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NOTE

PREPARATION AND DISPROPORTIONATION OF (2,2'-BIPYRIDINE)-ETHYLBERYLLIUM CHLORIDE

N. A. BELL
Department of Chemistry, College of Technology, Pond Street, Sheffield (Great Britain)

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There are few references in the literature to the organoberyllium halides. The reaction between equimolar proportions of dimethylberyllium and hydrogen chloride was surprisingly completed at 120–130° yielding methane and presumably methylberyllium chloride although the latter was not fully characterised[1]. Reactions between dimethylberyllium and iodine, and diethylberyllium and beryllium chloride in ether, have been suggested to yield alkylberyllium halides[2].

Alkyl halides (RX) react with beryllium above room temperature both in the presence or absence of ether[3]. The ether-free products (RBeX) are insoluble in alkyl halides and doubtless are coordination polymers. A report[4] that a sublimable by-product from the reaction used to prepare ether-free di-tert-butylberyllium from its etherate and anhydrous beryllium chloride was probably tert-butylberyllium chloride etherate has since been confirmed[5].

The report[6] by Ashby *et al.* concerning the redistribution reaction of dimethylberyllium with beryllium bromide in ether prompts this report of the preparation of EtBeCl·Bipy. Compounds of the type RMX, where M is a Group II metal Mg, Zn, Cd, Hg, and their complexes are now well characterised and in some cases their structure demonstrated by X-ray diffraction. A disturbing feature of the beryllium system has been the lack of exchange between Ph_2Be and isotopically labelled $BeBr_2$ (using ^7Be) in ether; the mixture was therefore formulated as $Ph_2Be \cdot BeBr_2$ rather than PhBeBr[7]. In a similar system, the lack of exchange between Et_2Mg and $MgBr_2$ using ^{28}Mg led to the product, which has the same characteristics as the Grignard reagent prepared from Mg and EtBr, being formulated as $Et_2Mg \cdot MgBr_2$ rather than EtMgBr[8]. Later work[9] showed that complete exchange took place using ^{25}Mg, and Ashby[10] has pointed out that the former redistribution reaction may have been inhibited by impurities in the ^{28}Mg rather than impurities in the ^{25}Mg catalysing the exchange as was suggested by the authors.

A similar state of affairs could exist in the beryllium case and Ashby[6] has provided conclusive evidence for the redistribution of $BeBr_2$ with Me_2Be in diethylether from NMR, and ebullioscopic molecular weight data, and by preparing a 1,4-dioxane complex of methylberyllium bromide. A few years ago EtBeCl·Bipy was prepared and is now reported. The addition of equimolar quantities of ethereal beryllium chloride to diethylberyllium in ether results in slight heat evolution, and after the addition of ligand, the orange-yellow complex separates thus confirming Ashby's report[6] that redistribution between a beryllium halide and dialkyl will take place in ethereal solution. The colour of the complex is quite different from the colours of diethylberyllium and beryllium chloride bipyridine complexes, the former being red and the latter colourless[11]. Since the former will be more soluble in benzene than the halide complexes, the slight excess of $Et_2Be \cdot Bipy$ was washed from $EtBeCl \cdot Bipy$ until the red colour in solution was barely perceptible.

Thus the Schlenk equilibrium

$$Et_2Be + BeCl_2 \rightleftarrows 2\ EtBeCl$$

in ether solution lies well to the right. However, after prolonged extraction with boiling benzene, the insoluble white disproportionation product $BeCl_2 \cdot Bipy$ was identified but the other product ($Et_2Be \cdot Bipy$) decomposed in the benzene solution. Bipyridine is prone to attack by some Group II metal dialkyls[11] and alkylberyllium hydrides.

EXPERIMENTAL

All operations were carried out under dry, oxygen-free nitrogen, and solvents were carefully dried before use.

Beryllium chloride (3.43 g, 0.0043 mole) in ether (30 ml) was transferred by hypodermic syringe into diethylberyllium (2.7 ml of a 1.63 *M* solution in ether, 0.0044 mole) contained in one limb of a double Schlenk tube[12]. The mixture was stirred at room temperature for about 30 min, and 2,2'-bipyridine (1.4 g, 0.0090 mole) was added to the clear solution. An orange-yellow precipitate immediately formed leaving a red solution. This product was filtered off, washed with ether (5 × 10 ml) and then benzene (2 × 10 ml) until the filtrate was almost colourless. The complex, which decomposed at 167° and which slowly turns white in air, was dried under reduced pressure. (Found: Be, 3.95; Cl, 15.95; hydrolysable-ethyl, 12.4. $C_{12}H_{13}BeClN_2$ calcd.: Be, 3.93; Cl, 15.5; hydrolysable-ethyl, 12.6%.)

An attempt to crystallise the product by Soxhlet extraction with boiling benzene yielded after three days a dark-brown solution. The white material (1.35 g, 95% yield) remaining on the sinter of the Soxhlet apparatus was dried under reduced pressure, and identified as $BeCl_2 \cdot Bipy$[11]. (Found: Be, 3.82; Cl, 29.9. $C_{10}H_8BeCl_2N_2$ calcd.: Be, 3.81; Cl, 30.1%.)

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