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Synthesis of New Azines in Various Reaction Conditions and Investigation of their Cycloaddition Reaction

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A series of new azines were prepared by reaction of 2-ketoalkyl quinoline derivatives with some hydrazone in solvent free reaction conditions using ultrasonic irradiation. The application of ultrasonic irradiation improved the yields and reduced the reaction times. These azines, due to having α-acidic hydrogen next to azine group and heterocycle ring, have tautomeric forms the degree of each of which was determined on the basis of ^{13}C NMR, ^{1}H NMR, UV and IR spectrum. The results revealed that all compounds exist mostly in the enaminone form. We attempted to obtain criss-cross or probably Diels-Alder cycloaddition products through the reaction of some of these new azines with 2-chloroacrylonitrile as a dienophile. Some new diene systems developed from the said reactions.

Keywords: 2-Ketoalkyl quinoline, Azine, Tautomer, Criss-cross cycloaddition, Diels-Alder cycloaddition, Dienophile

INTRODUCTION

Azines are a class of compounds that have been receiving increasing attention in recent years for their antibacterial, antifungal and antitumor properties [1-2]. Azines have also been extensively used in bond formation reaction [3], polymerization [4], in the design of liquid crystal [5] and the synthesis of heterocyclic compounds [6-8]. Few studies have been done on the reaction of azines with dienophile. The pseudo-diene structure of azines is considered to be the main factor of the most interesting reactions of azines; and it is predictable that many of the reactions with dienes occur with azines as well. However, in comparison with an ordinary diene, the diene part of azines, which is in fact a hetero diene, acts differently. Due to the high electronegativity of nitrogen to carbon, the electron density around nitrogen is more than the carbon and the lone pairs of nitrogen also act as a sigma donor.

One of the known reactions of azines is the criss-cross cycloaddition [9-10]. In this reaction, the dienophile containing electron withdrawing groups are added to an azine molecule and make two five-member cycles on two sides of N=N bond. Most of the aromatic aldazines have been used to produce this reaction but aliphatic or aliphatic-aromatic aldazine can not cause the criss-cross cycloaddition reaction. For instance, acetoneazine, in reaction with alkenes can not produce a criss-cross cycloaddition. But it has been established that hexafluoroacetoneazine, which is an electron poor azine, reacts with electron rich olefins or acetylene under heat or photochemical conditions and gives the criss-cross cycloaddition product in more than 80% yield [11].

Schimizu and co-workers have obtained the criss-cross

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cycloaddition and Diels-Alder addition product by the reaction of styrene with azine [12]. In this article, we wish to report the synthesis of some new azines from 2-methylquinoline and investigate tautomeric forms of these new azines based on ^{13}C NMR, ^{1}H NMR, UV and IR spectrum in $CDCl_3$. We will also describe the cycloaddition reaction of some of these compounds with 2-chloroacrylonitrile.

EXPERIMENTAL

Chemicals and Apparatus

All solvents were dried using literature procedures and distilled before use. Reactions were produced under an atmosphere of argon unless otherwise specified. 2-Ketoalkyl quinoline was prepared according to the reported procedure [14]. Elemental analyses for C, H and N were performed using Heraeus CHN-O-Rapid analyzer. ^{1}H NMR spectra were recorded at 500 MHz on Bruker and ^{13}C NMR spectra were recorded at 125 MHz with tetramethylsilane as the internal standard. Mass spectra were recorded using a VG70-SE spectrometer operating at nominal accelerating voltage of 70 eV. Thin layer chromatography (TLC) was run on silica percolated aluminium plates (Merck Kieselgel F254). Melting points were determined on a Kofler hot-stage apparatus. The ultrasonic device used was a UP 400 S instrument from Dr. Hielscher GmbH. An S3 immersion horn emitting 24 kHz ultrasound at intensity levels tunable to maximum sonic power density of 460 W cm^{-2} was used. Ultraviolet spectra were obtained by a Shimadzu 160 UV spectrometer. Infrared spectra were taken with a Shimadzu PU 9716 spectrophotometer, Model 435.

General Procedure for the Preparation of Azines, Method 1

Glacial acetic acid (3 drops) was added to 2-ketoalkyl quinoline derivatives (10 mmol). After grinding for 5 min, aromatic hydrazone (10 mmol) was added and grinding continued for 30-60 min. After completion of the reaction (monitored by TLC), the mixture was recrystallised from 95% ethanol to afford the pure azine compound.

General Procedure for the Preparation of Azines, Method 2

Glacial acetic acid (3 drops) was added to the solution of 2-ketoalkyl quinoline derivatives (10 mmol) in ethanol. After 5 min aromatic hydrazone (10 mmol) was added and the reaction mixture was irradiated with ultrasound for 10-20 min. After completion of the reaction (monitored by TLC), the mixture was recrystallised from 95% ethanol to afford the pure azine compound.

