A MECHANISTIC STUDY OF THE OLEFIN METATHESIS REACTION

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Terence K. Brunck
1972

A MECHANISTIC STUDY OF THE OLEFIN METATHESIS REACTION

by

Terence K^{EVIN}. Brunck

AN ABSTRACT OF A THESIS

Submitted to Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1972

ABSTRACT

A MECHANISTIC STUDY OF THE OLEFIN METATHESIS REACTION

by

Terence K. Brunck

The olefin metathesis reaction is a reaction in which the carbon-carbon double bonds of an olefin are broken and then remade with the substituents scrambled. The catalysts for this reaction are generally either heterogeneous or homogeneous complexes of tungsten or molybdenum.

The mechanism has been suggested to be a concerted [2 + 2]cycloaddition of the olefins in the coordination sphere of the metal followed by a retro-[2 + 2]cycloaddition which could give the rearranged products observed.

This research primarily studied an alternate mechanism in which a metallocycle would be formed. The metallocycle intermediate was formed by a reaction of 1,4-dilithiobutane with tungsten hexachloride and was found to give "metathesis-like" products when deuterated starting materials were used. All the results indicate that the metallocycle is the likely intermediate for the metathesis reaction.

A MECHANISTIC STUDY OF THE OLEFIN METATHESIS REACTION

by

Terence K$^{\text{evin}}$. Brunck

A THESIS

Submitted to Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1972

To the woman who will spend
the rest of her life with me

ACKNOWLEDGEMENT

The author wishes to express his special thanks to Dr. Robert H. Grubbs, without whose guidance and continuing understanding this thesis would never have existed.

The author also wishes to express his gratitude to Mr. Dale D. Carr for technical cooperation on portions of this work.

A final expression of thanks from the author is given to his parents, who gave him support and understanding for twenty-one years.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

Page

TABLE OF CONTENTS (Continued)

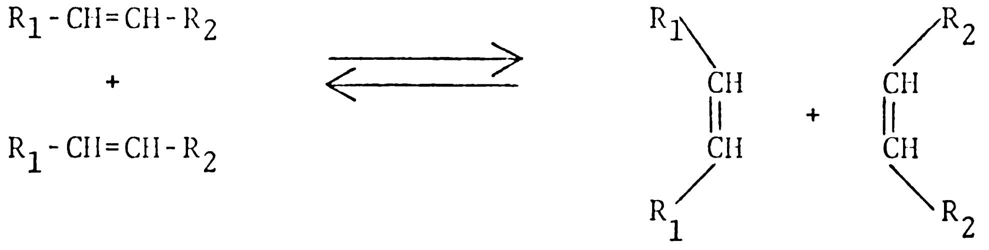
LIST OF TABLES

LIST OF SPECTRA

SPECTRA Page

I. INTRODUCTION

Olefin metathasis is a reaction in which carbon-carbon double bonds in two olefins are catalyticlly broken and then remade with the substituents scrambled.[1] Several types of



both heterogeneous and homogeneous complexes of transition metals[2,3] have been found to catalyze this type of rearrangement. Mechanisms for the observed reaction can be generally classified into two groups; 1) transalkylidenation, where the double bonds are actually broken and remade and 2) transalkylation, where the bonds to the substituents are involved.

It was shown by Calderon <u>et.al</u>. that the true mechanism is of the type 1 classification. 2-butene and 2-butene-d_8 were mixed in the presence of a catalyst, and only one new compound was observed.[4] As shown by the following reactions, this confirms the general reaction classification.

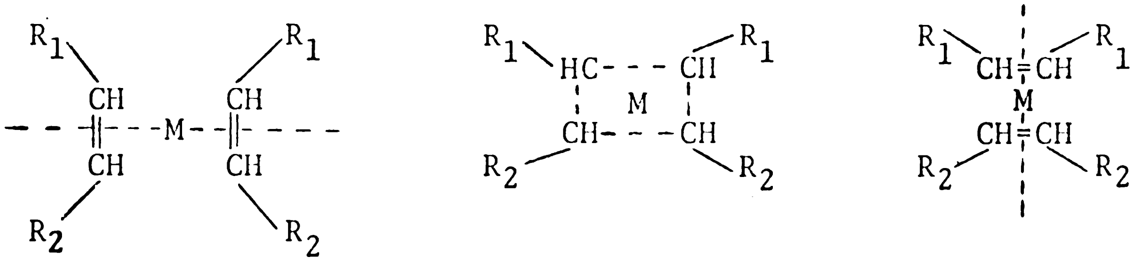
$$\begin{array}{c} CH_3-CH=CH-CH_3 \\ + \\ CD_3-CD=CD-CD_3 \end{array} \rightleftharpoons 2\ CD_3-CD=CH-CH_3 \qquad \text{Type 1}$$

1 new compound

$$\begin{array}{c} \mathrm{CH_3{-}CH{=}CH{-}CH_3} \\ + \\ \mathrm{CD_3{-}CD{=}CD{-}CD_3} \end{array} \rightleftharpoons \begin{array}{l} \mathrm{CH_3{-}CH{=}CH{-}CD_3} + \mathrm{CH_3{-}CD{=}CD{-}CD_3} + \\ \\ \mathrm{CD_3{-}CH{=}CH{-}CD_3} + \mathrm{CH_3{-}CD{=}CD{-}CH_3} \end{array}$$

4 new compounds

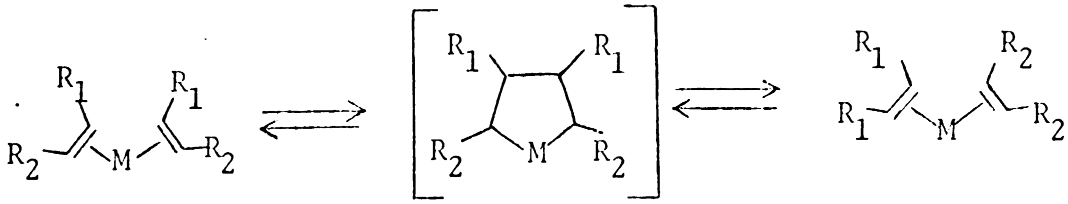
A mechanism for the reaction has been formulated as a (2 + 2) cycloaddition of the two olefins in the coordination sphere of the metal to form a "quasicyclobutane" intermediate,[5] which can decompose by a retro (2 + 2) cycloaddition. If a change in the symmetry plane of the intermediate is included, the rearranged products will be observed.[17,18]



Although the (2 + 2) cycloaddition is not observed thermally, the presence of the metal in this reaction permits a scheme to be written which conserves orbital symmetry.

An alternate mechanism of type 1 is suggested by the work of Katz[6] and Eaton.[7] Their work with the rhodium catalyzed rearrangement of strained carbocyclic rings systems has demonstrated that these reactions involve metal-carbon sigma bonded intermediates rather than a metal catalyzed electrocyclic reaction.

The analogous intermediate in the metathesis reaction is given in the general scheme below.



The general goals of this research were to a) prepare the metallocycle intermediate and b) determine if it gives the metathesis products. Secondary interests were to prepare stable metallocycles and search for new catalysts.

Metathesis catalysts to-date have been primarily heterogeneous or homogeneous tungsten or molybdenum compounds (for homogeneous, see Table). The mechanism for the second reaction proposed by Wang and Menapace[8] exposes an interesting route to the desired metallocycle intermediate.

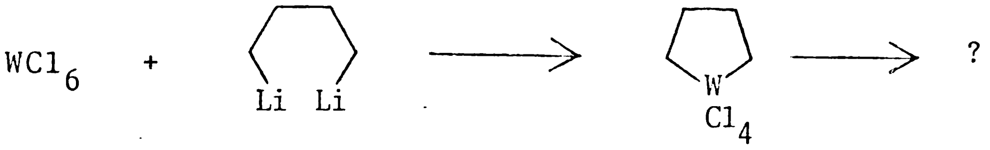
TABLE 1

Metathesis Catalysts

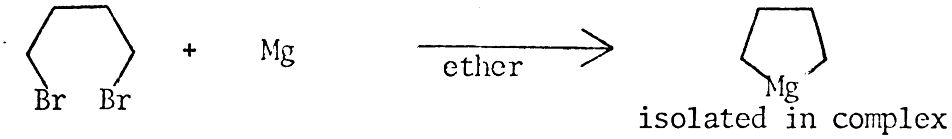
WCl_6 + EtOH + $EtAlCl_2$[1]
WCl_6 + 2 n-buLi [8]
$L_2Cl_2(NO)_2M$ + $RAlX_2$ [9]
L = ϕ_3P, PY, ϕ_3PO; M = M or W

$$WCl_6 + 2BuLi \rightarrow [WCl_4Bu_2] \rightarrow WCl_4 + C_4H_{10} + C_4H_8$$

This mechanism suggests that tungsten hexachloride, when treated with an equivalent of a 1,4-dilithio alkane, would yield the metallocycle intermediate.



It is also clear that this reaction could be generalized to any metal compound containing two displaceable groups. It was also noticed that magnesium compounds had already been prepared from the di-halide,[10] as follows, so that a metal-metal exchange reaction might also be useful.

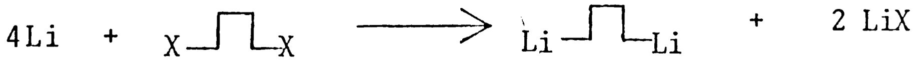


The specific thrust of this research was a) to prepare the 1,4-dilithiobutane reagent and b) to react this reagent with a variety of metal complexes to see if they yield the metathesis products. The second part requires deuterium labeling to gain evidence for the necessary rearrangement of the metallocycle intermediate in the metathesis reaction.

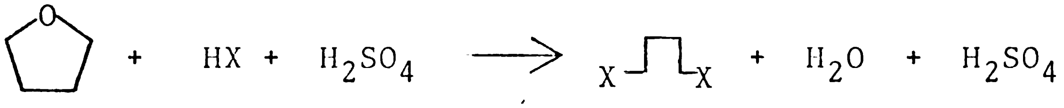
II. RESULTS AND DISCUSSION

A. Preparation of the di-lithium Reagents

The basic approach to the production of the 1,4-dilithio alkanes was a simple reaction between metallic lithium and the corresponding 1,4-dihaloalkane.



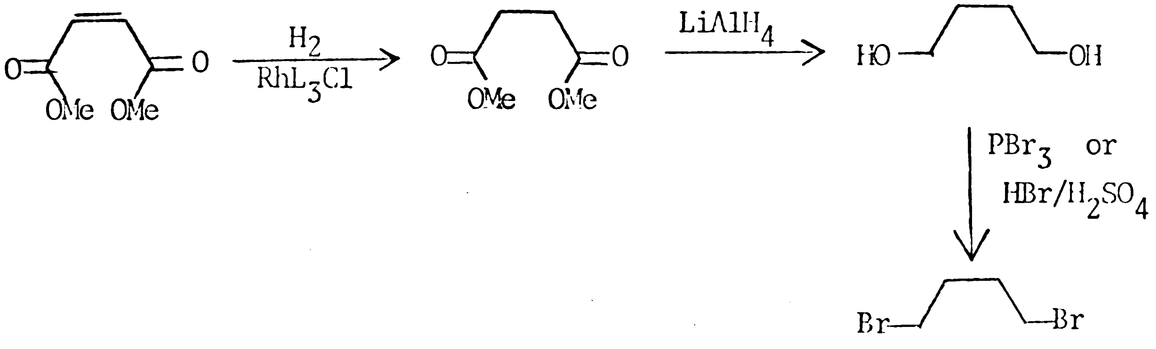
The production of the 1,4-dihalobutane was attempted by the cleavage of tetrahydrofuran by the appropriate acid halide.[11]



X = Cl, Br

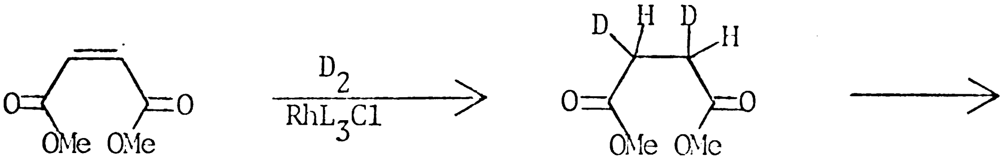
The high yields for these reactions (80-95%) made this the method of choice for bulk production of the 1,4-dihalobutane.

An alternate synthesis, as given below, was also worked out for the production of 1,4-dibromobutane.

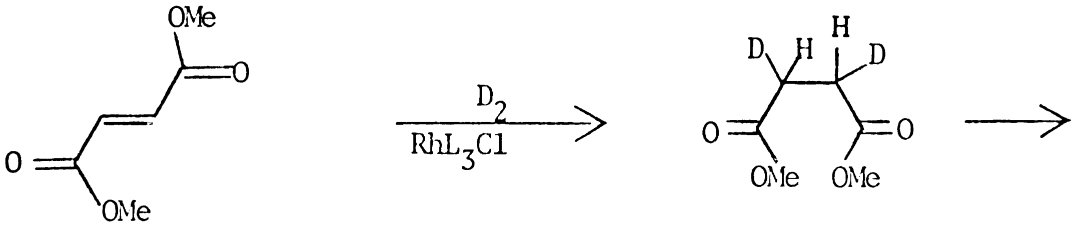


The overall yield for this sequence of reactions was at best 66%. The major difficulty with this route is the tendency of the diol to remain complexed to the aluminum hydroxide precipitate in the basic work up of the lithium aluminum hydride reaction. Acid work up was not feasible due to the extremely high solubility of the diol in water. The problem of complexation to the precipitate was attached successfully with the use of the continuous extraction technique using ether as the solvent. After 72 hours, nearly all of the diol product could be isolated.

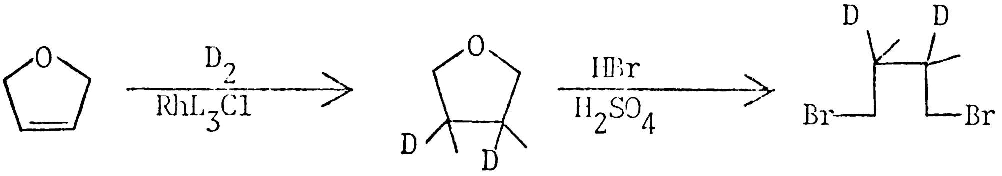
The advantage of this route lies in its utility for incorporating meso deuteriums into the dilithium reagents.



