Registry No.—III, 17392-80-2; IV, 17392-81-3; cyclopentadienylidene, 1729-01-5; 4-methyl-*cis*-pentene-2, 691-38-3; hexafluorobenzene, 392-56-3; octafluorocyclobutane, 115-25-3; acrylonitrile, 107-13-1.

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The Composition of Grignard Compounds. V. In Triethylamine Solution

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For the first time Grignard compounds have been prepared directly in triethylamine solvent. In some cases side reactions occur during the preparation in triethylamine (quaternary salt formation and dehydrohalogenation); however, the reaction readily produces the desired product in 50–90% yield. The lower solubility of the Grignard compounds in triethylamine (0.1–0.9 *m*) as compared to diethyl ether (2–4 *m*) limits somewhat the useful concentration range in which the reagent can be employed. Nevertheless, reaction of the material with a carbonyl compound proceeds smoothly and results in a ratio of addition to reduction product that is significantly lower than that found when the reagent is prepared and reacted in diethyl ether. The composition of Grignard compounds in tertiary amine solvent was shown to be best represented by the equilibrium $R_2Mg + MgX_2 \rightleftarrows 2RMgX$. This equilibrium was shown to lie almost completely to the right when X = Cl and Br but not nearly so much to the right when X = I. The redistribution of $(CH_3)_2Mg$ and $(C_2H_5)_2Mg$ with $MgBr_2$ and MgI_2 was shown to take place readily in triethylamine and as the tetramethylethylenediamine complexes in diethyl ether and benzene.

The preparation of Grignard reagents in ether solvents and the reaction of these compounds with various organic functional groups have been known to chemists for decades. However, it is only recently that the composition of this highly useful reagent has been elucidated. The controversy surrounding the composition problem, coupled with the reagent's popularity for organic syntheses, have resulted in the accumulation of a great deal of data concerning, directly or indirectly, the Grignard reagent in ether solvents.[3] In addition, recent effort has been directed toward the discovery of new solvents, particularly nitrogen-containing solvents, that might function in place of ethers for the preparation and reaction of Grignard compounds; hexamethylphosphoramide[4] and disubstituted amides[4b] have been investigated for this purpose. Surprisingly, little effort has been directed toward the use of pure amine solvents for Grignard compounds[5] although tertiary amines, substituted amides, and nitrogen heterocycles have been used in stoichiometric amounts for the preparation and/or reaction in ether[6] and hydrocarbon[7] diluents. Some reactions in nitrogen-containing solvents have been studied with Grignard compounds that were just prepared in diethyl ether which was subsequently displaced with the secondary solvent.[8] This method of preparation was used to obtain ethylmagnesium bromide triethylaminate which was then crystallized for the only reported structural study[9] of Grignard compounds complexed to an amine.

The scant information available gives little indication of either the consequences of using an amine rather than an ether solvent for the direct preparation and reaction of Grignard reagents or the reagent's composition when prepared directly in amine solution. This lack of information, as well as our continued interests in the composition of Grignard compounds in various solvents, prompted this study with triethylamine, the nitrogen analog of diethyl ether. The synthetic aspects will be considered first, followed by a presentation of the evidence pertaining to the composition of Grignard reagents in amine solvents.

Results and Discussion

Examination of Table I reveals that the preparation of Grignard reagents in triethylamine suffers some limitations compared to diethyl ether or tetrahydrofuran as a solvent. The yields for the ethylmagnesium halides are reasonably high but decrease for the *sec*-butyl-, *t*-butyl-, and phenylmagnesium halides. The yields are highest for the alkylmagnesium chlorides but generally show a decrease for the bromides and iodides. Although dehydrohalogenation of the alkyl halide by triethylamine appears to be a very minor reaction even with the *t*-butyl halides, quaternary salt formation can be more serious. Since quaternary salt formation increases in the order *t*-alkyl < *sec*-alkyl < *n*-alkyl and Cl < Br < I, alkyl halides such as ethyl iodide must have minimum contact with the tertiary amine prior to reaction.

Perhaps the most notable feature of triethylamine as a solvent for Grignard compounds is the low solubility of some of the compounds in this solvent. Whereas Grignard compounds in diethyl ether usually have a solubility in the range 2–4 *m*, in triethylamine the solubility for the compounds investigated range from

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(1) To whom all inquiries should be sent.

(2) Taken from a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree.

(3) (a) E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967); (b) B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966); (c) R. M. Salinger in "Survey of Progress in Chemistry," Vol. 1, A. F. Scott, Ed., Academic Press, Inc., New York, N. Y., 1963, pp 301–324; (d) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Inc., Englewood Cliffs, N. J., 1954.

(4) (a) G. Fraensel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, **87**, 1406 (1965); (b) H. Normant, *Bull. Soc. Chim. Fr.*, 1434 (1963); (c) J. Fauvarque and J. F. Fauvarque, *C. R. Acad. Sci., Paris*, **263**, 488 (1966).

(5) Reference 3d, p 49.

(6) (a) F. Drahowyal, *Monatsh. Chem.*, **82**, 794 (1951); (b) F. Drahowyal and H. Konig, *ibid.*, **85**, 654 (1954).

(7) (a) E. C. Ashby and R. Reed, *J. Org. Chem.*, **31**, 985 (1966); (b) ref 3d, p 50.

(8) A. Kirmann and J. Robesiaka, *Bull. Soc. Chim. Fr.*, 2370 (1967).

(9) J. Torey and G. D. Stucky, *Chem. Commun.*, 1168 (1967).

Table I

Grignard Compounds Prepared in Triethylamine[a]

Grignard	Registry no.	Yield, %	Solubility, *m*
C_2H_5MgCl	2386-64-3	90	0.72
C_2H_5MgBr	925-90-6	90	0.30
C_2H_5MgI	10467-10-4	80	0.41
sec-C_4H_9MgCl	15366-08-2	82	0.78
sec-C_4H_9MgBr	922-66-7	70	0.92
sec-C_4H_9MgI	14753-38-9	72	0.60
t-C_4H_9MgCl	677-22-5	72	0.11
t-C_4H_9MgBr	2259-30-5	52	*b*
C_6H_5MgBr	100-58-3	55	0.23

[a] Registry no., 121-44-8. [b] Solubility too low to measure accurately.

0.1 to 0.9 *m*. The *t*-butyl compounds have an especially low solubility as does phenylmagnesium bromide. The *sec*-butyl compounds are more soluble than their ethyl counterparts, but any effect of the halogen atom on the solubility appears to be random.