2-(4-Nitrobenzylidene)-1-(1-(quinolin-2-yl)propan-2-ylidene)hydrazine (1c). A/B 0:100; 97% yield, m.p.: 183-184 °C (EtOH). υ_{max} (KBr): 1515, 1560, 1590, 1635 cm^{-1}. λ_{max} (95% EtOH): 410, 385, 250. ^{13}C NMR ($CDCl_3$): δ (ppm) 20.2, 98.2, 123.5, 125.5, 126.1, 126.1, 128.1, 128.4, 128.9, 130.9, 137.2, 139.9, 143.3, 147.7, 148.0, 150.5, 159.4. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.32 (s, 3H, CH_3), 5.48 (s, 1H, CH), 7.22-8.27 (m, 10H, aromatic-H), 8.40 (s, 1H, HC=N) 14.36 (bs, 1H, NH). MS (EI), *m/z* (%) = 332 (M^+), 183, 143, 115, 69 (100), 44. Anal. Calcd. for $C_{19}H_{16}N_4O_2$: C, 68.7; H, 4.8; N; 16.9. Found: C, 68.8; H, 4.8; N, 16.8.

2-(2-Nitrobenzylidene)-1-(1-(quinolin-2-yl)propan-2-ylidene)hydrazine (2c). A/B 0:100; 95% yield, m.p.: 174-176 °C (EtOH). υ_{max} (KBr): 1570, 1575, 1595, 1638 cm^{-1}. λ_{max} (95% EtOH): 415, 384, 250. ^{13}C NMR ($CDCl_3$): δ (ppm) 20.1, 97.8, 123.5, 125.8, 126.0, 126.1, 128.0, 128.1, 129.5, 130.3, 130.5, 131.0, 134.4, 137.1, 137.2, 147.7, 148.7, 150.7, 159.4.^{1}H NMR ($CDCl_3$): δ (ppm) 2.25 (s, 3H, CH_3), 5.45 (s, 1H, CH), 7.22-8.09 (m, 10H, aromatic-H), 8.49 (s, 1H, HC=N), 14.29 (bs, 1H, NH). MS (EI), *m/z* (%) = 332 (M^+), 183, 168, 143 (100), 128, 115, 102, 77, 51. Anal. Calcd. for $C_{19}H_{16}N_4O_2$: C, 68.7; H, 4.8; N; 16.9. Found: C, 68.7; H, 4.8; N, 16.7.

2-(1-(4-Bromophenyl)ethylidene)-1-(1-(quinolin-2-yl) propan-2-ylidene)hydrazine (3c). A/B 0:100; 85% yield, m.p.: 150-151 °C (EtOH). υ_{max} (KBr): 1510, 1550, 1575, 1635 cm^{-1}. λ_{max} (95% EtOH): 400, 375, 248. ^{13}C NMR ($CDCl_3$): δ (ppm) 14.9, 20.2, 97.2, 122.9, 123.2, 125.0, 125.7, 127.4, 128.1, 128.5, 129.0, 129.1, 130.2, 132.3, 132.4, 136.0, 142.8, 147.9, 151.8, 159.9. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.33 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 5.46 (s, 1H, CH), 7.24-8.08 (m, 10H, aromatic-H), 13.74 (bs, 1H, NH). MS (EI), *m/z* (%) = 381 (M^++2), 379 (M^+), 183 (100), 169, 143, 119, 69. Anal. Calcd. for $C_{20}H_{18}BrN_3$: C, 63.2; H, 4.8; N; 11.0. Found: C, 63.1; H, 4.8; N, 11.2.

2-(1-(4-Nitrophenyl)ethylidene)-1-(1-(quinolin-2-yl) propan-2-ylidene)hydrazine (4c). A/B 0:100; 85% yield, m.p.: 178-179 °C (EtOH). υ_{max} (KBr): 1565, 1570, 1590, 1638

cm^{-1}. λ_{max} (95% EtOH): 420, 380, 252. ^{13}C NMR ($CDCl_3$): δ (ppm) 14.8, 20.0, 98.8, 123.3, 124.6, 125.4, 125.9, 126.7, 127.5, 128.3, 128.6, 136.3, 140.9, 146.0, 147.8, 147.8, 151.1, 159.6.^1H NMR ($CDCl_3$): δ (ppm) 2.37 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 5.57 (s, 1H, CH), 7.29-8.24 (m, 10H, aromatic-H), 13.90 (bs, 1H, NH). MS (EI), *m/z* (%) = 346 (M^+), 183 (100), 143 (100), 117, 76. Anal. Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.4; H, 5.2; N; 16.2. Found: C, 69.3; H, 5.2; N, 11.1.