Using the dimethylmaleate starting material, meso 2,3-dideutero products are obtained as identified by nmr and ir, while using dimethylfumarate leads to d,1-product.

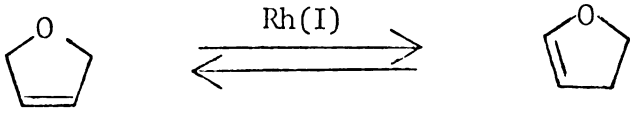


The di-deutero di-bromobutanes were also approached by the reduction of dihydrofuran with deuterium followed by hydrobromic acid cleavage. The reduction step, however,



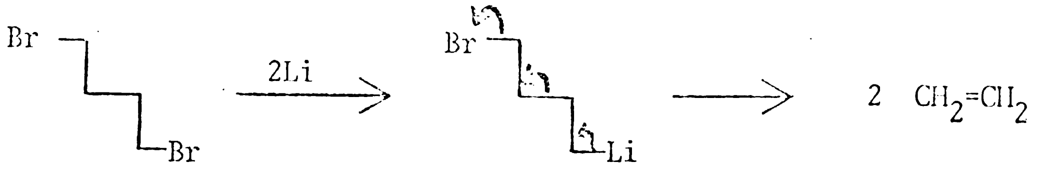
gave scrambled products as might be expected due to the isomerization of the double bond.

Isomerization of the oxacyclopentene-3 to the oxacyclopentene-2 was attempted with a rhodium(I) catalyst, $Rh_2(C_2H_4)_4Cl_2$, with little success as a mixture of the isomers always resulted.



The reaction between metallic lithium and the 1,4-dihalobutane proved to be the difficult step in the production of the dilithioalkanes. Several important side reactions kept the yields of this reaction low. (A significant portion of the research was carried out using yields of about 10% for this step.)

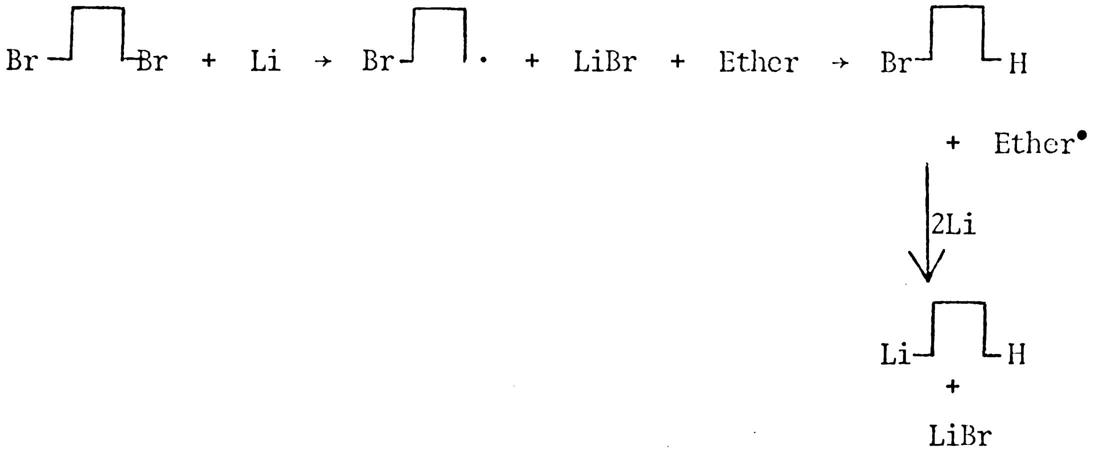
Two of the important side reactions are given below. The first is a Grob type fragmentation reaction which involves the breaking of a carbon-carbon single bond to form 2-molecules of ethene. This side reaction is aided by highly polar solvents and/or a good leaving group.



The obvious difficulty lies in choosing a solvent polar enough to form the lithium reagent without being so polar as to be able to solvate $Li^{\oplus}$ easily, facilitating the fragmentation. Along these lines, a variety of solvents were studied. Diethyl ether at -(5 → 10)°C was found to give the highest yields (30-40%) of dilithium reagent and a minimum of monolithium reagent (butyllithium). Tetrahydrofuran was found to give predominantly Grob fragmentation, while butyl ether gave no reaction.

The other method of slowing the Grob fragmentation reaction is by lowering the leaving ability of the substituents. Along these lines, 1,4-dichlorobutane was prepared by cleaving tetrahydrofuran with hydrochloric acid and sulfuric acid. It was found, however, that the yields of 1,4-dilithiobutane were still lower than if the dibromo compound were used. This was attributed to the lower reactivity of the chloride and to the fact that, due to the difference in solubilities of the lithium halides, the lithium chloride tended to obstruct the metal surface more. N-propyl ether was used for a portion of the research due to the observation that little Grob fragmentation occurred at -10°C in this solvent. However, it was discovered that this solvent gives a 60% yield of butyl lithium and only a

10% yield of the dilithium reagent from 1,4-dibromobutane. It is postulated that the monolithium compound might arise from the radical reaction shown below.

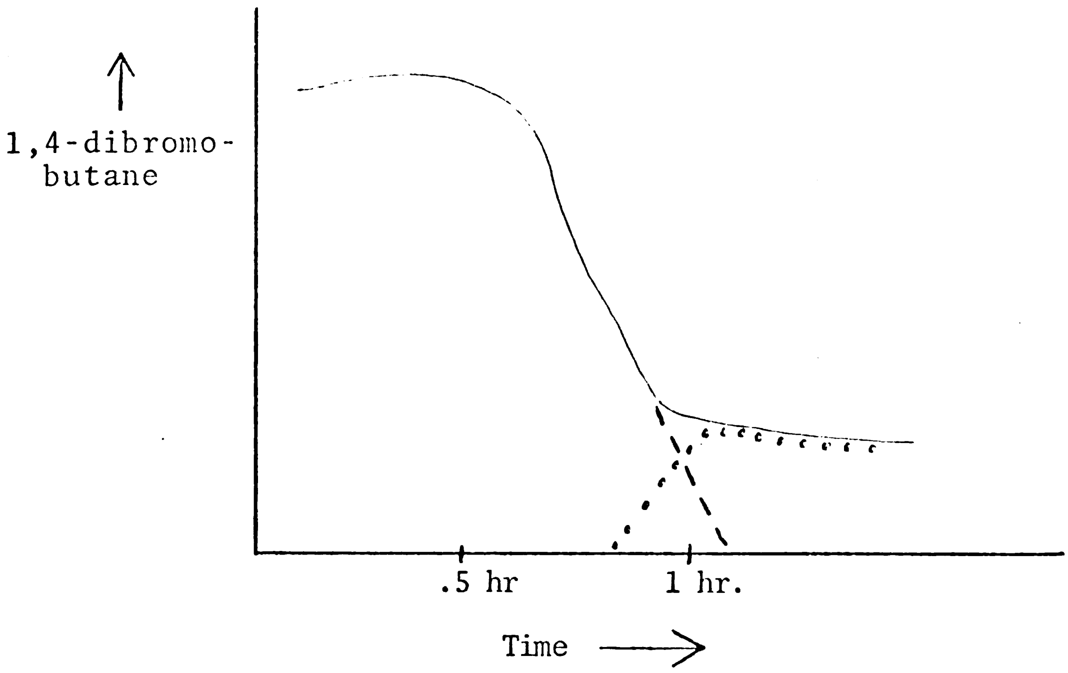


In order to eliminate this pathway, an ether could be used with no easily abstracted hydrogens, or warmer temperatures and more vigorous stirring could be employed.

For the above discussions it was, of course, necessary to measure the yields of the 1,4-dilithiobutane. This was performed in three ways. First, a system was developed for quenching a sample of the reagent (in ether) with water. The butane evolved was measured against a propane standard. This method, it is clear, does not actually give the yield of the dilithio reagent, but the combined yields of the dilithio reagent and the butyllithium also formed in the reactions. It was then decided to quench the ether solution with a benzene solution of bromine. The total titration of bromine gives the same information as the water quench, but, after appropriate work up procedures, gas chromatography of the solution with o-xylene as a standard gives the amount of di-bromobutane reactant remaining plus dibromobutane formed in the quench. The course of a typical reaction between lithium and 1,4-dibromobutane at -5° in diethyl ether was followed by quenching with bromine and the results are given in graph 1 below.

Graph 1

Amount of 1,4-Dibromobutane in Quench vs. Time of Reaction



The reaction seems to be slow to initiate, but relatively rapid thereafter. The graph indicates the decreasing amount of reactant by the dashed line and the likely formation of the dilithium reagent by the dotted line. This curve would indicate a maximum yield of dilithio butane of about 30% is possible under these conditions. The 1,4-

dibromobutane not accounted for here (70%) has probably been used in the Grob reaction and radical butyllithium formation mentioned above.

This result indicated that we should attempt to get a secure number for the yield of the dilithium reagent. A procedure worked out by West[12] produced 1,4-bis(trimethylsilyl)butane from 1,4-dibromobutane, lithium, and trimethyl silyl chloride. It might appear that his procedure gave a method for producing the dilithio reagent, but careful examination of the experimental section shows that he has not proven that he has made the reagent of interest to us. However, we successfully produced and isolated the disilylbutane product to be used as a standard using his method (see Spectra).

When quenching our ether solutions of the dilithium reagent, we added only the liquid part of the reaction mixture (i.e. no lithium was added) to a solution of trimethyl silyl chloride and a known amount of durene in ether. Simple gas chromatographic analysis of this quenching solution gives the yield of the disilylbutane, and, hence, the yield of dilithio reagent. As stated previously, yields measured in this manner varied from 25% to 40% depending on the reaction conditions.

B) Reactions of 1,4-dilithiobutanes with Tungsten Compounds

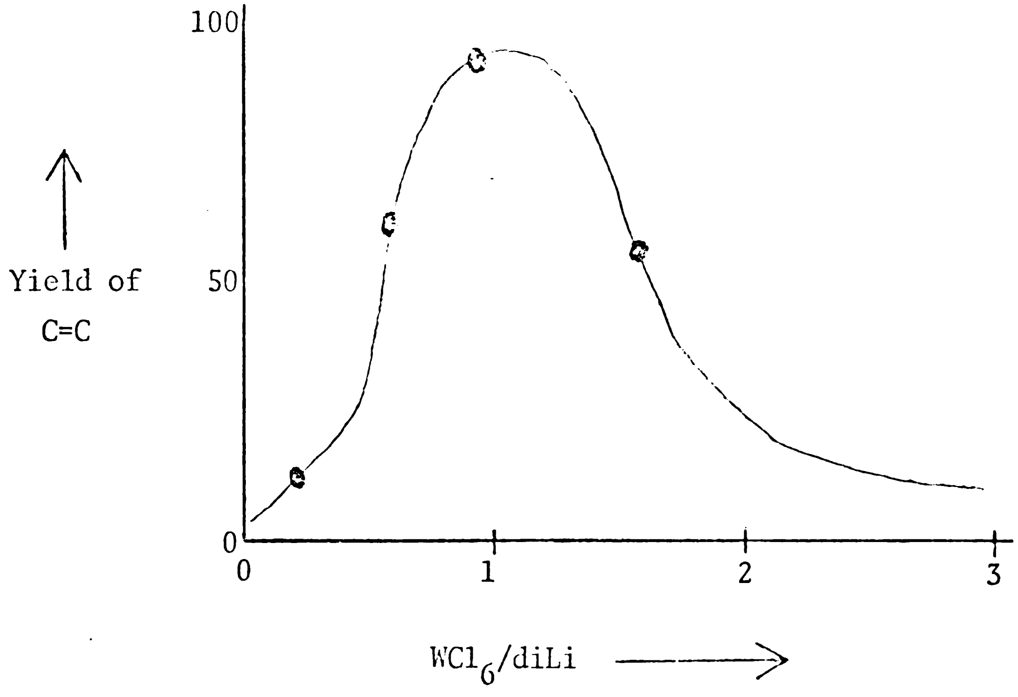
The second major phase of research involved the reaction of the dilithiobutane with various metal compounds, primarily tungsten hexachloride, as it should give a metallocycle of a known metathesis catalyst. The most important question to begin with is the yield of ethene.

Using a .05M solution of 1,4-dilithiobutane in dipropyl ether which also contained .52M butyllithium, it was found that, when added to tungsten hexachloride in benzene, a near quantitative yield of ethene was obtained (based an dilithium reagent). It should be noted that the yield of ethene is highly dependent on the purity of the tungsten hexachloride. For most work to be reported here, re-sublimed tungsten hexachloride stored in solution under nitrogen was used. Yield trials were run using crude tungsten which resulted in 10-15% yields of ethene.

Initially, there was some doubt about the origion of the ethene observed, as the total quantity was not large. There were two possible sources of ethene aside from the metathesis products. One would be a Grob fragmentation in the reaction vessel as described previously, and the other was the possible decomposition of ether in the presence of tungsten hexachloride. The first possibility was checked by placing a sample of the ethereal dilithio solution in benzene and observing any ethene production. After two days there was a trace amount of ethene measured while the yield data mentioned before could be obtained in roughly five minutes.

There was remaining the possibility that the solvent was decomposing in the strongly basic conditions. Several experiments were performed to exclude this possibility. 1,5-dibromopentane was reacted with lithium to form the 1,5-dilithiopentane compound in ether. This solution was added to tungsten hexachloride in benzene and no ethene was observed. A similar experiment using n-butyllithium in ether was run with the same result. The obvious and conclusive proof that the ethene was not coming from the decomposition of diethyl ether was to use a different solvent. Hence, some of the work to be discussed later was performed using dipropyl ether as the solvent. As mentioned previously, dipropyl ether does not give good yields of the dilithio reagent and the solution usually contains a large amount of n-butyllithium. It should be clear from the experiments above that diethyl ether is an appropriate solvent for forming the metallocycle intermediate.