An attempt was made to compare the addition properties of Grignard compounds prepared in triethylamide with those displayed by reagents prepared in diethyl ether. Benzaldehyde was selected as the compound with which to react the amine solutions of Grignard reagents since addition rather than reduction is the predominant reaction in diethyl ether and because it contains no α hydrogens and hence enolization cannot occur. The only reactions that can occur then are reduction to form a primary alcohol (benzyl alcohol) and addition to form a secondary alcohol (a phenyl alkyl carbinol). Examination of Table II reveals that the identity of the Grignard has a strong influence on the course of the reaction. The ethylmagnesium halides give more reduction and less addition as the halide is changed from chloride to bromide to iodide. An increase in reduction product results in going from *sec*-butylmagnesium chloride to the bromide, but the amount of addition product is about the same with either compound. As with the other Grignards, *t*-butylmagnesium chloride yields less reduction product than does the bromide; however, the most striking feature is the complete lack of addition with either the chloride or bromide. Inspection of the alkylmagnesium halides reveals greater reduction and less addition as the alkyl group is changed from ethyl to *sec*-butyl to *t*-butyl.

Table II

Reaction of Grignard Compounds Prepared in Triethylamine with Benzaldehyde

Grignard	Recovered benzaldehyde, %[a]	Reduction product $C_6H_5CH_2OH$, %	Addition product C_6H_5CHROH, %	Addition product in $(C_2H_5)_2O$, %[b]
C_2H_5MgCl	...	10	81	...
C_2H_5MgBr	...	12	64	78
C_2H_5MgI	5	29	12	...
sec-C_4H_9MgCl	...	22	35	...
sec-C_4H_9MgBr	...	32	41	60
t-C_4H_9MgCl	33	16	...	55
t-C_4H_9MgBr	8	35	...	...

[a] Dots indicate that no material was detected by glpc (estimated to be less than 1% if present). [b] Dots indicate that this reaction was not studied.

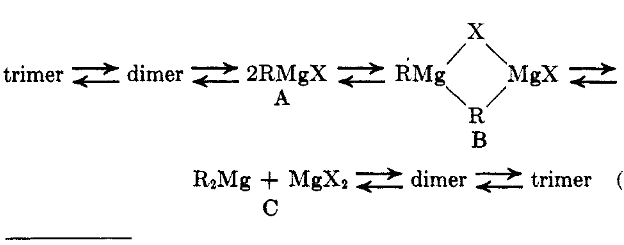
It will be noted that, in some of the reactions, the mass balance is poor; the reason for the low recovery of material is not known. However, it is interesting to note that similar results have been previously reported. Thus, a low over-all yield was found[8] when isopropylmagnesium bromide was prepared in diethyl ether and, after displacing the ether with N,N-diethylaniline, was allowed to react with 2-pentanone in N,N-diethylaniline. Also the reaction between benzaldehyde and butylmagnesium bromide in diethyl ether in the presence of pyridine[6a] resulted in the isolation of several side products, the composition of which varied if pyridine was mixed with the Grignard before or during the aldehyde addition.

Although the poor mass balance in several of the reactions precludes an exact interpretation of the effects of the alkyl group and/or halogen atom on the competition between reduction and addition, it can be said that the results generally paralleled those found for Grignard compounds in diethyl ether,[10] *i.e.*, an increase in the steric requirements of the alkyl group results in an increase in reduction product.

When the Grignard compound is first prepared in triethylamine, isolated, and then mixed with benzaldehyde in diethyl ether, the yield of addition product is markedly improved. Thus, ethylmagnesium bromide gives a 15% increase and *sec*-butylmagnesium bromide gives a 20% increase in yield of the addition product. The most dramatic change is found with *t*-butylmagnesium chloride which yields 55% of the addition product in diethyl ether compared with no addition product in triethylamine. One possible explanation is that, when the Grignard–triethylamine complex is dissolved in diethyl ether, the triethylamine is displaced from the magnesium by the ether in a small fraction of the compound. Although triethylamine should still be the stronger base, the difference in Lewis basicity between diethyl ether and triethylamine should be diminished somewhat due to the large steric requirement of the Grignard compound functioning as the Lewis acid. The fact that diethyl ether is the solvent and is therefore present in large excess should force equilibrium 1 even further to the right. Thus the addition reaction proceeds in a manner similar to that observed when the Grignard is prepared and allowed to react directly in diethyl ether.

$$\begin{aligned} &RMgX \cdot (C_2H_5)_3N + n[(C_2H_5)_2O] \rightleftharpoons \\ &\quad RMgX \cdot m(C_2H_5)_2O + (C_2H_5)_3N + (n - m)[(C_2H_5)_2O] \quad (1) \end{aligned}$$

Several factors must be considered before discussing the composition of Grignard compounds in triethylamine. In ether solvents the Grignard compound is actually a system of equilibria with the interconversion of A to C (eq 2) thought to occur *via* intermediate B.[11]



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[10] D. O. Cowan and H. S. Mosher, *J. Org. Chem.*, **27**, 1 (1962), and other papers in this series.

[11] (a) E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.*, **86**, 4363 (1964); (b) E. C. Ashby and F. Walker, *J. Organometal. Chem.*, **7**, 17 (1967).

It is also known that Grignard reagents exist in diethyl ether as molecular aggregates with the degree of association dependent on the concentration; however, in tetrahydrofuran the compounds are predominantly monomeric.[12] This difference in association results from a stronger coordination of the magnesium atom by tetrahydrofuran than by diethyl ether which prevents the formation of an appreciable concentration of bridged compounds. Since triethylamine is also a good Lewis base toward certain Lewis acids, coordination with the magnesium atom might be strong enough to not only inhibit association as does tetrahydrofuran, but also strong enough to stop completely the formation of bridged compounds such as B. As this would eliminate any interconversion of A and C, the Grignard in triethylamine would be composed of the initial species formed when an alkyl halide reacts with magnesium in this solvent.

The relative insolubility of magnesium halides and the solubility of magnesium alkyls in triethylamine offer a convenient method for studying the interconversion of A and C. If the magnesium halide and dialkylmagnesium are mixed in triethylamine, the formation of A can be determined by following the change in magnesium and halogen content of the solution.

Results from molecular weight studies in amines[13] and THF[11] show that magnesium compounds are monomers in solution when complexed with a solvent that is a stronger Lewis base than diethyl ether. Therefore, an increase in the magnesium and halogen content of the solution cannot be attributed to some type of association or ion-pairing phenomena which would result in the formation of dimers or other associated forms in solution but must be indicative of redistribution to form the monomeric RMgX compound. Thus, when diethylmagnesium triethylaminate was combined with either magnesium bromide triethylaminate or magnesium iodide triethylaminate in triethylamine, redistribution occurred (Table III) to form the soluble ethylmagnesium bromide and partially soluble ethylmagnesium iodide, respectively.

