AN ABSTRACT OF THE THESIS OF

SALLY THOMAS for the Master of Science Degree in Chemistry presented on July 27th 1990.

Title: Reactions of Sesquixanthene And Related Compounds.

Abstract approved: Eric L. Trump

Abstract: Three different methods to protect the central carbon of sesquixanthene, which is a triphenylmethane dye, were tried. The three methods involved 1) the introduction of benzyl group using benzyl chloride, 2) the introduction of carboxylic acid group using dry ice, and 3) the introduction of benzyl group using benzyl magnesium chloride. In addition to these, the reduction of the cation of sesquixanthydrol was also tried.

Spectroscopic examination of the products gave evidence that one of the methods to protect the central carbon was successful. This was the method involving the introduction of benzyl group using benzyl magnesium chloride. The reduction of the cation of sesquixanthydrol using tetrafluoroboric acid by $NaBH_4/H_2O$ was successful.

DeWayne Backhus

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Committee Chairman

James L. Wolfe

Approved for the Graduate Council

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Sally Thomas

Signature of the Author

07-30-1990

Date

Reactions of sesquixanthene and related compounds

Title of Thesis/Research Project

Jackie Tolbert

Signature of Graduate Office Staff Member

July 30, 1990

Date Received

REACTIONS OF SESQUIXANTHENE

AND RELATED COMPOUNDS

A Thesis

Presented to

the Department of Chemistry

EMPORIA STATE UNIVERSITY

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

Sally Thomas
(M.Sc University of Agra)

July 1990

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Introduction

Triarylmethane dyes are useful as textile dyes, pH indicators[1], reagents for determining the presence of traces of halides[2], H_2S[3], Ga[4], Ge[5], In[6], etc. and also as ball point pen inks[7] and corrosion inhibitors[8]. We are interested in the dye called sesquixanthene and also substituted sesquixanthenes which have potential uses as laser dyes, staining agents for biological specimens, chemiluminiscent acceptors, and as redox indicators. Triarylmethane dyes are familiar as indicators in the titrations of Fe (II), Ti (III), Cr (III), and Cu (I) with Ce (IV) and also in the titrations of Fe (II), hydroquinone, Mo (V), U (IV), and Fe $(CN)_6^{4-}$ with dichromate. There are two problems frequently encountered in these types of titrations. First, they are not reversible in the course of the reaction. Secondly, they are not stable in oxidizing solutions. Yet they were commonly used as the indicator of choice[9,10] in the past.

Triarylmethane dyes are distinguished from other dyes by the unique property of the central carbon atom. If the central carbon is charged the resulting entity is very stable due to the delocalization of that charge on the aromatic rings. This stabilization is dependent on the angle of twist of each ring, and would be at a maximum when the rings are coplanar. Coplanarity of the rings is often not possible because of steric interactions at the ortho positions. This gives rise to "propeller shaped" molecules

as they are described in the organic literature[11,12].

The cation of sesquixanthydrol is very stable due to the delocalization of the positive charge and also due to the coplanarity of the rings. The oxygen between the rings locks the latter, resulting in their coplanarity. Computerized literature search from 1982 to the present did not give any information on sesquixanthene and sesquixanthydrol.

The delocalization of the charge at the central carbon is dependent on the ring substituents. In other words the properties of a triarylmethane dye are dependent on the ring substituents. In a basic medium, the proton on the central carbon is removed from the triarylmethane dye. The acidic nature of this proton is enhanced by electron withdrawing substituents on the benzene rings. As an example, tri (p-nitrophenyl) methane is acidic with a pKa of 14.3[13] whereas triphenylmethane has a pKa of 32.[14]. The pKa of the proton on the central carbon of sesquixanthene is not known.

When the central carbon is attached to a hydroxyl group, it is easily protonated under acidic conditions. This can be represented as

$$H^+ + Ar_3COH \rightleftharpoons Ar_3CO^+ \begin{matrix} H \\ H \end{matrix} \rightleftharpoons Ar_3C^+ + H_2O.$$

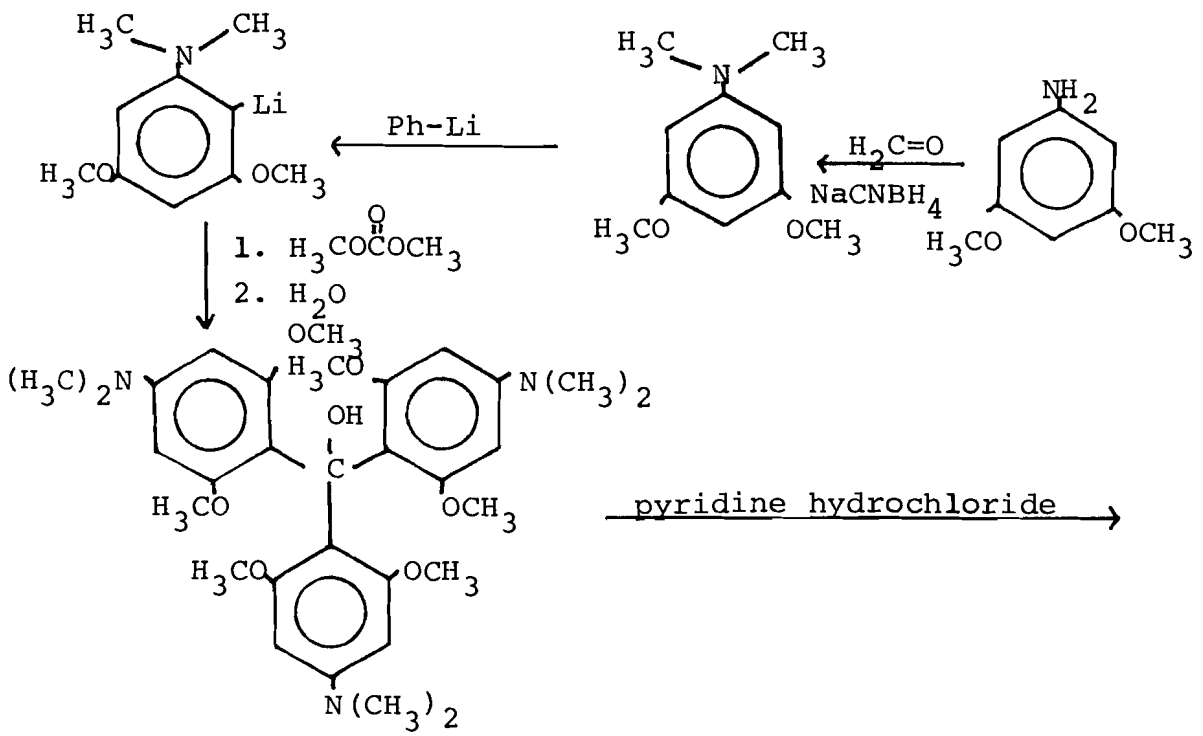
Compounds which undergo this type of reaction are called secondary bases and the equilibrium constant is expressed as K_{R+}[15] . The resulting triaryl carbonium ion is stable due

