Synthesis of new Azo compounds combining with heterocyclic groups

Cite as: AIP Conference Proceedings **2450**, 020001 (2022); https://doi.org/10.1063/5.0093536
Published Online: 12 July 2022

Batool S. Haddad and Mariam Abdul-bary

Synthesis of New Azo Compounds Combining with Heterocyclic Groups

Batool S. Haddad[1, a)] and Mariam Abdul-bary[2, b)]

[1] *Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq*
[2] *Department of Food Science, College of Agriculture, University of Basrah, Basrah, Iraq*

[a)] Corresponding author: *batoolsalih16@yahoo.com*
[b)] *maryamabd2018@gmail.com*

Abstract. Six compounds of Azo containing heterocyclic groups, as derivatives for α, β- unsaturated ketones (the chalcones analogs), were synthesized. The Azo compounds combining the α, β- unsaturated ketones were prepared by the reaction the diazonium salt with an aryl carbonyl compound, such as benzaldehyde, 2-chlorobenzaldehyde, and furfual. And then treated with acetone. The products were reacted with benzil to prepare two chalcone groups. The results were reacted with $NH_2OH.HC/EtOH$ and glacial HAC, as a catalyst. Several derivatives of azo compounds that containing heterocyclic group were syntheside. The newly synthesized compounds have been diagnosed by (FTIR, ^1H NMR, ^{13}CNMR, and MASS) spectroscopy.

INTRODUCTION

Azo compounds having the diazenyl group (R−N=N−R′), R and R′ are alkyl or aryl. The more stable azo compound contains two aryl groups [1]. Azo compounds were synthesized by the reaction between cation, aryldiazonium compounds, and aromatic compounds [2, 3]. Azo compounds have bright colors, red, yellow, and orange [4, 5]. They are used as an azo dye and as indicators such as methyl orange [6,7]. They have used to treat textiles and some foods due to their insolubility properties in water and many other solvents [8]. Synthesis of azo and heterocyclic compounds such as *isoxazole* derivatives received much of attention due to their important applications [9, 10]. Azo compounds and heterocyclic compounds such as *isoxazole* have ranked first among many types of organic compounds because of different biological and industrial activities [11, 12]. Heterocyclic compounds such as *isoxazole* have a significant place in the field of heterocyclic chemistry [13]. The azo and isoxazole compounds are established extensive applications in the scope of pharmacological activity [14, 15]. The oligomers for these compounds were used in photovoltaic cells due to their high stability [16]. *Isoxazole* compounds have been considered as a free radical's scavenger and as a prevent cancer [17, 18]. They possess the ability to decrease oxidative stress [19]. In this research, according to the above interesting observations, we combining these two interesting classes, azo and heterocyclic compounds. We synthesized azo compounds containing heterocyclic groups, as derivatives of α, β- unsaturated ketones.

MATERIALS AND METHODS

All materials used were supplied by Aldrich, merk,and sigma. All solvents used have been purified. Electro thermalIA 9200 was used to measure the melting point. The NMR spectra were recorded using BRUKER spectrometer 300 MHz. The FTIR spectra were recorded using BRUKER spectrometer. The mass spectra were recorded using Shimadzu. The reaction of the diazonium salt with the aromatic compounds containing the carbonyl group leads to the formation of an azo compound containing the carbonyl group, and then this product is treated with CH_3COCH_3 to form α, β- unsaturated ketones. Then the heterocyclic group was formed by adding $NH_2OH.HCl$ in EtOH and adding glacial HAC as catalysis. Nuclear magnetic resonance (in $CDCl_3$, 300 MHz Bruker NMR spectrometer), infrared, and mass spectroscopy were used to diagnose the compounds.

The General Method for Preparing Azo Compounds [20]

A solution of (2 mol, 2.0 ml) of amine compounds and (6.0 ml) of concentrated hydrochloric acid (6.0 ml) H_2O. The solution cooled to 5-0 ˚C and then added (1.0 g) of $NaNO_2$ in (10.0 ml) of H_2O. The mixture was stirred and added (1 mol, 1.0 gm) aromatic aldehyde in (2.0 ml) ethanol. The product is recrystallized from EtOH.

