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SYNTHESIS OF O,C-DILITHIUM DERIVATIVES OF 2-(α-HYDROXYALKYL)-1-METHYLBENZIMIDAZOLES

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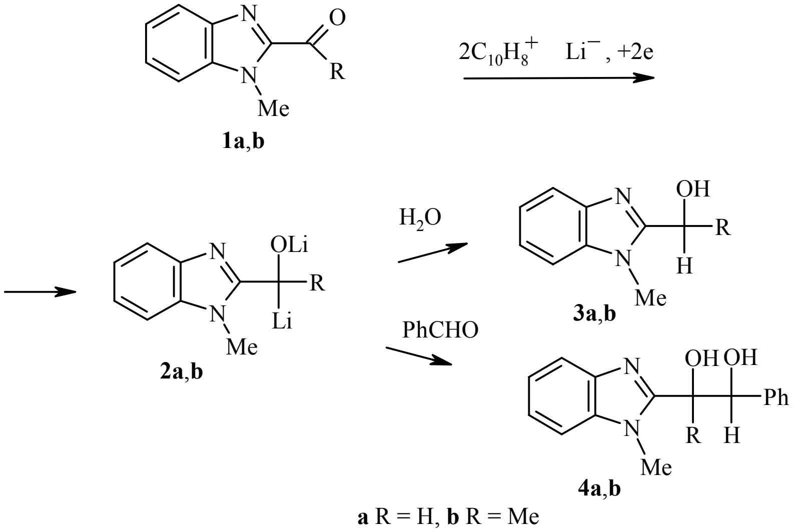
Diazoles and their halo derivatives form lithium organic compounds upon the action of lithium salts of arene radical–anions, in particular, lithium naphthalene [1, 2]. We have found that 2-acylbenzimidazoles react readily with lithium naphthalene to give O,C-dilithium derivatives, corresponding to a two-electron reduction of the substrates. Thus, 2-formyl-1-methyl- (**1a**) and 2-acetyl-1-methylbenzimidazoles (**1b**) react with lithium naphthalene in THF to give dilithium derivatives **2a** and **2b**, which undergo hydrolysis to give 2-hydroxymethyl-1-methyl- (**3a**) and 2-(α-hydroxyethyl)-1-methylbenzimidazoles (**3b**), respectively. The reaction of **2a** and **2b** with benzaldehyde gives diols **4a** and **4b**.



a R = H, **b** R = Me

1-(1-Methyl-1H-benzimidazol-2-yl)-2-phenylethane-1,2-diol (4a). A sample of 2-formyl-1-methylbenzimidazole (1.5 g, 9.4 mmol) in THF (10 ml) was added with stirring to a solution of lithium naphthalene obtained from naphthalene (3.6 g, 28.8 mmol) and lithium (0.2 g, 28.8 mmol) in THF (30 ml) at 0°C over 10 min and then, benzaldehyde (3.0 g, 28.3 mmol) in THF (10 ml) was added over 10 min. After 15 min, the mixture was hydrolyzed and the bases were extracted with a 1:1 mixture of conc. hydrochloric acid and water and, then, 1.7 g (68%) diol **4a** was isolated by the ordinary procedure; mp 177-180°C (acetonitrile).

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This compound is an approximately equimolar mixture of two diastereomeric racemates. The ^{1}H NMR spectrum of the mixture at 300 MHz (DMSO-d_6), δ, ppm, *J* (Hz): 3.4 (3H, s, NMe); 3.6 (3H, s, NMe); 4.7-4.9 (2H+2H, m, groups of CH–CH groups of both isomers); 5.4 (1H, d, OH, *J* = 4.8); 5.5-5.6 (2H, m, 2OH) and 5.6 (1H, d, OH, *J* = 6.0); 7.0-7.5 (9H+9H, m, arom. protons of both racemates). The signals of the hydroxyl groups disappear upon deuteration with D_2O, while the multiplet of the CH–CH fragments is simplified and converts into an eight-component superposition of the signals of the AB systems of the CH–CH groups of the two racemates (J_{vic} = 7.9 and 6.7 Hz). Found, %: C 71.9; H 5.7; N 10.7. $C_{16}H_{16}N_2O_2$. Calculated, %: C 71.6; H 6.0; N 10.4.

2-(1-Methyl-1H-benzimidazol-2-yl)-1-phenylpropane-1,2-diol (4b) was obtained analogously using ketone **1b** instead of aldehyde **1b** in 64% yield; mp 197-198°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 2.5 (3H, s, CMe); 3.9 (3H, s, NMe); 4.9 1H, d, CH($\underline{\text{OH}}$), *J* = 4.6); 5.4 (1H, d, C$\underline{\text{H}}$(OH), *J* = 4.6); 5.4 (1H, s, OH); 7.1-7.2 (7H, m, arom. protons); 7.4 (1H, d, *J* = 8) and 7.5 (1H, d, *J* = 8) (arom. protons). Found, %: C 72.3; H 6.5; N 10.2. $C_{17}H_{18}N_2O_2$. Calculated, %: C 72.3; H 6.4; N 9.9.

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