N-(1-Biphenyl-4-yl-ethylidene)-N′-(1-methyl-2-quinolin-2-yl-ethyylidene)-hydrazine (5c). A/B 15:85; 87% yield, m.p.: 173-174 °C (EtOH). υ_{max} (KBr): 1560, 1590, 1637 cm^{-1}. λ_{max} (95% EtOH): 440, 400, 252 ^{13}C NMR ($CDCl_3$): δ (ppm) 15.1, 15.7, 20.3, 20.8, 35.9, 96.9, 123.3, 124.9, 125.7, 127.1, 127.4, 127.9, 127.9, 127.9, 127.9, 128.0, 128.3, 128.5, 129.7, 129.8, 130.2, 135.9, 139.0, 141.5, 141.6, 148.0, 151.9, 160.0. ^1H NMR ($CDCl_3$): δ (ppm) 2.40 (s, 0.45H, CH_3, form A), 2.41 (s, 0.45H, CH_3, form A), 2.47 (s, 2.55H, CH_3, form B), 2.60 (s, 2.55H, CH_3, form B), 4.15 (s, 0.3H, CH_2, form A), 5.34 (s, 0.85H, CH, form B), 7.08-7.92 (m, 15H, aromatic-H, form A and B), 13.86 (bs, 0.85H, NH). MS (EI), *m/z* (%) = 377 (M^+), 235, 183, 152, 143 (100), 115, 77, 51. Anal. Calcd. for $C_{26}H_{23}N_3$: C, 82.7; H, 6.1; N; 11.2. Found: C, 82.8; H, 6.2; N, 11.2.

2-(1-(Pyridin-2-yl)ethylidene)-1-(1-(quinolin-2-yl) propan-2-ylidene)hydrazine (6c). A/B 0:100; 92% yield, m.p.: 159-160 °C (EtOH). υ_{max} (KBr): 1540, 1555, 1593, 1630 cm^{-1}. λ_{max} (95% EtOH): 413, 391, 249. ^{13}C NMR ($CDCl_3$): δ (ppm) 13.2, 20.1, 97.9, 121.0, 123.2, 123.2, 125.2, 125.8, 127.6, 128.4, 130.4, 136.1, 136.9, 145.2, 148.0, 149.1, 151.2, 157.3, 159.8. ^1H NMR ($CDCl_3$): δ (ppm) 2.43 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 5.38 (s, 1H, CH), 7.08-8.59 (m, 10H, aromatic-H), 13.89 (bs, 1H, NH). MS (EI), *m/z* (%) = 302 (M^+), 243, 183 (100), 156, 143, 115, 75. Anal. Calcd. for $C_{19}H_{18}N_4$: C, 75.5; H, 6.0; N; 18.5. Found: C, 75.4; H, 5.9; N, 18.6.

2-(1-(4-Nitrophenyl)ethylidene)-1-(1-(quinolin-2-yl) butan-2-ylidene)hydrazine (7c). A/B 0:100; 87% yield, m.p.: 155-156 °C (EtOH). υ_{max} (KBr): 1565, 1570, 1590, 1636 cm^{-1}. λ_{max} (95% EtOH): 423, 405, 250. ^{13}C NMR ($CDCl_3$): δ (ppm) 13.9, 14.6, 26.5, 97.3, 123.5, 124.6, 125.4, 125.9, 126.7, 127.5, 128.6, 130.4, 136.3, 140.8, 146.1, 147.7, 147.8, 156.1, 159.8.^1H NMR ($CDCl_3$): δ (ppm) 1.36 (t, *J* = 7.4 Hz, 3H, CH_3), 2.59 (s, 3H, CH_3), 2.82 (q, *J* = 7.4 Hz, 2H, CH_2), 5.43 (s, 1H, CH), 7.13-8.22 (m, 10H, aromatic-H), 13.95 (bs, 1H, NH). MS (EI), *m/z* (%) = 361 (M^+), 143 (100), 117, 76. Anal. Calcd. for $C_{21}H_{20}N_4O_2$: C, 70.0; H, 5.6; N; 15.6. Found: C, 69.9; H, 5.6; N, 15.5.

2-(1-(Pyridin-2-yl)ethylidene)-1-(1-(quinolin-2-yl) butan-2-ylidene)hydrazine (8c). A:B 0:100; 90% yield, m.p.: 161-162 °C (EtOH). υ_{max} (KBr): 1545, 1550, 1592, 1632 cm^{-1}. λ_{max} (95% EtOH): 415, 389, 253. ^{13}C NMR ($CDCl_3$): δ (ppm) 13.2, 14.0, 26.7, 96.5, 121.0, 123.2, 123.4, 125.2, 125.8, 127.7, 128.4, 130.4, 136.1, 137.0, 148.0, 149.0, 156.3, 157.2, 160.0. ^1H NMR ($CDCl_3$): δ (ppm) 1.37 (t, *J* = 7.4 Hz, CH_3), 2.35 (s, 3H, CH_3), 2.84 (q, *J* = 7.4 Hz, 2H, CH_2), 5.39 (s, 1H, CH), 7.12-8.60 (m, 10H, aromatic-H), 13.85 (bs, 1H, NH). MS (EI), *m/z* (%) = 317 (M^+), 197, 143, 77 (100), 50. Anal. Calcd. for $C_{20}H_{20}N_4$: C, 75.9; H, 6.4; N; 17.7. Found: C, 75.9; H, 6.4; N, 17.7.