International Conference of Chemistry and Petrochemical Techniques (ICCPT)
AIP Conf. Proc. 2450, 020001-1–020001-5; https://doi.org/10.1063/5.0093536
Published by AIP Publishing. 978-0-7354-4354-9/$30.00

The General Method for Preparing α, β- Unsaturated Ketones [21]

A solution of (1.0 mol) of azo compounds containing a carbonyl group was stirred with (1.0 mol, 30 ml) of CH_3COCH_3. After that (10.0 g) NaOH was added in (100.0 ml) H_2O and (80.0 ml) EtOH. The solution was stirred for half an hour. The reaction progression was followed up with thin layer chromatography. The solid resultant was recrystallized from EtOH.

A solution of (1.0 mol, 0.8 g) in (50.0 ml) EtOH of the last product was stirred with (1.0 mol, 1.0 g) of benzil. After that (10.0 g) NaOH was added. The solution was stirred for half an hour. The reaction progression was followed up with thin layer chromatography. The solid resultant was recrystallized from EtOH.

The General Method for Synthesis Heterocyclic Group [22]

(2.50 ml) glacial HAC, as a catalyst, was added to a solution of $NH_2OH.HCl$ (2.0 mol). The solution was stirred and added to a solution of α, β-unsaturated ketones (1.00 mol) in (10.0 ml) EtOH. The solution was refluxed for (18-24) hr. The reaction progression was followed up with thin layer chromatography. The solution was filtered. Then the solid resultant was recrystallized from ethanol. The reaction synthesis steps are shown in Fig. 1. The physical properties of newly synthesized compounds are listed in Table 1.

