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SYNTHESIS OF NOVEL FUSED PYRAZOLO[4,3-*d*][1,2,3]TRIAZIN-4-ONES: APPLICATION OF DIAZONIUM ION INDUCED HETEROCYCLISATION IN THE SYNTHESIS OF NOVEL HETEROCYCLES

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ABSTRACT

Synthesis of novel 10-chloro-3-methyl-1-*n*-propyl-4,5,7,12-tetrahydro-*H*-benzo[*d*]pyrazolo [3', 5': 5,6][1,2,3] triazino [1,2-a] [1, 2, 3] triazin-4, 12-dione (5) and 11-methyl-9-*n*-propyl-5,6,11,12-tetrahydro-8*H*-benzo[*e*] pyrazolo[4′,3′: 4, 5] [1, 2, 3] triazino [1,2-*a*] [1, 2, 3] triazin-5, 12-dione (11) by reacting 4-*N*-(2-amino-5-chlorobenzoyl)amino-1-methyl-3-*n*-propylpyrazole-5-carboxamide (4) and 5-*N*-(2-carboxamidophenyl)-1-methyl-4-amino-3-*n*-propyl-1*H*-pyrazole-5-carboxamide (10) with sodium nitrite in hydrochloric acid respectively is reported.

Key Words: Tetracyclic, Pyrazole**,** Fused pyrazolo [4, 3*d*] [1, 2, 3] triazine, Diazotization, Cyclization, Characterization.

INTRODUCTION

Synthesis of pyrazolo[4,3-*d*] [1,2,3]triazines derivatives were reported in the literature (Long RA, 1970; Buchaman JG, 1981; Baraldi, PG *et al.*, 1988; Kumar, KS *et al.*, 2012; Daniel M *et al.*, 2009. Manfredini and co-workers synthesised pyrazolo[4,3-d][1,2,3]triazin-4-one nucleosides and evaluated their cytostatic and antiviral activities (Manfredini S *et al.*, 1992). Since no work is reported, we got interested in the synthesis of novel fused pyrazolo[4,3-*d*][1,2,3]triazine derivatives. We report herein a facile and efficient synthesis of 10-chloro-3-methyl-1-*n*-propyl-4,5,7,12-tetrahydro-3H-benzo-[*d*] pyrazolo[3',4':5,6][1,2,3]triazino[1,2-*a*][1,2,3]triazin-4,12-dione (5) and 11-methyl-9-n- propyl-5,6,11,12-tetrahydro-8H-benzo[*e*]pyrazolo[4',3':4,5][1,2,3]triazino[1,2-*a*][1,2,3] triazin-5,12-dione (11) from readily accessible methyl 4-amino-1-methyl-3-*n*-propylpyrazole-5-carboxylate (1) and 1-methyl-4-nitro-3-*n*-propyl pyrazole-5-carboxylic acid (8) respectively.

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EXPERIMENTAL

All the melting points mentioned were determined in capillaries using Polman digital melting point apparatus (model-mp-96) and reported in degree centigrade. UV spectra were taken in methanol on Shimadzu 1601 PC model UV visible spectrometer, and the absorption maxima are presented in nm. Infrared spectra were obtained in KBr pellets on Shimadzu 435 instrument. The positions of absorptions are quoted to ± 2.5 cm^{-1}. ^{1}H-NMR Spectra were recorded on Varian Gemini (200 MHz) and ^{13}C-NMR spectra on Varian Gemini (50 MHz) spectrometers with TMS as internal standard. The solvent in which the NMR spectrum was recorded is indicated at the appropriate places. Mass spectra were recorded on Perkin-Elmer Hitachi RMU-6L instrument on direct inlet probe.

Preparation of methyl 4-N-(5-chloro-2-nitrobenzoyl) amino-1-methyl-3-n-propylpyrazole-5-carboxylate (2)