The decrease in solubility observed when dimethylmagnesium triethylaminate and magnesium bromide triethylaminate were mixed in triethylamine (Table III) is a little more difficult to interpret due to a report[9] that the addition of triethylamine to an ethereal solution of ethylmagnesium bromide produces, upon crystallization, solid material with the formula $(EtMgBr)_2(Et_3N)_2$. Dimer formation in the solid was attributed to a steric preference for the interaction of the magnesium atom with a triethylamine molecule and a bromine atom to that with two triethylamine molecules to form a dissolvated monomer. The possibility exists, therefore, that the decrease in solubility in the methyl system is due to the precipitation of a dimethylmagnesium–magnesium bromide complex rather than the precipitation of methylmagnesium bromide formed by redistribution.[14] However, there is no reason to believe that the methyl stystem would not be at least as prone to redistribution as the ethyl system. Certainly any requirement to form an intermediate with alkyl bridges (B, eq 2) should be met with ease by the methyl system due to the good bridging properties of the methyl group.[10b,11b,15]

TABLE III

REDISTRIBUTION OF DIALKYLMAGNESIUM COMPOUNDS AND MAGNESIUM HALIDES IN TRIETHYLAMINE

Reactants	Sample	Mg/g of soln, mmol	Halogen/g of soln, mmol	Mg/X[a]	Time, hr
$(C_2H_5)_2Mg + MgBr_2$	Initial	0.177	0.053	1.00:0.30	0
$(C_2H_5)_2Mg + MgBr_2$	1	0.252	0.236	1.00:0.94	18.0
$(C_2H_5)_2Mg + MgBr_2$	2	0.255	0.240	1.00:0.94	66.0
Calcd for 100% redistribution[c]		0.279	0.269	1.00:0.96	
$(C_2H_5)_2Mg + MgI_2$	Initial	0.130	0.024	1.00:0.18	0
$(C_2H_5)_2Mg + MgI_2$	1	0.186	0.159	1.00:0.86	18.0
$(C_2H_5)_2Mg + MgI_2$	2	0.168	0.138	1.00:0.82	66.0
$(C_2H_5)_2Mg + MgI_2$	3	0.164	0.128	1.00:0.78	108.0
Found for EtMgI[b]				1.00:0.92	
Calcd for 100% redistribution[c]		0.223	0.221	1.00:0.99	
$(CH_3)_2Mg + MgBr_2$	Initial	0.180	0.045	1.00:0.25	0
$(CH_3)_2Mg + MgBr_2$	1	0.130	0.017	1.00:0.13	0.5
$(CH_3)_2Mg + MgBr_2$	2	0.094	0.016	1.00:0.17	4.3
$(CH_3)_2Mg + MgBr_2$	3	0.066	0.032	1.00:0.48	21.0
$(CH_3)_2Mg + MgBr_2$	4	0.069	0.029	1.00:0.42	46.0
Found for MeMgBr[b]				1.00:0.31	
Calcd for 100% redistribution[c]		0.299	0.299	1.00:1.00	

[a] X = halide ion (Br or I). [b] Authentic Grignard prepared from the alkyl halide and magnesium in triethylamine. This value, when available, was inserted in the cases where the redistribution results in the precipitation of material and therefore makes difficult a meaningful comparison of the results with those calculated for 100% reaction. [c] These are the values expected if all of the material goes into solution.

Earlier it was reported[13a] that diethylmagnesium triethylaminate and magnesium bromide triethylaminate did not exchange in triethylamine solvent. The magnesium bromide used in this experiment was prepared by the often quoted method[16] which involves the reaction of magnesium metal and bromine in diethyl ether. Since then it has been found that this method produces an impure product when prepared according to the literature directions although the Mg/Br ratio of the product is 1:2. Unfortunately the determination of the Mg/Br ratio of the product in solution turned out to be a deceptive criteria of purity. The ether is highly brominated in this reaction resulting in the production of $MgBr_2$ which is complexed to highly reactive brominated ethers. This contaminant is believed to have been at least partly responsible for the misleading results reported earlier.[17] It is only on repeated fractional crystallization that the brominated

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[12] (a) E. C. Ashby and W. E. Becker, *J. Amer. Chem. Soc.*, **85**, 118 (1963); (b) E. C. Ashby and F. W. Walker, unpublished results.

[13] (a) E. C. Ashby, *J. Amer. Chem. Soc.*, **87**, 2509 (1965); (b) G. E. Coates and J. A. Heslop, *J. Chem. Soc., A*, 27 (1966); (c) D. F. Evans and M. S. Khan, *ibid.*, 1648 (1967).

[14] Although the diethylmagnesium–magnesium iodide system also precipitated some material, this presented no problem in interpreting the results since the magnesium content of the solution was greater than that due solely to the solubility of magnesium iodide and diethylmagnesium. The over-all result, then, was a substantial increase in the magnesium and iodine content of the solution which can be attributed only to the formation of EtMgI. In the methyl system, the solution has a magnesium and bromine analysis only a little greater than found for dissolved magnesium bromide and therefore prevents an easy interpretation of the results.

[15] L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **89**, 1607 (1967), and other papers in this series.

[16] (a) G. Swain and Henry B. Boyles, *ibid.*, **73**, 870 (1951); (b) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956); (c) M. Anteunis, *ibid.*, **27**, 596 (1962).

[17] The major conclusion of the previous study[13a] is still valid; namely, that the existence of RMgX species in solution has been definitely demonstrated and that this is the predominant species in triethylamine solution. However, the conclusion that RMgX is the species first formed in the reaction of RX and Mg in diethyl ether and is the predominant species in diethyl ether is not necessarily true since the RMgX could have been formed by the redistribution of R_2Mg and MgX_2.

ether can be removed from the product and 99+% pure $MgBr_2$ obtained.[18]

The interconversion of A and C suggests that there is an equilibrium in triethylamine similar to that found in ethers (eq 2). This equilibrium can be detected by taking advantage once again of the low solubility of magnesium halides in triethylamine. As pointed out earlier, all indications are that the various magnesium compounds in triethylamine are monomers in solution. Therefore, if the Grignard is a mixture of dialkylmagnesium and magnesium halide, they will be present as monomers and fractional crystallization of the solution will cause the magnesium halide (least soluble) to precipitate in the early fractions and the dialkylmagnesium (most soluble) to precipitate in the latter fractions. The first fractions then will have a magnesium to halogen ratio approaching 1:2, and the last fractions will have a magnesium to halogen ratio approaching 1:0. If all of the fractions are the same, as shown by a constant magnesium to halogen ratio of 1:1, this would indicate that the equilibrium lies entirely in the direction of a single monomeric compound, *i.e.*, the alkylmagnesium halide.

When the Grignard reagents prepared in triethylamine were fractionally crystallized, a magnesium to halogen ratio of 1:1 was found in every case except when the halogen was iodine. This can be seen by examining Tables IV, V, and VI for ethylmagnesium chloride, bromide, and iodide, respectively.

