WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
Coden USA: WJPRAP
Impact Factor 8.453
Volume 15, Issue 3, 102-124.
Review Article
ISSN 2277–7105

COUPLING REACTIONS OF ARYLDIAZONIUM SALT. PART-XIII: CINNAOLINE PRECURSORS USING CHEMOSELECTIVE CONDENSATION OF SUBSTITUTED DIAZONIUM SALT WITH ACETYLACETONE

C. J. Patil[1]*, A. N. Dhake[1], Anil H. Shinde[2], Chunilal Pawara[3], Balsing B. Valvi[1], Lalsing R. Vasave[1], Nandu R. Vasave[1], Kalpesh S. Salve[1]

*[1]Organic Research Laboratory, Department of Chemistry, MTES’, Smt. G. G. Khadse College, Muktainagar-425 306, (MS), India.
[2]Department of Chemistry, A. S. C. College, Varangaon-425 305.
[3]CSMCRI, Gijubhai Badheka Marg, Bhavnagar-364 002.

Article Received on 05 Jan. 2026,
Article Revised on 25 Jan. 2026,
Article Published on 01 Feb. 2026,
https://doi.org/10.5281/zenodo.18426944

***Corresponding Author**
C. J. Patil
Organic Research Laboratory,
Department of Chemistry, MTES',
Smt. G. G. Khadse College,
Muktainagar-425 306, (MS), India.

How to cite this Article: C. J. Patil[1]*, A. N. Dhake[1], Anil H. Shinde[2], Chunilal Pawara[3], Balsing B. Valvi[1], Lalsing R. Vasave[1], Nandu R. Vasave[1], Kalpesh S. Salve[1] (2026). Coupling reactions of aryldiazonium salt. Part-xiii: cinnaoline precursors using chemoselective condensation of substituted diazonium salt with acetylacetone. "World Journal of Pharmaceutical Research, 15(3), 102–124.

ABSTRACT

The aryldiazonium salt, $Ar\text{-}N2^{\oplus}Cl^{\ominus}$ are highly reactive compounds. It was used as intermediate in different reactions. In this work we have synthesized the varied aryldiazonium salt and coupled with an Active Methylene Group (AMG) containing compound viz. Pentane-2,4-dione or Acetyl acetone(AA). The synthesized compounds were characterized using TLC, UV-Vis, FTIR and 1H NMR techniques to arrive at the designated structures of the products formed. The final products formed, **C-1** to **C-6**, were potentially used as precursors for synthesis of cinnoline or derivatives thereof. These compounds were tested for the antibacterial activity showed moderate activity than ciprofloxacin.

KEYWORDS: Aryldiazonium salt, Azo compound, active methylene group, antibacterial activity.

INTRODUCTION

There are many classes of compounds in organic chemistry like aldehyde, ketone, nitrile, ester, lactone, anhydride, imine and azo compounds etc. likewise aryldiazonium compounds also plays an important role in synthetic organic chemistry. The aryldiazonium salt were synthesized and reacted upon with an AMG containing compound like Pentane-2,4-dione or Acetyl acetone(AA). Heterocyclic rings,[1-2], which were the reason for the activity of Most of the drugs of natural origin leads to the discovery of the many synthetic drugs possessing the heterocyclic rings. Heterocyclic nitrogenous[3-4] compounds and their fused analogues represent an important class of heterocyclic compounds that exist in numerous natural products displaying a wide range of biological and pharmaceutical activities.

The literature was done using google web site a series of azo coupling products have been prepared by reaction of substituted benzenediazonium tetrafluoroborates with N-alkyl-4-aminopent-3-en-2-ones or 3-amino-1-phenylbut-2-en-1-ones.[5] The structure and tautomerism of the reaction products were studied by means of single-crystal X-ray study and by NMR spectroscopy in $CDCl_3$ solution. The azo coupling products obtained from 4-methylaminopent-3-en-2-ones exist in $CDCl_3$ solution as E/Z isomer mixtures with the Z isomer strongly predominating. The major isomer is a mixture of enamino–azo and imino–hydrazo tautomers The proportion of the azo form depends on substitution of the benzene ring of the diazonium salt and decreases in the order of MeO > Me > Br > NO_2. In the solid phase, the azo form always predominates; substitution of diazonium salt and at N_3 nitrogen does not significantly affect the position of the tautomeric equilibrium. The azo coupling products always exist in the form of a single Z isomer.

3-Phenylpyrazole-5-(diazonium chloride couples with α-chloro derivatives of acetylacetone, ethyl acetoacetate and aceto-o-anisidine to yield the corresponding pyrazole-5-yl hydrazonyl chloride derivatives.[6] A few compounds were cyclized to yield either the pyrazolo[1,5-c]-1,2,4-triazole derivatives or the pyrazolo[1,5-c]-as-triazines depending on the applied reaction conditions. Compounds cyclized only under different cyclization conditions. The pyrazolo[1,5-c]-as-triazine derivatives could be prepared via condensation of potassium cyanide. The 4-chloro derivative reacted with aromatic thiols and with sodium benzene-sulphonate to yield the pyrazolo[1,5-c]-as-triazine derivatives. reacted with activated double bond systems to yield pyrazolo[1,5-c]-as-triazines.

A number of diazo coupled products of chromium(III) chelates of acetylacetone and benzoylacetone were prepared by using some aryl diazonium ions. The aryl diazonium ions of 4-chloro, 4-bromo, 2,5-dimethoxy, 4-nitro and 1-naphthyl were synthesized by diazotization of respective aniline groups. The prepared diazo coupled products were characterized on the basis of their analytical data, magnetic moment, 1H NMR spectra, molar conductance, infrared and electronic spectral studies. Considering all these data, the structures of the synthesized diazo coupled products of chromium(III) were proposed to be octahedral.[7]

It was reported that the cobalt bis(acetylacetonate)[Co(acac)$_2$], tert-butyl hydroperoxide(TBHP), and triethylsilane(Et$_3$SiH) constitute an inexpensive, general, and practical reagent combination to initiate a broad range of Markovnikov-selective alkene hydro functionalization reactions.[8] Cobalt bis(acetylacetonate)–*tert*-butyl hydroperoxide–triethylsilane: a general reagent combination for the Markovnikov selective hydro functionalization of alkenes by hydrogen atom transfer These transformations are believed to proceed by cobalt-mediated hydrogen atom transfer (HAT) to the alkene substrate, followed by interception of the resulting alkyl radical intermediate with a somophile. In addition, we report the first reductive couplings of unactivated alkenes and aryldiazonium salts by an HAT pathway. The simplicity and generality of the Co(acac)$_2$–TBHP–Et$_3$SiH reagent combination suggests it as a useful starting point to develop HAT reactions in complex settings.

Aryldiazonium salts, Ar-N2⊕Cl$^{\Theta}$ were used as intermediate in different reactions. To prepare the 3-(Substituted-phenyl azo) pentane-2,4-dione from pentane-2,4-dione or AA with aryldiazonium salt and to study their antibacterial activity.[9] Here, aryldiazonium salt was treated with an Active Methylene Group containing moiety viz. pentane-2,4-dione or AA and the antibacterial activity by diffusion cup method. The final product formed has potential to use as precursor for synthesis of 4-methyl-3-acetylcinnoline or derivatives thereof. These compounds were tested for the antibacterial activity against gram negative bacteria, *E. coli*. 3-(Substituted-phenyl azo) pentane-2,4-dione, tested for the antibacterial activity showed less activity than ciprofloxacin. Diazotization of p-amino benzoic acid was carried out in presence of sodium nitrite and hydrochloric acid followed by coupling reaction with activated methylene group in presence of sodium acetate and ethanol to yield the corresponding substituted arylazo. The coupling adducts were reacted with hydrazine hydrate under reflux in ethanol in presence of tri ethyl amine to yield the pyrazalone derivatives. Also, acetylation of the coupling adducts with acetic anhydride gave only while the rest of compounds did not react. The compounds were tested against microorganisms such as gram-negative bacteria (*E-coli* and *P. salmonella*) in comparison with different antibiotics, for example Ampicillin.

The aryldiazonium salt Ar-N2⊕Cl$^{\Theta}$ are highly reactive compounds. It is used as an intermediate in the different reactions These reactions, either, losses nitrogen containing function or without loss of nitrogen function. The first category includes replacement by H,-OH,-Br,-F,-I,-CN,-NO_2, Aryl-etc. and the latter involves reduction and diazo coupling type reaction. In the present piece of work, we have coupled the aryldiazonium salt with AMG bearing moiety, b-keto ester viz. Ethyl acetoacetate (EAA). The final product formed has potential to be used in some organic reaction to prepare derivatives of benzodiazepines.[10] These compounds were tested for the antibacterial activity against *E. coli* when compared with ampicillin as a standard drug.

