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Synthesis of Benzimidazoles Containing a Fused Alicyclic Ring By Rhodium - Catalysed Hydroformylation of N-Alkenyl-1,2-diaminobenzenes†,#,‡

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ABSTRACT

Rhodium-catalysed reactions of N-alkenyl-1,2-diaminobenzenes(3) with hydrogen and carbon monoxide give benzimidazoles containing a fused alicyclic ring ((8) and (9)) in excellent yields. In some cases intermediate bicyclic compounds can be isolated and the ^{1}H and ^{13}C n.m.r. spectra of one of these, the 3,4,5,6-tetrahydro-4-methyl-3H-1,6-benzodiazocine (6), shows evidence for unusual atropisomerism.

INTRODUCTION

The preparation of heterocyclic compounds containing two heteroatoms has been of interest for some time.[1] Transition-metal catalysed routes to heterocyclic compounds containing a single heteroatom have been extensively investigated[2,3,4] but this approach does not appear to have been applied extensively to the preparation of medium ring heterocycles containing more than one heteroatom. In this paper we describe a simple, high-yielding route to some benzimidazoles by rhodium-catalysed reaction of N-alkenyl-1,2-diaminobenzenes (3) with carbon monoxide and hydrogen.

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† Dedicated to Professor Charles W. Rees on the occasion of his 65th birthday.

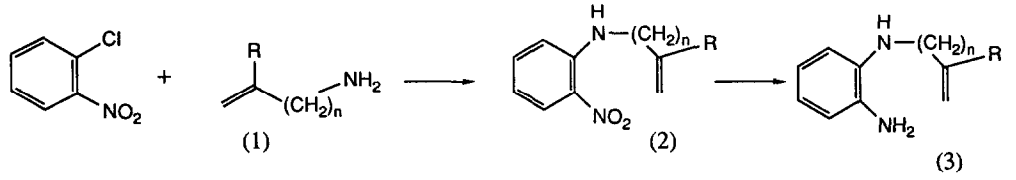
Part XXXIX of the series 'Stereochemistry of organometallic compounds. Part XXXVIII, Jackson, W.R. ; Moffat, M.R.; Perlmutter, P. and Tasdelen, E.E. *Aust J. Chem.*, 1992 (in press).

‡ Some of the work described in this paper has appeared in a communication, Anastasiou, D.; Chaouk, H.; and Jackson, W.R. *Tetrahedron Letters.*, 1991, **32**, 2499-2500.

RESULTS AND DISCUSSION

Preparation of N-Alkenyl-1,2-diaminobenzenes

The N-alkenyl-1,2-diaminobenzenes (3) were readily prepared by reaction of 2-chloronitrobenzene with an appropriate alkenylamine[5a] and subsequent reduction of the aminonitro compound (2) using iron powder and hydrochloric acid in 50% aqueous ethanol.[5b] (Scheme 1) Yields of the diamines (3) and the intermediate aminonitro compounds (2) are summarised in Table 1. All but a few of these reactions gave yields of >70% and many >80%.



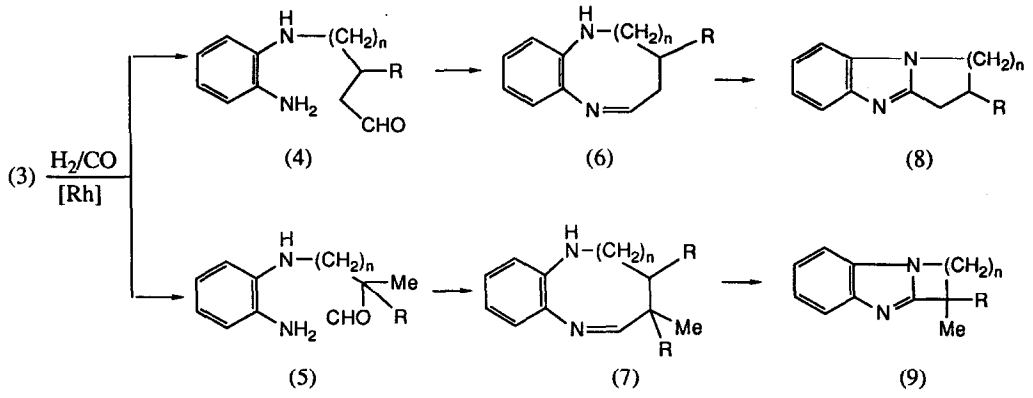
Scheme 1

Table 1 Yields of N-Alkenyl-1,2-diaminobenzenes (3) and intermediate nitroamines (2).

Reactant (1)		Yields of Products %	
n	R	(2)	(3)
1	H	88	91
1	Me	97	89
2	H	82	70
2	Me	51	85
3	H	88	64
3	Me	81	71

Rhodium-Catalysed Reactions of the Diamines with CO/H_2

Reactions were carried out at 70-100°C for 20 to 60 hours with CO/H_2 (1:1, 400 psi) and with alkene, $[Rh(OAc)_2]_2$ and PPh_3 in the ratio 200:1:4. The triphenylphosphine was added to lend stability to the catalyst system but as only 2 moles of phosphine were available for each rhodium atom, vacant sites were available on the metal for potential coordination to the amino nitrogen atoms.[6] Where mixtures of products were formed, their ratios were estimated from the ^1H (200 MHz) and ^{13}C (50 MHz) n.m.r. spectra. (Scheme 2)



Scheme 2

Reactions of N-(3-methylbut-3-enyl)-1,2-diaminobenzene (3; n=2; R=Me) and N-(4-methylpent-4-enyl)-1,2-diaminobenzene (3; n=3; R=Me) gave in each case a single benzimidazole product (8) in good yield (see Table 2). It is proposed that these arise from regioselective hydroformylation of (3) leading to the terminal aldehyde (4) which can cyclise to the cyclic imine (6).