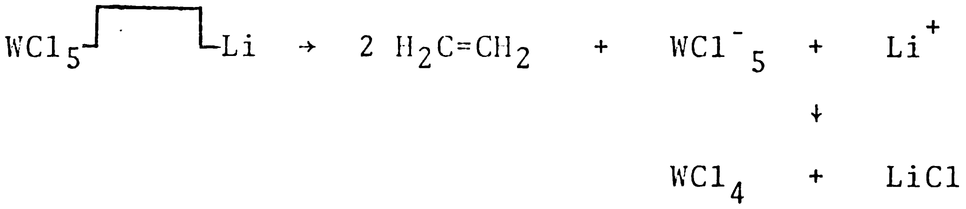
The following is a plot of yield of ethene as a function of the WCl_6 to di-Li ratio in the solution. The important result is that the highest yield of ethene occurs with equimolar amounts of the two reagents. This is another indication that the dilithium reagent is reacting stoichiometrically with the tungsten hexachloride and that the tungsten is not just a catalyst for another reaction.



Plot of Yield of C=C vs. WCl_6/diLi

Once it had been determined that ethene had been produced by some reactions of the 1,4-dilithioreagent and the tungsten, it became necessary to label the reagent to check for actual rearrangement products. To this end, 2,3-dideutero-1,4-dibromobutane (either meso or d,l) was reacted with lithium to form the dilithio reagent. When a solution of the dilithium compound in ether was added to tungsten hexachloride in benzene, ethene evolution proceeded as before. The ethene was purified by vapor phase chromatography and analyzed by mass spectroscopy at an ionization energy of 15ev. This ionization energy was chosen because it is roughly at this point that nitrogen ceases to be ionized. (This is important as the mass of N_2 and ethene D_0 are very nearly identical.) Also at this energy there is negligible fragmentation of the ethenes. The ethene products of the reaction described above was a mixture containing, on the average 6% D_2 ethene, 6% D_0 ethene and 88% D_1 ethene. Clearly, 12% of the total products were arising from a reaction which involved some type of rearrangement.

The question of a Grob type fragmentation reaction occurring with a lithio-tungsten butane compound as pictured below was raised.



$$\mathrm{WCl_5}\sqcap\mathrm{Li} \rightarrow 2\,\mathrm{H_2C{=}CH_2} + \mathrm{WCl^{-}{}_5} + \mathrm{Li^{+}}$$

$$\downarrow$$

$$\mathrm{WCl_4} + \mathrm{LiCl}$$

This type of reaction should be highly dependent on the reduction potential of the metal complex. With this in mind, several metal complexes of varying reduction potential were tried. If this were the major source of ethene, then metals with a reduction potential similar to that of tungsten hexachloride, might be expected to show evolution of ethenes. The table below gives the results of tests with various metal complexes and the reduction potential for the halides of the two states of interest as calculated from the change in heats of formation ($\Delta\Delta H_f{}^{\circ}$).

TABLE 2

Dilithium-Metal Reactions and Reduction Potentials

Complex	Yield of ethene	$\Delta\Delta H_8°$ (kcal/mole)
WCl_6	100%	-28
WCl_4	≈ 20%	-33.0
$TiCl_4$[a]	90%	-35.3
$(\phi_3P)_3RhCl_3$	0	-40.0[b,c]
$(\phi_3P)_2PtCl_2$	0	-35.5[d,c]

[a] $TiCl_4$ + reducing agent give a metathesis catalyst.[14]

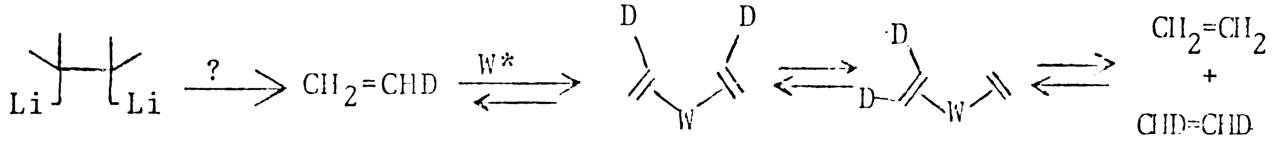
[b] Calculated from the $\Delta H_8°$ of $RhCl_3$ and RhCl.

[c] The phosphine ligands should stabilize the lower oxidation state and decrease the magnitude of $\Delta\Delta H_f°$.

[d] Calculated from the $\Delta H_8°$ of $PtCl_2$ and Pt(O).

It is clear from this table that there is no simple correlation between the reduction potential of the metal and the yield of ethene as one would expect if a Grob fragmentation were an important pathway in the production of the ethene. However, the Grob reaction may still have some importance in the overall reaction scheme.

The possibility existed that the dilithium reagent was reacting in some way to give only D_1 ethene, as the fragmentation would give, which then reacted further with the metathesis catalyst formed in the reaction to give the rearranged products observed.



A check of this possibility was made by preparing the metathesis catalyst with tungsten hexachloride and n-butyllithium in ether. To this was added 1,7-octadiene which should produce ethene if rearrangement were possible under these conditions.[19] None was observed.

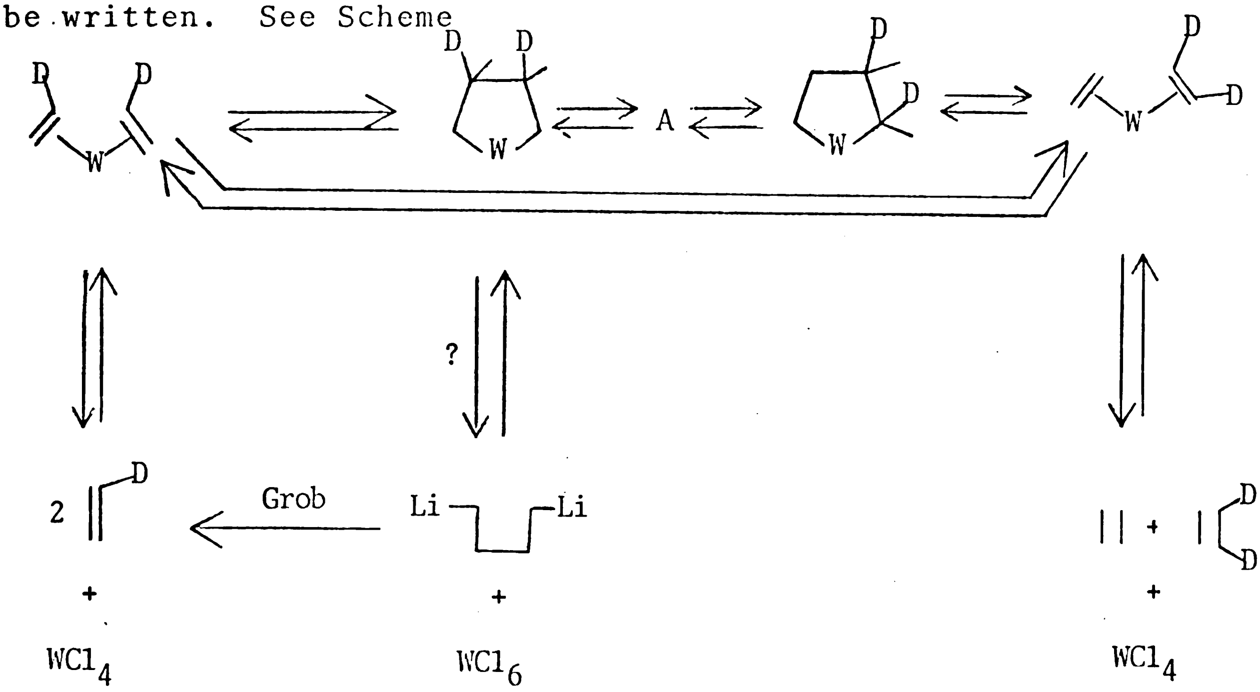
Further proof of this preferential complexation of ether over olefins was obtained by examining the stereochemistry of the D_2 ethenes produced by this reaction. If the ethenes were produced by some route which involved multiple complexation and de-complexation, there should be a random (50:50) distribution of <u>cis</u> and <u>trans</u> dideuteroethene formed. The meso and d,l-2,3-dideuterodilithiobutanes were produced as described above and added to tungsten hexachloride in benzene. The products were purified by vapor phase chromatography as before and the ethene collected in a liquid nitrogen trap. The sample was placed in a sodium chloride gas cell and an infrared spectra taken. These tests showed that the d,l-dideutero dilithiobutanes gave almost quantitatively <u>trans</u> dideutero ethene while the meso starting material gave mainly <u>cis</u> dideutero ethene.

Standards for this infrared work were obtained by the reduction of dideuteroethynes.[13] When calcium carbide is added to deuterium oxide (D_2O), D_2 ethyne results. If D_2

ethyne is reduced with zinc and hydrochloric acid, the cis isomer results with near perfect purity while if chromous chloride is used as the reducing agent, the trans isomer is found, also with very high purity. The products of these reactions were treated as metathesis products (purified and collected) and standard spectra were taken.

The work thus far demonstrates that the dilithium reagent can give metathesis like products from a reaction involving tungsten hexachloride and the mechanism does not involve multiple complexations of the ethenes. The information thus far does not exclude mechanisms which involve multiple reactions in the coordination sphere of the metal.

At this point, a preliminary mechanism for metathesis reaction containing all of the remaining possibilities can be written. See Scheme



SCHEME

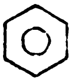
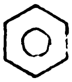
In this scheme, A is an intermediate or series of intermediates which, for the following kinetic discussion, will be assumed to be symmetrical.

In order to investigate the nature of A, it becomes essential to be assured that once the tungsten-olefin complex is formed, it is dissociated immediately by the ether. It is necessary to show that k_d is much larger than k_{-1}.

The most obvious method to check the rate of dissociation is to check the product ethene distribution at several solvent (benzene-ether) mixtures. If the dissociation is a significant step, then less rearrangement should occur as the ether concentration is increased. The table below gives the results at various ether concentrations.

TABLE 3

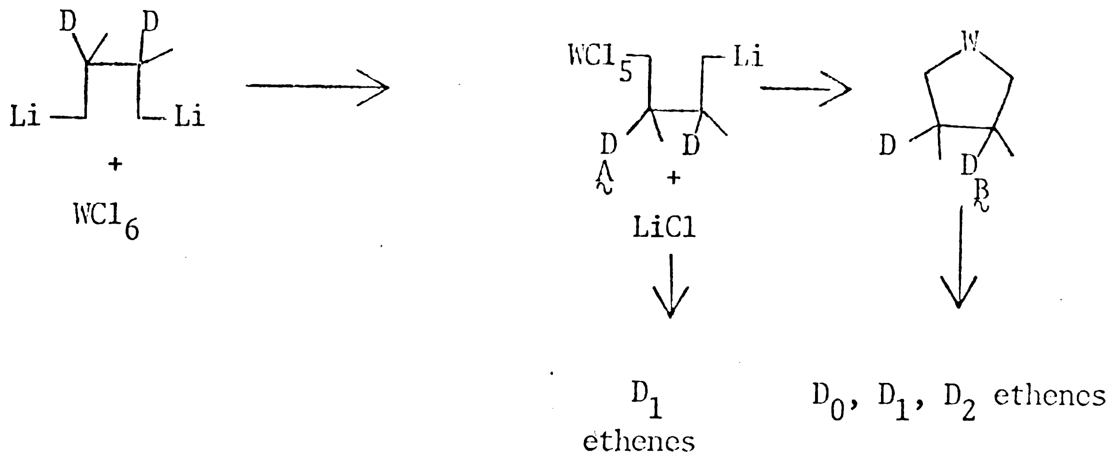
Deuterated Ethene Ratios from WCl_6

Isomer of 1,4 DiLi Reagent	Solvent	Ratio of Ethenes D_2/D_1
dl	Pr_2O/	1/17.5
meso	Et_2O/	1/16.6
dl	Et_2O/	1/17.5
dl	Et_2O/ = 1/3	1/7.3 1/4.8
dl	Et_2O/ = 2/5	1/4.8
dl	Et_2O/ = 1/2	1/2.75

It is clear that there is more rearrangement as the ether concentration increases and not less. Thus, no firm statement can be made about the dissociation step except that the change in rate of dissociation is less than other changes in rates which are due to the change in the solvent mixture.

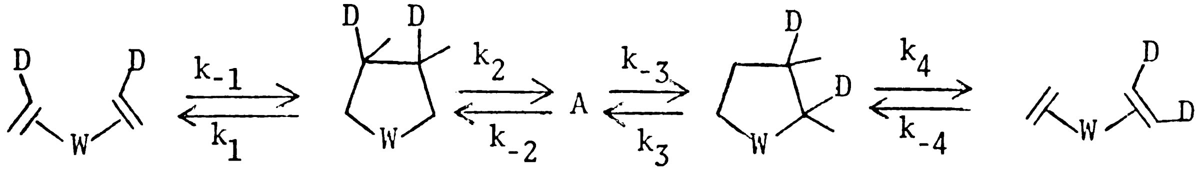
At this point, the actual deuterium ratio data must be carefully examined. As evident from the table given above, these ratios can vary depending on the solvent mixture. Before one can determine which values are most appropriate to be used in the kinetic work, some explanation of the observed variance in deuterium ratios must be given.

It has already been determined that the ethenes are evolving from some reaction between the dilithiobutanes and the tungsten hexachloride. This reaction can be broken into two general types, one being the reaction of only one end of the lithium reagent with the tungsten and the other being the reaction to form the metallocycle. A reaction of the first type, if it gives ethene by some direct reaction, can only give D_1 ethene as a product. However, the metallocycle can give all of the various ethene products by some reaction or combination of reactions. The sequence given below shows these possibilities.



It is generally true that good donating ligands can stabilize a high oxidation state in a metal where a withdrawing ligand will stabilize the lower oxidation state. In the case under examination, it is likely that the ether will stabilize the intermediate A so that it will have time to react again to give the metallocycle B. Thus, as the ether concentration increases, the amount of metallocycle increases, and more rearrangement may be observed.

It is possible to treat the basic rearrangement mathematically if a few simple assumptions are made. First



the assumption is made that A is symmetrical and present in a steady state; that is $k_2=k_3$ and $k_{-2}=k_{-3}$. Secondly the assumption is made that the secondary deuterium isotope effects are negligible. This is equivalent to setting $k_1=k_4$

and $k_{-1}=k_{-4}$. With these simplifications and the assumption that the olefin complex dissociates immediately ($k_{-1}=0$), one can solve for the ratio k_1/k_2 in terms of the observed deuterated ethenes produced in the reaction (see Appendix). From this treatment one obtains

$$k_1/k_2 = 1/4\ D_1/D_2 - 1/2$$

However, no substantial information about the rate of dissociation has been obtained yet, so the kinetic system may be somewhat more complicated. The treatment above also assumes that the formation of the metallocycle is essentially instantaneous. If this is not valid, the kinetics take on another degree of complexity.