From our laboratory, few reactions on Schiff bases or Aldimines,[11-15] Ketimines[16-18] as well as aryldiazonium salt[9-10,19-24] are reported. In the present work the aryldiazonium salt was reacted with an AMG containing compound, Pentane-2,4-dione viz. AA. Similar to Sitosterol[25] and Cholesterol etc. Cinnolines are from the class of bioactive compounds due to their remarkable biological[26] and pharmacological property.[27] Cinnoline and its derivatives also show biological activities such as antihypertensive and analgesic[28] activity. This type of compound requires the intermediates of the type (Phenylhydrazono)-acetyl acetone or similar compounds. In view of synthesis of newer 4-Methyl-3-acetylcinnoline or derivatives thereof are of importance, their intermediates are considered worthwhile to study their synthesis. Similar type of reactions were also reported by Mittal and Singhal[29], and recently from our laboratory.[30-31] In the present work the type of ketone compounds i.e the intermediates of the type (Phenylhydrazono)-acetylacetone, its varied derivatives are synthesized (**Scheme-l**). Review of literature indicated that such ketone derivatives are valuable synthons for the synthesis of 4-Methyl-3-acetylcinnoline or derivatives thereof.

MATERIALS AND METHODS

All the chemicals and solvents were obtained from E-Merck, India and are of synthesis and the Spectroscopic grade respectively. They were used without further purification. Silica gel-G was used to monitor the progress of reactions, by TLC and visualized by iodine vapour-chamber. The color observed was recorded by visual method and melting point range was taken in an one end open capillary tube. The purity of the compounds was ascertained by melting point range determination (in one end open capillary method), and by Silica gel-G TLC. The UV-Vis spectra were recorded on Shimadzu-1800 instrument Quartz cuvette of path length 1 cm was used for measurements in solution. The FTIR spectra were recorded on a Shimadzu FTIR 8400 spectrophotometer (Model-IRAffinity-1) using samples mixed in powder form with KBr powder, the frequency values, υ, are in cm^{-1}. The overall purity and structural assignment of the products was based respectively on the elemental (CHN) analyses, TLC and UV-Vis, FTIR spectral data. The biological strain used was gram negative (*E. Coli*, NCIM 2065) and compared with the standard drug, Ciprofloxacin.

Stage-I. General Procedure for Preparation of Diazonium Salt, B-1 to B-6

Charge 0.02 M aniline (or its derivative) in a beaker Add to it mixture of 10 ml con. HCl and 5 ml water and stir with the glass rod to get a clear solution, cool the solution to 0°C by keeping in an ice bath. Meanwhile dissolve (0.025 M) sodium nitrite in 8 ml water. Cool the solution in ice bath to 0°C, after attaining 0°C add $NaNO_2$ solution in to aniline hydrochloride solution drop wise with constant stirring (Do not allow to rise temperature above 5°C during addition) test the diazotized solution impart dark blue colour to starch iodide paper(blue colour is obtained on the potassium-iodide starch paper). Decompose the excess of nitrous acid by adding a pinch of urea, filter the solution and collect the filtrate which is diazonium salt solution.

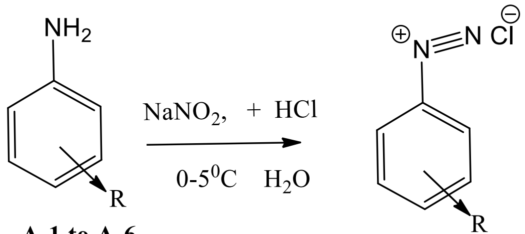
Stage-II. General Procedure for Synthesis of (Phenylhydrazono)-acetylacetone, C-1 to C-6

Add aryldiazonium salt solution (from **Stage-I**) slowly, to the well cooled mixture of, Pentane-2,4-dione viz. Acetyl acetone(AA) (0.018 M) dissolved in 5 ml ethanol and NaOAc, 8-10 gm in 4-5 ml of water(to keep the mixture alkaline to litmus), a coloured precipitate is separated, then add 20 ml of con. HCl then filters and checks the absence of ester and thus the product obtained is recrystallized by using solvent ethanol, dry it. Record the dried weight (in gms) and the physical constant i.e. m. p. range of the compound.

The synthesized compounds were tested for the antibacterial activity against *E. coli* as per the method described in literature and compared with ampicillin as standard drug.

Scheme of Present Work

Scheme-I: Formation of diazonium salt



A-1 to A-6

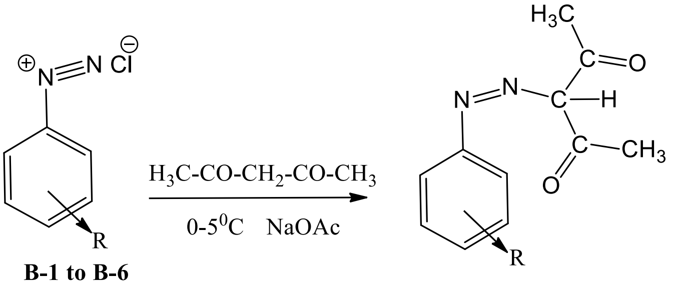
Substituted-aniline

B-1 to B-6

Substituted-phenyldiazonium chloride

where R- = 1) 2-F; 2) 4-F; 3) 3-Cl; 4) 4-Cl; 5) 3-OCH_3 6) 2-C_2H_5

Scheme-II: Chemoselective condensation of diazonium salt with Acetylacetone



B-1 to B-6

Substituted-phenyldiazonium chloride

C-1 to C-6

(*Z*)-3-(Substituted-phenyldiazenyl) pentane-2,4-dione

where R- = 1) 2-F; 2) 4-F; 3) 3-Cl; 4) 4-Cl; 5) 3-OCH_3; 6) 2-C_2H_5

RESULTS AND DISCUSSION

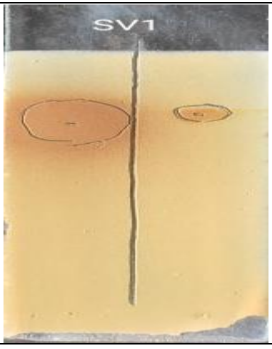
In the present study, diazonium intermediates of aniline and substituted anilines are synthesized, reacted with active methylene compound(acetyl acetone) and screened for antibacterial activity. All the compounds were obtained in high purity. The progress of reactions was monitored by Silica gel-G TLC, visualized by iodine vapour. The purity of the compounds was ascertained by melting point determinations (open capillary method), and by Silica gel-G TLC. The structural assignment of the products was based on UV-Vis and FTIR spectral data and elemental (CHN) analyses. The spectral data are in clos agreement with the structures of the synthesized compounds. All compounds gave satisfactory elemental analysis. Values are in close agreement with the values calculated for expected molecular formulae assigned to these compounds and are in 5 % in statistics.

The data showing results of synthesis study and their analytical details such as colour and physical constants etc. are depicted in the **Table 1**. Thin layer chromatography indicates the preparation of the final intermediates, compared with the starting raw material. Thus, the synthesized compounds viz. (Phenylhydrazono)-acetylacetone, or derivatives thereof, are synthesized and are now available for further use.

Table 1: Physical & analytical data for the azo compounds, 3-(Substituted-phenyldiazenyl) pentane-2, 4-dione, C-1 to C-6.

Sr No	Name of the Product, ID	Aniline used	Mol. Wt. of Aniline used	Product Mol. Wt.	Colour	Product wt, gm	m. p. ^{o}C	% Yield
1	**C-1**	2-Fluroaniline	111.12	222.2156	Brown	5.85	140	86.95
2	**C-2**	4-Fluroaniline	111.12	222.2156	Yellow	1.90	160	42.80
3	**C-3**	3-Chloroaniline	127.57	238.6702	Yellow	1.86	103	25.98
4	**C-4**	4-Chloroaniline	127.57	238.6702	Brown Dark	2.90	125	60.79
5	**C-5**	2-Anisidine	123.15	234.2512	Brown	1.51	175	32.27
6	**C-6**	2-Ethyl aniline	121.18	232.2783	Brown Red	4.70	> 250	67.46

Table-2: The TLC photograph and respective data for the 3-(Substituted-phenyldiazenyl) pentane-2, 4-dione, C-1 to C-6.

