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LETTERS

Preparation of N,N,N′,N′-2,3-Hexamethyl-2,3-butanediamine

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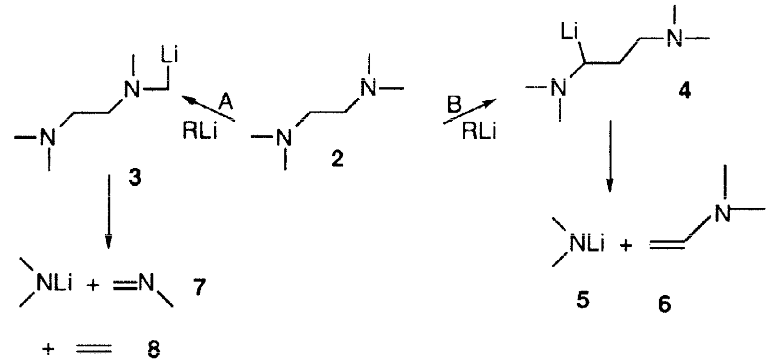
Abstract: The title compound has been prepared by aminolysis (dimethylamine) of the corresponding hexamethyl aziridinium iodide .

Keywords: diamines; aziridines; NMR; protonation

Although TMEDA is an effective catalyst for the reactions of organolithium compounds[1] it does, on prolonged exposure to these reagents, undergo different fragmentation reactions,[2,3] see **2** - **8**, initiated by C-metalation both at N-methyl, **3**, and methylene, **4**,



favored by the transient intermediacy of α-amino carbanionic species or of transition states with such characteristics. The title compound **1** is an attractive candidate for organolithium reaction systems in that the metalation of methylene route is unavailable since these protons have been replaced by methyls.

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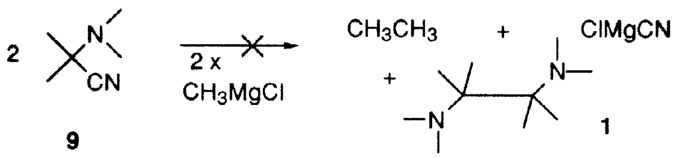
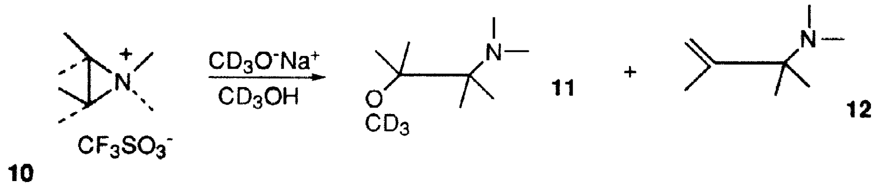
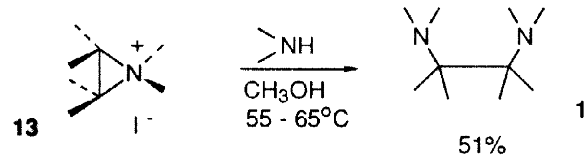
In 1925 Belgium workers reported compound **1** to result from the one electron reduction of 2,2-aminonitrile, **9**, by methylmagnesium chloride.[4,5]



We have been unable to repeat this claim, varying solvent, Grignard, and trying out CuI to promote one electron transfer; each such attempt resulted in recovery of aminonitrile.

Our approach to **1** is based on the well known cleavage of aziridines and aziridinium salts by amines or amide salts.[6,7] In fact the required aziridinium salt, **10**, has already been reported to cleave with methoxide to amino ether **11** with some elimination product, **12**, in a process first order in each of **10** and sodium methoxide.[8] Hence aziridinium iodide, **13**,[7] was allowed to react with dimethylamine in methanol. This clearly resulted in a 51% yield of the required diamine, **1**; NMR and MS data, are consistent for **1**, see Figure 1 which also shows the NMR data for aziridinium, **13**, and aziridine, **14**.





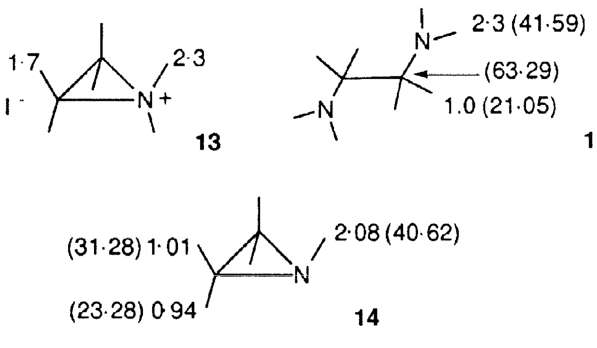
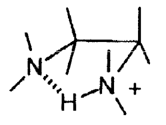
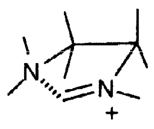


Figure 1 NMR chemical shifts ^{1}H and (^{13}C)

The three principal MS fragments, 173, 171 and 128 are in accord with proposed **15**, **16**, and cation **13**, respectively





m/z 173 171

15 **16**

We previously determined the pKa's of several tertiary vicinal diamines[9] and have now, for comparison, done so for **1**. In 50%/50% ethanol/water the values for **1** are found to be 11.2 and 3.3.[8] These data are similar to results for several cyclic cis tertiary vicinal diamine on five- and six-membered rings, typically 11 and 3. In contrast the pKa's for TMEDA, also in 1:1 ethanol/water, are 8.6 and 5.3. The increased pKa for the cis vicinal cyclic diamines was ascribed to intramolecular hydrogen bonding of the monoprotonated form. This effect may also explain the similar basicity of **1**, as proposed in structure **15**.

Selected Experimental

N,N,N′,N′-2,3-Hexamethyl-2,3-butanediamine,1. A mixture of 1,1,2,2,3,3-hexamethyl-aziridinium iodide[6,7] (25.8 g, 0.1 mole) and dimethylamine (30 g, 0.67 mole) in 220 mL methanol was refluxed at 55 to 65° C for 2.5 h. Concentration of the mixture to 40 mL, followed by treatment with NaOH pellets and extraction of product into diethyl ether, removed of ether, then distillation of the residue 39 °C/0.1 torr yielded 8.9 g of **1** in 51% yield; picrate, yellow needles from methanol, mp. 207 - 209 °C, dec.; ^{1}H NMR ($CDCl_3$) δ; 2.3 (s, 12H, $N(CH_3)_2$), 1.0 (s, 12H, $C(CH_3)_2$); ^{13}C NMR δ; 63.29 (s, C $(CH_3)_2$, 41.59 (s, $N(CH_3)_2$), 21.05 (s, $N(CH_3)_2$); IR, neat, 2988-2972, 1455, 1361, 1260, 1170, 1146, 1046 and 767 cm^{-1}; MS, m/z(%) 173, ($[M+1]^+$ 40), 171 ($[M-1]^+$, 25), 128 ($[M-N(CH_3)_2]^+$, 100).

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