The problem would seem to be that the Grob type of fragmentation reaction is occurring and is influencing the deuterium ratios in the products. This problem can be attacked in ways similar to those described in the preparation of the dilithium reagent. To help eliminate the fragmentation when reacting the dilithium reagent with tungsten hexachloride cooler temperatures could be used or a more polar solvent might be attempted. A different tungsten compound with less of a reduction potential would also help slow the fragmentation, however, this would most probably also alter the product ratios since this potential is important to the rearrangement. Research in this area would be difficult at best since factors influencing the fragmentation tend also to influence the rearrangement. Clearly this is an area for future examination.

To summarize the results of this portion of the research, it has been found that a reaction between 1,4-dilithiobutane and tungsten hexachloride give variable yields of ethene which can be nearly quantitative. It has been demonstrated by deuterium labeling that the various ethene products do not arise from multiple complexations of the olefins. Simultaneously, it has been clearly demonstrated that the above reaction does give metathesis like products, however, no unequivical kinetic information can be obtained due to the influences of solvents and side reactions.

The third, and final, section of this research was a search for other potential metathesis catalysts. The following table summarizes the result of some basic test reactions between the 1,4-dilithiobutane and some metal chlorides.

TABLE 4

Dilithium-Metal Reactions

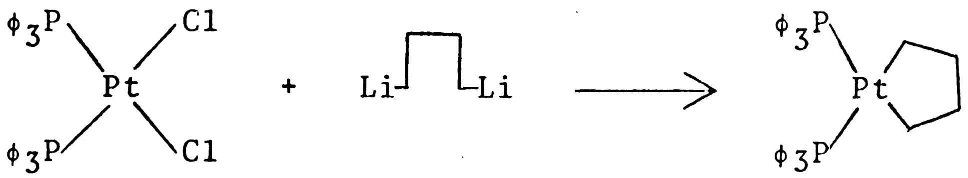
Metal Compound	Yield of C_2H_4 in %
WCl_4	$\approx$20%
$TiCl_4$[a]	$\approx$90% (D_2/D_1 = 1/20)
$(\phi_3P)_3RhCl_3$[b]	0%
$(\phi_3P)_2PtCl_2$[b]	0%
$SnCl_4$	0%
$(PY)_2MoCl_2$	trace

[a] $TiCl_4$ + reducing agent give a metathesis catalyst.[14]

[b] Evidence indicates a stable metallocycle is formed.

None of the systems listed above were studied in depth in this research due to the problems encountered with the tungsten hexachloride. It is important to note that titanium tetrachloride in benzene when reacted with a solution of d,l-2,3 dideutero-1,4-dilithiobutane in ether does give "metathesis-like" products as one would expect from other literature.[14]

One other interesting aspect of the trials with the rhodium and platinum complexes was the evidence found for the formation of stable metallocycle complexes. These reactions gave no ethenes even when heated in hot water baths. Proton magnetic resonance spectra were taken of both products in chloroform-d which indicated the possibility of a metallocycle. Analysis of the platinum complex, which is the most easily purified being air and water stable, also indicated the one to one reaction pictured below.



It is, of course, possible that a dimer of this complex was formed, but this would not seem to be statistically very probable. The crystal structure is presently being attempted to determine this point conclusively. If the platinum complex is in reality a metallocycle, the inference from proton magnetic resonance spectroscopy would be that the rhodium complex is also a metallocycle. Further enlightenment on these facts could lend excellent support to idea of the importance of metallocycle intermediates.

In conclusion, it has been demonstrated that in one reaction in particular, the metathesis reaction, and very possibly many more reactions, as indicated by the formation of the stable complexes of rhodium and platinum given above, metallocycle compounds must be considered the most likely intermediates in the reaction scheme. A general technique for probing suspected reactions in regard to their possibility of metallocycle intermediates has been developed using the dilithium reagent. This new technique should prove to be a useful tool for studying transition metal reaction mechanism.

II. EXPERIMENTAL

A. Physical Measurements

1. Spectra

Proton magnetic resonance spectra were obtained using a Varian T60 high resolution spectrometer with tetramethylsilane as an internal standard where important.

Mass spectra were performed using a Hitachi RMU-6-E mass spectrometer. The ethene samples were ionized with 15ev electrons since the nitrogen impurity is not ionized by this low energy bombardment and no observable fragmentation of the ethene occurs.

Infrared spectra of the ethenes were taken on a Beckman IR7 spectrometer using sodium chloride windows. All ether infrared spectra were taken with a Perkin Elmer 237B Grating Infrared Spectrophotometer using potassium bromide discs.

2. Vapor Phase Chromatography

All vapor phase chromatography work was performed using a Varian Aerograph (Model 90P) gas chromatograph with a helium carrier. The vapor samples were run using a ten foot column of 10% paraffin oil supported an alumina. Temperatures for good separation range from about 50°C to 105°C.

Columns used for liquid samples were Varian products containing FFAP and 10% SE30.

3. Collection of Vapor Samples

The ethene samples for mass spectrometry and infrared work were collected using two methods. First, a gas burrett was attached to the gas chromatograph and ethene collected at atmospheric temperature and pressure. These samples, as one might expect, were fairly dilute for most infrared work. The second method utilized a liquid nitrogen trap filled with standard Ottawa sand. This method was quite adequate for all work attempted.

B. Preparations and Reactions

1. 1,4-dibromobutane from Tetrahydrofuran[11]

A 50 ml. round-bottom flask equipped with a reflux condensor was warmed to 100°C after 15 ml. of 48% hydrobromic acid (conc.) (.111 moles) was added to 2.8 ml. (.029 moles) of tetrahydrofuran. When the proper temperature was reached, 5.4 ml. of sulfuric acid (conc.) was added with stirring and both heating and stirring was maintained for 3.5 hours. After cooling, about 20 ml. of methylene chloride was added and all of the liquids were transferred to a separation funnel. The layers were separated and the organic layer was washed once with water and once with a saturated sodium bicarbonate solution. The organic mixture was dried with magnesium sulfate and the solvent removed by roto-evaporation. 6.3 grams of crude product was obtained (Spectra 1). The pure product distills at about 43°C at .7 torr.

2. Meso-2,3-dideuterodimethylsuccinate from dimethyl Maleate[15]

A 250 ml. glass bomb was equipped with a safety valve, pressure guage, and gas valve and the system was checked for leaks. The system was then continuously flushed with nitrogen as .1995 grams of Wilkinson's Catalyst ($Rh(\phi_3P)_3Cl$) was added. 25 ml. of ethanol (purified) and 25 ml. of benzene (purified) were added to the bomb. The system was then pressurized to 8 psi with deuterium gas and the color of the solution was observed to change from deep maroon to yellow-orange. The pressure was then released and 5.3 ml. dimethyl maleate was added while flushing again with nitrogen. The system was then pressurized to 40 psi with deuterium. After the addition of the dimethyl maleate, the solution became deep red again. When the pressure reached nearly zero, the system was again pressurized with deuterium. After this final addition of deuterium the mixture can be distilled to obtain the desired product, or more dimethyl maleate can be added and the procedure repeated again. In general, this procedure can be repeated between five and ten times before the catalyst becomes poisoned. The solvents can be removed by roto-evaporation and the product distilled from the catalyst at 52°C at .9 torr. Yields for this reaction range from 90-95% (see Spectra 2). To eliminate any question about hydrogen-deuterium exchange in the solvent, pure benzene can also be used for the reduction.

3. d,l-2,3-dideuterodimethylsuccinate from dimethylfumarate[15]

The procedure here for the preparation of the catalyst and reduction system are identical with that given previously. However, since dimethyl fumarate is crystalline and not readily soluble in benzene, the entire portion of reactant can be added at one time to the activated catalyst. The system is pressurized with deuterium as before and when no further deuterium uptake is noted on the pressure guage the product can be worked up as described above (see Spectra 3 and 4). Yields for this reduction are similar to those above.

4. meso-2,3-dideutero-1,4-butanediol from meso-2,3-dideutero dimethyl succinate

A 1 liter 3-neck round-bottom flask was equipped with a reflux condensor, mechanical stirrer and 250 ml. addition funnel. The system is flushed with nitrogen and 5 grams of lithium aluminum hydride were added to about 300 ml dry ether with stirring. Along with 200 ml. of dry ether, 16.52 (.11 moles) of meso-2,3-dideuterodimethyl succinate were placed in the addition funnel. An ice bath was placed around the flask and the solution of ester was added dropwise until all had been added. The mixture was allowed to warm to room temperature for about two hours after which a basic work-up was performed. 5 ml. of water was added slowly with rigorous stirring to the reaction mixture after which, 5 ml. of 15% sodium hydroxide was added. Finally, 15 ml. of water were added and large flakey crystals appeared. The ether was filtered from the crystals after which the crystals were placed in a continious extractor for three days (ether solvent) to remove the diol product from the surface of the crystals. The solvent was removed using the roto-evaporation technique and the diol was distilled (B.P. 98-99°C at 1.5 torr). In general, it is not necessary to purify by distillation at this time since the following step involves the addition of water, which is probably the major impurity. Yields for this step range from 50%, if no continuous extraction is used, to about 90% if the precipitate is washed thoroughly as described above (see Spectra 5).

5. d,l-2,3-dideutero-1,4-butane diol from d,l-2,3-dideuterodimethyl succinate

The procedure for this reaction and yields are identical with that previously described for the meso compound (see Spectra 6).

6. meso-2,3-dideutero-1,4-dibromobutane from meso-2,3-dideutero-1,4-butane diol

a) Using phosphorous tribromide

A 100 ml. 3-neck round-bottom flask was equipped with a reflux condensor and a 25 ml addition funnel. 25 ml. of phosphorous tribromide were placed in the flask and cooled to -8°C. 20.5 ml. of crude diol were placed in the addition funnel and added dropwise to the cooled phosphorous tribromide. After the addition is complete, the mixture is permitted to warm to room temperature, at which point, it is heated to 80°C overnight. When cool, 50 ml. of water were added slowly to the reaction mixture. The organic layer was separated and the aqueous layer washed twice with methylene chloride. All organic portions are combined and dried with magnesium sulfate after which the solvent was removed by roto-evaporation. The crude product is distilled (43°C at .7 torr). Yields for this reaction are generally about 90%, however, if the reaction mixture is allowed to remain heating for and extended period of time, the yield may drop substantially (see Spectra 7).

b) Using hydrobromic acid

The procedure using hydrobromic acid on the diol is essentially the same as the hydrobromic acid cleavage of tetrahydrofuran described above. This reaction tends to be a bit more vigorous as the diol loses two moles of water rather than one. Yields are more consistantly about 90% than for the above reaction.

7. d,1-2,3-dideutero-1,4-dibromobutane from d,1-2,3-dideutero-1,4-butane diol.

Preparation of this compound was essentially the same as those for the meso compound (see Spectra 8).

8. 1,4-dilithiobutane from 1,4-dibromobutane

A 100 ml. 3-neck round-bottom flask was equipped with a 25 ml. addition funnel, a gas adaptor, and a serum cap over one of the necks. 1.2 grams of lithium ribbon was cut into small pieces and placed in the flask with 20 ml. of dry, purified ether. 2 ml. of dibromobutane (also deuterated compounds can be used) is mixed with 20 ml. of dry, purified ether in the addition funnel. The flask is cooled to 0°C and 2-3 ml. of the dibromobutane solution is added with vigorous stirring to initiate the reaction. When the solution becomes cloudy, it is cooled to -8°C and the remainder of the dibromobutane solution is added dropwise to the reaction mixture. Twenty-five minutes after the addition is complete, the yield of the dilithiobutane has maximized at about 30%. Quenching experiments described below indicate that only a small amount of butyllithium is formed using this method. Solutions of dilithiobutane in ether are stable for several hours at -78°C.

Reactions run in other solvents were procedurally very similar, however, none gave acceptable yields of the dilithio reagent.

9. Quenching reactions of 1,4-dilithiobutane

a) Water

2 ml. of freshly prepared dilithio reagent solution was injected by syringe into a half-pint evacuated bottle containing about 5 ml. water. After gas evolution ceased, 10 ml. of propane gas was added with a syringe. Gas chromatography gives the yield of butane forming reactants in the dilithio solution.

b) Bromine

2 ml. of the dilithium solution was placed in a pre-cooled, 3 neck 100 ml. round-bottom flask equipped with a stopper, burette, and gas adaptor. The system was flushed with nitrogen before the dilithium solution was added. A solution of 4.4 ml. of bromine was diluted with 20 ml of benzene (4.02 MBr_2) was placed in the burrette and titrated into the dilithium solution. The total titration values given the same information as the water quench. However, the titration mixture was worked up with a sodium sulfite solution and the organic portion dried and analyzed by gas chromatography. This procedure gives total yield of dilithium reagent plus unreacted starting compound. O-xylene was used as a standard for the gas chromatography work (10% Se-30 column at 125°C).

c) Trimethyl silyl chloride

In an evacuated 5 dram vial covered with a serum cap is placed .44 ml. of trimethylsilylchloride and an accurately measured amount (about 40 mg.) of durene. The components are then dissolved in about 2 ml. of dry ether. To this is added 2 ml. of the dilithium solution. The mixture is swirled for about 5 minutes after which the mixture is analyzed by gas chromatography (FFAP column at 80°C until disilyl product is off then jump to 100°C to observe durene standard). This technique give the actual yield of dilithium reagent. Standards of the 1,4-bis(trimethylsilyl) butane were prepared by the method of West.[12]

10. 2,3-dideutero-1,4-dilithiobutane from 2,3-dideutero-1,4-dibromobutane.

All dilithio compounds were made as previously described and quenched in a similar manner.

