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On reactions of triazoles: Synthesis of some new 3-aroyl-4, 5-dihydro-1H-1,2,4-triazole oximes and hydrazones

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ABSTRACT

A series of new 3-aroyl-4,5-dihydro-1H-1,2,4-triazoles oximes **(2a-l)** and hydrazones**(3a-j)** were synthesized from the reaction of corresponding 3-Aroyl-1,2,4-triazoles**(1a-l)**with hydroxylamine hydrochloride and hydrazine hydrate respectively. The structures of the synthesized compounds were confirmed by their spectral data and elemental analysis.

KEYWORDS

Oximes;
Hydrazones;
Tautomeric isomerism;
Hydroxylamine;
3-Aroyl-4,5-dihydro-1H-1,2,4-triazoles.

INTRODUCTION

The chemistry of triazole derivatives have been the subject of much interest in recent years due to use of such ring system as the core structure in many heterocyclic compounds covering wide range of pharmacological applications[1-9]. Recently, we have reported the synthesis of different substituted 1,2,4-triazoles employing nitrilimines and oximes or hydrazones[11-13]. In previous paper we reported the ring transformation of spirotriazoles to six-membered heterocycles[14]. In continuation of our work on the reaction of five membered aza heterocyclic compounds, we wish to report the reactivity of 3-aroyl-1,2,4-triazoles toward hydroxylamine and hydrazine.

EXPERIMENTAL

Melting points were determined on a Stuart Electrothermal Apparatus and are uncorrected. The IR spectra were obtained by using Satellite 3000 Mid infrared spectrophotometer in potassium bromide(KBr) pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer(400.13 MHz) at room temperature in $CDCl_3$ if not noted otherwise, using tetramethylsilane (TMS) as internal reference. All chemical shifts(δ) were reported in ppm from TMS.

Electron impact(EI) mass spectra were run on Shimadzu GCMS-QP1000 EX spectrometer at 70eV. Elemental analysis performed at Cairo University, Egypt and the results agreed with the calculated values within experimental errors. The 3-aroyl-1,2,4-triazoles(**1a-l)** were prepared according to previous described procedures[15].

General method for the synthesis of oximes(2a-l)

A solution of sodium acetate(0.025mol) was added to a stirred solution of 1,2,4-triazoles 1(0.005mol) and hydroxylamine hydrochloride(0.025mol) in absolute methanol(40ml). The reaction mixture was heated under reflux for 2-4h with efficient stirring. The solvent was then removed under vacuum and cold water(100ml) was added to the residue. The precipitated crude solid was collected, washed several times with water, dried and recrystallized from ethanol affording the desired oximes 2. The following compounds were synthesized using this method:

4-Acetylamino-1-(4-chlorophenyl)-5-methyl-3-(2-naphthoyl)-4,5-dihydro-1H-1,2,4-triazole oxime(2a)

Yield: 75%; m.p. 131-132^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.2/9.1(1H, s, OH), 8.8(1H, s, NH), 8.7-6.9 (4H, m, Ar-H), 5.5/5.2(1H, q, CH), 2.0/1.9(3H, s, CH_3), 1.6/1.5(3H, d, CH_3); ^{13}C NMR(δ/ppm): 177.5/173.3(N-C=O), 152.4/150.3(C=NOH), 146.4/145.9(triazole C-3), 142.2-115.4(C=C Ar), 81.0/80.5 (triazole C-5), 21.3/20.7(CH_3), 20.2 /20.0(CH_3); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1690(N-C=O), 1625, 1595(C=N); MS(M+=421/423); $C_{22}H_{20}ClN_5O_2$ (421.89): calcd. C 62.63, H 4.78, N 16.60. found: C 62.50, H 4.90, N 16.70.

4-Benzoylamino-1-(4-chlorophenyl)-5-ethyl-3-(2-naphthoyl)-4,5-dihydro-1H-1,2,4-triazole oxime(2b)

Yield: 79%; m.p. 154-156^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.3/9.7(1H, s, OH), 9.2/9.0(1H, s, NH), 8.8-7.0(4H, m, Ar-H), 5.4/5.1(1H, t, CH), 1.9/1.8(2H, m, CH_2), 1.0/0.9(3H, t, CH_3); ^{13}C NMR(δ/ppm): 169.3/167.1(N-C=O), 152.8/150.6(C=NOH), 146.3/146.2 (triazole C-3), 143.4-114.3(C=C Ar), 84.3/83.7 (triazole C-5), 26.40/25.6(CH_2), 11.2/11.0(CH_3); IR (ν/cm^{-1}): 3400-3200(NH, OH), 1675(N-C=O), 1620, 1590(C=N); MS(M+·=497/499); $C_{28}H_{24}ClN_5O_2$ (497.99): calcd. C 67.53, H 4.86, N 14.06. found: C 67.80, H 5.10, N 13.90.

