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I hereby recommend that the thesis prepared under my supervision by Howard A. Woltermann

entitled SOLVATION OF PSEUDO-GRIGNARD REAGENTS AND THE KINETICS OF PSEUDO-GRIGNARD REACTIONS

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Dayl H. McDaniel

John S. Thayer

Joseph E. Todd

Form 668—Grad. School—1M—8-67

SOLVATION OF PSEUDO-GRIGNARD REAGENTS AND THE KINETICS OF PSEUDO-GRIGNARD REACTIONS

A dissertation submitted to the

Division of Graduate Studies
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

in the Department of Chemistry
of the Graduate School of Arts and
Sciences

1972

BY

Howard A. Woltermann

A.B. Villa Madonna College, 1963

M.S. Xavier University, 1965

DEDICATION

This work is dedicated by the author to his wife, Maureen, whose encouragement and sacrifices made this thesis possible, and to his children who made it necessary.

ACKNOWLEDGMENT

The author wishes to thank Dr. Darl H. McDaniel for suggesting this work and for his guidance while the work was being completed. Also appreciation is expressed for Dr. McDaniel's understanding and patience with the author's work schedule at Monsanto.

The author thanks his wife, to whom this work is dedicated, as well as his father and mother who supported and encouraged much of his earlier education. He also thanks his fellow graduate students for their helpful discussions and their friendship which made this undertaking a pleasant experience.

The author also expresses his gratitude to the management of Monsanto Research Corporation, especially to his immediate supervisor, Wayne R. Amos, for their complete cooperation in allowing the author to work on a half time basis during this work.

He also thanks the Department of Chemistry, University of Cincinnati, for furnishing a scholarship covering the cost of tuition during the last two years of this thesis.

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Part I

SOLVATION OF PSEUDO-GRIGNARD REAGENTS

INTRODUCTION

Historical Background

The Grignard reagent has been extensively investigated since its discovery in 1900 by Victor Grignard[1]. More articles have been published on this reagent than on any other. Paradoxically, the structure of the Grignard reagent is still not completely understood and has been the subject of spirited controversy.

For an interesting history of this reagent, the reader is referred to a 1967 review article by Ashby[2]. A brief history of this reagent follows, as a backdrop to this thesis.

Jolibois[3] in 1903 proposed that the Grignard reagent has an assymetric dimer structure $R_2Mg \cdot MgX_2$, where R refers to an alkyl or aromatic group and X is Cl, Br, or I. This proposal was based on the degree of association of the RMgX as inferred from colligative properties and the similarity of Et_2Mg in diethylether with a Grignard prepared from EtI and magnesium in ether.

The quantitative precipitation of magnesium halide dioxonate from a Grignard reagent by the addition of excess 1,4-dioxane led Schlenk and Schlenk[4] to postulate that the equilibrium:

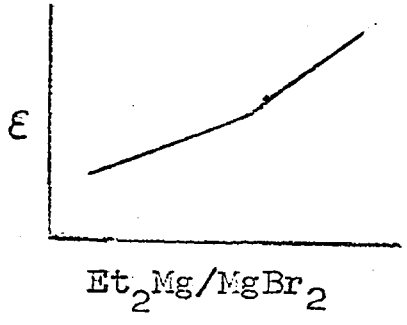
(1) $2RMgX \rightleftharpoons R_2Mg + MgX_2$

$R_2Mg + MgX_2 \rightleftharpoons R_2Mg \cdot MgX_2$

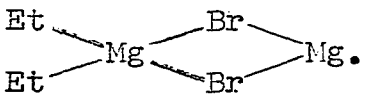
best described "RMgX".

In the late 1950's Dessy[5] and coworkers challenged the existence of the RMgX monomer in the equilibrium. A plot of the dielectric constant of a diethylether solution of $MgBr_2$ with varying amounts of Et_2Mg exhibited a distinct break at a 1:1 $Et_2Mg/MgBr_2$ mole ratio (2). This indicated a compound formation at the 1:1 mole ratio. This fact and the similarity of this 1:1 compound to the conventionally prepared Grignard reagent "EtMgBr" indicated that "EtMgBr" was the compound formed by the reaction of Et_2Mg and $MgBr_2$.

(2)



Using $^{28}MgBr_2$ and Et_2Mg Dessy[6] et al prepared the "EtMgBr" Grignard reagent . On precipitation of $MgBr_2$ dioxanate by 1,4-dioxane addition, he isolated 95% of the ^{28}Mg in the $MgBr_2$ precipitate. Thus the Grignard reagent was postulated as:

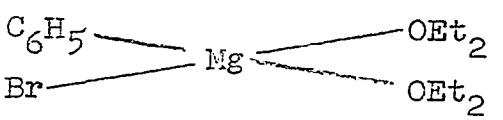
(3) 

If the monomer were present in the Schlenk equilibrium complete statistical exchange of ^{28}Mg between the Et_2Mg and $MgBr_2$ would have been observed.

Dessy's work was generally accepted, and in fact by 1962 it was thought that the structure of the Grignard reagent had been solved.

By 1963 the controversy was reopened by papers by Ashby[7,8] and coworkers, and by Stucky and Rundle[9]. Ashby *et al* showed by studies of boiling point elevation that EtMgCl was monomeric over a large concentration range in THF. In a later paper, Ashby[8] and coworkers then showed that EtMgI and EtMgBr were monomeric in dilute diethylether solutions. (0.2M).

Stucky and Rundle[9] obtained crystals from diethylether solution of the empirical formula $C_6H_5MgBr \cdot 2(Et_2O)$ and studied the structure by Xrays. From their data they found the structural units present to be

(4) 

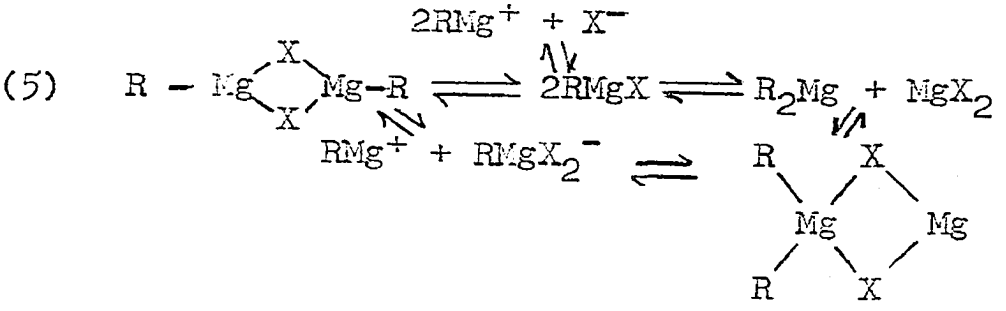
This proved that monomeric RMgX does exist at least in the solid phase.

Meanwhile Dessy was unable to reproduce his exchange work. Using a ^{25}Mg tracer he found complete statistical exchange. In 1964[10] he repeated the ^{28}Mg tracer work and found that only when a specific type of ^{28}Mg is used (Dow atomized shot) is there no exchange. High purity triply sublimed magnesium and Grignard grade turnings gave statistical exchange.

When the Dow atomized shot was mixed with the ^{28}Mg turnings, no statistical exchange was seen. Ashby[2] suggested that an inhibitor was present in the atomized shot. Dessy[10] did not find this explanation appealing but admitted it was a possibility.

Although RMgX monomer has only been shown to exist in THF and in dilute diethylether solutions it seems reasonable that some RMgX is present in more concentrated solutions by way of a Schlenk type equilibrium.

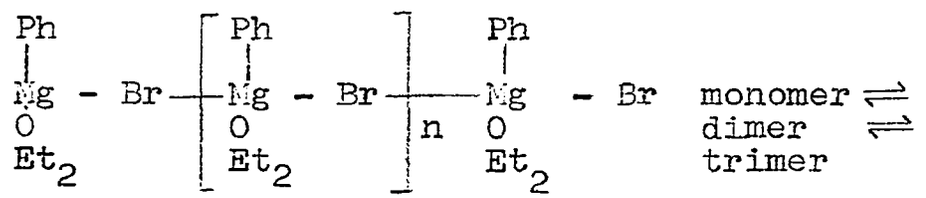
Wakefield[11] in review articles in 1966 and 1968 proposed that the Grignard reagent is best described by the extended equilibrium:



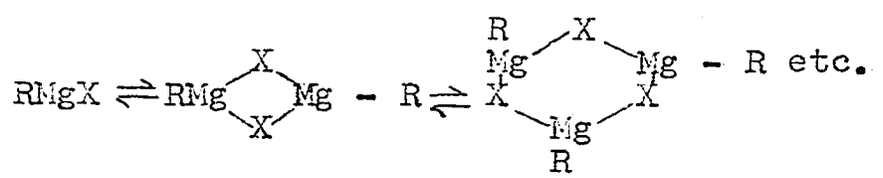
The $RMg^+ + X^-$ species in the equilibrium must be viewed with some skepticism. It is highly unlikely that the strong Lewis base, X^-, would exist except in trace concentrations in the presence of the strong Lewis acid, RMg^+.

Ashby[12] indicated that for some Grignard reagents as C_6H_5MgBr, a linear polymer or cyclic polymer equilibrium should be included:

(6)



(7) or



Very recently Parris and Ashby[13], and Evans and Fazakerley[14], in separate articles described low temperature NMR studies of various Grignard reagents which show the presence of R_2Mg and RMgX in Grignard solutions. Their results support the Schlenk equilibrium.

While progress has been made on elucidating structure of the reagent, until recently there has been very little understanding of the solvent molecules which are bound to the magnesium of the Grignard reagents. This is indeed unfortunate since the reactivity of Grignard reagents is

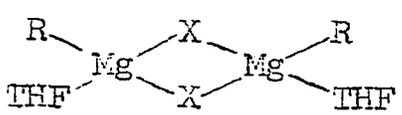
known to be very dependent upon the solvent in which they are found. The X-ray studies that have been performed on Grignard reagents show the number and bonding mode of solvent molecules in the solid phase but strict extrapolation to solution coordination is at best risky.

Guild[15] et al developed a gas chromatographic Henry's Law titration to determine the number of solvent molecules coordinated per magnesium atom.

By this method Guild[15] et al and later Chattoraj[16] were able to titrate diethylether solutions of Grignards with a stronger base, tetrahydrofuran (THF), and calculate the number of THF molecules coordinated per magnesium atom.

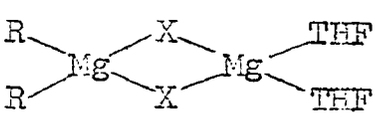
From these data they deduced the association of the Grignard reagent. If one THF molecule coordinated per magnesium atom, a dimer as shown in (8) I or II was postulated. If two THF molecules coordinated with each Mg atom, a monomer as shown in (8) III was suggested.

(8)



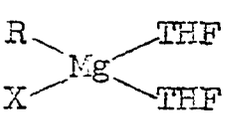
I

Sym. Dimer



II

Asym. Dimer



III

Monomer

These structures were deduced from the solvation data and the assumption of a four coordinated magnesium atom.

By such titrations, phenylmagnesium bromide, benzylmagnesium bromide, and ethylmagnesium bromide were found to coordinate one THF molecule per magnesium atom, and were assumed to have a dimeric structure. Methylmagnesium iodide was found to coordinate two THF molecules per magnesium atom and was assumed to have a monomeric structure.

Hollingsworth[17] et al explored Et_2Mg and found that it solvated one THF molecule per magnesium atom. Assuming Et_2Mg to be monomeric, Hollingsworth postulated the equilibria,

(9) $Et_2Mg \cdot 2Et_2O + THF \overset{K_1}{\rightleftharpoons} Et_2Mg \cdot Et_2O, THF + Et_2O$

$Et_2Mg \cdot Et_2O, THF \overset{K_2}{\rightleftharpoons} Et_2Mg \cdot 2THF + Et_2O.$

Mathematically Hollingsworth demonstrated that if $K_1 >> K_2$ the Henry's Law curve would intercept the abscissa at a mole ratio corresponding to one THF molecule per magnesium atom. Hollingsworth offered no explanation as to why the first diethylether molecule would be replaced much more easily than the second.

McPherson[18] in 1971 reported on the solvent coordination of a large number of Grignard reagents in various solvents (Table I).

TABLE 1

Work of McPherson

GRIGNARD	INIT. CONC(M)	ORIG. IN SOLVENT	TITR. SOLV.	T °C	SOLV/ Mg	ASSOCN.
EtMgBr	.0944	Et_2O	THF	42.25	2.09	1
EtMgBr	.472	Et_2O	THF	42.25	1.75	1&2
EtMgBr	.944	Et_2O	THF	42.25	1.44	1&2
EtMgBr	1.627	Et_2O	THF	42.25	1.01	2
nPrMgCl	.090	Et_2O	THF	44.60	1.10	2
nPrMgCl	.447	Et_2O	THF	44.60	1.05	2
nPrMgCl	.894	Et_2O	2-MeTHF	44.60	1.13	2
nPrMgCl	2.236	Et_2O	2-MeTHF	44.60	1.07	2
MeMgI	.100	Et_2O	THF	41.50	1.98	1
MeMgI	.738	Et_2O	THF	41.50	2.03	1
MeMgI	1.353	Et_2O	THF	41.50	2.00	1
MeMgI	2.706	Et_2O	THF		1.83	1&2
nAmMgCl	1.059	Et_2O	THF	42.25	2.12	1
nAmMgCl	.530	Et_2O	THF	42.25	1.95	1
nAmMgCl	.064	Et_2O	THF	42.25	1.99	1
tBuMgCl	.230	Et_2O	THF	41.20	1.07	2
secBuMgCl	.273	Et_2O	THF	42.50	1.09	2
nBuMgBr	1.180	Et_2O	THF	42.50	1.44	1&2
tBuMgBr	.284	Et_2O	THF	42.25	3.84	-
EtMgBr	.551	anisole	THF	25.95	2.07	1
EtMgBr	.990	nBu_2O	THF	25.95	1.01	2

TABLE 1 (cont.)

GRIGNARD	INIT. CONC(M)	ORIG. IN SOLVENT	TITR. SOLV.	T °C	SOLV./ Mg	ASSOCN.
EtMgBr	.476	iPr_2O	THF	74.50	.97	2
EtMgBr	.633	4Me,1,3,-diox.	THF	25.95	1.99	2
EtMgBr	.423	THT	THF	52.05	1.02	2

Like Guild et al, McPherson deduced the structure from the solvation data and the assumption of a four coordinated magnesium atom. Thus, solvent to magnesium ratios of one were represented as dimers and ratios of two as monomers. McPherson ignored the possibility of linear or cyclic polymers which also could exhibit ratios of one.

McPherson concluded from his work that the structure of the Grignard depends on many factors, the most important being 1) the nature of the solvent, 2) the nature of the halogen, 3) the nature of the alkyl of aryl substituent on magnesium and 4) the concentration of the Grignard reagent in solution. He cautioned that the Grignard reagents are complex systems and extrapolating results of one system to another could be misleading.

Thus at this stage of the study of the Grignard reagent, it seems certain that RMgX monomers do exist and are linked via a Schlenk type equilibrium to higher associated species as well as the disproportionation species R_2Mg and MgX_2. However, the reason for the apparent contradiction of the metal exchange work of Dessy is still not clear.

It may be argued that the high concentrations at which Dessy worked reduced the amount of monomer present to the point where metal exchange is very slow. However, this can not explain the complete statistical exchange obtained by

Dessy when other types of magnesium (both purer and less pure) were used.

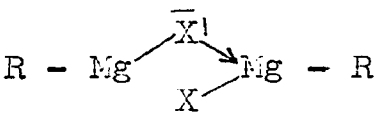
Although Dessy[10] claims that all exchange work was performed by identical methods, it is impossible to rule out a subtle change in technique which might result in the different results.

Ashby's[2] argument that an inhibitor was present in the Dow metal shot does account for the one obvious variable in Dessy's work but the concept of a trace impurity blocking the exchange reaction is unpalatable.

However it is noted by several workers[19,20,21] that trace impurities in magnesium can lead to the formation of Grignard reagents with distinctly different properties. Perhaps an impurity, such as surface oxide which can not be determined spectroscopically, catalyzed a change in the diethylmagnesium or magnesium bromide. Now the diethylmagnesium and the magnesium bromide would react to give a Grignard species not identical to the reagent prepared in the conventional manner. This reagent, perhaps due to an unusual degree of polymerization, or perhaps coordinated by a strongly basic by-product, then exchanged at a very slow rate.

Pseudo-Grignard Reagents

The dimeric Grignard species described earlier may be considered to be the product of a reaction of a Lewis acid (the magnesium in RMgX) having empty low lying orbitals and a Lewis base (the halide in RMgX) with a pair of electrons to share.

(10) 

It seems reasonable that other atoms or groups could serve equally well as either the acid or the base part of the complex. We chose in this study to vary the base, and have termed the RMgX reagents, where X≠ halide, "pseudo Grignard" reagents.

Accordingly in the preparation of associated pseudo-Grignard reagents, we need look only for an atom that will bond to magnesium and leave additional electron pairs available to form bridges to other magnesium atoms. The table below shows some possible bridging groups for associated Grignard reagents.

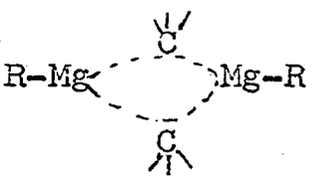
(11)

(CR_3)	NR_2	OR	F
	PR_2	SR	Cl
			Br
			I
			At

The halides have three pairs of unshared electrons

after bonding to magnesium. However, as seen from the previous section only one pair is used in bridges in associated Grignard reagents.

Oxygen and sulfur analogues have two unshared pairs available after bonding to magnesium while the amides and phosphides have but one pair. Although CR_3 has no unshared pair of electrons after bonding, association can occur by means of an electron deficient bridge (12).

(12) 

Thus we have included the dialkylmagnesium compounds in this study.

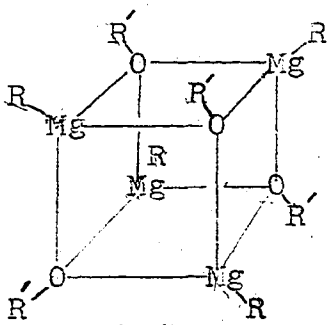
Organomagnesium alkoxides (X=OR)

Since orgomagnesium alkoxides (RMgOR) are featured as intermediates in most mechanisms for the reaction between Grignard reagents and carbonyl compounds there is much interest in their structure. They are conveniently prepared by partial alcoholysis or ketolysis of diorganomagnesium compounds (equations 13&14).

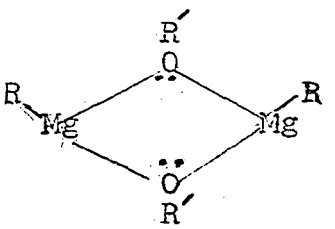
(13) $$R_2Mg + R^1OH \longrightarrow RMgOR^1 + RH$$

(14) $R_2Mg + R'-\overset{O}{\overset{\|}{C}}-R' \longrightarrow RMg-O-\overset{R}{\underset{R'}{C}}-R'$

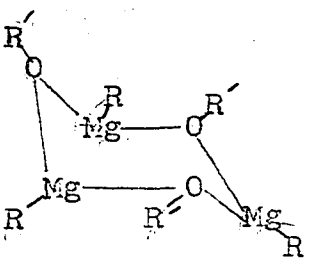
Like their beryllium analogues, they are usually associated in solution. Coates[22] has proposed the general rule that where the organic group is bonded to the oxygen by a primary carbon atom, polymerization on the order of 7 or 8 commonly occurs. Where there is chain branching α to the oxygen, tetrameric association is generally observed and is accounted for in the postulated structure (15).



(15)



(16)



(17)

However, Coates further states that if the steric requirements about the α carbon becomes great, as for example in $EtMgOCEt_3$, the dimeric structure (16) is preferred. Bryce-Smith[21] prepared and isolated $nBuMgO^iPr$ and found it to be trimeric (17).

Because of the strong competing basicity of both lone pair of electrons on the oxygen, the tetrameric and polymeric alkoxides do not coordinate diethylether. The dimeric

structure however, is isolated with coordinated ether. Bryce-Smith [21] postulated that the trimeric $nBuMgOPr^i$ was readily isolated free of ether because of back bonding of the oxygen lone pair to a vacant orbital on the magnesium.

Organomagnesium diorganoamides ($X=NR_2$)

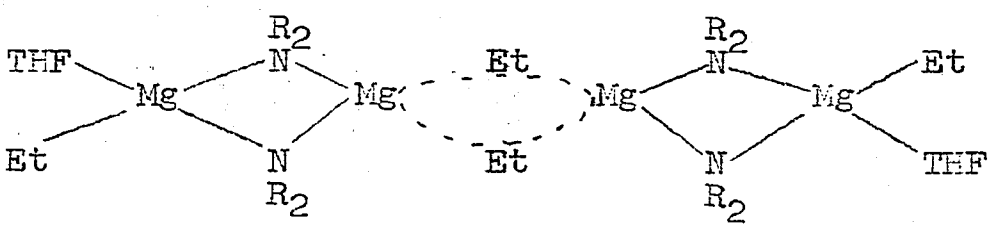
Coates[23] and coworkers isolated and studied the association of several alkylmagnesium diorganoamides. These compounds can be prepared by partial aminolysis of diethylmagnesium.

(18) $$R_2Mg + HNR'_2 \longrightarrow RMgNR'_2 + RH$$

In general these amido Grignard reagents are highly associated. Association is reduced by bulky groups on the nitrogen and by basic solvents which compete with the bridging amido group.

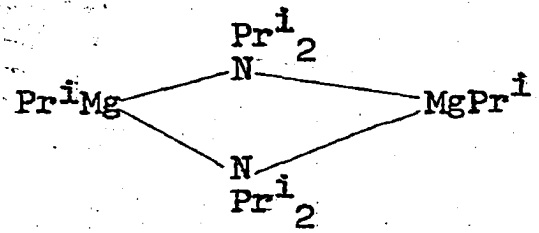
Ethylmagnesium diethylamide and ethylmagnesium diisopropylamide were found by Coates to strongly coordinate ether and THF. The THF aducts were determined to be tetramers in benzene and structure (19) was postulated.

(19)



Ethylmagnesium diphenylamide could be isolated from ether by vacuum stripping, forming the benzene insoluble polymer $(EtMgN\phi_2)_n$. A monomeric complex, $EtMgN\phi_2(THF)_2$, is formed with THF in benzene. Isopropylmagnesium diisopropylamide could be obtained free from ether and was freely soluble in benzene with dimeric association (20). This is the first reported tricoordinated organomagnesium compound (the structure being inferred from the molecular weight).

(20)



Dialkylmagnesium (X=R)

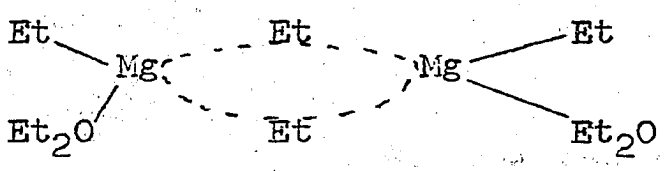
The most studied pseudo-Grignard reagent is the dialkylmagnesium compound. The preparation of this compound predates the Grignard reagent by forty years. It can be prepared by the reaction of dialkylmercury with magnesium metal in ether or by precipitation of the magnesium halide from a Grignard reagent by 1,4-dioxane.

R_2Mg coordinates with diethylether. However, in contrast to the Grignard reagents, dialkylmagnesium compounds can be readily desolvated. In the extreme case, dimethylmagnesium crystalizes from ether solutions without coordinated solvents.

Dialkylmagnesium compounds are reported to be more reactive than Grignard reagents toward carbonyl groups and active hydrogen compounds. Some dialkylmagnesium compounds are so reactive to oxidation that they spontaneously inflame in air.

The most throughly studied dialkylmagnesium, diethylmagnesium was determined by Ashby[12] to be monomeric over a large concentration range, in diethylether and THF. At higher concentrations (>1M) some association is seen in diethylether and is attributed to electron deficient carbon bridges (21).

(21)



Other Pseudo Grignard Reagents (X=SR,F)

Alkylmagnesium thioalkyls have been prepared and isolated by Coates[24] by the reaction:

(22) $R_2Mg + R'SH \longrightarrow RMgSR' + RH$

$tBuMgSPr^i \cdot Et_2O$, $MeMgSBu^t \cdot THF$ and $EtMgSBu^t \cdot THF$ were found to be dimeric in benzene. $EtMgSBu^t$ was found to be tetrameric in benzene when prepared in ether free reagents.

For years explanations have been tendered for the "non-existence" of organomagnesium fluorides. However, very recently, Ashby[25] has reported preparing a series of these fluorogrignards, by reacting alkylfluorides with magnesium in the presence of large (4 mole %) amounts of I_2 catalyst for several days in THF.

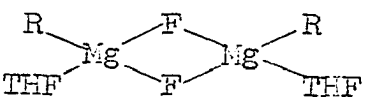
(23) $$RF + Mg \xrightarrow[THF]{I_2} RMgF.$$

Also Ashby[26] was able to prepare aromatic as well as alkyl derivatives by the reaction.

(24) $$3\ R_2Mg + BF_3 \xrightarrow[THF]{} RMgF + R_3B.$$

n-Hexylmagnesium fluoride[27] was determined to be dimeric. RMgF differs from conventional Grignard reagents in that no evidence is observed for a Schlenk equilibrium due to strong fluoride bridging.

(25)



STATEMENT OF THE PROBLEM

It has been shown by Guild, McPherson and others, that the gas chromatographic Henry's Law titration is a valuable tool for determining solvent coordination. It also is an excellent compliment to association studies in deducing the structure of Grignards reagents.

With the advent of the pseudo-Grignards, possible new synthetic tools have become available to the chemist. It is necessary to understand the structure and properties of these reagents in order to realize their full potential. By exploring a series of pseudo-Grignards this study hopes to elucidate the effects of changes in the X group upon the structure and properties of organomagnesium compounds. Also it is hoped to show the effects of various solvents upon the degree of association of these reagents.

Although basicities of various solvents have been well documented in solution for reaction with hydrogen ions, Virtually no work has been done on the relative basicities of solvents toward Grignard reagents. Until now, attributing differences in reactivity in various solvents to basicity required estimating the relative basicities of the solvents by analogy to their basicities toward protons or other Lewis acids[28]. By use of the gas chromatographic

Henry's Law titration it should be possible to catalogue the relative basicities of some of the more common solvents toward organomagnesium compounds.

EXPERIMENTAL

Materials

Magnesium powder: Purified grade magnesium powder was obtained from Baker Chemical Co.

Magnesium Turnings: Magnesium turnings (for Grignard's reaction) were obtained from Mallinckiodt Chemical Works.

Diethylether: Absolute ether (Baker or Mallinckiodt) was dried over sodium ribbon and used without further treatment.

Methylcyclohexane: Reagent grade methylcyclohexane (Baker) was dried over sodium ribbon and used without further treatment.

n-Butylchloride: Practical grade n-butylchloride (Matheson) was dried over phosphorous pentoxide and distilled at atmospheric pressure.

Ethylbromide: Practical grade ethylbromide (Eastman) was used as received.

n-Propyl alcohol: Reagent grade n-propyl alcohol (Baker) was dried by treatment with magnesium[29] and distilled.

Secondary and tertiary alcohols: Reagent grade Isopropyl and secbutyl and t-butyl alcohols (Baker) were dried over Drierite and distilled at atmospheric pressure.

1,4-Dioxane: Reagent grade 1,4-dioxane (Baker) was treated with activated aluminum oxide[30] in order to remove peroxides, dried for several days over calcium hydride, and distilled at atmospheric pressure.

2-Methyltetrahydrofuran and Tetrahydrofuran: Reagent grade (Baker) were dried for several days over calcium hydride and distilled at atmospheric pressure.

Triethylamine: Reagent grade triethylamine (Eastman) was dried for several days over calcium hydride and distilled at atmospheric pressure.

Pyridine: Reagent grade pyridine (Baker) was dried for several days over either anhydrous barium oxide or calcium hydride and distilled at atmospheric pressure.

Tetrahydrothiophene: Reagent grade tetrahydrothiophene was dried over Drierite and distilled at atmospheric pressure.

N-Methylpyrrolidine: Reagent grade N-methylpyrrolidine (Matheson) was dried over calcium hydride and distilled at atmospheric pressure.

Phenol: USP grade phenol (Baker) was used as received.

Di-n-propylamine and diisopropylamine: These amines (Eastman) were dried over Drierite and distilled at atmospheric pressure.

Diphenylamine: Reagent grade diphenylamine (Baker) was placed in a vacuum desicator for several hours at 100°C before use.

II. PREPARATION OF ORGANOMAGNESIUM COMPOUNDS

n-Butylmagnesium n-propoxide, isopropoxide and sec-butoxide were prepared by the method of Bryce-Smith[21]. Two moles of n-butylchloride and one mole of the alcohol were reacted with magnesium powder in methylcyclohexane at 100°C. The insoluble magnesium chloride and excess magnesium powder were centrifuged from the supernate containing the n-butylmagnesiumalkoxide.

Diethylmagnesium was prepared by the dioxane precipitation method described by Nesmeyanov and Kocheshkov[31]. The dioxane was stripped off at 150°C under vacuum. Diethylmagnesium was redissolved with methylcyclohexane and the minimum amount of diethylether to effect the dissolution. The compound was then recrystallized in a Schlenk tube. For the preparation in triethylamine, the diethylmagnesium was dissolved in methylcyclohexane and triethylamine.

Ethylmagnesium alkoxides and amides were prepared as described by Coates[22,23] by reaction of one mole of diethylmagnesium and one mole of alcohol or secondary amine.

All organomagnesium compounds were stored in septum-capped amber bottles which, in turn, were kept in jars containing Drierite and filled with nitrogen.

III. ANALYSIS GRIGNARD REAGENTS

The concentration of n-butylmagnesium alkoxides and diethylmagnesium compounds were determined by the double titration method of Vlismas and Parker[32]. Total basicity of the organomagnesium compound was determined by a Gilman titration. A separate aliquot of the organomagnesium reagent was reacted with carbon tetrachloride prior to another Gilman titration. The CCl_4 reacts with R-Mg bonds to yield neutral coupling products. Thus the concentration of R-Mg species as well as concentration of magnesium alkoxide was determined.

Halide content of the n-butylmagnesium alkoxides and diethylmagnesium compounds was semiquantitatively determined by addition of $AgNO_3$ to a sample hydrolyzed in 1 N nitric acid. The turbidity of the AgX precipitate in compound was compared to standard halide samples. The n-butylmagnesium alkoxides contained a chloride to RMg mole ratio of less than 0.01. The bromide content of the Et_2Mg compounds was undetectable.

Et_2Mg solutions were analyzed for dioxane by gas chromatography. 1.0 ml. of the Et_2Mg solution was reacted with 1.0 ml. of 95% ethanol. The precipitate was centrifuged

and 2 (μl) of the supernate was chromatographed on a 6 foot, ¼" OD, 10% UC-W on Chromasorb W colunm at 70°C. The dioxane peak was compared to peaks obtained from standard mixtures. In all cases the dioxane to Et_2Mg mole ratio was less than .01.

APPARATUS

The diagram of the gas chromatographic assembly is shown in Figure I. The titration vessel consisted of a 125 ml. flat bottomed flask connected to a cold finger condenser. The flask had three side arms. A thermometer graduated to the nearest .1°C was inserted into one side arm. A sample port with a silicone rubber sepatum was connected to one of the side arms through which samples could be introduced by means of a syringe. The remaining arm was connected to a length of ⅛" O.D. teflon tubing which in turn was connected to an on-off valve (Valve A). This valve was connected to the sample valve by ⅛" O.D. stainless steel tubing. All connections were made with Swagelok fittings.