Table 2 Yields of Benzimidazoles (8)

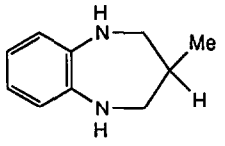
Reactant (3)		Ratio of Products		Yield
n	R	(8) : (9)		%
3	Me	>97	-	87
3	H	60	40	72
2	Me	>97	-	78
2	H	60	40	98

Intramolecular cyclisation with subsequent oxidation during workup leads to the product (8). Similar cyclisation of the eight-membered ring cyclic imine (6; R=H) with subsequent oxidation has been proposed by Kawamoto et. al.[7] as the mechanism of formation of the benzimidazole compound (8; n=2, R=H) from the Schmidt reaction of 1-aza-6,7-benzcycloheptan-5-one. Alternative syntheses of pyrrolo- and pyridobenzimidazoles have involved either ring-closure reactions of benzimidazole derivatives[8] or formation of the imidazole ring[9] as the final step.

The high regioselectivity shown in the initial hydroformylation reaction can mainly be ascribed to the established pattern of terminal aldehyde formation from a,a-disubstituted alkenes.[10] It was possible however, that chelation of one of the amino-nitrogen atoms to the rhodium catalyst was also promoting the high regioselectivity. Such effects have been noted for reaction of primary aliphatic amines[11] but were less pronounced for other rhodium-catalysed reactions of unsaturated anilines.[12] Reactions of the straight chain alkenes (3; n=2 and 3; R=H) suggested that this was again the case as mixtures of benzimidazoles (8) and

(9) were now formed presumably arising from an initial non-regioselective hydroformylation giving mixtures of the aldehydes (4) and (5).

Reactions of the propenyl compounds (3; n=1, R=H or Me) were more complex in that intermediate products e.g. (6; n=1, R=Me) could be isolated and the products varied with reaction conditions. Reaction of the terminal alkene (3; n=1, R=H) gave mixtures of the cyclic imine (6; n=1, R=H), the related benzimidazole (8; n=1, R=H) and the cyclic diamine (10), presumably resulting from hydrogenation of the intermediate imine (7; n=1, R=H).



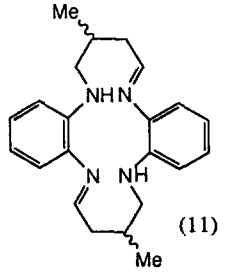
(10)

The three products were formed in the ratio (6) + (8) : (10), 70 : 30. The ratio of (6) : (8) varied with reaction conditions in a non-systematic manner. The formation of (10) presumably occurs because of the amount of strain in the precursor imine (7; n=1, R=H) which makes the $\rangle C{=}N-$ highly reactive. Such strain cannot be relieved by cyclisation as this would lead to formation of a 4-membered ring and thus hydrogenation occurs.

Reaction of the branch-chain compound was less sensitive to reaction conditions and gave mixtures of the cyclic imine (6; n=1, R=Me) and the related benzimidazole (8; n=1, R=Me) in approximately 70 : 30 ratio.

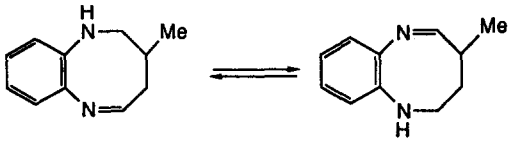
Atropisomerism in 3,4,5,6-tetrahydro-4-methyl-3H-1,6-benzodiazocine (6; n=1, R=Me)

The ^{1}H and ^{13}C n.m.r. spectra of this compound showed a doubling up of all signals suggesting that two isomers were present in ratio *ca.* 60 : 40. The signals did not broaden or coalesce when spectra were recorded at temperatures up to 100°C suggesting the presence of a significant barrier to interconversion. The existence of atropisomers in medium - sized heterocycles has been discussed recently.[13] The barriers to interconversion of atropisomers in a 1,3-diconstrained system can be significant but no previous examples of significant barriers arising from a benzene ring and an imino- group appear to have been observed. An alternative explanation was that the product was not the cyclic imine (6; n=1, R=Me) but was a mixture of the diastereoisomeric dimers (11) arising from intermolecular condensation of the intermediate aminoaldehyde (4; n=1, R=Me).



(11)

However, molecular weight determinations by vapour-phase osmometry and chemical ionisation mass spectroscopy did not support the dimeric structure. Another possible explanation was that in the presence of a rhodium catalyst the imine (6; n=1; R=Me) had partially isomerised to the related imine (12).



(6; n=1; R=Me) (12)

However no evidence for the isomeric benzimidazole that would result from intramolecular cyclisation/oxidation was observed. It thus appears that two atropisomers of the cyclic imine (6; n=1, R=Me) exist and that there is a substantial barrier to their interconversion.

EXPERIMENTAL

General conditions are as described previously.[12,14] The molecular weight of the cyclic imine was determined for solutions in toluene using a Knauer vapour pressure osmometer with benzil as the standard.

Alkenamines (1)

But-3-en-1-amine (1; n=2, R=H) b.p. 75°/760 mm (lit.,[15] 78°/760 mm); 3-methylbut-3-en-1-amine (1; n=2, R=Me) b.p. 83-85°/760 mm (lit.,[16] 85-90°/760 mm), pent-4-en-1-amine, b.p. 93-96°/760 mm (lit.,[17] 91-94°/760 mm) and 4-methylpent-4-en-1-amine, b.p. 40-45°/25 mm were prepared from the corresponding alcohols by a modified Mitsunobu procedure.[18]

N-Alkenyl-2-nitrobenzenamines (2)

These compounds were prepared by heating the amine (1) with 2-chloronitrobenzene in a Carius tube containing a stirring bead.[5a]

N-(Prop-2-enyl)-2-nitrobenzenamine (2; n=1, R=H) had ν_{max} 3365s, 1615s, 1575s, 1345s cm^{-1}. ^1H n.m.r. δ (200 MHz): 3.91, m, 2H, *J* 5.4, 1.7 Hz, H1'; 5.12-5.41, m, 2H, *J* 16.7, 10.5, 1.4 Hz, H3'; 5.84-6.04, m, 1H, *J* 17.1, 10.1, 5.2 Hz, H2'; 6.61, td, 1H, *J* 8.4, 1.2 Hz, H4; 6.84, bd, 1H, *J* 8.7 Hz, H6; 7.80, td, 1H, *J* 8.2, 1.4 Hz, H5; 8.00-8.36, dd and bs, 2H, *J* 8.7, 1.6 Hz, H3 and NH. Mass spectrum: *m/z* 178(M, 67%), 161(13), 151(20), 144(12), 132(17), 131(73), 130(100), 119(12), 106(19), 105(95), 104(30), 103(18), 92(22), 91(25), 78(27), 77(55), 65(23), 55(28), 51(31).