4-Benzoylamino-1-(4-chlorophenyl)-5-cyclohexyl-3-(2-naphthoyl)-4,5-dihydro-1H-1,2,4-triazole oxime (2c)

Yield: 70%; m.p. 146-148^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.3/9.8(1H, s, OH), 9.3/8.9(1H, s, NH), 8.7-6.9(4H, m, Ar-H), 5.4/5.2(1H, d, CH), 1.9-1.2(11H, m, cyclohexyl); ^{13}C NMR(δ/ppm): 168.9/157.0(N-C=O), 152.8/151.2(C=NOH), 146.2/146.0(triazole C-3), 143.2-114.90(C=C Ar), 87.3/85.7(triazole C-5), 40.4-24.7(cyclohexyl carbons); IR(ν/cm^{-1}): 3400-3000(NH, OH), 1675(N-C=O), 1625, 1590(C=N); MS(M+·=551/553); $C_{32}H_{30}ClN_5O_2$(552.08): calcd. C 69.62, H 5.48, N 12.69. found: C 69.90, H 5.30, N 12.80.

4-Benzoylamino-1-(4-chlorophenyl)-5-methyl-3-(2-thenoyl)-4,5-dihydro-1H-1,2,4-tri-azole oxime (2d)

Yield: 73%; m.p. 134-136^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.3/9.3(1H, s, OH), 8.8/8.5(1H, s, NH), 8.3-7.2(4H, m, Ar-H), 5.3/5.0(1H, q, CH), 1.5/1.3(3H, d, CH_3); ^{13}C NMR(δ/ppm): 170.6/168.9(O-C=O), 153.4/152.0(C=NOH), 146.5/146.3(triazole C-3), 141.8-115.4(C=C Ar), 84.6/82.3(triazole C-5), 20.7/20.5(CH_3); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1670 (O-C=O), 1630, 1595(C=N); MS(M+·=439/441); $C_{21}H_{18}ClN_5O_2S$(439.93): calcd. C 57.34, H 4.12, N 15.92. found: C 57.10, H 4.30, N 16.20.

1-(4-Chlorophenyl)-5-ethyl-4-methoxycarbonyl amino-3-(2-thenoyl)-4,5-dihydro-1H-1,2,4-triazole oxime (2e)

Yield: 71%; m.p. 129-130^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.0/8.9(1H, s, OH), 7.0/6.9(1H, s, NH), 8.3-7.2(4H, m, Ar-H), 5.2/5.0(1H, t, CH), 3.7/3.6(3H, s, OCH_3), 2.0/1.8(2H, m, CH_2), 1.0/0.80(3H, t, CH_3); ^{13}C NMR(δ/ppm): 158.6/157.4(O-C=O), 153.7/152.4(C=NOH), 146.1/145.2(triazole C-3), 141.0-113.9(C=C Ar), 84.8/84.1(triazole C-5), 53.2/52.6(OCH_3), 26.8/26.3(CH_2), 11.2/11.0(CH_3), 13.00/11.27(CH_3C=N); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1730(O-C=O), 1635, 1597(C=N); MS(M+·=407/409); $C_{17}H_{18}ClN_5O_3S$(407.88): C 50.06., H 4.45., N 17.17. found: C 49.80, H 4.60, N 17.30.