A mixture of 5-chloro-2-nitrobenzoic acid (1.97 g, 0.01 mol) and thionyl chloride (10 ml) was refluxed for 3h. The reaction mixture was cooled and excess thionyl chloride was removed in *vacuo*. The oily residue was dissolved in benzene (10 mL) and this acid chloride was cautiously added to the solution of methyl 4-amino-1-methyl-3-*n*-propylpyrazole-5-carboxylate (1, 1.82 g, 0.01 mol) in dry benzene (10 mL) at 20-25^{o}C. The precipitated methyl 4-*N*-(5-chloro-2-nitrobenzoyl)amino-1-methyl-3-*n*-propylpyrazole-5-carboxylate (2**)** was collected by filtration and recrystallized from methanol, yield 93%; mp. 205^{o}C; IR (KBr, cm^{-1}): 3228, 2959, 2869, 1725, 1662; ^{1}H-NMR ($CDCl_3$+DMSO-d_6, δ ppm): 0.82 (t, 3H, CH_3), 1.48 (m, 2H, CH_2), 2.35 (t, 2H, CH_2), 3.7 (s, 3H, OCH_3), 3.9 (s, 3H, N-CH_3), 7.4 (brs, 2H, Ar-H), 7.8 (brs, 1H, Ar-H), 9.5 (s, 1H, NH); MS: m/e 380 (M+), 333, 301, 195, 164, 136, 100.

Preparation of methyl 4-N-(2-amino-5-chlorobenzoyl)amino-1-methyl-3-n-propyl-1H pyrazole-5-carboxylate (3)

To a solution of ester 2 (3.8 g, 0.01 mol) in methanol (40 mL), was added Raney nickel (0.5 g) and the reaction mixture was placed under a hydrogen (30 psi) atmosphere in a Paar hydrogenation apparatus for 0.5h and then filtered through a celite bed. The catalyst was washed with methanol (15 mL) and the combined filtrates were evaporated to dryness *in vacuo*. The resulting residue was taken in water (30 mL) and extracted with chloroform (3 x 50 mL). The organic extracts were combined, dried (Na_2SO_4) and evaporated. Trituration of the residue with benzene gave methyl-4-*N*-(2-amino-5-chlorobenzoyl) amino-1-methyl-3-*n*-propyl-1*H*-pyrazole-5-carboxylate (3) which on recrystallisation from methanol gave colourless needles, yield 3.3 g (95%); mp. 156°C; IR (KBr, cm^{-1}): 3465, 3372, 3226, 2950, 2868, 1713, 1647; ^{1}H-NMR ($CDCl_3$, δ ppm): 0.9 (t, 3H, CH_3), 1.6 (m, 2H, CH_2), 2.65 (t, 2H, CH_2), 3.9 (s, 3H, OCH_3), 4.1 (s, 3H, N-CH_3), 5.5 (brs, 2H, NH_2), 6.6 (d, 1H, Ar-H), 7.2 (m, 2H, Ar-H), 7.5 (brs, 1H, NH), 8.1 (brs, 1H, NH); MS: m/e 350 (M+), 197, 168, 154,126, 99.

Preparation of 4-N-(5-chloro-2-aminobenzoyl)amino-1-methyl-3-n-propyl-1H-pyrazole-5-carboxamide (4)

A mixture of methyl 4-*N*-(2-amino-5-chloro-benzoyl) amino-1-methyl-3-*n*-propyl pyrazole-5-carboxylate (3, 3g) and concentrated ammonia (40 mL) was heated under reflux for 3h. The reaction mixture was then cooled and poured in ice cooled water (50 mL). The separated solid was filtered, washed with cold water (2 x 15 mL), dried and recrystallised from benzene to give 4-*N*-(5-chloro-2-aminobenzoyl)amino-1-methyl-3-*n*-propyl pyrazole-5-carboxamide (4), yield 1.5 g (87%); mp. 199°C; UV (MeOH, λ_{max}): 296, 240, 214 nm; IR (KBr, cm^{-1}): 3462, 3366, 3282, 3202, 2961, 2862, 1662; ^{1}H-NMR ($CDCl_3$, δ ppm): 0.9 (t, 3H, CH_3), 1.3 (brs, 2H, amine NH_2), 1.7 (m, 2H, CH_2), 2.6 (t, 2H, CH_2), 4.0 (s, 3H, N-CH_3), 5.6 (brs, 2H, amide NH_2), 6.7 (d, 1H, Ar-H), 7.3 (brs, 1H, NH), 7.6 (m, 2H, Ar-H); MS: m/e 335 (M+), 318, 182, 154, 126, 99.

