1, 3-Dipolar cycloaddition reactions: Synthesis of 5-benzyl-1-(2',4'-dibromophenyl)-3-(4''-substituted phenyl)-3a,4,6,6a-tetrahydro-1H, 5H-pyrrolo[3,4-c]pyrazole-4,6-dione derivatives

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Abstract. 1,3-Dipolar cycloaddition of nitrilimines **3** with *N*-benzyl maleimide **4** has provided 5-benzyl-1-(2',4'-dibromophenyl)-3-(4''-substituted phenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione derivatives **5** in excellent yield as the only isomer through a concerted pathway.

Keywords. Nitrilimine; cycloaddition; stereo-controlled; pyrrolo pyrazole.

1. Introduction

1,3-Dipolar cycloaddition reaction has found an extensive use as a high-yielding, efficient, regio and stereo-controlled method for the synthesis of many heterocyclic compounds.^{1–4} 1,3-Dipolar cycloaddition reaction has been described as 'the single most important method for the construction of heterocyclic five-membered rings in organic chemistry'.⁵ These reactions proceed through 'conservation of orbital symmetry'.⁶ Nitrilimines **3** are well-known labile intermediates which are generated *in situ* in the presence of the dipolarophile to form cycloadducts.⁷ It has been reported that the orientation during 1,3-dipolar cycloaddition reaction observed for alkenes substituted with electron-donor conjugating and electron acceptor substituents provides the 5-substituted regioisomer, while on other occasions, these cycloadditions of nitrilimines to highly electron-deficient alkenes give 4-substituted products.⁸ The active dipolarophile maleimides are known to be a class of substrates having biological importance along with their synthetic utility.⁹ Besides, using chiral maleimides, synthesis of pyrazoles have also been explored.¹⁰ The nitrilimines 1,3-dipole have been synthesised by various methods such as thermal decomposition of substituted tetrazole,¹¹ treatment of diarylhaloformazans¹² with tertiary amine, use of triphenylphosphine and carbon tetrachloride¹³ and treatment of aryl hydrazone with chloramine-T,¹⁴ but more conveniently, nitrilimines can be synthesised *in situ* by treating

hydrazidoyl halides^{15,16} with a tertiary base (table 1, scheme 1).

2. Experimental

2.1 General

Melting points reported are uncorrected. IR spectra were recorded on a Perkin Elmer RXIFT infrared spectrophotometer using KBr pellets. ¹H-Nuclear magnetic resonance (¹H-NMR) spectra were recorded on a 400 MHz Bruker Advance II Spectrometer using tetramethylsilane (TMS) as internal standard. ¹³C-NMR spectra were recorded on a Bruker Advance II 100 NMR Spectrometer, SAIF Punjab University, Chandigarh. Mass spectra were recorded on LCQ FINNIGAN MAT (ESI), NIPER, Mohali. Thin layer chromatography (TLC) plates were coated with silica gel-G suspended in methanol–chloroform. Elemental analysis was carried out using Elementar vario MICRO cube CHN analyser.

2.2 General procedure for synthesis of *N*-benzyl maleimide (**4**)

Equimolar quantities of benzylamine and maleic anhydride were stirred in toluene at room temperature for 1 h to yield *N*-benzyl maleanilic acid. Maleanilic acid thus obtained was cyclised to maleimide in acetic anhydride in the presence of anhydrous sodium acetate under reflux for 1.5 h and then the contents were poured into ice cold water and kept over night to afford the solid, which was filtered, washed with water and finally

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Table 1. Characterisation data of 5-benzyl-1-(2',4'-dibromophenyl)-3-(4''-substituted phenyl)-3a,4,6,6a-tetrahydro-1*H*,5*H*-pyrrolo[3,4-*c*]pyrazole-4,6-dione derivatives.

Compounds	X	Yield (%)	Melting point (°C)
5a	4-Cl	70	193–195
5b	3-Cl	67	185–187
5c	2-Cl	72	132–133
5d	4-CH ₃	68	194–196
5e	3-CH ₃	64	142–144
5f	2-CH ₃	66	162–163
5g	4-NO ₂	70	230–232
5h	3-NO ₂	66	190–191
5i	H	73	168–169

Scheme 1. Schematic diagram describing the synthesis of 5-benzyl-1-(2',4'-dibromophenyl)-3-(4''-substituted phenyl)-3a,4,6,6a-tetrahydro-1*H*,5*H*-pyrrolo[3,4-*c*]pyrazole-4,6-dione derivatives.

recrystallized from petroleum ether to give *N*-benzyl maleimide **4**.