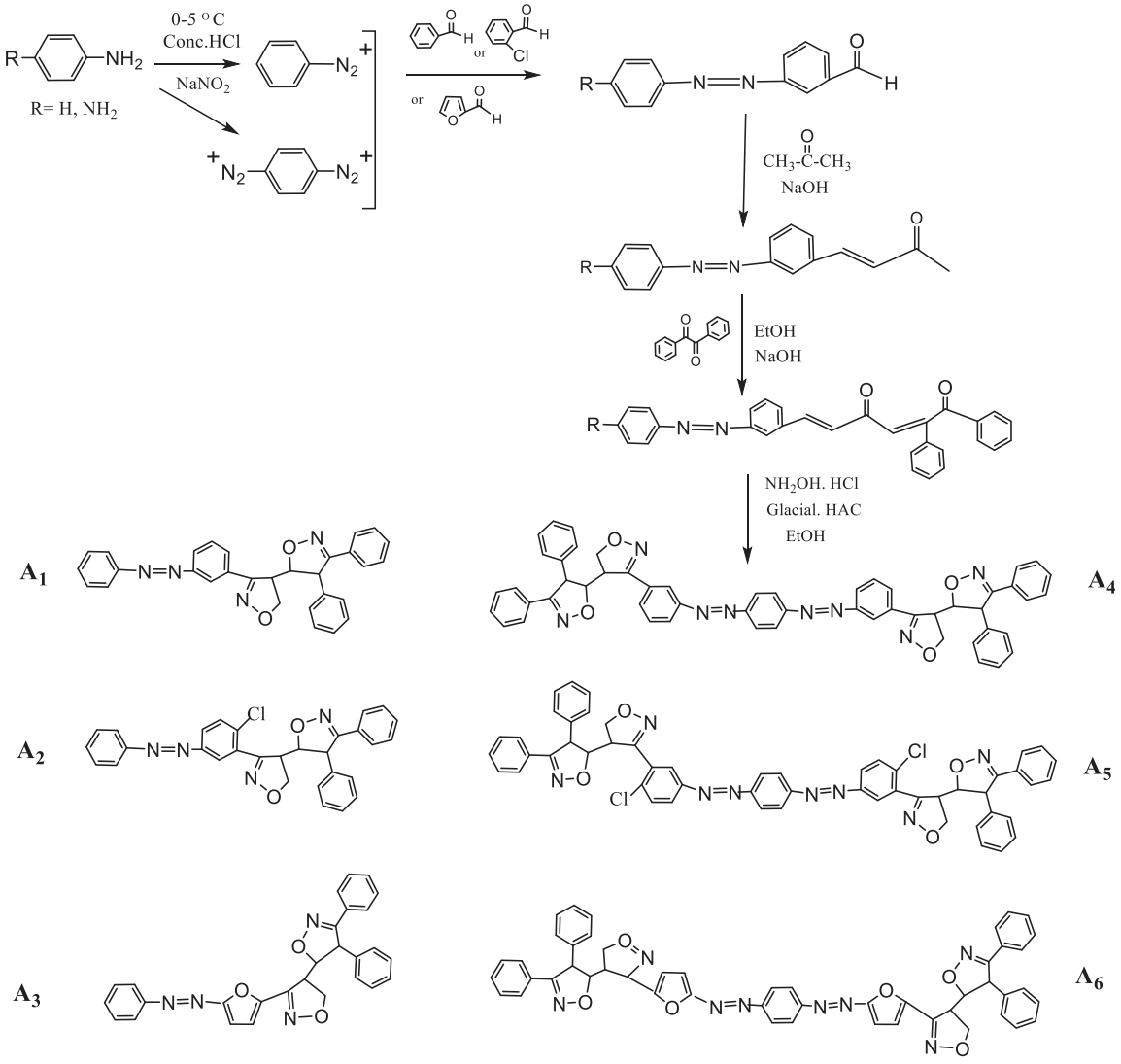

FIGURE 1. The synthesis steps of azo compound combining heterocyclic group.

TABLE 1. The physical data of the synthesized azo compounds combining with a heterocyclic group.

Comp.	M. p ^{O}C	Time of reacting. Hr.	Yield (%)
A_1	185	18	72
A_2	190	18	74
A_3	80	20	65
A_4	90	19	71
A_5	80	21	74
A_6	100	24	67

A_1 3', 4'-diphenyl-3-(3-(phenyldiazenyl)phenyl)-4,4',5,5'-tetrahydro-4,5'-biisoxazole

Orange powder; yields: 72 %; Melting point. 185 °C; FTIR (ν cm^{-1}): 1280 (C--N), 1464 (N==N), 1567(C=C), 1600 (C=N), 1187 (N-O), 1116 (C-O), 3100 (CH aromatic), 2885-2867 (CH aliphatic); "^{1}H NMR ($CDCl_3$) ppm: 7.71 "(m,5H, ph)", 6.83 "(m,5H, ph)", 6.80 "(m,5H, ph)," 6.53 (m,5H, ph), 2.72 "(m 2H, CH_2)", 2.40 "(m 1H, CH)", 2.10 "(m 1H, CH)", 1.90 "(1 H, CH)"; ^{13}C NMR ($CDCl_3$) ppm :54.52, 67.13, 110.53, 112.97, 118.64, 119.06, 120.31, 121.07, 123.81, 124.69, 125.21, 127.25, 128.70, 129.09, 130.40, 130.92, 131.94, 132.63, 133.75, 134.11, 134.90, 139.10, 141.26, 161.84; MS: m/z: 472 (M^+).

A_2 3-(2-chloro-5-(phenyldiazenyl)phenyl)-3',4'-diphenyl-4,4',5,5'-tetrahydro-4,5'-biisoxazole

Orange powder; yields: 74 %; Melting point. 190 °C; FTIR (ν cm^{-1}): 1288 (C-N), 1460 (N=N), 1577(C=C), 1609 (C=N), 1189 (N-O), 1126 (C-O), 3106 (CH aromatic), 2880-2871 (CH aliphatic), 796 (C-Cl); ^{1}H NMR ($CDCl_3$ δ ppm) δ: 8.15 (m,4H, ph), 7.85 (m,5H, ph), 7.57 (m,5H, ph) 7.23 (m,5H, ph), 2.70 (m 2H, CH2), 2.53 (m 1H, CH), 2.25 (m 1H, CH), 1.82 (1 H, CH); ^{13}C NMR ($CDCl_3$ δ ppm):53.54, 63.32, 100.03, 112.43, 117.73, 119.79, 120.35, 122.74, 123.75, 124.32, 126.11, 127.33, 128.97, 129.75, 130.02, 130.95, 131.28, 131.92, 132.06, 132.99, 134.43, 140.10, 141.54, 160.43; MS: m/z: 506 (M^+).

A_3 3-((phenyl diazenyl)furan-2-yl)-3',4'-diphenyl-4,4',5,5'-tetrahydro-4,5'-biisoxazole

Orange powder; yields: 65 %; Melting point. 80 °C; FTIR (ν cm^{-1})": 1278 (C--N), 1458 (N==N), 1585(C=C), 1612 (C=N), 1186 (N-O), 1130 (C-O), 3114 (CH aromatic), 2891-2883 (CH aliphatic); "^{1}H NMR (CDH_3 δ. ppm) δ": 7.63 "(m,5H, ph)", 7.39 "(m,5H, ph)", 7.06 "(m,5H, ph)" 6.85 "(m,2H, furan)", 3.00 "(m 2H, CH_2)", 2.26 "(m 1H, CH)", 2.02 "(m 1H, CH)", 1.73 "(1 H, CH)", 1.62 "(m 1H, CH)", 1.47 "(m 1H, CH"); ^{13}C NMR (CDH_3 δ ppm):49.53, 53.93, 111.64, 113.73, 118.94, 119.75, 120.32, 121.04, 123.74, 124.46, 127.19, 128.97, 129.05, 130.43, 130.85, 132.62, 132.93, 133.90, 134.32, 140.74, 160.03, 161.86; MS: m/z: 462 (M^+).