Sr. No	Aniline Used	Name of the Product, ID	TLC* of the amine with Product	Solvent Front	Dist. Travelled by aniline Spot	Dist. Travelled by Product Spot	R_f value	
							Aniline	Product
1	**2-Fluroaniline**	**C-1**		**4.5**	**3.1**	**3.5**	**0.68**	**0.77**

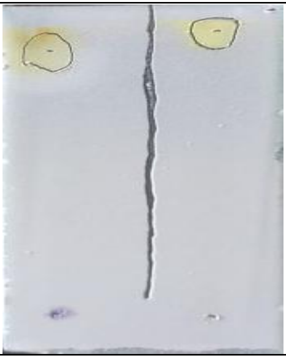
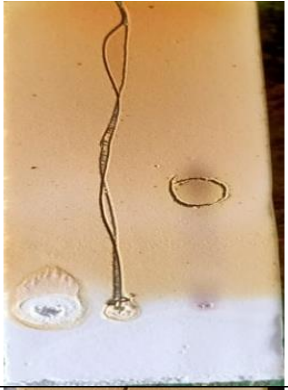
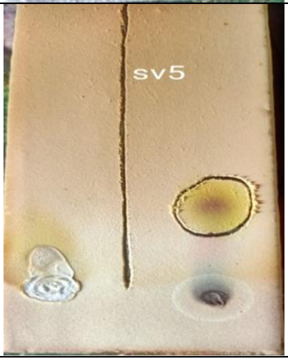
2	**4-Fluroaniline**	**C-2**		**4.9**	**4.1**	**4.5**	**0.83**	**0.91**
3	**3-Chloroaniline**	**C-3**		**4.1**	**2.5**	**3.8**	**0.60**	**0.92**
4	**4-Chloroaniline**	**C-4**		**4.6**	**0.4**	**2**	**0.09**	**0.43**
5	**2-Anisidine**	**C-5**		**3.6**	**0.5**	**1.4**	**0.14**	**0. 34**
6	**2-Ethyl aniline**	**C-5**		**4.2**	**1.2**	**1.4**	**0.30**	**0.33**

Table 3: Photographic representation of the Recrystallized Products, 3-(Substituted-phenyldiazenyl) pentane-2, 4-dione C-1 to C-6.

Sr.No	Aniline used	Product Name and ID	Method for purification	Pure product
1	2-Fluroaniline	C-1	Recrystallization using ethanol	
2	4-Fluoroaniline	C-2	Recrystallization using ethanol	
3	3-Chloroaniline	C-3	Recrystallization using ethanol	
4	4-Chloroaniline	C-4	Recrystallization using ethanol	
5	2-Anisidine	C-5	Recrystallization using ethanol	

6	**2-Ethyl aniline**	**C-6**	**Recrystallization using ethanol**	

Thus, the ketonic compounds viz. (Aryldiazenyl)pentane-2,4–dione and its varied derivatives are prepared and characterized by TLC, physical constant and FTIR spectra and are now available for further use. The UV and Visible absorption of the compounds under investigation display mainly three bands observed in ethanol within the range 200-500 nm. The UV-Vis spectral data for the compounds, **C-1** to **C-5** is depicted in **Table 5** collected from **Fig 1** to **Fig 6.**

Table 4: The Characteristic UV Spectral data of the synthesized compounds, C-1 to C-5 (Concentration = 4.0 mg/ml).

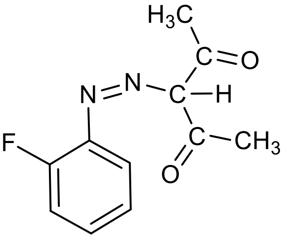
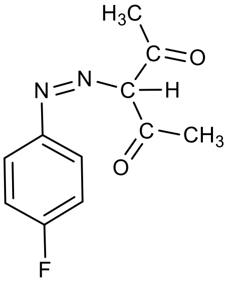
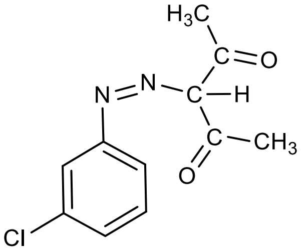
Sr. No.	**Product Name and ID**	**Full Name of Compound**	**UV max**	**Absorbance**	**Molar Absorptivity (€)**
1	**C-1**	(2–Fluorophenyl)diazenyl)pentane-2,4–dione	359.50	2.808	0.702 x 10^4
			240.50	1.829	0.457 x 10^4
			290.50	0.256	0.064 x 10^4
			204.00	0.623	0.156 x 10^4
2	**C-2**	(4–Fluorophenyl)diazenyl)pentane-2,4–dione	364.40	2.112	0.528 x 10^4
			362.40	2.114	0.529 x 10^4
			243.20	1.112	0.278 x 10^4
			201.60	0.706	0.528 x 10^4
			194.00	0.607	0.152 x 10^4
3	**C-3**	(3-Chlorophenyl)diazenyl)pentane-2,4-dione	361.60	1.797	0.449 x 10^4
			246.40	1.109	0.277 x 10^4
			203.80	1.472	0.368 x 10^4
			223.80	0.431	0.108 x 10^4
4	**C-4**	(4–Chlorophenyl)diazenyl)pentane-2,4–dione	368.40	1.886	0.472 x 10^4
			364.60	1.908	0.477 x 10^4
			244.60	1.097	0.274 x 10^4
			203.40	0.804	0.201 x 10^4
5	**C-5**	(2-Methoxyphenyl)diazenyl)pentane-2,4–dione	395.20	1.966	0.492 x 10^4
			249.80	1.116	0.279 x 10^4
			228.60	0.612	0.153 x 10^4
			204.80	1.662	0.416 x 10^4

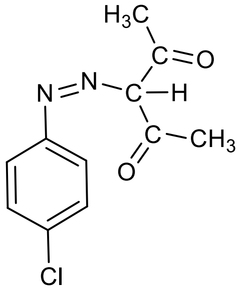
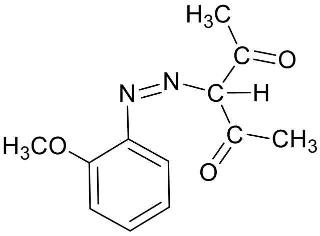
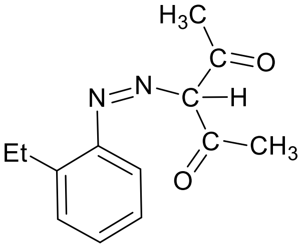
Energy transition of the aromatic ring, while the second shoulder peak band was observed in the range 310-320 nm(shoulder peak) and the third long wavelength band in the range 450-

530 nm was assigned to the transition of azo group and the overall effect of methoxy and chloro auxochromes, in analogy to the case of simple azo compound.

The FITR spectra of the synthesized final products are depicted below in Fig. **C-1 to C-6**. The related data of FTIR characteristic frequency (in cm^{-1}) of the groups indicated in **Table 5** collected from **Fig 6** to **Fig 10**.

Table 5: The Characteristic FTIR Spectral data of the synthesized compounds C-1 to **C-6.**

Sr. No.	**Product Name and ID**	**FTIR Frequencies in (cm^{-1})**	**Structure of Compound and Name**
1	**C-1**	$V_{-C=O} = 1612$ $V_{-C-N} = 1308$ $V_{-C-F} = 1410$ $V_{-N=N} = 1354$ $V_{-C-H} = 3037$ $V_{-C-CH3} = 1469$	 (2–Fluorophenyl)diazenyl)pentane-2,4–dione
2	**C-2**	$V_{-C=O} = 1667$ $V_{-C-N} = 1312$ $V_{-C-F} = 1404$ $V_{-N=N} = 1358$ $V_{-C-H} = 3011$ $V_{-C-CH3} = 1431$	 (4–Fluorophenyl)diazenyl)pentane-2,4–dione
3	**C-3**	$V_{-C=O} = 1640$ $V_{-C-N} = 1359$ $V_{-C-Cl} = 770$ $V_{-N=N} = 1359$ $V_{-C-H} = 3077$ $V_{-C-CH3} = 1446$	 (3 – Chlorophenyl) diazenyl) pentane 2,4 – dione

4	C-4	$V_{\text{-C=O}}$ = 1663 $V_{\text{-C-N}}$ = 1353 $V_{\text{-C-Cl}}$ = 773 $V_{\text{-N=N}}$ = 1353 $V_{\text{-C-H}}$ = 3059 $V_{\text{-C-CH3}}$ = 1437	 (4–Chlorophenyl)diazenyl)pentane2,4–dione
5	C-5	$V_{\text{-C=O}}$ = 1663 $V_{\text{-C-N}}$ = 1354 $V_{\text{-C-CH3O}}$ = 1251 $V_{\text{-N=N}}$ = 1354 $V_{\text{-C-H}}$ = 3002 $V_{\text{-C-CH3}}$ = 1440	 (2-Methoxyphenyl)diazenyl)pentane2,4–dione
6	C-6	$V_{\text{-C=O}}$ = 1748 $V_{\text{-C-N}}$ = 1335 $V_{\text{-N=N}}$ = 1393	 (2-Ethylphenyl) diazenyl)pentane2,4–dione

These structures of were confirmed by elemental analysis and IR spectra showing an absorption band at 1616-1645 cm^{-1} (C=N), 2879-3095 cm^{-1} (C-H of Ar.), 2779-2875 cm^{-1} (-OCH_2), 2931-2945, 1367-1391 cm^{-1} (-CH_3,-CH_2-), 1645-1703 cm^{-1} (>C=O). The synthesized compounds were tested for the antimicrobial activity in order to determine their potential application in microbial chemotherapy. The antimicrobial result indicated that all the synthesized compounds found moderately active against *E. coli* in comparison with ciprofloxacin, as standard antibacterial agents.