4-Acetylamino-1-(4-chlorophenyl)-5-cyclohexyl-3-(2-thenoyl)-4,5-dihydro-1H-1,2,4-triazole oxime (2f)

Yield: 74%; m.p. 166-168^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.1/8.9(1H, s, OH), 8.8/8.5(1H, s, NH), 8.3-7.2(4H, m, Ar-H), 5.4/5.2(1H, d, CH), 2.1/1.9(3H, s, OCH_3), 1.8/1.1(11H, m, cyclohexyl); ^{13}C NMR(δ/ppm): 178. 2/176.4(N-C=O), 154.1/152.7(C=NOH), 146.5/145.9(triazole C-3), 141.4-114.2(C=C Ar), 87.4/85.1(triazole C-5), 41.0/24.6(cyclohexyl carbons), 21.5/20.8(CH_3); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1690(N-C=O), 1635, 1597(C=N); MS (M+·=445/447); $C_{21}H_{24}ClN_5O_2S$(445.97): calcd. C 56.56, H 5.42, N 15.70. found: C 56.40, H 5.60, N 15.80.

4-Acetylamino-1-(4-chlorophenyl)-3-(2-furoyl)-5-methyl-4,5-dihydro-1H-1,2,4-tri-azole oxime (2g)

Yield: 72%; m.p. 148-150 °C(from EtOH); ^{1}H NMR(δ/ppm): 10.1/9.0(1H, s, OH), 8.7/8.4(1H, s, NH), 8.2-7.1(4H, m, Ar-H), 5.4/5.2(1H, q, CH), 1.9/1.8(3H, s, OCH_3), 1.6/1.5(3H, d, CH_3); ^{13}C NMR(δ/ppm): 178.1/177.0(N-C=O), 155.3/153.4(C=NOH), 146.4/146.0(triazole C-3), 141.2-115.3(C=C Ar), 80.9/80.1(triazole C-5), 21.3/20.9(CH_3), 20.2/20.0(CH_3); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1680(N-C=O), 163, 1590(C=N); MS($M^{+\cdot}$=361/363); $C_{16}H_{16}ClN_5O_3$ (361.79): calcd. C 53.12, H 4.46, N 19.36. found: C 52.90, H 4.60, N 19.40.

4-Benzoylamino-1-(4-chlorophenyl)-5-ethyl-3-(2-furoyl)-4,5-dihydro-1H-1,2,4-tri-azole oxime (2h)

Yield: 75%; m.p. 133-134 °C(from EtOH); ^{1}H NMR(δ/ppm): 9.9/9.4(1H, s, OH), 8.9/8.7(1H, s, NH), 8.4-7.2(4H, m, Ar-H), 5.4/5.1(1H, q, CH), 1.9/1.8(2H, m, CH_2), 1.2/1.0(3H, t, CH_3); ^{13}C NMR(δ/ppm): 169.0/168.5(N-C=O), 153.5/152.0(C=NOH), 146.1/145.7(triazole C-3), 141.0-114.8(C=C Ar), 85.2/85.0 (triazole C-5), 27.2/26.7(CH_2), 11.5/11.3(CH_3); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1670(N-C=O), 1640, 1600(C=N); MS($M^{+\cdot}$=437/439); $C_{22}H_{20}ClN_5O_3$ (437.89): calcd. C 60.35, H: 4.60, N: 15.99. found: C 60.10, H 4.50, N 16.20.

4-methoxycarbonylamino-1-(4-chlorophenyl)-5-cyclohexyl-3-(2-furoyl)-4,5-dihydro-1H-1,2,4-triazole oxime (2i)

Yield: 72%; m.p. 197-198 °C(from EtOH); ^{1}H NMR(δ/ppm): 9.8/9.2(1H, s, OH), 7.0/6.9(1H, s, NH), 8.3-7.2(4H, m, Ar-H), 5.3/5.1(1H, d, CH), 3.6/3.5(3H, s, OCH_3), 1.9/1.2(11H, m, cyclohexyl); ^{13}C NMR(δ/ppm): 159.4/158.5(O-C=O), 154.3/153.0(C=NOH), 145.8/145.0(triazole C-3), 141.3-115.6(C=C Ar), 86.9/85.7(triazole C-5), 53.8/52.6(OCH_3), 41.3-24.7(cyclohexyl carbons); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1725(O-C=O), 1635, 1598(C=N); MS($M^{+\cdot}$= 445/447); $C_{21}H_{24}ClN_5O_4$(445.91): calcd. C 56.57, H 5.43, N 15.71. found: C 56.40, H 5.50, N 15.80.