N-(2-Methylprop-2-enyl)-2-nitrobenzenamine (2; n=1, R=Me), b.p. (oven) 85-95°/0.3 mm (Found: C, 62.9; H, 6.6; N, 14.2. $C_{10}H_{12}N_2O_2$ requires C, 62.5; H, 6.3; N, 14.6%). ν_{max} 3389s, 1659m, 1619s, 1574s, 1511s, 1353s cm^{-1}. ^1H n.m.r. δ (300 MHz): 1.81, s, 3H, Me; 3.87, s, 1H and 3.89, s, 1H, H1'; 4.97, m, 2H, *J* 1.3 Hz, H3'; 6.65, td, 1H, *J* 8.4, 1.3 Hz, H4; 6.78, d, 1H, *J* 8.6 Hz, H6; 7.41, 1H, td, *J* 8.6, 1.5 Hz, H5; 8.18, dd, 1H, *J* 8.5, 1.5 Hz, H3; 8.29, bs, 1H, NH. ^{13}C n.m.r. δ (50 MHz): 20.15 (Me); 48.59 (C1'); 111.55, 114.09 (Arom. CH); 115.34 (C3'); 128.57 (Arom. CH); 131.74 (Arom.

C); 135.88 (Arom. CH); 140.37 (C2'); 145.41 (Arom. C). Mass spectrum: *m/z* 192(M, 100%), 177(10), 151(75), 146(33), 145(58), 144(61), 131(56), 130(64), 119(35), 118(23), 106(29), 105(92), 104(49), 93(54), 92(35), 91(42), 79(71), 78(31), 77(75), 69(80), 55(77), 53(22), 52(31), 51(54).

N-(But-3-enyl)-2-nitrobenzenamine (2; n=2, R=H) b.p. (oven) 60-65°/0.08 mm (Found: C, 62.6; H, 6.2; N, 14.4. $C_{10}H_{12}N_2O_2$ requires C, 62.5; H, 6.3; N, 14.6%). ν_{max} 3375s, 1619s, 1573m, 1513s, 1353s cm^{-1}. ^1H n.m.r. δ (200 MHz): 2.49, qd, 2H, *J* 5.6, 1.1 Hz, H2'; 3.26-3.48, m, 2H, H1'; 5.14-5.27, m, 2H, *J* 17.0, 10.3, 1.7 Hz, H4'; 5.75-5.95, m, 1H, *J* 17.0, 10.1, 7.0 Hz, H3'; 6.63, td, 1H, *J* 8.4, 1.2 Hz, H4; 6.86, dd, 1H, *J* 8.7, 0.8 Hz, H6; 7.43, td, 1H, *J* 8.6, 1.5 Hz, H5; 8.06, bs, 1H, NH; 8.15, dd, 1H, *J* 8.6, 1.5 Hz, H3. ^{13}C n.m.r. δ (50 MHz): 33.18, 42.12 (CH_2); 113.79, 115.22 (Arom. CH); 117.98 (C4'); 126.86 (Arom. CH); 131.84 (Arom. C); 134.60 (C3'); 136.20 (Arom. CH); 145.38 (Arom. C). Mass spectrum: *m/z* 192(M, 11%), 152(10), 151(100), 121(7), 120(3), 105(8), 93(13), 91(8), 78(15), 77(10), 51(8).

N-(3-Methylbut-3-enyl)-2-nitrobenzenamine (2; n=2, R=Me). b.p. (oven) 90-95°/0.1 mm (Found: C, 64.0; H, 7.2; N, 13.3. $C_{11}H_{14}N_2O_2$ requires C, 64.1; H, 6.8; N, 13.6%). ν_{max} 3382s, 1619s, 1573s, 1513s, 1353s cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.79, s, 3H, Me; 2.46, t, 2H, *J* 6.8 Hz, H2'; 3.39, m (AB of ABX), 2H, *J* 6.9 Hz, H1'; 4.89, d, 1H, *J* 1.0 Hz and 4.93, d, 1H, *J* 1.2 Hz, H4'; 6.64, td, 1H, *J* 8.4, 1.3 Hz, H4; 6.85, dd, 1H, *J* 8.7, 0.7 Hz, H6; 7.44, td, 1H, *J* 8.5, 1.5 Hz, H5; 8.03, bs, 1H, NH; 8.17, dd, 1H, *J* 8.6, 1.5 Hz, H3. ^{13}C n.m.r. δ (50 MHz): 21.91 (Me); 36.93, 40.83 (CH_2); 113.32 (C4'); 113.78, 115.19, 126.93 (Arom. CH); 131.75 (Arom. C); 136.14 (Arom. CH); 141.84 (C2'); 145.00 (Arom. C). Mass spectrum: *m/z* 207(M+1, 3%), 206(M, 30), 189(2), 171(2), 152(13), 151(100), 135(4), 121(11), 105(20), 104(28), 93(32), 91(17), 78(31), 77(28).