The tubing from the titration vessel to the sample port to the gas chromatograph was wrapped with electrical heating tape to prevent condensation of vapors.

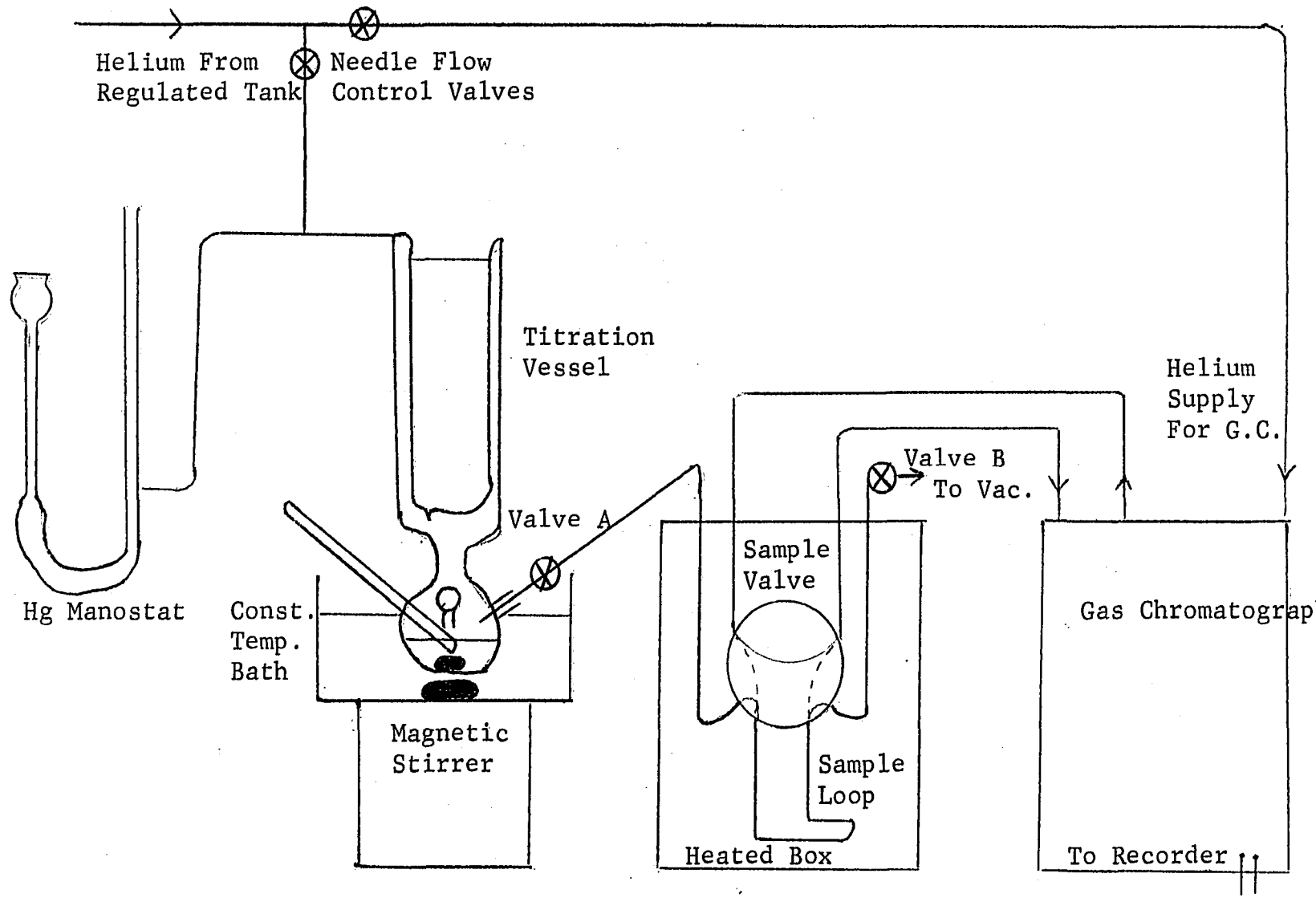


Figure I Gas Chromatographic Assembly

The titration vessel was kept at constant temperature by means of a small constant temperature bath. This bath was on top of a magnetic stirrer. This permitted simultaneous stirring of the bath and solution in the titration vessel by magnetic stir pills in the bath and in the titration vessel.

The cold finger of the titration vessel was filled with an ice water slurry. A slow flow of helium through the manostat allowed a constant pressure of inert gas to blanket the air sensitive reagents in the titration vessel.

The sample valve, a rotary valve (Consolidated Electrodynamics Corporation), was contained in an electrically heated box, the temperature of which was maintained high enough to prevent condensation of vapors.

Samples could be injected into the gas chromatograph by the following operation. The sample valve and sample loop were evacuated by means of a vacuum pump. The toggle valve "B" was closed and valve "A" was opened to fill the sample loop with the gas above the liquid in the titration vessel. The sample valve was then switched (dotted lines in figure I) to sweep the gases in the sample loop into the gas chromatograph. After fifteen seconds the sample valve was switched to it's original position, valve "A" was closed

and valve "B" was opened to reevacuate the system in preparation for the next sample.

The gas chromatograph was a Gow Mac Model 69-500 equipped with a thermal conductivity detector. A six foot ¼" O.D. aluminum column, packed with 20% w/w Penwalt 223, 4%w/w KOH on Gas Chrom R, was used for all titrations. Flow rates of carrier gas and temperature of the columns and detector were adjusted depending upon the mixture to be separated. The gas chromatograph was attached to a Micro Cord 44, 0.5-10 millivolt recorder (Photovolt Corporation).

Gas Chromatographic Henry's Law Titration

A predetermined volume of solvent was first injected into the titration vessel by a syringe. In the same way a known volume of Grignard reagent was injected. When the solution had been brought to the temperature of the constant temperature bath, a sample of the gas above the solution was sent through the gas chromatograph and analyzed. An appropriate amount of the complexing solvent was injected into the titration vessel and after fifteen minute equilibrium time, the process was repeated. The carrier gas flow rate, sample valve temperature, column temperature, detector

temperature, and detector current were maintained constant throughout the titration.

Obtaining Data From Chromatograms

The peak height of the solvent and complexing agent were measured in millimeters and were multiplied by the correction factor (V+v)/V, where V is the initial volume of the solution and v is the total volume of complexing solvent added. This factor corrects for the dilution effect occuring during the titration. The corrected peak heights of the complexing solvent were plotted versus the total amount of complexing solvent added. The straight line portion of this curve was extrapolated to the abscissa. The value of the intercept thus obtained was used to calculate the mole ratio of complexing solvent to magnesium in the Grignard reagent.

The apparatus and operation for the Henry's Law titration described above were essentially the same as described by McPherson. One new development was the use of a constant temperature bath instead of constant temperature reflux for most of this work. Use of the constant temperature bath allowed selection of titration temperature and did not require adjustment of pressure during titration.

Also the lower temperatures permitted by the constant temperature bath resulted in better precision especially for higher boiling titrants.

RESULTS AND DISCUSSIONS

Organomagnesium alkoxides

nButylmagnesium n-propoxide: Listed in Tables V, VI, and VII and plotted in figure III are the results of the gas chromatographic titration of n-butylmagnesium n-propoxide in diethylether, methylcyclohexane solvent. With tetrahydrofuran as the titrant a straight line Henry's Law plot passing through the origin indicated no complexation of THF with this reagent. This is consistent with the polymeric structure postulated for primary alkoxides by Coates[22] involving tetra coordinated magnesium and oxygen atoms. This implies that THF is not basic enough to replace either of the lone pairs on the alkoxide oxygen coordinated with magnesium.

Since triethylamine and pyridine are more basic toward a proton, they were used as titrants. With triethylamine as the titrant, the straight line Henry's Law plot intercepts the abscissa at a Et_3N/Mg ratio of 0.05 which is indicative of little or no co-ordination with n-butylmagnesium n-propoxide. The low basicity of triethylamine toward this reagent is probably due to the steric requirements of the three ethyl groups about the nitrogen on the amine.

Figure II:: BLANK GAS CHROMATOGRAPHIC TITRATION CURVE IN DIETHYLETHER SOLVENT

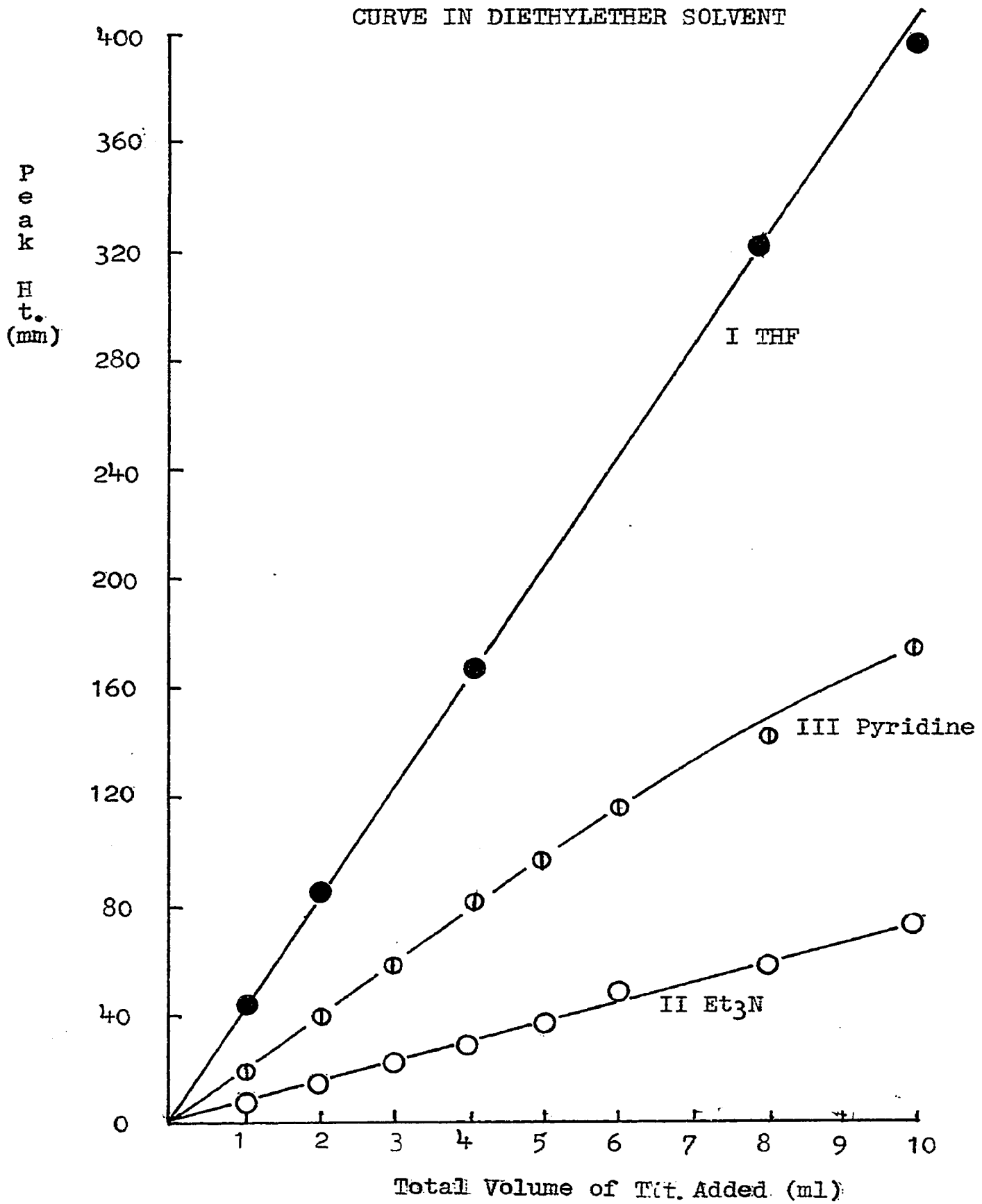
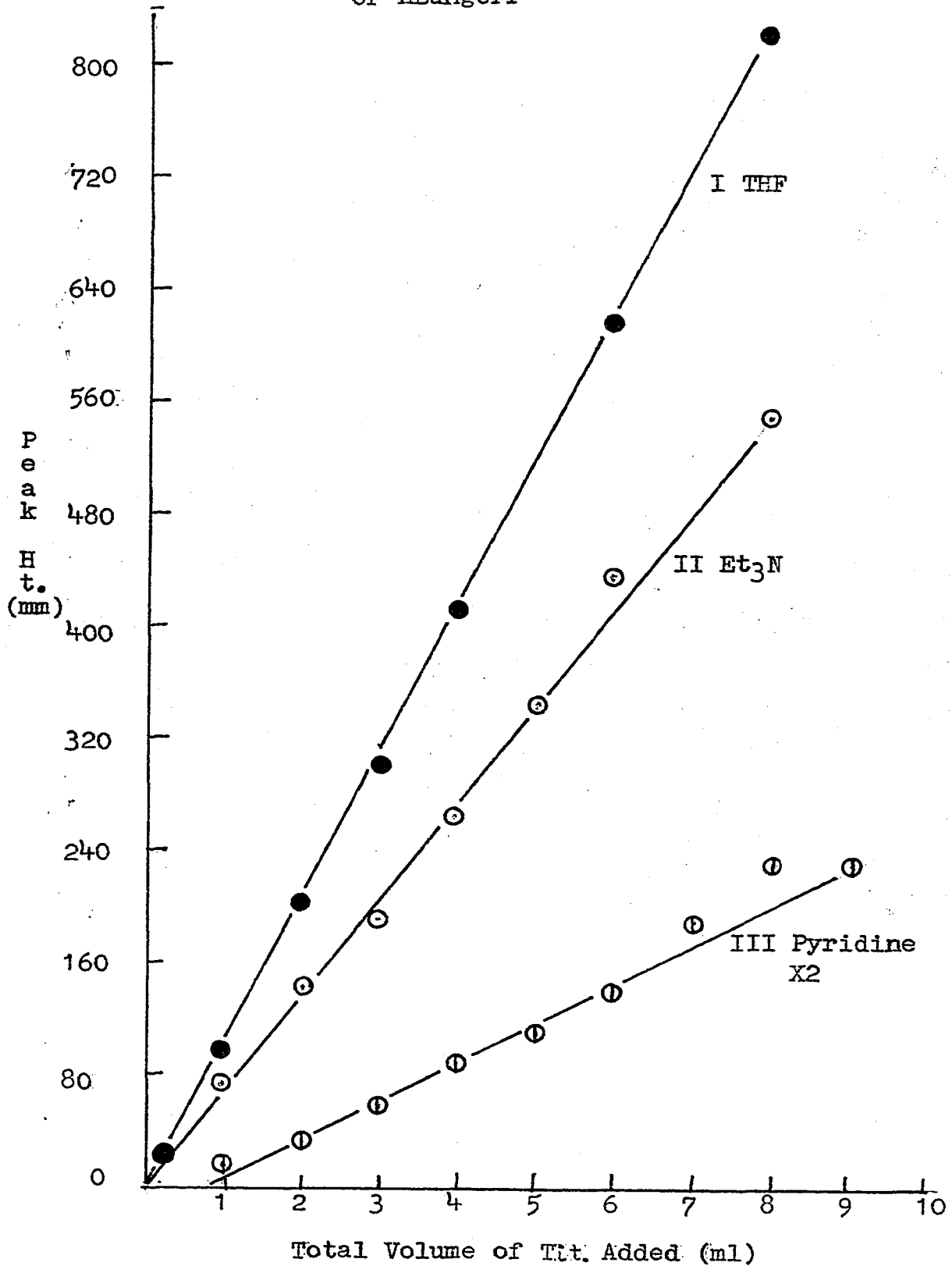
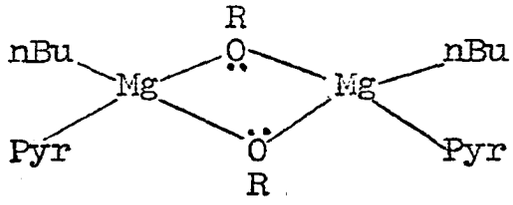


Figure III: GAS CHROMATOGRAPHIC TITRATION CURVES OF $nBuMgOPr^n$



Pyridine coordinates to nBuMgOPr^n with a pyridine/Mg mole ratio of .98 or one molecule of pyridine coordinated per every magnesium atom. This could be explained by structure (26) which would be analogous to the dimers found in traditional Grignard reagents.

(26)



n Butylmagnesium isopropoxide: Listed in Tables VIII, IX, X, XI, XII and XIII and plotted in Figures IV and V are the results of the gas chromatographic titration of n-butylmagnesium isopropoxide in diethylether/methylcyclohexane solvent.

With THF as the titrant at 24 °C extropalation of the straight line portion of the Henry's Law plot intercepted the abscissa at a volume of THF corresponding to a THF/Mg mole ratio of 0.22. This plot is indicative of an equilibrium

$$(27) \quad RMgOR' + THF \rightleftharpoons RMgOR' \cdot THF,$$

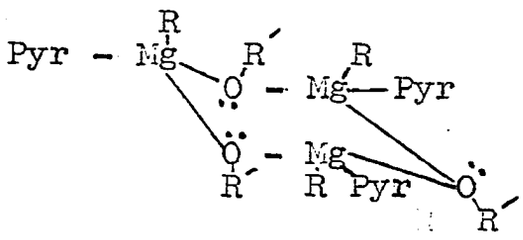
with the equilibrium lying to the left. nBuMgOPr^i is known to be trimeric in benzene with a possible structure (17 pg. 14) suggested by Bryce-Smith[21]. Although Mg is pre-

sumably tricoordinated and seemingly quite susceptible to solvent coordination, Bryce-Smith attributes its weak Lewis acidity toward diethylether as due to back bonding of the lone pair of electrons on the oxygen to the vacant p orbital on the magnesium. The stronger base THF could be visualized as competing with this back bonding to partially coordinate the reagent.

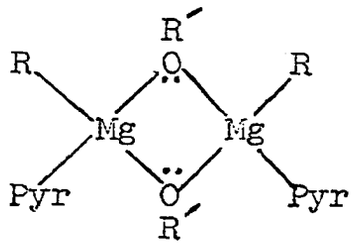
Titration with triethylamine at 49.40 °C yields a Et_3N/Mg mole ratio of 0.0. Titration at 24.4 °C shows a mole ratio of 0.05. Once again this indicates little or no coordination of Et_3N to the reagent. Also this indicates that steric factors make Et_3N a weaker base toward these Grignard reagents than THF.

Pyridine coordinates with nBuMgOPr at 24.4 °C with a pyridine/Mg mole ratio of 1.06. This can be explained by structure (27) where pyridine merely overcomes the backbonding of oxygen, or by rearrangement of the molecule to a dimeric structure (29). These data can not distinguish between the two structures.

(28)



(29)



The possibility occurred that nBuMgOPr^{i} may coordinate diethylether and might appear to have only a weak coordination with THF due to the large excess of diethylether solvent. Although excess diethylether did not cause incomplete coordination by THF in the work done by McPherson and others, the possibility remained that for unexplained reasons the basicity of THF relative to diethylether might not be as great with organomagnesium alkoxides as with traditional Grignard reagents.

Accordingly, n-BuMgOPr^{i} was titrated with THF in methylcyclohexane solvent without diethylether. A THF/Mg mole ratio = 0.0 was obtained (Figure V, curve II). This proves that excess diethylether does not inhibit the apparent coordination of THF to nBuMgOPr^{i}.

The THF/Mg mole ratio of 0.0 as compared to a mole ratio of 0.22 in excess diethylether is due to the positive deviation from Henry's Law for the MCH system as shown by the blank run (Figure V, curve I). An attempt was made to empirically correct for this positive deviation.

The peak heights for the blank run were multiplied by 0.770. This generated curve III where the peak heights for THF at 7.0 ml are the same for blank and sample run. Now a straight line (curveIV) was drawn between the origin and the THF peak height at 7.0 ml to represent a well behaved,

linear, Henry's Law blank. The differences between the curve III, and curve IV were subtracted from curve II (the sample run). Curve V is now generated which represents what the sample run would look like if the system obeyed Henry's Law. A mole ratio of 0.24 THF/Mg is now seen which is in excellent agreement with results in the diethylether/ methylcyclohexane system.

Figure IV: GAS CHROMATOGRAPHIC TITRATION CURVES OF nBuMgOPr^{i}

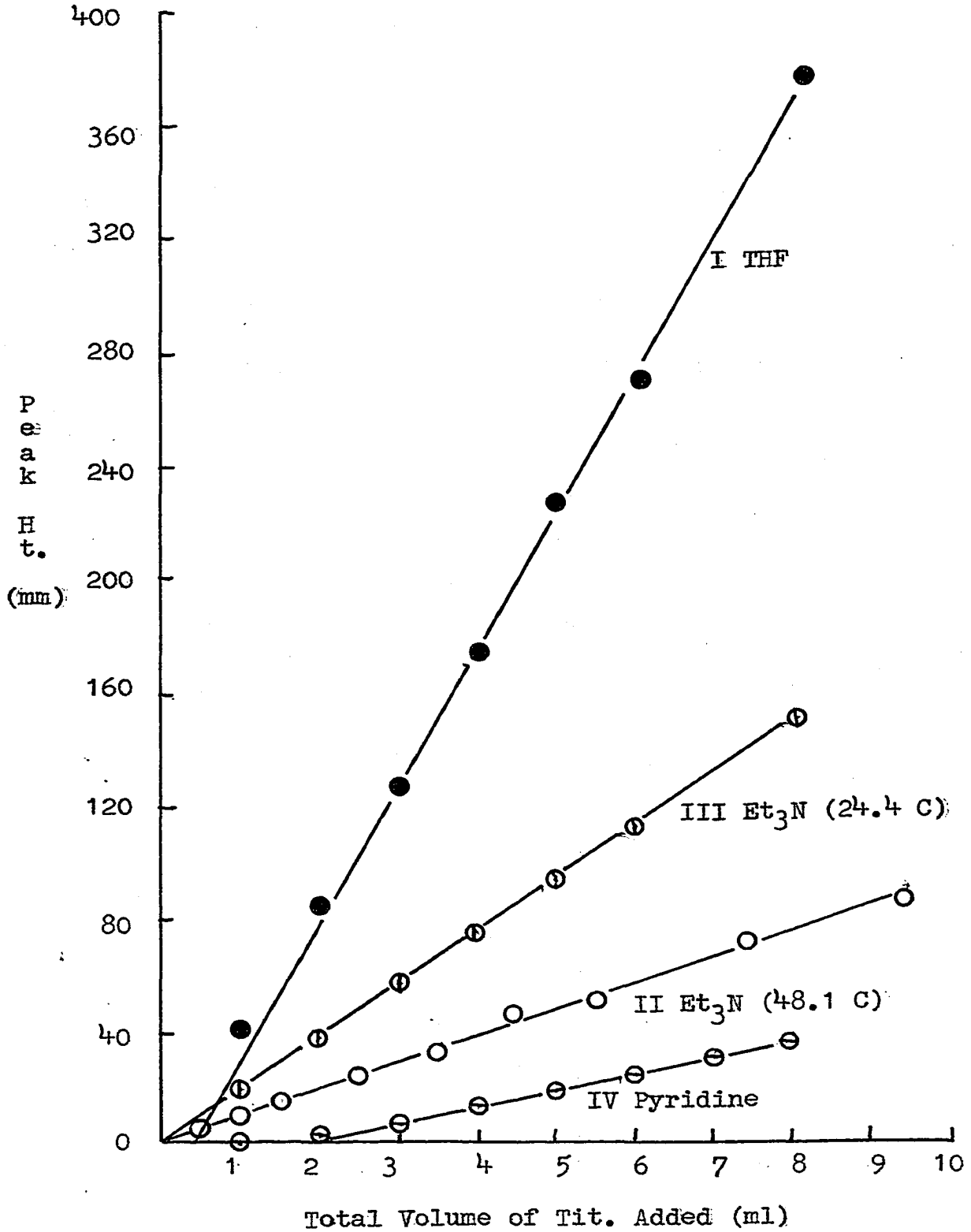
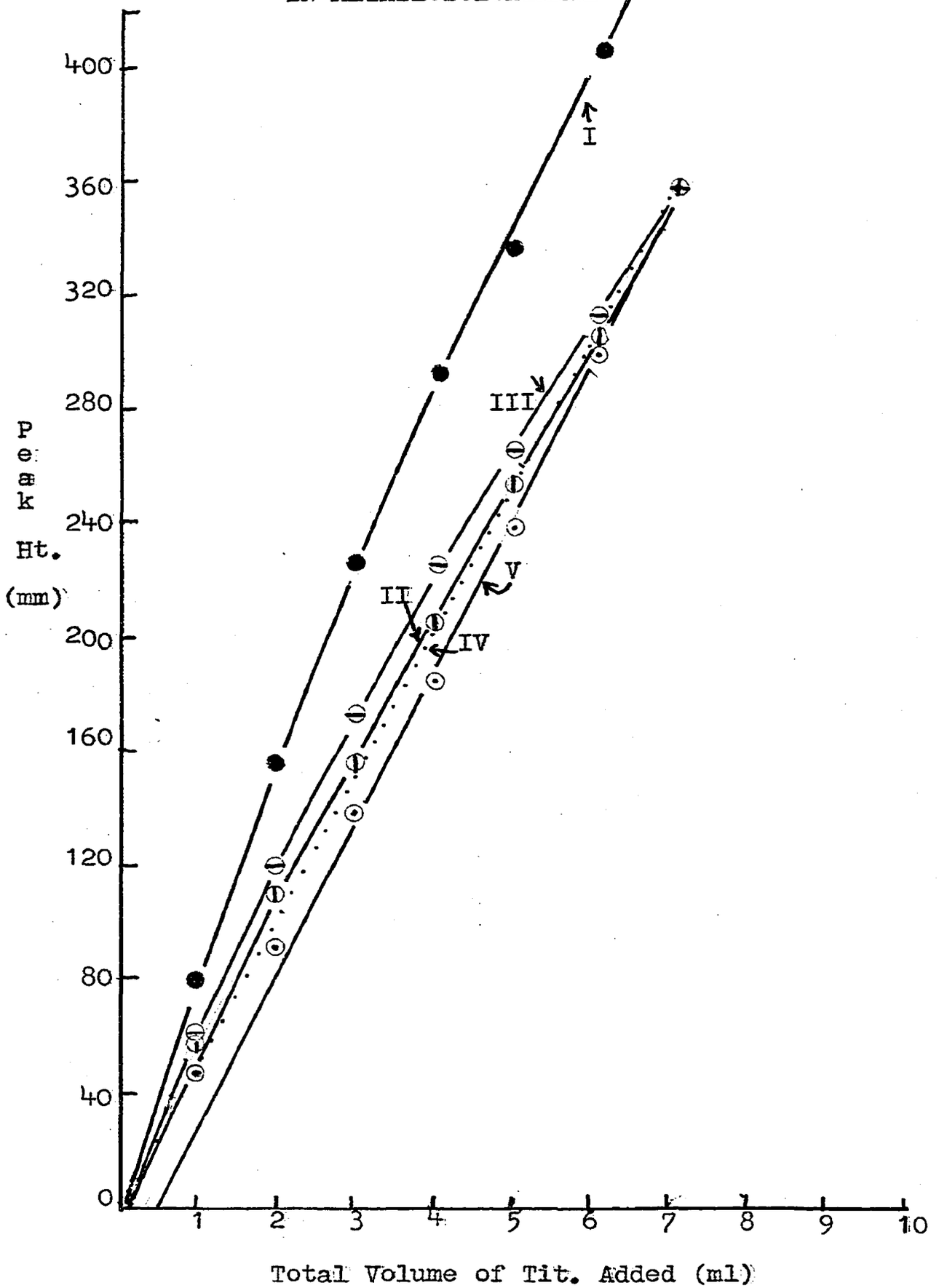


Figure V: G.C. TITRATION CURVES OF $nBuMgOPr^i_2$ IN METHYLCYCLOHEXANE



n Butylmagnesium sec-butoxide: Listed in Tables XIV, XV and XVI and plotted in Figure VI are the results of the gas chromatographic titration of n-butylmagnesium sec-butoxide in diethylether/ methycyclohexane solvent.

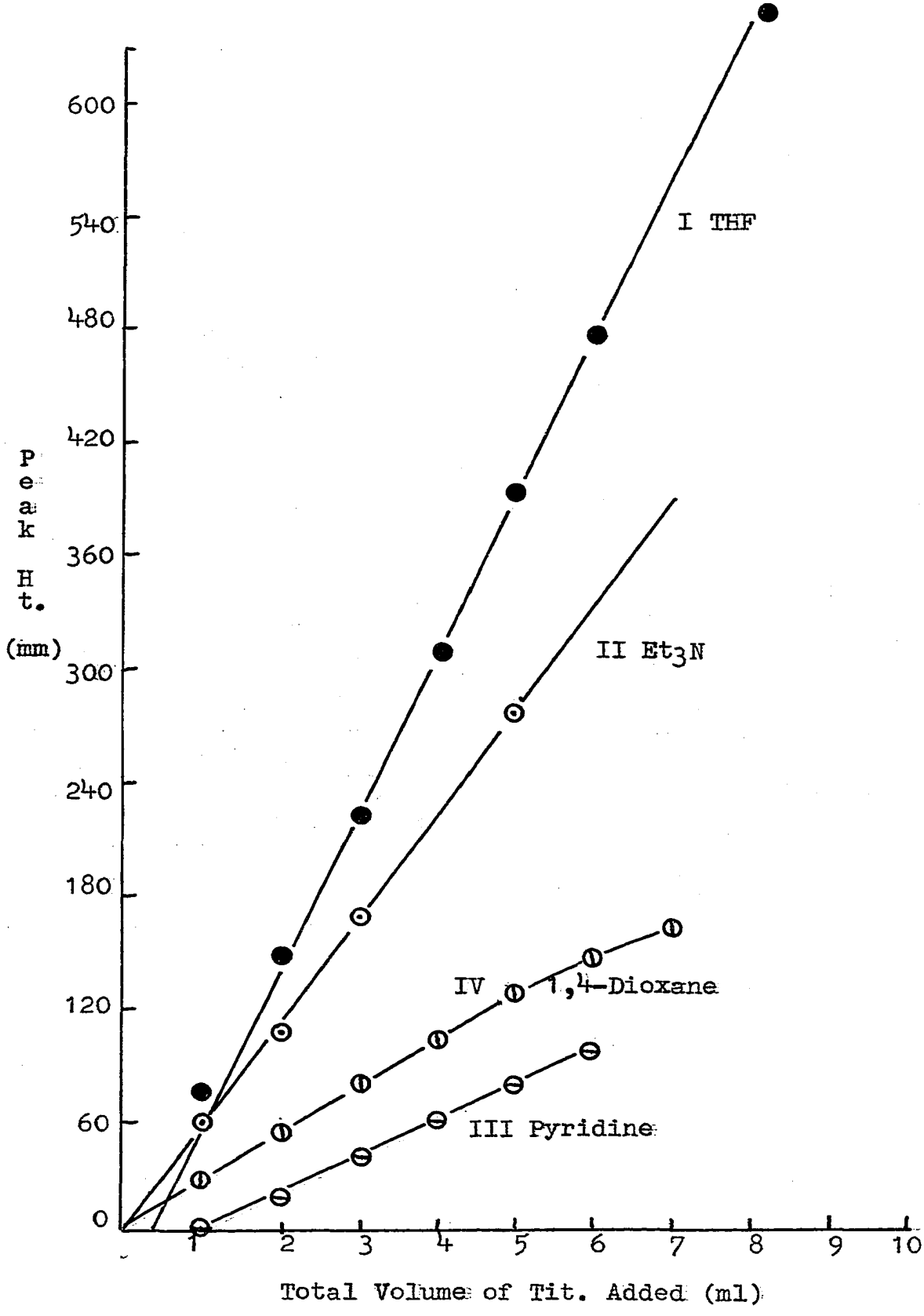
THF was found to coordinate to $nBuMgOBu^{sec}$ at 24.4°C with a THF/Mg mole ratio 0.36. Similar to the isopropoxide derivative, the sec-butoxide weakly coordinates THF. Although the association of $nBuMgOBu^{sec}$ has not been determined, it was found that the compound when isolated from ether is a colorless oil as is the isopropoxide. These facts and the molecular similarity between $nBuMgOPr^{i}$ and $nBuMgOBu^{sec}$ suggest the most probable structure for $nBuMgOBu^{sec}$ is similar to that suggested for $nBuMgOPr^{i}$(17 pg.14).