Preparation of 10-chloro-3-methyl-1-n-propyl-4,5,7,12-tetrahydro-3H-benzo[d]pyrazolo[3',4':5,6][1,2,3]triazino [1,2-a][1,2,3]triazin-4,12-dione (5)

A solution of 4-*N*-(2-amino-5-chlorobenzoyl) amino-1-methyl-3-*n*-propylpyrazole-5-carboxamide (4, 1.73 g, 0.005 mol) in 2N hydrochloric acid (25 mL) was stirred for 15 min and cooled to 0°C. An aqueous solution of sodium nitrite (0.4 g, 0.006 mol in 5 mL of water) was added dropwise to the above solution over a period of 5 min at 10 °C. After the addition, the solution was stirred for an additional 15 min and the temperature was allowed to rise to 25°C and stirred for 3h. On cooling the reaction mixture at 0 °C for 30 min compound 10-chloro-3-methyl-1-*n*-propyl-4,5,7,12-tetrahydro-3*H*-benzo[*d*]pyrazolo [3',4':5,6][1,2,3]triazino [1,2-*a*][1,2,3]- triazin-4,12-dione (**5**) separated out. It was filtered, dried and recrystallised from methanol. yield 1.5 g (84%); mp. 208°C; UV (MeOH, λ_{max}): 290, 221 nm; IR (KBr, cm^{-1}): 3439, 3329, 2954, 2873, 1669; ^{1}H-NMR (DMSO-d_6, δ ppm): 0.8 (t, 3H, CH_3), 1.5 (m, 2H, CH_2), 2.5 (t, 2H, CH_2), 4.0 (s, 3H, N-CH_3), 7.5 (brs, 1H, NH), 7.7 (brs, 1H, NH), 8.2 (d, 1H, Ar-H), 8.35 (m, 2H, Ar-H); ^{13}C-NMR (DMSO-d_6, δ ppm): 13.6, 21.1, 27.2, 38.7, 117.8, 121.2, 124.3, 130.7, 133.7, 135.8, 137.9, 141.8, 146.7, 153.5, 159.7; MS: m/e 346 (M^+), 303, 289, 274, 260, 246, 232, 164, 136, 110, 95, 75, 67; Anal. calcd. for $C_{15}H_{15}ClN_6O_2$: C, 51.95; H, 4.36; N, 24.24. Found : C, 51.82; H, 4.51; N, 24.42.

Preparation of N-(2-carbamoylphenyl)-1-methyl-4-nitro-3-n-propyl-1H-pyrazole-5-carboxamide (9)

A mixture of 1-methyl-4-nitro-3-n-propyl pyrazole-5-carboxylic acid (8, 0.01 mol) and thionyl chloride (10 mL) was refluxed for 3h. The reaction mixture was cooled and excess thionyl chloride was removed in vacuo. The oily residue was dissolved in benzene (10 mL) and this acid chloride was cautiously added to 2-aminobenzamide (0.01 mol) in benzene (10 mL) at 5-10°C. The precipitated *N*-(2-carbamoylphenyl)-1-methyl-4-nitro-3-*n*-propyl-1*H*-pyrazole-5-carboxamide (9) was collected by filtration and recrystallised from benzene. yield 84%; mp 135^{o}C; UV (MeOH, λ_{max}): 285, 254, 210 nm; IR (KBr, cm^{-1}): 3486, 3348, 3182, 1670, 1618; ^{1}H-NMR (DMSO-d_6, δ ppm): 1.0 (t, 3H, CH_3), 1.7 (m, 2H, CH_2), 2.9 (t, 2H, CH_2), 4.05 (s, 3H, N-CH_3), 7.1 (t, 1H, Ar-H), 7.4 (t, 1H, Ar-H), 7.7 (d, 1H, Ar-H), 8.0 (brs, 2H, NH_2), 8.5 (d, 1H, Ar-H), 12.5 (brs, 1H, NH).

Preparation of 5-N-(2-carboxamidophenyl)-1-methyl-4-amino-3-n-propyl-1H-pyrazole-5-carboxamide (10)

To a solution of compound 9 (0.01 mol) in methanol (25 mL), was added Raney nickel (0.5 g) and reaction mixture was placed under a hydrogen (30 psi) atmosphere in a Parr hydrogenation apparatus for 1.5h and then filtered through a celite bed. The catalyst was washed with methanol (10 mL) and the combined filtrates were evaporated to dryness *in vacuo*. The resulting residue was taken in water (25 mL) and extracted with chloroform (2 x 25 mL). The organic extracts were combined, dried (Na_2SO_4) and evaporated under reduced pressure. Trituration of the residue with benzene gave the corresponding 5-*N*-(2-carboxamidophenyl)-1-methyl-4-amino-3-*n*-propyl-1*H*-pyrazole-5-carboxamide (10) which was recrystallised from dichloromethane, yield 77%; mp. 116^{o}C; UV(MeOH, λ_{max}): 310, 268, 216 nm; IR (KBr, cm^{-1}): 3484, 3410, 3260, 3237, 2961, 1684, 1651; ^{1}H-NMR (DMSO-d_6, δ ppm): 0.9 (t, 3H, CH_3), 1.6 (m, 2H, CH_2), 2.4 (t, 2H, CH_2), 3.9 (s, 3H, N-CH_3), 4.2 (brs, 2H, NH_2), 7.2 (t, 1H, Ar-H), 7.4 (t, 1H, Ar-H), 7.8 (d, 1H, Ar-H), 8.2 (brs, 2H, NH_2), 8.4 (d, 1H, Ar-H), 11.8 (brs, 1H, NH).