4-Acetylamino-3-benzoyl-5-methyl-1-(4-chlorophenyl)-4,5-dihydro-1H-1,2,4-tri-azole oxime (2j)

Yield: 72%; m.p. 144-146^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.0/9.5(1H, s, OH), 8.7/8.4(1H, s, NH), 8.1-6.8(4H, m, Ar-H), 5.5/5.2(1H, q, CH), 1.9/1.8(3H, s, OCH_3), 1.6/1.5(3H, d, CH_3); ^{13}C NMR(δ/ppm): 179.4/178.2(N-C=O), 152.5/151.0(C=NOH), 146.7/146.1(triazole C-3), 141.3-114.8(C=C Ar), 81.2/80.5 (triazole C-5), 21.1/20.8(CH_3), 20.2/19.9(CH_3); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1685(O-C=O), 1630, 1598(C=N); MS($M^{+\cdot}$=371/373) $C_{18}H_{18}ClN_5O_2$ (371.83): calcd. C 58.15, H 4.88, N: 18.83. found: C 57.90, H 5.00, N 18.70.

3-Benzoyl-4-benzoylamino-1-(4-chlorophenyl)-5-ethyl-4,5-dihydro-1H-1,2,4-tri-azole oxime (2k)

Yield: 72%; m.p. 151-152^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.2/9.7(1H, s, OH), 9.2/8.8(1H, s, NH), 8.2-7.0(4H, m, Ar-H), 5.4/5.2(1H, t, CH), 1.9/1.80(2H, m, CH_2), 1.1/0.9(3H, t, CH_3); ^{13}C NMR(δ/ppm): 169.4/168.5(N-C=O), 152.3/150.7(C=NOH), 146.5/146.0(triazole C-3), 141.0-114.6(C=C Ar), 84.9/84.2 (triazole C-5), 27.2/26.3(CH_2), 11.2/10.9(CH_3); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1675(N-C=O), 1635, 1598(C=N); MS($M^{+\cdot}$=447/449); $C_{24}H_{22}ClN_5O_2$ (447.93): C 64.36, H 4.95, N 15.63. found: C 64.20, H 5.10, N 15.80.

3-Benzoyl-4-benzoylamino-1-(4-chlorophenyl)-5-cyclohexyl-4,5-dihydro-1H-1,2,4-triazole oxime (2l)

Yield: 72%; m.p. 175-177^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 10.3/9.8(1H, s, OH), 9.0/8.7(1H, s, NH), 8.2-7.1(4H, m, Ar-H), 5.4/5.2(1H, q, CH), 1.9/1.1(11H, m, cyclohexyl); ^{13}C NMR(δ/ppm): 169.1/168.2(N-C=O), 152.8/151.0(C=NOH), 146.3/145.6(triazole C-3), 141.0-114.8(C=C Ar), 86.9/85.7(triazole C-5), 41.2-24.2(cyclohexyl carbons); IR(ν/cm^{-1}): 3400-3200(NH, OH), 1670(O-C=O), 1630, 1598(C=N); MS($M^{+\cdot}$=502/504); $C_{28}H_{28}ClN_5O_2$(502.02): C 66.99, H 5.62, N 13.95. found: C 67.20, H 5.50, N 14.10.

Synthesis of 3-acetyl-1,2,4-triazoles hydrazones (3a-j)

General method: Hydrazine monohydrate 98% (0.02mol) was added to a stirred solution of 1,2,4-triazoles 1(0.004mol) in absolute ethanol(50ml) with few drops of glacial acetic acid. The reaction mixture was heated under reflux for **(2-3h)**. The solvent was then removed under vacuum. The residual solid product was collected and recrystallized from ethanol or methanol affording the desired hydrazones **(3)**. The following compounds were synthesized using this method:

4-Acetylamino-1-(4-chlorophenyl)-3-(2-naphthoyl)-5-methyl-4,5-dihydro-1H-1,2,4-triazole hydrazone (3a)

Yield: 60%; m.p. 133-134^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 8.9(1H, s, NH), 8.5-6.95(5H, m, Ar-H), 5.6(2H, s, NH$_2$), 5.3(1H, q, CH), 2.0(3H, s, CH$_3$), 1.5(3H, d, CH$_3$); ^{13}C NMR(δ/ppm): 177.6(N-C=O), 147.5 (C=NNH$_2$), 145.3(triazole C-3), 142.8-115.7(C=C Ar), 81.0(triazole C-5), 20.9(CH$_3$), 20.1(CH$_3$);IR(ν/cm^{-1}): 3414, 3290, 3227(NH, NH$_2$), 1730(O-C=O), 1598(C=N); MS(M+˙=420/422); $C_{22}H_{21}ClN_6O$ (420.91): calcd. C 62.78, H 5.03, N 19.97. found: C 63.00, H 4.90, N 20.10.