Table IV

Fractional Crystallization of Ethylmagnesium Chloride in Triethylamine[a]

Fraction	Sample wt, g	Mg, %	Cl, %	N, %[b]	Mg/Cl/N
1	7.0	17.4	27.2	6.0	1.00:1.01:0.90
2	8.9	14	19.8		1.00:0.95:0
3	31.1	17.9	24.7		1.00:0.94:0
4	16.5	12.0	17.8	7.3	1.00:1.01:1.06
5	8.4	13.1	18.3		1.00:0.96:0
6 (residue)	10.2	13.5	19.5		1.00:0.98:0
Aliquot (10 ml)					1.00:0.98:0
Calcd for $C_2H_5MgCl \cdot N(C_2H_5)_3$		12.8	18.7	7.4	1.00:1.00:1.00

[a] The variation in absolute values of the elemental analysis appears to be due to the extent of drying of each sample. The important consideration here is the Mg/Cl/N ratio. [b] The lack of values for nitrogen content of some of the fractions is due to an inability to dry completely these fractions. In these cases the value would be meaningless as it would include the triethylamine solvent along with the triethylamine complexed with the magnesium compound.

Table V

Fractional Crystallization of Ethylmagnesium Bromide in Triethylamine

Fractions	Sample wt, g	Mg, %	Cl, %	N, %	Mg/Br/N
1	15.0	11.2	36.6	6.55	1.00:0.99:1.02
2	10.1	11.5	39.2	6.71	1.00:1.04:1.01
3	32.4	13.4	41.8	7.47	1.00:0.93:1.01
4	11.7	12.3	37.9	7.10	1.00:0.94:1.00
5	9.1	10.6	34.8	5.87	1.00:1.00:0.94
6	12.0	10.8	35.1	6.12	1.00:0.99:0.98
7	10.7	12.2	38.2	6.98	1.00:0.95:0.99
Calcd for $C_2H_5MgBr \cdot N(C_2H_3)_3$		10.4	34.1	5.97	1.00:1.00:1.00

Table VI

Fractional Crystallization of Ethylmagnesium Iodide in Triethylamine[a]

Fractions	Sample wt, g	Mg, %	I, %	Mg/I
1	6.4	7.1	59.7	1.00:1.61
2	4.7	7.9	52.2	1.00:1.26
3	24.0	8.2	48.2	1.00:1.13
4	7.8	9.0	48.7	1.00:1.03
5	3.7	9.1	45.2	1.00:0.95
6	4.2	10.1	41.1	1.00:0.78
Aliquot (10 ml)				1.00:0.92
Calcd for $C_2H_5MgI \cdot N(C_2H_5)_3$		9.46	47.9	1.00:1.00

[a] None of the alkylmagnesium iodide data includes values for nitrogen content. The reason for this omission is discussed in the first section of the Experimental Section.

When the alkyl group is changed from ethyl to *sec*-butyl, a magnesium to halogen ratio of 1:1 is found for all fractions for the chloride (Table VII); however, the bromide shows a high halogen analysis in the first fraction (Table VIII). This high halogen analysis in the first fraction is not due to magnesium bromide from a di-*sec*-butylmagnesium–magnesium bromide equilibrium since the last fraction does not show a corresponding high magnesium analysis demanded by precipitation of di-*sec*-butylmagnesium. The high halogen content of the first fraction could be due to dehydrohalogenation of the alkyl halide by the amine to form triethylammonium bromide, coupling of the alkylmagnesium halide with the alkyl halide to form magnesium halide, and/or quaternary ammonium salt formation from the amine and the alkyl halide.

Table VII

Fractional Crystallization of *sec*-Butylmagnesium Chloride in Triethylamine

Fractions	Sample wt, g	Mg, %	Cl, %	N, %	Mg/Cl/N
1	25.3	11.4	15.9	4.8	1.00:0.96:0.73
2	38.2	11.3	15.7	6.6	1.00:1.01:0.95
3	4.7	11.9	17.1		1.00:0.98:0
4	15.1	12.4	18.1		1.00:1.00:0
Aliquot (10 ml)					1.00:1.01:0
Calcd for *sec*-$C_4H_9MgCl \cdot N(C_2H_5)_3$		11.1	16.3	6.5	1.00:1.00:1.00

Table VIII

Fractional Crystallization of *sec*-Butylmagnesium Bromide in Triethylamine[a]

Fraction	Sample wt, g	Mg, %	Br, %	Mg/Br
1	12.2	5.8	35.7	1.00:1.88
2	23.9	9.4	41.6	1.00:1.35
3	28.7	10.8	33.0	1.00:1.05
4	29.4	10.0	34.2	1.00:1.04
Calcd for *sec*-$C_4H_9MgBr \cdot N(C_2H_5)_3$		9.3	30.5	1.00:1.00

[a] Nitrogen content was not determined.

The results from *sec*-butylmagnesium iodide (Table IX) offer a convenient comparison. As with ethylmagnesium iodide but not *sec*-butylmagnesium bromide, the high halogen analysis found in the first fractions is accompanied by a high magnesium analysis in the later fractions. The compounds *t*-butylmagnesium chloride (Table X) and *t*-butylmagnesium bromide (Table XI) also displayed high halogen analysis in the first fraction without the required low halogen analysis in the

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[18] See E. C. Ashby and R. Arnott, *J. Organometal. Chem.*, in press.

TABLE IX

FRACTIONAL CRYSTALLIZATION OF *sec*-BUTYLMAGNESIUM IODIDE IN TRIETHYLAMINE

Fraction	Sample wt, g	Mg, %	I, %	Mg/I
1	56.3	8.2	47.5	1.00:1.11
2	14.3	8.6	45.4	1.00:1.01
3	7.7	7.8	46.6	1.00:1.15
4	26.3	9.0	38.0	1.00:0.81
Calcd for *sec*-$C_4H_9MgI\cdot N(C_2H_5)_3$		7.9	41.0	1.00:1.00

TABLE X

FRACTIONAL CRYSTALLIZATION OF *t*-BUTYLMAGNESIUM CHLORIDE IN TRIETHYLAMINE[a]

Fraction	Sample wt, g	Mg, %	Cl, %	Mg/Cl
1	2.8	...	...	1.00:2.06
2	37.8	14.3	23.5	1.00:1.13
3	21.5	12.0	20.5	1.00:1.17
4	4.6	16.2	25.4	1.00:1.09
Calcd for *t*-$C_4H_9MgCl\cdot N(C_2H_5)_3$		11.2	16.3	1.00:1.00

[a] Nitrogen content not determined.

TABLE XI

FRACTIONAL CRYSTALLIZATION OF *t*-BUTYLMAGNESIUM BROMIDE IN TRIETHYLAMINE

Fractions	Sample wt, g	Mg, %	Br, %	N, %	Mg/Br/N
1	65.6	5.7	52.2	4.3	1.00:2.81:1.02
2	2.6	9.0	43.0	3.0	1.00:1.48:0.60
Aliquot (10 ml)					1.00:1.48:0
Calcd for *t*-$C_4H_9MgBr\cdot N(C_2H_5)_3$		9.3	30.4	5.3	1.00:1.00:1.00

final fractions. The only aromatic Grignard studied, phenylmagnesium bromide (Table XII), displayed an analysis similar to the *sec*-butylmagnesium bromide and *t*-butylmagnesium bromide and chloride. This probably results from coupling of the aromatic Grignard with bromobenzene to form magnesium bromide and biphenyl.