Triethylamine exhibited a Et_3N/Mg mole ratio of 0.0 when titrated into the $nBuMgOBu^{sec}$ reagent. Again triethylamine behaves as a weaker base than THF.

Pyridine coordinates to $nBuMgOBu^{sec}$ with a pyridine/ magnesium mole ratio of 0.96. This indicates a structure similar to the isopropoxide derivative. A structure analogous to (28) is consistant with the data.

$nBuMgOBu^{sec}$ was also titrated with 1,4-dioxane. A 0.0 dioxane/Mg mole ratio shows little or no coordination between dioxane and this Grignard reagent.

Figure VI:- G.C. TITRATION CURVES OF nBuMgOBu^{sec}



Ethylmagnesium t-butoxide: The results for the titration of ethylmagnesium t-butoxide in diethylether/methylcyclohexane solvent are listed in Table XVII and Figure VII. With THF as the titrant a THF/Mg mole ratio of 0.11 was calculated. Little coordination of THF is indicated. $EtMgOBu^t$ was found to be tetrameric in diethylether by Coates[22] (15 pg. 15).

Ethylmagnesium phenoxide: Listed in Table XVIII and Figure VIII are the results of the titration of ethylmagnesium phenoxide.

With THF as the titrant a THF/Mg mole ratio of 0.94 indicates one THF molecule coordinated per magnesium atom. This compound is unique among the organomagnesium alkoxides studied to date. The only alkoxides known to strongly coordinate THF are those in which the steric requirements about the oxygen are very large (eg $C(Et)_3$). The phenyl group is obviously less bulky than the t-butyl group in the $EtMgOBu^t$ above. The most logical explanation is a resonance displacement of a lone pair of electrons on the oxygen (structure 30) thus making the lone pair less basic for coordinating with magnesium.

(30)

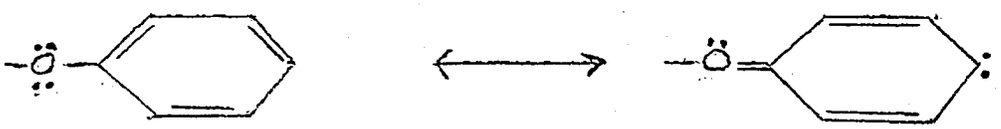


Figure VII: G.C. TITRATION CURVE OF $EtMgOBu^t$ WITH THF

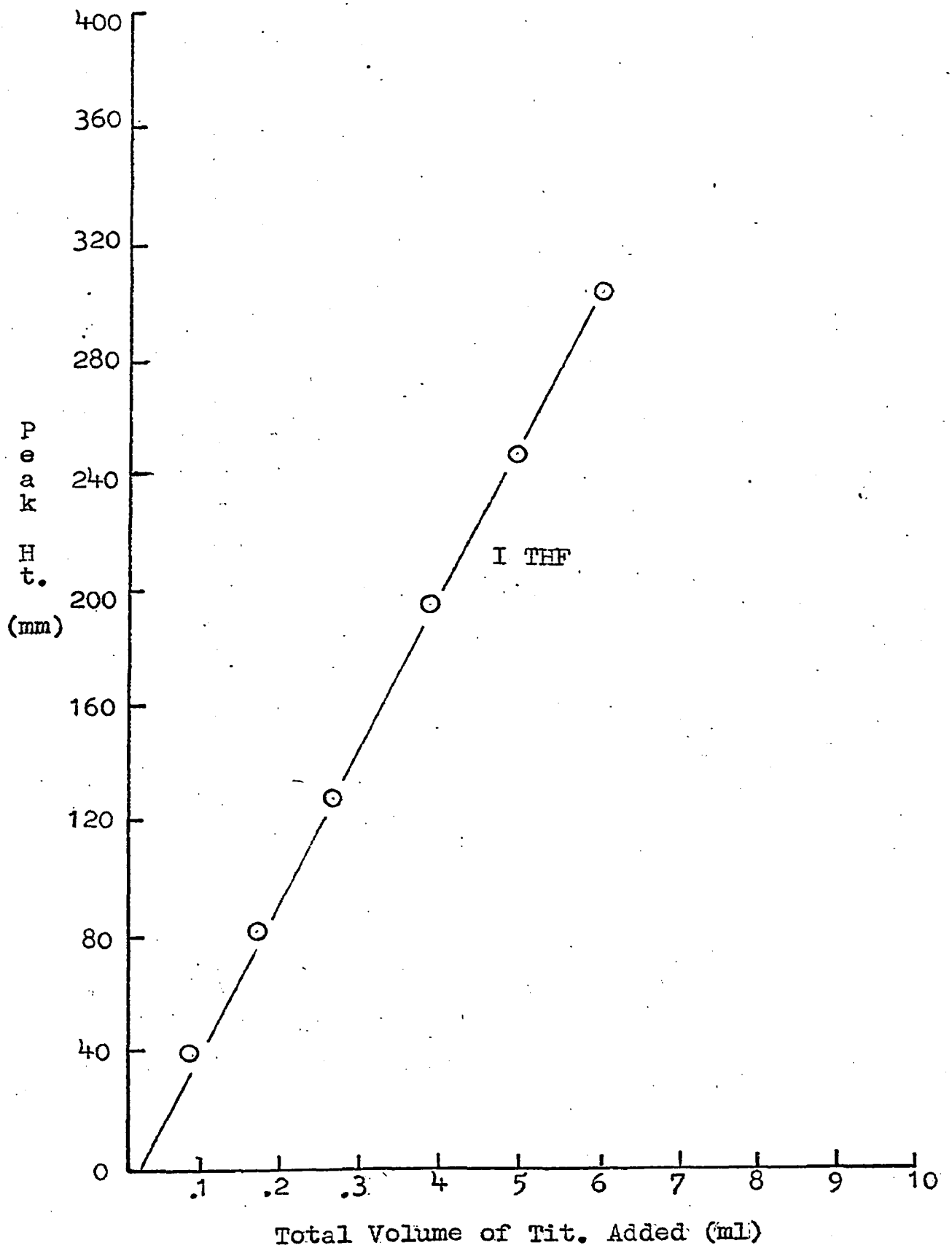
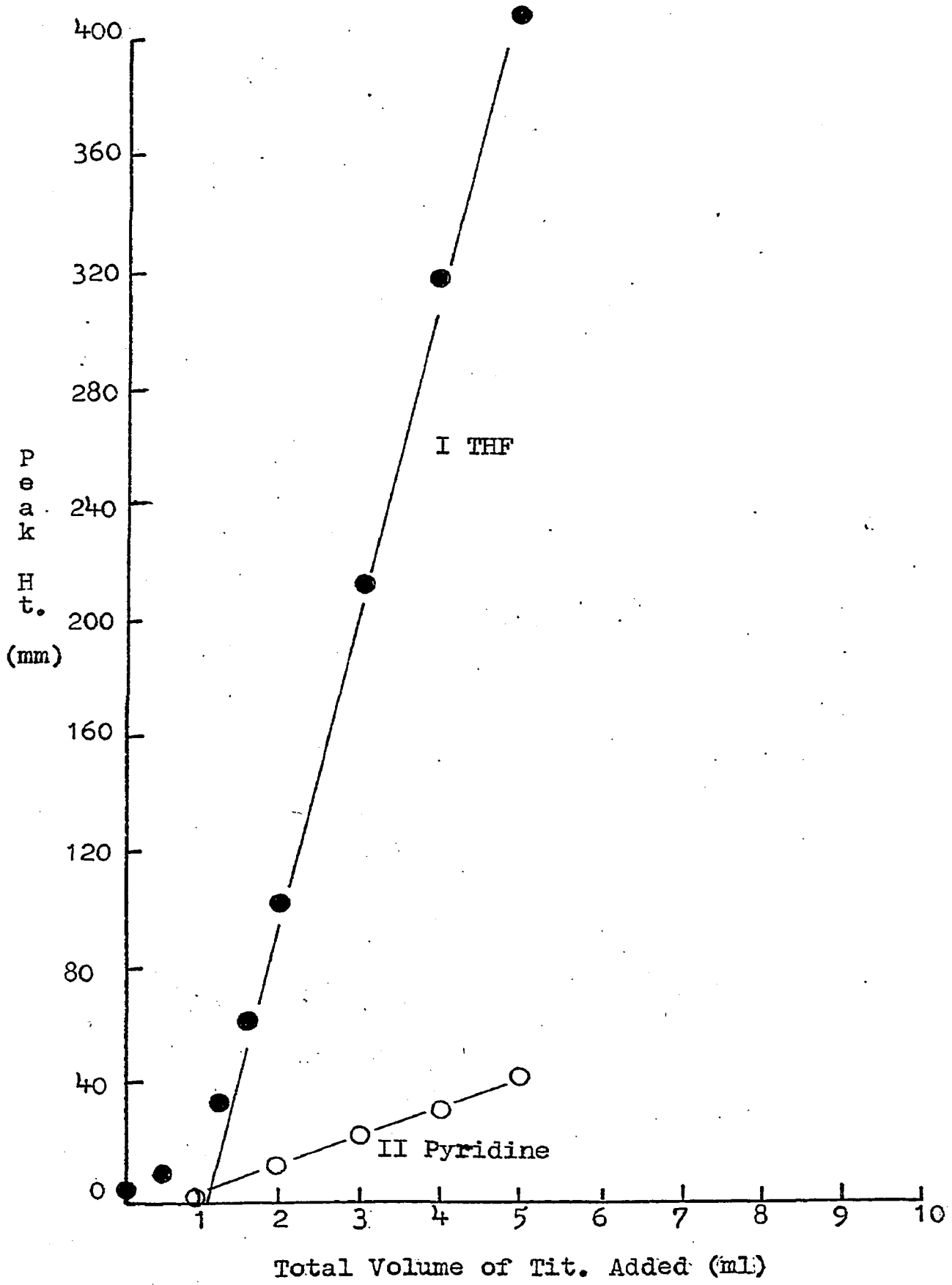
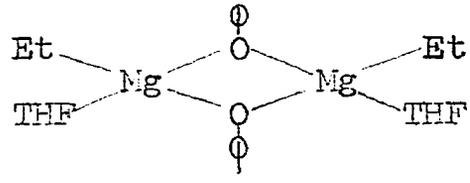


Figure VIII: G.C. TITRATION OF EtMgOΦ



Consequently THF is now more basic than one of the remaining lone electron pairs on oxygen. A dimeric structure (31) seems most likely.

(31)



Subsequent titration of this THF complex with pyridine yields a pyridine/Mg mole ratio of 0.86 or close to one. The stronger base, pyridine, merely replaces the THF molecules. As with previously studied alkoxides the pyridine is not basic enough to cleave the oxygen bridge. That is, pyridine is still less basic than the first lone pair of electrons.

Organomagnesium alkoxide coordination with THF as a function of temperature: The effect of different temperatures on the coordination of THF with n-butylmagnesium sec-butoxide is shown in Tables XIV, XX, XXI and Figure IX. At 54.6°C the mole ratio of THF/Mg was 0.17. At 24.3°C the mole ratio was 0.36, and at 0°C, 0.56. Thus coordination of THF with magnesium increases with decreasing temperature. This is consistent with experimental facts that solvents can be stripped off of some organomagnesium compounds (eg. Et_2Mg) only at higher temperatures.

The equilibrium constant for the reaction

$$RMgOR' + THF \rightleftharpoons RMgOR' \cdot THF,$$

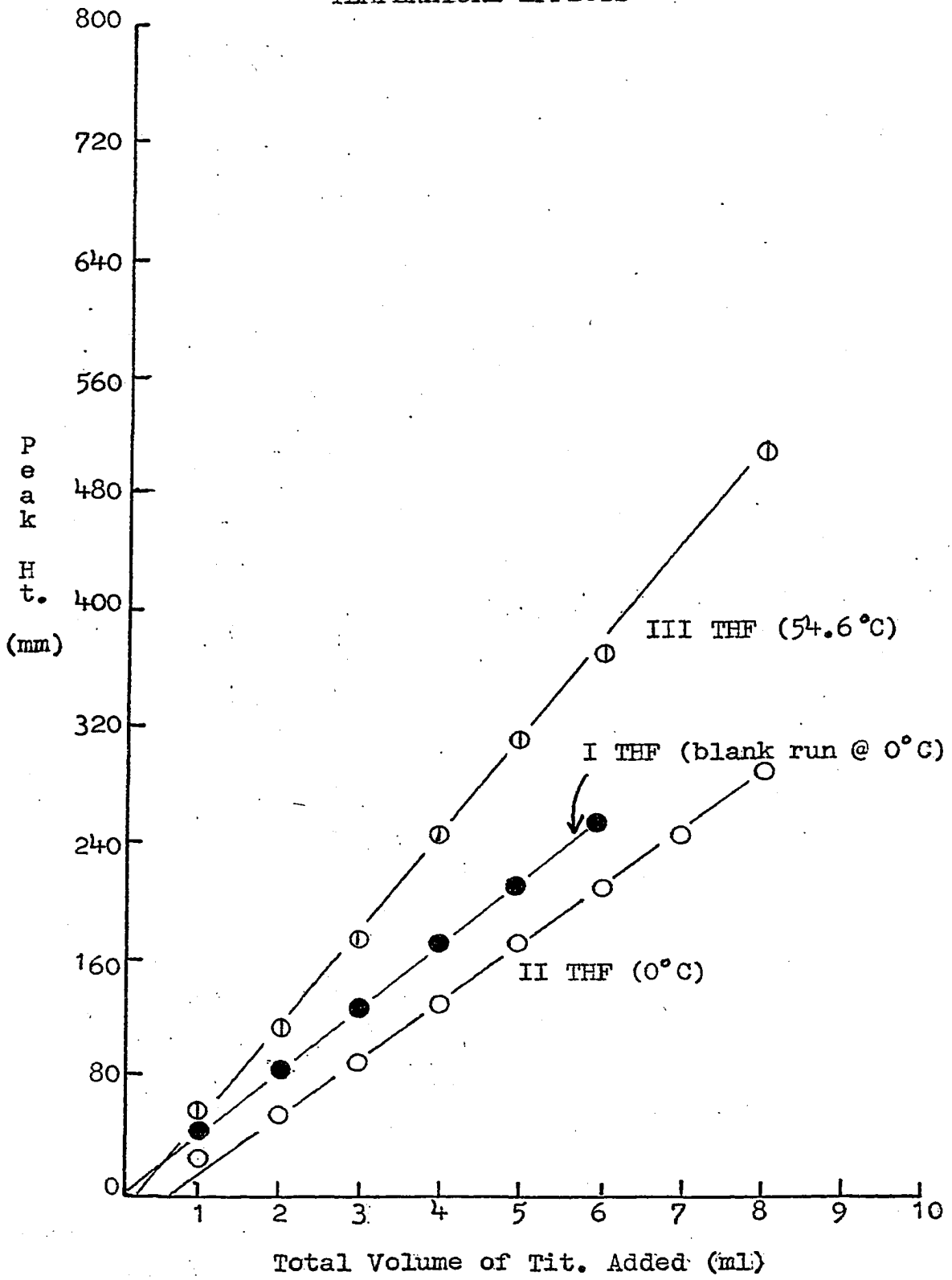
was estimated from the THF peak height at a 1:1 mole ratio of THF to magnesium. This value could be related to the amount of free THF at 1:1 mole ratio by dividing by the slope of the straight line portion of the Henry's Law plot. Thus the proportion of free and cocrdinated THF is known and the equilibrium constant for the reaction can be calculated.

The equilibrium constants estimated for nBuMgOPr at three temperatures are listed below.

T °C	K_1 eq.
54.6	0.75
24.3	1.01
0	3.60

Figure IX:: G.C. TITRATION CURVES OF nBuMgOBu^{sec}

TEMPERATURE EFFECTS



Diethylmagnesium

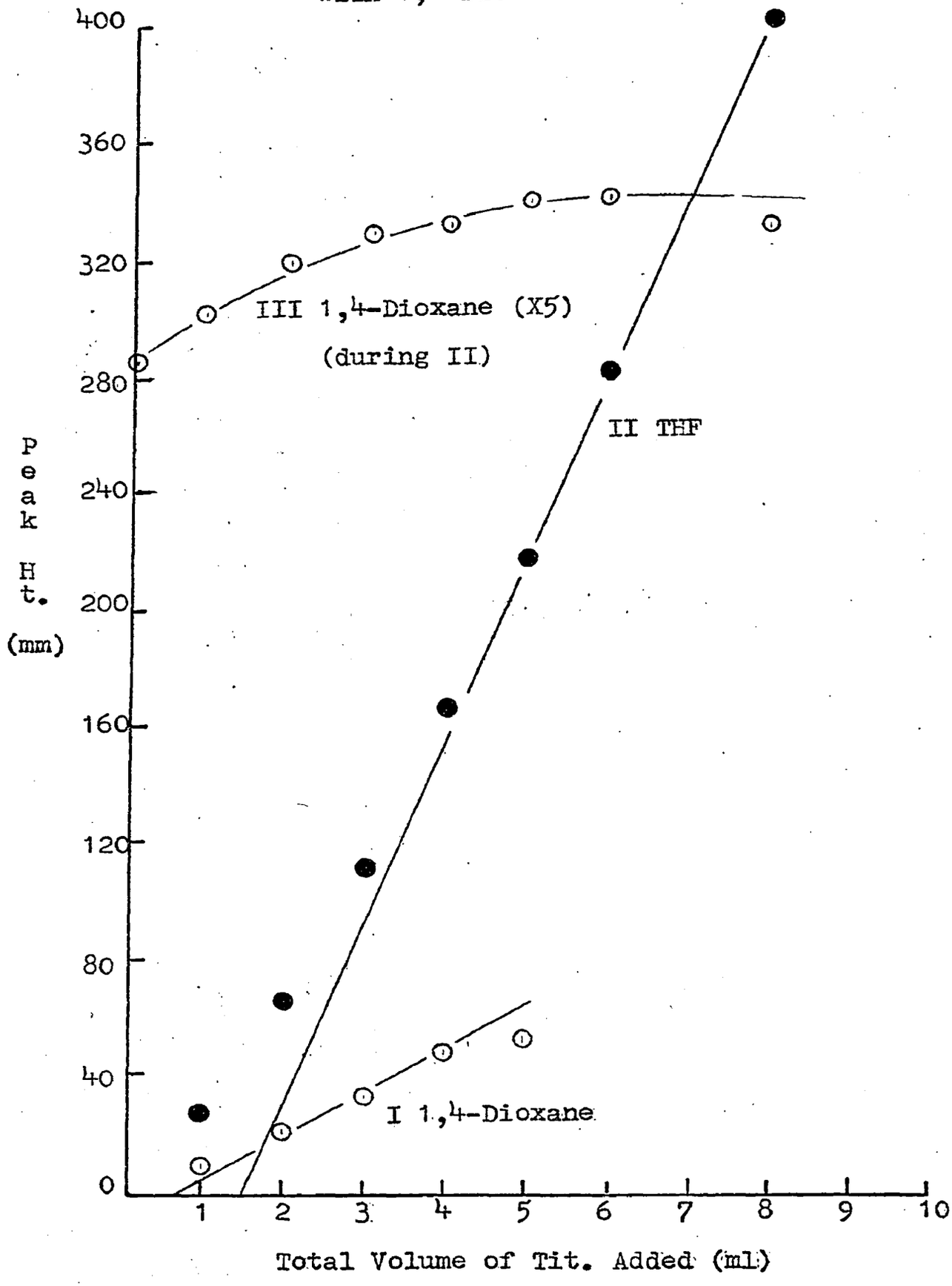
1,4-Dioxane tetrahydrofuran titrations. Table XXII and Figure X lists the results when 1,4-dioxane is titrated against diethylmagnesium in a diethylether solvent, followed by the titration of this resulting mixture with tetrahydrofuran. Curve I indicates a nondistinct break in the Henry's Law plot for dioxane. An extrapolation of a rather arbitrarily chosen straight line yields an intercept corresponding to a mole ratio of dioxane to magnesium of 0.41. Subsequent titration with THF yields curve II where the intercept of the straight line portion of the curve corresponds to a THF/Mg mole ratio of 0.94. Curve III shows the increase in the dioxane peak with THF additions. Several conclusions can be reached from the data. Dioxane is a stronger base toward Et_2Mg than diethylether. However, in the very large excess of diethylether, the Henry's Law plot continues to curve, thus making extrapolation very difficult. This is due to the equilibrium,

$$Et_2Mg \cdot Et_2O + \text{dioxane} \rightleftharpoons Et_2Mg \cdot \text{dioxane} + Et_2O,$$

being shifted to the left by the excess diethylether.

THF is a stronger base than dioxane and replaces it from Et_2Mg.

Figure X: G.C. TITRATION CURVES OF Et_2Mg WITH 1,4-DIOXANE THEN THF



(34) $Et_2Mg \cdot \text{dioxane} + THF \rightleftharpoons Et_2Mg \cdot THF + \text{dioxane}$

The THF/Mg ratio of 0.94 is close to one. This agrees with the THF/Mg mole ratio obtained by Hollingsworth et al[17]. However, as discussed in the background section of this thesis, it is hard to rationalize the mixed solvent equilibrium postulated by Hollingsworth.

Our data do not support this mixed THF-Et_2O species and the equilibrium is most likely:

(35) $R_2Mg \cdot Et_2O + THF \rightleftharpoons R_2Mg \cdot THF + Et_2O$

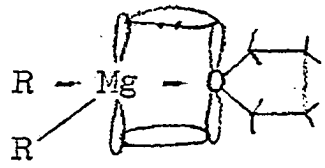
$R_2Mg \cdot THF + THF \rightleftharpoons R_2Mg \cdot 2\ THF$

The addition of a second THF molecule is postulated to account for the reported isolation of some $R_2Mg \cdot 2\ Et_2O$ crystals from solution[52].

The favored species $R_2Mg \cdot THF$ involves a three coordinated magnesium atom which is not observed in the traditional Grignard reagent studied by Guild, McPherson and Chattoraj. The dialkylmagnesium compounds are a much weaker Lewis acids than are the traditional RMgX compounds. Carbon has a much lower electronegativity than the halides, consequently the formal charge on magnesium in Et_2Mg is less positive, reducing its effective basicity compared to RMgX.

Thus when one THF molecule coordinates to magnesium in Et_2Mg the positive character of magnesium is further reduced. The $Et_2Mg \cdot THF$ species now behaves as a very weak acid towards a second THF molecule.

The basicity of the $Et_2Mg \cdot THF$ could be further reduced if π bonding similar to that suggested by Bryce-Smith[21] for trimeric $nBuMgOPr^i$ occurs.

(36) 

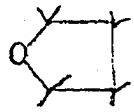
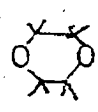
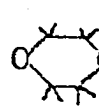
$R_2Mg =$ 

Table XXIII and Figure XI list the results when 1,4-dioxane and subsequently THF were titrated into diethylmagnesium in methylcyclohexane solvent containing the minimum amount of diethylether necessary to solublize the Et_2Mg.

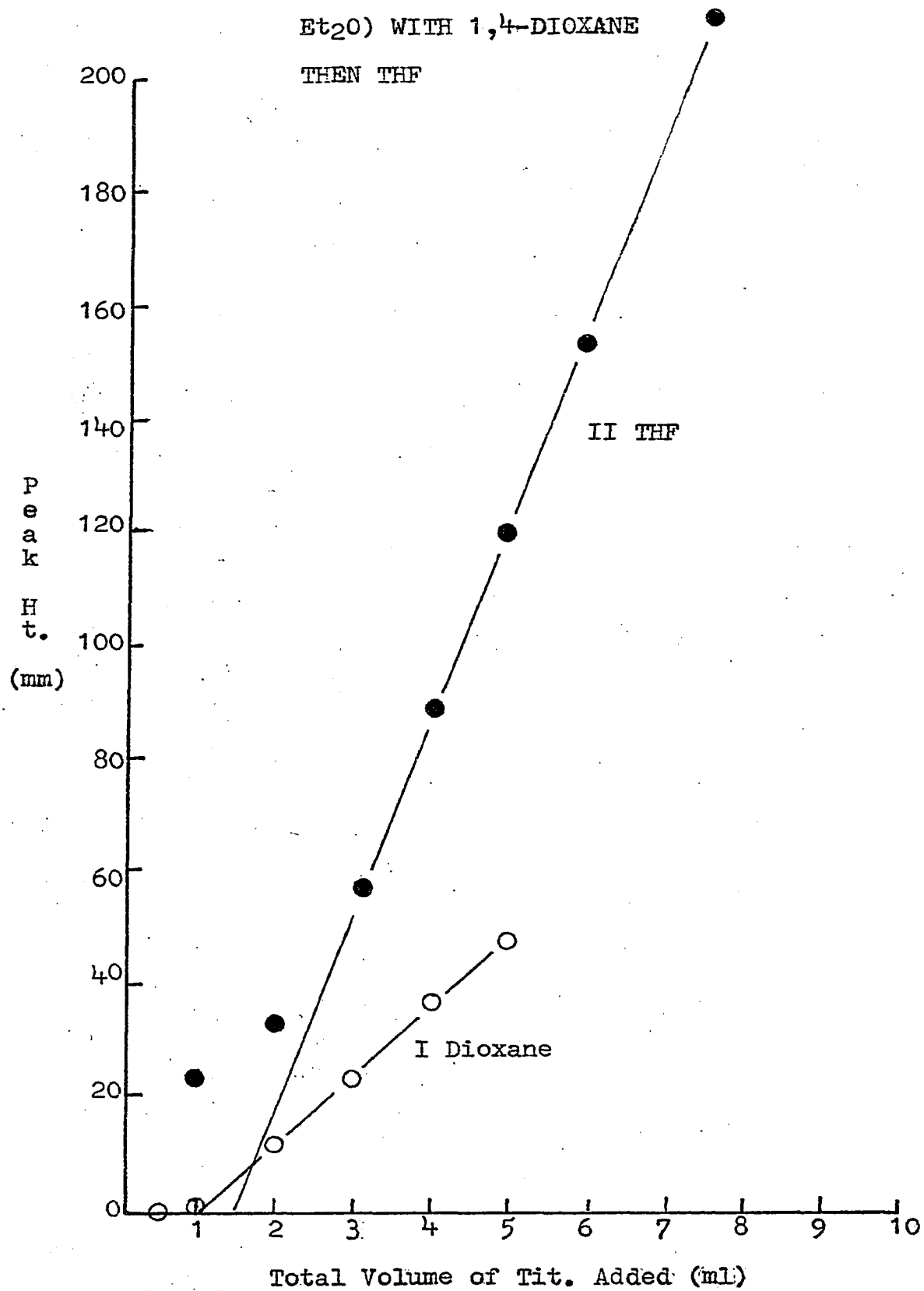
Curve I shows the Henry's Law plot of the dioxane titration. A dioxane/Mg mole fraction of 0.63 was found. Henry's Law plot of the subsequent THF titration, shown by Curve II, yields a THF/Mg mole fraction of 0.96.

Titration by dioxane with only limited diethylether present yields a sharp Henry's Law plot. The mole ratio of 0.63 may indicate that both oxygens in the dioxane are coordinating.

(37) $R_2Mg :$  $: MgR_2 \rightleftharpoons R_2Mg :$ 

The above equilibrium between dioxane/Mg mole fractions of 0.5 and 1.0 could explain this noninteger number

Figure XI: G.C. TITRATION CURVES OF Et_2Mg (IN LIMITED Et_2O) WITH 1,4-DIOXANE THEN THF



coordination. The subsequent THF titration again suggests a THF/Mg mole ratio of one.

Table XXIV and Figure XII show the results when the order of titration of Et_2Mg in methylcyclohexane is reversed.

Curve I shows the Henry's Law plot for THF with a THF/Mg mole fraction of 0.99. Curve II shows that there is no coordination of dioxane in the subsequent dioxane titration.

Addition of THF titrant prior to dioxane in methylcyclohexane solvent with limited diethylether indicates a THF/Mg mole ratio of one. Thus the total amount of diethylether present seems to have little or no effect on the THF to Mg coordination.

If Hollingsworth's equilibrium were present and if the replacement of the second diethylether molecule were retarded by gross excess of diethylether, the observed THF/Mg ratio should become greater with lower ether concentrations.

Subsequent titration with dioxane yields expected results. Since dioxane is a weaker base than THF it can not replace THF and no coordination is observed.

Triethylamine and Pyridine Titrations: Table XXV and Figure XIII list the results for the titration of Et_2Mg with triethylamine and subsequently with pyridine in diethylether solvent.