4-Benzoylamino-1-(4-chlorophenyl)-5-ethyl-3-(2-naphthoyl)-4,5-dihydro-1H-1,2,4-triazole hydrazone (3b)

Yield: 65%; m.p. 142-144^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 9.2(1H, s, NH), 8.5-7.0(4H, m, Ar-H), 5.6(2H, s, NH$_2$), 5.1(1H, t, CH), 1.85(2H, m, CH$_2$), 0.9(3H, d, CH$_3$); ^{13}C NMR(δ/ppm): 168.9(N-C=O), 147.8(C=NNH$_2$), 145.3(triazole C-3), 143.0-114.8(C=C Ar), 85.3(triazole C-5), 26.8(CH$_2$), 10.8 (CH$_3$); IR(ν/cm^{-1}): 3425, 3250, 3243(NH, NH$_2$), 1734 (O-C=O), 1605(C=N); MS(M+˙=496/498); $C_{28}H_{25}ClN_6O$(497.00): calcd. C 67.67, H 5.07, N 16.91. found: C 67.50, H 4.80, N 17.00.

4-Benzoylamino-1-(4-chlorophenyl)-5-methyl-3-(2-thenoyl)-4,5-dihydro-1H-1,2,4-triazole hydrazone (3c)

Yield: 50%; m.p. 134-135^{0}C(from MeOH); ^{1}H NMR (δ/ppm): 9.1(1H, s, NH), 8.3-7.1(4H, m, Ar-H), 5.5 (2H, s, NH$_2$), 5.2(1H, q, CH), 1.6(3H, d, CH$_3$); ^{13}C NMR(δ/ppm): 168.5(N-C=O), 147.7(C=NNH$_2$), 144.3(triazole C-3), 141.5-115.3(C=C Ar), 81.2 (triazole C-5), 20.7(CH$_3$); IR(ν/cm^{-1}): 3414, 3398, 3241(NH, NH$_2$), 1731(O-C=O), 1595(C=N); MS (M+˙=438/440); $C_{21}H_{19}ClN_6OS$(438.94): calcd. C 57.46, H 4.36, N: 19.15. found: C 57.60, H 4.50, N 19.10.

1-(4-Chlorophenyl)-5-ethyl-4-methoxycarbonyl amino-3-(2-thenoyl)-4,5-dihydro-1H-1,2,4-triazole hydrazone (3d)

Yield: 86%; m.p. 149-151^{0}C(from MeOH); ^{1}H NMR (δ/ppm): 6.8(1H, s, NH), 8.3-7.0(4H, m, Ar-H), 5.5(2H, s, NH$_2$), 5. 2(1H, t, CH), 3.6(3H, s, OCH$_3$), 1.9(2H, m, CH$_2$), 1.0(3H, t, CH$_3$); ^{13}C NMR(δ/ppm): 156.8(O-C=O), 147.9(C=NNH$_2$), 144.5(triazole C-3), 141.6-114.3(C=C Ar), 85.7(triazole C-5), 52.7(OCH$_3$), 26.8(CH$_2$), 10.9(CH$_3$); IR(ν/cm^{-1}): 3315, 3248, 3239(NH, NH$_2$), 1720(O-C=O), 1595(C=N); MS(M+˙=406/408); $C_{17}H_{19}ClN_6O_2S$ (406.90): calcd. C 50.18, H: 4.71, N: 20.65. found: C 49.90, H 4.80, N 20.70.

4-Acetylamino-1-(4-chlorophenyl)-3-(2-furoyl)-5-methyl-4,5-dihydro-1H-1,2,4-tri-azole hydrazone (3e)

Yield: 72%; m.p. 128-130 ^{o}C(from MeOH); ^{1}H NMR (δ/ppm): 8.7(1H, s, NH), 8.2-7.2(4H, m, Ar-H), 5.5 (2H, s, NH$_2$), 5.1(1H, q, CH), 1.6(3H, d, CH$_3$); ^{13}C NMR(δ/ppm): 176.9(N-C=O), 146.8(C=NNH$_2$), 143.9(triazole C-3), 142.3-115.2(C=C Ar), 80.9 (triazole C-5), 20.6(CH$_3$), 19.8(CH$_3$); IR(ν/cm^{-1}): 3300, 3287, 3244(NH, NH$_2$), 1716(O-C=O), 1590 (C=N); MS(M+=360/362); $C_{16}H_{17}ClN_6O_2$(360.81): calcd. C 53.26, H 4.75, N 23.29. found: C 53.00, H 4.90, N 23.20.