Preparation of 11-methyl-9-n-propyl-5,6,11,12-tetrahydro -8H-benzo[e]pyrazolo[4',3':4,5][1,2,3]triazino[1,2-a][1,2, 3] triazin-5,12-dione (11)

A solution of compound 10 (3.01 g, 0.01 mol) in 2N hydrochloric acid (25 mL) was stirred vigorously for 15 min. The solution was cooled to 0°C and an aqueous solution of sodium nitrite (0.75 g, 0.011 mol in 10 mL of water) was added dropwise over a period of 10 min at 10°C. After the addition, the solution was stirred for an additional 15 min and temperature was allowed to rise 25°C and stirred for 2h at this temperature. The reaction mixture was cooled at 10°C for overnight and the obtained solid,11-methyl-9-*n*-propyl-5,6,11,12-tetrahydro-8*H*-benzo [*e*]pyrazolo[4',3':4,5][1,2,3]triazino[1,2-*a*][1,2,3]triazin-5,12-dione (11) was filtered, dried and recrystallised from C_2H_5OH, yield 2.7 g (89%); mp. 114°C; UV (MeOH, λ_{max}): 285, 220 nm; IR (KBr, cm^{-1}): 3396, 3163, 2961, 1706, 1671; ^{1}H-NMR ($CDCl_3$, δ ppm): 1.0 (t, 3H, CH_3), 1.8 (m, 2H, CH_2), 3.0 (t, 2H, CH_2), 4.2 (s, 3H, N-CH_3), 5.6 (br s, 1H, NH), 6.0 (br s, 1H, NH), 7.4 (d, 1H, Ar-H), 7.5 (t, 1H, Ar-H), 7.6 (t, 1H, Ar-H), 7.7 (d, 1H, Ar-H); ^{13}C-NMR (DMSO-d_6, δ ppm) :13.7, 21.7, 27.3, 38.6, 124.0, 128.5, 129.0, 129.3, 130.8, 133.5, 134.9, 136.4, 146.9, 149.8, 167.5; MS: m/e 312 (M^+), 286, 268, 241, 239, 212, 165, 151, 149, 120, 118, 81, 77, 65, 53; Anal. calcd. for $C_{15}H_{16}N_6O_2$: C, 57.68; H, 5.16; N, 26.91. Found: C, 57.54; H, 5.28; N, 27.01.

RESULTS AND DISCUSSION

Methyl 4-amino-1-methyl-3-*n*-propylpyrazole-5-carboxylate (1) was reacted with 5-chloro-2-nitrobenzoyl chloride and the resulted crystalline compound was characterized as methyl 4-*N*-(5-chloro-2-nitrobenzoyl) amino-1-methyl-3-*n*-propyl-1*H*-pyrazole-5-carboxylate (2). IR spectrum showed amide NH (3228 cm^{-1}) besides ester carbonyl (1725 cm^{-1}) and amide carbonyl (1662 cm^{-1}) peaks. Presence of amide NH and ester methoxy groups in the compound is also discerned from the ^{1}H-NMR spectrum ($CDCl_3$ + DMSO-d_6) with the corresponding peaks at δ 9.5 (s, 1H, NH) and 3.7 (s, 3H, OCH_3). In the mass spectrum, the molecular ion peak at m/e 380 is weak. Loss of nitro and hydrogen units from the molecular ion leads to the ion corresponding to base peak at m/e 333.

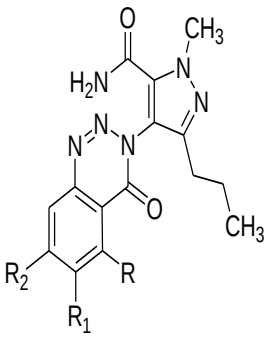
Catalytic reduction of nitroaroylaminopyrazole derivative 2 in presence of Raney Ni smoothly yielded a compound, which is characterised as methyl 4-*N*-(2-amino-5-chlorobenzoyl)amino-1-methyl-3-*n*-propyl-1*H*-pyrazole-5-carboxylate (3) based on the IR, mass and ^{1}H-NMR spectral data.