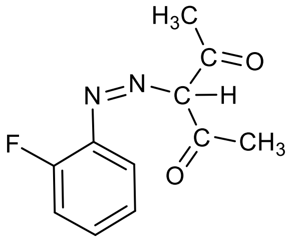
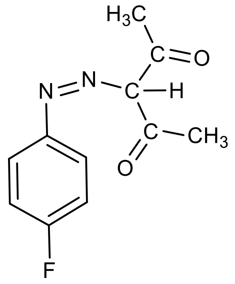
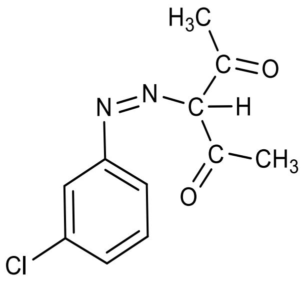
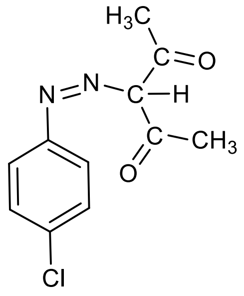
Table 6: The Characteristic 1H NMR Spectral data of the synthesized compounds, C-1 to C-5.

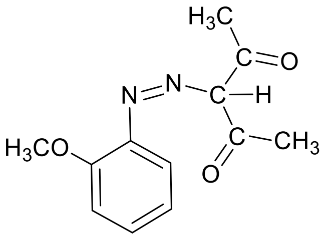
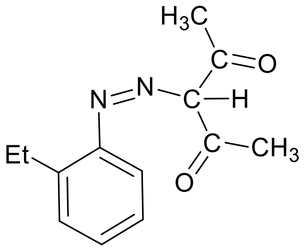
Sr. No.	Product Name and ID	Full Name of Compound	δ Values in ppm			
			Ar-H	CH_3 from Acetyl-	Central Proton of Acetylacetone part of molecule	Misc protons
1	C-1	(2–Fluorophenyl) diazenyl)pentane-2,4–dione	7.13-7.79	2.51-2.62	14.71	--
2	C-2	(4–Fluorophenyl)	7.10-	2.49-	14.81	--

		diazenyl)pentane-2,4-dione	7.41	2.61		
3	**C-3**	(3-Chlorophenyl) diazenyl)pentane-2,4–dione	7.18-7.46	2.51-2.62	14.61	--
4	**C-4**	(4-Chlorophenyl) diazenyl)pentane-2,4-dione	7.27-7.40	2.50-2.62	14.62	--
5	**C-5**	(2-Methoxyphenyl) diazenyl)pentane-2,4-dione	7.22-7.48	2.51-2.62	14.72	H from MeO-3.82

The synthesized Azo derivatives of acetylacetone product, **C-1** to **C-5**, were screened by ^{1}H NMR, to know about newly formed compounds and the respective protons. These spectra are respectively depicted in **Fig 11** to **Fig 15.** The chemical shifts, δ values are given in **Table 6** and the respective protons are assigned in the structure of **C-1** to **C-5**.

From the 1H NMR in $CDCl_3$ solvent with TMS as internal standard, the spectrum of the ligand exhibits signals at δ = (2.13) ppm belong to proton of methyl groups ($-CH_3$) of acetyl, the phenyl multiples at δ = 7.22-7.75 ppm is endorsed for aromatic protons, the peaks at δ = (1.7) ppm is belong to central protons of the acetylacetone part of molecule, (>C-H) (3.2). From all above analysis and the spectral data one arrives on the following structures of the product synthesized in the work….

 (2–Fluorophenyl)diazenyl)pentane-2,4–dione	 (4–Fluorophenyl)diazenyl)pentane-2,4–dione
C-1	C-2
 (3–Chlorophenyl)diazenyl)pentane2,4–dione	 (4–Chlorophenyl)diazenyl)pentane2,4–dione
C-3	C-4

 (2-Methoxyphenyl)diazenyl)pentane2,4–dione	 (2-Ethylphenyl)diazenyl)pentane2,4–dione
C-5	C-6

The UV-Vis Spectra for the Synthesized Substituted azo compounds, **C-1** to **C-5** are as depicted in **Fig 1** to **Fig 5** below

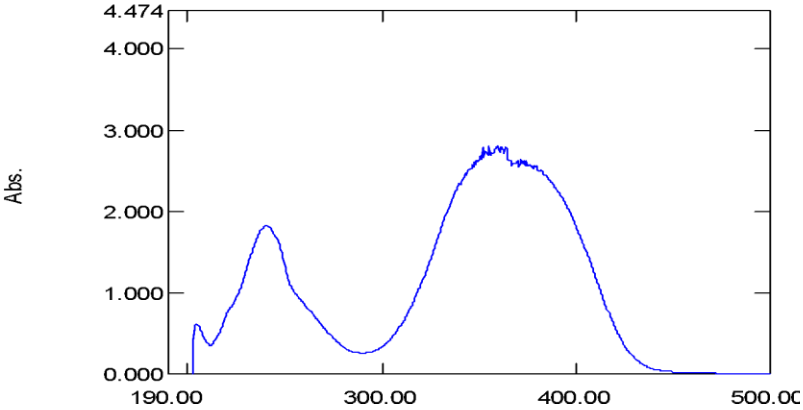


Fig. 1: UV-Vis Spectra of (2–Fluorophenyl)diazenyl)pentane-2,4–dione, C-1.

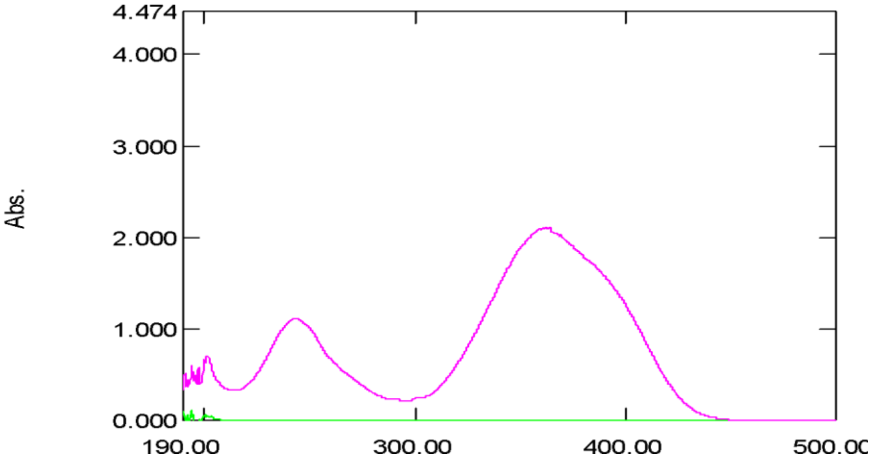


Fig. 2: UV-Vis Spectra of (4–Fluorophenyl)diazenyl)pentane-2,4–dione, C-2.

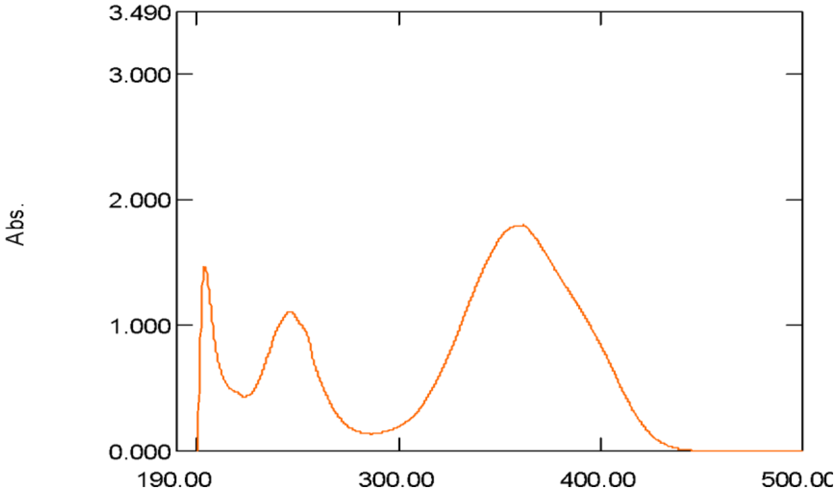


Fig. 3: UV-Vis Spectra of (3–Chlorophenyl)diazenyl)pentane2,4–dione, C-3.