4-Benzoylamino-1-(4-chlorophenyl)-5-ethyl-3-(2-furoyl)-4,5-dihydro-1H-1,2,4-tri-azole hydrazone (3f)

Yield: 72%; m.p. 164-165^{0}C(from MeOH); ^{1}H NMR (δ/ppm): 9.1(1H, s, NH), 8.1-6.9(4H, m, Ar-H), 5.6 (2H, s, NH$_2$), 5.1(1H, q, CH), 1.9(2H, m, CH$_2$), 0.95 (3H, t, CH$_3$); ^{13}C NMR(δ/ppm): 169.2(N-C=O), 146.8(C=NNH$_2$), 143.8(triazole C-3), 142.33-115.23 (C=C Ar), 85.4(triazole C-5), 27.0(CH$_2$), 11.1(CH$_3$); IR(ν/cm^{-1}): 3300, 3287, 3244(NH, NH$_2$), 1716(O-C=O), 1590(C=N); MS(M+˙=436/438); $C_{22}H_{21}ClN_6O_2$(436.90): calcd. C 60.48, H 4.84, N 19.24. found: C 60.60, H 5.00, N 19.10.

1-(4-chlorophenyl)-5-cyclohexyl-3-(2-furoyl)-4-methoxycarbonylamino-4,5-di-hydro-1H-1,2,4-triazole hydrazone (3g)

Yield: 72%; m.p. 138-140 ^{o}C(from MeOH); ^{1}H NMR (δ/ppm): 7.0(1H, s, NH), 8.4-7.2(4H, m, Ar-H), 5.5 (2H, s, NH$_2$), 5.2(1H, d, CH), 3.7(3H, s, CH$_3$), 1.9-1.1(11H, m, cyclohexyl); ^{13}C NMR(/ppm): 156.9(O-C=O), 146.7(C=NNH$_2$), 143.9(triazole C-3), 142.1-115.1(C=C Ar), 88.2(triazole C-5), 52.6(OCH$_3$), 41.1-24.4(cyclohexyl carbons); IR(ν/cm^{-1}): 3300, 3287, 3244(NH, NH_2), 1716(O-C=O), 1590(C=N); MS(M+˙=444/446); $C_{21}H_{25}ClN_6O_3$(444.92): calcd. C 56.69, H 5.66, N 18.89. found: C 56.50, H 5.80, N 19.00.

4-Acetylamino-3-benzoyl-1-(4-chlorophenyl)-5-methyl-4,5-dihydro-1H-1,2,4-tri-azole hydrazone (3h)

Yield: 72%; m.p. 171-172^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 8.8(1H, s, NH), 8.1-6.9(4H, m, Ar-H), 5.5(2H, s, NH_2), 5.2(1H, q, CH), 2.0(3H, s, CH_3), 1.6(3H, d, CH_3); ^{13}C NMR(δ/ppm): 177.2(N-C=O), 147.1 (C=NNH_2), 145.6(triazole C-3), 142.3-114.9(C=C Ar), 81.2(triazole C-5), 20.6(CH_3), 19.7(CH_3); IR(ν/cm^{-1}): 3300, 3287, 3244(NH, NH_2), 1716(O-C=O), 1590(C=N); MS(M+˙=370/372); $C_{18}H_{19}ClN_6O$ (370.84): calcd. C 58.30, H 5.16, N 22.66. found: C 58.50, H 5.10, N 22.60.