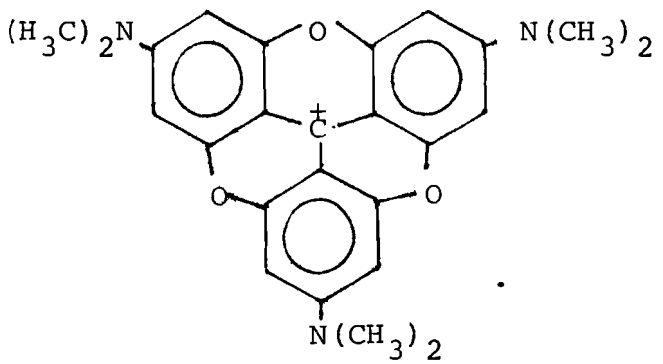
to the delocalization of the positive charge.

Experimental Section

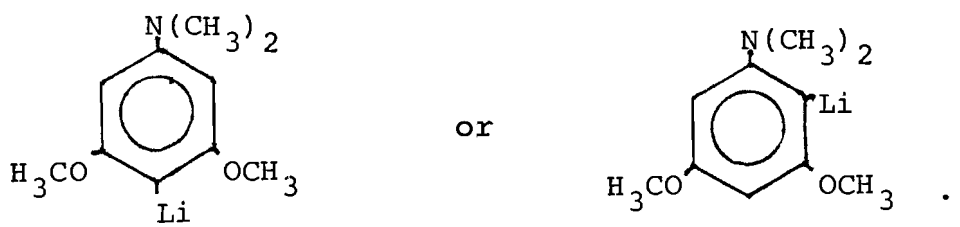
1. A proposed method for the synthesis of substituted triphenylmethane dye.

One of the methods which was tried to prepare a substituted triarylmethane system may be outlined as follows. The starting material was 3,5 dimethoxy benzene. It was to be subjected to reductive amination, then the lithium substituted compound was to be prepared using phenyl lithium[16]. This product was to be subjected to reaction with dimethyl carbonate and the compound was to be hydrolyzed. This compound was to be separated and allowed to react with pyridine hydrochloride to demethylate it. The final product was expected to be a planar triarylmethane system. The above sequence of reactions may be represented as follows:





It was not possible to carry out this synthesis because the starting material 3,5 dimethoxy aniline was light sensitive. When purified using column chromatography, it turned black immediately due to polymerization; moreover, there is difficulty in assigning the structure of the compound formed after the n-butyl lithium reaction. There are two possibilities:



2. A successful method for the synthesis of the dye.

In this method the triphenylmethane dye formed has no substituents on the rings.

a. Preparation of 2, 6, 2, 6', 2'', 6'' hexamethoxy triphenyl carbinol.

A solution of phenyl lithium[16] was prepared by the

addition of bromobenzene (39.2 g, 0.250 mole) in 125 ml of ether to lithium wire (4.0 g, 0.577 mole) in 60 ml of ether. Resorcinol dimethyl ether (30.0 g, 0.218 mole) was added and the reaction mixture was allowed to stand at room temperature under nitrogen for about 60 hours. 2,6-dimethoxy phenyl lithium was formed as white crystals.[17] Ethyl carbonate (8.50 g, 0.072 mole) in 400 ml of benzene was added and the reaction mixture was refluxed for three days under nitrogen. A white solid formed in the reaction mixture during this time. After cooling, the reaction mixture was poured into about 600 ml of water to produce an aqueous layer and an organic layer. The organic layer was separated and mixed with the ether extract from the aqueous layer, washed twice with water, dried over anhydrous sodium sulfate, and concentrated by evaporating the ether to yield a grey residue. The residue was recrystallized from ether to yield 18.0 g (57%) of 2 ,6 ,2', 6', 2'', 6''-hexa methoxy triphenyl carbinol with a melting point of 163.0-164.8°C.

b. Preparation of sesquixanthydrol from 2, 6, 2', 6', 2'', 6'' hexamethoxy triphenyl carbinol.