TABLE XII

FRACTIONAL CRYSTALLIZATION OF PHENYLMAGNESIUM BROMIDE IN TRIETHYLAMINE

Fractions	Sample wt, g	Mg, %	Br, %	N, %	Mg/Br/N
1	7.1	8.9	30.8		1.00:1.05:0
2	25.6	8.4	33.5	4.9	1.00:1.22:1.02
3	20.1	8.0	32.8		1.00:1.25:0
4	25.4	8.9	30.8		1.00:1.05:0
Aliquot (10 ml)		8.9	30.8		1.00:1.05:0
Calcd for $C_6H_5MgBr\cdot N(C_2H_5)_3$		8.6	28.2	5.0	1.00:1.00:1.00

TABLE XIII

FRACTIONAL CRYSTALLIZATION OF ETHYLMAGNESIUM BROMIDE PREPARED IN DIETHYL ETHER AND QUENCHED IN TRIETHYLAMINE

Fractions	Sample wt, g	Mg, %	Br, %	N, %	Mg/Br/N
1	10.2	10.9	35.8	6.12	1.00:1.00:0.97
2	11.6	11.2	39.0	6.62	1.00:1.06:1.03
3	23.7	11.8	43.9	6.91	1.00:1.11:1.02
Calcd for $C_2H_5MgBr\cdot N(C_2H_5)_3$		10.4	34.1	5.97	1.00:1.00:1.00
Recovery: 90.0%					

TABLE XIV

FRACTIONAL CRYSTALLIZATION OF PHENYLMAGNESIUM BROMIDE PREPARED IN DIETHYL ETHER AND QUENCHED IN TRIETHYLAMINE

Fractions	Sample wt, g	Mg, %	Br, %	N, %	Mg/Br/N
1	24.3	9.2	30.9	4.2	1.00:1.02:0.80
2	1.0	12.1	39.8	5.8	1.00:1.00:0.81
3	21.1	10.2	35.3	6.1	1.00:1.05:1.04
Calcd for $C_6H_5MgBr\cdot N(C_2H_5)_3$		8.6	28.2	5.0	1.00:1.00:1.00
Recovery: 96.9%					

TABLE XV

FRACTIONAL CRYSTALLIZATION OF *t*-BUTYLMAGNESIUM CHLORIDE PREPARED IN DIETHYL ETHER AND QUENCHED IN TRIETHYLAMINE

Fractions	Sample wt, g	Mg, %	Cl, %	N, %[a]	Mg/Cl/N
1	2.2	19.6	32.4	3.1	1.00:1.13:0.28
2	2.0	15.2	24.1	2.4	1.00:1.09:0.27
3	10.8	13.6	22.5	5.8	1.00:1.13:0.74
Calcd for *t*-$C_4H_9MgCl\cdot N(C_2H_5)_3$		11.2	16.3	6.4	1.00:1.00:1.00
Recovery: 99.8%					

[a] The reason for the low nitrogen content of the fractions is not known.

TABLE XVI

FRACTIONAL CRYSTALLIZATION OF ISOPROPYLMAGNESIUM CHLORIDE PREPARED IN DIETHYL ETHER AND QUENCHED IN TRIETHYLAMINE

Fractions	Sample wt, g	Mg, %	Cl, %	N, %	Mg/Cl/N
1	2.3	13.9	20.8	5.1	1.00:1.02:0.64
2	11.6	13.4	20.3	6.0	1.00:1.04:0.78
Calcd for *i*-$C_3H_7MgCl\cdot N(C_2H_5)_3$		12.0	17.5	6.9	1.00:1.00:1.00
Recovery: 83.8%					

Somewhat similar results were observed when a series of Grignard reagents was prepared in diethyl ether and then added to triethylamine. After fractional crystallization of the triethylamine solutions, 1:1 magnesium to halogen ratios were obtained in every case except when the halogen was iodine. Thus, ethylmagnesium bromide (Table XIII), phenylmagnesium bromide (Table XIV), *t*-butylmagnesium chloride (Table XV), and isopropylmagnesium chloride (Table XVI) gave, within experimental error, Mg/halogen ratios of 1:1. The high halogen analyses in the first fractions that were found when phenylmagnesium bromide (Table XII) and *t*-butylmagnesium chloride (Table X) were prepared by reacting the halide with magnesium directly in triethylamine are absent for these compounds prepared in diethyl ether and then added to triethylamine.

The only compound to give a different result was *n*-butylmagnesium iodide (Table XVII) where the magnesium to iodide ratio approached 1:2 in the initial fraction and the last fraction displayed a high mag-

TABLE XVII

FRACTIONAL CRYSTALLIZATION OF *n*-BUTYLMAGNESIUM IODIDE PREPARED IN DIETHYL ETHER AND QUENCHED IN TRIETHYLAMINE

Fractions	Sample wt, g	Mg, %	I, %	Mg/I
1	6.3	7.1	57.7	1.00:1.56
2	1.4	7.9	48.0	1.00:1.17
3	12.1	10.8	40.2	1.00:0.71
Calcd for *n*-$C_4H_9MgI\cdot N(C_2H_5)_3$		7.9	41.0	1.00:1.00
Recovery: 91.7%				

nesium analysis. This result for *n*-butylmagnesium iodide compares favorably with the previously mentioned results obtained when ethylmagnesium iodide (Table VI) and *sec*-butylmagnesium iodide (Table IX) were prepared directly in triethylamine.

Due to the monomeric nature of the solutions, the empirical formula ratios obtained by analysis of the solid fractions are equivalent to the molecular formula ratios of the material in solution. Thus, in the cases where only RMgX was isolated from the Grignard–triethylamine system (when X = Cl, Br), it can be concluded that the predominant species in solution is RMgX and that the Schlenk equilibrium (eq 2) lies far to the left. This conclusion is supported by the redistribution studies (Table III). This agrees with the previously mentioned report[9] that the material obtained by adding triethylamine to an ether solution of ethylmagnesium bromide produces solid material formulated as dimeric EtMgBr. This isolation of magnesium iodide and dialkylmagnesium from the alkylmagnesium iodides must be interpreted with care. The precipitation of magnesium iodide simply indicates its presence; the amount isolated does not necessarily reflect the equilibrium concentration in solution. This is so because removal of this compound from the equilibrium system would simply result in shifting the equilibrium to regenerate more magnesium iodide.[19,20] Thus, a large amount of magnesium iodide could be isolated by fractional crystallization, although only a small quantity may be present in solution at equilibrium. This is observed when dioxane is added to ethereal Grignards to isolate the dialkylmagnesium compound. Although the exact position of the equilibrium cannot be stated, the fact that diethylmagnesium and magnesium iodide redistribute (Table III) and that alkylmagnesium iodides have a much greater solubility than magnesium iodide in triethylamine suggest an appreciable concentration of RMgX in the alkylmagnesium iodide solutions.[21,22]