4-Benzoyl-3-benzoylamino-1-(4-chlorophenyl)-5-ethyl-4,5-dihydro-1H-1,2,4-tri-azole hydrazone (3i)

Yield: 72%; m.p. 143-145^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 9.2(1H, s, NH), 8.2-7.1(4H, m, Ar-H), 5.5(2H, s, NH_2), 5.1(1H, t, CH), 1.9(2H, m, CH_2), 1.0(3H, t, CH_3); ^{13}C NMR(δ/ppm): 169.2(N-C=O), 147.2 (C=NNH_2), 145.4(triazole C-3), 142.4-115.0(C=C Ar), 85.1(triazole C-5), 26.8(CH_2), 10.9(CH_3); IR(ν/cm^{-1}): 3300, 3287, 3244(NH, NH_2), 1716(O-C=O), 1590(C=N); MS(M+˙=446/448); $C_{24}H_{23}ClN_6O$ (446.94): calcd. C 64.50, H 5.19, N 18.80. found: C 64.40, H 5.30, N 19.00.

4-Benzoyl-3-benzoylamino-1-(4-chlorophenyl)-5-cyclohexyl-4,5-dihydro-1H-1,2,4-triazole hydrazone (3j)

Yield: 72%; m.p. 188-190^{0}C(from EtOH); ^{1}H NMR(δ/ppm): 9.3(1H, s, NH), 8.2-7.2(4H, m, Ar-H), 5.6(2H, s, NH_2), 5.2(1H, q, CH), 2.0-1.2(11H, m, cyclohexyl); ^{13}C NMR(δ/ppm): 169.4(N-C=O), 147.4(C=NNH_2), 145.6(triazole C-3), 142.2-115.5(C=C Ar), 88.4 (triazole C-5), 41.5-24.6(cyclohexyl carbons); IR (ν/cm^{-1}): 3300, 3287, 3244(NH, NH_2), 1716(O-C=O), 1590(C=N); MS(M+˙=500/502); $C_{28}H_{29}ClN_6O$ (501.04): calcd. C 67.12, H 5.83, N 16.77. found: C 66.90, H 6.00, N 16.60.

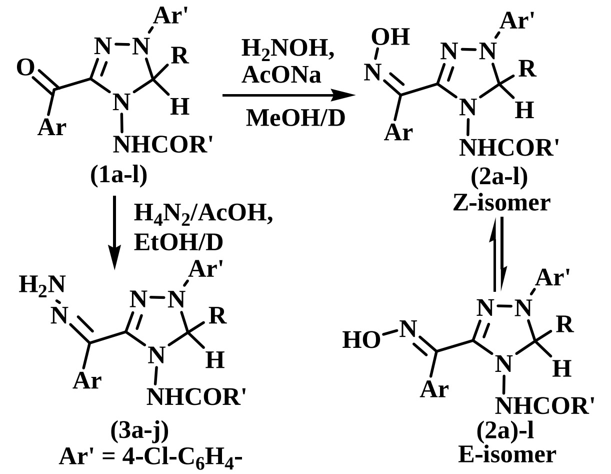
RESULTS AND DISCUSSION

3-aroyl-4,5-dihydro-1H-1,2,4-triazoles 1a-l were prepared by the reaction of C-aroyl-N-arylnitrilimines with alkanal or cycloalkanal hydrazones[15]. The treatment of these triazoles**(1a-l)** with hydroxylamine hydrochloride in presence of sodium acetate in refluxing methanol afforded oxime derivatives**(2a-l)**(SCHEME 1). No ring transformation was observed as occurred with spirotriazoles which reported in previous paper[14].

On the other hand, the condensation reaction of 3-aroyl-4,5-dihydro-1H-1,2,4-triazoles 1a-l with five fold of hydrazine hydrate in presence of catalytic amount of acetic acid in refluxing ethanol gave the corresponding hydrazone derivatives **(3a-j)** (SCHEME 1).

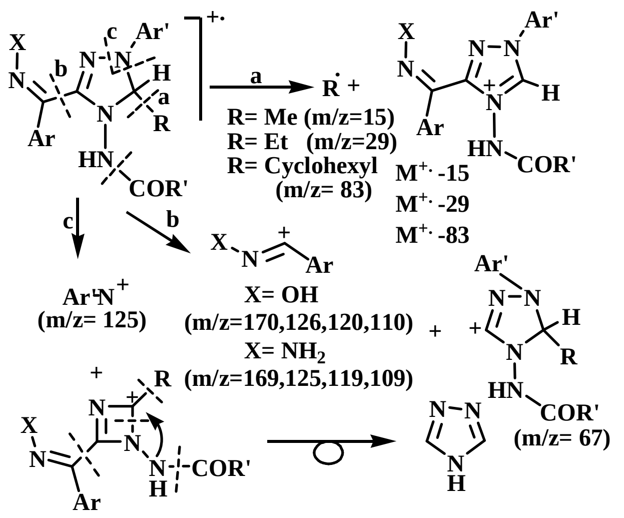
Spectral data analysis

The structure of synthesized 1,2,4-triazole oximes **(2a-l)** was assigned by their spectral data and elemental microanalysis(experimental section). In their ^{1}H NMR spectra the signal of hydroxyl proton(C=NOH) resonates at 10.3-9.0ppm and NH proton observed at 9.0-