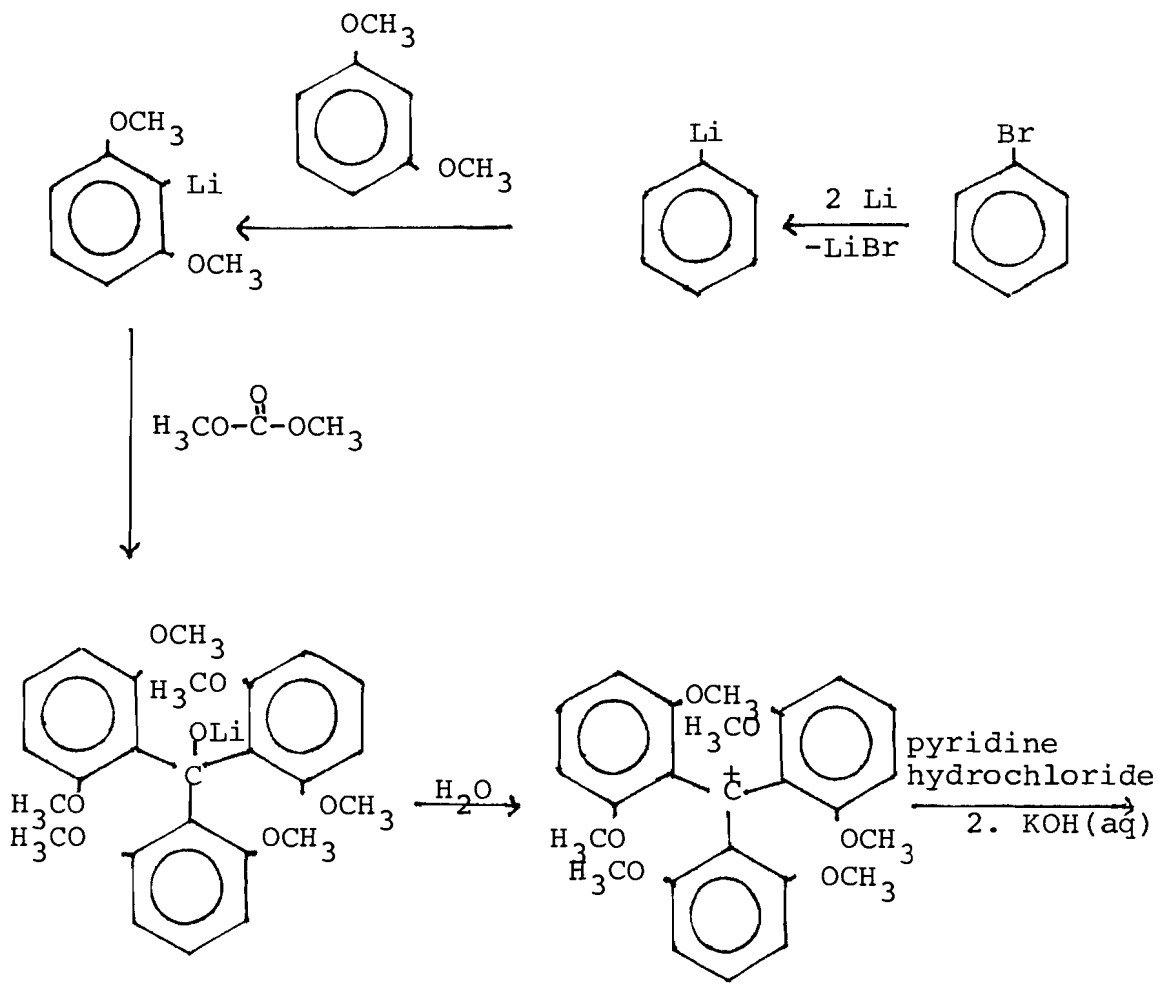
Pyridine hydrochloride[18,19] (50.0 g, 0.435 mole) and 2, 6, 2', 6', 2'', 6''-hexamethoxy triphenyl carbinol (about 10.0 g, 0.023 mole) were mixed and heated with stirring at about 195°C for one hour. The purple solid mass gradually became a liquid under these conditions and developed on a red color. The reaction mixture was washed into 1 liter of

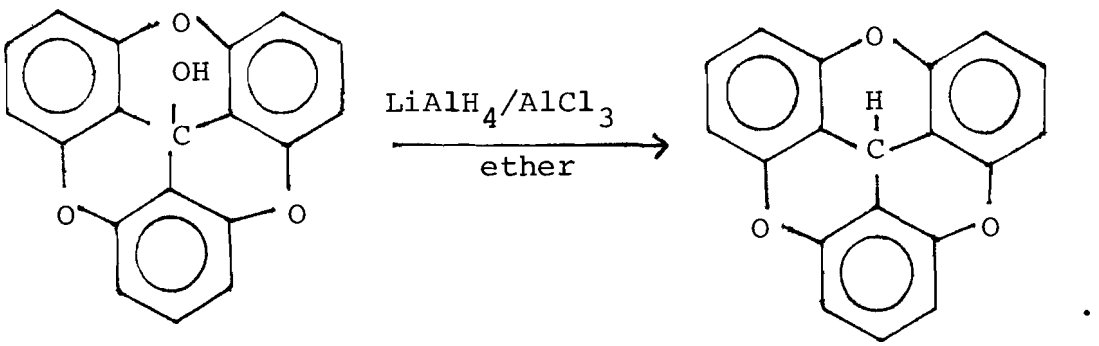
water to produce a red solid (2.40 g) and yellow aqueous solution. The solution was filtered to remove the red solid and was basified with potassium hydroxide to produce a white solid 4.22 g (61.4% of theoretical yield). This product was purified by recrystallization from benzene-ethanol to yield 3.45 g (50.3%) of pure material which was then identified as sesquixanthydrol by infra-red (IR) and nuclear magnetic resonance (NMR) spectroscopic techniques. The melting point was 245°C.