2.3 General procedure for synthesis of substituted benzaldehyde-2',4'-dibromophenyl hydrazoneyl bromide (**2a–i**)

All these compounds were prepared by reacting an equimolar amount of corresponding benzaldehyde and

phenyl hydrazine in ethanol. The product obtained after recrystallization (0.1 mol) was dissolved in cold glacial acetic acid (100 ml). To this solution a solution of acetic bromine (0.3 mol/30 ml glacial acetic acid) was added dropwise within 30 min. The reaction mixture was stirred for about 2.5 h and kept for an overnight period. On usual work-up, the reaction mixture provided crude product which on recrystallisation from ethanol gave **2a–i**.

2.4 General procedure for cycloadditions (**5a-i**)

To the substituted benzaldehyde-2',4'-dibromophenyl hydrazone bromide **2a-i** (0.01 mol) were added *N*-benzyl maleimide **4** (0.01 mol) in tetrahydrofuran (75 mL). To the cold mixture was added triethylamine (0.01 mol) in tetrahydrofuran (25 mL) and the mixture was stirred for 2–3 h and allowed to stand overnight. The crude product that separated out was recrystallised from ethanol to give cycloadducts **5a-i**.

2.4a 5-Benzyl-1-(2',4'-dibromophenyl)-3-(4''-chlorophenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5a): Compound obtained as white solid (3.7 g, 64.5%), m.p. 193–195°C; IR (KBr pellets): 1716, 1782 cm⁻¹ (C=O); 1610 cm⁻¹ (C=N); 1579 cm⁻¹ (C=C); ¹H-NMR (400 MHz, CDCl₃), δ 5.8 (d, 1H, *J* = 10.36 Hz); 4.8 (d, 1H, *J* = 10.32 Hz); 4.6 (s, 2H); 8.0–7.1 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.5, 171.2, 145.4, 140.6, 135.8–119.3, 131.3, 127.1, 63.3, 53.9, 43.2; MS(ESI): *m/z* 572[M]⁺, 574[M+2]⁺, 576[M+4]⁺, Anal. Calc. for C₂₄H₁₆N₃Br₂ClO₂: C, 50.21; H, 2.79; N, 7.32, Found: C, 50.35; H, 2.77; N, 7.35.

2.4b 5-Benzyl-1-(2',4'-dibromophenyl)-3-(3''-chlorophenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5b): Compound obtained as white solid (3.9 g, 67.9%), m.p. 185–187°C; IR (KBr pellets): 1708, 1778 cm⁻¹ (C=O); 1608 cm⁻¹ (C=N); 1575 cm⁻¹ (C=C); ¹H-NMR (400 MHz, CDCl₃), δ 5.8 (d, 1H, *J* = 10.40 Hz); 4.8 (d, 1H, *J* = 10.36 Hz); 4.6 (s, 2H); 7.9–7.1 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.6, 171.4; 143.7, 142.7, 135.8–118.2, 130.5, 126.8, 62.4; 53.6, 43.1; MS(ESI): *m/z* 572[M]⁺, 574[M+2]⁺, 576[M+4]⁺, Anal. Calc. for C₂₄H₁₆N₃Br₂ClO₂: C, 50.21; H, 2.79; N, 7.32, Found: C, 50.20; H, 2.81; N, 7.31.

2.4c 5-Benzyl-1-(2',4'-dibromophenyl)-3-(2''-chlorophenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5c): Compound obtained as white solid (3.3 g, 57.5%), m.p. 132–133°C; IR (KBr pellets): 1699, 1771 cm⁻¹ (C=O); 1606 cm⁻¹ (C=N); 1574 cm⁻¹ (C=C); ¹H-NMR (400 MHz, DMSO-*d*₆), δ 5.9 (d, 1H, *J* = 10.20 Hz); 5.3 (d, 1H, *J* = 10.20 Hz); 4.5 (s, 2H); 7.6–7.1 (m, 12H); ¹³C-NMR (100 MHz, DMSO-*d*₆), δ 171.8, 171.6, 144.6, 141.9, 134.9–16.2, 132.1, 127, 62.9, 55.3, 41.8; MS(ESI): *m/z* 572[M]⁺, 574[M+2]⁺, 576[M+4]⁺, Anal. Calc. for C₂₄H₁₆N₃Br₂ClO₂: C, 50.21; H, 2.79; N, 7.3, Found: C, 50.15; H, 2.78; N, 7.29.