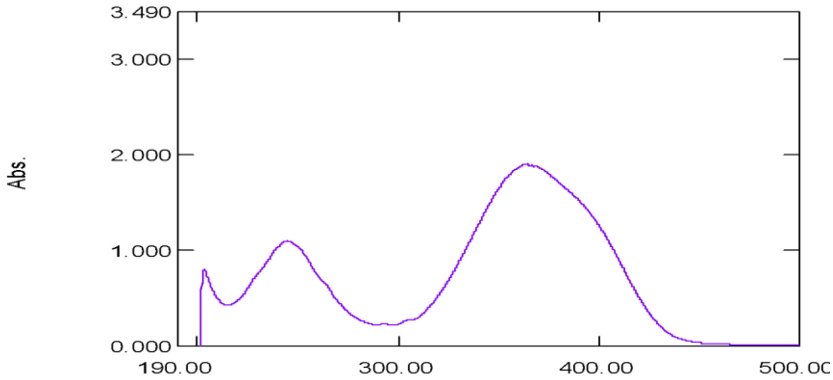


Fig. 4: UV-Vis Spectra of (4–Chlorophenyl)diazenyl)pentane2,4–dione, C-4.

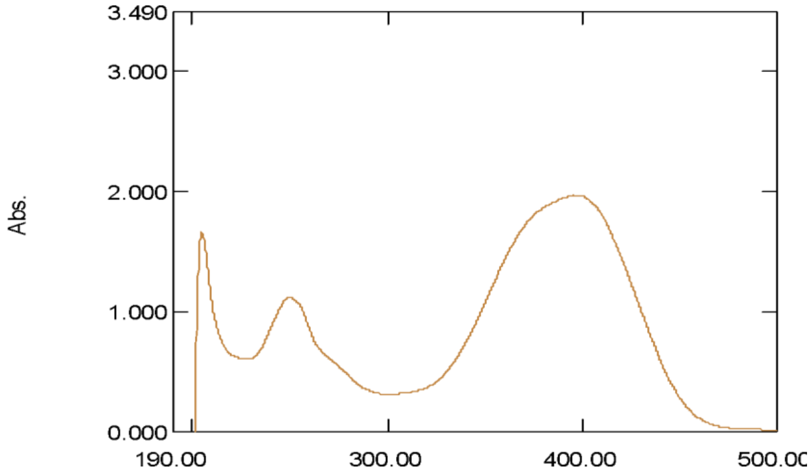


Fig. 5: UV-Vis Spectra of (2-Methoxyphenyl)diazenyl)pentane2,4–dione, C-5.

The FTIR Spectra for the Synthesized Substituted azo compounds, **C-1** to **C-5** are as depicted in **Fig 6** to **Fig 10** below

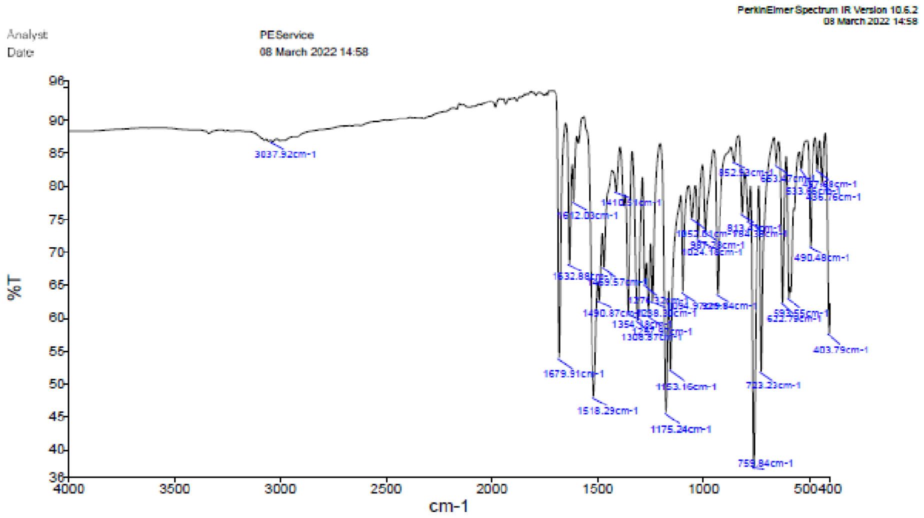


Fig. 6: FTIR Spectra of (2–Fluorophenyl)diazenyl)pentane-2,4–dione, C-1.

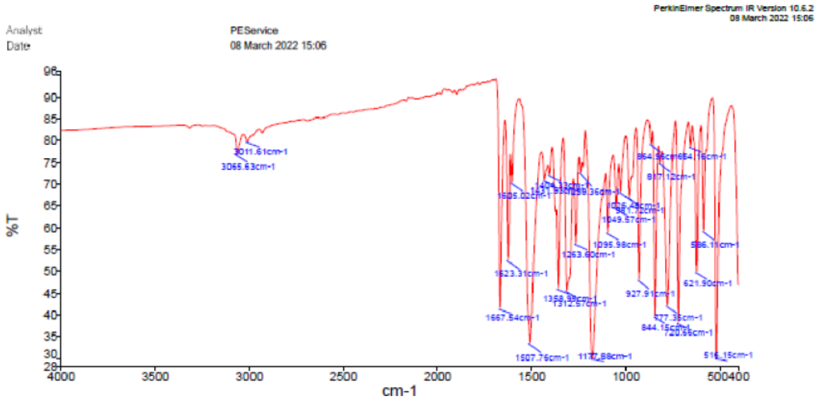


Fig. 7: FTIR Spectra of (4–Fluorophenyl)diazenyl)pentane-2,4–dione, C-2.

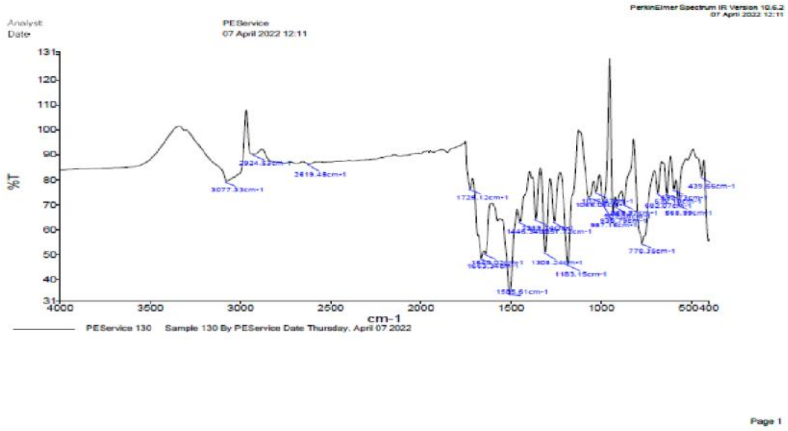


Fig. 8: FTIR Spectra of (3–Chlorophenyl)diazenyl)pentane2,4–dione, C-3.

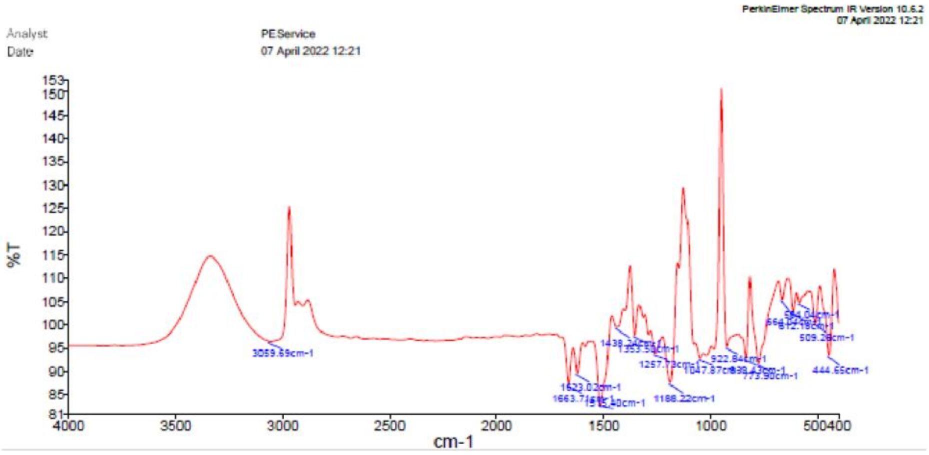


Fig. 9: FTIR Spectra of (4–Chlorophenyl)diazenyl)pentane2,4–dione, C-4.