Sesquixanthydrol was reduced to sesquixanthene using $LiAlH_4$ and $AlCl_3$ in diglyme as follows: Anhydrous aluminum chloride (10.6 g, 0.80 mole) was dissolved in 200 ml of dry diglyme (purified by distillation from calcium hydride) and placed in a flask which contained a magnetic stirrer. Lithium aluminum hydride (1.61 g, 0.042 mole) was added with several injections through a septum cap. This was stirred for five minutes and sesquixanthydrol (2.0 g, 0.0066 mole) in 400 ml of dry diglyme was added over a period of one hour. The reaction mixture was allowed to stand overnight under nitrogen. The excess of lithium aluminum hydride was decomposed by the addition of water. The reaction mixture was filtered and the resultant colorless solution was poured into two liters of water to produce a white solid. The solid was collected by suction filtration and dried under vacuum to yield 1.33 g (70% of theoretical yield) of sesquixanthene.

The compound was purified by recrystallization from benzene-acetone solution to give 0.95 g (50% of theoretical yield) of sesquixanthene, which was identified using IR and NMR spectroscopic techniques. The compounds showed decomposition between 280 and 300°C.

The reactions involved in the formation of sesquixanthene can be represented as follows:



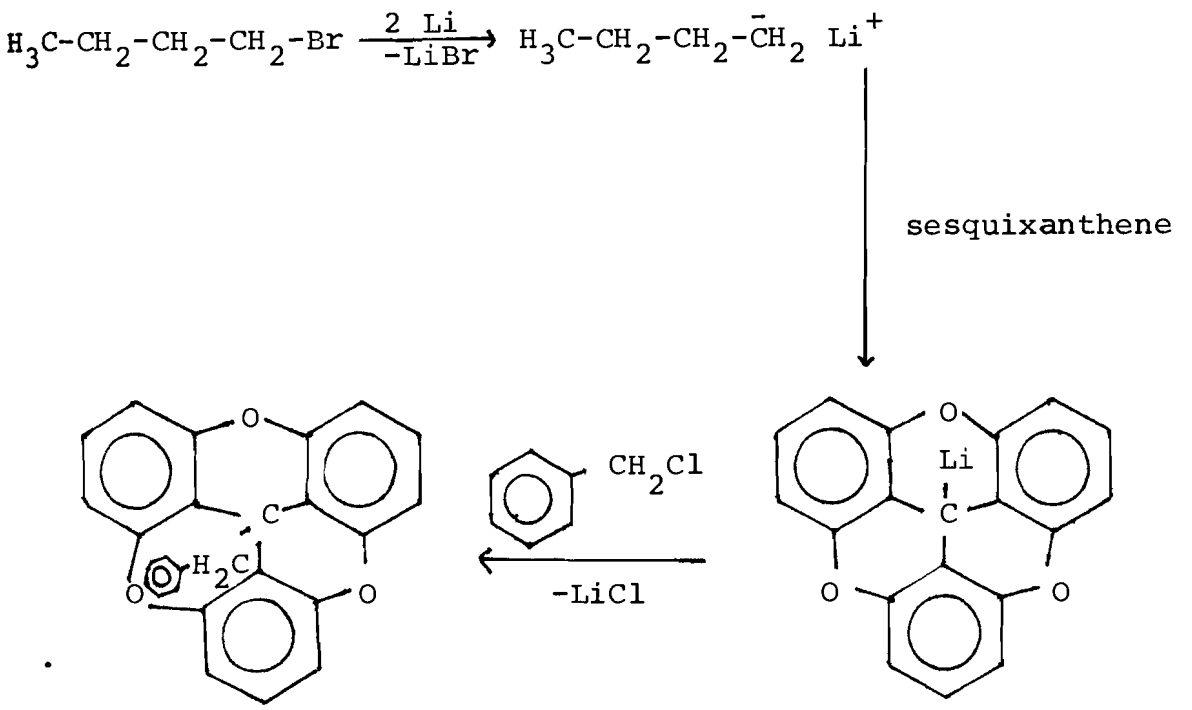


3. Reactions of Sesquixanthene.

a. Reaction with benzyl chloride.

5 ml of n-butyl bromide in 30 ml of ether and 0.6 gm of lithium were allowed to react in a three-necked flask under nitrogen until no more lithium dissolved. Then 0.5 gm of sesquixanthene dissolved in a minimum amount of ether was added over a period of one hour through an addition funnel. This was allowed to stand for one hour. 3 ml of benzyl chloride was added to the reaction mixture and was allowed to stand overnight under nitrogen. On hydrolysis the organic and aqueous layers were separated. The solution was subjected to steam distillation to yield a solid product. The dried product was analyzed spectroscopically.

