture of freshly fused and powdered $ZnCl_2$ (10g) in dry propionic anhydride (14ml) 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 15 minutes. The viscous red solution was allowed to cool to room temperature. 80ml 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 4,6-dipropionylresorcinol as a colorless solid. Yield 90%, m.p. 125 ˚C.

2-(substituted phenyl)azo-4,6-dipropionyl resorcinol

Substituted aniline (0.001mol) was dissolved in 2ml HCl and to it was added 1ml of H_2O. The solution was cooled to 0-5˚C in an ice bath and maintained this temperature. Sodium nitrite (0.002mol) in water (2ml) was then added drop wise. Stirring was continued for 20 minutes to produce diazonium salt at the same temperature. To this mixture, 4,6-dipropionylresorcinol (0.001mol, 0.222g) dissolved in 10% NaOH was added drop wise with stirring at 0-5˚C. The mixture was stirred for 15 minutes (**Scheme I**). The precipitated crude azo product was collected by filtration at vacuum and recrystallised from appropriate solvent.



R= I: hydrogen,
II:para methyl
III: ortho methyl
IV:ortho carboxy
V: para carboxy
VI: para nitro

(I - VI)

Scheme I

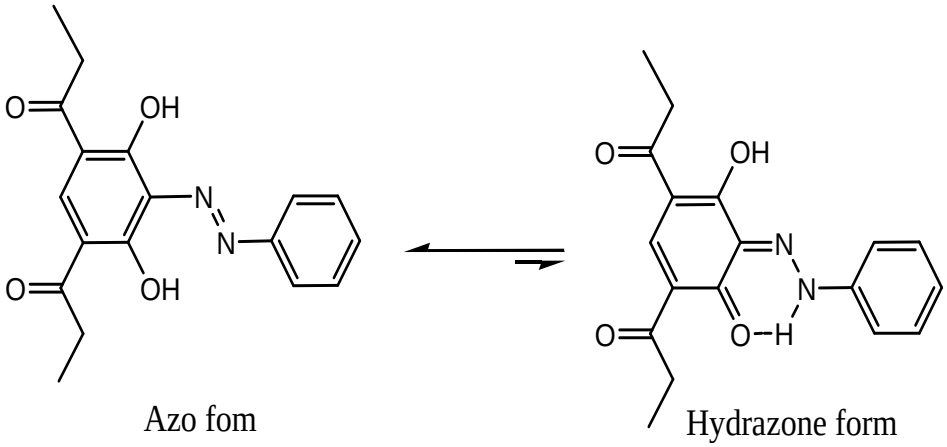
RESULTS AND DISCUSSION

As a representative case, the spectral identification of 2-phenylazo-4,6-dipropionyl resorcinol**(I)** has been discussed.

2-phenylazo-4,6-dipropionylresorcinol (I)

In IR spectrum, it shows a weak absorption band at 3444cm^{-1} indicating the presence of O–H group. The absorption peaks at 3057 cm^{-1} and 2980 cm^{-1} are due to Ar–H and CH_3 stretching vibrations, respectively. A strong absorption peak at 1676 cm^{-1} is assigned for C=O stretching vibration. This low absorption frequency for C=O is due to chelating effect between C=O and

–OH group.[19-21] The presence of N=N group is evidenced by a stretching absorption peak at 1590 cm^{-1}. Aromatic C=C stretching frequency appears at 1570cm^{-1}. Absorption peaks at 1371 cm^{-1} and 1188 cm^{-1} are due to C–N and C–O stretching vibrations respectively. In ^1H NMR, the chemical shift values at δ 1.1 and 3.1 as triplet and quadruplet, respectively are due to the presence of six protons of two methyl and four protons of two CH_2 groups of resorcinol moiety. Two doublets at δ 8.0 and 7.6 are assigned to $C_{2'}$, $_{6'}$-H and $C_{3'}$, $_{4'}$, $_{5'}$-H of phenyl moiety respectively. A singlet at δ 8.5 ppm corresponds to C_5 hydrogen of resorcinol moiety. The -OH proton appears as a broad peak at δ 14.5.[22-27] 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 6.4 of C_2 hydrogen of parent compound 4,6-dipropionylresorcinol shows that diazo group is attached at C_2 -carbon of 4,6-dipropionyl resorcinol and further confirms the product formation.



Scheme II

In general azo compounds can exist in azo-hydrazone tautomeric forms.[28-30] In compound **I,** absence of a band at N-H region of the IR spectrum shows the absence of N-H hydrazone formation and absence of N-H hydrogen peak in the ^1H NMR spectrum also shows the absence of N-H hydrazone formation. This shows that compound **I** exists in the azo form (**Scheme II)**. Similarly spectral data of all the synthesised compounds conform the azo structure for 2-(substituted phenyl)azo-4,6-dipropionylresorcinol derivatives (**II-VI**).