N-(1-Biphenyl-4-yl-ethylidene)-N′-(1-quinolin-2-ylmethyl-propylidene)-hydrazine (9c). A:B 18:82; 85% yield, m.p.: 155-156 °C (EtOH). υ_{max} (KBr): 1540, 1555, 1594, 1632 cm^{-1}. λ_{max} (95% EtOH): 440, 416, 260. ^{13}C NMR ($CDCl_3$): δ (ppm) 11.6, 14.1, 15.1, 15.9, 25.3, 25.9, 36.4, 95.3, 120.6, 121.1, 123.4, 123.5, 124.3, 124.9, 125.0, 125.3, 125.8, 126.2, 127.0, 127.5, 127.9, 127.9, 127.9, 127.9, 128.0, 128.2, 128.5, 129.7, 129.7, 129.7, 130.0, 130.2, 131.2, 135.9, 136.3, 138.4, 139.0, 141.6, 148.0, 149.1, 156.2, 157.0, 158.1, 158.5, 159.2, 160.2. ^1H NMR ($CDCl_3$): δ (ppm) 1.24 (t, *J* = 7.4 Hz, 0.54H, CH_3, form A), 1.40 (t, *J* = 7.4 Hz, 2.46H, CH_3, form B), 2.25 (q, J = 7.4 Hz, 0.36H, CH_2, form A), 2.39 (s, 0.54H, CH_3, form A), 2.63 (s, 2.46H, CH_3 form B), 2.86 (q, J = 7.4 Hz, 1.64H, CH_2, form B), 4.22 (s, 0.36H, CH_2, form A), 5.35 (s, 0.82H, CH, form B)), 7.11-7.93 (m, 15H, aromatic-H, form A and B), 13.81 (bs, 0.82H, NH, form B). MS (EI), *m/z* (%) = 391 (M^+), 373, 197 (100), 152(100), 143, 115, 44. Anal. Calcd. for $C_{27}H_{25}N_3$: C, 82.8; H, 6.4; N; 10.7. Found: C, 82.7; H, 6.3; N, 10.7.

2-(4-Nitrobenzylidene)-1-(1-(quinolin-2-yl)butan-2-ylidene)hydrazine (10c). A:B 0:100; 90% yield, m.p.: 153-154 °C (EtOH). υ_{max} (KBr): 1545, 1555, 1590, 1635 cm^{-1}. λ_{max} (95% EtOH): 420, 410, 251. ^{13}C NMR ($CDCl_3$): δ (ppm) 13.9, 26.6, 96.7, 123.3, 124.8, 125.5, 126.1, 127.2, 127.7, 128.4, 129.7, 130.4, 136.4, 137.1, 142.9, 147.9, 155.7, 159.3. ^1H NMR ($CDCl_3$): δ (ppm) 1.25 (t, *J* = 7.4 Hz, 3H, CH_3), 2.70 (q, *J* = 7.4 Hz, 2H, CH_2), 5.28 (s, 1H, CH), 7.01-8.12 (m, 10H,

aromatic-H), 8.14 (s, 1H, HC=N), 14.40 (bs, 1H, NH). MS (EI), *m/z* (%) = 346 (M^+), 197, 143 (100), 115, 76. Anal. Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.3; H, 5.2; N; 16.1. Found: C, 69.4; H, 5.3; N, 16.2.

2-(2-Nitrobenzylidene)-1-(1-(quinolin-2-yl)butan-2-ylidene)hydrazine (11c). A:B 0:100; 85% yield, m.p.: 153-155 °C (EtOH). υ_{max} (KBr): 1535, 1540, 1588, 1636 cm^{-1}. λ_{max} (95% EtOH): 423, 405, 250. ^{13}C NMR ($CDCl_3$): δ (ppm) 13.9, 26.6, 96.4, 123.2, 125.4, 125.5, 125.8, 125.9, 127.9, 128.3, 128.4, 129.0, 130.5, 131.5, 133.8, 134.9, 136.3, 148.0, 155.6, 159.3. ^1H NMR ($CDCl_3$): δ (ppm) 1.25 (t, *J* = 7.4 Hz, 3H, CH_3), 2.68 (q, *J* = 7.4 Hz, 2H, CH_2), 5.25 (s, 1H, CH), 6.99-8.12 (m, 10H, aromatic-H), 8.44 (s, 1H, HC=N), 14.47 (bs, 1H, NH). MS (EI), *m/z* (%) = 346 (M^+), 197, 182, 168, 143 (100), 115, 51. Anal. Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.3; H, 5.2; N; 16.1. Found: C, 69.2; H, 5.1; N, 16.0.

2-(2-Nitrobenzylidene)-1-(1-(quinolin-2-yl)pentan-2-ylidene)hydrazine (12c). A:B 0:100; 80% yield, m.p.: 138-139 °C (EtOH). υ_{max} (KBr): 1510, 1555, 1595, 1637 cm^{-1}. λ_{max} (95% EtOH): 415, 390, 253. ^{13}C NMR ($CDCl_3$): δ (ppm) 15.0, 22.6, 35.5, 97.5, 123.1, 125.5, 125.8, 125.9, 127.9, 128.2, 128.4, 129.0, 130.5, 131.6, 133.8, 134.9, 136.3, 147.8, 148.1, 154.1, 159.2. ^1H NMR ($CDCl_3$): δ (ppm) 0.98 (t, *J* = 6.8 Hz, 3H, CH_3), 1.70 (sec, *J* = 6.9 Hz, 2H, CH_2), 2.61 (t, *J* = 7.2 Hz, 2H, CH_2), 5.25 (s, 1H, CH), 6.98-8.10 (m, 10H, aromatic-H), 8.45 (s, 1H, HC=N), 14.48 (bs, 1H, NH). MS (EI), *m/z* (%) = 360 (M^+), 211, 169, 168, 143 (100), 115, 77, 51. Anal. Calcd. for $C_{21}H_{20}N_4O_2$: C, 69.9.7; H, 5.6; N; 15.5. Found: C, 70.0; H, 5.5; N, 15.6.