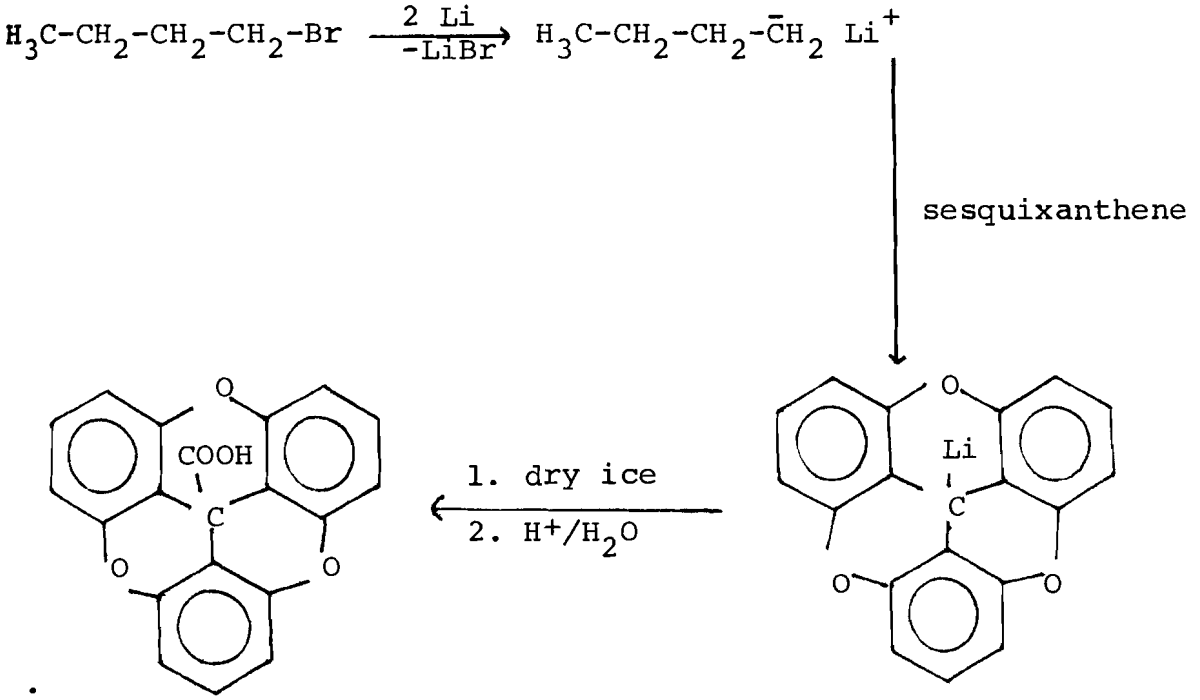
The reactions involved can be represented as follows:



b. Reaction with dry ice[20].

10 ml of n-butyl bromide in 30 ml of ether and 0.85 g of lithium were allowed to react under nitrogen in a three necked flask until no more lithium dissolved. 0.72 g of sesquixanthene dissolved in a minimum amount of ether was added over a period of one hour through an addition funnel. This was allowed to stand for one hour. Dry ice was added and allowed to stand for 4 hours under nitrogen. The resulting solution was hydrolyzed and the product was collected by suction filtration and dried under vacuum. Analysis was done using spectroscopic methods.

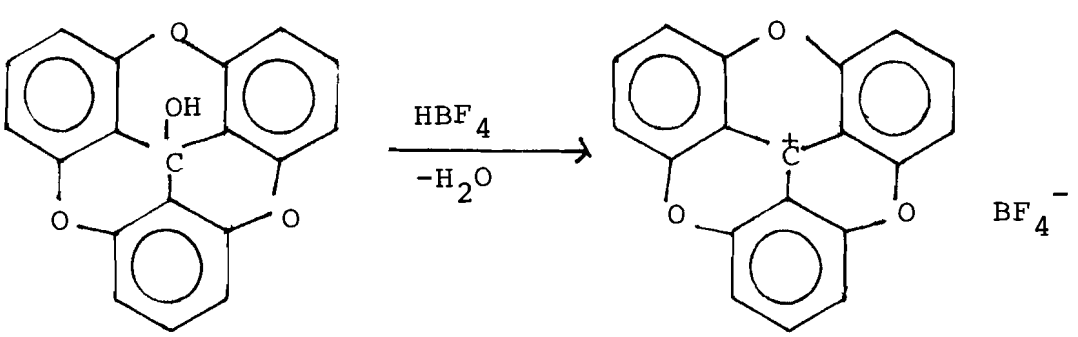
The reactions involved can be represented as follows:



4. Reactions of Sesquixanthydrol.

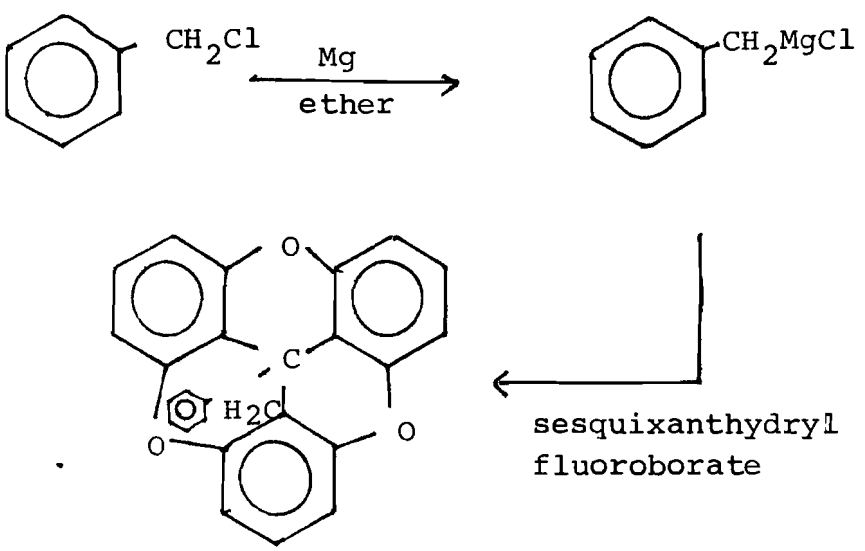
a. Preparation of the salt of sesquixanthydrol[21].

