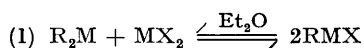


## Redistribution of Dimethylberyllium with Beryllium Bromide in Diethyl Ether

By E. C. ASHBY,\* R. SANDERS, and J. CARTER

(School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332)

REDISTRIBUTION of this type shown in equation (1) is known to occur for systems of the Group II metals, Mg, Zn, Cd, Hg.



where R = alkyl, X = halogen

Only in the case of M = Be is this redistribution reported not to take place. Radioactive tracer studies,<sup>1</sup> using labelled beryllium, show that the

beryllium system does not undergo redistribution in diethyl ether, when R = phenyl and X = bromide.

Further study of the anomalous behaviour of beryllium provides evidence that redistribution does occur in the system  $\text{Me}_2\text{Be}-\text{BeBr}_2$  in diethyl ether. The evidence results from (i) low temperature n.m.r. spectra, (ii) ebullioscopic molecular association data and (iii) selective precipitation experiments using 1,4-dioxan as the precipitating agent.

All operations were carried out under conditions involving rigorous exclusion of moisture and oxygen.  $\text{Me}_2\text{Be}$  was prepared *via* the reaction of electrorefined (99.99% pure) beryllium flake and  $\text{Me}_2\text{Hg}$  at  $110^\circ$ . Traces of residual  $\text{Me}_2\text{Hg}$  were removed by heating at reduced pressure, and the product was purified by vacuum sublimation.  $\text{BeBr}_2$  was synthesized by treating hot beryllium flake with bromine vapour. The white, fluffy crystalline product was purified by sublimation and dissolved in cold  $\text{Et}_2\text{O}$ . Gas chromatographic analysis of the  $\text{BeBr}_2$ - $\text{Et}_2\text{O}$  solution showed that the ether was not cleaved or halogenated on standing.  $\text{Me}_2\text{Be}$  and  $\text{BeBr}_2$  solutions were combined volumetrically to give stable, clear, colourless solutions, markedly less reactive than ethereal  $\text{Me}_2\text{Be}$ .

Ebullioscopic molecular association measurements for a (1:1) mixture of  $\text{Me}_2\text{Be}$  and  $\text{BeBr}_2$  in diethyl ether over a concentration range of 0.05–0.10 molal in Be gave *i*-values of 1.0–1.1, based on  $\text{MeBeBr}$ . Similarly,  $\text{Me}_2\text{Be}$  was monomeric in ether over the same range.

The addition of 1,4-dioxan to a (1:1, 0.1M solution)  $\text{Me}_2\text{Be}$  and  $\text{BeBr}_2$  in ether resulted in the precipitation of a fine white solid which on analysis established a Be:Br ratio of 1:1. This was observed when dioxan was in great molar excess, in exact molar equivalence, or in molar excess of Be. When  $\text{Me}_2\text{Be}/\text{BeBr}_2 > 1$ , the excess  $\text{Me}_2\text{Be}$ , *n*-dioxan is easily washed from the (1:1) precipitate.

N.m.r. spectra (60 Mc./sec.) were observed over a temperature range of  $+35^\circ$  to  $-75^\circ$  for  $\text{Me}_2\text{Be}$  in ether, (1:1) mixture of  $\text{Me}_2\text{Be}$  and  $\text{BeBr}_2$

in ether, and (2:1) mixtures of  $\text{Me}_2\text{Be}$  and  $\text{BeBr}_2$ , respectively, in ether. Comparison of the spectra, with internal and external  $\text{Me}_4\text{Si}$  as reference standard, showed identical spectra, and the values quoted here are in c./sec. upfield from the internal  $\text{Me}_4\text{Si}$  singlet. Concentration of beryllium in the mixtures was 0.1 molar. For  $\text{Me}_2\text{Be}$  in ether, a sharp singlet was observed which shifted with temperature from 70.5 at  $35^\circ$  to 78 c./sec. at  $-75^\circ$ . Similarly the (1:1) mixture displayed a singlet which moved from 71 at  $35^\circ$  to 75 c./sec. at  $-75^\circ$ . The (2:1) mixture, however, was markedly different, for a singlet was observed at 71 c./sec. at  $35^\circ$ , which shifted upfield with decreasing temperature and split into a doublet of equal peak height at  $-75^\circ$ , the low field peak being at 75 and the high field peak at 79 c./sec.

The monomeric nature of the (1:1) mixture of  $\text{Me}_2\text{Be}$  and  $\text{BeBr}_2$  in ether and the stoichiometry of the dioxan-precipitation product, leads us to conclude that redistribution does occur in this system according to equation (1). We suggest that the n.m.r. spectra of the (2:1) mixture is indicative of the  $\text{Me}_2\text{Be}$  species, mixed with the redistribution product  $\text{MeBeBr}$ . The downfield shift of the Me resonance singlet expected for electron withdrawal by Br in the species  $\text{MeBeBr}$  is small but definite. In the  $-75^\circ$  spectrum of the 2:1 mixture, the signal at 78 c./sec. is attributed to the excess of  $\text{Me}_2\text{Be}$  and the signal at 75 c./sec. is attributed to  $\text{MeBeBr}$ .

Further work on this system with  $\text{R} = \text{Ph}$  is being performed.

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<sup>1</sup> R. E. Dessy, *J. Amer. Chem. Soc.*, 1960, **82**, 1580.