11. Tungsten tetrachloride from Tungsten hexachloride

A thirty-two millimeter Pyrex tube was sealed at one end and filled with 21 grams of tungsten hexachloride and 1.12 grams of aluminum. The tube was evacuated to about 1 torr and sealed. The tube was placed in a dual temperature oven with the reactants at the hot end (475°C) and the receiving end at 275°C. This heating was maintained for 48 hours. The tube was then placed in a smaller oven at 225°C to sublime the aluminum trichloride away from the product. A black product was formed in about a 30% yield. This being a standard preparation, no analysis was performed.

12. Tris-triphenylphosphinerhodiumtrichloride from rhodium trichloride trihydrate

.501 grams of rhodium trichloride trihydrate, 1.61 grams of triphenylphosphine and 12 ml. ethanol were placed in a 25 ml. flask which was flushed with nitrogen. Heating to boiling for ten minutes and cooling produced 1.07 grams of product (57% yield).

13. Bis-triphenylphosphine platinum dichloride from potassium tetrachloroplatinete(II)[16]

1 gram of potassium tetrachloroplatinate (II) was dissolved in 10 ml. of water and 5 ml. glacial acetic acid. 1.5 grams of triphenylphosphine was added to the warm solution. The reaction was refluxed for about 20 minutes until the solution was slightly pink. After cooling 1.12 grams of white crystalline product was collected and washed with water, ethanol, and ether.

14. Reactions of various metal complexes with 1,4-dilithiobutane

The reactions of metal compounds with 1,4-dilithiobutane were all carried out in a similar fashion. The metal compound is placed in a 25 mm x 200 mm test tube with a known amount of solvent, usually benzene. The test tubes were covered with a serum cap and evacuated. A known amount of dilithium reagent is added by syringe to the metal compound solution. The vapors are then analyzed by gas chromatography

12. Tris-triphenylphosphinerhodiumtrichloride from rhodium trichloride trihydrate

.501 grams of rhodium trichloride trihydrate, 1.61 grams of triphenylphosphine and 12 ml. ethanol were placed in a 25 ml. flask which was flushed with nitrogen. Heating to boiling for ten minutes and cooling produced 1.07 grams of product (57% yield).

13. Bis-triphenylphosphine platinum dichloride from potassium tetrachloroplatinete(II)[16]

1 gram of potassium tetrachloroplatinate (II) was dissolved in 10 ml. of water and 5 ml. glacial acetic acid. 1.5 grams of triphenylphosphine was added to the warm solution. The reaction was refluxed for about 20 minutes until the solution was slightly pink. After cooling 1.12 grams of white crystalline product was collected and washed with water, ethanol, and ether.

14. Reactions of various metal complexes with 1,4-dilithiobutane

The reactions of metal compounds with 1,4-dilithiobutane were all carried out in a similar fashion. The metal compound is placed in a 25 mm x 200 mm test tube with a known amount of solvent, usually benzene. The test tubes were covered with a serum cap and evacuated. A known amount of dilithium reagent is added by syringe to the metal compound solution. The vapors are then analyzed by gas chromatography

12. Tris-triphenylphosphinerhodiumtrichloride from rhodium trichloride trihydrate

.501 grams of rhodium trichloride trihydrate, 1.61 grams of triphenylphosphine and 12 ml. ethanol were placed in a 25 ml. flask which was flushed with nitrogen. Heating to boiling for ten minutes and cooling produced 1.07 grams of product (57% yield).

13. Bis-triphenylphosphine platinum dichloride from potassium tetrachloroplatinete(II)[16]

1 gram of potassium tetrachloroplatinate (II) was dissolved in 10 ml. of water and 5 ml. glacial acetic acid. 1.5 grams of triphenylphosphine was added to the warm solution. The reaction was refluxed for about 20 minutes until the solution was slightly pink. After cooling 1.12 grams of white crystalline product was collected and washed with water, ethanol, and ether.

14. Reactions of various metal complexes with 1,4-dilithiobutane

The reactions of metal compounds with 1,4-dilithiobutane were all carried out in a similar fashion. The metal compound is placed in a 25 mm x 200 mm test tube with a known amount of solvent, usually benzene. The test tubes were covered with a serum cap and evacuated. A known amount of dilithium reagent is added by syringe to the metal compound solution. The vapors are then analyzed by gas chromatography

for ethene, methane, ethane, propane, butane and butenes.

One reaction involving tungsten hexachloride was quenched with 5 ml. of 10% sodium hydroxide solution and the organic layer analyzed by gas chromatography for butylchloride. There were no compounds of boiling point higher than benzene found in the mixture.

15. Formation of Stable Metallocycles

a) Using Platinum

In a test tube containing .5 millimoles of bis-triphenylphosphine platinum dichloride and 10 ml. of benzene was added .5 millimoles of 1,4-dilithio butane in ether. The solvents were removed using vacuum to dryness. Chloroform-d was then added and a sample taken for NMR (see Spectra 9). The solution was then washed with water and a second spectrum taken (see Spectra 10). Integration suggests that the metallocycle had been formed.

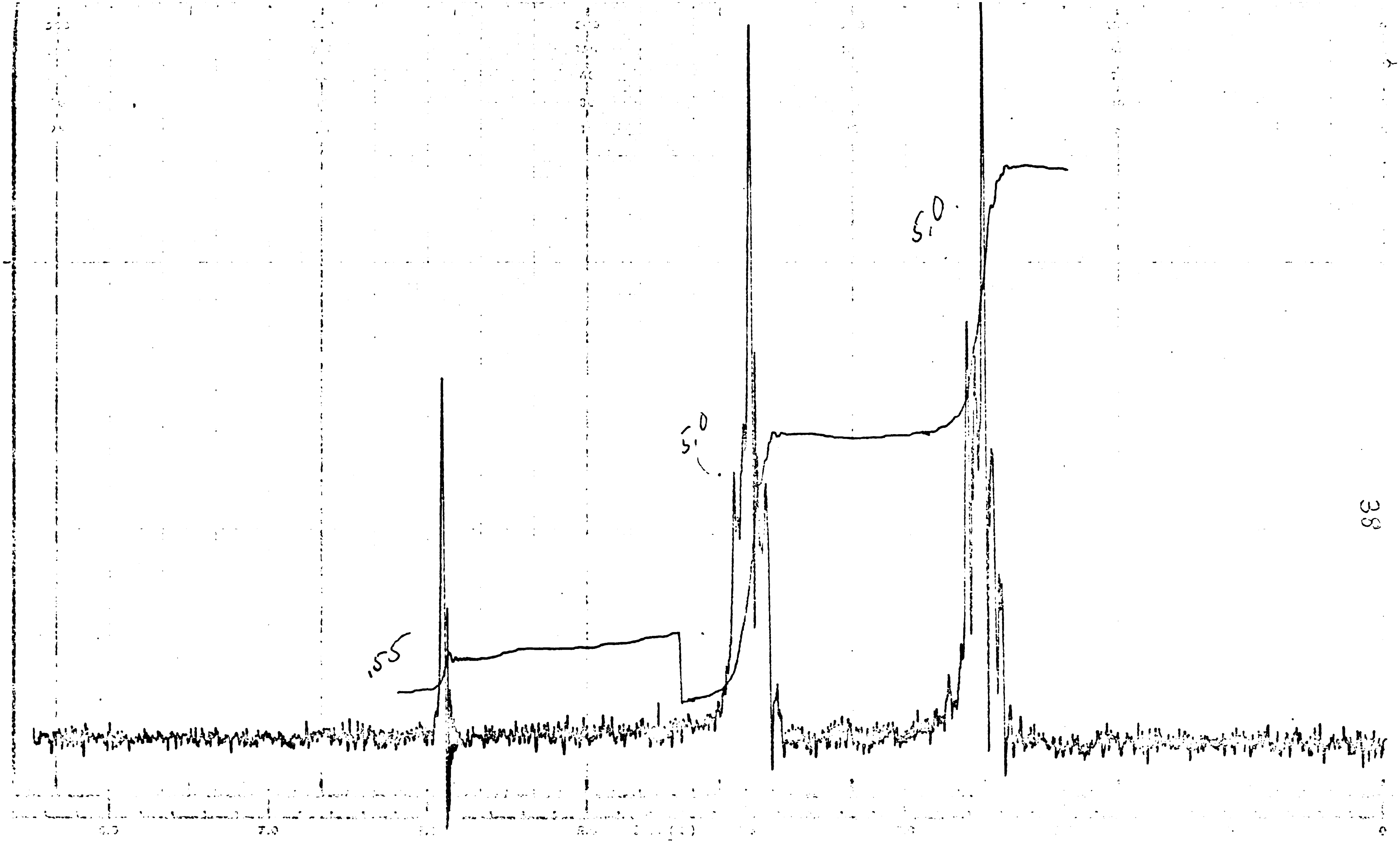
Anal. Calcd.: C, 61.93; H, 4.93; P, 7.98; Pt, 25.14.
Found: C, 61.82; H, 4.86; P, 7.90; Pt, 25.10.

b) Using Rhodium

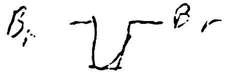
The reaction was run identically with that above except that tris-triphenylphosphine rhodium trichloride was used. The spectra was quite similar to the platinum complex, however, the rhodium metallocycle was not stable to water (see Spectra 11 and 12).

16. Ethene d_2, Cis and trans[13]

The procedure used was identical to that in the reference except that a glass bomb was used as the reaction vessel. The samples for the infrared work were purified by gas chromatography and collected in liquid nitrogen traps. The main absorbtion for cis d_2 ethene occurs at 843 cm^{-1} and for trans d_2 ethene at 989 cm^{-1}. D_1 ethene has a major absorbtion at 943 cm^{-1} and D_0 ethene at 952 cm^{-1}.