The pyrazole ester **3** was refluxed in ammonia followed by usual workup furnished a crystalline compound with mp. 199°C. IR spectrum (KBr) of the compound showed NH (3462, 3366, 3282 and 3202 cm^{-1}) and amide carbonyl (1662 cm^{-1}) absorptions. UV spectrum displayed absorption maxima at 296, 240 and 214 nm. In the mass spectrum, the highest peak at m/e 335 corresponds to the molecular ion (MF-$C_{15}H_{18}N_4O_2Cl$) of the expected product, 4-*N*-(2-amino-5-chlorobenzoyl) amino-1-methyl-3-*n*-propyl-1*H*-pyrazole-5-carboxamide (**4**). Broad singlets at δ 1.3, 5.6 and 7.3 in the ^{1}H-NMR spectrum ($CDCl_3$) due to amine NH_2, amide NH_2 and amide NH also supporting the diamide structure 4.

Treatment of pyrazole diamide derivative 4 with sodium nitrite in hydrochloric acid yielded a crystalline compound. In the mass spectrum of this compound, peak at m/e 346 conforming to molecular formula $C_{15}H_{15}N_6ClO_2$ corresponds to the molecular weight of the expected tetracyclic derivative **5**. In this spectrum, intensity of M+2 ion is 1/3 rd that of molecular ion confirming the presence of one chlorine atom in the molecule. UV spectrum with absorption maxima at 290 and 221 nm is different from that of its precursor 4. IR spectrum of the compound displayed two NH absorptions (3329 and 3439 cm^{-1}) besides an intense carbonyl peak (1669 cm^{-1}). ^{1}H-NMR spectrum (DMSO-d_6) with two deuterium exchangeable broad singlets at δ 7.5 and 7.7 indicates the presence of two distinct NH protons, favouring the 10-chloro-3-methyl-1-*n*-propyl-4,5,7,12-tetrahydro-3*H*-benzo[*d*]pyrazolo[3',4':5,6] [1,2,3]triazino[1,2-*a*] [1,2,3]triazin-4,12-dione (5, scheme-1) structure. Other signals in the spectrum are due to *n*-propyl [(δ 0.8 (t, 3H, CH_3), 1.5 (m, 2H, CH_2), 2.5 (t, 2H, CH_2)], *N*-methyl group (δ 4.0, s, 3H) and aromatic protons [δ 8.2 (d, 1H), 8.35 (m, 2H)].

Two other alternate isomeric structures, 6 and **7** are discarded on the basis of following factors. The NH_2 protons signal of pyrazolecarboxamides, such as 1-benzyl-3-methyl-4-nitropyrazole-5-carboxamide is known to appear as a broad singlet at δ 6.1-7.0 in the ^{1}H-NMR (100 MHz, $CDCl_3$) spectrum unlike in the present case, where two distinct NH signals are oberved in the ^{1}H-NMR

spectrum. Pyrazole carboxamide derivative structure 6 is ruled out on this basis. Formation of triazine **7** requires the diazotisation of an amide NH_2 in preference to aniline NH_2, which is highly unlikely and thus possibility of structure 7 is discounted. Further, aniline NH_2 signal of precursor 4 appeared as a singlet at δ 1.3 in the ^{1}H-NMR spectrum unlike in the present case.Proton decoupled ^{13}C-NMR spectrum of the compound is complementary to the aforementioned spectral data. Two carbonyl carbon signals appeared at δ153.5 and 159.7. Among the remaining nine signals in the down field region, signals at δ 124.3, 133.7 and 146.7 correspond to the carbons of pyrazole nucleus and remaining six signals, δ 117.8, 121.2, 130.7, 135.8, 137.9 and 141.8 are due to phenyl ring carbons. The chemical shift values δ 13.6, 21.1 and 27.2 correspond to *n*-propyl group. It is reasoned that, N-CH_3 carbon signal at δ 38.7 was overlapped with DMSO carbon signals like in all previous cases. Thus, fused pyrazolotriazine derivative is obtained via intramolecular attack of the electrophilic nitrogen of a diazo group on a carboxamide function.



