Tetrahedron Letters,Vol.26,No.3,pp 275-278,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

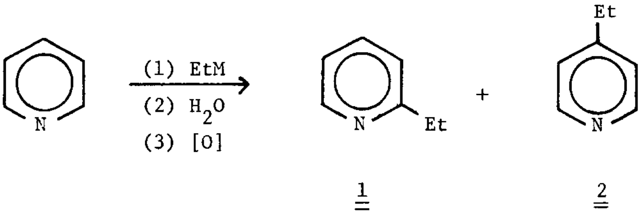
REACTIONS OF DIETHYLMAGNESIUM - ETHYLLITHIUM SOLUTIONS WITH PYRIDINE

Herman G. Richey, Jr.,* and Julius Farkas, Jr.

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

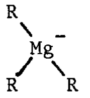
Abstract: In contrast to the reactions of pyridine with diethylmagnesium or ethyllithium alone, which lead only to 1,2-addition, reactions with diethylmagnesium-ethyllithium solutions lead to significant amounts of 1,4-addition; magnesium ate species are proposed to be responsible.

Reactions with pyridine of Et_2Mg - EtLi solutions differ strikingly from those of either organometallic compound alone. Et_2Mg and pyridine react slowly to produce exclusively 1, a product resulting from 1,2-addition. EtLi and pyridine react far more rapidly but also to produce only 1. As evident from the results summarized in the Table, however, Et_2Mg - EtLi solutions and pyridine form significant amounts of 2, a product resulting from 1,4-addition.[1,2]

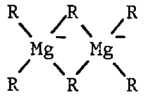


(1)

Earlier observations[3] that addition of 15-crown-5 to solutions of dialkylmagnesium compounds profoundly affected some of their reactions led to these experiments and to our expectation that mixtures of a magnesium and a lithium compound might form a product not produced by either compound alone. The effects observed with 15-crown-5 included a considerable acceleration of the reaction with pyridine and the production of even more 2 than of 1. We suggested that the effects of 15-crown-5 might be due to formation of "ate" species, such as 3 or 4, the impetus for their formation being a particularly great ability of



3



4

15-crown-5 to coordinate to Mg^{2+} or RMg^+ (e.g., equations 2 and 3).

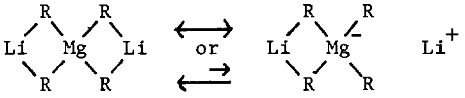
$$3\ R_2Mg\ +\ 15\text{-}C\text{-}5\ \rightleftarrows\ Mg^{2+}(15\text{-}C\text{-}5)\ +\ 2\ R_3Mg^-\ (\text{or } R_6Mg_2^{\ 2-}) \tag{2}$$

$$3\ R_2Mg\ +\ 15\text{-}C\text{-}5\ \rightleftarrows\ RMg^+(15\text{-}C\text{-}5)\ +\ R_5Mg_2^{\ -} \tag{3}$$

To try to convert organomagnesium compounds to solutions with similar reactivities by adding compounds quite different from a crown ether, we first chose organometallic compounds of alkali metals. NMR investigations by Brown, Seitz, and Little of solutions prepared from mixing organolithium and organomagnesium compounds in various ratios have established the formation of mixed metal species of at least three stoichiometries (5-7); the composition of

$$R_2Mg\ +\ RLi\ \longrightarrow\ \underset{5}{R_3MgLi}\ +\ \underset{6}{R_4MgLi_2}\ +\ \underset{7}{R_5MgLi_3} \tag{4}$$

a particular solution depends on the nature of R and the solvent.[4] These mixed-metal species are thought to have structures with bridging alkyl groups. Structure 8, for example, has



8 9

been proposed for R_4MgLi_2 (6).[4] It is reasonable that such species could have significant ate character (e.g., 8↔9) and exhibit the ability to react with pyridine in a fashion similar to that induced by 15-crown-5. Ionization (e.g., 8→9) might even be significant.

The 2:1 product ratio varies somewhat with the Et_2Mg:EtLi ratio and is increased by addition of crown ethers or 2,1,1-cryptand but not by tetramethylethylenediamine or hexamethylphosphoramide. Of these additives, only 15-crown-5 and 2,1,1-cryptand lead to formation of any 2 in the reaction of pyridine with Et_2Mg alone. No addition products are observed when 12-crown-4 is used with EtLi alone, apparently because of rapid destruction of EtLi by attack on the crown ether. An additive better able to coordinate with Li^+ than with other solution components could enhance an ionization such as 8→9. It is possible that the crown ethers and the cryptands are functioning in this manner.