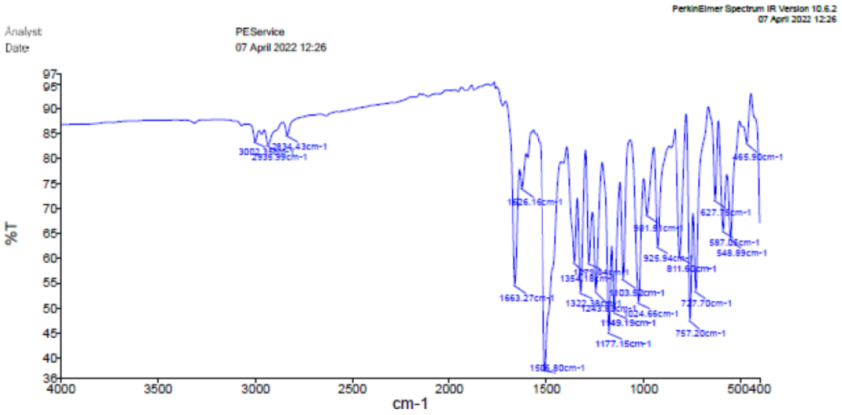


Fig. 10: FTIR Spectra of (2-Methoxyphenyl)diazenyl)pentane2,4–dione, C-5.

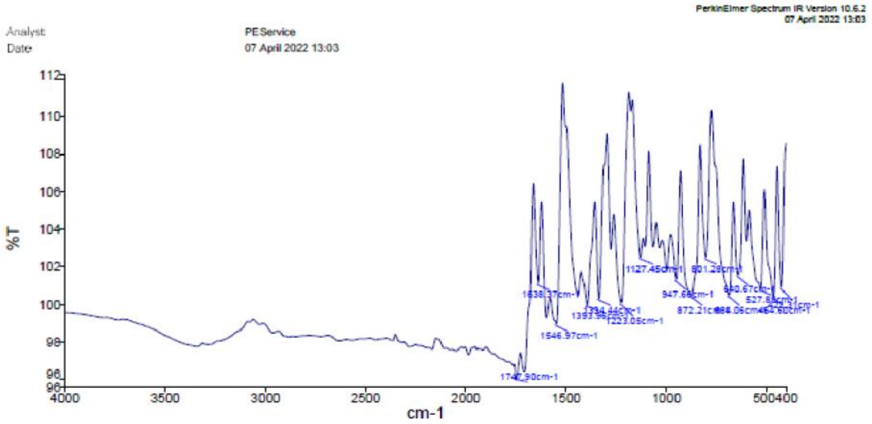


Fig. 11: FTIR Spectra of (2-Ethylphenyl)diazenyl)pentane2,4–dione, C-6.

The 1H NMR Spectra for the Synthesized Substituted azo compounds, **C-1** to **C-5** are as depicted in **Fig 12** to **Fig 16** below

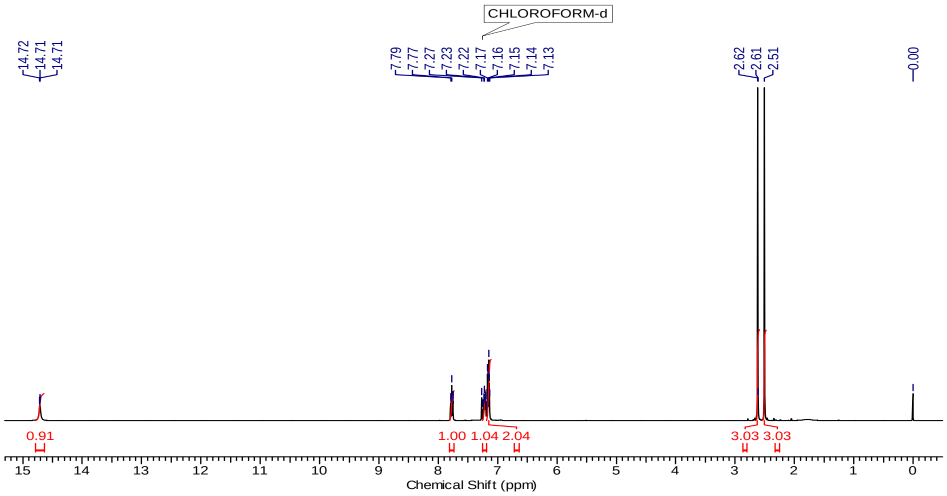


Fig. 12: NMR Spectra of (2–Fluorophenyl)diazenyl)pentane-2,4–dione, C-1.

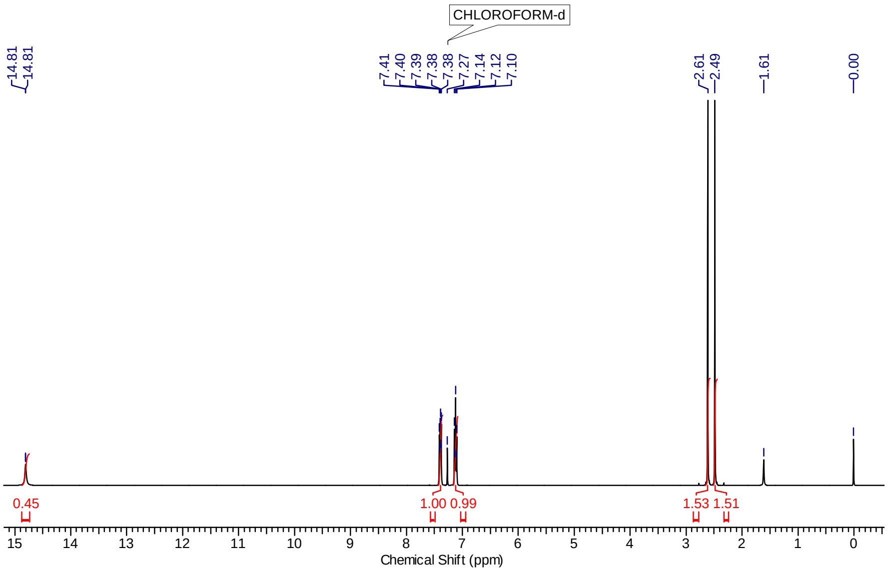
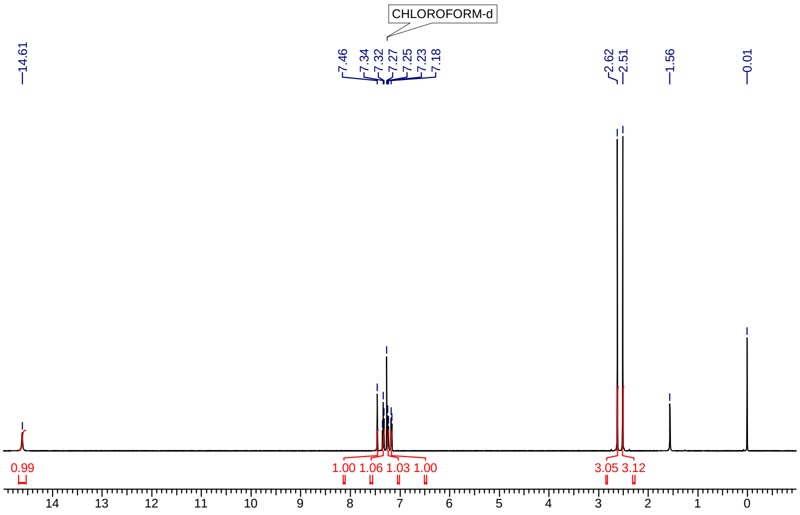


Fig. 13: NMR Spectra of (4 – Fluorophenyl)diazenyl)pentane-2,4–dione, C-2.