SCHEME 1: Synthetic pathway of compounds (2a-l) and (3a-j)

Entery	Ar	R	R'	Entery	Ar	R	R'
2a	2-Naphthyl	CH_3	CH_3	2l	Ph	C_6H_{11}	Ph
2b	2-Naphthyl	C_2H_5	Ph	3a	2-Naphthyl	CH_3	CH_3
2c	2-Naphthyl	C_6H_{11}	Ph	3b	2-Naphthyl	C_2H_5	Ph
2d	2-Thienyl	CH_3	Ph	3c	2-Thienyl	CH_3	Ph
2e	2-Thienyl	C_2H_5	OCH_3	3d	2-Thienyl	C_2H_5	OCH_3
2f	2-Thienyl	C_6H_{11}	CH_3	3e	2-Furyl	CH_3	CH_3
2g	2-Furyl	CH_3	CH_3	3f	2-Furyl	C_2H_5	Ph
2h	2-Furyl	C_2H_5	Ph	3g	2-Furyl	C_6H_{11}	OCH_3
2i	2-Furyl	C_6H_{11}	OCH_3	3h	Ph	CH_3	CH_3
2j	Ph	CH_3	CH_3	3i	Ph	C_2H_5	Ph
2k	Ph	C_2H_5	Ph	3j	Ph	C_6H_{11}	Ph



SCHEME 2: Fragmentation pattern of compounds (2a-l) and (3a-j)

7.0ppm. The structures of these oximes **(2a-l)** were supported by ^{13}C NMR spectra, which displayed the characteristic signals for imino carbon(Ar-C=N) at about 154-150ppm instead of 185-173ppm for(C=O) in compounds **(1a-l)**. The signal doubling is observed in both ^{1}H and ^{13}C NMR spectra of synthesized oximes due to Z:E tautomeric isomerism around C=N[16]. The entire ^{1}H and ^{13}C NMR data were presented in experimental section.

The IR spectra of oximes **(2a-i)** revealed absorption bands for OH and NH in the 3400-3200cm^{-1} region, and C=N stretching band appears in the region 1630-1600cm^{-1}. The electron impact(EI) mass spectra of compounds **(2a-l)** displayed the corrected molecular ions in accordance with the suggested structures. The base peak of these compounds occurs at($M^{+\cdot}$-15, $^{\cdot}CH_3$) for compounds containing methyl moiety,($M^{+\cdot}$-29, $^{\cdot}CH_2CH_3$) for compounds containing ethyl moiety, ($M^{+\cdot}$-83, $^{\cdot}C_6H_{11}$) for compounds containing cyclohexyl moiety and another important fragments Ar'N^{+}, Ar-$^{+}$C=NOH and $^{+}$COR'[17](SCHEME 2).

The structure assignment of synthesized hydrazones is based on analytical and spectroscopic data (experimental section). The ^{1}H NMR spectra of these compounds**(3a-j)** revealed a characteristic signal of(NNH_2) protons at 5.6-5.5ppm. In ^{13}C NMR spectra, the carbon of($C=NNH_2$) appeared at about 148 ppm. The IR spectra of compounds **(3a-j)** showed three NH absorption bands in the region 3400-3200cm^{-1} and two absorption bands for two C=N in the region 1620-1590cm^{-1}. The mass spectra of produced hydrazones **(3a-j)** displayed the correct molecular ions suggested by their formulas. The fragmentation occurs in similar manner of oximes **(2a-l)**, in addition to Ar-$^{+}$C=NNH_2 fragment[17](SCHEME 2).

In conclusion, the oximation and hydrazonation occurred on true carbonyl(ArCO-) at C-3 of triazoles ring instead of carbonyl of amide group(R'CONH-) at C-4 of those azoles.

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