Salt of sesquixanthydrol was prepared in the following manner: 0.94 g of sesquixanthydrol was mixed with 2 ml of tetrafluoroboric acid. The yellow salt was separated by suction filtration, washed with ether, and dried under reduced pressure. The reaction may be represented as follows:



b. Reaction with benzyl magnesium chloride.

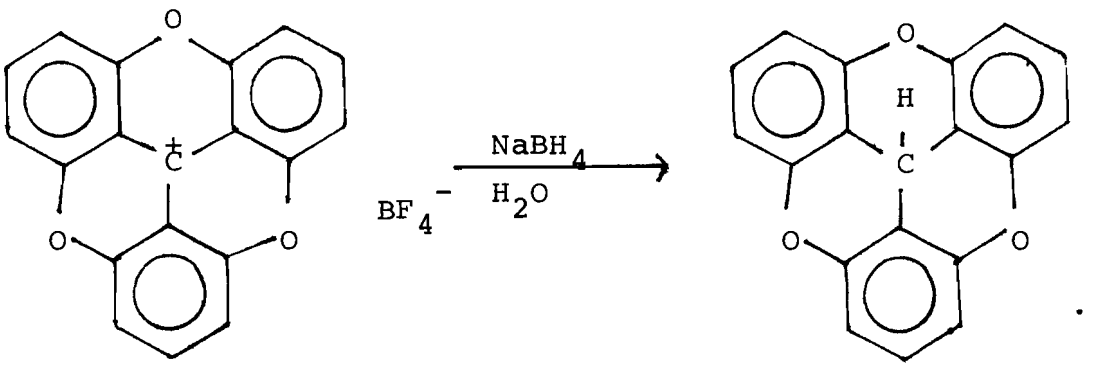
0.075 g of magnesium was weighed into a three-necked flask containing about 50 ml of ether. 0.4 ml of benzyl chloride was added and the magnesium turnings were crushed using a glass rod. The product formed is benzyl magnesium chloride[22]. 0.76 g of the salt of sesquixanthydrol was added and allowed to stand for eight hours. The solution was hydrolyzed using very dilute HCl. The product was collected by suction filtration and dried under vacuum. The product was analyzed spectroscopically using IR and NMR. The reaction involved may be represented as follows:



c. Reduction of the cation of sesquixanthydrol.

A saturated solution of the cation in water was made.

Sodium borohydride dissolved in water was added to the above solution. A white solid was formed which was analyzed spectroscopically. The reaction may be represented as follows:



Results

a. Introduction.

The structure of the compounds formed after the synthesis and the products formed as a result of the reactions were investigated by using spectroscopic methods to confirm their identities. The spectroscopic instruments used included a NMR spectrophotometer (Hitachi, Perkin-Elmer, high resolution model number 12-24B), a UV-Visible spectrophotometer (GCA-Mcpherson instrument model number EU-700 series), and a FTIR spectrophotometer (BOMEM model MB-100). Given below are the spectral details of the compounds sesquixanthydrol, sesquixanthene, and the products formed after each reaction. The solvent used for NMR spectra was deuterated chloroform ($CDCl_3$)

b. Spectral details of solvent $CDCl_3$.

The NMR spectrum of the solvent (Figure 1) had prominent peaks around 0.5 ppm, 1.5 ppm , and 7.2 ppm.

c. Spectral details of sesquixanthydrol.

The NMR spectrum of sesquixanthydrol (Figure 1) had prominent peaks around 7 ppm, and a broad peak around 2.2 ppm. There were peaks around 1.5 ppm, 1 ppm, 0.5 ppm, and one at zero.

The IR spectrum (Figure 3) of sesquixanthydrol had peaks at 3478.1 cm^{-1}, 3396.2 cm^{-1}, 3053.6 cm^{-1}, 1609 cm^{-1}, 1467.6 cm^{-1} , and 1266.5 cm^{-1}.

Figure 1: NMR spectrum of the solvent $CDCl_3$.