A_4 1,4-bis((4-(3',4'-diphenyl-4,4',5,5'-tetrahydro-[4,5'-biisoxazol]-3-yl)phenyl-1-yl)diazenyl) benzene

Orange powder; yields: 71 %; Melting point. 90 °C; FTIR (ν cm^{-1})": 1290 (C--N), 1462 (N==N), 1553(C=C), 1698 (C=N), 1161 (N-O), 1112 (C-O), 3120 (CH aromatic), 2894-2881 (CH aliphatic); "^{1}H NMR ($CDCl_3$ δ ppm) δ": 7.84 "(m,4H, ph)", 7.60 "(m,4H, ph)", 7.00 "(m,5H, ph)" 6.62 "(m,5H, ph)", 3.02 "(m 2H, CH_2)", 2.30 "(m 1H, CH)", 2.11 "(m 1H, CH)", 1.85 "(1 H, CH)"; "[^{13}C NMR ($CDCl_3$ δ ppm)]":47.95, 64.94, 117.96, 118.53, 118.99, 119.76, 122.11, 122.09, 123.65, 124.08, 125.00, 127.56, 128.67, 129.57, 130.35, 130.92, 131.54, 132.32, 134.05, 139.33, 140.36, 161.56; MS: m/z: 866 (M^+).

A_5 1,4-bis(4-chloro((4-(3',4'-diphenyl-4,4',5,5'-tetrahydro-[4,5'-biisoxazol]-3-yl))phenyl-1-yl) diazenyl)benzene

Orange powder; yields: 74 %; Melting point. 80 °C; FTIR (ν cm^{-1})": 1276 (C--N), 1447 (N==N), 1567(C=C), 1601 (C=N), 1186 (N-O), 1112 (C-O), 3126 (CH aromatic), 2890-2866 (CH aliphatic), 786 (C-Cl); "[^{1}H NMR ($CDCl_3$ δ. ppm) δ] ": 7.90 "(m,4H, ph)", 7.82 "(m,3H, ph)", 7.20 "(m,5H, ph)" 6.97 "(m,5H, ph)", 2.86 "(m 2H, CH_2)", 2.16 "(m 1H, CH)", 2.11 "(m 1H, CH)", 1.37 "(1 H, CH)"; "[^{13}C NMR ($CDCl_3$ δ ppm)]" :50.53, 60.34,

110.75, 113.75, 118. 54, 119.45, 121.54, 122.24, 123.47, 125.07, 126.06, 127.06, 129.49, 130.04, 130.20, 131.86, 132.99, 133.73, 134.93, 140.84, 141.04, 162.74; MS: m/z: 934 (M^+).

A_6 1,4-bis((5-(3',4'-diphenyl-4,4',5,5'-tetrahydro-[4,5'-biisoxazol]-3-yl)furan-2-yl) diazenyl)benzene

Orange powder; yields: 67 %; Melting point. 100 ° C; FTIR (ν cm^{-1})": 1298 (C--N), 1478 (N==N), 1589(C=C), 1602 (C=N), 1176 (N-O), 1140 (C-O), 3100 (CH aromatic), 2882-2861 (CH aliphatic); "^{1}H NMR ($CDCl_3$ δ ppm) δ": 7.10 "(m,4H, ph)", 6.90 "(m,5H, ph)", 6.64 "(m,5H, ph)" 6.28 "(m,2H, furan)", 2.54 "(m 2H, CH2)", 2.37 "(m 1H, CH)", 2.08 "(m 1H, CH)", 2.01 "(1 H, CH)", 1.86 "m 1H, CH)", 1.52 "(m 1H, CH)"; ^{13}C NMR ($CDCl_3$ δ. ppm):59.86, 60.09, 112.60, 113.32, 117.47, 119.74, 120.94, 121.95, 123.43, 124.49, 127.74, 129.77, 130.25, 130.63, 131.48, 132.90, 132.93, 133.51, 134.73, 142.45, 161.73, 163.27; "MS: m/z: 846 (M^+)".