Table. Product Compositions from Reactions of Diethylmagnesium, Ethyllithium, and Pyridine in Diethyl Ether[a] at 25 °C.[b]

Relative molar amounts					[Pyridine]		
Et_2Mg :	EtLi :	pyridine :	additive	Additive[c]	M	**1**,[d] %	**2**,[d] %
1	0	1	0		0.30	0.3	0
0	1	2	0		0.57	47	0
1	0	1	1.5	12-crown-4	0.08	~0.1	0
0	1	1	1.5	12-crown-4	0.09	0	0
1	1	1	0		0.20	37 (31)	6 (7)
2	1	2	0		0.25	51 (43)	21 (20)
4	1	4	0		0.22	69[e] (63)	18[e] (14)
2	1	2	1.5	12-crown-4	0.18	24	13
4	1	4	1.5	12-crown-4	0.15	26[f]	46[f]
4	1	4	1.5	15-crown-5	0.17	18	37
4	1	4	1.5	18-crown-6	0.17	18	42
4	1	4	1.5	2,1,1-cryptand	0.16	44	38
4	1	4	1.5	$Me_2NCH_2CH_2NMe_2$	0.25	73 (78)	23 (23)
4	1	4	1.5	$(Me_2N)_3P{=}O$	0.17	79	12

[a] Since a benzene solution of EtLi was used, some benzene was also present in those solutions containing EtLi but never exceeded 25% of the volume. [b] Reaction times were ~22 h. [c] A second liquid phase was observed upon addition of 12-crown-4 or 2,1,1-cryptand to Et_2Mg - EtLi solutions. [d] Yields are based on EtLi if it is present and on Et_2Mg (assuming that only one Et will react) when EtLi is not present. Values in parentheses are from duplicate experiments. [e] The composition after 0.5 h was 21% of **1** and 3% of **2**, after 4 h was 52% and 9%, and after 8 h was 62% and 12%. [f] The composition after 0.5 h was 6% of **1** and 7% of **2**, after 4 h was 15% and 24%, and after 9 h was 22% and 38%.

The proposal that "ate-like" species are responsible for the effects of 15-crown-5 on dialkylmagnesium reactions did lead to the surprising but accurate prediction that reactions of dialkylmagnesium-alkyllithium combinations could differ qualitatively from those of either component. Compared to dialkylmagnesium or organolithium compounds, the ate species may be (a) stronger bases, (b) more powerful nucleophiles, (c) weaker coordinating agents for electron-pair donors, and (d) more effective electron transfer agents. Of these particular possibilities, the last seems the most likely to be related to the behavior noted with pyridine.[5] While their particular mode of reaction with pyridine is not established, it is evident that the ate species should be regarded not as R_2Mg or RLi with slightly modified reactivities, but rather as very different organometallic species that exhibit unique behavior.

Acknowledgement. We are grateful to the National Science Foundation for support of this research.

References and Notes

1. We have found a few prior reports of diorganomagnesium-organolithium reactions. In a study of stereochemistry (cis or trans) of the products formed on addition of methyl organometallic compounds to substituted cyclohexanones, the mixed species and the individual organometallics formed essentially identical product mixtures [E. C. Ashby, L.-C. Chao, and J. Laemmle, J. Org. Chem., 39, 3258 (1974)]. Another study was of metalation of fluorene and addition to benzophenone and benzalacetophenone by phenyl organometallic compounds [G. Wittig, F. J. Meyer, and G. Lange, Justus Liebigs Ann. Chem., 571, 167 (1951)]. With benzalacetophenone, Ph_2Mg and the mixed species both gave principally 1,4-addition but PhLi principally 1,2-addition. All gave the same products with fluorene and benzophenone, of course. Organomagnesium plus organolithium or other organoalkali compounds have been used in a few instances as catalysts for alkene or diene polymerizations [for examples, see D. B. Malpass, J. Organomet. Chem. Libr., 9, 1 (1980)].
2. Addition to pyridine by Et_2Mg - EtLi is faster than addition by Et_2Mg alone but slower than by primary organolithium compounds alone. For example, compare with the rapid addition to pyridine of butyllithium [G. Fraenkel and J. C. Cooper, Tetrahedron Lett., 1825 (1968)].
3. H. G. Richey, Jr., and B. A. King, J. Am. Chem. Soc., 104, 4672 (1982).
4. L. M. Seitz and T. L. Brown, J. Am. Chem. Soc., 88, 4140 (1966). L. M. Seitz and T. L. Brown, Ibid., 89, 1602 (1967). L. M. Seitz and B. F. Little, J. Organomet. Chem., 18, 227 (1969).
5. The pyridine radical anion has been suggested to be an intermediate in reactions of pyridine, an alkyl halide, and magnesium in which formation of 4-alkylpyridines rather than of 2-alkylpyridines predominates [D. Bryce-Smith, P. J. Morris, and B. J. Wakefield, J. Chem. Soc., Perkin Trans. 1, 1977 (1976)].

(Received in USA 13 August 1984)