Reference: TMS

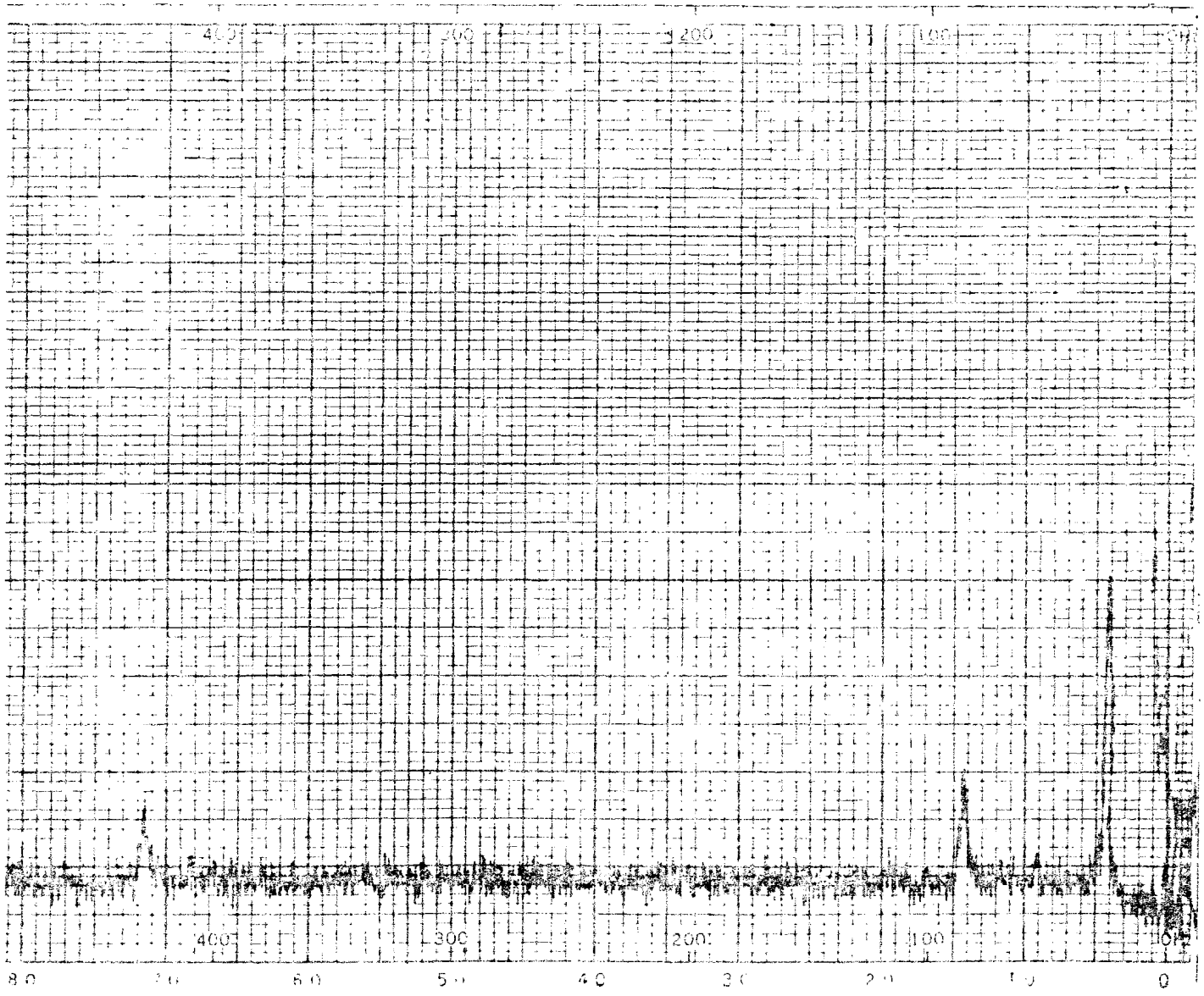

400
300
200
100
0
ppm

Figure 2: NMR spectrum of sesquixanthydrol.