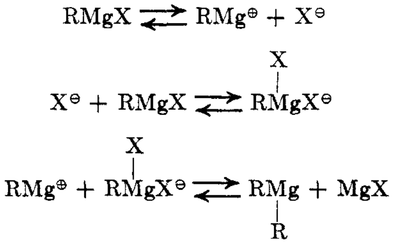
Apparently triethylamine is not a Lewis base of sufficient strength to prevent the formation of B and thus stop the interconversion of A and C. The discovery of a complexing agent that would stop the interconversion of A and C would allow the determination of equilibrium constants for the Grignard reagent in various solvents by simply complexing the reagent with the base and then fractionally crystallizing the solution. Tetramethylethylenediamine (TMED) was used with success for a similar study with the zinc analog of Grignard reagents.[23] The feasibility of using TMED as the complexing agent for Grignard reagents in diethyl ether was demonstrated by finding that magnesium halide–TMED complexes are only slightly soluble and dialkylmagnesium–TMED complexes are very soluble in diethyl ether. However, dimethylmagnesium–TMED and magnesium bromide–TMED redistributed in diethyl ether to form the relatively insoluble methylmagnesium bromide–TMED complex (Table XVIII).[24] The attempted use of triethylenediamine proved unsuccessful when it was found that both dimethylmagnesium and magnesium bromide form complexes that are insoluble in diethyl ether, hexane, and benzene.

Table XVIII

Redistribution of Dimethylmagnesium–TMED and Magnesium Bromide–TMED

Solvent	Sample	Mg/g of soln, mmol	Br/g of soln, mmol	Mg/X	Time, hr
Diethyl ether	Initial	0.180	0.013	1.00:0.07	0
Diethyl ether	1	0.064	0.037	1.00:0.58	18.0
Diethyl ether	2	0.062	0.046	1.00:0.74	42.0
Diethyl ether	3	0.060	0.049	1.00:0.82	120.0
Calcd for 100% redistribution		0.338	0.344	1.00:1.02	
Benzene	Initial	0.116	0.045	1.00:0.39	0
Benzene	1	0.182	0.171	1.00:0.94	18.0
Benzene	2	0.187	0.194	1.00:1.04	45.0
Calcd for 100% redistribution		0.183	0.187	1.00:1.02	

The failure of complexing agents to prevent the interconversion of A and C raises the possibility that redistribution and disproportionation may follow a mechanism other than the one shown by eq 2. The presence of ions in ether solvents has been reported,[25] so that it is reasonable to expect that the greater complexing ability of tertiary amines would stabilize and thus inhance formation of charged species in solution. An ionic mechanism can be envisioned (eq 3), based on



$$\mathrm{RMgX} \rightleftarrows \mathrm{RMg}^{\oplus} + \mathrm{X}^{\ominus}$$
$$\mathrm{X}^{\ominus} + \mathrm{RMgX} \rightleftarrows \mathrm{R}\overset{\mathrm{X}}{\overset{|}{\mathrm{M}}}\mathrm{gX}^{\ominus} \qquad (3)$$
$$\mathrm{RMg}^{\oplus} + \mathrm{R}\overset{\mathrm{X}}{\overset{|}{\mathrm{M}}}\mathrm{gX}^{\ominus} \rightleftarrows \mathrm{R}\underset{\mathrm{R}}{\underset{|}{\mathrm{M}}}\mathrm{g} + \mathrm{MgX}$$

the principal ions reported in ether solvents. Therefore if the compounds are first complexed with an amine, isolated, and then brought together in a suitable solvent of low dielectric constant and low-solvating power, interconversion of A and C *via* a pathway involving bridged species (eq 2) and *via* an ionic mecha-

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[19] This would not be true if the interconversion of A and C is so slow that the fractionation could be completed before the equilibrium system could compensate for the material removed. The redistribution studies and other recent work[13,20] indicate that the interchange is probably too rapid for this to occur.

[20] H. O. House, R. A. Latham, and G. M. Whitsides, *J. Org. Chem.*, **32**, 2481 (1967).

[21] The use of nmr spectroscopy would be the obvious method for determining the equilibrium composition of Grignard reagents in triethylamine. However, in the case of methylmagnesium bromide in triethylamine, any difference in the nmr spectra of methylmagnesium bromide and dimethylmagnesium solutions could not be observed owing to the low solubility of the Grignard compound prepared either by redistribution of dimethylmagnesium and magnesium bromide or by a direct combination of magnesium and methyl bromide in triethylamine. Further, in the soluble ethyl system, the diethylmagnesium and ethylmagnesium bromide solutions gave spectra that were similar enough so as to prevent an easy interpretation of the results. This latter finding agrees with earlier reports[20,22] on similar systems in ether solvents.

[22] (a) D. F. Evans and J. P. Maker, *J. Chem. Soc.*, 5125 (1962); (b) G. Fraeusel, D. G. Adams, and J. Williams, *Tetrahedron Lett.*, **No. 12**, 767 (1963); (c) H. O. House and D. D. Traficante, *J. Org. Chem.*, **28**, 355 (1963); (d) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).

[23] M. H. Abraham and P. H. Rolfe, *J. Organometal. Chem.*, **7**, 35 (1967).

[24] These findings agree with other recent reports[12c,19] with alkyl exchange in dialkylmagnesium systems;[18] it was found that exchange in diethyl ether–THF mixtures is retarded but not stopped by complexing agents such as TMED. The acceleration of the exchange by added magnesium bromide[18] suggests that the alkyl–halogen interchange studied here might be even more facile and therefore more difficult to stop than the alkyl–alkyl interchange.

[25] (a) W. V. Evans and F. H. Lee, *J. Amer. Chem. Soc.*, **55**, 1474 (1933); (b) R. E. Dessy and R. M. Jones, *J. Org. Chem.*, **24**, 1685 (1959).

nism (eq 3) might be prevented. To test this possibility, dimethylmagnesium–TMED was prepared and dissolved in benzene. Since this complex is monomeric in benzene,[13b] the concentration of bridged species is small. When mixed with magnesium bromide–TMED, which has a low solubility in benzene, redistribution was observed (Table XVIII). Whichever mechanism is operative for the redistribution–disproportionation, the process is too facile to be stopped by any of the methods studied.