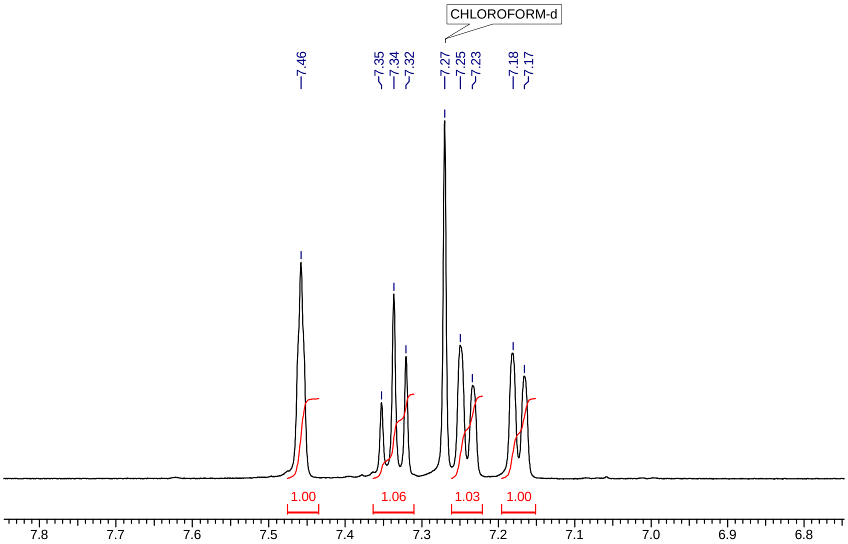


Fig. 14: NMR Spectra of (3 – Chlorophenyl)diazenyl)pentane2,4–dione, C-3.

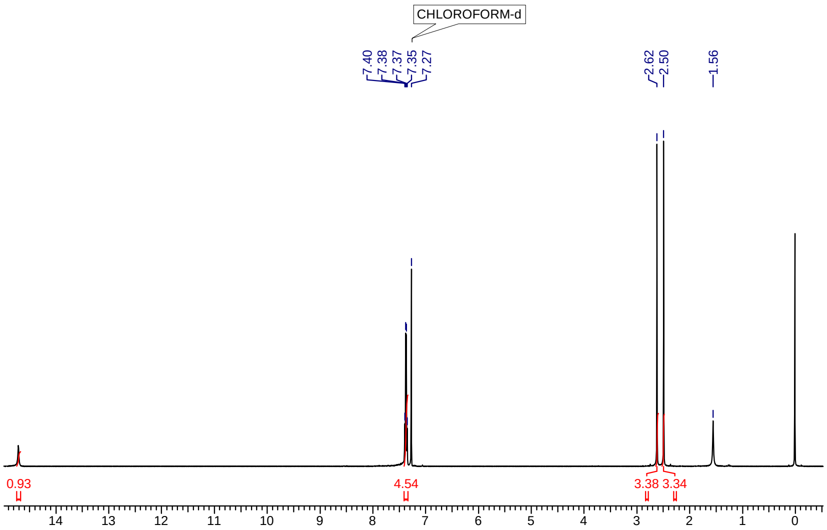
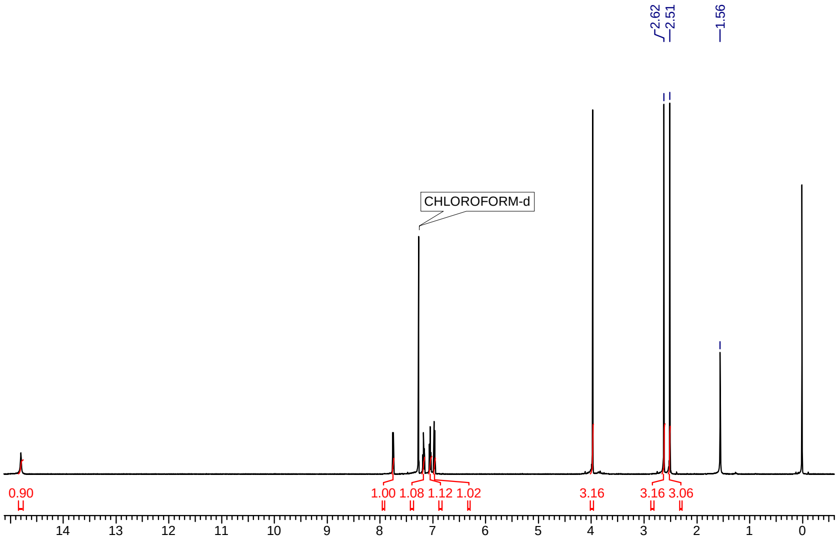


Fig. 15: NMR Spectra of (4–Chlorophenyl)diazenyl)pentane2,4–dione, C-4.



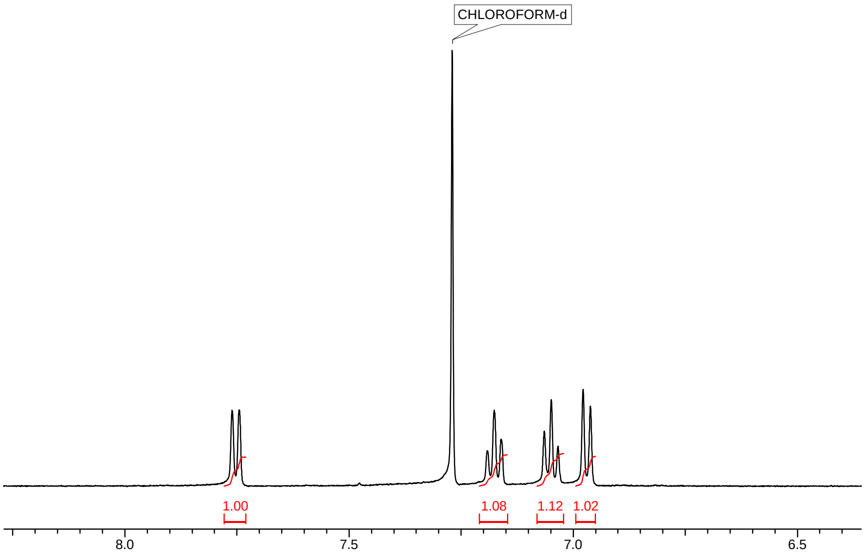


Fig. 16: NMR Spectra of (2-Methoxyphenyl)diazenyl)pentane2,4–dione, C-5.

CONCLUSION

In summary, we have used a more convenient method for synthesis of azo-acetylacetone by using a catalyst. The main advantage of this procedure is simple and convenient. The synthesized azo-acetylacetone from diazonium salt of varied anilines, directly or indirectly, may serve as a building block.

Aniline and substituted anilines are used for the preparation of diazoninium salt then they are reacted upon with Acetyl acetone to give (Substitutedphenyl-diazenyl)pentane-2,4–dione, derivatives thereof like cinnaolines heterocycle. These compounds will be useful as building blocks for organic researchers in the near future.

ACKNOWLEDGEMENTS

The authors are thankful to Chairman, The Muktainagar Taluka Education Society, Muktainagar for continuous encouragement and appreciation of our work and Principal, Smt. G. G. Khadse College, Muktainagar for providing laboratory facilities.

PERSONAL IDENTITY

Google Scholar: C. J. Patil; ORCID ID: orcid.org/0000-00027535-698X; Researcher ID: G-6274-2015; Scopus ID: 56810689600, Google Scholar: A. N. Dhake; ORCID ID: orcid.org/0000-0001-5993-1676. Google Scholar: Anil H. Shinde.

REFERENCES

1. a) A. R. Katritzky, W. R. Charles, Comprehensive Heterocyclic Chemistry, 1990, 3, 22, Trend in Heterocyclic Chemistry, 248; b) A. R. Katritzky, Chairman of the Editorial

Board, W. R. Charles, FRS Co Chairman of the Editorial Board, FRS, Comprehensive Heterocyclic Chemistry the Structure Reaction Synthesis & Use of Heterocyclic Compounds Vol-3 (Pergamon Press) UK, p. 2.