Curve I shows the Henry's Law plot for Et_3N. No coordination is observed. Et_3N does not replace diethylether

Figure XII: G.C. TITRATION CURVES OF Et_2Mg WITH THF THEN 1,4-DIOXANE

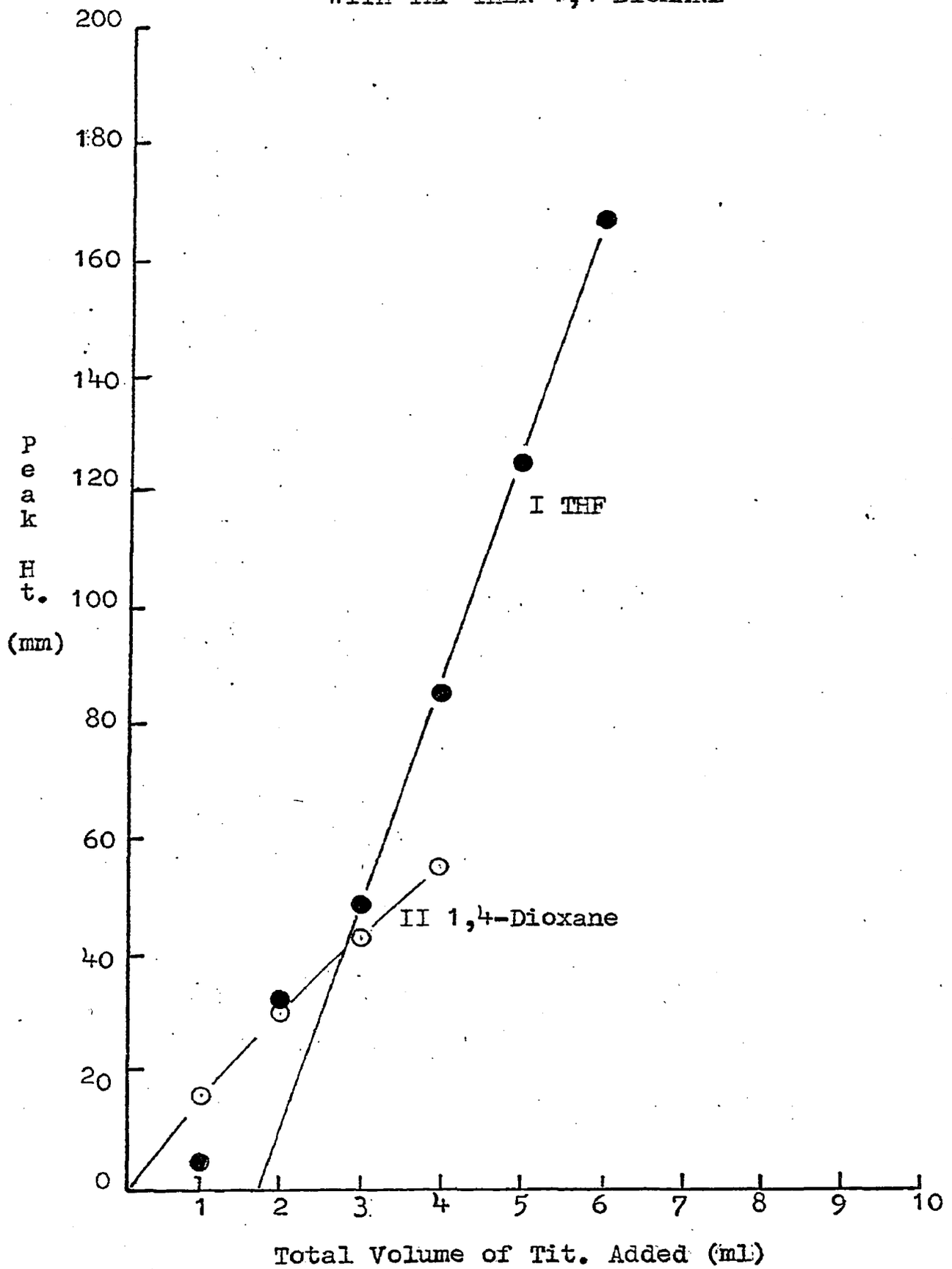
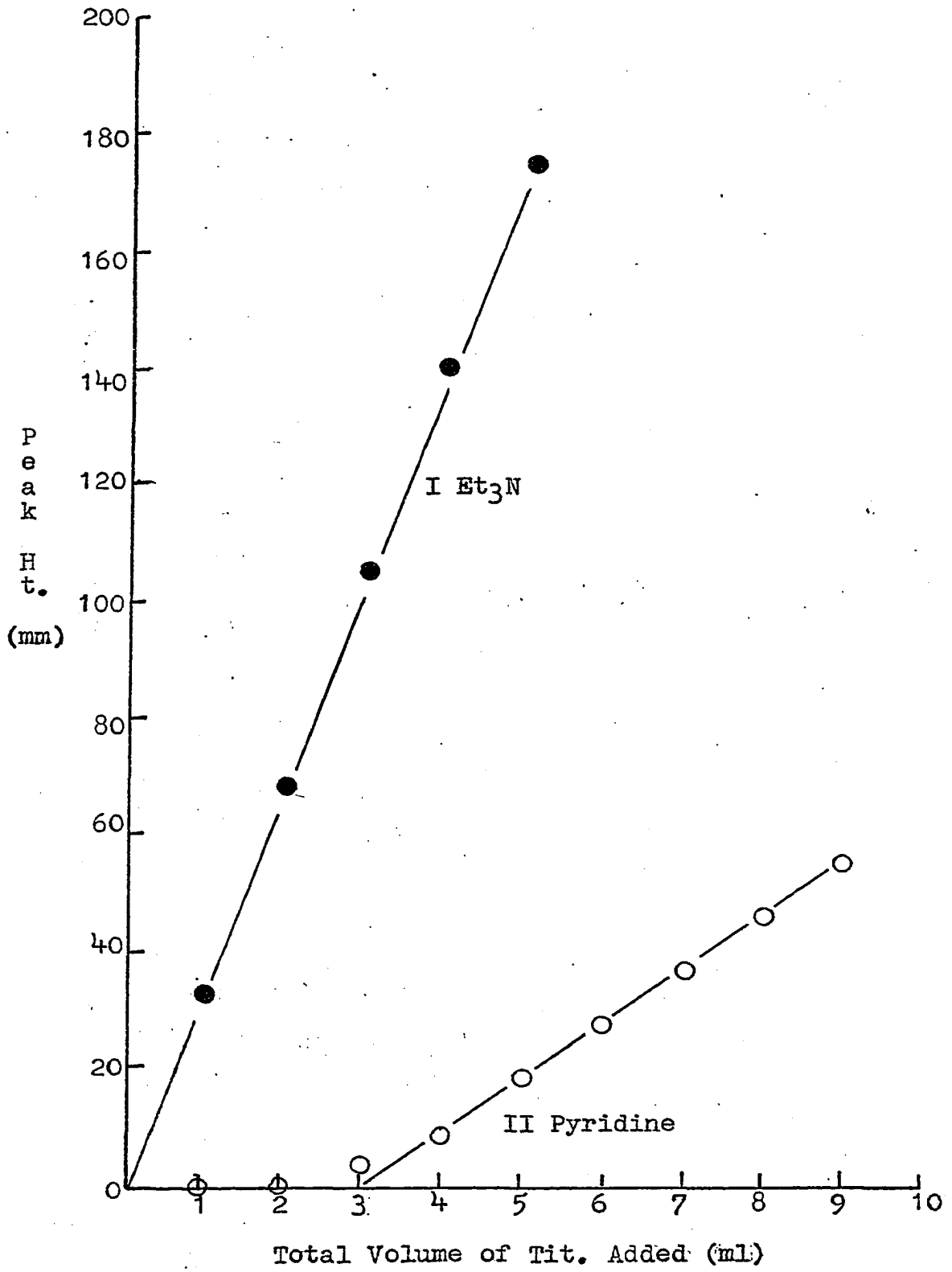
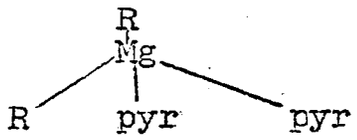


Figure XIII: G.C. TITRATION CURVES OF Et_2Mg WITH Et_3N THEN PYRIDINE



due to the steric effects of the three ethyl groups.

Pyridine in Curve II is shown to coordinated with magnesium with a pyr/Mg mole ratio of 1.89 or close to 2. This is best explained by structure

(38) 

Triethylamine and Diethylether Titrations: Table XXVI and Figure XIV list the results for the titration of Et_2Mg with triethylamine in methylcyclohexane with a minimum amount of diethylether present. The Henry's Law plot for Et_3N, Curve I, shows no Et_3N coordination, while Curve II shows no increase in the diethylether peak during the titration. This indicates that Et_3N is a weaker base than diethylether, and cannot replace it from Et_2Mg.

Table XXVIII and Figure XV list the results of the titration of Et_2Mg with diethylether in methylcyclohexane, with the minimum amount of triethylamine required to dissolve the Et_2Mg.

The Henry's Law plot, Curve II, indicates a mole ratio $\frac{(Et_2O)}{Mg}$ of 0.28. Curve III shows the increase in the Et_3N peak during this titration. Thus,

(39) $Et_2Mg \cdot Et_3N + Et_2O \rightleftharpoons Et_2Mg \cdot Et_2O + Et_3N.$

Figure XIV: G.C. TITRATION CURVES OF Et_2Mg (IN LIMITED Et_2O) WITH Et_3N

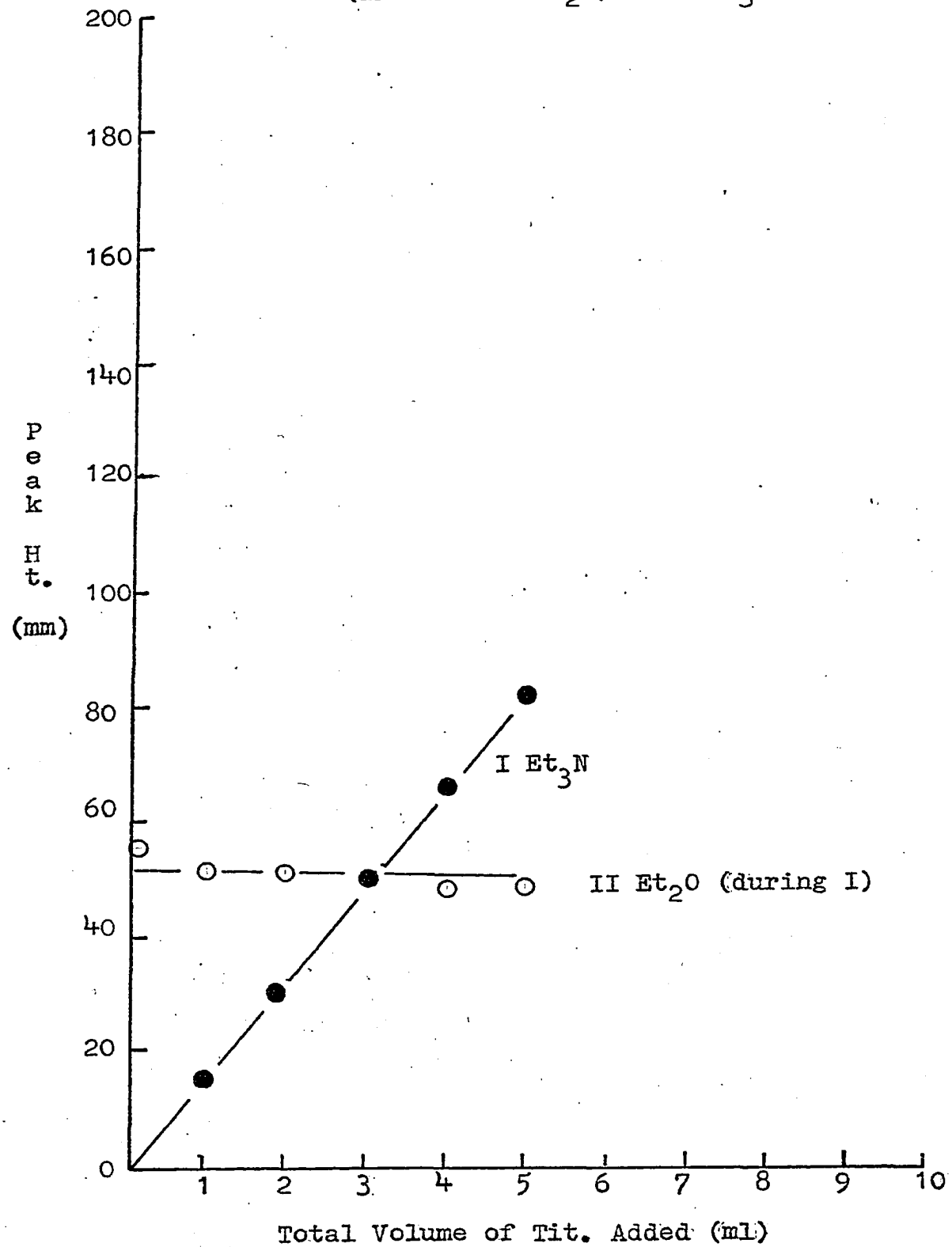
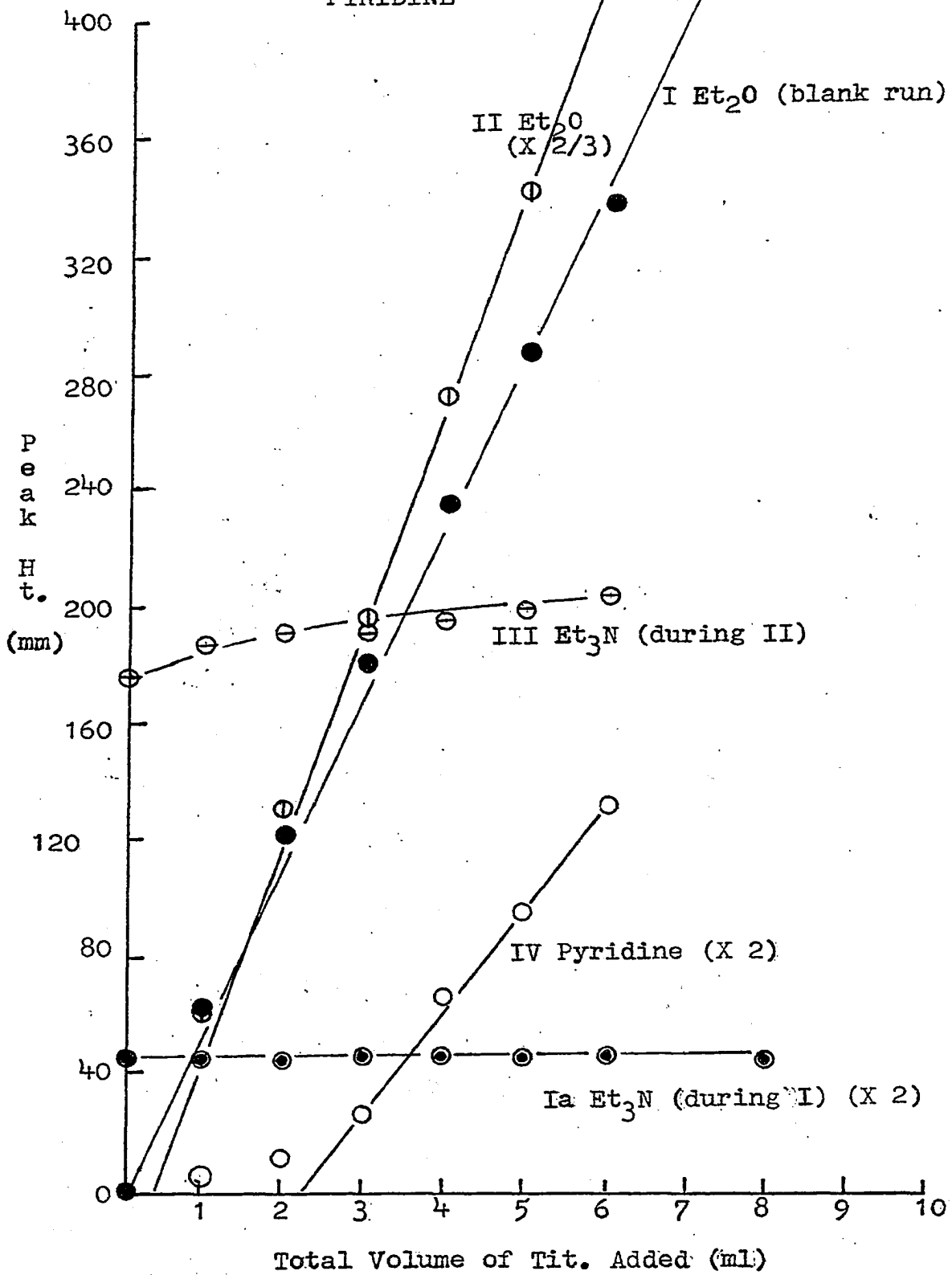


Figure XV: G.C. TITRATION CURVES OF Et_2Mg WITH Et_2O THEN PYRIDINE



The fractional mole ratio of 0.28 is due to the above equilibrium being forced to the left by excess Et_3N. Since diethylether is a weak base and Et_2Mg is a weak Lewis acid compared to traditional Grignard reagents, the equilibrium

$$(40) \qquad Et_2Mg \cdot Et_2O \rightleftharpoons Et_2Mg + Et_2O,$$

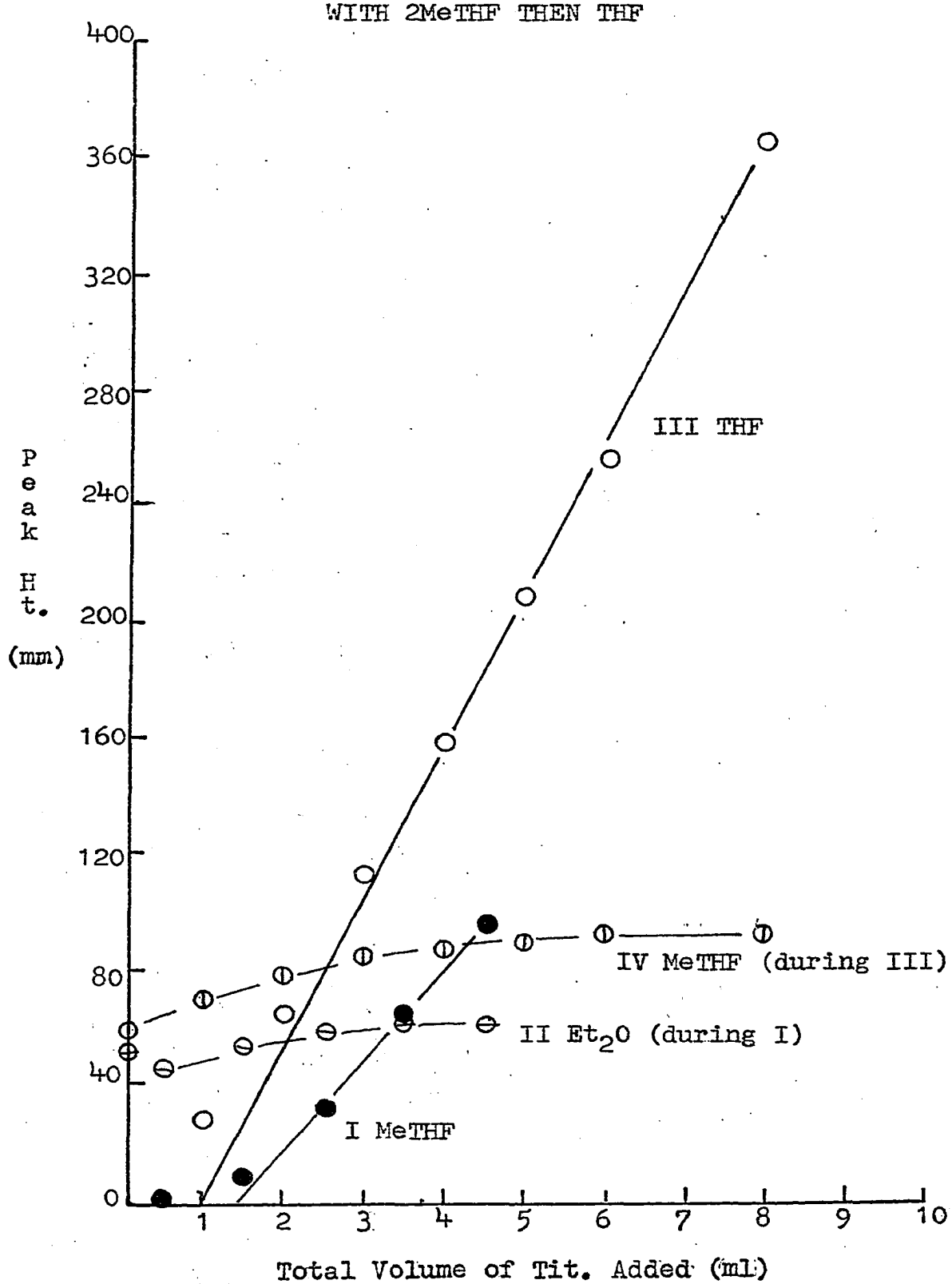
also contributes to the small mole ratio. The relative importance of these two factors can not be determined from the data.

Subsequent pyridine titration of this mixture, Curve IV, was used to establish the concentration of R_2Mg present since the Et_3N would interfere with the normal analysis.

2-Methyltetrahydrofuran and Tetrahydrofuran Titrations: Table XXIX and Figure XVI list the 2-methyltetrahydrofuran titration and subsequent tetrahydrofuran titration of Et_2Mg in methylcyclohexane solvent with a minimum amount of diethylether.

Curve I shows the Henry's Law plot for MeTHF with MeTHF/Mg mole ratio of 0.93. Curve II shows the increase in diethylether peak during this titration. Curve III relates the Henry's Law plot of THF during THF titration of this mixture. A mole ratio of 0.87 is obtained. Curve IV, shows the increase in MeTHF during the THF titration.

Figure XVI: G.C. TITRATION CURVES OF Et_2Mg WITH 2MeTHF THEN THF



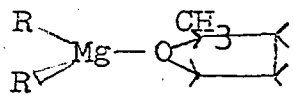
The above results show that MeTHF is a stronger base than diethylether but a weaker base than THF toward Et_2Mg.

(41) $Et_2Mg \cdot Et_2O + MeTHF \longrightarrow Et_2Mg \cdot MeTHF + Et_2O$

$Et_2Mg \cdot MeTHF + THF \longrightarrow Et_2Mg \cdot THF + MeTHF$

The methyl group on the THF ring would donate electrons and should make MeTHF a stronger base than THF. However, the methyl group in the two position evidently causes steric hindrance with Et_2Mg that overshadows this inductive effect.

(42)

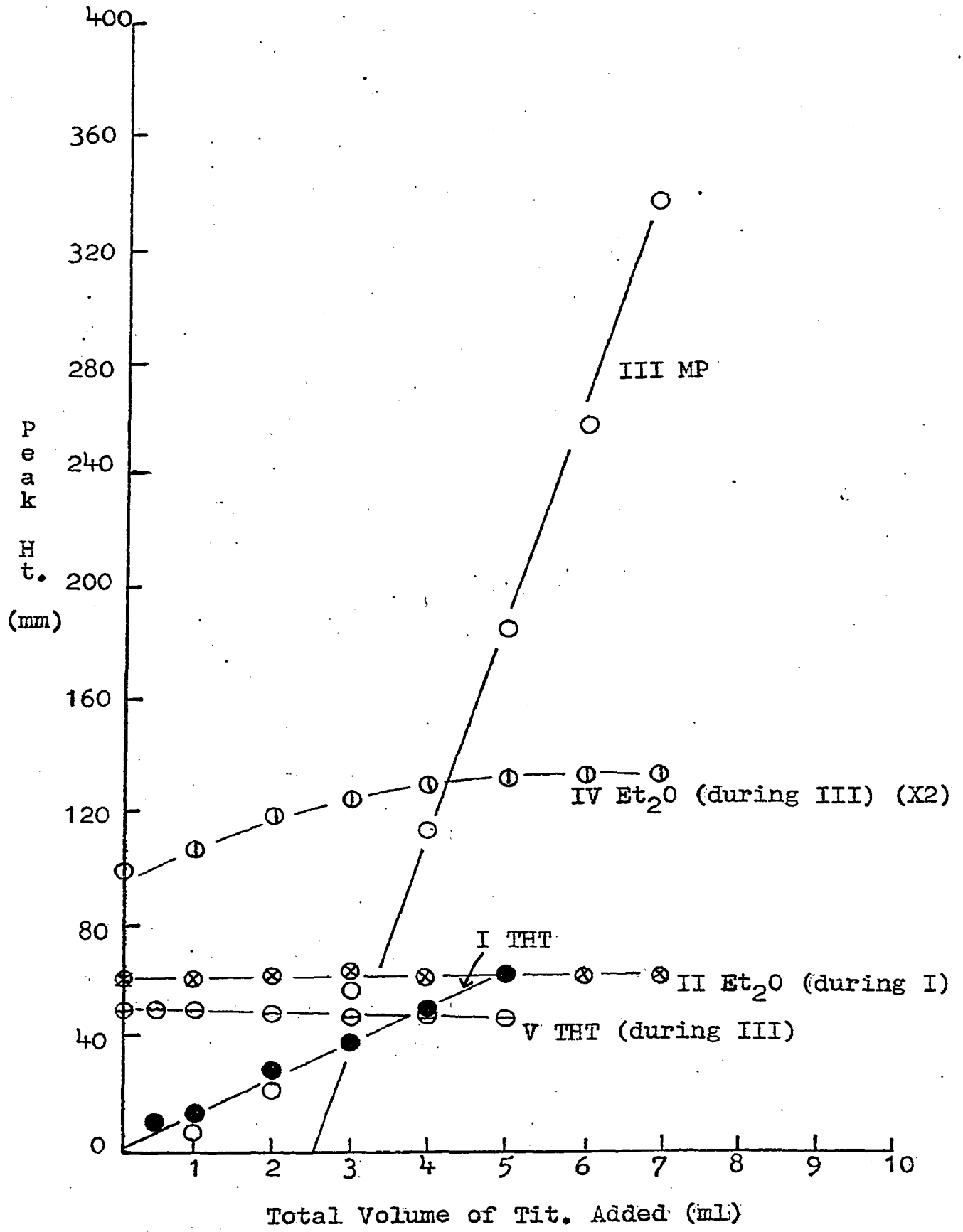


Tetrahydrothiophene and N-Methylpyrrolidine Titrations: Table XXX and Figure XVII list the results for the titration of Et_2Mg with tetrahydrothiophene (THT) and subsequently with N-methylpyrrolidine (MP) in methylcyclohexane.

The Henry's Law plot for the THT, Curve I, shows no coordination of this solvent with Et_2Mg. Curve II shows no increase in diethylether peak height during the THT titration.

The subsequent MP titration yields Henry's Law plot given in Curve III. A MP/Mg mole ratio of 1.04 is obtained from the extrapolation. Curve IV shows the increase in di-

Figure XVII: G.C. TITRATION CURVES OF Et_2Mg WITH THT THEN N-METHYLPYRROLIDINE (MP)



ethylether peak during the MP titration while Curve V shows that the THF peak remains constant.

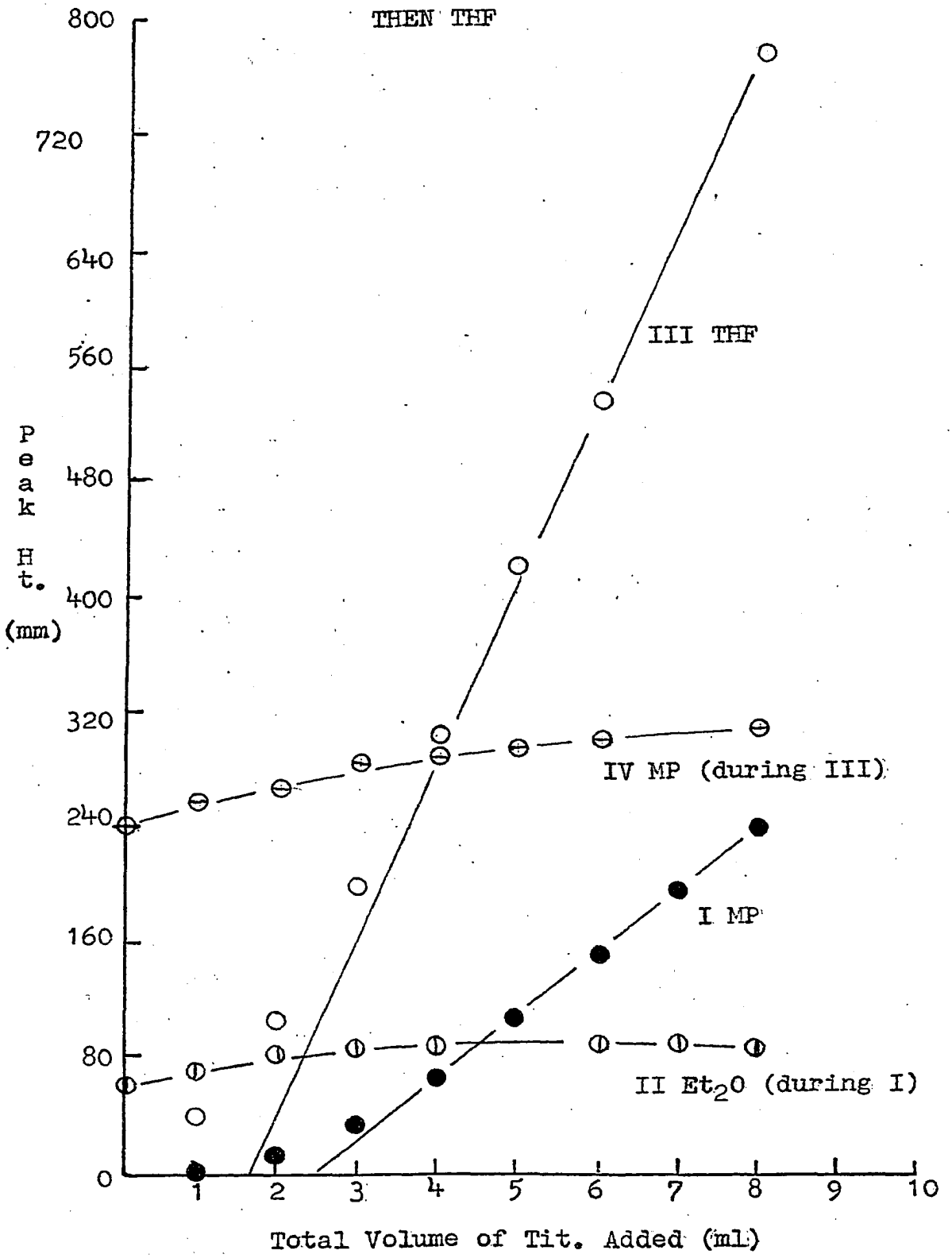
Therefore THT is a weaker base toward Et_2Mg than diethylether. Since THT would be less sterically hindered than diethylether, the sulfur atom in this molecule must be a poorer electron donor toward magnesium than the oxygen atom in ethers.

The MP/Mg mole ratio of 1.04 found in the MP titration indicates that MP is a stronger base toward Et_2Mg than diethylether. This amine is less sterically crowded than Et_3N.

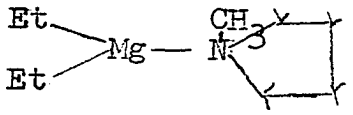
N-Methylpyrrolidine and Tetrahydrofuran Titrations: Listed in Table XXXI and Figure XVIII are the results of the titration of Et_2Mg in methylcyclohexane with N-methylpyrrolidine (MP) and subsequently with tetrahydrofuran.

Curve I shows the Henry's Law plot for the MP titration with an intercept corresponding to a mole ratio of 1.04. Curve II shows the increase in diethylether peak during this titration. A THF/Mg mole ratio of 0.98 is calculated from Curve III, the Henry's Law plot for the THF titration. Curve IV shows the increase inMP peak height during the THF titration.

Figure XVIII: G.C. TITRATION CURVES OF Et_2Mg WITH N-METHYLPYRROLIDINE (MP) THEN THF



From these data it can be seen that N-methylpyrrolidine coordinates with Et_2Mg with a mole ratio of one. Structure 43 seems likely.