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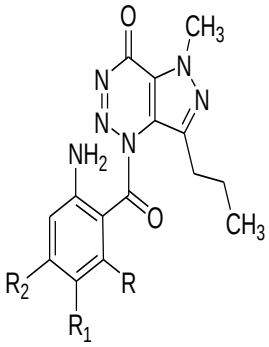

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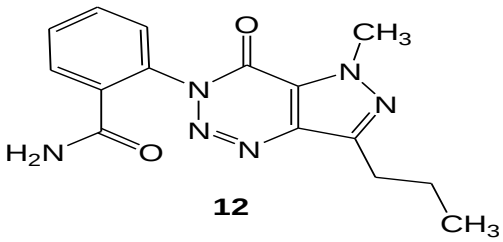
Success of the above approach in the synthesis of a angularly fused tetracyclic heterocycle **5** prompted us to apply a similar strategy in the synthesis of another novel linearly fused 11-methyl-9-*n*-propyl-5,6,11,12-tetrahydro-8*H*-benzo[*e*]pyrazolo[4',3':4,5][1,2,3]triazino-[1,2-*a*]. [1,2,3] triazin-5,12-dione (**11**) as shown in the scheme-2.

1-Methyl-4-nitro-3-*n*-propylpyrazole-5-carboxylic acid (**8**) (Bell AS, Terrett NK, 1993) was reacted with thionyl chloride followed by condensation with 2-aminobenzamide proceeded smoothly as before and provided 1-methyl-4-nitro-3-*n*-propylpyrazole-5-(*N*-2-carboxamidophenyl)carboxamide (**9**). The structural assignment was based on the IR, UV and mass spectral data. Catalytic hydrogenation of 4-nitropyrazole-5-carboxamide derivative **9** in the presence of Raney Ni smoothly afforded the 4-aminopyrazolecarboxamide derivative **10**. [IR (KBr, cm^{-1}), 3484, 3410, 3360, 3237 (NH_2 & NH), 1684 and 1651 (C=O); UV (MeOH, λ_{max} : 310 and 268 nm].

Treatment of 4-aminopyrazole-5-carboxamide derivative 10 with sodium nitrite in hydrochloric acid followed by usual workup yielded a crystalline compound with mp. 114°C. IR spectrum of the compound indicated the presence of two NH functions (3396 and 3163 cm^{-1}) and two carbonyl groups (1706 and 1671 cm^{-1}). In the electronic spectrum (MeOH, λ_{max}) the absorption maxima were at 285 and 220 nm. In the mass spectrum the molecular ion peak at m/e 312 corresponds to the molecular weight of the expected fused tetracyclic system 11. The base peak at m/e 151 may be attributed to 1-methyl-3-*n*-propyl-5-pyrazoloyl ion. Thus, IR and mass spectral data suggest 11-methyl-9-*n*-propyl-5,6,11,12-tetrahydro-8*H*-benzo[*e*]pyrazolo[4',3':4,5] [1,2,3]triazino [1,2-*a*][1,2,3]triazin-5,12-dione (11) structure to the product. An alternate isomeric 5-methyl-3-(2-carboxamidophenyl)-7-*n*-propyl-4,5-dihydro-3*H*-pyrazolo [4,3-*d*][1,2,3]triazin-4-one (12), structure was ruled out on the basis of ^{1}H-NMR spectrum which showed two distinct NH signals at δ 5.6 and 6.0 each integrating for one proton, thus favouring the structure 11. Appearance of benzamide NH_2 as two distinct peaks at those chemical shift values is highly unlikely. Other signals in the ^{1}H-NMR spectrum are due to N-CH_3 (δ 4.2, s, 3H), *n*-propyl [δ 1.0 (t, 3H, CH_3), 1.8 (m, 2H, CH_2), 3.0 (t, 2H, CH_2)] and aromatic (δ 7.4-7.7, m, 4H) protons. Proton decoupled ^{13}C-NMR spectrum recorded in DMSO is in agreement with the assigned structure 11. Two carbonyl carbon peaks appeared at δ 149.8 and 167.5. Signals at δ 124, 134.9 and 146.9 are due to three carbons of pyrazole nucleus (Bell AS, Terrett NK, 1992). Rest of the six signals in the downfield region (δ 128.5, 129.0, 129.3, 130.8, 133.5 and 136.4) correspond to the six carbons of phenyl ring. Peaks of *n*-propyl group carbons appeared in the upfield region at δ 13.7, 21.7 and 27.3. The peak for *N*-CH_3 was overlapped with DMSO-d_6 carbon signals at δ 38.6 as in the case of earlier *N*-CH_3 pyrazole derivatives.