N-(Pent-4-enyl)-2-nitrobenzenamine (2; n=3, R=H) b.p. (oven): 90-95°/1 mm) (Found: C, 64.1; H, 6.7; N, 13.5. $C_{11}H_{14}N_2O_2$ requires C, 64.1; H, 6.9; N, 13.6%). ν_{max} 3381m, 3078w, 1619s, 1573s, 1512s, 1354m, 742s cm^{-1}. ^1H n.m..r. δ (200 MHz): 1.84, p, 2H, *J* 7.3Hz, H2'; 2.22, qd, 2H, *J* 7.1, 1.0Hz, H_3'; 3.33, t, 2H, *J* 7.1Hz, H1'; 5.01-5.14, m, 2H, H5'; 5.74-5.94, m, 1H, H4'; 6.63, td, 1H, *J* 7.8, 1.2Hz, H4; 6.85, dd, 1H, *J* 8.5, 1.0Hz, H6; 7.43, td, 1H, *J* 7.8, 1.8Hz, H5; 8.07, bs, 1H, NH; 8.17, dd, 1H, *J* 8.7, 1.6Hz, H3. ^{13}C n.m.r. δ (75 MHz): 27.93, 30.99, 42.20 (CH_2); 113.67, 115.06 (Arom. CH); 115.71 (C5'); 126.88 (Arom. CH); 131.60 (Arom. C); 136.14 (C4'); 137.17 (Arom. CH); 145.49 (Arom. C). Mass spectrum: *m/z* 206(M, 21%), 160(6), 151(100), 121(10), 105(25), 93(40), 77(36).

N-(4-Methylpent-4-enyl)-2-nitrobenzenamine (2; n=3, R=Me) b.p. (oven): 90-95°/0.2 mm) (Found: C, 65.6; H, 7.2; N, 12.9. $C_{12}H_{16}N_2O_2$ requires C, 65.3; H, 7.3; N, 12.7%). ν_{max} 3380s, 3076m, 1618s, 1571s, 1509s, 1263s, 1037s, 891s, 741s cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.75, s, 3H, CH_3; 1.86, p, 2H, *J* 7.1Hz, H2'; 2.16, t, 2H, *J* 7.5Hz, H3'; 3.29, qd, 2H, *J* 6.5, 1.7Hz, H1'; 4.74, m, 1H and 4.77, m, 1H, H5'; 6.61, td, 1H, *J* 7.8, 1.3Hz, H4; 6.83, dd, 1H, *J* 8.7, 1.0Hz, H6; 7.41, td, 1H, *J* 7.9, 1.7 Hz, H5; 8.14, dd, 1H, *J* 8.7, 1.7Hz, H3. ^{13}C n.m.r. δ (50 MHz): 22.12 (CH_3); 26.49, 34.84, 42.27 (CH_2), 110.76 (C4'), 113.61, 114.94, 126.67 (Arom. CH); 131.51 (Arom. C); 136.07 (Arom. CH); 144.20 (Arom. C); 145.41 (C5'). Mass spectrum: *m/z* 220(M, 16%), 151(100), 134(46), 119(12), 106(34), 93(38), 77(27), 67(11), 55(10), 51(13).

N-Alkenyl-1,2-diaminobenzenes (3)

These compounds were prepared by reaction of nitro amine (2) with iron powder and concentrated hydrochloric acid in 50% aqueous ethanol.[5b]

N-(Prop-2-enyl)benzene-1,2-diamine (3; n=1, R=H) b.p. (oven) 85-95°/0.9 mm (lit.[19] 88-92°/0.3 mm). ν_{max} 3350bs, 1620s, 1600sh cm^{-1}. ^1H n.m.r. δ (200 MHz): 3.48, bs, 3H, NH and NH_2; 3.78, dt, 2H, *J* 5.4, 1.6 Hz, H1'; 5.18, dq, 1H, *J* 10.5, 1.7 Hz, E-H3'; 5.32, dq, 1H, *J* 17.0, 1.4 Hz, Z-H3'; 5.89-6.14, m, 1H, *J* 16.9, 10.4, 5.5 Hz, H2'; 6.60-6.80, m, 4H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 46.82 (C1'); 112.09, 116.27 (Arom. CH); 116.50 (C3'); 118.76, 120.64 (Arom. CH); 134.30 (Arom. C); 135.59 (C2'); 137.50 (Arom. C). Mass spectrum: *m/z* 148(M, 47%), 132(10), 131(25), 130(27), 119(63), 118(13), 108(23), 107(100), 92(12), 91(13), 83(10), 80(54), 77(22), 65(23), 51(18).

N-(2-Methylprop-2-enyl)benzene-1,2-diamine (3; n=1, R=Me) b.p. (oven) 80-90°/0.4 mm (Found: C, 74.3; H, 8.9; N, 16.9. $C_{10}H_{14}N_2$ requires C, 74.0; H, 8.7; N, 17.3%). ν_{max} 3384s, 3350s, 1599s cm^{-1}. ^1H n.m.r. δ (300 MHz): 1.04, s, 3H, Me; 3.29, bs, 2H, NH_2; 3.57, bs, 1H, NH; 3.65, s, 2H, H1'; 4.88, d, 1H, *J* 0.7 Hz and 4.96, d, 1H, *J* 0.6 Hz, H3'; 6.60, dd, 1H, *J* 7.7, 1.5 Hz, H3; 6.68, m, 2H, H5 and H6; 6.79, td, 1H, *J* 7.8, 1.2 Hz, H4. ^{13}C n.m.r. δ (50 MHz): 20.66 (Me); 50.10 (C1'); 110.87, 111.98 (Arom. CH); 116.55 (C3'); 118.52, 120.68 (Arom. CH); 134.02, 137.75 (Arom. C); 142.84 (C2'). Mass spectrum: *m/z* 162(M, 60%), 144(5), 130(4), 121(13), 119(28), 108(10), 107(100), 94(12), 80(36), 65(12), 53(4).

