A METAL CATALYSED ROUTE TO BENZIMIDAZOLES CONTAINING A FUSED ALICYCLIC RING

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Rhodium catalysed reactions of N-alkenyl-1,2-diaminobenzenes (1) with hydrogen and carbon monoxide give benzimidazoles containing a fused alicyclic ring (6,7) in excellent yields.

There is much current interest in generating new, general routes to heterocyclic compounds.¹ We wish to report a general, high-yielding route to benzimidazoles containing a fused alicyclic ring (6,7) by rhodium catalysed reaction of readily available N-alkenyl-1,2-diaminobenzenes (1) with H_2/CO .



The N-alkenyl-1,2-diaminobenzenes (1) were prepared in high yields by reaction of 2-chloronitrobenzene with an alkenylamine and subsequent reduction of the nitro compound following the general method of Ashton.² Reaction of N-(3-methylbut-3-enyl)-1,2-diaminobenzene (1; n=3; R=Me) and N-(4-methylpent-4-enyl)-1,2-diaminobenzene (1; n=2; R=Me) gave in each case a single product, *i.e.* 1,2,3,4-tetrahydro-3-methylpyrido[1,2-*a*]benzimidazole (6; n=2, R=Me) and 7,8,9,10-tetrahydro-7-methyl-6H-azepino[1,2-*a*]benzimidazole (6; n=2, R=Me) and 7,8,9,10-tetrahydro-7-methyl-6H-azepino[1,2-*a*]benzimidazole (6; n=2, R=Me) and 7,8,9,10-tetrahydro-7-methyl-6H-azepino[1,2-*a*]benzimidazole (6; n=2, R=Me) in good yield (see Table). These products are visualised as arising from initial highly regioselective aldehyde formation at the terminal carbon atom (2) followed by intramolecular cyclisation with subsequent oxidation to the benzimidazole (6). A similar cyclisation of the eight - membered ring cyclic imine (4; n=2, R=H) with concurrent or subsequent oxidation was proposed by Kawamoto *et al*³ to explain the formation of the benzimidazole derivative (6; n=2, R=H) from Schmidt reaction of the ketone (8).

Other syntheses of the pyrrolo- and pyridobenzimidazoles have either involved ring closure reactions of benzimidazole derivatives⁴ or formation of the imidazole ring, e.g. by oxidation of 2-(N-pyrrolidino or Npiperidino) benzenamine with trifluoroperacetic acid5.

Reactions of the straight chain alkenes (1; n-2 & 3, R=H) gave high yields of benzimidazoles (6 and 7) presumably arising from non-regiospecific hydroformylation leading to a mixture of aldehydes (2 & 3) and imines (4 & 5).

Direct evidence for the involvement of the cyclic imines (4 and 5) came from reactions of N-(allvl)benzene-1.2-diamine (1; n=1, R=H) and N(methylallyl)benzene-1,2-diamine (1; n=1, R=Me). Intermediate imines (or their reduction products) were isolated as well as pyrrolobenzimidazoles. A typical reaction of N-(methylallyl)-1,2-diaminobenzene (1; n=1, R=Me) at 70° gave the 1,6-benzodiazocine (4; n=1, R=Me) and the pyrrolobenzimidazole (6; n=1, R=Me) in 65% and 29% yields respectively after preparative t.l.c. Reaction of N-(allyl)-1,2-diaminobenzene (1; n=1, R=H) gave a mixture (85%) of the 1,6-bendiazocine (4; n=1, R=H), the pyrrolobenzimidazole (6; n=1, R=H), and a saturated 1,5-benzodiazepine resulting from hydrogenation of the cyclic-imine (5; n=1, R=H). The eight-membered ring cyclic-imines cyclise more slowly than their nine - and ten - membered homologues and the seven-ring imine does not cyclise and is readily hydrogenated.

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	IABLE	Yields of Denzimidazoles				
Reactant (1)		Ratio of 1	Yield			
n	R	(6) :	(7)	%		
3	Me	>97	-	87%		
3	Н	60	40	72%		
2	Me	>97	-	78%		
2	Н	60	40	98%		

TA	BL	E	Yi	ele	ds	of	benzi	imi	ida	zol	es†

- Reactions were carried out with alkene, [Rh(OAc)2]2, PPh3 in ratio 200: 1: 4 for 20 to 60 hours at † 70° with 400 psi initial CO/H2 pressure.
- Estimated from ¹H and ¹³C n.m.r. spectra. İ

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