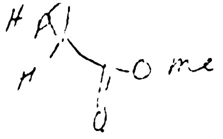
0
4
47
.05



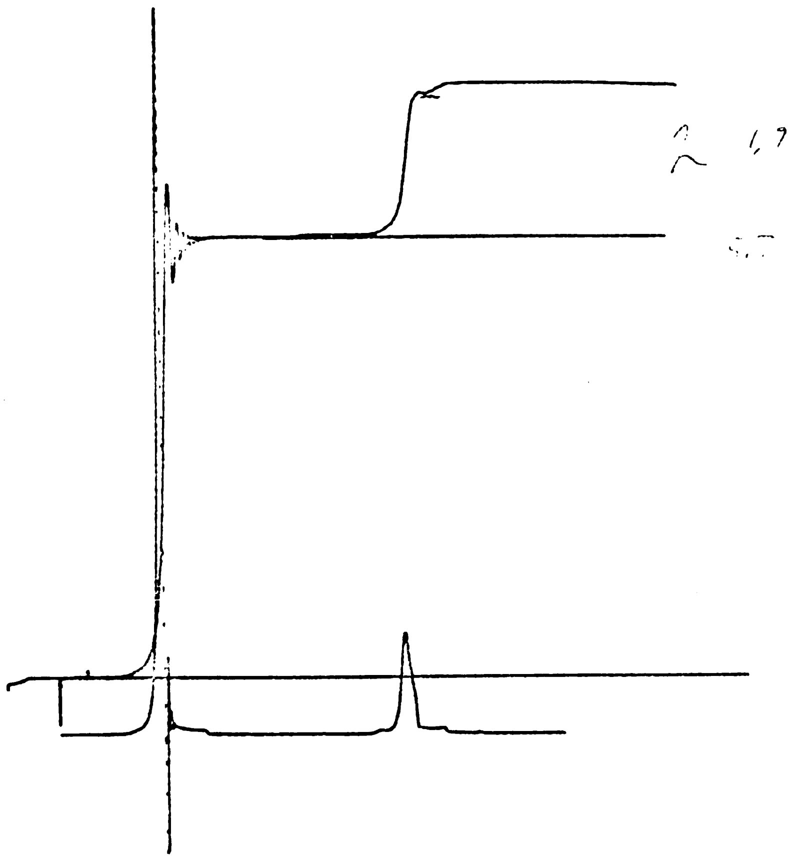
CCl_2H_2

6/25

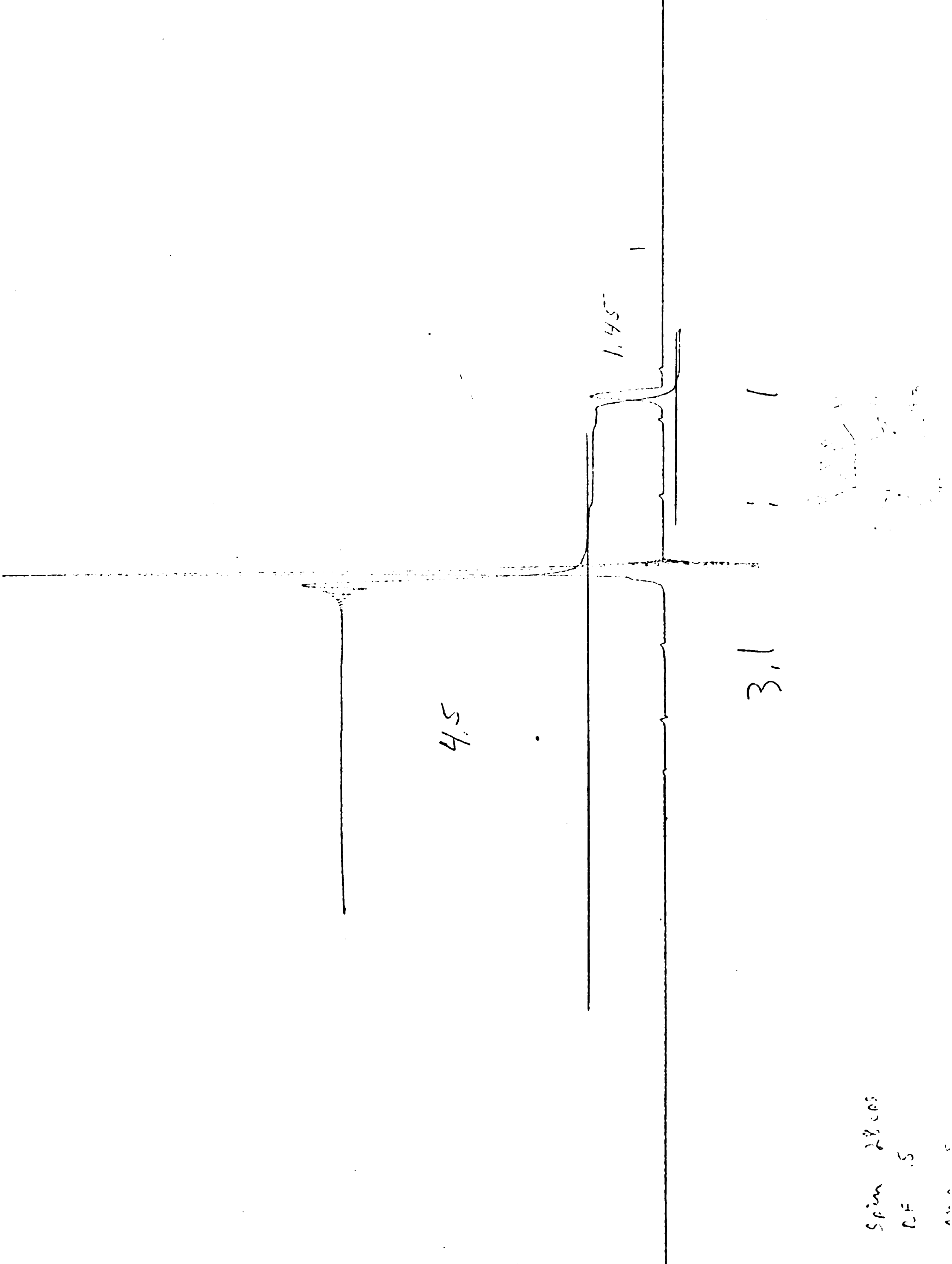
Su 71-3

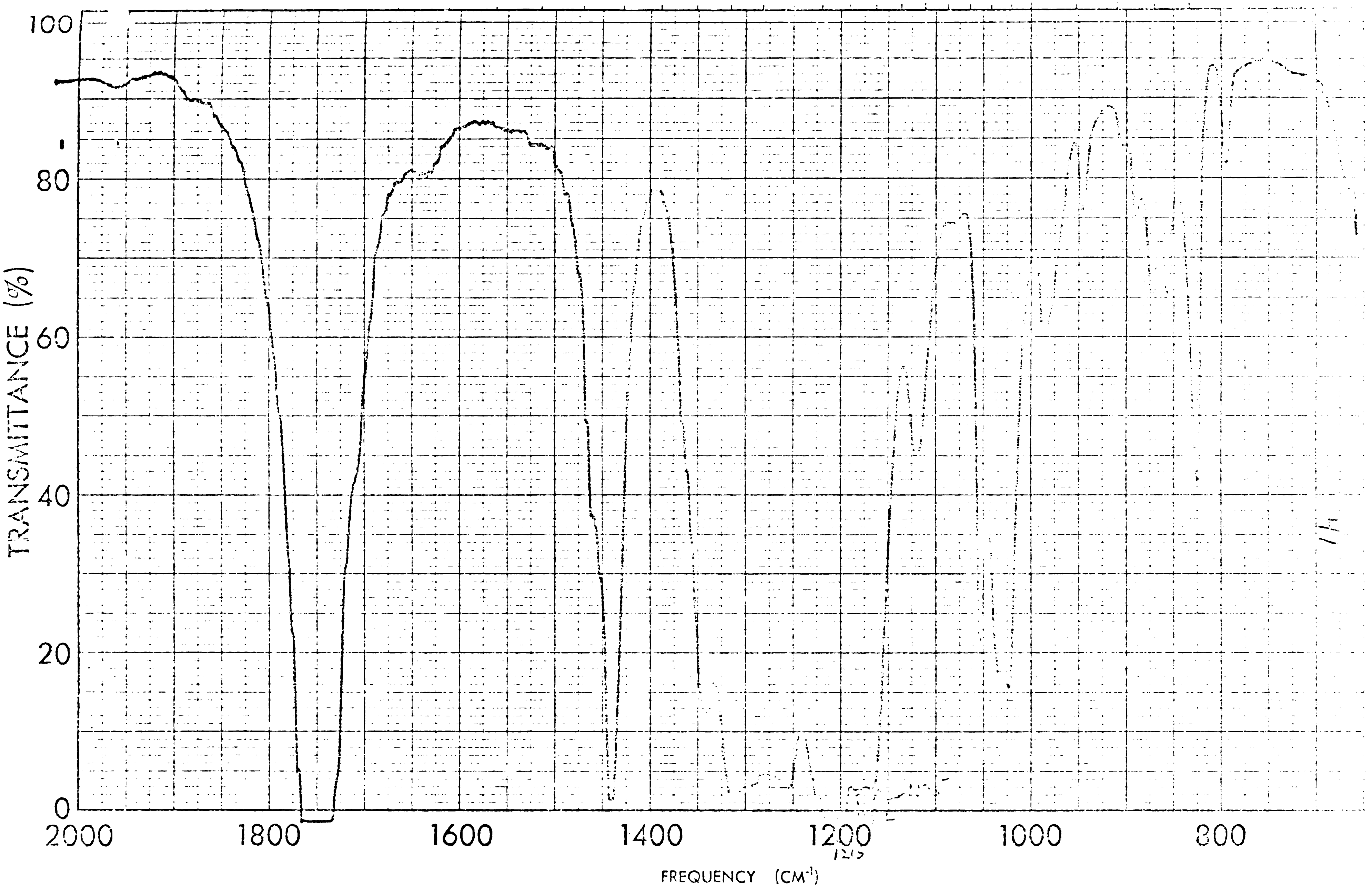


small run



40





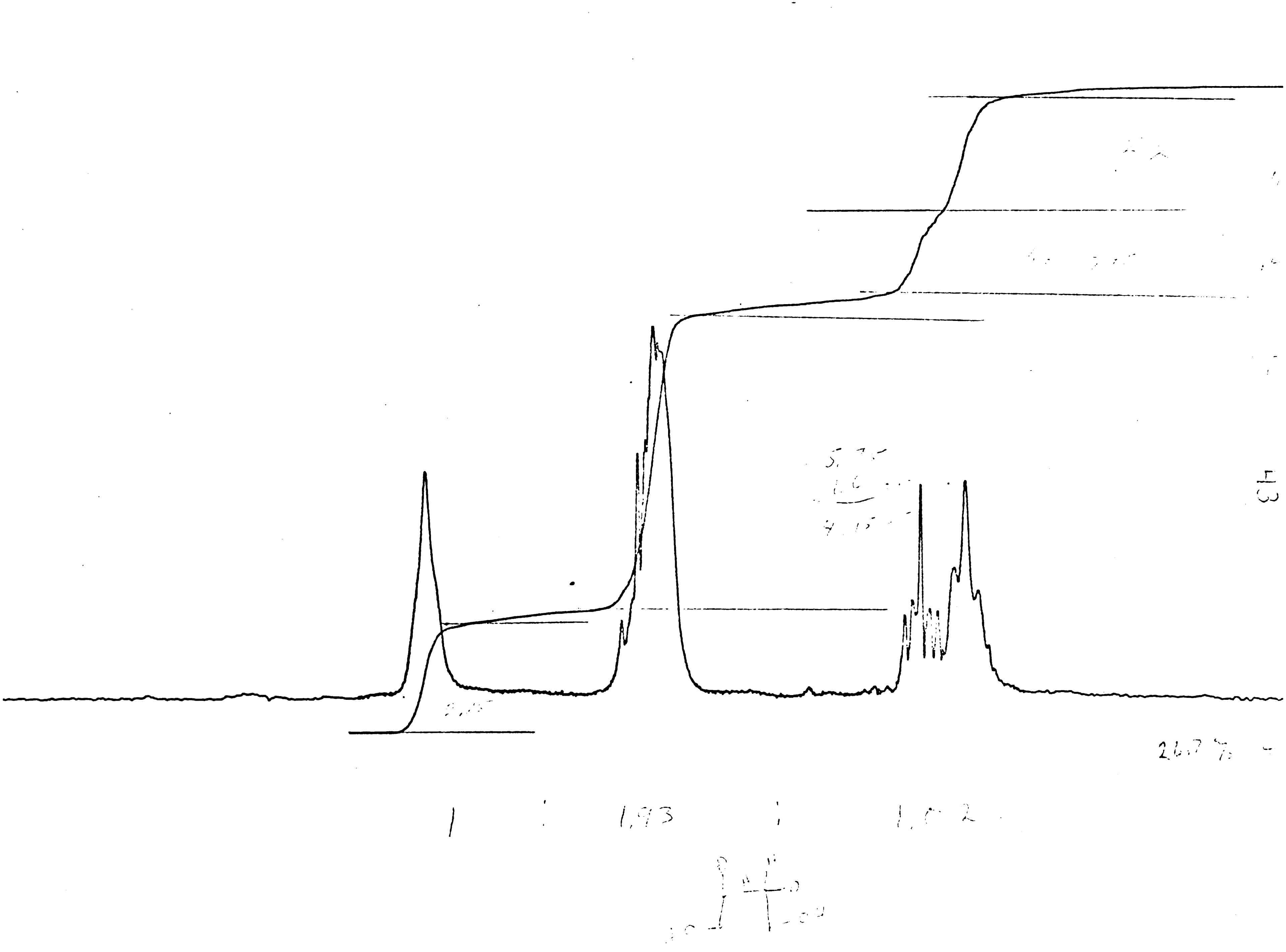
SAMPLE [illegible]
[illegible]
ORIGIN
SOLVENT [illegible]

CURVE NO.
CONC.
CELL PATH
REFERENCE

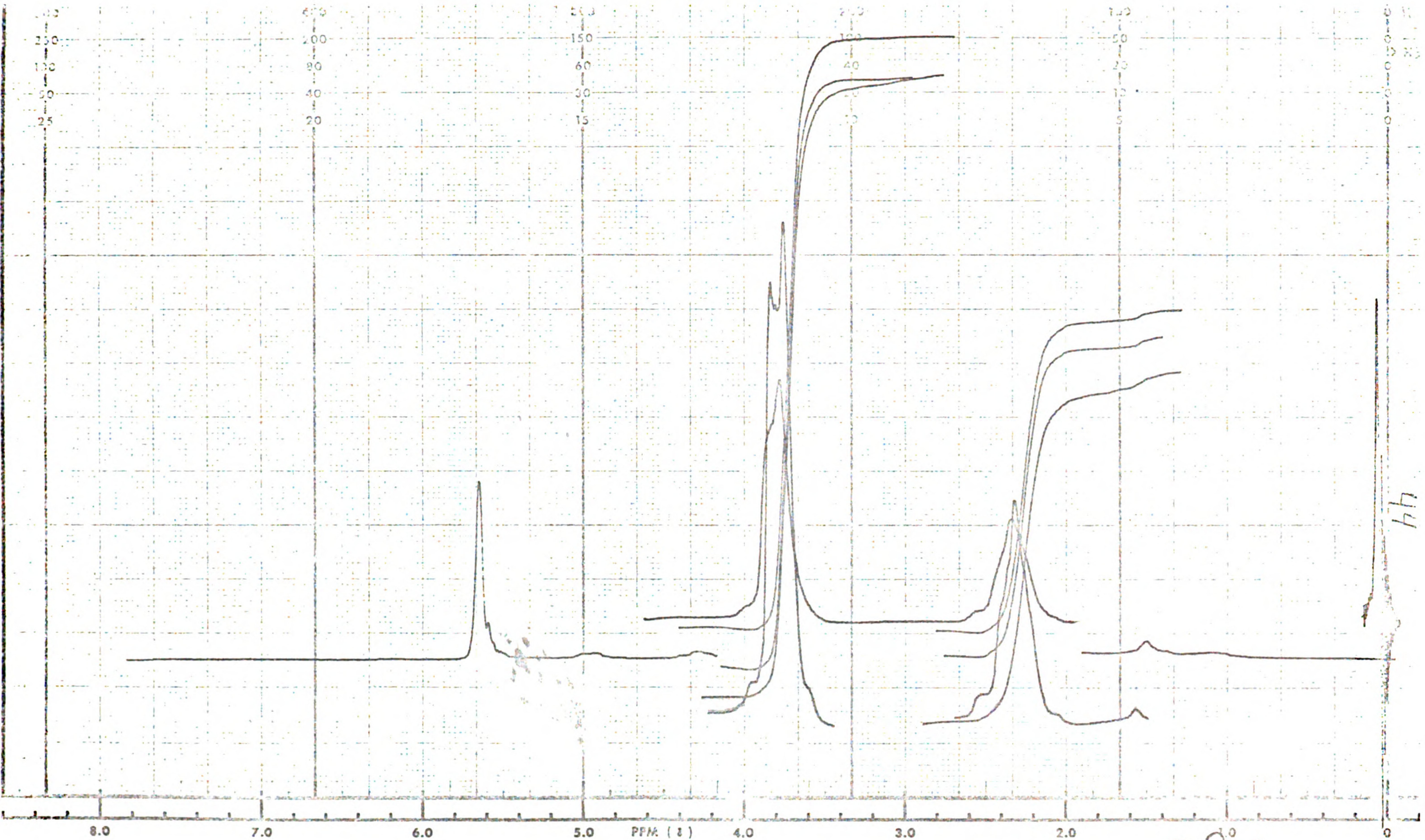
SCAN SPEED [illegible]
SLIT [illegible]
REMARKS 5G-71-13

OPERATOR
DATE [illegible]


meso
5.4
3.3 CH2 peak
1.1
5.2
CHC peak
1.4
.4


1 : 1,93 : 1,02
267 %

44



MANUAL

SWEEP OFFSET (Hz): -------

SPECTRUM AMPLITUDE: -------

INTEGRAL AMPLITUDE: -------

SPINNING RATE (RPS): -------

SWEEP TIME (SEC): 50 | 250

SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500

FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8

RF POWER LEVEL: ---------------

AUTO ☐

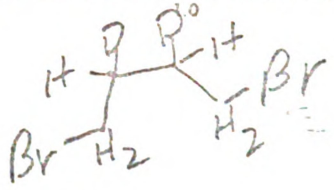
(250)
(500)
(2)
(.05)

SAMPLE:

SOLVENT:

From

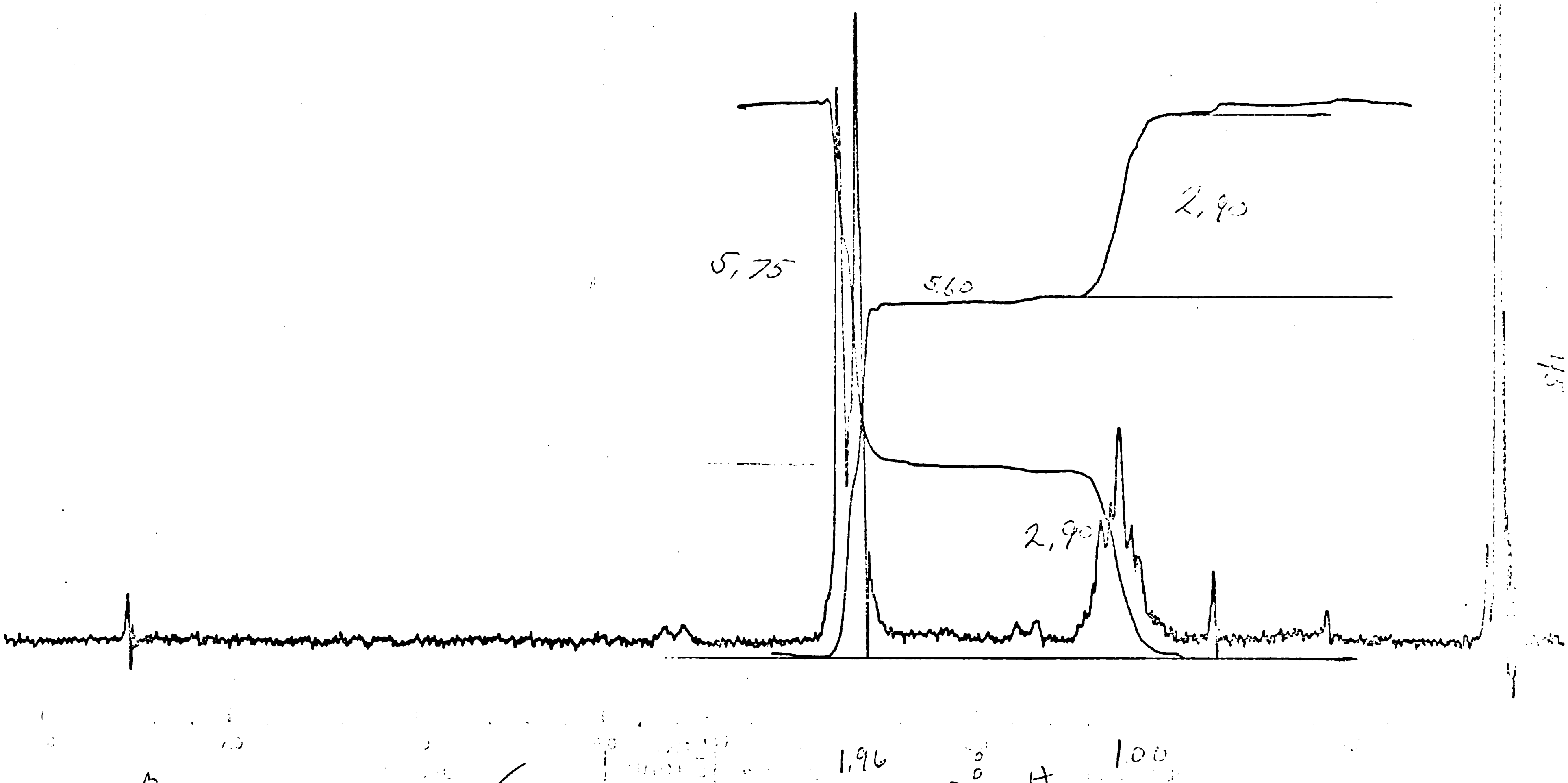

REMARKS:

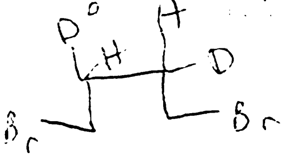


60 MHz NMR
SPECTRUM NO. ---------------

DATE: ---------------

OPERATOR: ---------------

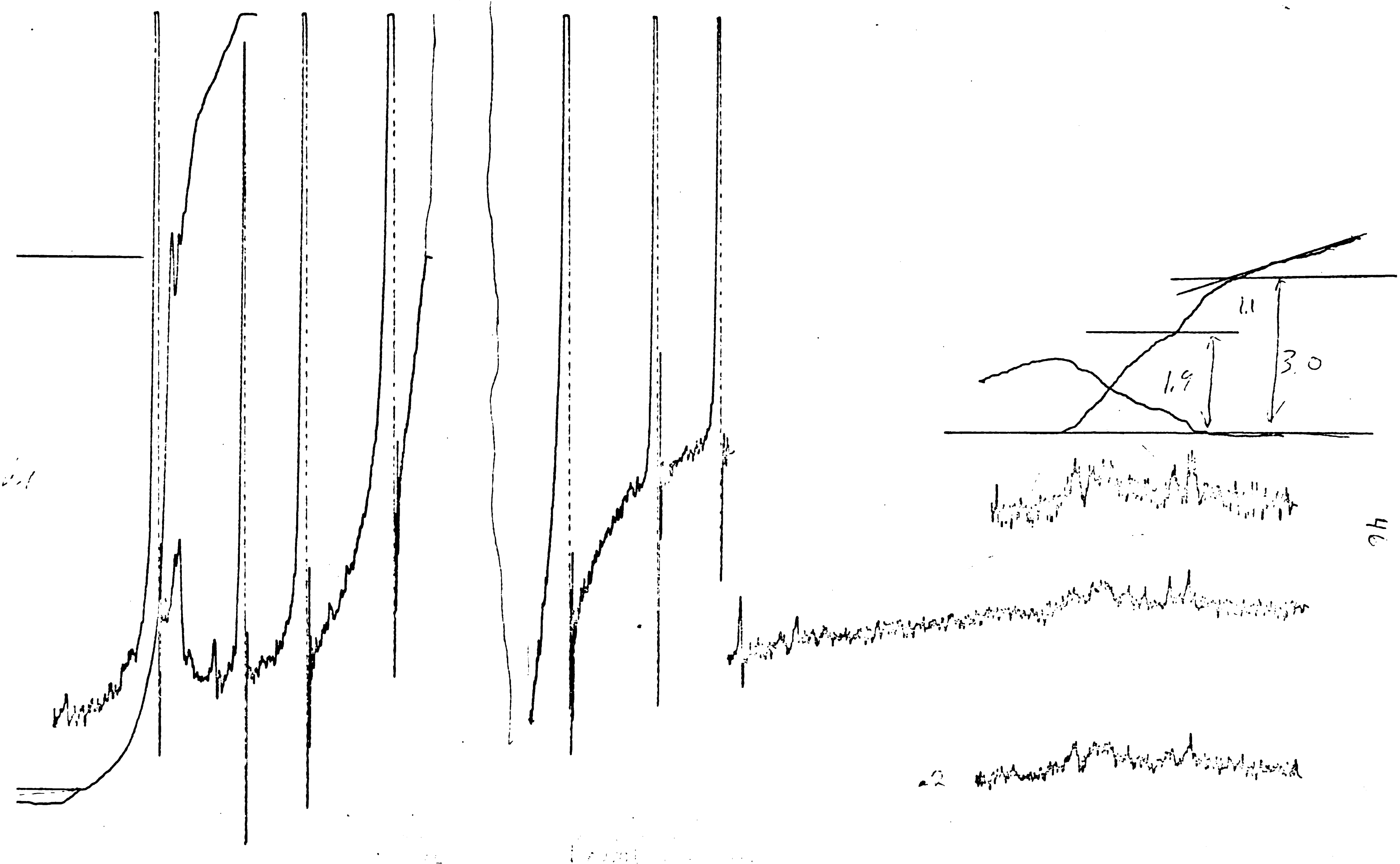


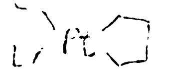


C
20
6
55

1.0

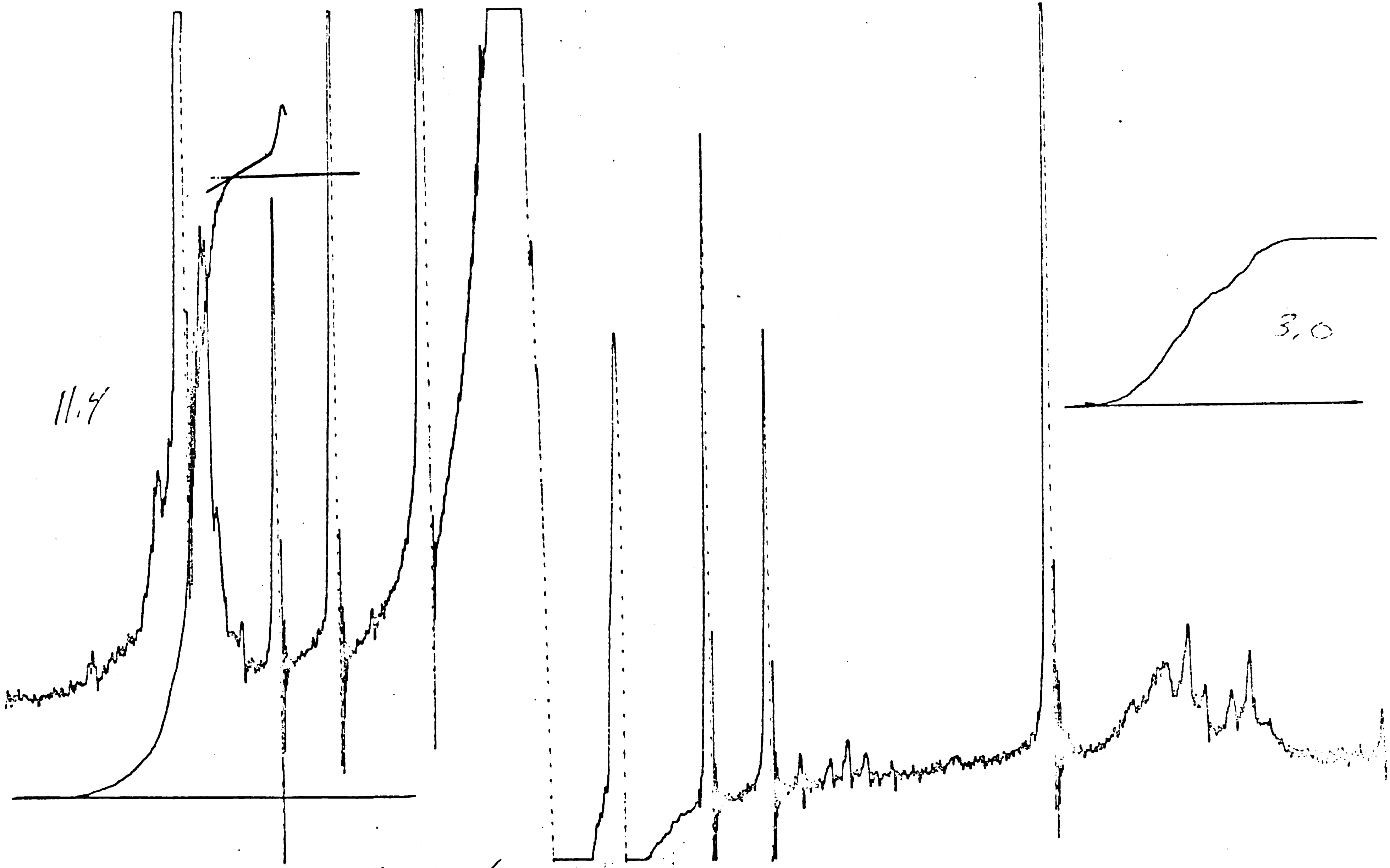
2-6-72





30 1.87
3.35 1.13
2.37 1.1

Sa-71-15

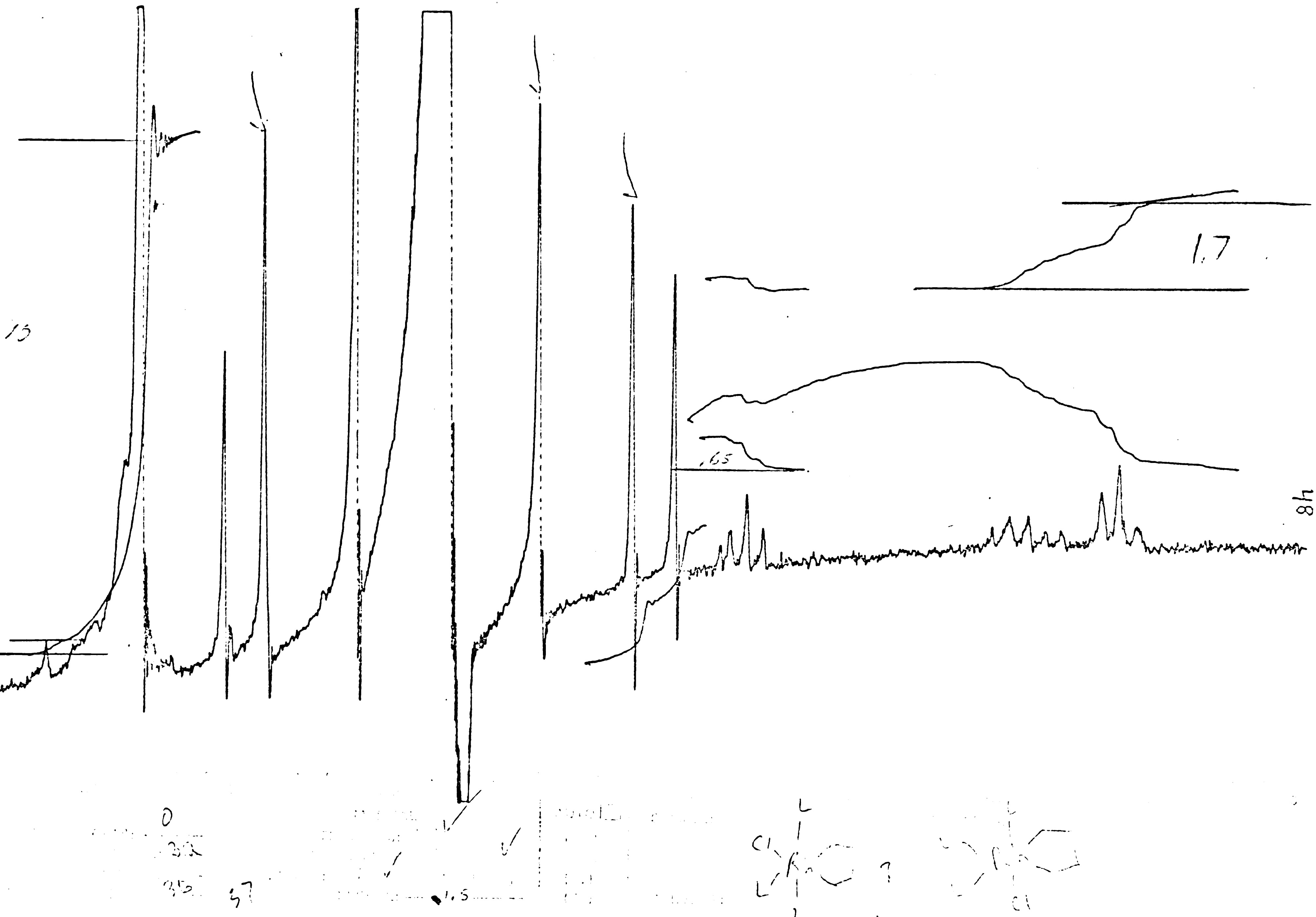


8-3-71

PtL2  9 : 30 } theo
1 : 3.75 }

CH2Cl2 1 : 3.80 } obs

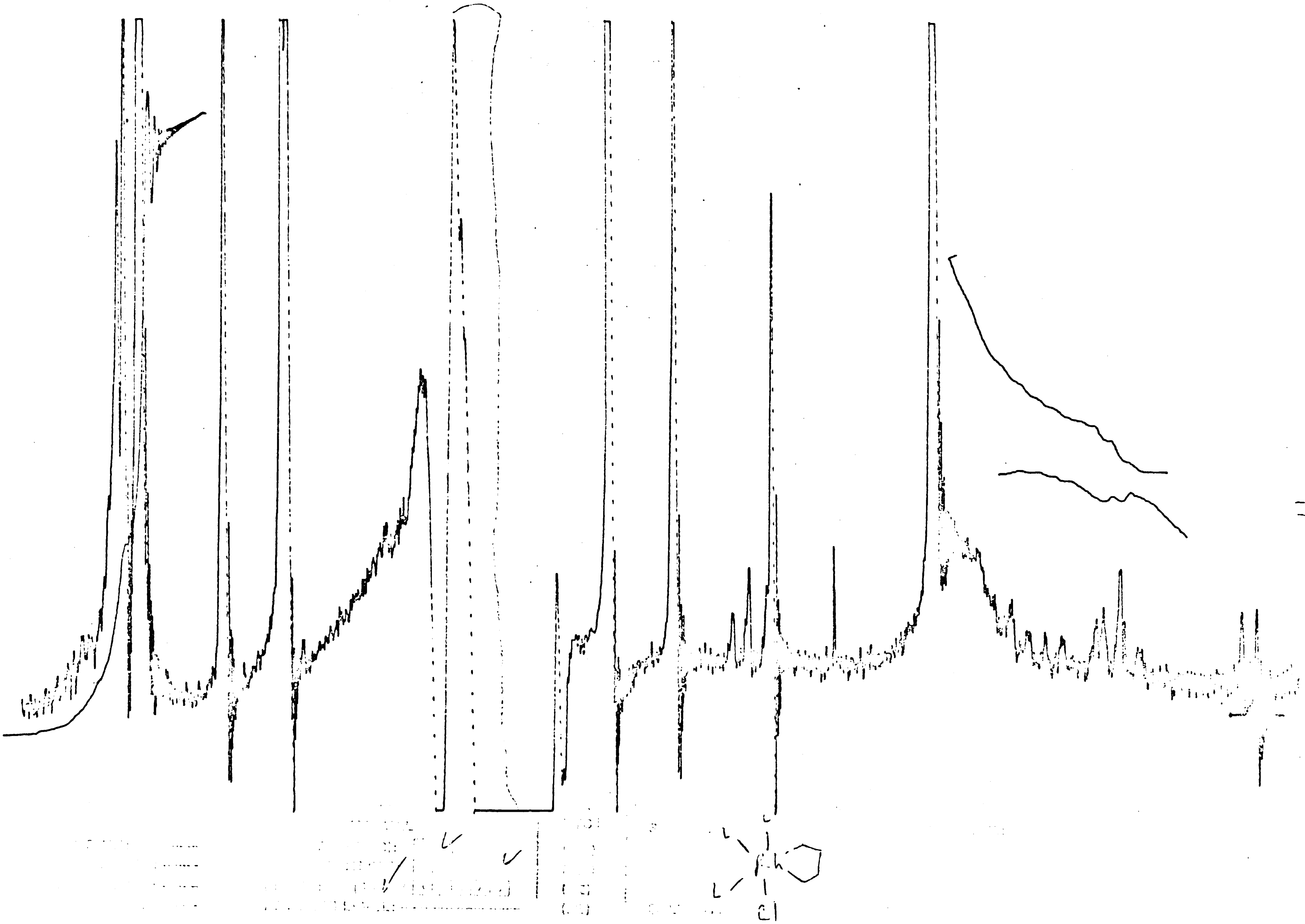
Su 71-15



7-28-71

5.62 : 1 theo

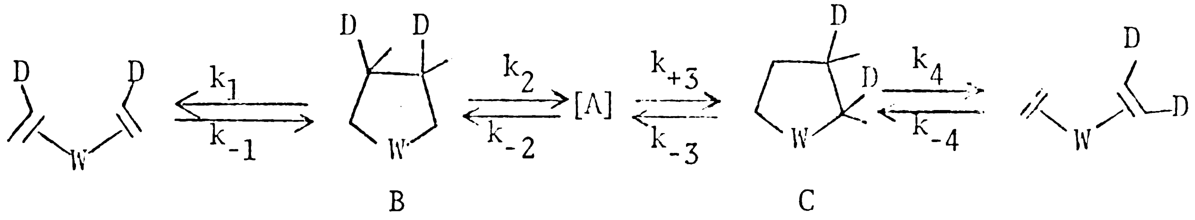
36-71-1b



CH₂Cl₂

Sn-71-19

APPENDIX



Assume $k_{-1} = k_{-4} = 0$ due to ether displacement

Assume $k_1 = k_4$ no D isotope effect

Assume $k_2 = k_{-3}$, $k_3 = k_{-2}$ symmetrical [A]

1) $$\frac{d(D_1)}{dt} = 2k_1(B)$$

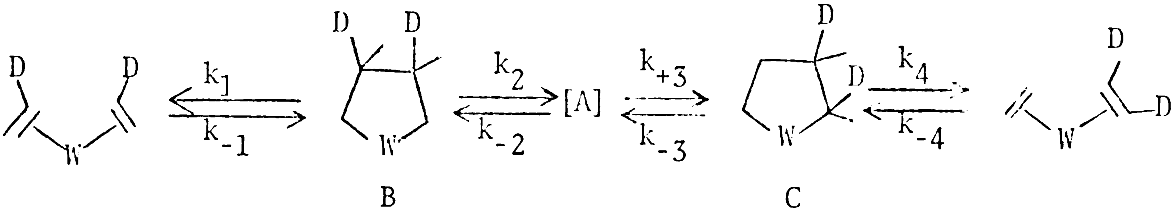
2) $$\frac{d(B)}{dt} = k_{-2}(A) - (k_1 + k_2)(B)$$

3) $$\frac{d(A)}{dt} = k_2(B + C) - 2k_{-2}(A) = 0$$

$$(A) = \frac{k_2}{2k_{-2}}(B + C)$$

4) $$\frac{d(C)}{dt} = k_{-2}(A) - (k_1 + k_2)(C)$$

APPENDIX



Assume $k_{-1} = k_{-4} = 0$ due to ether displacement

Assume $k_1 = k_4$ no D isotope effect

Assume $k_2 = k_{-3}$

$k_3 = k_{-2}$ symmetrical [A]

1) $$\frac{d(D_1)}{dt} = 2k_1(B)$$

2) $$\frac{d(B)}{dt} = k_{-2}(A) - (k_1 + k_2)(B)$$

3) $$\frac{d(A)}{dt} = k_2(B + C) - 2k_{-2}(A) = 0$$

$$(A) = \frac{k_2}{2k_{-2}}(B + C)$$

4) $$\frac{d(C)}{dt} = k_{-2}(A) - (k_1 + k_2)(C)$$

5) $\frac{d(D_2)}{dt} = k_1(C)$

rewrite 2 $\frac{d(B)}{dt} = \frac{k_2}{2}(B + C) - (k_1 + k_2)(B)$

$$= \frac{k_2}{2}(C) - (k_1 + \frac{k_2}{2})(B)$$

rewrite 4 $\frac{d(C)}{dt} = \frac{k_2}{2}(B) - (k_1 + \frac{k_2}{2})(C)$

define $(Q) = (B + C)$

$(P) = (B - C)$

then $\frac{d(Q)}{dt} = \frac{d(B)}{dt} + \frac{d(C)}{dt} = \frac{k_2}{2}(Q) - (k_1 + \frac{k_2}{2})(Q)$

$$= (\frac{k_2}{2} - k_1 - \frac{k_2}{2})(Q) = - k_1 Q$$

$$= K_1(Q)$$

$\frac{d(P)}{dt} = \frac{d(B)}{dt} - \frac{d(C)}{dt} = -\frac{k_2}{2}(P) - (k_1 + \frac{k_2}{2})(P)$

$$= -(\frac{k_2}{2} + k_1 + \frac{k_2}{2})(P) = -(k_2 + k_1)P$$

$$= -K_2(P)$$

then $Q = C_1e^{K_1t}$ and $P = C_2e^{-K_2t}$

$$B = \frac{(P + Q)}{2} = (\frac{C_1}{2})e^{k_1t} + (\frac{C_2}{2})e^{-k_2t}$$

$$C = \frac{(P-Q)}{2} = (\frac{C_1}{2})e^{k_1t} - (\frac{C_2}{2})e^{-k_2t}$$

at $t = 0$ $\quad B = \frac{C_1}{2} + \frac{C_2}{2} = 1$ (relatively)

$$C = \frac{C_1}{2} - \frac{C_2}{2} = 0$$

$\therefore \quad C_1 = C_2 = 1$ $\quad$ since only B is formed from the dilithium reagent

at $t = \infty$, (B) must be finite $\therefore \quad K_1 < 0$

$$\frac{d(D_1)}{dt} = 2\,k_1\,(\tfrac{1}{2}e^{k_1t} + \tfrac{1}{2}e^{-K_2t}$$

$$= k_1\,(e^{k_1t} + e^{-K_2t})$$

$$(D_1)_{\text{final}} = [{}_0^{\infty}k_1(e^{k_1t} + e^{-K_2t})dt]$$

$$= [\frac{k_1}{K_1}e^{k_1t} + \frac{-k_1}{K_2}e^{-K_2t}]_0^{\infty}$$

$$= \frac{k_1}{K_2} - \frac{k_1}{K_1}$$ since K_1CO

$$(D_2)_{\text{final}} = [{}_0^{\infty}\frac{k_1}{2}(e^{k_1t} - e^{-K_2t})dt]$$

$$= [\frac{k_1}{2K_1}e^{k_1t} + \frac{k_1}{2K_2}e^{-K_2t}]_0^{\infty}$$

$$= \; - \left(\frac{k_1}{2K_1} \; + \; \frac{k_1}{2K_2}\right)$$

Then $\quad D_1/D_2 \; = \; - \dfrac{k_1\left(\frac{1}{K_2} - \frac{1}{K_1}\right)}{\frac{k_1}{2}\left(\frac{1}{K_2} + \frac{1}{K_1}\right)} \; = \; - 2 \; \dfrac{(K_1 - K_2)}{(K_1 + K_2)}$

Substitute for K_1 and K_2

$$D_1/D_2 \; = \; \frac{- 2 \; (-k_1 - k_1 \; - k_2)}{(-k_1 + k_1 + k_2)} \; = \; \frac{2(2k_1 + k_2)}{k_2}$$

$$D_1/D_2 \; = \; \frac{4k_1}{k_2} \; + \; 2$$

$$1/4D_1/D_2 \; - \; 1/2 \; = \; \frac{k_1}{k_2}$$

Thus, the D_1/D_2 ratio measured gives the ratio of the rate constants.

If one uses the appropriate dilithium reagent to form (C), then one would expect, by an argument similar to the one above, that the D_1/D_0 ratio would be consistent with ratio above. That is, if the mechanism is essentially correct, the ratio of k_1/k_2 will be the same whether measured starting with B or C. This would be proof of the assumptions used for the calculations.

REFERENCES

1. N. Calderon, H. Y. Chen and K. W. Scott, *Tet. Lett.*, **34**, 3327 (1967).
2. G. C. Bailey, *Catalysis Reviews*, **3**, 37 (1969).
3. W. B. Hughes, *Chem. Comm.*, 431 (1969).
4. N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).
5. C. P. C. Bradshaw, E. J. Howman and L. Turner, *J. of Catalysis*, **7**, 269 (1967).
6. T. Katz and S. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6320 (1969).
7. Z. Cassor, P. E. Eaton and J. Halpern, *ibid.*, **92**, 3515 (1970).
8. J. T. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).
9. E. A. Zeuch, *Chem. Comm.*, 1182 (1968).
10. B. Denise, J. Fauvarque and J. Ducom, *Tet. Lett.*, **5**, 335 (1970).
11. C. L. Wilson, *J. Chem. Soc.*, 48, (1945).
12. R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).
13. R. S. Rabinovitch and F. S. Zooney, *J. Amer. Chem. Soc.*, **75**, 2652 (1953).
14. W. B. Hughes, E. A. Zeuch, E. T. Kittelman and D. H. Kerbirek, Presented at the XXIII IUPAC Conference, Paper 566, Boston, MA, August 1971.
15. J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966).
16. J. Chatt and L. M. Venazi, *J. Chem. Soc.*, 2787 (1955).

17. F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967).

18. G. S. Zewandos and R. Pettit, *Tet. Lett.*, 780 (1971).

19. W. B. Hughes, *J. Amer. Chem. Soc.*, **92**, 532 (1970).