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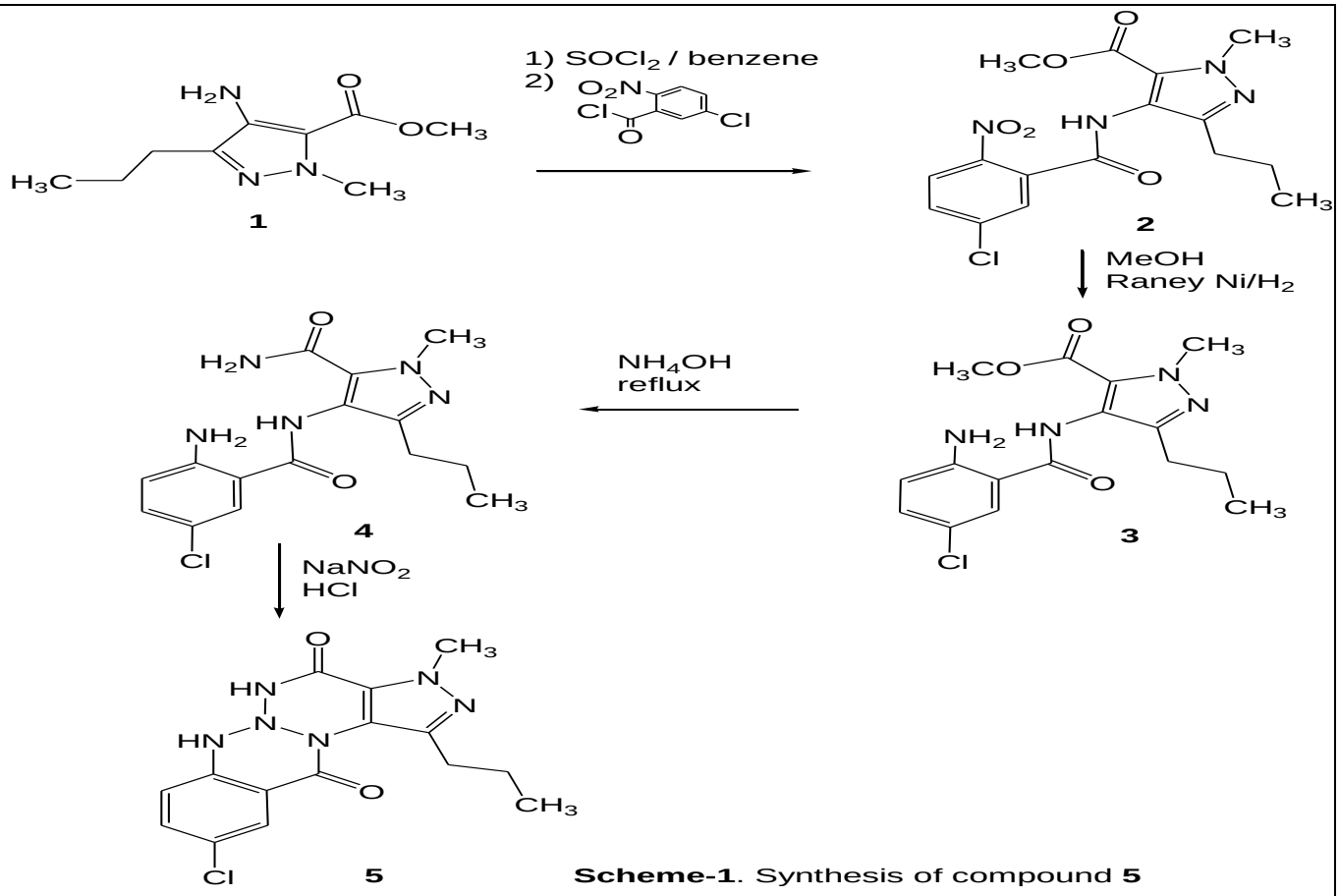
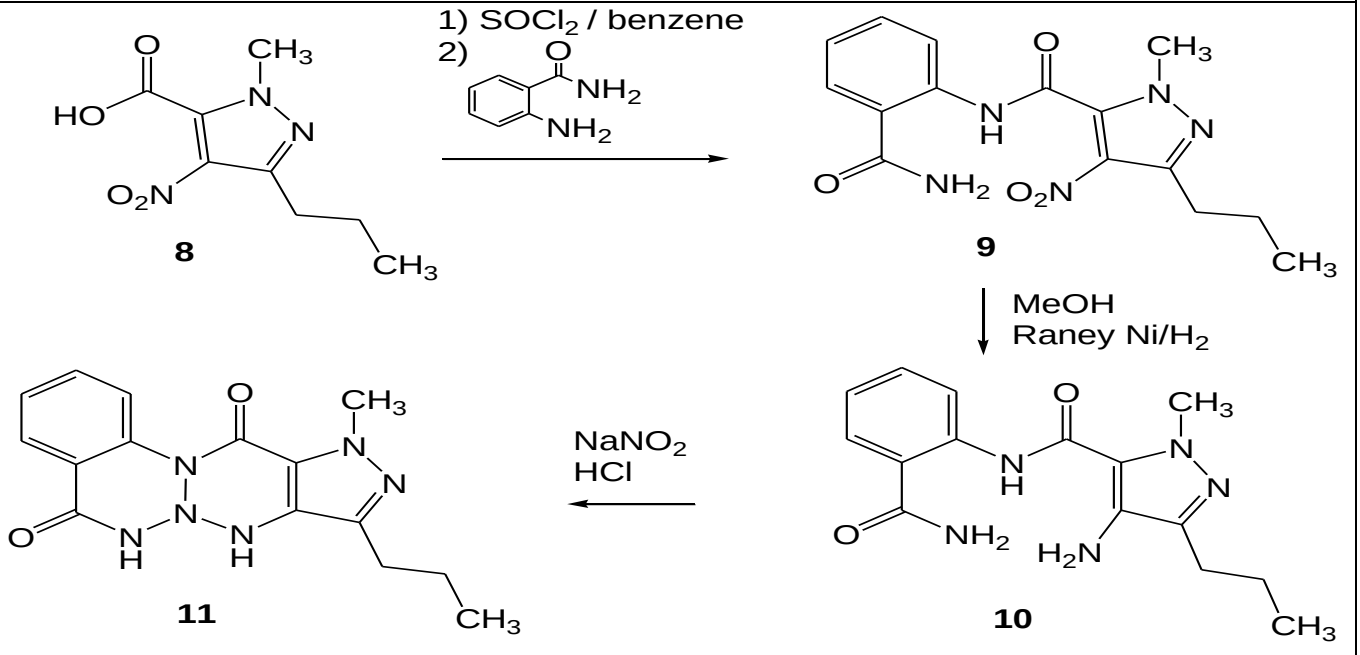
Formation of compound 11 may involve the intermediacy of pyrazolotriazine 12. However, compound 11 was isolated as the sole product under the reaction conditions. Generalizations of these methods are under progress.