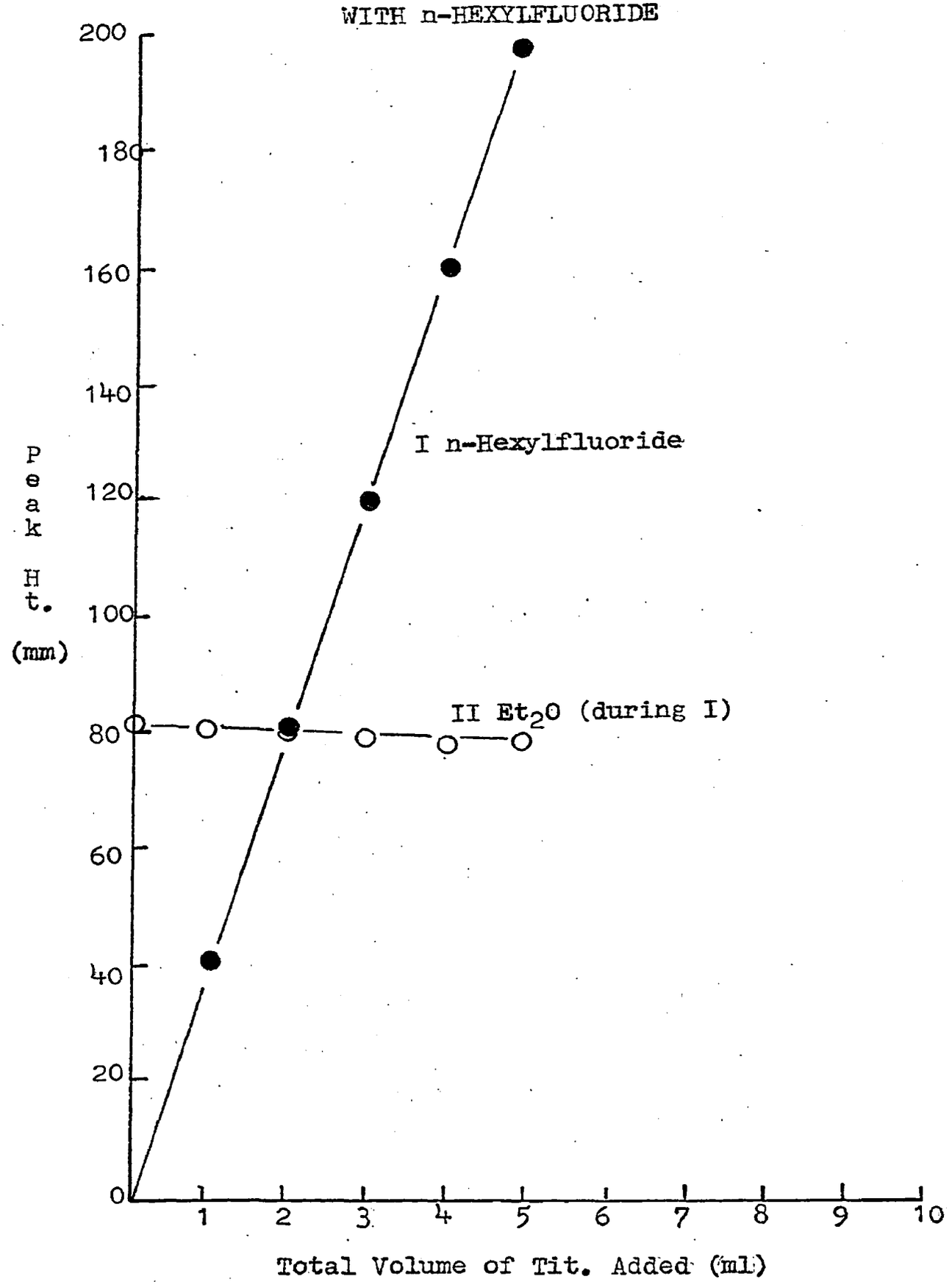
(43) 

THF is a stronger base than MP and displaces it from Et_2Mg. This can be attributed to a more favorable steric situation for THF and possibly due to THF's ability to double bond to magnesium.

n-Hexylfluoride Titration: Listed in Table XXXII and Figure XIX are the results of the titration of n-hexylfluoride with Et_2Mg in methylcyclohexane solvent. Curve I, the Henry's Law plot for n-hexylfluoride, shows no coordination of n-hexylfluoride with Et_2Mg. Curve II shows no increase in diethylether peak height.

n-Hexylfluoride was chosen as a representative of the halogen series since unlike chlorides, bromides, and iodides, it will not react with Grignard reagents via a Wurtz coupling. The steric strain for n-hexylfluoride coordination would be the smallest studied (Structure 44). However the weak basicity of the lone pairs of electrons on the fluorine atom overcomes the steric advantage. Thus n-hexylfluoride is a weaker base than diethylether.

Figure XIX: G.C. TITRATION CURVES OF Et_2Mg WITH n-HEXYLFLUORIDE



(44)

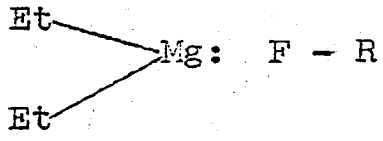


Table XXXIII and Figure XX show the results of the titration of n-hexylfluoride into a heterogenous mixture of insoluble ether free Et_2Mg and methylcyclohexane. A zero intercept indicates there is no coordination of n-hexylfluoride with Et_2Mg.

However this does not exclude the possibility that stronger Lewis acid Grignard reagents might coordinate with organofluorides, analogous to the antimony pentafluoride complexes with organofluorides recently reported by Olah et al[33].

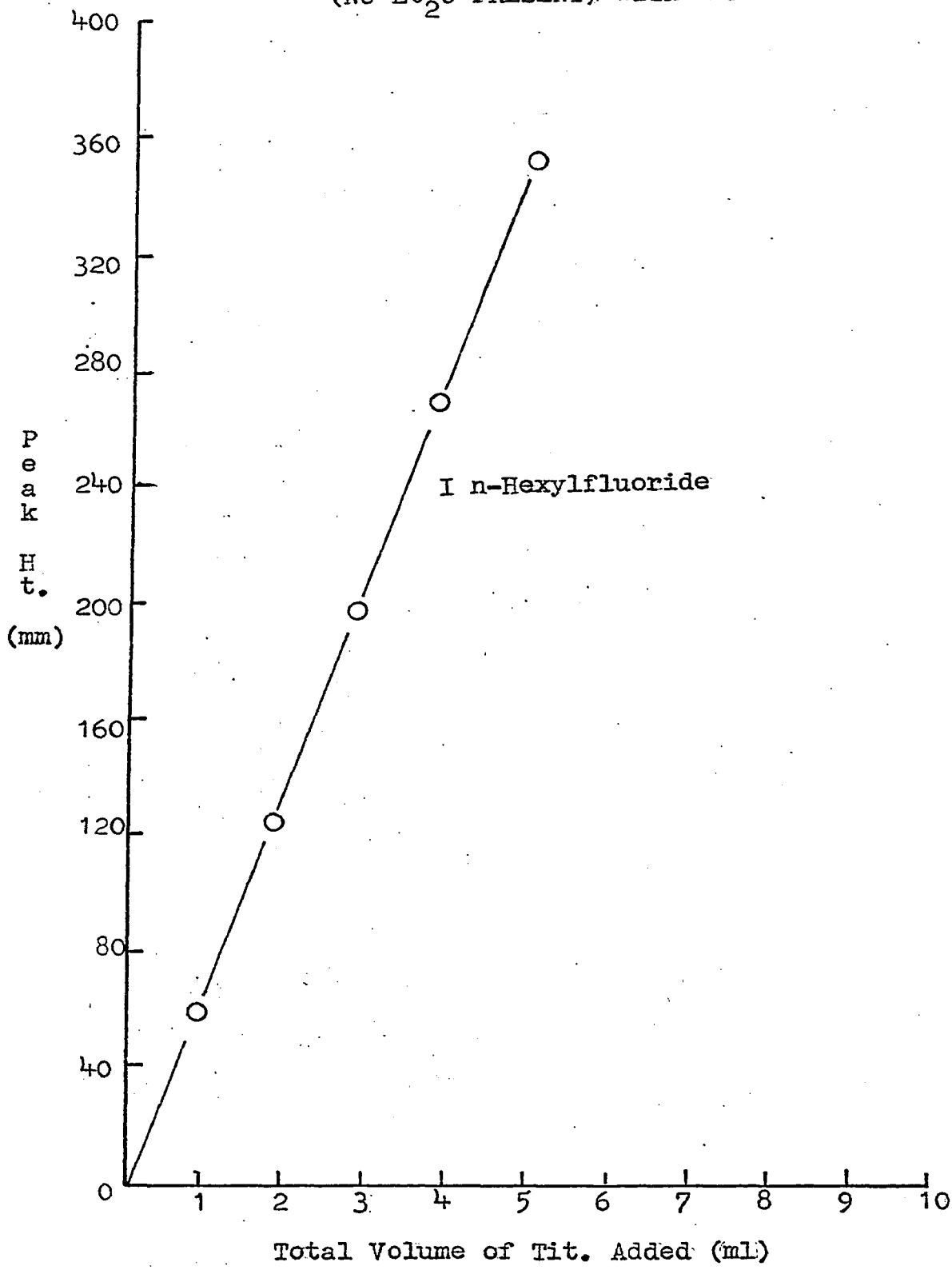
A subsequent titration with THT yielded anomolous results. It is thought that this might be due to longer time to achieve equilibrium in this heterogenous system. Some Et_2Mg appeared to dissolve with addition of large amounts of THT.

These facts coupled with the reported preparations of traditional Grignards in THT indicated that some solvation by THT is occurring and THT is a stronger base than n-hexylfluoride.

Ethylmagnesium diorganoamides

Ethylmagnesium diisopropylamide: Listed in Table XXXIV

Figure XX: G.C. TITRATION CURVES OF Et_2Mg (NO Et_2O PRESENT) WITH n-HEXYLFLUORIDE

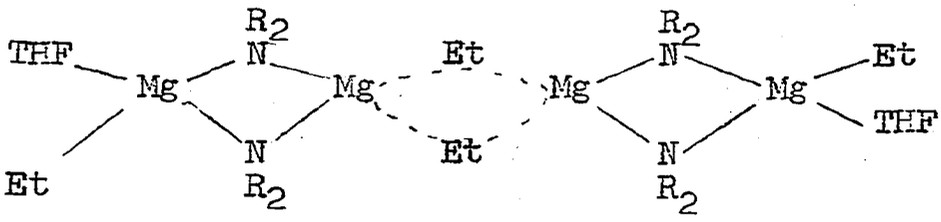


and Figure XXI are the results of the titration of $EtMgNPr^i_2$ in diethylether/methylcyclohexane solvent with THF and subsequently with pyridine.

With THF as the titrant a Henry's Law plot (Curve I) has an intercept on the abscissa corresponding to a THF/Mg mole ratio of 0.55. The Henry's Law plot for the subsequent pyridine titration (Curve II) exhibits an intercept corresponding to a pyridine/magnesium mole ratio of 1.06.

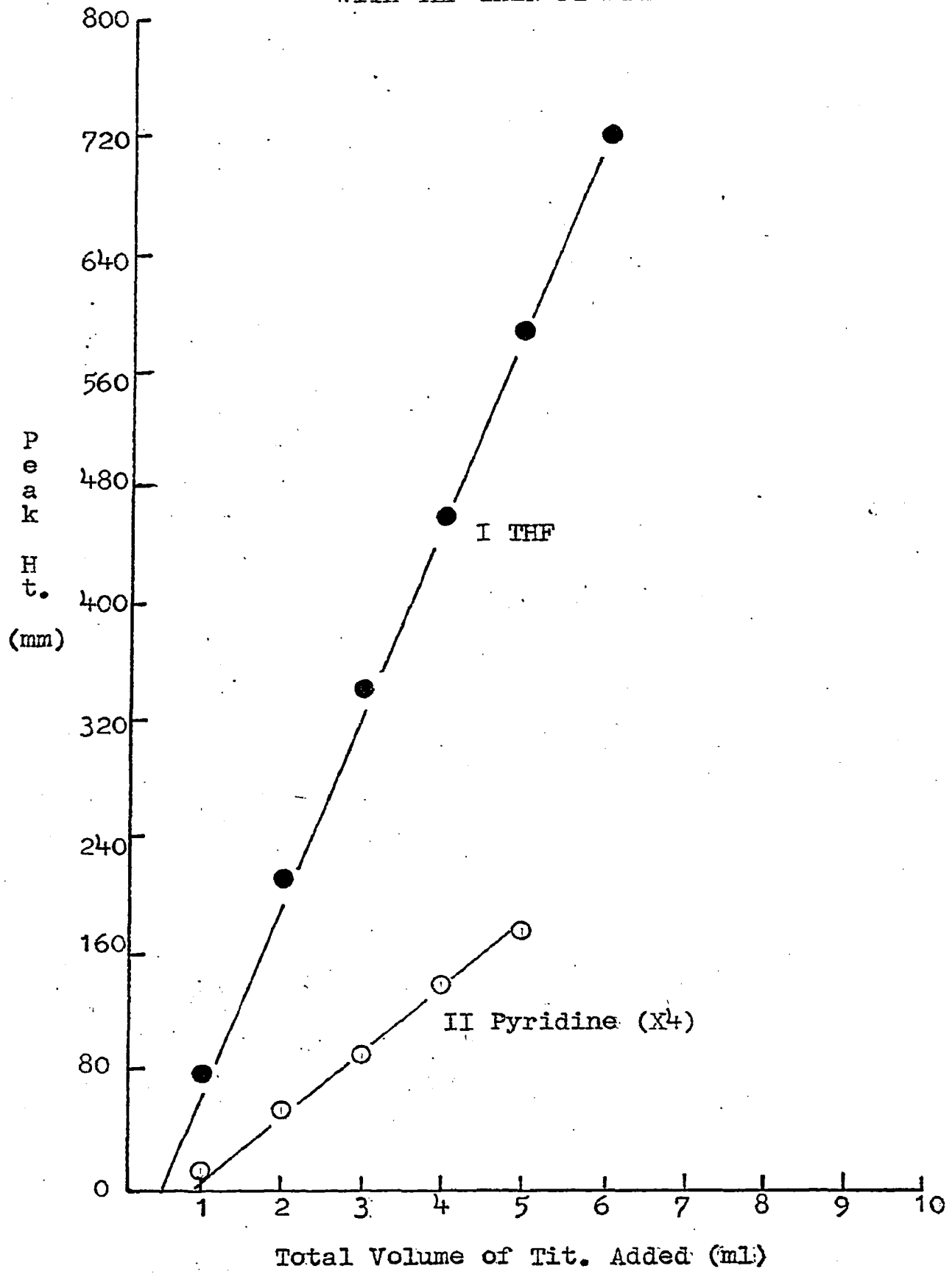
The THF/Mg mole ratio of 0.55 corresponds well with the tetrameric association found by Coates[23] et al in benzene. Coates has suggested structure (45) for the tetramer.

(45)

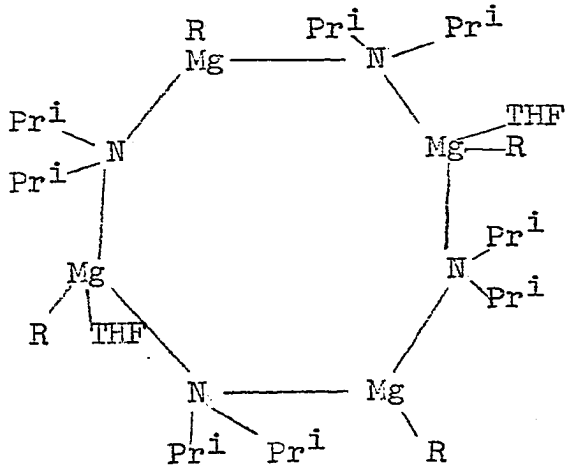


The structure postulated by Coates requires existance of electron deficient carbon bridges in the presence of THF. This is unlike other organomagnesium systems (eg. dialkyls) where THF is basic enough to cleave the electron deficient bridges. Perhaps a better explanation would be a cyclic tetramer similiar to one postulated for some conventional Grignard reagents.

Figure XXI: G.C. TITRATION CURVES OF Et-MgNPr$^{i}_{2}$ WITH THF THEN PYRIDINE



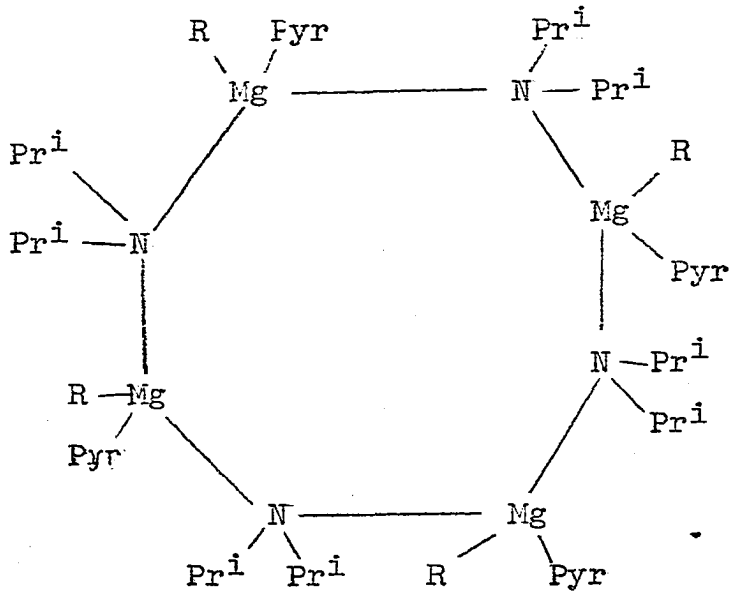
(46)



The stoichiometry of the THF solvate suggests that the steric requirements of the two isopropyl groups on nitrogen are such that only alternate magnesium atoms can be coordinated by THF. The alpha branching of the isopropyl groups can be pictured as pointing away from the two THF coordinated magnesium atoms thus "shielding" the remaining two magnesium atoms from THF cocrdination.

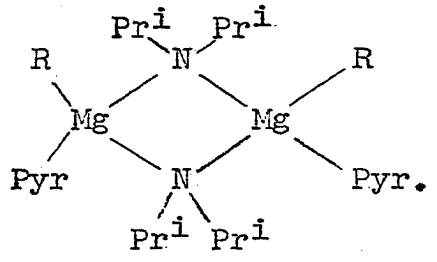
Subsequent pyridine titration of $EtMgNPr_2^i$ produced a yellow color which proceeded to deep red during the course of titration. A very early peak adjoining the air peak increased after each pyridine injection. This suggests a reaction between pyridine and $EtMgNPr_2^i$. A Michler ketone test at the conclusion of the titration indicated that some Grignard reagent remained. A normal Henry's Law plot was obtained which suggested this structure.

(47)



Here the very basic pyridine overcomes the steric strain to coordinate all four magnesium atoms. Alternately pyridine could cause rearrangement of the $(EtMgNPr_2^i)_4 \cdot 2$ THF with replacement of THF to form the dimer

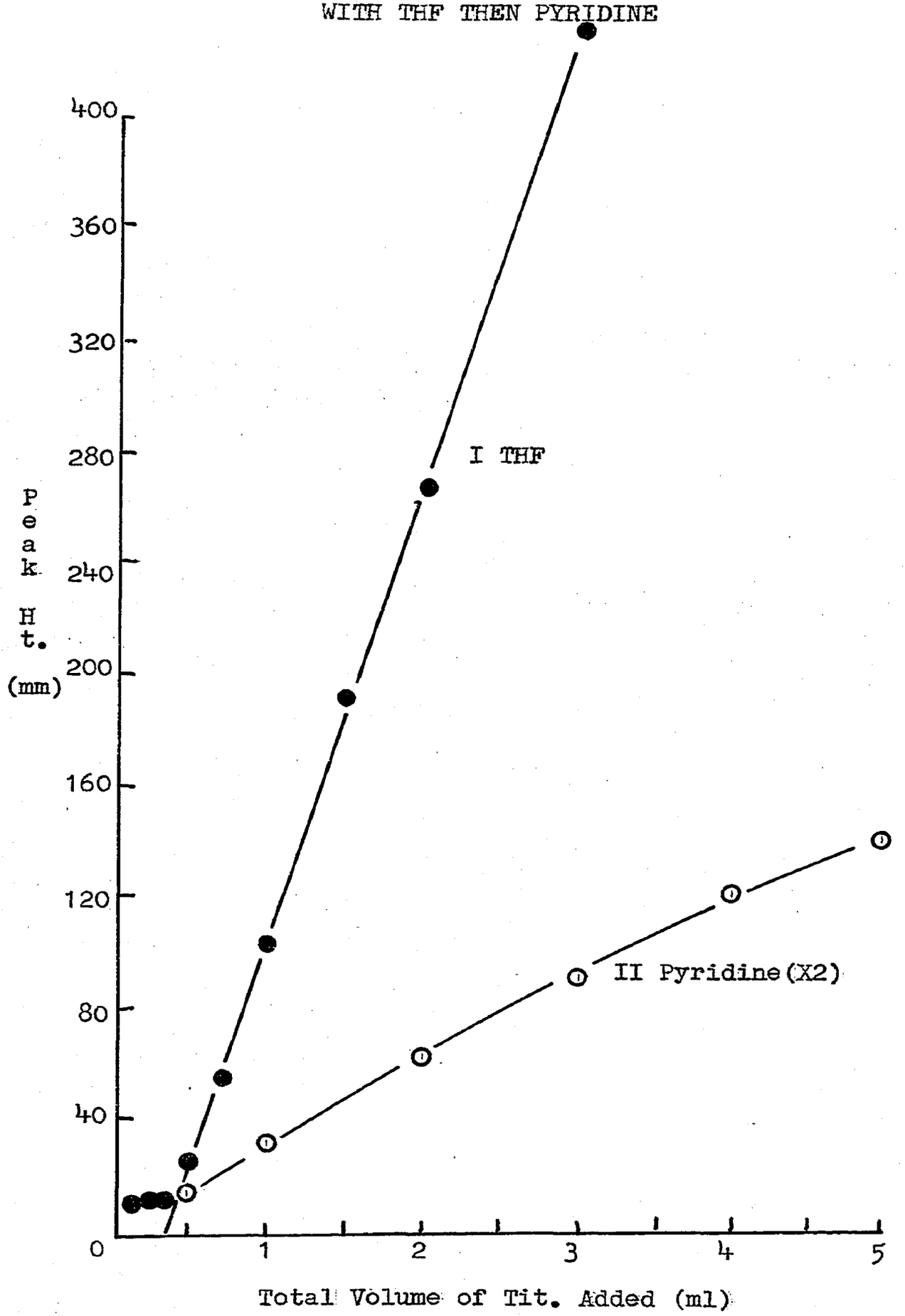
(48)



Listed in Table XXXV and Figure XXII are the results of the titration of $EtMgNPr_2^n$ in diethylether/methylcyclohexane solvent with THF and subsequently pyridine.

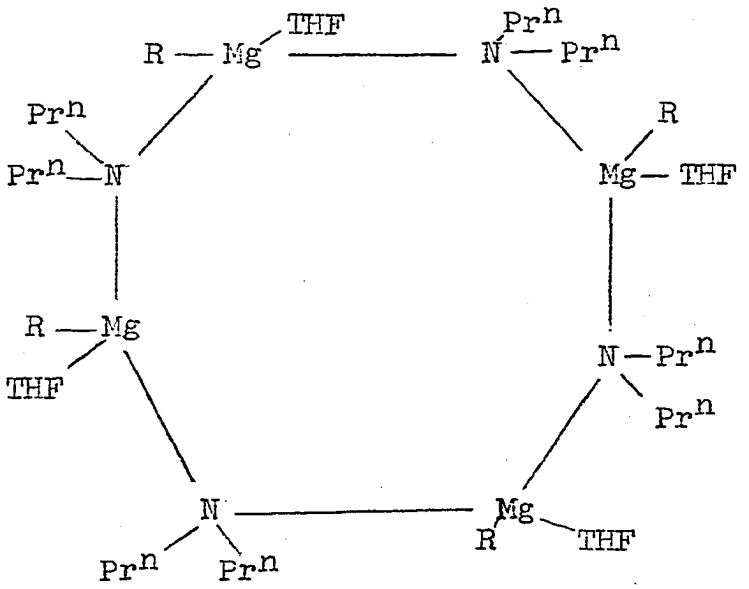
With THF as the titrant (Curve I) an intercept is obtained that corresponds to a THF/Mg mole ratio of 0.89. Curve II which depicts the pyridine titration has an anomolous shape.

Figure XXII: G.C. TITRATION CURVES OF $EtMgNPr^n_2$ WITH THF THEN PYRIDINE



$EtMgNPr_2^n$ would be very similar sterically and electronically to $EtMgNEt_2$ studied by Coates[23] and found to be tetrameric. The THF/Mg mole ratio of 0.89 could indicate a structure similar to (49) seen for $EtMgNPr_2^i$.

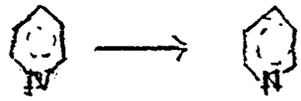
(49)

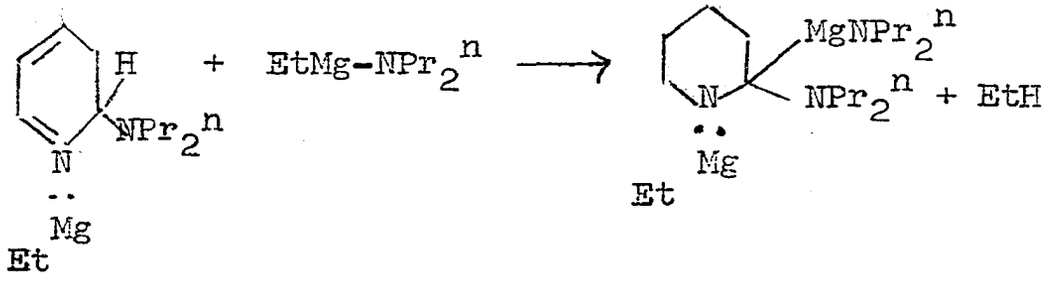


Unlike $EtMgNPr_2^i$ there is no branching of the alkyl group and less steric crowding about nitrogen. Thus coordination of all four magnesium atoms is possible.

Again pyridine addition causes a yellow to red color change and an early peak in the gas chromatograph. The anomolous curve indicates that the reaction of pyridine with $EtMgNPr_2^n$ proceeds too quickly to permit meaningful Henry's Law data. Some of the gas evolved during the reaction was submitted to mass spectrometry and found to be ethane.

A Tschichibaben type attack on the pyridine ring followed by abstraction of hydrogen by the ethyl group of the Grignard reagent might explain this reaction.

(50) "$EtMgNPr_2^n$" + 

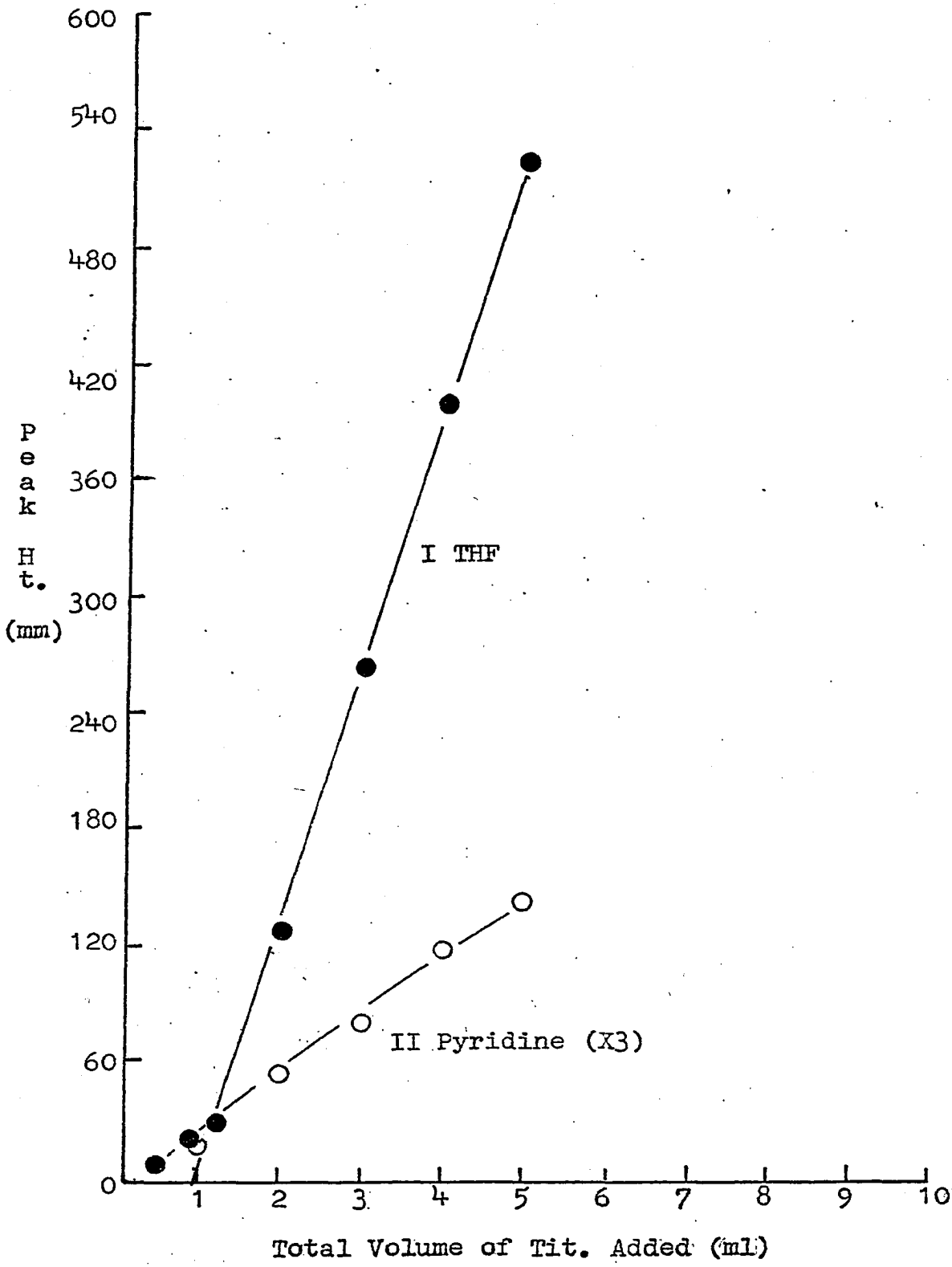


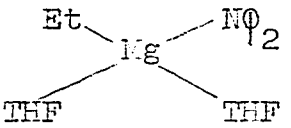
Ethylmagnesium diphenylamide: Listed in Table XXXVI and Figure XXIII are the results of the titration of $EtMgN\Phi_2$ in diethylether/methylcyclohexane solvent with THF and subsequently pyridine.

With THF as the titrant (Curve I) an intercept is obtained that corresponds to a THF/Mg mole ratio of 2.00. Curve II depicting the pyridine titration again shows an anomolous shape .

The THF/Mg mole ratio of 2.00 agrees well with the observation by Coates[23] that $EtMgN\Phi_2 \cdot 2$ THF isolated from THF solution is a monomer (structure 51) in benzene. Presumably the phenyl rings tend to withdraw the lone pair of electrons on the nitrogen so that the amide can no longer compete with THF in coordinating magnesium.

Figure XXIII: G.C. TITRATION CURVES OF $EtMgNO_2$ WITH THF THEN PYRIDINE



(51) 

The pyridine titration again produces a yellow to red color change with a meaningless Henry's Law plot. No ethane peak is observed, however, suggesting a somewhat different reaction.