N-(But-3-enyl)benzene-1,2-diamine (3; n=2, R=H) b.p. (oven) 60-70°/0.2 mm (Found: C, 73.8; H, 8.4; N, 16.9. $C_{10}H_{14}N_2$ requires C, 74.0; H, 8.7; N, 17.3%). ν_{max} 3400s, 3333s, 1618s, 1598s cm^{-1}. ^1H n.m.r. δ (200 MHz): 2.43, qt, 2H, *J* 6.9, 1.2 Hz, H2'; 3.17, t, 2H, *J* 6.8 Hz, H1'; 3.31, bs, 3H, NH and NH_2; 5.01-5.25, m, 2H, *J* 17.3, 9.9, 1.2 Hz, H4'; 5.74-5.98, m, 1H, *J* 17.1, 10.1, 6.9 Hz, H3'; 6.97-7.30, m, 4H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 33.77, 43.14 (CH_2); 111.87, 116.46 (Arom. CH); 116.96 (C4'); 118.62, 120.67 (Arom. CH); 134.25 (Arom. C); 135.94 (C3'); 137.69 (Arom. C). Mass spectrum: *m/z* 162(M, 21%), 122(8), 121(100), 119(12), 107(3), 94(37), 93(7), 92(5), 80(8), 77(10), 65(11), 53(4), 52(3).

N-(3-Methylbut-3-enyl)benzene-1,2-diamine (3; n=2, R=Me) b.p. (oven) 85-90°/0.1 mm (Found: C, 75.2; H, 9.2; N, 15.8. $C_{11}H_{16}N_2$ requires C, 75.0; H, 9.2; N, 15.9%). ν_{max} 3394s, 3333s, 1622s, 1599s cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.77, s, 3H, Me; 2.40, t, 2H, *J* 6.7 Hz, H2'; 3.21, t, 2H, *J* 6.8 Hz, H1'; 3.27, bs, 3H, NH and NH_2; 4.82, d, 1H, *J* 1.1 Hz and 4.85, d, 1H, *J* 1.6 Hz, H4'; 6.64-6.72, m, 3H and 6.76-6.87, m, 1H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 22.02 (Me); 37.51, 41.51 (CH_2); 111.67 (Arom. CH); 112.19 (C4'); 116.36, 118.47, 120.62 (Arom. CH); 134.16, 137.68 (Arom. C); 143.11 (C3'). Mass spectrum: *m/z* 176(M, 23%), 131(3), 122(8), 121(100), 119(20), 108(10), 107(17), 94(30), 93(6), 92(7), 80(10), 77(9), 65(11).

N-(Pent-4-enyl)benzene-1,2-diamine (3; n=3, R=H) b.p. (oven) 85-90°/0.4 mm (Found: C, 74.8; H, 8.8; N, 15.8. $C_{11}H_{16}N_2$ requires C, 75.0; H, 9.2; N, 15.9%). ν_{max} : 3389s, 3331s, 3073s, 1621s, 1598s, 1508s, 1269s, 911s, 740s cm^{-1}. ^1H n.m.r. δ (300 MHz): 1.76, p, 2H, *J* 7.2Hz, H2'; 2.20, qt, 2H, *J* 7.1, 1.3Hz, H3'; 3.11, t, 2H, *J* 7.1 Hz, H1'; 3.27, bs, 3H, NH and NH_2; 4.96-5.10, m, 2H, H5'; 5.78-5.91, m, 1H, H4'; 6.63-6.71, m, 3H, and 6.79-6.85, m, 1H, Arom. H. ^{13}C n.m.r. δ (75 MHz):

28.80, 31.41, 43.69 (CH_2); 111.68 (Arom. CH); 114.99 (C5'); 116.47, 118.40, 120.71 (Arom. CH); 134.04, 137.91 (Arom. C); 138.08 (C4'). Mass spectrum: *m/z* 176(M, 30%), 121(100), 108(9), 94(29), 80(10), 65(10), 53(4).

N-(4-Methylpent-4-enyl)benzene-1,2-diamine (3; n=3, R=Me) b.p. (oven) 125-130°/0.3 mm. (Found: C, 75.5; H, 9.5; N, 15.0. $C_{12}H_{18}N_2$ requires C, 75.7; H, 9.5; N, 14.7%). ν_{max} : 3393s, 3330s, 3070s, 1647s, 1620s, 1599s, 1510s, 1448s, 1269s, 887s cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.74, s, 3H, CH_3; 1.77, m, 2H, H_2'; 2.13, t, 2H, *J* 7.5 Hz, H3'; 3.07, t, 2H, *J* 7.1 Hz, H1'; 3.28, bs, 3H, NH and NH_2; 4.73, m, 2H, H5'; 6.60-6.69, m, 3H, and 6.74-6.87, m, 1H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 22.41 (CH_3); 27.46, 35.37, 43.86 (CH_2); 110.30 (C5'); 111.57, 116.44, 118.34, 120.70 (Arom. CH); 134.04, 137.99, (Arom. C); 145.22 (C4'). Mass spectrum: *m/z* 190(M, 27%), 175(4), 134(3), 121(100), 108(9), 94(28), 80(9), 65(10), 53(4).

Hydroformylations

N-(Prop-2-enyl)benzene-1,2-diamine (3; n=1, R=H). In a typical reaction, rhodium(II) acetate dimer (0.0073 g, 0.017 mmol), triphenylphosphine (0.017 g, 0.066 mmol) and N-(prop-2-enyl)benzene-1,2-diamine (3; n=1, R=H) (0.49 g, 3.31 mmol) in ethyl acetate (10ml) were reacted with carbon monoxide and hydrogen (400 p.s.i.) at 70° for 20 h. The ratio of the products (6) : (8) : (10) was 50 : 30 : 20 as determined from the ^1H and ^{13}C n.m.r. spectra of the crude reaction mixture. The mixture of compounds was separated from the spent catalyst by preparative t.l.c. (Alumina; ether) to yield the product in a good mass recovery (0.42 g). The individual components were separated by preparative t.l.c. (Alumina; ether/light petroleum 1:1, graded to ether only) and obtained analytically pure after sublimation.