2. P. Matyus, K. Czako, Trend in Heterocyclic Chemistry, 1993; 2(3): 249.
3. M. Tisler and B. Stanovic, In: A. R. Katritzky and A. J. Boulton (Ed.), Advance in Heterocyclic Chemistry, (Academic Press, 1979): 408.
4. A. Stanczak, W. Pakulska, B. Pietrzak and W. Lewgowd, Die Pharmazie, 2001, 56(6): 501-505, Comparison of pharmacophore cinnoline and quinoline systems on the basis of computer calculation and pharmacological screening of their condensed systems.
5. P. Šimůnek, M. Svobodová, V. Bertolasi, L. Pretto, A. Lyčka and V. Macháčeka, New J. Chem., 2007; 31: 429-438, doi: 10.1039/B613346, Structure and tautomerism of azo coupling products from N-alkylenaminones derived from acetylacetone and benzoylacetone in solid phase and in solution.)
6. H. Elnagdi, R. H. Elmoghayar, E. M. Kandeel and M. K. A. Ibrahim, J. Heterocyc. Chem., 14(2): 227-230, doi: 10.1002/jhet.5570140212, Reactions with heterocyclic diazonium salts: New routes for the synthesis of pyrazolo[1,5-c]-1,2,4-triazoles and pyrazolo[1,5-c]-as-triazines.
7. A. K. L. Rahman, M. B. Hossain, M. A. Halim, D. A. Chowdhury and M. A. Salam, Afr. J. Pure Appl. Chem., 2010, 4(10): 216-220, doi: 10.5897/AJPAC.9000141, Article Number: 1283D732326, Studies on some diazo coupled products of chromium(III) chelates of acetylacetone and benzoylacetone.
8. X. Ma and S. B. Herzon, Beilstein J. Org. Chem., 2018; 14: 2259–2265, doi: 10.3762/bjoc.14.201, Cobalt bis(acetylacetonate)–tert-butyl hydroperoxide–triethylsilane: a general reagent combination for the Markovnikov selective hydro functionalization of alkenes by hydrogen atom transfer.
9. C. J. Patil, Dipak S. Talele, Satyajit P. Talele, Pradnya R. Pohekar, Ankur S. Patil, Int. J. Pharm. Sci. Rev. Res., 2017; 45(1): Article No. 13, 64-73, Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-IV. Chemoselective Synthesis and Antibacterial Activity of 3-(Substituted-phenylazo)-pentane-2,4-diones.
10. C. J. Patil, Pooja A. Patil, Pravin B. Patil and Manisha C. Patil, Der Chemica Sinica, 2015; 6(5): 108-114, Coupling reactions involving aryldiazonium salt: Part-I. Chemoselective condensation to synthesize 2-(phenylhydrazono)-3-oxo-butyricacid ethylester, its derivatives and their antibacterial activity.

11. C. J. Patil, C. A. Nehete and H. A. Mahajan, Int J Green and Herbal Chem, 2013, 2(2), 241-246. Azomethines and Biological Screening: Part-1. An approach towards green sustainable chemistry by environmental friendly grindstone method compared with conventional method and screening of the Benzylideneanilines.
12. C. J. Patil, Manisha C. Patil, Mrunmayee C. Patil and Sanjivani N. Patil, J. Chem. Biol Phy. Sci., 2015; 6(1): 220-227, Azomethines and Biological Screening: Part-2. Evaluation of Biological Properties of Schiff Bases from 2-Aminobenzothiazoles and 4-Chlorobenzaldehyde.
13. C. J. Patil, Manisha C. Patil and Mrunmayee C. Patil, Rec. Res. Sci. Tech., 2018; 10: 23-27, DOI:10.25081/rrst.2018.10.3489, Studies on Synthesis of Aldimines: Part-I. Synthesis, Characterization and Biological Activity of Aldimines from Benzaldehyde with variedly substituted Anilines.
14. S. S. Kolate, G. P. Waghulde, C. J. Patil, C. H Sarode, V. S. Waghulde, N. K Patil, S. P. Chaudhari and P. J. Patil, Int. Multidisc. E- Res. J., Special Issue, Rec. Trends Chem. Environ., 2017, UGC Approved No. 40705 & 44117, 49-54, Studies on Synthesis of Aldimines: Part-IV. Synthesis, Spectral Characterization and Biological Activity of Salicylideneaniline Derivatives.
15. C. J. Patil, A. S. Madhava, G. Ramachandriah and D. N. Vyas, Bull. Electrochem., 1993; 9(2&3): 95 - 98, ISSN: 0256-1654, Electrochemical Studies of Schiff Bases: Part-2. Voltammetric Studies of Schiff Bases.
16. C. J. Patil, M. C. Patil, RG Mahale, Der Pharma Chemica, 2016; 8(1): 99-103, Studies on Aromatic Ketimines from Methyl-1-Naphthyl Ketone: Part-II. Synthesis & characterization of ketimines from 1-acetyl naphthalene with derivatives of aniline.
17. C. J. Patil, Manisha C. Patil and Mrunmayee C. Patil, Acta Velit, 2017; 3(3): 52-59, Studies on Synthesis of Aromatic Schiff Bases: Part-II. Synthesis, Characterization and Biological Evaluation of Ketimines from Benzophenone with Substituted-anilines
18. H. A. Mahajan, C. J. Patil and G. P. Waghulde, Asian J. Chem. Envir. Res., 2012; 5(1 - 2): 15 - 19, ISSN No.- 0974-3049, Kinetic Study of Oxidation of Schiff Bases. Part-I: 5-Chloro-2-hydroxy-4-methyl acetophenone anil by Ce+4 in aq. Sulphuric acid.
19. C. J. Patil, Dipak S. Talele, Satyajit P. Talele, Pradnya R. Pohekar and D. S. Kolhe, J. Pharm. Sci. & Res., 2019; 11(6): 2213-2219, Coupling Reactions Involving Aryldiazonium Salt: Part-VII. Products of Chemoselective Reaction of Aryldiazonium Chloride with Active Methylene Group containing Moiety.

20. C. J. Patil, Manisha C. Patil, Nilesh R. Pachpole and Vilas S. Waykole, Der Chemica Sinica, 2015; 6(5): 115-121, Coupling reactions involving aryldiazonium salt: Part-II. Chemoselective condensation with acetyl acetone and antibacterial activity.
21. C. J. Patil and Sujay V. Rajput, Int. J. Rec. Sci. Res., 2019; 10(4-G): 32144-156, 10.24327/ijrsr.2019.1004.3105, Coupling Reactions Involving Aryldiazonium Salt: Part-IX. Review on Synthesis of Azo-Phenolic derivatives, their Applications and Biological activities.
22. A. H. Shinde, C. J. Patil, Asian Journal of Chemistry, 2020; 32(6): 1520-1524, Study on Azo-aldehyde: Part-II. Synthesis and Characterization of Azo Schiff Bases and their β-Lactam Derivatives.
23. C. A. Nehete and C. J. Patil, Int. J. Pharma Biol. Arch., 2015; 8(1): 20 - 26, Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-V. Synthesis of Novel Azo-Aniline with Different Substituted Anilines and study of their Biological Activity.
24. A. H. Gheath, O. O. El-Abedy, N. M. Alarafi, Hind Elzletni, ISSN(Online) : 2347-2995, J. Res. Pharmaceut. Sci., 2016; 3(03): 10-19, Coupling of PABA Diazonium Chloride with Active Methylenes and Their Microbial Evaluations.
25. M. C. Patil, C. J. Patil and R. T. Mahajan, Int. J. Pharmacogn. Phytochem. Res., 2018; 10(8): 309-316, Phytochemical Investigation and Validation of Antioxidant Potential of Beta-Sitosterol from Tubers of *Eulophia Herbacea* and *Eulophia Ochreata*.
26. W. Lewgowd and A. Stanczak, Arch. Pharm., 2007; 340: 65–80, doi: 10.1002/ardp.200500194, Cinnoline derivatives with biological activity.
27. A. M. Amer, A. F. El-Farargy, N. M. Yousif and A. A. Fayed, Synthesis and pharmacological activities of some dibenzopyrazolocinnolines and dibenzopyridazoquinoxalines. Chem. Heterocycl. Compd., 2011; 47: 101–107. doi: 10.1007/s10593-011-0726-z.
28. M. F. Zayed, Chem Engin., 2022; 6(6): 94, doi: 10.3390/chemengineering6060094, Medicinal Chemistry of Quinazolines as Analgesic and Anti-Inflammatory Agents.
29. A. K. Mittal and O. P. Singhal, J. Ind. Chem. Soc, 1982, 59, 711-712, Synthesis of Some New 1-Phenyl-3-methyl/phenyl-4-(o/m/p-substituted benzeneazo)-5-pyrazolones, 1-Phenyl-3-(o/m/p-substituted anilic)-5-pyrazolones and 3-Methyl/phenyl-4-(o/m/p-substituted benzeneazo)-5-isoxazolones as Possible Biological Agents.
30. A. N. Dhake, C. J. Patil and G. R. Chaudhari, Heterocyc. Lett., 2022; 12(2): 415-443, Coupling Reactions of Aryldiazonium Salt. Part-XII: Review on Coupling of Aryldiazonium Salt of Aminobenzothiazoles with Aromatic or Heteroaromatic

Mofits[Link: chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://www.heteroletters.org/issue122/review1.pdf].

31. A. N. Dhake, C. J. Patil and G. R. Chaudhari, Int. J. Pharma. Sci. Rev. Res., 2021; 70(2): 75-99, doi: 10.47583/ijpsrr.2021.v70i02.011, Coupling Reactions of Aryldiazonium Salt. Part-XI: Review on Coupling of Aryldiazonium Salts of Aminobenzothiazoles with Aromatic and Heterocyclic Components.