Experimental Section

All equipment used was dried by flash flaming under vacuum or under a flow of dry nitrogen. In the preparation of the Grignard reagents, the magnesium was added prior to the drying procedure. Triethylamine, TMED, THF, and benzene were distilled from $NaAlH_4$ through a 2-ft Vigreux column under dry nitrogen just prior to use. Anhydrous diethyl ether was distilled in a similar manner from $LiAlH_4$. The alkyl and aryl halides, after drying over Na_2CO_3, were distilled under dry nitrogen through a 1.5-ft column packed with glass helices. All manipulations of materials were carried out either in a glove box (dry nitrogen atmosphere) or on the bench top in sealed systems under nitrogen. The analysis for magnesium was accomplished by titration with EDTA and halide analyses were completed by titration with silver nitrate (potentiometrically or Volhard). Analysis for nitrogen was carried out by adding an aliquot of standard acid to the sample and then back-titrating with NaOH solution. The difference between the acid consumed and the total Mg content (by EDTA) indicated the amount of complexed amine. However, the alkylmagnesium iodides gave uninterpretable results as the first fractions gave either a very small value or a negative number for the nitrogen content. In contrast, the latter fractions gave very large values. A reasonable explanation for these results rests with the conclusions drawn about the composition of the alkylmagnesium iodide fractions from the Mg/halogen ratios. Thus, since the first fractions contain mainly MgI_2 and very little of any material with an active carbon–magnesium bond, the relatively small amount of acid consumed is due mainly to the complexed triethylamine. When the value for the Mg content is subtracted, a very small value or negative number results for the nitrogen content. The later fractions, composed mainly of R_2Mg, require a large amount of acid, and subtraction of the total Mg content results in a value suggesting an unreasonably large amount of triethylamine complexed with the magnesium compound.

Preparation of Grignard Reagents in Triethylamine.—The methods used for the preparation of Grignard compounds in triethylamine are very similar to those used for the preparation in ethers. The only additional precaution that must be observed is that the alkyl halide should not be in contact with the solvent any longer than is necessary, especially in the cases where the alkyl halide is prone to quaternary salt formation and/or dehydrohalogenation. The preparation of ethylmagnesium bromide is typical of the methods employed. Two addition funnels, one with ethyl bromide (54.5 g, 0.5 mol) and one with triethylamine (400.0 ml), were placed on opposite sides of a 1-l. three-necked flask containing magnesium (36.4 g, 1.5 g-atoms). The funnel containing triethylamine shared a Claissen adapter with a water-cooled condenser; the funnel with the alkyl halide was connected directly to the flask so that the liquid dropped directly into the reaction mixture. After adding 50 ml of triethylamine to the magnesium, the reaction was initiated by adding 5 ml of ethyl bromide. After the reaction initiated, as evidenced by a spontaneous evolution of heat, stirring (motor assembly with an oil-sealed bearing) was started, and the addition rates of solvent and halide were adjusted to maintain a reaction temperature of 45–50°. A precipitate formed at the very beginning of the reaction, and the quantity was increased throughout the addition step. When addition was complete, the stirring was continued for 12 hr while maintaining a temperature of 50° with external heating.

Fractional Crystallization of Grignard Reagents Prepared in Triethylamine.—The crystallization results reported in the tables were obtained in the following manner. The solid–liquid mixture formed in the Grignard preparation reactions was separated by filtration. The solid material was separated from the excess magnesium used in the reactions by solution of the Grignard component in benzene, followed by filtration of the magnesium. The benzene filtrate was then subjected to vacuum distillation to produce the solid that was labeled fraction 1. The other fractions were obtained by slow removal of the triethylamine solvent from the original filtrate under vacuum until crystallization had begun. In this way usually several fractions were isolated. The last fraction was always the residue obtained after complete removal of the benzene solvent under vacuum.

Reaction of Grignard Reagents with Benzaldehyde in Triethylamine.—A portion of the triethylamine-soluble ethylmagnesium bromide (0.125 mol) was allowed to react with benzaldehyde (14.8 g, 0.14 mol) by adding the aldehyde *via* an addition funnel to the Grignard compound contained in a 500-ml three-necked flask equipped with a water-cooled condenser. The reaction mixture was stirred (motor assembly, oil-sealed bearing) at room temperature during the addition and for 2 hr after completion of addition. After hydrolysis of the reaction mixture with 10% aqueous NH_4Cl, the aqueous layer was extracted with diethyl ether and the product composition was determined by glpc.

Reaction of Grignard Reagents (Isolated from Triethylamine) with Benzaldehyde in Diethyl Ether.—After removal of the triethylamine from a portion of the ethylmagnesium bromide solution, the solid (0.125 mol) was dissolved in diethyl ether. Reaction with benzaldehyde (0.14 mol) was accomplished using the same procedure and apparatus employed for the reaction in triethylamine; product analysis was accomplished by glpc.

Preparation of Grignard Reagents in Diethyl Ether.—The preparation of *n*-butylmagnesium iodide will illustrate the method employed. Two addition funnels, one with 1-iodobutane (368.1 g, 2.0 mol) and one with diethyl ether (900.0 ml), were connected to a 1-l. three-necked flask containing magnesium (53.5 g, 2.2 g-atoms). After initiating the reaction by adding 50 ml of ether and 5 ml of 1-iodobutane, stirring (motor assembly with an oil-sealed bearing) was started. The ether and the halide were added simultaneously at a rate to maintain gentle boiling as evidenced by a slow solvent return from the tip of the Dry Ice condenser. After being stirred overnight at room temperature, the solution was filtered through a glass wool plug to remove unreacted magnesium.

Fractional Crystallization of Ethereal Grignard Reagents from Triethylamine.—This operation will be illustrated with *n*-butylmagnesium iodide. An addition funnel containing the Grignard compound in ether (50.0 ml, 89.0 mmol) was connected to a 1-l. three-necked flask equipped with a stirring assembly (oil-sealed bearing) and a water-cooled condenser. Triethylamine (500.0 ml) was stirred rapidly while the Grignard was dripped slowly into the flask at room temperature. After being stirred overnight, the solution was fractionally crystallized by slowly removing the triethylamine under vacuum at room temperature. The fractions were dried for 3 days on a vacuum manifold.

Preparation of Dialkylmagnesium Compounds.—To a 200-ml round-bottom flask containing 10.6 g (0.43 g-atom) of triply sublimed Mg was added 50.0 g (0.22 mol) of dimethylmercury in a drybox. The flask was connected to a water-cooled condenser and mixed with a magnetic stirrer at room temperature. The reaction started within 15 min as evidenced by heat release and formation of a white solid accompanied by the appearance of free mercury in the flask. Stirring was continued for 2 days. The flask was then transferred to a small distillation unit. The receiver was cooled by Dry Ice–acetone, and the system was evacuated overnight to remove any unreacted dimethylmercury. The procedure for the preparation of diethylmagnesium was the same except that the reaction mixture was heated with an oil bath to 65–70° during the reaction. The triethylamine and diethyl ether solutions were prepared by adding a sufficient quantity of solvent directly to the flask to dissolve the solid magnesium alkyl. Dimethylmagnesium–TMED was prepared by adding the amine (14.5 g, 0.125 mol) to an ether solution of dimethylmagnesium (0.056 mol); a portion of the solution was removed *via* syringe for the redistribution studies in diethyl ether. The remainder was isolated and dried under vacuum for the study in benzene.