3,4,5,6-Tetrahydro-3H-1,6-benzodiazocine (6; n=1, R=H) (0.21g, 40%) m.p. 60° dec. (Found: C, 75.1; H, 7.2; N, 17.2. $C_{10}H_{12}N_2$ requires C, 75.0; H, 7.6; N, 17.5%). ν_{max} 3150w, 1600m, 735s cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.58-1.87, m, 3H, 1.94-2.14, m, 1H, 3.13, m, 1H and 3.26-3.38, m, 1H, H3, H4 and H5; 4.01, bs, 1H, NH; 5.22, t, 1H, *J* 5.4 Hz, H2; 6.44-6.61, m, 2H and 6.61-6.79, m, 2H, Ar. ^{13}C n.m.r. δ (50 MHz): 23.68, 34.41, 54.25 (CH_2); 82.03 (C2); 109.59, 111.65, 120.41, 121.01 (Arom. CH); 142.18, 144.74 (Arom. C). Mass spectrum: *m/z* 160(M, 4%), 159(17), 158(100), 157(70), 156(13), 145(3), 132(13), 131(11), 130(10), 118(12), 103(11), 90(7), 77(12), 66(12).

2,3-Dihydro-1H-pyrrolo[1,2-a]benzimidazole (8; n=1, R=H) (0.15g, 29%) m.p. 114.5 - 115.0° (lit.[20] 115°) sublimed 50-60°/0.15 mm (Found: C, 75.8; H, 6.6; N, 17.7. Calculated for $C_{10}H_{10}N_2$ C, 75.9; H, 6.4; N, 17.7%). ν_{max} 1610w, 1520m, 740s cm^{-1}. ^1H n.m.r. δ (200 MHz): 2.65, m, 2H, *J* 7.4, 4.1 Hz, H2; 3.00, m, 2H, *J* 7.3, 4.5 Hz, H3; 4.02, m, 2H, *J* 7.1, 4.1 Hz, H1; 7.16-7.28, m, 3H, H6, H7 and H8; 7.66-7.71, m, 1H, H5. The ^1H n.m.r. spectrum was in good agreement with the spectrum reported in the literature.[7] ^{13}C n.m.r. δ (50 MHz): 23.27, 25.85, 42.51 (CH_2); 109.34, 119.32, 121.46, 121.56 (Arom. CH); 132.18, 148.67 (Arom. C); 161.00 (C=N). Mass spectrum: *m/z* 159(M+1, 12%), 158(M, 100), 157(78), 156(11), 132(5), 131(4), 130(10), 129(6), 118(2), 103(11), 102(6), 90(8), 77(10), 76(7), 66(10), 63(8), 51(9).

2,3,4,5-Dihydro-3-methyl-1H-1,5-benzodiazepine (10) (0.09g, 17%) m.p. 86.5-87.0° sublimed 50-60°/0.25 mm (Found: C, 74.1; H, 9.0; N, 16.9. $C_{10}H_{14}N_2$ requires C, 74.0; H, 8.7; N, 17.3%). ν_{max} 3319s, 1595m, 746s cm^{-1}. ^1H n.m.r. δ (200 MHz): 0.90, d, 3H, *J* 6.6 Hz, Me; 1.86-2.09, m, 1H,

H3; 2.57, dd, 2H, *J* 12.4, 8.8 Hz, H2 and H4; 3.17-3.34, m, 2H, *J* 12.4, 5.6 Hz, H2' and H4'; 3.62, bs, 2H, NH; 6.62-6.83, m, 4H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 18.37 (Me); 36.18 (CH_2); 53.67 (C3); 119.51, 120.91 (Arom. CH); 140.40 (Arom. C). Mass spectrum: *m/z* 162(M, 48%), 145(5), 144(4), 130(6), 120(23), 119(100), 93(3), 92(13), 91(4), 65(13).

N-(2-Methylprop-2-enyl)benzene-1,2-diamine (3; n=1, R=Me). Reaction of this compound (0.36g) gave a crude reaction mixture (0.38g) whose ^{1}H and ^{13}C n.m.r. spectra suggested that the compounds (6) and (8) were present in the ratio 70:30, the former as a 60:40 mixture of isomers. The ^{1}H n.m.r. spectrum was re-run four days after the reaction and indicated that (8) was now the major product. The products were separated by preparative t.l.c. (Alumina; ether/light petroleum, 1:1 graded to ether only) and obtained analytically pure after sublimation. Due to the inherent instability of (6), isolated yields and isomer ratios of purified material serve only as an approximate guide.

3,4,5,6-Tetrahydro-4-methyl-3H-1,6-benzodiazocine (6; n=1, R=Me) (0.25g, 65%) m.p. the melt solidifies at 65° and remelts at 75.5-78.0° sublimed 50-60°/0.25 mm (Found: C, 76.1; H, 8.4; N, 16.3. $C_{11}H_{14}N_2$ requires C, 75.8; H, 8.1; N, 16.1%). ν_{max} 3189m, 1659m, 1621s, 1596s, 1529s cm^{-1}. The ^{1}H and ^{13}C n.m.r. spectra indicated the presence of a 52.48 mixture of isomers which could not be separated. ^{1}H n.m.r. δ (200 MHz): the signals belonging to each of the isomers were not distinguishable thus no definite assignments were attempted; 1.02, d, *J* 6.6 Hz, 1.06, d, *J* 6.4 Hz, Me; 1.29-1.44, m, *J* 11.2, 8.5 Hz, 1.62-1.76, m, *J* 9.3, 7.0 Hz, 1.86-1.97, m, *J* 7.0, 2.1 Hz, 2.09-2.38, bm, *J* 2.0 Hz, 2.63, t, *J* 9.4 Hz, 2.84, dd, *J* 11.1, 8.8 Hz, 3.31, m, *J* 11.1, 7.2 Hz and 3.59, dd, *J* 9.2, 7.0 Hz, H3, H4 and H5; 3.98, bs, NH; 5.25, dd, *J* 8.4, 5.2 Hz and 5.38, dd, *J* 5.8, 2.8 Hz, H2; 6.49-6.60, m, and 6.62-6.72, m, Arom. H. ^{13}C n.m.r. δ (50 MHz): the major isomer has been quoted first: 17.12 (Me); 31.60, 43.34 (CH_2); 62.60 (C4); 81.52 (C2); 109.26, 112.29, 120.61, 121.25 (Arom. CH); 142.69, 144.70 (Arom. C). 17.76 (Me); 32.67, 42.73 (CH_2); 60.74 (C4); 82.55 (C2); 110.05, 110.90, 120.69 (Arom. CH); 141.39, 145.24 (Arom. C). Mass spectrum: *m/z* 174(M, 43%), 173(29), 172(17), 171(18), 159(22), 158(8), 157(13), 145(7), 133(11), 132(100), 131(73), 130(9), 119(10), 118(13), 104(7), 92(7), 77(16), 65(8). Mass spectrum (CI, methane): m/z 174(M, 20), 173(100). Vapour phase osmometry measurements gave values in the range 145-150 (monomer 174).