2-(4-Nitrobenzylidene)-1-(1-(quinolin-2-yl)pentan-2-ylidene)hydrazine (13c). A:B 0:100; 83% yield, m.p.: 177-178 °C (EtOH). υ_{max} (KBr): 1575, 1580, 1590, 1635 cm^{-1}. λ_{max} (95% EtOH): 421, 395, 255. ^{13}C NMR ($CDCl_3$): δ (ppm) 15.0, 22.6, 35.4, 97.8, 123.3, 124.8, 125.0, 125.5, 126.0, 127.2, 127.7, 128.4, 129.7, 130.4, 136.4, 137.0, 142.9, 147.9, 154.18, 159.3. ^1H NMR ($CDCl_3$): δ (ppm) 0.99 (t, *J* = 7.3 Hz, 3H, CH_3), 1.71 (sec, *J* = 7.4 Hz, 2H, CH_2), 2.62 (t, *J* = 7.3 Hz, 2H, CH_2), 5.25 (s, 1H, CH), 6.99-8.12 (m, 10H, aromatic-H), 8.13 (s, 1H, HC=N), 14.40 (bs, 1H, NH). MS (EI), *m/z* (%) = 360 (M^+), 211, 143 (100), 115, 103, 76, 41. Anal. Calcd. for $C_{21}H_{20}N_4O_2$: C, 69.9; H, 5.6; N; 15.5. Found: C, 68.9; H, 5.5; N, 15.4.

2-(1-(4-Nitrophenyl)ethylidene)-1-(1-(quinolin-2-yl)pentan-2-ylidene)hydrazine (14c). A:B 0:100; 85% yield, m.p.: 149-150 °C (EtOH). υ_{max} (KBr): 1550, 1560, 1585, 1635 cm^{-1}. λ_{max} (95% EtOH): 425, 413, 256. ^{13}C NMR ($CDCl_3$): δ (ppm) 14.7, 15.1, 22.6, 35.4, 98.4, 123.4, 124.6, 125.3, 125.9, 126.6, 127.4, 128.6, 130.4, 136.2, 140.7, 146.0, 147.7, 147.8, 154.5, 159.7. ^1H NMR ($CDCl_3$): δ (ppm) 1.00 (t, *J* = 7.3 Hz, 3H, CH_3), 1.72 (sec, *J* = 7.5 Hz, 2H, CH_2), 2.49 (s, 3H, CH_3), 2.67 (t, *J* = 7.1 Hz, 2H, CH_2), 5.33 (s, 1H, CH), 7.03-8.13 (m, 10H, aromatic-H), 13.85 (bs, 1H, NH). MS (EI), *m/z* (%) = 374 (M^+), 211, 143 (100), 128, 115, 76, 44. Anal. Calcd. for $C_{22}H_{22}N_4O_2$: C, 70.6; H, 5.9; N; 14.9. Found: C, 70.5; H, 5.8; N, 14.9.

2-(1-(Pyridin-2-yl)ethylidene)-1-(1-(quinolin-2-yl)pentan-2-ylidene)hydrazine (15c). A:B 0:100; 80% yield, m.p.: 148-149 °C (EtOH). υ_{max} (KBr): 1550, 1565, 1590, 1630 cm^{-1}. λ_{max} (95% EtOH): 418, 402, 255. ^{13}C NMR ($CDCl_3$): δ (ppm) 13.2, 15.1, 22.7, 35.6, 97.5, 120.9, 123.2, 123.3, 125.2, 125.8, 127.6, 128.4, 130.4, 136.0, 136.8, 144.9, 148.0, 149.2, 145.7, 157.4, 159.9. ^1H NMR ($CDCl_3$): δ (ppm) 0.99 (t, *J* = 7.3 Hz, 3H, CH_3), 1.75 (m, 2H, CH_2), 2.64 (s, 3H, CH_3), 2.68 (t, *J* = 7.3 Hz, 2H, CH_2), 5.29 (s, 1H, CH), 7.01-8.50 (m, 10H, aromatic-H), 13.76 (bs, 1H, NH). MS (EI), *m/z* (%) = 330 (M^+), 211, 188, 168, 143, 115, 77 (100), 51. Anal. Calcd. for $C_{21}H_{22}N_4$: C, 76.3; H, 6.7; N; 17.0. Found: C, 76.3; H, 6.7; N, 16.9.