Scheme-1. Synthesis of compound **5**



Scheme-2. Synthesis of compound **11**

CONCLUSION

A simple method involving diazonium ion mediated hetero cyclization was provided for the synthesis of two novel 10-chloro-3-methyl-1-*n*-propyl-4, 5, 7, 12-tetrahydro-3*H*-benzo [*d*] pyrazolo [3′, 4′, 5, 6] [1, 2, 3] triazino [1, 2*a*] [1, 2, 3] triazin-4, 12-dione (**5**) and 11-methyl-9-*n*-propyl-5, 6, 11, 12-tetrahydro-8*H*-benzo [*e*] pyrazolo [4′,3′, 4, 5] [1, 2, 3] triazino [1, 2-*a*] [1, 2, 3] triazin-5, 12-dione (**11**).

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REFERENCES

Baraldi PG, Casolari A, Guarneri M, Manfredini S, Pollini GP, Simoni D, Zanirato V. *Synthesis*. 1988; 78.
Bell AS, Terrett NK. *Eur. Pat. Appl.* 1993; 526: 004.
Buchaman JG, Stobie A, Wightman RH. *J.C.S. Perkin Trans I.* 1981; 2374.
Daniel M, Marcus B, Heinrich M, Dirk S, Niels S, Dieter H. *Heterocycles.* 2009; 78: 71.
Kumar KS, Raju A, Sandhya S, Rambabu D, Rama Krishna G, Malla Reddy C, Misra P, Patel M. *Bioorganic & Medicinal Chemistry Letters*. 2012; 22: 1146.
Long RA, Gerster JF, Townsend LB. *J. Heterocycl. Chem.* 1970; 7: 863.
Manfredini S, Bazzanini R, Baraldi PG, Guarneri M, Simoni D, Marongiu E, Pani A, Tramontano E, La Colla P. *J. Med. Chem.* 1992; 35: 917.
Pier GB, Daniele S, Vittorio P, Stefano M, Mario G, Roberto M, Enzo C. *J. Med. Chem.* 1984; 27: 986.