RESULTS AND DISCUSSION

Azo compound (combining with a group of α, β- unsaturated ketones) reacted with $NH_2OH.HCl$ and that leads to the formation of the corresponding Azo compounds Containing Heterocyclic group. The resulting compounds were colored powder recrystallized from EtOH in (65-74) % yield. The infrared spectra of the azo compounds containing the heterocyclic group showed the disappearance of the absorption band that attributed to the stretching of C=O (of α, β- unsaturated ketones), group which appeared at (1702-1679) cm^{-1}. All heterocyclic spectra indicated a peak related to (N = N) stretching in the azo group in the region (1463) cm^{-1}. The infrared spectra indicated a peak attributed to "C == N" and "N--O" stretching of the bonds of the heterocyclic group at "1599-1611 and 1151-1201" cm^{-1}. Aliphatic (C-H) bonds showed peaks appeared at (2874-2887) cm^{-1} and the aromatic (C-H) in the region (3100-3120) cm^{-1}. All the spectra of ^{1}H nuclear magnetic resonance of the synthesized compounds indicated multiples signals related to the benzene rings' protons at "6.52-7.79" ppm. The spectra showed the multiples signals attributed to the CH_2 protons in the heterocyclic group at "2.01-3.22" ppm. All the spectra of ^{13}C nuclear magnetic resonance of the synthesized compounds are confirmed to the expected structures. The structures of the synthesized compounds were diagnosed by mass spectra, and the results are confirmed the expected structures.

CONCLUSION

In the current study, six new azo compounds containing the heterocyclic group were synthesized. These new compounds were diagnosed using mass, infrared, and nuclear magnetic resonance spectroscopy, and the results are confirmed to the expected structure.

ACKNOWLEDGMENTS

We thank colleagues in the Chemistry Department for their support.

REFERENCES

1. V. Bargmann, Proc. Natl. Acad. Sci. USA **38**, 961–966 (1952).
2. P. Shamugam, N. Somiyaa, Elavarasana and K. Elavarasana, Journal of Molecular Structure **1224**,129016 (2021).
3. Y. Kucheryayyi, Kaplaushenko, A. and E. Pruhlo, Problems of Pharmacy **6**, 101-104 (2014).
4. Prabhu, V.V. Prabbu, N. Kannan and C. Guruvayoorappan, Pharmacological Reports **65**, 980-990 (2013).
5. R. Maccari, R. M.Vitale, R. Ottanà, M. Rocchiccioli, A. Marrazzo, V. Cardile and V. Graziano, European Journal of Medicinal Chemistry **81**, 1-14 (2014).
6. R. Malik, N. Pal, G. Singh and C. Singh, IOSR Journal of Pharmacy **3**, 27-30 (2013)
7. M. Rakesh and A. Wahab, Indian Journal of Heterocyclic Chemistry **13**, 29-32 (2003).
8. M. Ordonez, R. Cabrera and C. Cativiela, Tetrahedron **65**, 1749 (2009).
9. P. Sagar, B. Vilasrao, S. Ramesh and P. Sachin, International Journal of Pharmacy and Pharmaceutical Sciences **2**,19-26 (2017).
10. F. Fringe, F.Piematti and V. Pizzo, European Journal of Organic Chemistry **3**, 439–455 (2001).
11. C. Li, Chemical Reviews **105**, 3095–3166 (2005).
12. A. Dandia, K. Arya, M. Sati and P.Sarangi, Fluorine Chemistry **125**, 1273–1277 (2004).

13. C. Cho, C. Kim and N.Yoon, Tetrahedron **56**, 7747–7750 (200).
14. R. Lalit Gupta and C. Singh, International Journal of Applied Research **4**, 20-22 (2014).
15. S. Bhatt, C. P. Singhand D. Kumar, IOSR Journal of Pharmacy **2**, 60-64 (2012).
16. S. Nilufer and R, Sevim, Arkivoc**12**, 173-181 (2006).
17. Y. Vibhute and M. Basser, Indian Journal of Chemistry **4**, 205 (2003).
18. D. Guolan, X. Qiang, X. Yukun and H. Zhibin, Molecules **18**, 13645-13653 (2013).
19. D. Shi and H. Wang, J. Heterocycl. Chem **49**, 1086–1090 (2012).
20. V. Anna, J. Org. Chem**84**, 15567–15577 (2019).
21. R. Satyanarayana and G. Sravya, Environmental Chemistry Letters **18**, (2020).
22. Z. Xuan, L. Wei and Z. Dawei, Molecules**25**, 1594 (2020).