General Procedure for Preparation Diene from Azines

2-Chloroacrylonitrile (10 mmol) was added to the solution of azine (5 mmol) in benzene (10 ml) and refluxed for 24 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature. The precipitate was filtered, and recrystallised from 95% ethanol to afford the pure diene compound.

4-(4-Bromophenyl)-2-(1-(quinolin-2-yl)propan-2-ylidene)pent-3-enenitrile (1g). 80% yield, m.p.: 159-160 °C (EtOH). υ_{max} (KBr): 1500, 1510, 1560, 1640, 2150 cm^{-1}. λ_{max} (95% EtOH): 500, 390, 270, 255. ^{13}C NMR ($CDCl_3$): δ (ppm) 15.2, 17.3, 36.4, 105.3, 118.9, 119.2, 120.0, 121.7, 124.0, 124.3, 126.4, 126,4, 127.3, 137.0, 138.6, 139.0, 139.1, 140.2, 143.5, 148.8, 153.7. ^1H NMR ($CDCl_3$): δ (ppm) 2.25 (m, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.42 (s, 2H, CH_2), 5.00 (s, 1H, CH), 6.71-8.68 (m, 10H, aromatic-H). MS (EI), *m/z* (%) = 403 (M^+),

405, 388, 356, 207, 192 (100), 166, 128, 89, 63, 44. Anal. Calcd. for $C_{23}H_{19}BrN_2$: C, 68.5; H, 4.7; N; 6.9. Found: C, 68.4; H, 4.7; N, 6.8.

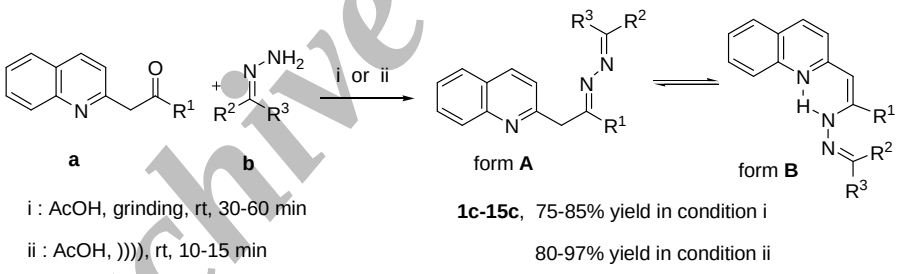
4-(4-Nitrophenyl)-2-(1-(quinolin-2-yl)propan-2-ylidene) pent-3-enenitrile (2g). 75% yield, m.p.: 168-169 °C (EtOH). υ_{max} (KBr): 1500, 1510, 1555, 1645, 2150 cm^{-1}. λ_{max} (95% EtOH): 518, 345, 284, 257. ^{13}C NMR ($CDCl_3$): δ (ppm) 16.8, 17.2, 38.6, 104.1, 116.8, 120.0, 121.9, 122.2, 124.6, 125.3, 126.6, 127,4, 128.9, 139.3, 139.5, 139.9, 140.6, 141.4, 143.9, 149.5, 150.4. ^1H NMR ($CDCl_3$): δ (ppm) 2.26 (m, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.57 (s, 2H, CH_2), 4.96 (m, 1H, CH), 6.59-8.12 (m, 10H, aromatic-H). MS (EI), *m/z* (%) = 369 (M^+), 321, 192, 162, 145, 117, 69 (100), 51. Anal. Calcd. for $C_{23}H_{19}N_3O_2$: C, 74.8; H, 5.2; N; 11.4. Found: C, 74.7; H, 5.1; N, 11.3.

4-(Pyridin-2-yl)-2-(1-(quinolin-2-yl)propan-2-ylidene) pent-3-enenitrile (3g). 75% yield, m.p.: 159-160 °C (EtOH). υ_{max} (KBr): 1505, 1510, 1560, 1640, 2140 cm^{-1}. λ_{max} (95% EtOH): 510, 350, 289, 254. ^{13}C NMR ($CDCl_3$): δ (ppm) 17.1, 18.1, 39.6, 105.1, 117.2, 121.0, 122.1, 123.2, 124.2, 125.4, 126.3, 129.4, 128,8, 129.6, 137.3, 138.4, 139.4, 139.5, 143.4, 144.6, 149.9, 151. ^1H NMR ($CDCl_3$): δ (ppm) 2.26 (m, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.46 (s, 2H, CH_2), 5.21 (m, 1H, CH), 6.72-8.55 (m, 10H, aromatic-H). MS (EI), *m/z* (%) = 325 (M^+), 283, 192, 169, 147, 119, 69 (100), 51. Anal. Calcd. for $C_{22}H_{19}N_3$: C, 81.2; H, 5.9; N; 12.9. Found: C, 81.3; H, 6.0; N, 12.8.

RESULTS AND DISCUSSION

Azines were synthesized from the reaction of some aromatic hydrazone with 2-ketoalkyl quinoline derivatives under solvent free reaction conditions by grinding. Moreover, these new azines were synthesized under ultrasonic irradiation in shorter reaction time (Scheme 1 and Table 1).