2,3-Dihydro-2-methyl-1H-pyrrolo[1,2-a]benzimidazole (8; n=1, R=Me) (0.11g, 29%) m.p. 88.2-88.5° sublimed 60-65°/0.1 mm (Found: C, 77.0; H, 7.4; N, 16.6. $C_{11}H_{12}N_2$ requires C, 76.7; H, 7.0; N, 16.3%). ν_{max} 1616m, 1580w, 1523m, 757s cm^{-1}. ^{1}H n.m.r. δ (200 MHz): 1.34, d, 3H, *J* 6.8 Hz, Me; 2.65, m, 1H, *J* 9.8, 5.4, 1.2 Hz, H2; 3.07-3.30, m, 2H, *J* 8.0, 5.7, 1.6 Hz, H3; 3.62, dd, 1H, *J* 10.1, 6.2 Hz, H1; 4.21, dd, 1H, *J* 10.0, 7.6 Hz, H1'; 7.12-7.34, m, 3H, H6, H7 and H8; 7.70, m, 1H, H5. ^{13}C n.m.r. δ (50 MHz): 19.52 (Me); 32.12 (C3); 35.68 (C2); 50.06 (C1); 109.42, 119.52, 121.58, 121.76 (Arom. CH); 137.27, 148.43 (Arom. C); 160.57 (C=N). Mass spectrum: *m/z* 172(M, 100%), 171(36), 157(38), 156(8), 145(8), 144(4), 132(5), 131(9), 130(24), 118(4), 103(17), 102(7), 90(8), 77(13), 76(10), 63(5), 51(8).

Similar reactions conducted at 80° and 100° both resulted in the formation of (6) and (8) in the ratio 80:20 with the former as a 60:40 isomeric mixture. The mass recovery in both cases was >95%. A reaction however, conducted at 60° resulted in the recovery of only the starting material.

N-(But-3-enyl)benzene-1,2-diamine (3; n=2, R=H). Reaction of this compound (0.15g) gave a mixture of (8 and 9; n=2, R=H) (0.16g) which were separated by preparative t.l.c. (Alumina; ether/light petroleum, 3:4) and obtained spectroscopically pure after sublimation.

1,2,3,4-Tetrahydro-1H-pyrido[1,2-a]benzimidazole (8; n=2, R=H) (0.13g, 62%) m.p. 99.8-100.1° (lit.[21], 99-100°) (Found: C, 76.7; H, 6.7; N, 16.1. Calculated for $C_{11}H_{12}N_2$ C, 76.7; H, 7.0; N, 16.3%). ν_{max} 1615w, 1509s, 756s cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.93-2.26, m, 4H, *J* 6.4, 1.8, 1.0 Hz, H2 and H3; 3.14, t, 2H, *J* 6.4 Hz, H4; 4.10, t, 2H, *J* 6.0 Hz, H1; 7.14-7.40, m, 3H, H7, H8 and H9; 7.63-7.81, m, 1H, H6. ^{13}C n.m.r. δ (50 MHz): 20.70, 22.61, 25.39 (CH_2); 42.38 (C1); 108.71, 118.77, 121.62, 122.04 (Arom. CH); 135.54, 142.70 (Arom. C); 151.67 (C=N). Mass spectrum: *m/z* 173(M+1, 12%), 172(M, 100), 171(56), 170(8), 144(30), 143(12), 131(4), 117(12), 90(6), 77(11), 51(7).

2,3-Dihydro-3-methyl-1H-pyrrolo[1,2-a]benzimidazole (9; n=2, R=H) (0.05g, 24%) m.p. 39.9-40.2° (lit.[22] 35-40°) ν_{max} 1618m, 1527s cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.50, d, 3H, *J* 7.0 Hz, Me; 2.19-2.41, m, 1H, *J* 12.9, 8.6, 7.9 Hz, H2; 2.81-3.02, m, 1H, *J* 11.8, 7.9, 3.6 Hz, H2'; 3.40, sextet, 1H, *J* 7.6 Hz, H3; 3.94-4.24, m, 2H, *J* 10.3, 8.8, 3.8 Hz, H1; 7.16-7.35, m, 3H, H6, H7 and H8; 7.66-7.79, m, 1H, H5. ^{13}C n.m.r. δ (50 MHz): 18.02 (Me); 30.97 (C3); 35.33, 41.93 (CH_2); 109.51, 119.61, 121.72, 121.90 (Arom. CH); 132.24, 148.39 (Arom. C); 164.35 (C=N). Mass spectrum: *m/z* 173(M+1, 8%), 172(M, 65), 171(19), 158(12), 157(100), 156(6), 144(5), 143(6), 129(9), 118(5), 102(7), 90(4), 77(13), 63(5), 51(9).

N-(3-Methylbut-3-enyl)benzene-1,2-diamine (3; n=2, R=Me). Reaction of this compound (0.11g) gave a crude product (0.1g) whose ^1H and ^{13}C n.m.r. spectra indicated that compound (8; n=2, R=Me) was present as the major component (> 95%). The product was purified by preparative t.l.c. (Alumina; ether/light petroleum, 3:2) and obtained analytically pure after sublimation.