Table 1: Analytical data of compounds I-VI

Compound	Molecular Formula	Molecular Weight	Melting Point (˚C)	IR (KBr) (cm^{-1})		Purification Solvent
				C=O	N=N	
I	$C_{18}H_{18}N_2O_4$	326	155	1676	1590	Ethanol
II	$C_{19}H_{20}N_2O_4$	340	160	1668	1577	Methanol
III	$C_{18}H_{16}N_2O_5$	340	190	1674	1589	Ethyl acetate
IV	$C_{19}H_{18}N_2O_6$	370	217	1666	1598	Chloroform
V	$C_{19}H_{18}N_2O_6$	370	220	1660	1585	Dioxane
VI	$C_{18}H_{17}N_3O_6$	371	210	1676	1589	Ethanol

2-phenylazo-4,6-dipropionylresorcinol (I)

IR (cm^{-1}) : 3444(O-H), 3057(Ar-H), 2980 (CH_3), 1676 (C=O), 1590 (N=N), 1570 (C....C), 1371(C–N), 1188(C–O) **^{1}H NMR (δ) :** 1.1(t, 6H, 2-CH_3), 3.1 (q, 4H,2-CH_2) 7.6 (m, $C_{3', 4', 5'}$-H, 3H), 8.0 (d, $C_{2', 6'}$-H, 2H), 8.5 (s, C_5-H, 1H), 14.5(hump, –OH), **^{13}C NMR(δ):** 8.6, 34, 116, 120, 122, 130, 147, 164, 202. **Mass:** m/e 326**,** $C_{18}H_{18}N_2O_4$.

2-(4-methylphenyl)azo-4,6-dipropionylresorcinol (II)

IR (cm^{-1}) : 3452(O-H), 3070 (Ar-H), 2978 (CH_3), 1668(C=O), 1577 (N=N), 1334 (C–N), 1190(C–O) **^{1}H NMR (δ) :** 1.2(t, 6H, 2-CH_3), 3.1 (q, 4H, 2-CH_2), 3.8 (s, 3H, $C_{4'}$–CH_3), 7.1 (d, $C_{3', 5'}$ -H, 2H), 8.0 (d, $C_{2', 6'}$ -H, 2H), 8.4 (s,1H,C_5-H), 14.7(hump, –OH), **^{13}C NMR (δ)** 8.6, 34, 115, 120, 122, 130, 147, 164, 200. **Mass:** m/e 340, $C_{19}H_{20}N_2O_4$

2-(2-methylphenyl)azo-4,6-dipropionyl resorcinol (III)

IR (cm^{-1}) : 3444(O-H), 3066(Ar-H), 2980 (CH_3), 1674 (C=O), 1589(N=N), 1541 (C....C), 1375(C–N), 1193(C–O), **^{1}H NMR (δ) :** 1.2 (t, 6H, 2-CH_3), 2.6 (s, 3H, $C_{4'}$–CH_3), 3.1 (q, 4H, 2-CH_2), 7.3(m, 3H, $C_{4', 5',6}$–H), 7.9(d, 1H, $C_{3'}$–H), 8.5 (s,1H,C_5-H), 14.5(hump, –OH), **^{13}C NMR (δ) :** 8.2, 18, 34, 116, 127, 131, 146, 199. **Mass:** m/e 340, $C_{18}H_{16}N_2O_5$.

2-(4-nitrophenyl)azo-4,6-dipropionyl resorcinol (VI)

IR (cm^{-1}): 3448(O-H), 3026(Ar-H), 2981 (CH_3), 1676 (C=O), 1589(N=N), 1560 (C....C), 1373(C–N), 1186(C–O), 1546 ($NO_{2(asym)}$), 1309 ($NO_{2\ (sym)}$). **^{1}H NMR (δ) :** 1.2 (t, 6H, 2-CH_3), 3.1 (dd, 4H, 2-CH_2), 8.0(dd, 2H, $C_{2', 6'}$ –H), 8.4(q, 2H, $C_{3', 5'}$ –H), 8.6 (s,1H,C_5-H), 14.5(hump, –OH), **^{13}C NMR (δ) :** 8.2, 34, 122, 125, 127, 140, 148, 152, 200. **Mass:** m/e 371, $C_{18}H_{17}N_3O_6$.

CONCLUSION

2-(substituted phenyl)azo-4,6-dipropionylresorcinol derivatives (**I-VI)** have been synthesized and confirmed by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectral analysis. The spectral data reveal that 2-(substituted phenyl)azo-4,6-dipropionylresorcinol derivatives (I-VI) exist in the azo form.

ACKNOWLEDGEMENT

The authors are thankful to the Principal and Management Committee, Jamal Mohamed College, Trichy-20 for providing necessary facilities.

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