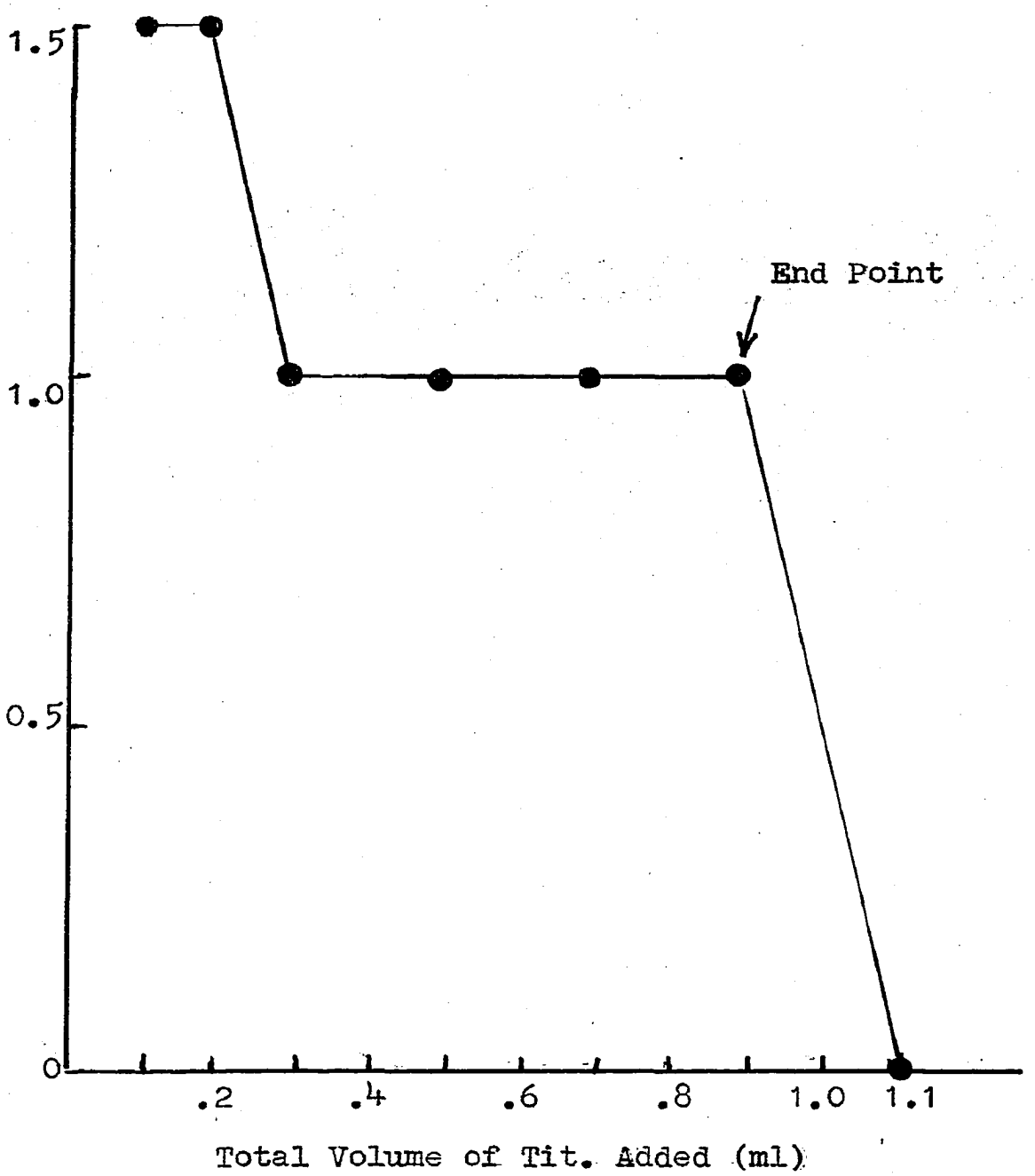
Thermal titrations to elucidate solvent coordination

After the addition of some of the coordinating solvents in the gas chromatographic titrations under constant temperature bath conditions, an increase in the temperature of the titration mixture was noted. The feasibility of using a thermal titration to study solvent coordination was explored.

The resultant mixture (Table XXVI, Figure XIV) of the titration of Et_2Mg with Et_3N was titrated with small increments of THF. After each addition the temperature increase of the titration mixture was noted. This temperature was allowed to return to bath temperature between additions.

An end point of 0.82 ml of THF would correspond moderately well to the expected THF/Mg mole ratio of 1.0. The last injection to generate a temperature rise (Table XXXVII) was the increase in total THF from 0.7 to 0.9 ml. This is consistant with an end point around 0.82.

Figure XXIV: THERMAL TITRATION CURVE OF Et_2Mg WITH THF



Because of integral injections and insensitive temperature monitoring (the thermometer described in the experiment section), precise results can not be obtained. However, a constant delivery syringe pump to titrate the coordination solvent and a thermocouple or thermistor voltage output to a strip chart recorder, with the titration vessel under adiabatic conditions, should allow precise, meaningful data. The thermal titration would prove a valuable compliment to the Henry's Law approach. The thermal titration could explore coordination of nonvolatile agents such as quinuclidine and HMPT.

SUMMARY AND CONCLUSIONS

Lewis Basicity and the Grignard Reagents

Both solvation and association of Grignard reagents are due to Lewis acid base interactions. Studies carried out permit assesment of not only relative basicities of the solvents but also the relative basicities of the possible bridging groups of the Grignard reagents. (i.e. $R - Mg - \overset{R}{O}$, $R - Mg - \overset{R}{O}-Mg$, $R - MgNR_2$ etc.)

It has been shown that electron deficient carbon bridges do not compete well with strong Lewis bases. Even Et_3N and Et_2O are effective in disassociating the Et_2Mg polymer. This is evidenced by the dissolution and solvation of Et_2Mg by these solvents.

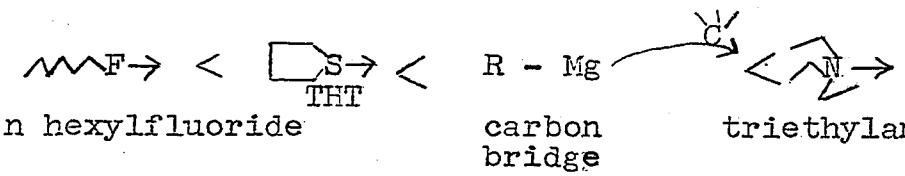
However, this carbon bridge can not be broken by n-hexylfluoride which shows no indication of solvating Et_2Mg. Tetrahydrothiophene (THT) was able to dissolve and presumably solvate Et_2Mg but only with gross excess of this solvent.

1,4-Dioxane and 2-methyltetrahydrofuran are stronger bases than diethylether and displace it from Et_2Mg, however both are weaker than tetrahydrofuran. N-methylpyrrolidine (MP) showed much stronger basicity than triethylamine due to more favorable steric requirements about the nitrogen atom, but again it is a weaker base than THF.

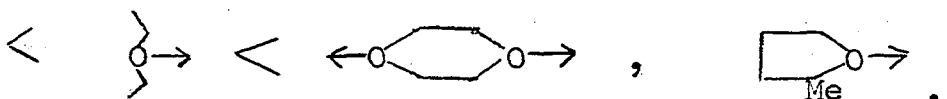
THF, however, is unable to compete with the two lone pairs of electrons on oxygen or the one lone pair on nitrogen in most of alkoxide and amide Grignard reagents. Pyridine is a stronger base than THF and is even more basic than one of the two lone pair of electrons on oxygen in the alkoxide Grignard reagents. Even pyridine was unable to compete with the strong bridges of the amide's nitrogen and one of the oxygen bridges.

A series of relative basicities would be:

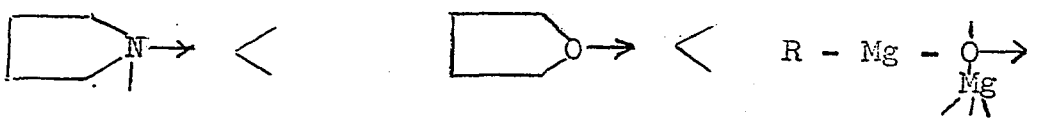
(52)



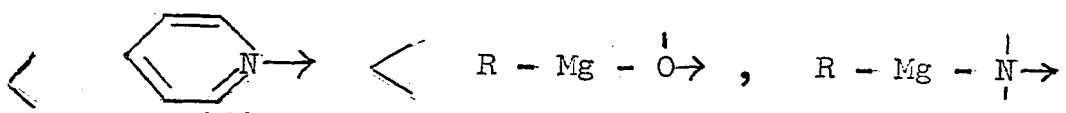
n hexylfluoride — carbon bridge — triethylamine



diethylether — 1,4 dioxane — 2 MeTHF



MP — THF — second oxygen bridge



pyridine — first oxygen bridge — amide's nitrogen bridge

In the work done by McPherson[18] the strength of halide bridges was seen to be:

$$RMgI < RMgBr < RMgCl \quad .$$

THF was able to compete with MgI and MgBr bridges and the chloride bridges of some RMgCl compounds. This indicates that the basicity of the iodide and bromide of the Grignard reagents are between diethylether and THF while the basicity of the chloride bridge is similar to THF. Ashby reports the fluoride Grignard reagents bridge stronger than the chloride thus indicating a basicity greater than chloride bridges.

Structure of Psuedo Grignard Reagents

Organomagnesium alkoxides are in general only weakly, if at all, coordinated with ether type solvents. This is attributed to the strong coordination of both lone pairs of electrons on the oxygen of $RMgOR$ to magnesium atoms of other RMgOR units. Alternately, it can be stated that the alkoxide group is a stronger base than the ethers studied.

RMgOR can be found with coordinated solvents in several cases:

1. When steric requirements about the carbon atom alpha to the oxygen becomes great (ie , $R-MgO-CMe_2Et$). Coates isolated several of these compounds with solvated diethylether.

2. If a group bonded to the oxygen atom delocalizes one of the electron pairs, the coordinating ability of this electron pair can be reduced enough to allow strong ether

coordination. In this work EtMgOϕ was found to coordinate one THF molecule per magnesium atom and was presumed to be dimeric.

3. Solvent coordination is found if the solvent used is basic enough to replace one or both of alkoxide lone pairs of electrons. Pyridine was found to coordinate the organomagnesium alkoxides studied in this work with a pyridine to magnesium mole ratio of one. A dimer with bridging oxygen atom is postulated. This indicates that pyridine is more basic than one of the two alkoxide lone pairs but not basic enough to replace the other lone pair.

Diethylmagnesium, shown by Ashby to be a monomer in diethylether, was found to coordinate several solvents with a solvent to magnesium mole ratio of one. Much interest has been shown of late in demonstrating the presence of magnesium in organomagnesium reagents with other than four bonds. It is somewhat ironic that a tricoordinate magnesium has been shown in this work to account for the solution structure of one of the first known organomagnesium compounds. Even if π bonding arguments are used, it is clear that Et_2-Mg·N-methylpyrrolidine must be a magnesium species with three sigma bonds and no pi bonds.

In general, organomagnesium amides exhibit strong bridging via coordination of nitrogen's lone pairs of electrons to magnesium. This bridge can be weakened by electron withdrawing groups bonded to nitrogen as in $EtMgNPh_2$. Two THF molecules coordinate to magnesium in $EtMgNPh_2$ indicating a monomeric structure.

An alternate proposal to Coates' was postulated for the structure of the tetramer $(EtMgNPr^i_2)_4 \cdot 2$ THF. A cyclic tetramer was postulated in which steric requirements about the nitrogen atom control the degree of solvation. In the case of $EtMgNPr^i_2$, with branching α to the nitrogen, the crowding allows only two of the four magnesium atoms to coordinate THF. $EtMgNPr^n_2$ steric requirements are much less severe, thus all the magnesium atoms can achieve full four coordination by coordination to THF.

Part II

THE KINETICS OF PSEUDO-GRIGNARD REACTIONS

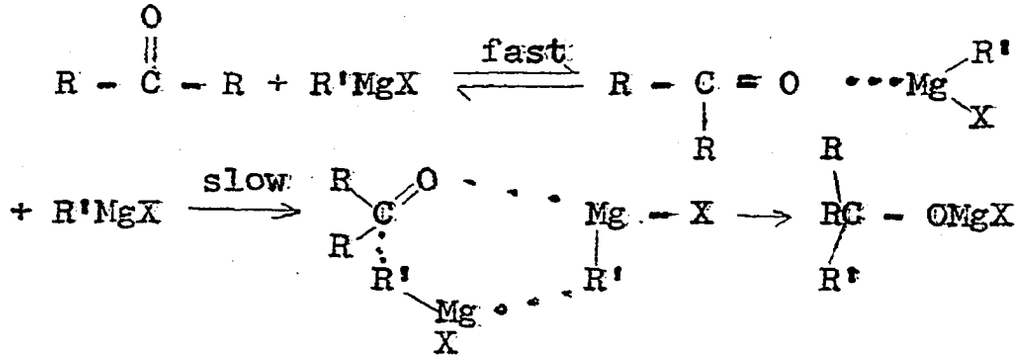
BACKGROUND

Considering the confusion concerning the structure of the Grignard reagent which we have reviewed in the previous section, it is not suprising to note controversy in regard to the mechanism of Grignard reactions.

The attack of the Grignard reagent on a carbonyl group has been studied since the first part of the century, culminating in the mechanism of Swain and Boyles in 1951[35].

They suggested the reaction to be third order, first order in the carbonyl compound and second order in R-Mg.

(53)



+ $R'MgX$.

After 1957, when Dessy's exchange work indicated that the Grignard reagent might best be represented by $R_2Mg \cdot MgX_2$, Swain and Boyle's mechanism fell under attack.

Miller et al[35], Bikales and Becker[36], and Hamelin and Hayes[37] suggested a bimolecular mechanism involving one molecule of ketone and one of the $R_2Mg \cdot MgX_2$.

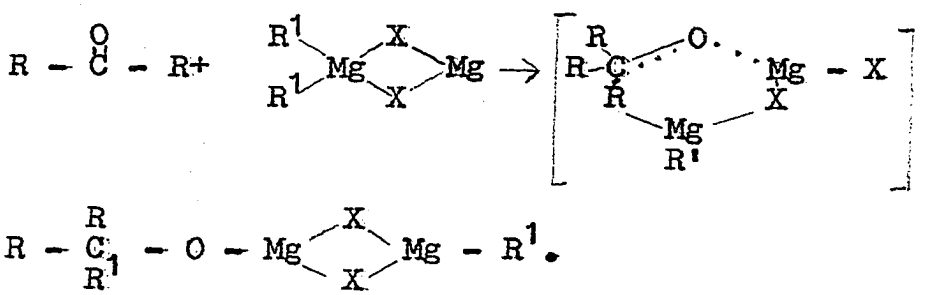
Bikales and Becker[36] followed the reaction of methylmagnesium bromide with benzophenone in THF solvent. They found that the last 50% of the R-Mg groups reacted at a rate of 1/85 of the first R-Mg groups. Thus half of the R-Mg groups were considered kinetically inactive.

Bikales and Becker[36] found the reaction to be second order, first order in benzophenone and first order in $Me_2Mg \cdot MgBr_2$. The kinetics deviated severely from second order behavior after the first third of the reaction. No simple order could describe the entire reaction.

By varying the concentrations of Grignard reagent and ketone, they obtained a series of rate constants consistant with a second order reaction over the first third of the reaction.

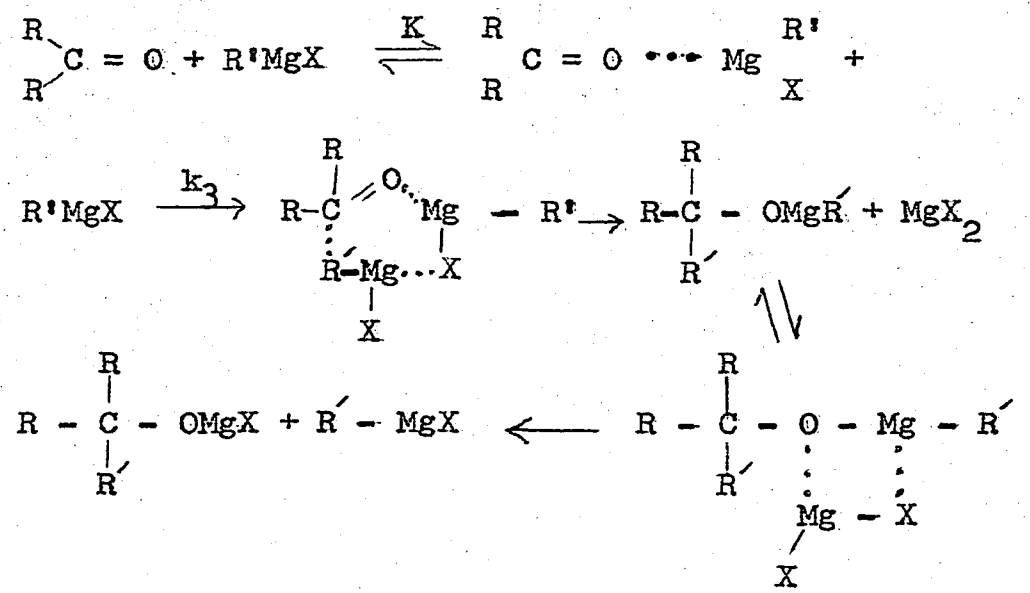
The mechanism was postulated:

(54)



Ashby[37] working at concentrations where all Grignard reagent is in the monomeric form, postulated a mechanism similar to Swain's mechanism.

(55)

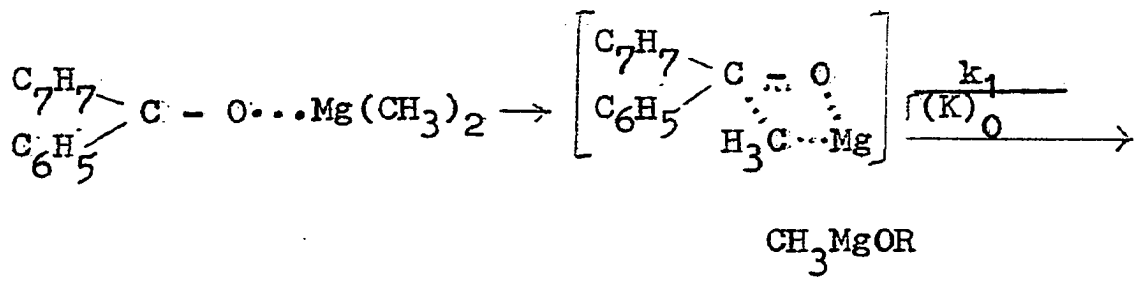


Where: $K_{obs} = \frac{k_3 K (G)^2}{1 + K(G)}$

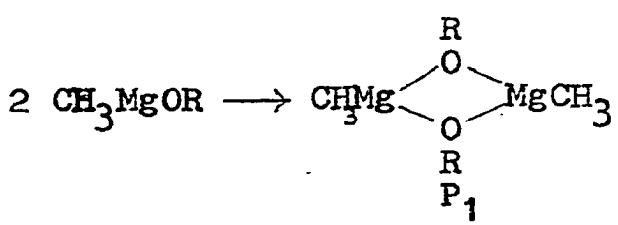
Ashby indicated that if $K(G) \gg 1$ then the reaction is first order in G, second order overall, if $K(G) \ll 1$ then the reaction appears second order in G, third order overall.

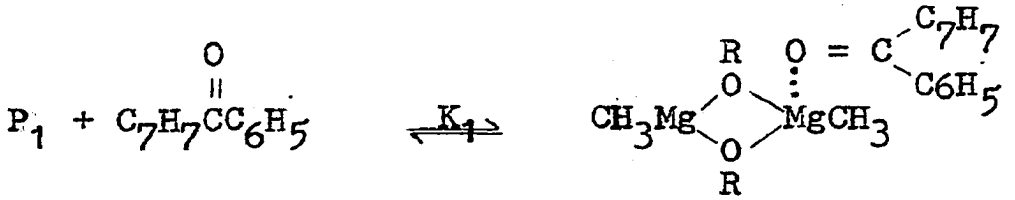
Very recently Ashby[38] has claimed new insight into this reaction. By following spectrophotometrically the disappearance of a Grignard reagent-ketone complex, Ashby explored the kinetics of Me_2Mg with 2-methylbenzophenone using a large excess of ketone. By the large excess of ketone, the reaction was unambiguously determined to be first order in Me_2Mg. The mechanism (56) was suggested;

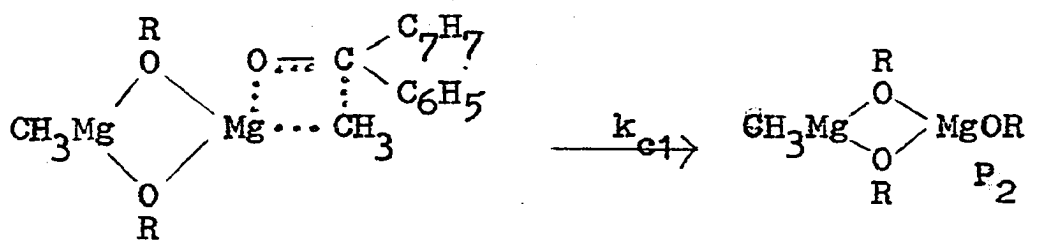
(56) $(CH_3)_2Mg + C_7H_7 - \overset{O}{\overset{\|}{C}} - C_6H_5 \rightleftharpoons C_7H_7(C_6H_5)C = O \cdots Mg(CH_3)_2$

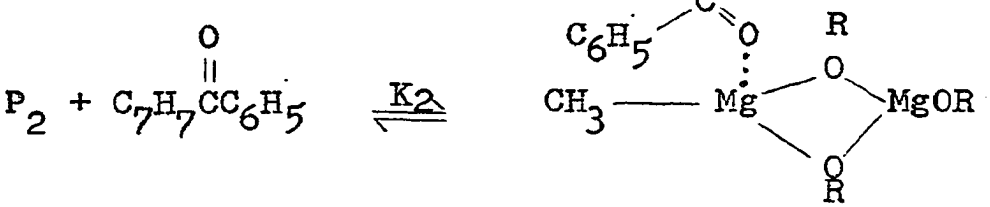


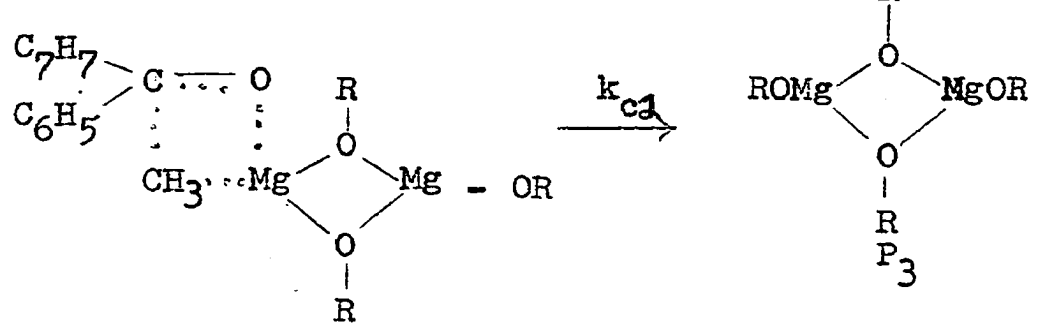
CH_3MgOR







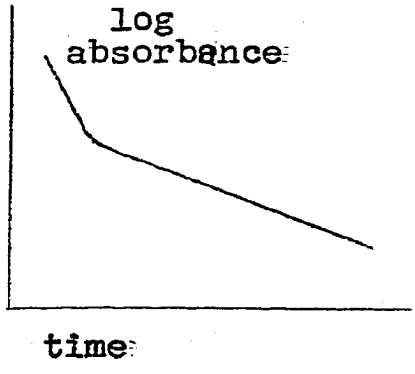




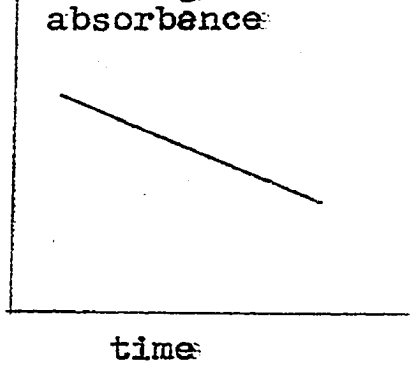
Quenching studies established the formulas of P_1, P_2 and P_3.

Armed with these data, Ashby[39] and coworkers explored the MeMgBr reaction with 2-methylbenzophenone. Again following the disappearance of the Grignard reagent-ketone complex and working in large excess of ketone, they found two competing reactions. The Me_2Mg formed by virtue of Schlenk's equilibrium reacted at a rapid rate, but a slower reaction of MeMgBr was also seen.

(57)



(58)



Addition of excess $MgBr_2$ produced curve (58), which is the reaction of MeMgBr alone with 2-methylbenzophenol. The rate constant calculated for the MeMgBr species attacking the ketone from (57) agreed well with rate constant where all the Me_2Mg had been removed by $MgBr_2$ addition (58).

It must be cautioned that these kinetic results apply strictly to the 2-methylbenzophenone, Me_2Mg and MeMgBr

systems only. Extrapolations to other systems must be made with care. The reactions studied by Ashby yielded 100% addition products. Quite often Grignard reagent ketone reactions are complicated by side reactions as enolization and reduction.

It is of interest to note that all of the proposed Grignard alkylation reactions involve as the first step the coordination of the ketone with the Grignard reagent, presumably by solvent displacement. Thus it is felt future workers in this field will find the conclusions of section I of this thesis valuable in relating the alkylation reactions of Grignard reagents with various bridging groups in various solvents.

The reaction of Grignard reagents with active hydrogen compounds has been extensively studied by Wotiz, Hollingsworth, and coworkers[40,-47], and by Hashimoto et al[48]. Wotiz, Hollingsworth et al in a series of articles explored the relative reactivity of Grignard reagents with terminal alkynes. They found the rate of reaction to be a function of the structure of the Grignard reagent[40], the structure of the alkyne[41] and the solvent used[42].

They determined the relative reaction rates toward 1-hexyne as RMgCl > RMgBr > RMgI. Et_2Mg was found to react

about three times as fast with 1-hexyne as EtMgBr. The relative reaction rates were determined in diethylether at 1 M concentration of Grignard reagent and 1-hexyne.

(59)

EtMgI	71
EtMgBr	100
EtMgCl	155
Et_2Mg	300

These relative reactivities were reported to be virtually independent of concentration.

A four centered intermediate was proposed[43] to account for the large deuterium isotope effect noted.

(60)

$$R - C \equiv C - H + Mg - R^1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R - C = C(H) \cdots Mg(R^1) \xrightarrow{k_2}$$

$$R - C \equiv C - Mg - + R^1H$$

The rate of reaction of EtMgBr with 1-hexyne in various solvents was related by Wotiz et al[44] directly to the basicity of the solvent. More basic solvents caused a slower reaction. The basicity of the solvents used was predicted

by analogy to known basicities of other Lewis acids of comparable size.

(61) Rate in $iPr_2O > Bu_2O > Et_2O >$ THF > MeTHF

In light of the order of basicity THF > MeTHF found in the first part of this work, this conclusion of Wotiz must be looked upon with some skepticism.

Hashimoto et al[48] also made a kinetic study of the reactions of EtMgBr with 1-hexyne. They found the reactions to be second order in diethylether and dibutylether solvents but 2.5 order in diethyleneglycol ether and third order in THF solvent. The mechanism in THF proposed was:

(62) (1) $(EtMgBr)_2 \rightleftharpoons 2\ EtMgBr$

(2) $EtMgBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Bu-C\equiv C-H$ (Et–Mg(solvent)–Br)

(3) $EtMgBr \xrightarrow{k_2} BuC\equiv CMgBr + EtH + EtMgBr$.

The reaction in Et_2O could proceed by the same mechanism if $k_1 << k_2$. However, Hashimoto et al rationalized that this assumption was unlikely due to the high degree of dimerization of EtMgBr in Et_2O and the activation energy required for the second step. The postulated reaction occurred by mechanism (63) in diethylether solvent.

(63) $(EtMgBr)_2 + BuC \equiv C - H \xrightarrow{k_1} BuC \equiv CMgBr + EtH + EtMgBr$

$2\ EtMgBr \xrightarrow{fast} (EtMgBr)_2$

Pseudo-Grignard Reagents

Except for R_2Mg and RMgOR' virtually no work has been done concerning the mechanism of the reaction of pseudo-Grignard reagents.

R_2Mg's reactions with ketones has been extensively studied. R_2Mg reacts approximately ten times as fast as RMgBr with ketones, presumably with a similar mechanism[49].

RMgOR' has been identified as an intermediate attacking species in the reaction of R_2Mg with ketones by Ashby[37,38] and also by House[49]. House found that RMgOR' reacted with ketone at a rate comparable to RMgBr but found that enolization and reduction side reaction were much more prominent than with R_2Mg and RMgBr compounds.

Only traditional Grignard reagents and R_2Mg have been investigated in reactions with active hydrogens.

STATEMENT OF THE PROBLEM

The aim of this part of the thesis work was to initiate the study of the kinetics of reactions of various pseudo-Grignard reagents.

The reaction of pseudo-Grignard reagents with 1-alkynes was studied since this system has been thoroughly explored with traditional Grignard reagents thus giving a base of comparison. Also the reaction can be conveniently followed by measurement of evolved hydrocarbon and should not be complicated by as many side reactions as, for example, the alkylation reactions.

EXPERIMENTAL

Materials: All the materials used were the same as in section I of this thesis.

1-Hexyne: 1-Hexyne obtained from the Chemical Procurement Company was distilled from Drierite and stored in a refrigerator.

Apparatus: The kinetic runs were similar to those of Wotiz et al[141]. The titration vessel described in section I of this thesis was used as the reaction vessel. The temperature of the reaction vessel was maintained ± 0.2 C by the constant temperature bath also described in section I. Grignard reagents and reactants were introduced through

the septum side arm. The cold finger contained a Dry Ice acetone slurry which was kept at a constant level during all experiments. The outlet at the top of the cold finger was attached to a capillary line, the other end of which was placed in the neck of a 100 ml, graduated, gas buret. Ethane evolved in the reactions was collected by displacement of water in the gas buret. A small tube of indicating Drierite was inserted in the capillary line to insure no water vapor from the gas burets would diffuse back into the reaction vessel.

After the Grignard reagent had been injected and the reaction vessel and temperature equilibrium had been obtained, the reactant was injected and the timer was started. A jump in temperature of several degrees was noted in some cases. The temperature took up to 10 minutes to reequilibriate. The volume of the gas evolved was measured at appropriate intervals.

Time infinity values for ethane evolution in the 1-hexyne reactions were obtained by slow addition of excess water to the reaction mixture.

In cases where the reaction mixture temperature increased (i.e. the $RMgNR'_2$ and $R_2Mg + R'_2NH$ reactions) the time at which the reaction temperature returned to equilibrium was noted. This time and volume of evolved ethane were

subtracted from all subsequent values to effectively remove initial higher temperature conditions from the kinetic data. All ethane volume measurements were corrected to STP conditions.