2.4d 5-Benzyl-1-(2',4'-dibromophenyl)-3-(4''-methylphenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5d): Compound obtained as white solid (4.0 g, 72.3%), m.p. 194–196°C; IR (KBr pellets): 1710, 1780 cm⁻¹ (C=O); 1605 cm⁻¹ (C=N); 1567 cm⁻¹ (C=C); ¹H-NMR (400 MHz, DMSO-*d*₆), δ 5.8 (d, 1H, *J* = 10.16 Hz); 5.0 (d, 1H, *J* = 10.16 Hz); 4.5 (s, 2H); 2.4 (s, 3H); 7.9–7.2 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.5, 171.2, 147.4, 144.4, 135.7–116.4, 133.7, 129, 63.2, 54.1, 43.3, 24.9; MS(ESI): *m/z* 553[M]⁺, 554[M+1]⁺, 555[M+2]⁺, Anal. Calc. for C₂₅H₁₉N₃Br₂O₂: C, 54.25; H, 3.44; N, 7.60, Found: C, 54.05; H, 3.45; N, 7.65.

2.4e 5-Benzyl-1-(2',4'-dibromophenyl)-3-(3''-methylphenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5e): Compound obtained as white solid (4.2 g, 75.9%), m.p. 142–144°C; IR (KBr pellets): 1717, 1779 cm⁻¹ (C=O); 1603 cm⁻¹ (C=N); 1565 cm⁻¹ (C=C); ¹H-NMR (400 MHz, CDCl₃), δ 5.8 (d, 1H, *J* = 10.08 Hz); 4.9 (d, 1H, *J* = 10.12 Hz); 4.5 (s, 2H); 2.5 (s, 3H); 7.8–7.1 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.8, 171.6, 146.8, 145.4, 138.3–116.8, 131.3, 128.8, 63.2, 54.0, 43.1, 25.3; MS(ESI): *m/z* 553[M]⁺, 554[M+1]⁺, 555[M+2]⁺, Anal. Calc. for C₂₅H₁₉N₃Br₂O₂: C, 54.25; H, 3.44; N, 7.60, Found: C, 54.10; H, 3.41; N, 7.61.

2.4f 5-Benzyl-1-(2',4'-dibromophenyl)-3-(2''-methylphenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5f): Compound obtained as white solid (3.6 g, 65%), m.p. 162–163°C; IR (KBr pellets): 1699, 1771 cm⁻¹ (C=O); 1603 cm⁻¹ (C=N); 1574 cm⁻¹ (C=C); ¹H-NMR (400 MHz, CDCl₃), δ 5.8 (d, 1H, *J* = 10.28 Hz); 4.8 (d, 1H, *J* = 10.24 Hz); 4.6 (s, 2H); 2.43 (s, 3H); 7.8–7.2 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.7, 171.4, 146.4, 142.2, 135.3–117.1, 132.9, 128.5, 63.0, 54.1, 43.2, 25.1; MS(ESI): *m/z* 553[M]⁺, 554[M+1]⁺, 555[M+2]⁺, Anal. Calc. for C₂₅H₁₉N₃Br₂O₂: C, 54.25; H, 3.40; N, 7.60, Found: C, 54.17; H, 3.23; N, 7.58.