1,2,3,4-Tetrahydro-3-methyl-1H-pyrido[1,2-a]benzimidazole (8; n=2, R=Me) (0.09g, 78%) m.p. 133.5-134.0° sublimed 60°/0.05 mm (Found: C, 77.4; H, 7.5; N, 15.1. $C_{12}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%). ν_{max} 1614m, 1516s, 740s cm^{-1}. ^1H n.m.r. δ (300 MHz): 1.19, d, 3H, *J* 6.5 Hz, Me; 1.76-1.86, m, 1H, *J* 5.8 Hz, H3; 2.09-2.23, bm, 2H, H2; 2.64, dd, 1H, *J* 17.1, 10.3 Hz, H4; 3.21, m, *J* 17.1, 10.5, 4.8 Hz, H4'; 3.96, m, 1H, *J* 11.4, 4.8 Hz, H1; 4.22, m, 1H, *J* 5.8, 2.8 Hz, H1'; 7.18-7.32, m, 3H, H7, H8 and H9; 7.68, m, 1H, H6. ^{13}C n.m.r. δ (50 MHz): 21.10 (Me); 27.63 (C3); 30.48, 33.46, 41.58 (CH_2); 108.75, 118.92, 121.65, 122.04 (Arom. CH); 134.51, 143.06, (Arom. C); 151.81 (C=N). Mass spectrum: *m/z* 187(M+1, 10%), 186(M, 100), 185(20), 171(14), 169(10), 157(7), 145(12), 144(96), 143(36), 132(13), 131(9), 118(13), 117(34), 103(6), 102(10), 90(11), 89(6), 77(26), 76(15), 65(8), 64(9), 63(10), 51(14).

N-(Pent-4-enyl)benzene-1,2-diamine (3; n=3, R=H). Reaction of this compound (0.2g) gave crude product (0.15g) shown by ^1H and ^{13}C n.m.r. spectroscopy to be a mixture of (8 and 9; n=3, R=H) in the ratio 60:40. The components were separated by preparative t.l.c. (alumina: ether/light petroleum 1:1).

7,8,9,10-Tetrahydro-6H-azepino[1,2-a]benzimidazole (8; n=3, R=H) m.p. 124-125°C (lit.[23] 124-125°C). ν_{max} 1615w, 1510w, 1240w, 1190w cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.74-1.97, m, 6H, H7, H8 and H9; 3.07-3.12, m, 2H, H6; 4.11-4.16, m, 2H, H10; 7.16-7.30, m, 3H, and 7.65-7.74, m, 1H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 25.52, 28.69, 30.10, 30.88 (CH_2); 44.42 (C10); 108.62, 119.19,

121.46, 121.81 (Arom. CH); 135.71, 142.37 (Arom. C); 157.45 (C=N). Mass spectrum: *m/z* 186(M, 100%), 171(38), 157(33), 145(11), 132(11), 118(4), 103(6), 97(3), 90(4), 77(13), 57(3), 51(8).

1,2,3,4-Tetrahydro-4-methyl-1H-pyrido[1,2-a]benzimidazole (9; n=3, R=H) m.p. 82.3-82.5°C (Found: C, 77.5; H, 7.9; N, 14.7. $C_{12}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%). ν_{max} 1654w, 1147w, 734w cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.54, d, 3H, *J* 7.1 Hz, Me; 1.59-2.32, bm, 4H, H2 and H3; 3.10-3.21, m, 1H, H4; 3.89-4.09, m, 1H, and 4.10-4.20, m, 1H, H1; 7.17-7.30, m, 3H, and 7.69-7.76, m, 1H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 19.38 (Me); 21.57, 29.49 (CH_2); 31.15 (C4); 42.60 (C1); 108.83, 119.03, 121.71, 121.98 (Arom. CH); 134.57, 142.82 (Arom. C); 156.07 (C=N). Mass spectrum: *m/z* 186 (M, 75%), 171(100), 157(34), 143(5), 132(16), 118(3), 102(10), 77(14), 71(3), 65(5), 51(9).

N-(4-Methylpent-4-enyl)benzene-1,2-diamine (3; n=3, R=Me). Reaction (0.2g) gave a crude product (0.2g) which n.m.r. spectroscopy indicated was a single compound. The product was purified by preparative t.l.c. (alumina: ethyl acetate/light petroleum, 1:1) to give a cream solid.

7,8,9,10-tetrahydro-7-methyl-6H-azepino[1,2-a]benzimidazole (8; n=3, R=Me) (0.12g, 55%) m.p. 133-134°C (Found: C, 77.9; H, 8.1; N, 14.0. $C_{13}H_{16}N_2$ requires C, 78.0; H, 8.1; N, 14.0%). ν_{max} 1613w, 1509w, 1326w, 1271w, 924w cm^{-1}. ^1H n.m.r. δ (200 MHz): 1.05, d, 3H, *J* 6.7 Hz, Me; 1.55-2.10, m, 4H, H8 and H9; 2.81, dd, 1H, J 14.7, 10.0 Hz, H7; 3.03-3.21, m, 2H, H6; 3.95, dd, 1H, J 14.2, 9.8 Hz and 4.28, dd, 1H, J 14.4, 5.9 Hz, H10; 7.15-7.26, m, 3H, and 7.66-7.71, m, 1H, Arom. H. ^{13}C n.m.r. δ (50 MHz): 22.48 (Me); 27.36 (CH_2); 31.36 (C7); 37.36, 38.98, 44.27 (CH_2); 108.56 118.32, 120.63, 121.80 (Arom. CH); 135.61, 142.38 (Arom. C); 155.99 (C=N). Mass spectrum: *m/z* 200(M, 100%), 185(32), 171(24), 157(25), 146(69), 132(38), 117(10), 103(8), 90(8), 84(4), 77(22), 65(6), 51(12).

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