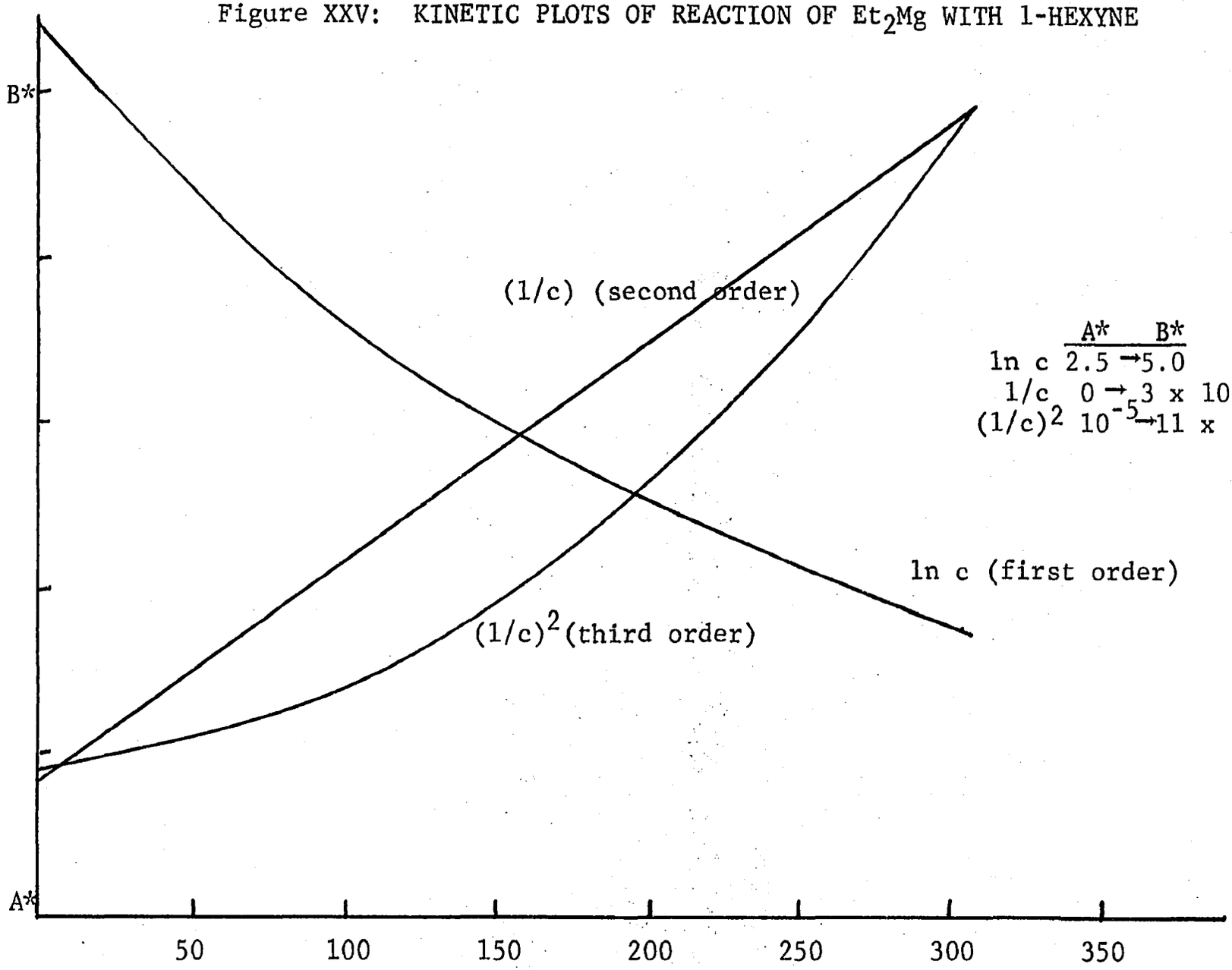
RESULTS AND DISCUSSIONS

Table XXXVIII and Figure XXV list the results for the reaction of diethyl magnesium (0.1M) and 1-hexyne (0.2M). The reaction was followed to about three half lives.

A plot of the reciprocal of the amount of ethane not yet evolved versus time was linear indicating second order kinetics. In all probability the reaction is first order in hexyne and first order in Et-Mg. The second order rate constant is $1.68 \cdot 10^{-3}$ l. mole^{-1} sec^{-1}. The second order rate constant for EtMgBr with 1-hexyne in diethylether at 24.8°C is $5.06 \cdot 10^{-4}$ l mole^{-1} sec^{-1} as determined by Hashimoto et al[48]. Thus Et_2Mg reacts 3.32 times as fast as EtMgBr with 1-hexyne. This is in good agreement with the relative reactivities of Wotiz et al[40].

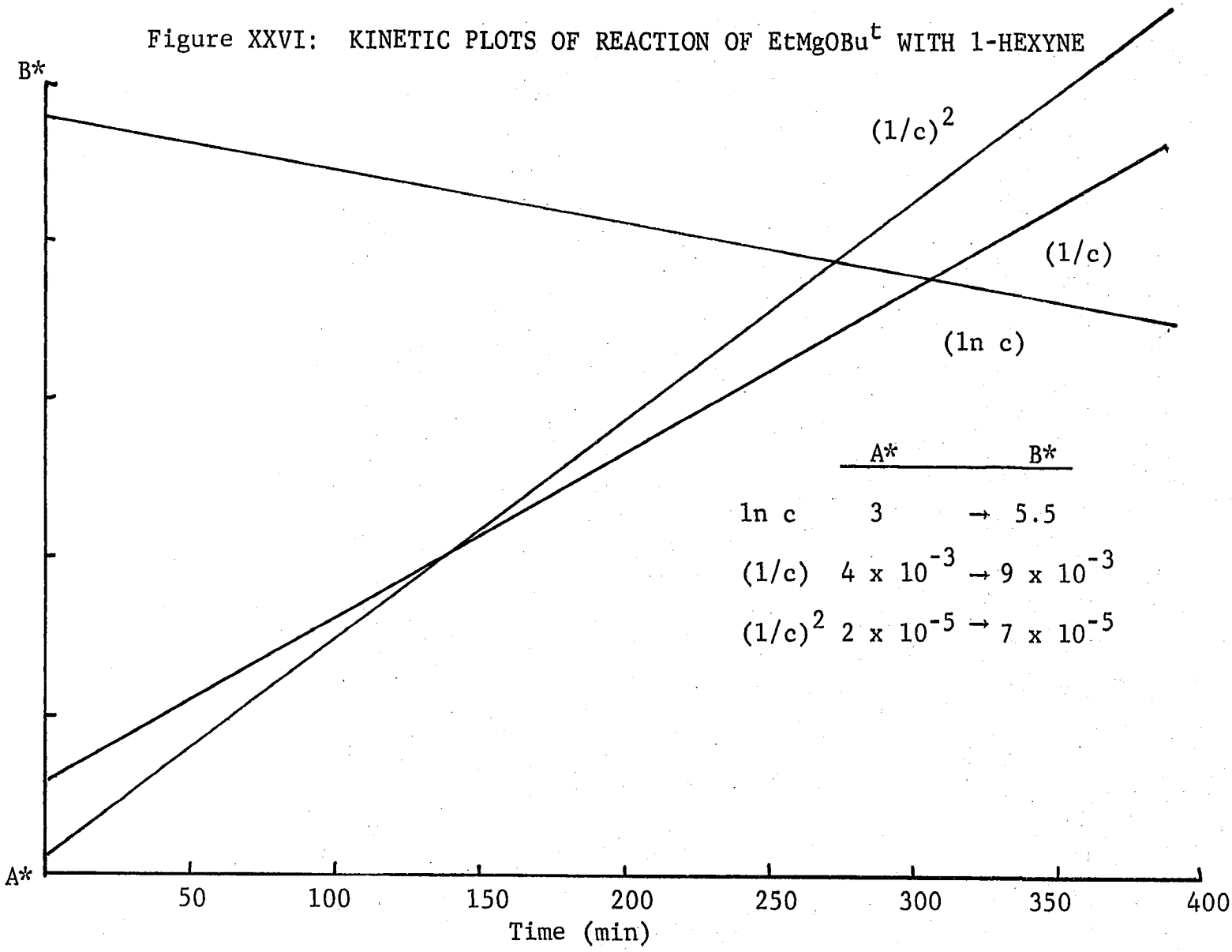
Ethylmagnesium t-Butoxide: Table XXXIX and Figure XXVI list the results of ethylmagnesium t-butoxide (0.2 M) and 1-hexyne (0.2 M). The reaction was slow and followed only to one half life.

Figure XXV: KINETIC PLOTS OF REACTION OF Et_2Mg WITH 1-HEXYNE



	A*	B*
ln c	2.5	5.0
1/c	0	3×10^{-2}
$(1/c)^2$	10^{-5}	11×10^{-5}

Figure XXVI: KINETIC PLOTS OF REACTION OF $EtMgOBu^t$ WITH 1-HEXYNE



	A*	B*
ln c	3	→ 5.5
(1/c)	4×10^{-3}	→ 9×10^{-3}
$(1/c)^2$	2×10^{-5}	→ 7×10^{-5}

The plot of the reciprocal of the amount of ethane not yet evolved versus time was linear in agreement with second order kinetics. However, third order kinetics could not be excluded as a possibility. The second order rate constant is $2.15 \cdot 10^{-4}$ l mole^{-1} sec^{-1}. The reactivity is .128 times as fast as Et_2Mg and 0.426 as fast as EtMgBr.

Ethylmagnesium diisopropylamide: Listed in Table XXXX and Figure XXVII are the results for the reaction of Et_2Mg (.2 M) and diisopropylamine (.2 M) to form ethylmagnesium diisopropylamide. Table XXXXI and Figure XXVIII list the results of the subsequent reaction of $EtMgNPr_2^i$ with 1-hexyne (.2 M).

The reaction of Et_2Mg with $HNPr_2^i$ was followed to completion. The second order rate constants hold fairly constant over several half lives at $8.5 \cdot 10^{-3}$ l.mole^{-1} sec^{-1}.

The reaction of the $EtMgNPr_2^i$ with 1-hexyne in equimolar amounts was complicated by a side reaction. The reaction appeared to procede to completion. Gas chromatography of the vapor above the reaction mixture indicated that no hexyne is present after 100 minutes. However, addition of more 1-hexyne caused a vigorous reaction with evolution of more ethane.

Figure XXVII: KINETIC PLOTS OF THE REACTION OF Et_2Mg WITH $HNPr^i_2$

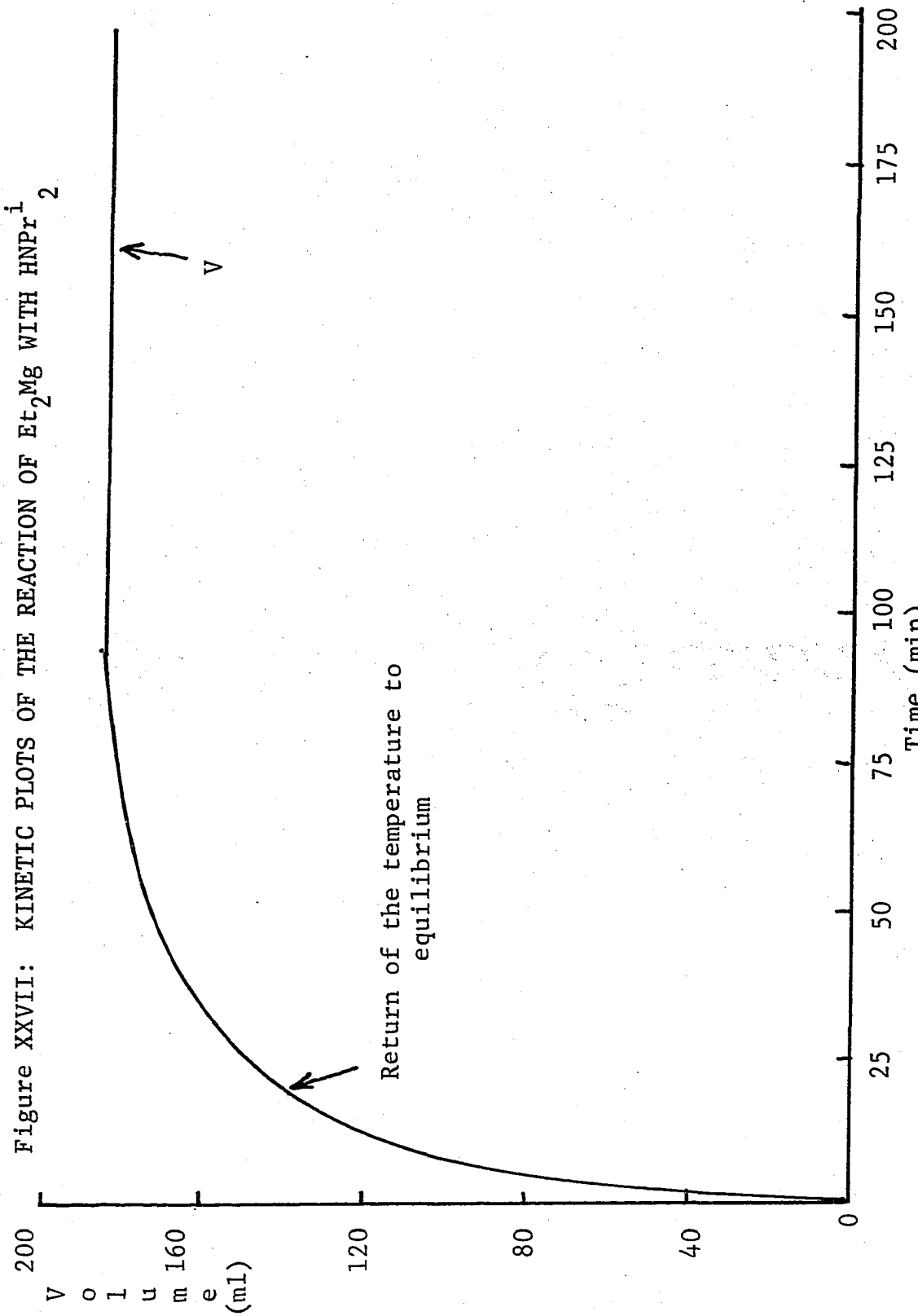
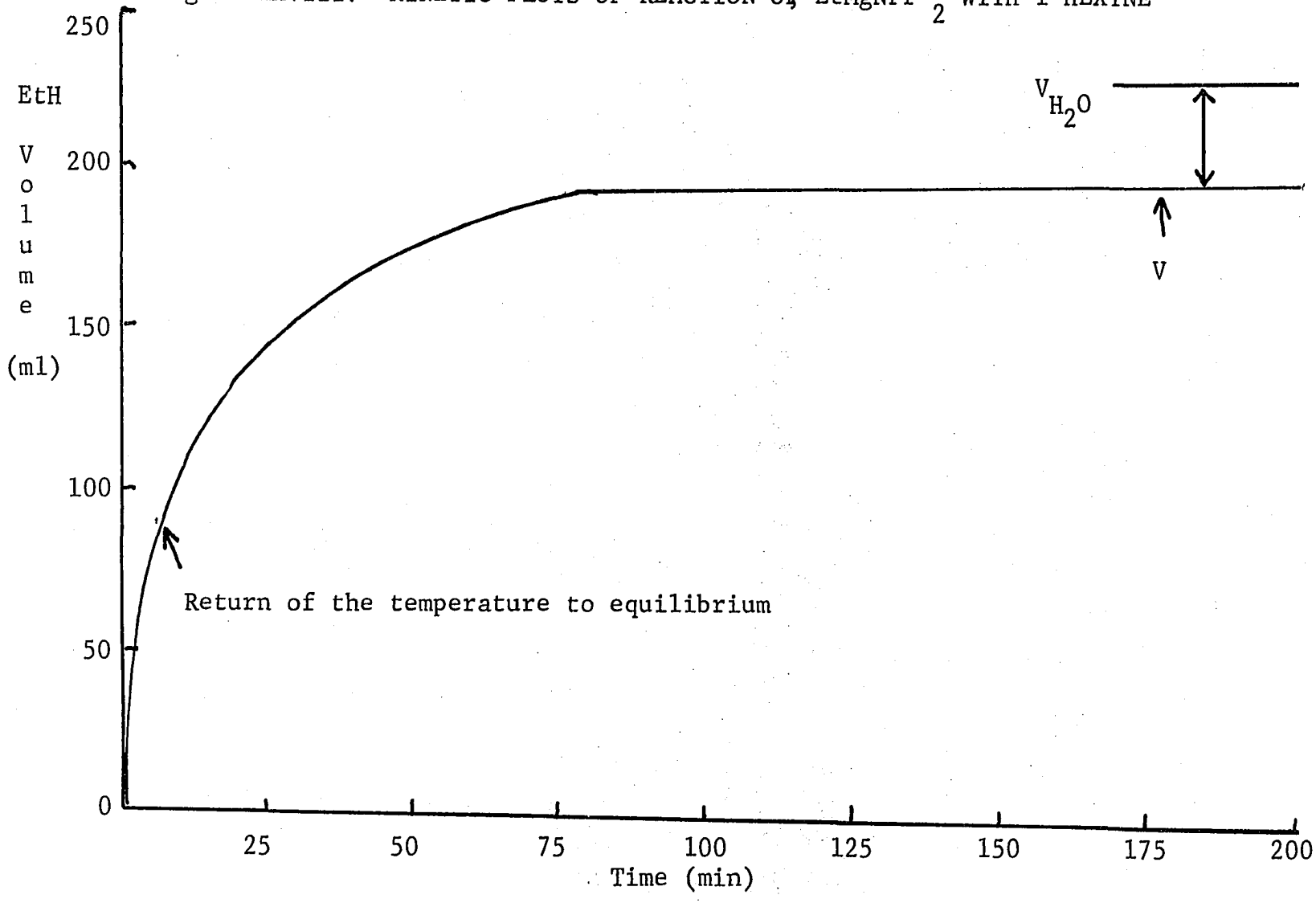


Figure XXVIII: KINETIC PLOTS OF REACTION OF $EtMgNPr^{i}_{2}$ WITH 1-HEXYNE



Since other organomagnesium compounds studied reacted with the active hydrogen without side reactions, it is thought that the amide group destroyed some hexyne. Addition reactions and coupling reactions caused by amines are common in primary acetylene chemistry. Since 3-hexyne was not attacked by this same reagent, the reaction must be peculiar to terminal acetylenes.

As an approximation, the amount of 1-hexyne initially present was calculated by the amount of ethane evolved when the reaction with Grignard reagent ceased (at > 100 minutes). The total Grignard reagent initially present was calculated by the ethane evolved during the reaction and after water addition. The second order rate constants calculated remained fairly constant over several half lives. The rate constant was $6.3 \cdot 10^{-3}$ l. $mole^{-1}$ sec^{-1}. Thus the rate of reaction of $EtMgNPr_2^i$ with 1-hexyne is almost as fast as the reaction of Et_2Mg with $HNPr_2^i$. The reaction with 1-hexyne is 3.75 times the rate of Et_2Mg.

The fast rate of $EtMgPr_2^i$ is not suprising in light of the observation by Smith et al[50] that even catalytic amounts of ammonia, amines, primary and secondary amines, and amine N-oxides greatly increase the rate of reaction of $LiAlH_4$ with 1-hexyne.

Amido compounds are intermediate to alkylmetals and alkynyl metals in the basic series: $C\equiv C-\underset{|}{Mg} < -\underset{|}{N}-Mg < R-\underset{|}{Mg}$. As can be seen from the previously studied reactions R-Mg reacts slower with 1-alkynes than with secondary amines. Perhaps the secondary amine acts as a catalyst by the reaction:

$$(64)\quad RMgNR'_2 + R''C\equiv CH \longrightarrow RMg - C\equiv CR'' + HNR'_2$$

$$\longrightarrow R'_2N - Mg - C\equiv CR'' + RH.$$

It is clear that a more thorough kinetic study of this system with a study of the side reactions involved will be necessary before a firm mechanism can be postulated.

SUMMARY AND CONCLUSIONS

The relative rates of reactions for organomagnesium compounds with 1-hexyne in diethylether solvent at 24.3 °C are:

$EtMgO^tBu$	43
EtMgI	71
EtMgBr	100
EtMgCl	155
Et_2Mg	332
$EtMgNPr^i_2$	1245

An explanation of this order has not been proposed in the literature. However, if the acidity of the magnesium is in the order RMgI> RMgBr> RMgCl> R_2Mg, as is the case with boron, aluminum, gallium and most other metals[51], the ability of R- to migrate as a carbanion in the mechanism proposed by Dessy et al[43] (60) would be, RMgI< RMgBr< RMgCl< R_2Mg. The rate determining step (k_2) would be increased with decreasing acidity of the RMgX compound. Thus the rate of reaction would be R_2Mg > RMgCl> RMgBr > RMgI as is observed.

EtMgOBu^t would be expected to have a low magnesium acidity. However, as discussed in section I of this thesis, EtMgOBu^t is highly associated due to the very strong basicity of the alkoxide oxygen. This strong coordination of the magnesium would shift the equilibrium (k_1, k_{-1}) to the left thus lowering the concentration of the intermediate involved in the rate determining step. Thus the rate of EtMgOBu^t with 1-hexyne would be much slower than expected on the basis of the acidity of the magnesium alone.

The very fast rate of EtMgNPr$^i_2$ is explained by the action of the amide as a catalyst (64) in transfer of the proton.

The Effect of Degree of Association on Kinetics - Directions for Further Research.

The main body of this work has been concerned with determining the degree of solvation and polymerization of pseudo Grignard reagents. The specific implication of polymerization in regards to the body of kinetic data on Grignard reagents has not been reinvestigated here. However, the following example indicates the kinetic order may be misinterpreted if the degree of association is improperly formulated.

If the attacking Grignard species is a polymer, the hypothetical reaction between $(RMgX)_n$ and R'H might be pictured as:

(65) $$(RMgX)_n + R'H \xrightarrow{k_1} R'MgX \cdot (RMgX)_{n-1} + RH$$

$$R'MgX \cdot (RMgX)_{n-1} + R'H \xrightarrow{k_2} (R'MgX)_2 \cdot (RMgX)_{n-2} + RH$$

etc.

The above reaction is an example of a competitive, consecutive second order reaction. The identical reaction with a Grignard reagent postulated as a monomer would be seen as

(66) $$RMgX + R'H \longrightarrow R'MgX + RH.$$

This could well be a simple second order reaction.

The reaction (65) would behave the same kinetically as reaction (66) only if $k_1 = (n/n-1)k_2$ in reaction (65). This is to say that the R-Mg group reacts with equal speed whether in the $(R\text{-}MgX)_n$ or $R\text{-}MgX \cdot (R'MgX)_{n-1}$ species. If $k_1 >> k_2$ and the RMgX species is mistakenly postulated as a monomer when in fact, it is a dimer, a plot of $1/(R'H)$ would exhibit considerable curvature indicating a different order than second order.

The reactions studied in this work could be considered in this catagory. Et_2Mg is monomeric but has two reactive groups per molecule. $EtMgOBu^t$ and $EtMgNPr^i_2$ are tetrameric thus having four reactant groups per molecule. The straight line plots of $1/c$ vs t indicate the condition $k_1 = \frac{n}{n-1} k_2$ holds in these reactions.

Dessy et al[43] has found this to be true for traditional Grignard reagents. However, Dessy reported that for $Et_2Mg + R'H$ $k_1 \approx 5k_2$ causing considerable curvature in the $1/(R'H)$ vs t plot.

The Et_2Mg results of Dessy et al were not observed in this work. Dessy performed these reactions at 1.0N concentrations where there is some association of Et_2Mg in diethylether. Et_2Mg would be principally monomeric at concentrations reported in this work. Dessy also allowed variations of several degrees during his kinetic runs, where the kinetic runs here were controlled to $\pm$ 0.2 °C. It is unclear at this point whether this discrepancy is due to the above mentioned facts or if there is another factor which we have

overlooked. The semiquantitative nature of the kinetic runs in this work would not be seriously affected however.

It is clear that serious mechanistic studies of all Grignard reactions must have knowledge of the degree of association of the Grignard species as well as the Lewis acid-solvent coordination properties of these species. Consequently, much of the kinetic work previously reported on traditional Grignard reagents needs to be reinterpreted in light of the contributions of Ashby, Guild, McPherson and others. Future workers on the kinetics of pseudo Grignard reagents should find the results and conclusions of this work noteworthy.

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PART III: APPENDIX

TABLE II

Gas Chromatographic Titration Data

Initial Mixture: 40.0 ml of diethylether

10.0 ml of methylcyclohexane (Blank run)

Titrating solvent: tetrahydrofuran

Titration temperature: 27.6 °C

Volume of THF added (ml.)	Time of equilibration (min.)	Corrected peak height of THF (mm)
0.0	---	0.0
1.0	15	44.4
1.0	30	43.0
2.0	15	90.0
4.0	15	168
4.0	30	171
8.0	15	325
8.0	30	322
10.0	15	392
10.0	39	388.5

From Figure II, curve I, the intercept on the abscissa is 0.0 ml. THF.

TABLE III

Gas Chromatographic Titration Data

Initial mixture: 30.0 ml. of diethylether

10.0 ml. of methylcyclohexane (Blank run)

Titrating solvent: triethylamine

Titration temperature: 47.1 °C

Volume of Et_3N added (ml)	Corrected peak height of THF (mm)
0.0	0.0
1.0	7.0
2.0	13.6
3.0	21.2
4.0	28.6
5.0	37.4
6.0	48.9
8.0	58.3
10.0	73.0

From Figure II, curve II, the intercept on the abscissa is 0.0 ml. of Et_3N.

TABLE IV

Gas Chromatographic Titration Data

Initial mixture: 40.0 ml. of diethylether

20.0 ml. of methylcyclohexane (Blank run)

Titrating solvent: pyridine

Titration temperature: 53.20 °C

Volume of pyridine added (ml.)	Corrected peak height of pyridine (mm)
0.0	0
1.0	18.3
2.0	39
3.0	57.2
4.0	79.4
5.0	93.9
6.0	114.5
8.0	172.9

From Figure II, curve III, the intercept on the abscissa is 0.0 ml of pyridine.

TABLE V

Gas Chromatographic Titration Data

Initial mixture: 10.0 ml of $nBuMgOPr^n$(0.75) in methylcyclohexane

30.0 ml of diethyl ether

Initial concentration of $nBuMgOPr^n$: 0.187 M

Titrating solvent: tetrahydrofuran

Titration temperature: 48.81 °C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0	0
0.2	20
1.0	107
2.0	210
3.0	299
4.0	418
6.0	621
8.0	828

From Figure III, curve I, the intercept on the abscissa is 0.0 ml of THF. THF=12.32 mm/ml.

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{0.0}{7.50} = 0.0$$

TABLE VI

Gas Chromatographic Titration Data

Initial mixture: 10.0 ml of $nBuMgOPr^n$ (1.20M) in methylcyclohexane

40.0 ml of diethylether

Initial concentration of $nBuMgOPr^n$: 0.24M

Titrating solvent: triethylamine

Titration temperature: 49.4 °C

Volume of Et_3N added (ml)	Corrected peak height of Et_3N (mm)
0.0	0.0
0.5	29.0
1.0	64.3
2.0	142.5
3.0	182.0
4.0	263.9
5.0	348.2
6.0	452.0
8.0	547.0

From Figure III, curve II, the intercept on the abscissa is 0.0 Et_3N. Et_3N = 7.11 mmo/ml

$$\text{Mole ratio} = \frac{Et_3N}{Mg} = \frac{0.0}{12.0} = 0.0$$

TABLE VII

Gas Chromatographic Titration Data

Initial mixture: 10.0 ml of $nBuMgOPr^n$ (1.20M) in methylcyclohexane

50.0 ml of diethylether

Initial concentration of $nBuMgOPr^n$: 0.20M

Titrating solvent: pyridine

Titration temperature: 47.2 °C

Volume of pyridine added (ml)	Corrected peak height of pyridine (mm)
0.0	2.5
1.0	8.4
2.0	17.5
3.0	29.7
4.0	45.6
5.0	55.2
6.0	70.0
7.0	94.6
8.0	115.0
9.0	117.2

From Figure III, curve III, the intercept on the abscissa is .95 ml pyridine = 12.39 mmo/ml.

$$\text{Mole ratio} = \frac{\text{pyridine}}{\text{Mg}} = \frac{11.8}{12.0} = .98$$

TABLE VIII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of nBuMgOPr^{i} (1.17M) in methylcyclohexane

40.0 ml of diethylether

Initial concentration of nBuMgOPr^{i} :- 0.39M

Titrating solvent: tetrahydrofuran

Titration temperature: 24.4°C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	0.0
1.0	41.9
2.0	83.0
3.0	125.3
4.0	172.9
5.0	225.5
6.0	269.5
8.0	376.0

From Figure IV, curve I, the intercept on the abscissa is 0.411 ml of THF. THF = 12.32 mmo/ml.

$$\text{Mole ratio} = \text{THF/Mg} = \frac{5.06}{23.4} = 0.22$$

TABLE IX

Gas Chromatographic Titration Data

Initial mixture: 10 ml of nBuMgOPr^i (1.53M) in methylcyclohexane

30 ml of diethylether

Initial concentration of nBuMgOPr^i :0.38M

Titrating solvent: triethylamine

Titration temperature: 48.1 °C

Volume of Et_3N added (ml)	Corrected peak height of Et_3N (mm)
0.0	0.0
0.5	3.6
1.0	8.2
1.5	13.5
2.5	23.0
3.5	31.5
4.5	42.8
5.5	48.4
7.5	69.8
9.5	84.2

From Figure IV, curve II, the intercept on the abscissa is 0.1 ml of Et_3N. Et_3N = 7.11 mmo/ml.

$$\text{Mole ratio} = \frac{Et_3N}{Mg} = \frac{.7}{15.3} = .05$$

TABLE X

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of nBuMgOPr^i (1.17 M) in methylcyclohexane

Initial concentration of nBuMgOPr^i : 0.39M

Titrating solvent: triethylamine

Titration temperature: 24.4 °C

Volume of Et_3N added (ml)	Corrected peak height of Et_3N (mm)
0.0	0
1.0	16.3
2.0	35.6
3.0	53.7
4.0	74.1
5.0	92.4
6.0	110.5
8.0	149.5

From Figure IV, curve III, the intercept on the abscissa is 0.15 ml of Et_3N. Et_3N = 7.11 mmo/ml.

$$\text{Mole ratio} = \frac{Et_3N}{Mg} = \frac{1.07}{23.4} = 0.05$$

TABLE XI

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of nBuMgOPr^i :• (1.17M) in methylcyclohexane

40.0 ml of diethylether

Initial concentration of nBuMgOPr^i: 0.39M

Titrating solvent: pyridine

Titration temperature: 24.4 °C

Volume of pyridine added (ml)	Corrected peak height of pyridine (mm)
0.0	0.0
1.0	0.0
2.0	2.1
3.0	5.8
4.0	12.4
5.0	17.1
6.0	23.8
7.0	29.0
8.0	35.2

From Figure IV, curve IV, the intercept on the abscissa is 2.00 ml of pyridine. pyriding = 12.39 mmo/ml

$$\text{Mole ratio} = \frac{\text{pyridine}}{\text{Mg}} = \frac{24.78}{23.4} = 1.06$$

TABLE XII

Gas Chromatographic Titration Data

Initial mixture: 60 ml methylcyclohexane
(Blank run)

Titrating solvent: tetrahydrofuran

Titration temperature: 24.8 °C

Volume of THF added (ml)	Corrected peak height of THF (mm)	X 0.77
0.0	0.0	0.0
1.0	79.8	61.4
2.0	155	119
3.0	224	172
4.0	292	224
5.0	346	266
6.0	406	312
7.0	464	357

From Figure V, curve I, the intercept on the abscissa is 0.0 of THF.

TABLE XIII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of nBuMgOPr^i (1.39M) in methylcyclohexane

40.0 ml of methylcyclohexane

Initial concentration of nBuMgOPr^i : 0.46M

Titrating solvent: tetrahydrofuran

Titration temperature: 24.3 C

Volume of THF added (ml)	Corrected peak height of THF (mm)	THF peak height Corr. for linearity of blank
0.0	0.0	0
1.0	58	47
2.0	109	907
3.0	155	137
4.0	204	183
5.0	254	239
6.0	305	298
7.0	357	357

From Figure V, curve II, the intercept on the abscissa is 0.0 ml of THF. THF = 12.32 mmo/ml

$$\text{Mole ratio} = \frac{\text{mmoTHF}}{\text{mmoMg}} = \frac{0.0}{27.8} = 0.0$$

From Figure V, curve III, the intercept on the abscissa is .55 ml of THF.