Preparation of Magnesium Halides.—Triply sublimed magnesium (24.3 g, 1.0 g-atom) was placed in a 500-ml round-bottomed flask containing a large stirring bar. The flask was connected *via* two Claisen adapters to a water-cooled condenser, an addition funnel containing 79.9 g (0.5 mol) of bromine, and an addition funnel containing 500 ml of diethyl ether. Initially, 75 ml of ether was added to the magnesium and cooled with an ice bath. A few drops of bromine were added to the cooled ether–magnesium mixture; decolorization was immediate. The ether and bromine were added simultaneously while moderating the reaction with the ice bath. After filtration to remove the unreacted magnesium, the reaction product was recrystallized from ether four times to yield white magnesiumb romide etherate. A glpc analysis of a portion of the hydrolyzed material revealed no impurities in the organic layer.

A 500-ml round-bottom flask containing 19.4 g (0.8 g-atom) of triply sublimed magnesium and a stirring bar was connected *via* a Claisen adapter to an addition funnel filled with 101.5 g (0.4 mol) of iodine in 450 ml of diethyl ether and to a water-cooled condenser. After the small initial addition had decolorized, the iodine solution was added to the stirred magnesium at a rate to maintain gentle boiling of the ether. After filtration to remove unreacted magnesium, the reaction product was recrystallized three times from ether to yield white magnesium iodide etherate. A glpc analysis detected no impurities in the hydrolyzed material.

Ether was displaced from magnesium bromide with triethylamine by dissolving a portion of the magnesium bromide etherate (27.1 g, 0.10 mol) in a minimum of diethyl ether in a 200-ml round-bottom flask. The flask was connected to a Claisen adapter fitted with an addition funnel containing 350 ml of triethylamine and a distillation unit with a 5-cm distilling column packed with glass helices. The ether solution was heated to boiling with mixing by a magnetic stirrer. When the ether started to distil, the triethylamine was introduced at a rate to maintain a constant volume of solution in the distilling flask. Addition of the triethylamine was continued until the temperature of the distillate remained constant. The remainder of the solvent was removed by distillation and by drying the solid product on a vacuum manifold overnight. A portion of the tan powder was hydrolyzed, and glpc analysis revealed that displacement of the ether was complete.

Anal. Calcd for $MgBr_2 \cdot NEt_3$: Mg, 8.52; Br, 56.02; Mg/Br, 1.00:2.00. Found: Mg, 8.16; Br, 53.42; Mg/Br, 1.00:1.99. The same treatment of the magnesium iodide etherate followed by a glpc analysis of the hydrolysate indicated that 99.6+% of the ether had been replaced by triethylamine.

Anal. Calcd for $MgI_2 \cdot NEt_3$: Mg, 6.41; I, 66.91; Mg/I, 1.00:2.00. Found: Mg, 6.29; I, 66.44; Mg/I, 1.00:2.02.

Magnesium bromide–TMED was prepared by adding the amine (5.1 g, 0.044 mol) *via* syringe to an ether solution of the halide (0.022 mol) and was not isolated for the redistribution study with dimethylmagnesium–TMED in diethyl ether. A second sample of the compound was prepared in the same manner but was isolated and dried under vacuum for the exchange study in benzene.

Redistribution Studies.—The apparatus and procedure employed was the same for all of the redistribution studies. A 500-ml round-bottomed flask was equipped with a septum cap opening for addition and withdrawal of samples by syringe. The nitrogen was supplied through the top of a water-cooled condenser, and the reaction mixture was mixed by a stirring bar. Thus, a magnesium bromide triethylaminate (0.019 mol)–triethylamine mixture was treated with a triethylamine solution of dimethylmagnesium triethylaminate (0.019 mol), and samples were withdrawn periodically for analysis. Similarly, a triethylamine solution of diethylmagnesium triethylaminate (0.022 mol) was added to a triethylamine–magnesium bromide triethylaminate (0.021 mol) mixture and diethylmagnesium triethylaminate (0.021 mol) in triethylamine was added to magnesium iodide triethylaminate (0.020 mol) in triethylamine. Redistribution of dimethylmagnesium–TMED and magnesium bromide–TMED in diethyl ether was examined by adding 100% excess of TMED to ether solutions of the compounds and then mixing the solution of dimethylmagnesium (0.019 mol) with the magnesium bromide (0.022 mol)–ether mixture. The exchange study in benzene was conducted by adding a benzene solution of dimethylmagnesium–TMED (0.019 mol) to a mixture of magnesium bromide–TMED (0.020 mol) in benzene.

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Chemistry of Cyclopropanes. I.[1] Synthesis and Deamination of Spiroamines

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Four spirocyclopropylamines in which the adjacent spiro ring was varied from cyclopropyl to cyclohexyl have been synthesized and deaminated. Three of the amines, 1-aminospirohexane, 1-aminospiro[2.4]heptane, and 1-aminospiro[2.5]octane, were obtained by adding ethyl diazoacetate to the appropriate methylenecycloalkane, and converting the resulting spiro esters by hydrolysis and Curtius rearrangement into the corresponding spiroamines. Similarly spiropentylamine was prepared from ethyl spiropentanecarboxylate. Deamination (aqueous nitrous acid–sodium nitrite) of three of the spirocyclopropylamines (excepting spiropentylamine) gave mixtures of unsaturated alcohols in which the adjacent cycloalkyl moiety remained intact. Spiropentylamine gave predominantly a mixture of 2- and 3-methylenecyclobutanols. These results are discussed in terms of the collapse or rearrangement of an initially formed spirocyclopropyl cation.

Since the initial report of Roberts and Chambers[3] in 1951 that cyclopropyl tosylate gave only allyl acetate upon acetolysis at a rate of 10^{-5} that of cyclohexyl tosylate, a considerable amount of research has been devoted to the carbonium ion chemistry of cyclopropyl systems.[4–7] Although the solvolysis of cyclopropyl derivatives is relatively slow, several investigators have offered strong evidence that these reactions proceed with considerable anchimeric assistance.[4–7] It appears that these solvolyses are a concerted process with ionization and ring opening taking place concurrently.[4,5] Recent studies have further indicated that opening of a cyclopropyl cation is a disrotatory process[8] with the groups *trans* to the leaving group rotating outward.[4,5] The transition state has generally been represented in terms of the delocalized structure

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[2] (a) Abstracted, in part, from the Ph.D. Thesis of L. M. Konzelman, Seton Hall University, 1966. (b) To whom inquiries should be addressed.

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