Due to having α-acidic hydrogen next to azine group and heterocycle ring, these azines had tautomeric forms and the ratio of each form was determined on the basis of ^{13}C NMR, ^1H NMR, UV and IR spectrum. This study showed that all



Scheme 1. Preparation of azines from 3-keto alkyl quinolines

Table 1. Ratio of Tautomeric Forms

Entry	R^1	R^2	R^3	A:B[a]	Entry	R^1	R^2	R^3	A:B[a]
1c	Me	H	*p*-$NO_2C_6H_4$	0:100	**9c**	Et	Me	*p*-PhC_6H_4	18:82
2c	Me	H	*o*-$NO_2C_6H_4$	0:100	**10c**	Et	H	*p*-$NO_2C_6H_4$	0:100
3c	Me	Me	*p*-BrC_6H_4	0:100	**11c**	Et	H	*o*-$NO_2C_6H_4$	0:100
4c	Me	Me	*p*-$NO_2C_6H_4$	0:100	**12c**	*n*-Pr	H	*o*-$NO_2C_6H_4$	0:100
5c	Me	Me	*p*-PhC_6H_4	15:85	**13c**	*n*-Pr	H	*p*-$NO_2C_6H_4$	0:100
6c	Me	Me	2-pyridyl	0:100	**14c**	*n*-Pr	Me	*p*-$NO_2C_6H_4$	0:100
7c	Et	Me	*p*-$NO_2C_6H_4$	0:100	**15c**	*n*-Pr	Me	2-Pyridyl	0:100
8c	Et	Me	2-pyridyl	0:100					

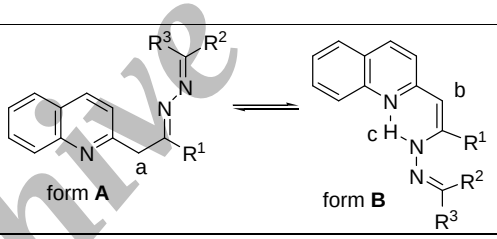
[a]The ratio of tautomeric forms was determined based on ^1H NMR spectra.

compounds exist mainly in enaminone form (form B) in $CDCl_3$. ^1H NMR spectra of compounds 1-15 (Table 2) showed the signals of the vinyl protons at δ = 5.2-5.5 ppm and the signals of methylene protons at δ = 4.1-4.2 ppm. The enaminone forms exhibited NH resonances in the range δ = 13.7-14.4 ppm due to the strong intramolecular hydrogen bonding between the NH proton and nitrogen. The ^{13}C NMR spectra of these compounds (Table 2) revealed signals in the range δ = 95-98 ppm for vinyl carbon and δ = 147-160 ppm for C=N carbon. The signals of methylene carbon appeared at δ = 35-37 ppm. In the IR spectra of the above compounds, the C=N band appeared in the range 1630-1637 cm^{-1} (Table 3) that was consistent with a previous report [13]. The UV spectrum of the compounds showed strong peaks at 300-470 nm which was also consistent with the conjugated system (Table 3).

In the course of our research we tried to obtain criss-cross or perhaps Diels-Alder cycloaddition products from reaction of some ofthese new azines with 2-chloroacrylonitrile as a dienophile. The reaction of **3c** with 2-chloroacrylonitrile took place under the same conditions as mentioned in the literature [12], but no product was formed and the starting material was obtained. Then this reaction was created under different conditions such as changing the solvent and reaction time (Table 4).

Our study indicated that this reaction was not possible in solvents such as ethanol, chloroform, ethyl acetate and a mixture of these solvents and also with different reaction times. However, in benzene solvent (a completely non-polar solvent) after 6 h, a new product was formed in a small amount. After 24 h, the new product with a yield above 85% was obtained. But what could this product be? Is it a criss-

Table 2. Some ^1H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) Chemical Shift of **1c-15c**



No	δ H (ppm)			δ C (ppm)			Ratio
	a	b	c	**a**	b	C=N	A:B
1c	-	5.4	14.3	-	98.8	150,159	0:100
2c	-	5.4	14.3	-	97.8	150,159	0:100
3c	-	5.4	13.7	-	97.2	151,159	0:100
4c	-	5.5	13.9	-	98.8	151,159	0:100
5c	4.1	5.3	13.8	35	96.9	151,158	15:85
6c	-	5.3	13.8	-	97.9	157,159	0:100
7c	-	5.4	13.9	-	97.3	156,159	0:100
8c	-	5.3	13.8	-	96.5	156,160	0:100
9c	4.2	5.3	13.8	36	95.3	157,160	18:82
10c	-	5.2	14.4	-	96.7	155,159	0:100
11c	-	5.2	14.4	-	96.4	155,159	0:100
12c	-	5.2	14.4	-	97.5	154,159	0:100
13c	-	5.2	14.4	-	97.8	154,159	0:100
14c	-	5.3	13.8	-	98.4	154,159	0:100
15c	-	5.2	13.8	-	97.5	157,159	0:100

Table 4. IR (KBr, cm^{-1}) and UV ($CHCl_3$, nm) Maximum Absorption Band of **1c-15c**