2.4g 5-Benzyl-1-(2',4'-dibromophenyl)-3-(4''-nitrophenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5g): Compound obtained as yellow solid (4.0 g, 68.5%), m.p. 230–232°C; IR (KBr pellets): 1709, 1781 cm⁻¹ (C=O); 1609 cm⁻¹ (C=N); 1562 cm⁻¹ (C=C); ¹H-NMR (400 MHz, DMSO-*d*₆), δ 6.0 (d, 1H, *J* = 10.44 Hz); 5.2 (d, 1H, *J* = 10.44 Hz); 4.6 (s, 2H); 8.3–7.2 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.2, 171, 145.9, 143.2, 136.2–116.9, 131.7, 127.3,

62.7, 53.8, 42.9; MS(ESI): m/z 581[M]⁺, 583[M+2]⁺, 585[M+4]⁺, Anal. Calc. for C₂₄H₁₆N₄Br₂O₄: C, 49.32; H, 2.74; N, 9.59, Found: C, 49.15; H, 2.74; N, 9.60.

2.4h 5-Benzyl-1-(2',4'-dibromophenyl)-3-(3''-nitrophenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5h): Compound obtained as yellow solid (3.6 g, 61.6%), m.p. 190–191°C; IR (KBr pellets): 1700, 1775 cm⁻¹ (C=O); 1606 cm⁻¹ (C=N); 1565 cm⁻¹ (C=C); ¹H-NMR (400 MHz, DMSO-*d*₆), δ 5.9 (d, 1H, *J* = 10.44 Hz); 5.2 (d, 1H, *J* = 10.44 Hz); 4.6 (s, 2H); 8.3–7.2 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.4, 171.1, 147.2, 144.9, 133.3–116.1, 130, 127.1, 63.5, 52.9, 43.3; MS(ESI): m/z 581[M]⁺, 583[M+2]⁺, 585[M+4]⁺, Anal. Calc. for C₂₄H₁₆N₄Br₂O₄: C, 49.32; H, 2.74; N, 9.59, Found: C, 49.45; H, 2.73; N, 9.57.

2.4i 5-Benzyl-1-(2',4'-dibromophenyl)-3-(phenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione (5i): Compound obtained as white solid (3.5 g, 64.9%), m.p. 168–169°C; IR (KBr pellets): 1709, 1781 cm⁻¹ (C=O); 1605 cm⁻¹ (C=N); 1562 cm⁻¹ (C=C); ¹H-NMR (400 MHz, CDCl₃), δ 6.0 (d, 1H, *J* = 10.16 Hz); 5.2 (d, 1H, *J* = 10.16 Hz); 4.6 (s, 2H); 8.3–7.2 (m, 12H); ¹³C-NMR (100 MHz, CDCl₃), δ 171.7, 171.4, 145.2, 141.9, 135.7–118.8, 131.4, 128.0, 63.2, 54.1, 43.2; MS(ESI): m/z 539[M]⁺, 540[M+1]⁺, 541[M+2]⁺, Anal. Calc. for C₂₄H₁₇N₃Br₂O₂: C, 53.43; H, 3.15; N, 7.79, Found: C, 53.60; H, 3.13; N, 7.77.

3. Results and discussion

In the present study, a convenient and facile method for the synthesis of *C*-aryl-*N*-(2',4'-dibromophenyl)-nitrilimines¹⁷ and their 1,3-dipolar cycloaddition with *N*-benzyl maleimide¹⁸ has been carried out, which has provided the synthesis of 5-benzyl-1-(2',4'-dibromophenyl)-3-(4''-substituted phenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione derivatives **5** in excellent yield. The phenyl hydrazones are treated with bromine¹⁹ in glacial acetic acid to give hydrazonyl bromide derivatives which subsequently on treatment with triethyl amine in cold tetrahydrofuran has given *C*-aryl-*N*-(2',4'-dibromophenyl)-nitrilimines *in situ* which undergo cycloaddition with activated double bond of *N*-benzyl maleimide to form five-membered fused bicyclic heterocycles which have been

characterised as 5-benzyl-1-(2',4'-dibromophenyl)-3-(4''-substituted phenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione derivatives through their melting point, elemental analysis, IR, ¹H-NMR, ¹³C-NMR, 2D-COSY and mass spectra. All the compounds gave satisfactory results for their elemental analysis.