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{6.79}{27.8} = .24$$

TABLE XIV

Gas Chromatographic Titration Data

Initial Mixture: 20.0 ml of $nBuMgOBu^{sec}$ (.708M) in methylcyclohexane

40.0 ml of diethylether

Initial concentration of $nBuMgOBu^{sec}$: 0.236M

Titrating solvent: tetrahydrofuran

Titration temperature: 24.4 °C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	0.0
1.0	75
2.0	147
3.0	220
4.0	306
5.0	390
6.0	475
8.0	646

From Figure VI, curve I, the intercept on the abscissa is .41 ml of THF. THF = 12.32 mmo/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{.5}{14.16} = .357$$

TABLE XV

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of $nBuMgOBu^{sec}$ (708M) in methylcyclohexane

40.0 ml of diethylether

Initial concentration of $nBuMgOBu^{sec}$: 0.236M

Titrating solvent: triethylamine and subsequently pyridine

Titration temperature: 24.4°C

Volume of Et_3N added (ml)	Corrected peak height of Et_3N (mm)
0.0	0.0
1.0	58.1
2.0	109.5
3.0	166
5.0	273

Volume of pyridine added (ml)	Corrected peak height of pyridine (mm)
0.0	0.0
1.0	3.3
2.0	19.6
3.0	37.8
4.0	57.8
5.0	76.1
6.0	93.5

From Figure VI, curve II, the intercept on the abscissa is 0.0 ml Et_3N. Et_3N = 7.11 mmo/ml

TABLE XV contd.

$$\text{Mole ratio} = \frac{Et_3N}{Mg} = \frac{0.0}{14.16} = 0.0$$

From Figure VI, curve III, the intercept on the abscissa is 1.1 ml pyridine. Pyridine = 12.39 mmo/ml

$$\text{Mole ratio} = \frac{\text{pyridine}}{Mg} = \frac{13.60}{14.16} = .96$$

TABLE XVI

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of $nBuMgOBu^{sec}$ (0.708 M) in methylcyclohexane

40.0 ml of diethylether

Initial concentration of $nBuMgOBu^{sec}$: 0.236M

Titrating solvent: 1,4 dioxane

Titration temperature: 24.4 C

Volume of dioxane added (ml)	Corrected peak height of dioxane (mm)
0.0	0.0
1.0	27.6
2.0	55.2
3.0	77.7
4.0	101
5.0	125
6.0	145
7.0	159

From Figure VI, curve IV, the intercept on the abscissa is 0.0 ml dioxane. dioxane = 11.7 mmo/ml

$$\text{Mole ratio} = \frac{\text{dioxane}}{\text{Mg}} = \frac{0.0}{14.16} = 0.0$$

TABLE XVII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of $EtMgOBu^t$ (0.83M) in diethylether

40.0 ml of methylcyclohexane

Initial concentration of $EtMgOBu^t$: 0.28M

Titrating solvent: tetrahydrofuran

Titration temperature: 24.3 C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	0.0
1.0	47
2.0	102
3.0	157
4.0	211
5.0	266
6.0	312

From Figure VII, curve I, the intercept on the abscissa is 0.15 ml of THF. THF = 12.32 mmo/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{1.85}{16.6} = .11$$

TABLE XVIII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of EtMgOφ(0.722M) in diethyl ether

40.0 ml of methylcyclohexane

Initial concentration of EtMgOφ: 0.24M

Titrating solvent: tetrahydrofuran and subsequently pyridine

Titration temperature: 24.3°C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	6.5
0.4	11
0.8	21
1.2	36
1.6	64
2.0	105
3.0	214
4.0	320
5.0	412

Volume of pyridine added (ml)	Corrected peak height of pyridine
0.0	2
1.0	4
2.0	13.0

TABLE XVIII contd.

Volume of pyridine added (ml)	Corrected peak height of pyridine
3.0	23.5
4.0	32.2
5.0	41.8

From Figure VIII, curve I, the intercept on the abscissa is 1.10 ml of THF. THF = 12.32 mmo/ml

$$\text{Mole ratio} = \frac{13.60}{14.44} = 0.94$$

From Figure VIII, curve II, the intercept on the abscissa is 1.00 of pyridine. Pyridine = 12.39 mmo/ml

$$\text{Mole ratio} = \frac{12.39}{14.44} = .86$$

TABLE XIX

Gas Chromatographic Titration Data

Initial mixture: 40.0 ml diethylether

20.0 ml methylcyclohexane
(Blank run)

Titrating solvent: THF

Titration temperature: 0.0 °C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	0
1.0	44.2
2.0	86.8
3.0	130
4.0	174
5.0	209
6.0	252

From Figure IX, curve I, the intercept on the abscissa is 0.0 ml of THF.

TABLE XX

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of $nBuMgOBu^{sec}$ (0.708M) in methylcyclohexane

40.0 ml of diethylether

Initial concentration of $nBuMgOBu^{sec}$ = 0.236M

Titrating solvent: tetrahydrofuran

Titration temperature: 0.0 °C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	0.0
1.0	25
2.0	56.1
3.0	92.4
4.0	132
5.0	173
6.0	209
7.0	248
8.0	290

From Figure IX, curve II, the intercept on the abscissa is .64 ml of THF. THF = 12.32 mmo/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{7.89}{14.16} = 0.56$$

TABLE XXI

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of $nBuMgOBu^{sec}$ (0.81M)

40.0 ml of diethylether

Initial concentration of $nBuMgOBu^{sec}$: 0.27

Titrating solvent: tetrahydrofuran

Titration temperature: 54.6 C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	2.2
1.0	58
2.0	116
3.0	176
4.0	248
5.0	313
6.0	374
8.0	516

From Figure IX, curve III, the intercept on the abscissa is 0.23 ml of THF. THF = 12.32 mmo/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{2.84}{16.2} = 0.17$$

TABLE XXII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of Et_2Mg (1.00M) in diethylether/methylcyclohexane

40.0 ml of diethylether

Initial concentration of Et_2Mg: 0.33M

Titrating solvent: 1,4-dioxane and subsequently THF

Titration temperature: 24.3 C

Volume of diox. added (ml)	Corrected peak ht. of diox. (mm)
0.0	0.0
1.0	9.7
2.0	21.7
3.0	33.6
4.0	48.2
5.0	57.4

Volume of THF added (ml)	Corrected peak ht. of diox. (mm)	Corrected peak ht. of THF (mm)
1.0	61	27.7
2.0	64.5	66.8
3.0	66.9	113
4.0	67.3	166
5.0	68.8	220
6.0	69.2	283
8.0	66.9	406

TABLE XXII (cont.)

From Figure X, Curve I, the intercept on the abscissa is 0.70 ml of 1,4-dioxane. 1,4-dioxane = 11.7 mm/ml.

$$\text{Mole fraction} = \frac{\text{dioxane}}{\text{Mg}} = \frac{8.18}{20} = .41$$

From Figure X, Curve II, the intercept on the abscissa is 1.50 ml of THF. THF = 12.32 mm/ml

$$\text{Mole fraction} = \frac{\text{THF}}{\text{Mg}} = \frac{18.5}{20} = .92$$

TABLE XXIII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of Et_2Mg(1.00M) in diethylether/methylcyclohexane

40.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: 0.33M

Titrating solvent: 1,4-dioxane and subsequently THF

Titration temperature: 24.3 C

Volume of dioxane added (ml)	Corrected peak ht. of ether (mm)	Corrected peak ht. of dioxane
0.0	58.7	0.0
0.5	65.4	0.0
1.0	80.2	1.6
2.0	80.9	11.3
3.0	80.8	23.7
4.0	79.4	36.7
5.0	77.1	47.1

Volume of THF added (ml)	Corrected peak ht. of dioxane (mm)	Corrected peak of THF (mm)
1.0	46.4	23.5
2.0	45.3	32.8
3.0	47.5	58.2
4.0	47.7	89.7
5.0	48.8	120
6.0	47.9	154
8.0	47.7	228

TABLE XXIII (cont.)

From Figure XI, Curve I, the intercept on the abscissa is 1.07ml of dioxane. 1,4-dioxane = 11.7 mm/ml

$$\text{Mole fraction} = \frac{\text{dioxane}}{\text{Mg}} = \frac{12.5}{20} = 0.63.$$

From Figure XI, Curve II, the intercept on the abscissa is 1.55 ml of THF. THF = 12.32 mm/ml

$$\text{Mole fraction} = \frac{\text{THF}}{\text{Mg}} = \frac{19.1}{20} = 0.96$$

TABLE XXIV

Gas Chromatographic Titration Data

Initial mixture: 20.0ml of Et_2Mg (1.07M) in diethylether/ methylcyclohexane

40.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: 0.36M

Titrating solvent: tetrahydrofuran and subsequently 1,4-dioxane

Titration temperature: 24.3 C

Volume of THF added (ml)	Corrected peak ht. of THF (mm)
0.0	0.0
1.0	4.3
2.0	33.6
3.0	49.0
4.0	86.4
5.0	126
6.0	168

Volume of dioxane added (ml)	Corrected peak ht. of dioxane (mm)
1.0	16.7
2.0	30.4
3.0	43.3
4.0	56.0

From Figure XII, Curve I , the intercept on the abscissa is 1.72 ml of THF. THF = 12.32 mm/ml

TABLE XXIV (cont.)

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{21.2}{21.4} = 0.99$$

From Figure XII, Curve II, the intercept on the abscissa is 0.0 ml dioxane. dioxane = 11.7

$$\text{Mole ratio} = \frac{0.0}{21.4} = 0.0$$

TABLE XXV

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of Et_2Mg (1.00M) in diethylether/methylcyclohexane

40.0 ml of diethylether

Initial concentration of Et_2Mg: 0.33M

Titrating solvent: triethylamine and subsequently pyridine

Titration temperature: 24.3 C

Volume of Et_3N added (ml)	Corrected peak ht. of Et_3N (mm)
0.0	0.0
1.0	33.5
2.0	69.5
3.0	106
4.0	141
5.0	177

Volume of pyridine added (ml)	Corrected peak ht. of pyridine (mm)
1.0	0.0
2.0	0.3
3.0	2.3
4.0	8.1
5.0	18.4
6.0	27.4
7.0	37.0

TABLE XXV (cont.)

Volume of pyridine added (ml)	Corrected peak ht. of pyridine (mm)
8.0	46.5
9.0	55.5

From Figure XIII, Curve I, the intercept on the abscissa is 0.00 ml of Et_3N. Et_3N = 7.11 mm/ml

$$\text{Mole ratio} = \frac{Et_3N}{Mg} = \frac{0.00}{20} = 0.00$$

From Figure XIII, Curve II, the intercept on the abscissa is 3.05 ml pyridine. Pyridine = 12.39 mm/ml

$$\text{Mole ratio} = \frac{pyr}{Mg} = \frac{37.8}{20} = 1.89$$

TABLE XXVI

Gas Chromatographic Titration Data

Initial mixture: 10.0 ml of Et_2Mg (1.07M) in diethylether/methylcyclohexane

40.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: 0.215M

Titrating solvent: triethylamine

Titration temperature: 24.3 C

Volume of Et_3N added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. of Et_3N (mm)
0.0	55.8	0.0
1.0	52.7	16.6
2.0	51.5	33.3
3.0	50.4	48.2
4.0	48.8	65.4
5.0	49.0	82.8

From Figure XIV, Curve I, the intercept on the abscissa is 0.0 ml of Et_3N. Et_3N = 7.11 mm/ml

$$\text{Mole ratio} = \frac{Et_3N}{Mg} = \frac{0.0}{10.7} = 0.0$$

TABLE XXVII

Gas Chromatographic Titration Data

Initial mixture: 10.0 ml of triethylamine (Blank run)

50.0 ml of methycyclohexane

Titrating solvent: diethylether

Titration temperature: 24.3 °C

Volume of Et_2O added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. of Et_3N (mm)
1.0	64	23.2
2.0	124	22.8
3.0	182	23.0
4.0	238	22.8
5.0	290	22.9
6.0	342	22.9
8.0	435	22.6

From Figure XV, Curve I, the intercept on the abscissa is 0.0 ml of Et_2O. Et_2O = 9.62 mm/ml

TABLE XXVIII

Gas Chromatographic Titration Data

Initial mixture: 10.0 ml of Et_2Mg (1.37M) in triethylamine/methylcyclohexane

50.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: 0.23M

Titrating solvent: diethylether and subsequently pyridine

Titration temperature: 24.3 °C

Volume of Et_2O added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. of Et_3N (mm)
0.0	0.1	89
1.0	94	94.5
2.0	198	96.7
3.0	297	96.8
4.0	410	98.2
5.0	519	100.3
6.0	638	102.4

Volume of pyridine added (ml)	Corrected peak ht. of Et_2O (mm)	Et_3N	Pyr.
1.0	716	1043	2.3
2.0	733	106	5.6
3.0	760	112	13.8
4.0	739	110	33.0
5.0	725	109	48.2
6.0	712	108	66.3

TABLE XXVIII (cont.)

From Figure XV, Curve IV, the intercept on the abscissa is 2.22 ml of pyridine. Pyridine = 12.39 mm/ml

$$\text{Mole ratio} = \frac{\text{pyridine}}{Et_2Mg} = 2 \quad \therefore \text{ mm of } Et_2Mg = 13.7$$

From Figure XV, Curve II, the intercept on the abscissa is 0.42 ml. Et_2O = 9.62 mm/ml

$$\text{Mole ratio} = \frac{Et_2O}{Et_2Mg} = \frac{3.80}{13.7} = .28$$

TABLE XXIX

Gas Chromatographic Titration Data

Initial mixture: 16.0 ml of Et_2Mg (.92M) in diethylether/methycyclohexane

40.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: 0.263M

Titrating solvent: 2-methyltetrahydrofuran and subsequently tetrahydrofuran

Titration temperature: 24.3 C

Volume of MeTHF added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. of MeTHF (mm)
0.0	51.0	0.0
0.5	46.0	1.5
1.5	54.4	8.7
2.5	59.6	33.4
3.5	61.6	64.8
4.5	61.6	97.2

Volume of THF added (ml)	Corrected peak ht. of MeTHF (mm)	Corrected peak ht. of THF (mm)
0.0	59.0	0.5
1.0	71.2	28
2.0	78	66
3.0	85	113
4.0	88	160
5.0	90	210
6.0	92.5	244
8.0	92	368

TABLE XXIX (cont.)

From Figure XVI, Curve I, the intercept on the abscissa is 1.42 ml of MeTHF. MeTHF = 9.62 mm/ml

$$\text{Mole ratio} = \frac{\text{MeTHF}}{\text{Mg}} = \frac{13.7}{14.72} = 0.93$$

From Figure XVI, Curve III, the intercept on the abscissa is 1.04 ml of THF. THF = 12.32 mm/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{12.8}{14.72} = 0.87$$

TABLE XXX

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of Et_2Mg (1.16M) in diethylether/methylcyclohexane

40.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: 0.39

Titrating solvent: tetrahydrothiophene (THT) and subsequently N-methylpyrrolidine (MP)

Titration temperature: 24.3 C

Volume of THT added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. of THT (mm)
0.0	50	1.0
0.5	49.4	9.1
1.0	48.8	13.7
2.0	48.1	26.8
3.0	47.5	38.0
4.0	46.8	50.0
5.0	46.8	62.1

Volume of MP added (ml)	Corrected peak ht. Et_2O (mm)	Corrected peak ht. THT	MP
1.0	53.7	60.9	4.4
2.0	59.5	61.7	21.1
3.0	62.7	62.7	56.5
4.0	65.3	61.5	117
5.0	66.2	61.5	187
6.0	66.5	61.2	259
7.0	66.8	61.4	339

TABLE XXX (cont.)

From Figure XVII, Curve I, the intercept on the abscissa is 0.0 ml of THT. THT = 12.6 mm/ml

$$\text{Mole ratio} = \frac{\text{THT}}{\text{Mg}} = 0.0$$

From Figure XVII, Curve III, the intercept on the abacissa is 2.50 ml of MP. MP = 9.60 mm/ml

$$\text{Mole ratio} = \frac{\text{MP}}{\text{Mg}} = \frac{24.0}{23.2} = 1.04$$

TABLE XXXI

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of Et_2Mg (1.16M) in diethylether/methycyclohexane

40.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: 0.39

Titrating solvent: N-methypyrrolidene and subsequently tetrahydrofuran

Titration temperature: 24.3 °C

Volume of MP added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. of MP (mm)
0.0	61.5	0.0
1.0	71.6	2.0
2.0	80.5	10.8
3.0	84.9	33.5
4.0	87.8	66.5
5.0	88.6	108
6.0	89.9	153
7.0	90.1	197
8.0	90.3	242

Volume of THF added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. MP	Corrected peak ht. THF
1.0	89.9	258.8	40.1
2.0	91.5	267	106
3.0	90.1	284	200
4.0	89.5	291.2	305

TABLE XXXI (cont.)

Volume of THF added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. MP	Corrected peak ht. THF
5.0	88.3	297.6	423
6.0	88.3	301.5	539
8.0	87.1	312	785

From Figure XVIII, Curve I, the intercept on the abscissa is 2.50 ml of MP. MP = 9.60 mm/ml

$$\text{Mole ratio} = \frac{24.0}{23.2} = 1.04$$

From Figure XVIII, Curve III, the intercept on the abscissa is 1.85 ml of THF. THF = 12.32 mm/ml

$$\text{Mole ratio} = \frac{22.8}{23.2} = 0.98$$

TABLE XXXII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of Et_2Mg (1.05M) in diethylether/methylcyclohexane

40.0 ml of methylcyclohexane

5.0 ml of diethylether

Initial concentration of Et_2Mg: 0.323

Titrating solvent: n-hexylfluoride

Titration temperature: 24.3 °C

Volume of $C_6H_{13}F$ added (ml)	Corrected peak ht. of Et_2O (mm)	Corrected peak ht. of $C_6H_{13}F$
0.0	82.0	0.5
1.0	81.3	41.6
2.0	80.4	82.4
3.0	80.0	121
4.0	79.6	162
5.0	79.2	200

From Figure XIX, Curve I, the intercept on the abscissa is 0.00 ml of $C_6H_{13}F$. $C_6H_{13}F$ = 7.22 mm/ml

$$\text{Mole ratio} = \frac{C_6H_{13}F}{Mg} = \frac{0.00}{21.0} = 0.0$$

TABLE XXXIII

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of Et_2Mg (1.05 M) stripped of solvent

50.0 ml of methylcyclohexane

Initial concentration of Et_2Mg: Heterogeneous mixture

Titrating solvent: n-hexylfluoride and subsequently tetrahydrothiophene

Titration temperature: 23.4 C

Volume of $C_6H_{13}F$ added (ml)	Corrected peak height of THT (mm)
0.0	0.0
1.0	71.5
2.0	144
3.0	215
4.0	281
5.0	356

Volume of THT added (ml)	Corrected peak height of THT (mm)
0.0	0
1.0	25.2
2.0	57.6
3.0	59.7
4.0	64.9
5.0	84.0
10.0	87.0

TABLE XXXIII (cont.)

From Figure XX, Curve I, the intercept on the abscissa is 0.0 ml of $C_6H_{13}F$. $C_6H_{13}F$ = 7.22 mm/ml

$$\text{Mole ratio} = \frac{C_6H_{13}F}{Mg} = \frac{0.0}{21.0} = 0.0$$

TABLE XXXIV

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of $EtMgNPr^i_2$ (0.553M) in diethylether/ methylcyclohexane

40.0 ml of methylcyclohexane

Initial concentration of $EtMgNPr^i_2$: 0.184 M

Titrating solvent: tetrahydrofuran and subsequently pyridine

Titration temperature: 24.3 °C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	8.0
1.0	78.3
2.0	214
3.0	346
4.0	465
5.0	592
6.0	728

Volume of pyridine added (ml)	Corrected peak height of pyridine (mm)
0.0	0.0
1.0	2.6
2.0	13.1
3.0	22.3
4.0	35.6
5.0	44.3

TABLE XXXIV (cont.)

From Figure XXI, Curve I, the intercept on the abscissa is 0.50 ml of THF. THF = 12.32 mm/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{6.06}{11.06} = 0.55$$

From Figure XXI, Curve II, the intercept on the abscissa is 0.95 ml of pyridine. Pyridine = 12.39 mm/ml

$$\text{Mole ratio} = \frac{\text{pyridine}}{\text{Mg}} = \frac{11.76}{11.06} = 1.06$$

TABLE XXXV

Gas Chromatographic Titration Data

Initial mixture: 10.0 ml of $EtMgNPr_2^n$ (0.553M) in diethylether/methylcyclohexane

40.0 ml of methycyclohexane

Initial concentration of $EtMgOPr_2^n$: 0.138

Titrating solvent: tetrahydrofuran and subsequently pyridine

Titration temperature: 24.3 °C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	8.7
0.1	10.2
0.2	11.2
0.3	12.3
0.4	16.4
0.5	25.8
0.7	55.7
1.0	104
1.5	192
2.0	268
3.0	435

Volume of pyridine added (ml)	Corrected peak height of pyridine (mm)
0.0	4.0
0.5	7.3

TABLE XXXV (Cont.)

Volume of pyridine added (ml)	Corrected peak height of THF (mm)
1.0	16.2
2.0	31.9
3.0	46.5
4.0	60.2
5.0	70.2

From Figure XXII, Curve I, the intercept on the abscissa is 0.39 ml of THF. THF = 12.32 mm/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{4.82}{5.53} = 0.87$$

TABLE XXXVI

Gas Chromatographic Titration Data

Initial mixture: 20.0 ml of $EtMgNO_2$ (.284M) in diethylether/methylcyclohexane

40.0 ml of methylcyclohexane

Initial concentration of $EtMgNO_2$: .0947M

Titrating solvent: tetrahydrofuran and subsequently THF

Titration temperature: 24.3 C

Volume of THF added (ml)	Corrected peak height of THF (mm)
0.0	8.0
0.4	9.1
0.8	22.3
1.2	29.6
2.0	130
3.0	266
4.0	401
5.0	528

Volume of pyridine added (ml)	Corrected peak height of pyridine (mm)
0.0	4.1
1.0	6.05
2.0	17.9
3.0	27.2
4.0	39.1
5.0	49.0

TABLE XXXVI (cont.)

From Figure XXIII, Curve I, the intercept on the abscissa is 0.92 ml of THF. THF = 12.32 mm/ml

$$\text{Mole ratio} = \frac{\text{THF}}{\text{Mg}} = \frac{11.34}{5.68} = 2.00$$

TABLE XXXVII

Thermal Titration Data

Initial mixture: 10.0 ml of Et_2Mg (1.07 M) in diethylether/methylcyclohexane

40.0 ml of methylcyclohexane

5.0 ml of triethylamine

Initial concentration of Et_2Mg: 0.195 M

Titrating solvent: tetrahydrofuran

Titration temperature: 24.3°C

Volume of THF added (ml)	T (°C)	T/0.1 ml addition
.1	1.5	1.5
.2	1.5	1.5
.3	1.0	1.0
.5	2.0	1.0
.7	2.0	1.0
.9	2.0	1.0
1.1	0	0

From Figure XXIV, Curve I, the end point would occur at about .9 ml which would correspond to a THF/Mg mole ratio of 1.1.

TABLE XXXVIII

Kinetic Data

Reaction: $Et_2Mg + 2BuC{\equiv}C{-}H \rightarrow (BuC{\equiv}C)_2Mg + EtH$

Initial Concentrations: Et_2Mg = 0.105 M Et-Mg= 0.210 M

1-Hexyne = 0.210 M

Solvent: Diethylether Temperature: 24.3 °C

$V_{STP}@_\infty$ = 190 ml

Time (min)	V_{STP}(ml)	$c(=V_{STP_\infty} - V_{STP})$	ln c	$\frac{1\cdot10^{-3}}{c}$	$\frac{1\cdot10^{-6}}{c^2}$
5	9.4	180.6	5.20	5.50	30.0
10	21.0	169	5.13	5.90	35.0
15	31.7	158.3	5.06	6.30	40.0
20	42.0	148.0	5.00	6.75	45.5
25	48.7	141.3	4.93	7.08	50.1
30	56.6	133.4	4.89	7.49	56.1
35	63.6	126.4	4.84	7.91	62.5
40	69.6	120.4	4.79	8.31	69.1
45	74.7	115.3	4.75	8.67	75.1
50	78.9	111.1	4.71	9.00	81.0
55	84.2	105.8	4.66	9.45	89.3
60	88.3	101.7	4.62	9.83	96.6
65	93.9	96.1	4.75	10.4	108
70	97.5	92.5	4.53	10.8	117
75	98.9	91.3	4.51	11.0	121
95	112.1	77.9	4.36	12.8	164

TABLE XXXVIII (cont.)

Time (min)	V_{STP} (ml)	$c(=V_{STP_\infty}-V_{STP})$	ln c	$\frac{1\cdot10^{-3}}{c}$	$\frac{1\cdot10^{-6}}{c^2}$
110	120.8	69.2	4.24	14.5	210
125	126.8	63.2	4.15	15.8	250
140	131.4	58.6	4.07	17.1	292
155	136.0	54.0	3.99	18.5	342
185	142.0	48.0	3.87	20.8	433
207	146.8	43.2	3.76	23.1	534
242	151.4	38.6	3.65	25.9	671
265	154.5	35.5	3.57	28.2	795
309	160	30.0	3.40	33.3	110.8

From Figure XXV and curve II the slope is $0.085 \cdot 10^{-3}$

$$\frac{52 \text{ ml(soln)}}{\text{ml (EtH) min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{22400 \text{ ml}}{n} \times \frac{1}{52(19.3)\text{ml}} =$$

$1.68 \cdot 1/n \text{ sec} = k_2$.

TABLE XXXIX

Kinetic Data

Reaction: $EtMgOBu^t + BuC{\equiv}C{-}H \longrightarrow BuC{\equiv}CMgOBu^t + EtH$

Initial Concentrations: $EtMgOBu^t$ = 0.210 M Et-Mg = 0.210

1-Hexyne = 0.210 M

Solvent: Diethylether Temperature: 24.3 °C

$V_{STP}@\infty = 224.16$

Time (min)	V_{STP} (ml)	$c(=V_{STP\infty} - V_{STP})$	ln c	$\frac{1}{c} \times 10^{-3}$	$\frac{1}{c^2} \times 10^{-6}$
15	9.78	214.4	5.37	4.66	21.7
25	16.04	208.20	5.34	4.80	23.0
35	22.33	201.87	5.31	4.95	24.5
45	28.32	195.88	5.28	5.11	26.1
65	35.30	188.9	5.24	5.29	28.0
75	40.55	183.65	5.21	5.45	29.7
85	44.24	179.96	5.19	5.56	30.9
97	46.00	178.20	5.18	5.61	31.5
115	51.83	172.37	5.15	5.80	33.6
136	58.40	165.80	5.11	6.03	36.4
154	62.24	161.96	5.09	6.18	38.2
182	69.31	154.89	5.04	6.46	41.7
205	70.81	153.39	5.03	6.65	44.2
220	77.05	147.15	4.99	6.80	46.2

TABLE XXXIX (cont.)

Time (min)	V_{STP} (ml)	$c(=V_{STP_\infty}-V_{STP})$	ln c	$\frac{1}{c} \times 10^{-3}$	$\frac{1}{c^2} \times 10^{-6}$
240	81.58	142.62	4.96	7.01	49.1
260	88.79	135.41	4.91	7.39	54.6
280	92.28	131.92	4.88	7.58	57.5
300	95.62	128.58	4.87	77.78	60.5
320	99.13	125.07	4.83	8.00	64.0
340	102.31	121.89	4.80	8.21	67.4
360	105.50	118.70	4.78	8.47	71.7
381	107.23	116.97	4.76	8.55	73.1
385	108.96	115.24	4.75	8.68	75.3

From Figure XXVI and curve II the slope is

$$1.06 \cdot 10^{-5} \frac{52 \text{ ml(soln)}}{\text{ml(EtH) min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{22400 \text{ ml}}{n} \times \frac{1}{52(19.3) \frac{\text{ml}}{\text{ml}}}$$

$$= 2.15 \cdot 10^{-4} \text{ l/n sec} = k_2$$

TABLE XL

Kinetic Data

Reaction $Et_2Mg + HNPr^i_2 \longrightarrow EtMgNPr^i_2 + EtH$

Initial Concentrations: Et_2Mg=0.210 M Et-Mg=0.420M

1-Hexyne = 0.210 M

Solvent: Diethylether Temperature: 24.3 °C

V_{STP_∞} = 50.3 ml

t* corr (min)	V_{STP}* corr(ml)	$k_2 \cdot 10^{-4}$	$k_3 \cdot 10^{-6}$
5	9.8	4.45	10.1
8	13.8	3.87	9.80
11	16.0	3.77	9.23
14	20.0	4.01	10.6
17	23.5	4.24	11.9
20	25.8	4.18	12.5
23	28.8	4.43	14.2
26	31.6	4.65	16.4
40	38.9	4.93	23.9
48	42.8	5.57	35.9
67	44.2	4.53	33.7
77	46.4	4.99	51.2
95	48.5	5.58	101.0
122	50.3		
156	50.3		
176	50.3		

TABLE XL (cont)

$$\text{Second order rate constant} = 4.0 \times 10^{-4} \frac{52 \text{ ml (soln)}}{\text{ml (EtH) min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{22400 \text{ ml}}{n} \times \frac{1}{52(19.3)\text{ml}} = 8.5 \cdot 10^{-3} \frac{1}{n \text{ sec}}$$

*Corrected values are actual values minus t = 14 min and V_{STP} = 133.8 ml when the temperature of solution returned to 24.3°C.

TABLE XLI

Kinetic Data

Reaction: $EtMgNPr^i_2 + BuC{\equiv}C\text{-}H \longrightarrow EtH + BuC{\equiv}C\text{-}MgNPr^i_2$

Initial Concentrations: $EtMgNPr^i_2 = 0.210$ Et - Mg = 0.210

1-Hexyne = 0.210

Solvent: Diethylether Temperature: 24.3 °C

$V_{STP_\infty} = 100.8$ $V_{STP\ H_2O} = 141.7$

t corr(min)	V_{STP} corr(ml)	$k_2 \cdot 10^{-4}$	$k_3 \cdot 10^{-6}$
5	21	3.46	4.01
9	31.1	3.23	3.98
14	41.8	3.24	4.33
19	51.4	3.37	5.02
24	58.4	3.41	5.58
34	68.1	3.36	6.58
39	71.1	3.28	6.84
44	73.6	3.20	7.07
49	79.1	3.58	9.27
69	86.4	3.55	12.4
80	88.1	3.35	12.8
89	92.1	3.84	19.4
107	93.8	3.61	21.5
119	93.8	3.25	19.4
129	95.8	3.55	27.3
139	97.6	4.01	43.4

TABLE XLI (cont.)

t corr(min)	V_{STP} corr (ml)	$k_2 \cdot 10^{-4}$	$k_3 \cdot 10^{-6}$
149	99.0		
184	100.8		
204	100.8		

Second order rate constant = $3.2 \times 10^{-4} \frac{52 \text{ml (soln)}}{\text{ml(EtH) min}}$

$\times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{22400 \text{ ml}}{n} \times \frac{1}{52(19.3) \text{ ml}} = 6.3 \cdot 10^{-3} \frac{1}{n \text{ sec}}$

Corrected values are actual values minus t=6 min and V_{STP} = 90.5 ml when the temperature of solution returned to 24.3 °C.

SOME ABBREVIATIONS USED

cont.	continued
Et_3N	triethylamine
Et_2O	diethylether
G.C.	gas chromatograph or gas chromatographic
HMPT	hexamethylphosphorotriamide
l	liter
MeTHF	2-methyltetrahydrofuran
min	minute
ml	milliliter
mm	millimeter or millimole
MP	N-methylpyrrolidine
n	mole
pyr	pyridine
THF	tetrahydrofuran
THT	tetrahydrothiophene
tit	titrant
sec	second