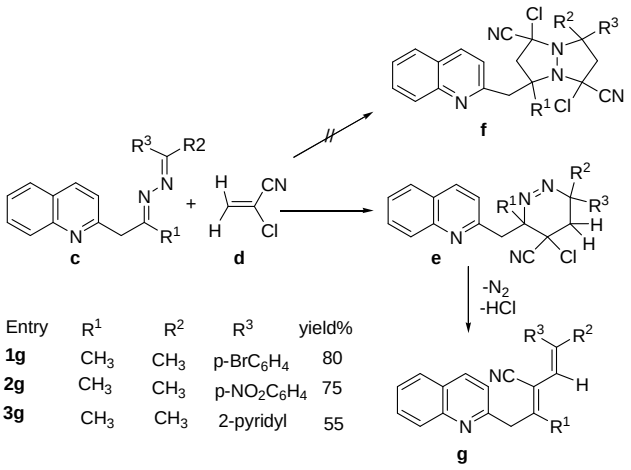
No.	IR (cm^{-1})		UV (nm)		
	C=N	C=C, Ar	λ_{max1}	λ_{max2}	λ_{max3}
1c	1635	1515, 1560, 1590	410	385	250
2c	1635	1510, 1550, 1575	415	384	250
3c	1630	1570, 1575, 1595	400	375	248
4c	1635	1565, 1570, 1590	420	380	252
5c	1637	1560, 1550, 1590	440	400	252
6c	1630	1540, 1555, 1593	413	391	249
7c	1636	1565, 1570, 1590	423	405	255
8c	1632	1545, 1550, 1592	415	389	253
9c	1632	1555, 1540, 1594	440	416	260
10c	1635	1545, 1545, 1590	420	410	251
11c	1636	1535, 1540, 1588	423	405	250
12c	1637	1510, 1555, 1595	415	390	253
13c	1635	1575, 1580, 1590	421	395	255
14c	1635	1550, 1560, 1585	425	413	256
15c	1630	1550, 1565, 1590	418	402	255

Table 4. The Effect of Solvent on Cycloaddition Reaction of Azine **3c**

No.	Solvent	Time (h)	Conversion (%)
1	EtOH	6	-
2	MeOH	6	-
3	$CHCl_3$	6	-
4	CH_3CO_2Et	6	-
5	$EtOH/CHCl_3$	6	-
6	Benzene	6	20
6	Benzene	24	80

cross cycloaddition product? Or, is it a Diels-Alder cycloaddition product?

Purification of **1g** (Scheme 2) was attained by recrystallization of the crude product mixture from ethanol. The observation of molecular ion peak at *m/z* = 403 and 405 in the mass spectrum of **1g** compound, almost rejected the formation of criss-cross cycloaddition product **f** as well as the Diels-Alder cycloaddition product. A more precise analysis of mass spectrum and expected fragmentation of Diels-Alder cycloaddition product showed that this product probably has been formed as an intermediate. Perhaps, in the first stage, Diels-Alder reaction has occurred and azo cyclic compound **e** has been made. This azo cyclic, due to its low stability, is decomposed in reaction conditions and makes a new diene system by eliminating HCl and N_2 molecules. It should be mentioned that in the process of reaction, the emission of HCl and N_2 gases was observed. Moreover, the nonexistence of chlorine in this product has been affirmed through qualitative



Entry	R^1	R^2	R^3	yield%
1g	CH_3	CH_3	p-BrC_6H_4	80
2g	CH_3	CH_3	p-$NO_2C_6H_4$	75
3g	CH_3	CH_3	2-pyridyl	55

Scheme 2. Cycloaddition of some azines with 2-chloro-acryllonitrile

elemental analysis. The mass molecule of the resulting product corresponds to the mass molecule shown in the mass spectrum. The suggested structure **1g-3g** compounds has been verified by spectroscopy methods such as ^{1}H and ^{13}C NMR, Mass, UV, IR and elemental analysis.

^{1}H NMR spectra of compounds **1g-3g** show the signals of the methylene protons at δ = 3.4-3.5 ppm, the signals of vinyl protons at δ = 4.9-5.2 ppm and the signals of methyl protons at δ = 2.2-2.4 ppm. It is worth mentioning that vinylic hydrogen, due to having allylic coupling with hydrogens of methyl group appears as a multiple. ^{13}C NMR spectra of compounds **1g-3g** show the signals of methylene carbon at δ = 36.4-39.6 ppm and the signals of methyl carbon at δ = 15.2-18.1 ppm. IR spectrum of these compounds shows the nitrile group absorption bond in 2150 cm^{-1} and C=C diene absorption system in 1640 cm^{-1}. According to UV spectrum data, these compounds clearly show the effect resulting from the conjugation of diene structure with aromatic cycle.

CONCLUSIONS

We have explored a simple, practical and efficient method for the preparation of some new azines. Based on the spectral data, all the compounds exclusively have the enaminone form (B form) in solution. The intramolecular hydrogen bonding is the only factor that can stabilize the enaminone form. New diene systems (**1g-3g**) may be accessed very readily by the reaction of azines with 2-chloroacrylonitrile, following the strategy outlined in Scheme 2.

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