In their IR spectra, these derivatives display two absorption bands in the region of 1782–1771 cm⁻¹ and 1717–1699 cm⁻¹, which have been assigned to two carbonyl groups stretching vibrations of succinimide moiety. Absorption bands in the range of 1603–1609 cm⁻¹ have been assigned to imino stretching vibrations of pyrazole ring, while the absorption bands in the region of 1575 cm⁻¹ have been assigned to aromatic carbon-carbon double bond skeletal stretching vibrations. In their ¹H-NMR spectrum, these derivatives display C_{3a}-H and C_{6a}-H as doublets at δ 5.3–4.8 with *J* = 10.08–10.44 Hz and δ 6.0–5.8 with *J* = 10.12–10.44 Hz, respectively, on coupling with protons C_{6a}-H and C_{3a}-H. C_{6a}-H proton, appears downfield in comparison to C_{3a}-H proton due to electronegative nitrogen atom attached to C_{6a}-H. Aromatic protons appear as multiplets at δ 8.3–7.1 (equivalent to 12H). A two protons singlet at δ 4.6–4.5 has been assigned to methylene protons of benzyl moiety; while a singlet at δ 2.5 has been assigned to methyl group (**5d–f**).

Their ¹³C-NMR spectra of these 5-benzyl-1-(2',4'-dibromophenyl)-3-(4''-substituted phenyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo[3,4-c]pyrazole-4,6-dione derivatives **5** display characteristic signals in the range of δ 171.2–171.8 and 171.0–171.6 which have been assigned to two succinimide carbonyl carbons, signals in the range of δ 143.7–147.4 have been assigned to ipso carbon of substituted phenyl attached to C-3, signals in the range of δ 140.6–145.4 have been assigned to carbon of dibromophenyl ring, signals in the range of δ 116.1–136.2 have been assigned to carbon atom of aromatic ring, signals in the range of 130.0–133.7 have been assigned to C-3 of C = N, signals in the range of δ 127.0–129.0 have been assigned to ipso carbon directly attached to benzylic carbon of *N*-benzyl moiety, signals in the range of δ 62.7–63.5 and 52.9–55.3 have been assigned to C-5 pyrazoline and C-4 pyrazoline, signals in the range of δ 41.8–43.3 have been assigned to benzylic carbon. Signals at δ 24.9–25.3 have been assigned to carbon of methyl group (**5d–f**).

Mass spectra of all the synthesised compounds in **5a–i** display correct molecular ion peaks. As a representative case, high resolution mass spectrum of **5d** is discussed which displays molecular ion peak at m/z 554 (100%) forming base peak, with other

Figure 1. Mass fragmentation pattern of compound **5d**.

isotopic ion peaks at m/z 553 (57%), 555 (48%) showing the relative abundance of bromine atoms present in the molecule. Ion peaks at m/z 392, 393 and 394 are formed with the loss of $C_9H_7NO_2$ from the parent molecule. Presence of all these peaks shows the presence of two isotopic bromine atoms again. Peaks at m/z 463 appears due to loss of benzyl moiety from the parent molecular ion peak. Other prominent mass ion peaks present in the mass spectrum are at m/z 473, 392, 302, 187, 96, etc. The probable mode of fragmentation pattern of compound **5d** is shown in figure 1. Only one isomer has been obtained in all cases as evidenced by TLC analysis showing single spot in each case, thus this reaction is stereospecific in nature. 2D-NMR (COSY) of parent compound **5d** shows mutual coupling of proton H_{3a} with H_{6a} with $J = 10.16$ Hz, which indicates that both protons are *cis* to each other (figure 2). The single isomer seems to arise through endo transition state where maximum double bond accumulation occurs (TS, scheme 2). Since the N-benzyl maleimide is a symmetrical molecule, it does not matter whether the C-phenyl or N-phenyl ring of dipole lies parallel to one of the carbonyl groups of succinimide moiety of dipolarophile; and the secondary

interactions in either case leads to the formation of only *cis* product following *cis*-endo addition rule.

Figure 2. 400-MHz 2D-NMR COSY spectrum of **5d** in $CDCl_3$.

Scheme 2. Transition states of **5a-i**.

4. Conclusion

1,3-Dipolar cycloaddition reaction of nitrilimine generated *in situ* with *N*-benzyl maleimide has provided one regioisomer following *cis*-endo addition rule, wherein there is maximum accumulation of double bonds and reaction seems to follow least non-bonding steric interactions. Besides, during bromination of hydrazone, *N*-phenyl ring also gets brominated at 2',4'- positions.

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