Solvent: $CDCl_3$

Reference: TMS

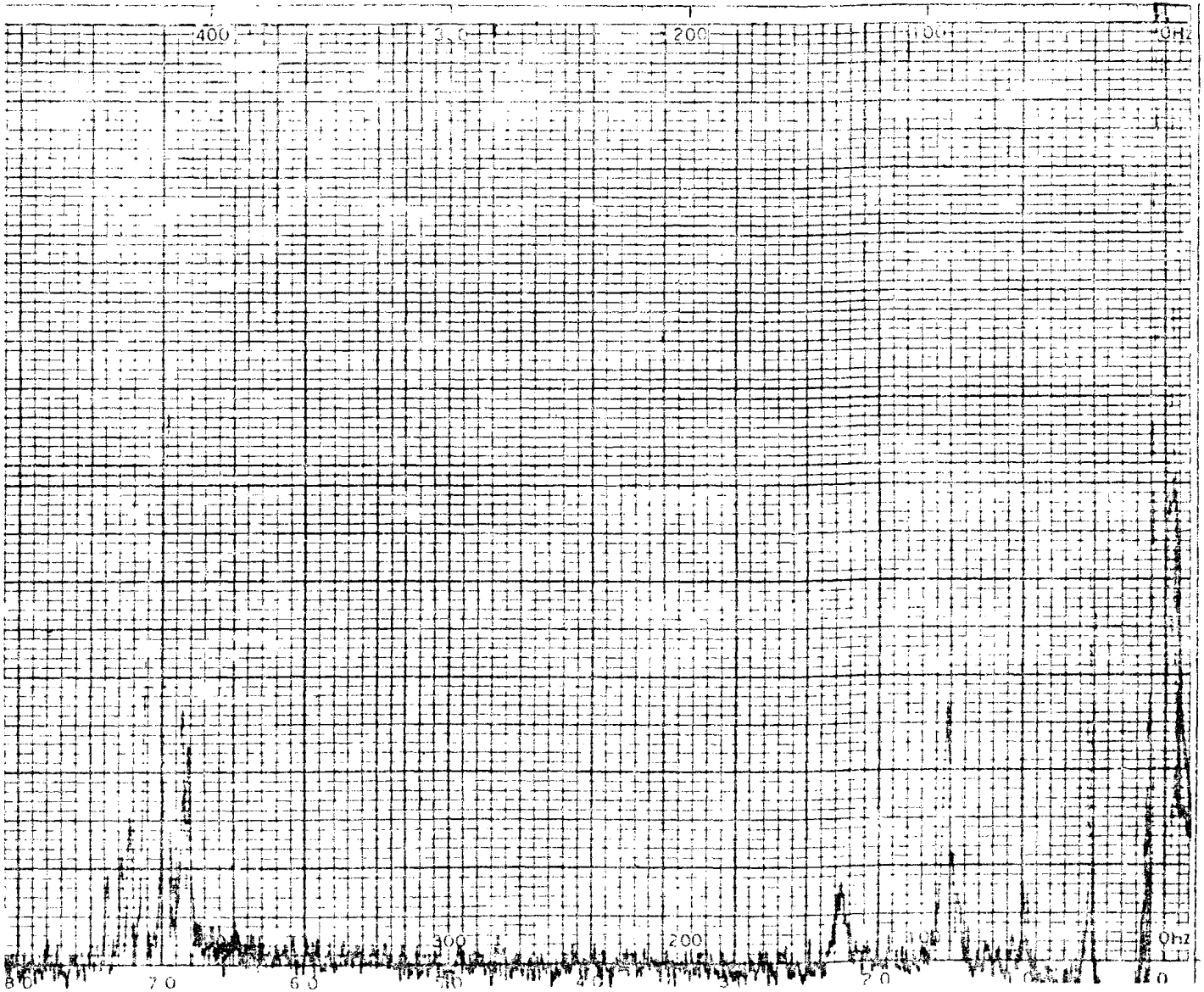
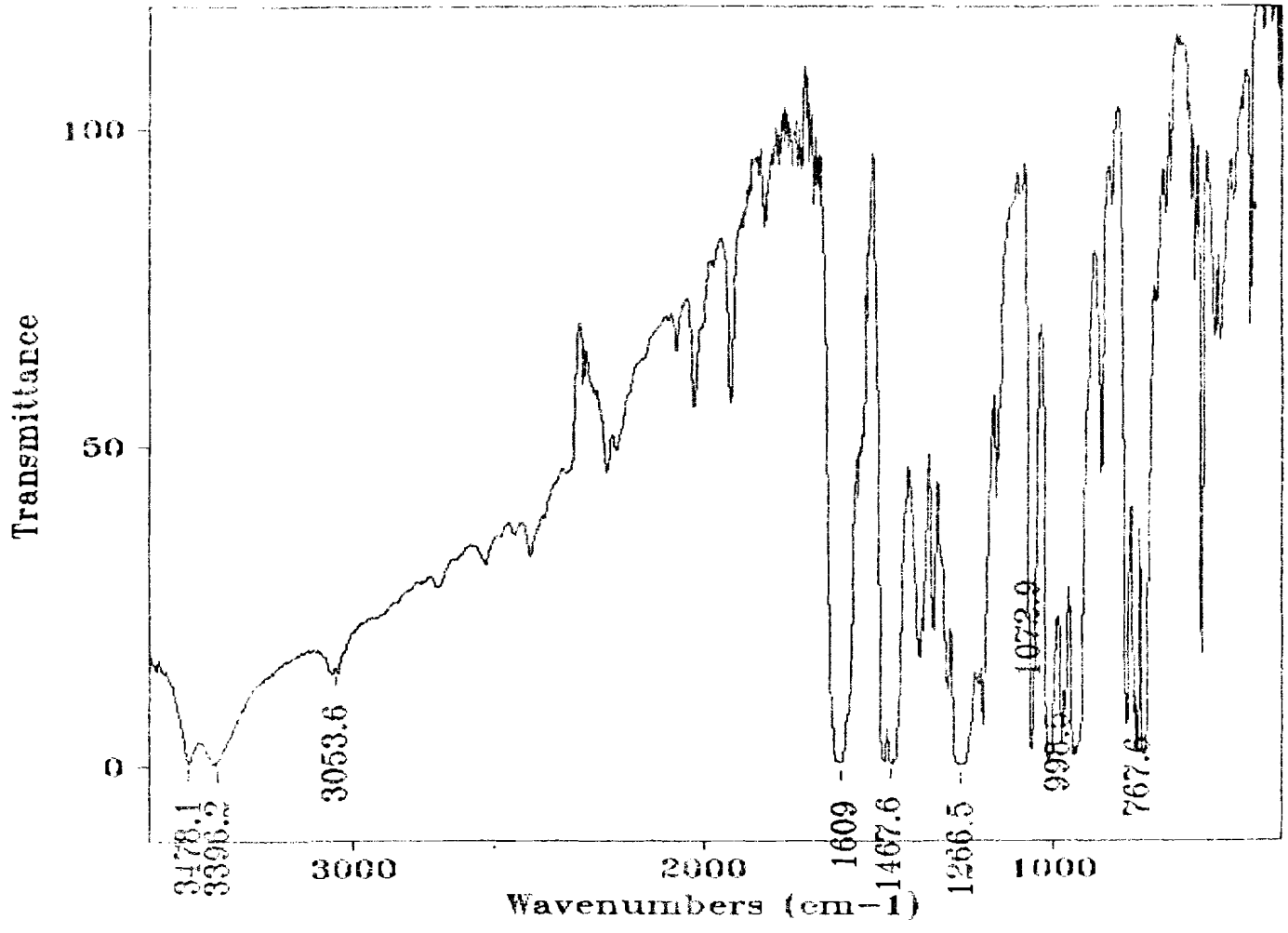

400
200
0Hz
300
200
0Hz
80
70
60
50
40
30
20
0
ppm

Figure 3: IR spectrum of sesquixanthydrol, KBr pellet.



Res= 4 cm-1

sesquixanthydrol, KBr pellet

d. Spectral details of sesquixanthene.

The NMR spectrum of sesquixanthene (Figure 4) had prominent peaks around 7 ppm, 4.8 ppm, 1.5 ppm, 1 ppm , and 0.5 ppm.

The IR spectrum of sesquixanthene (Figure 5) had peaks at 3066.7 cm^{-1}, 1618.1 cm^{-1}, 1467.7 cm^{-1} , and 1269.8 cm^{-1}.

Figure 4: NMR spectrum of sesquixanthene obtained from $LiAlH_4$ reduction.

Solvent: $CDCl_3$

Reference: TMS

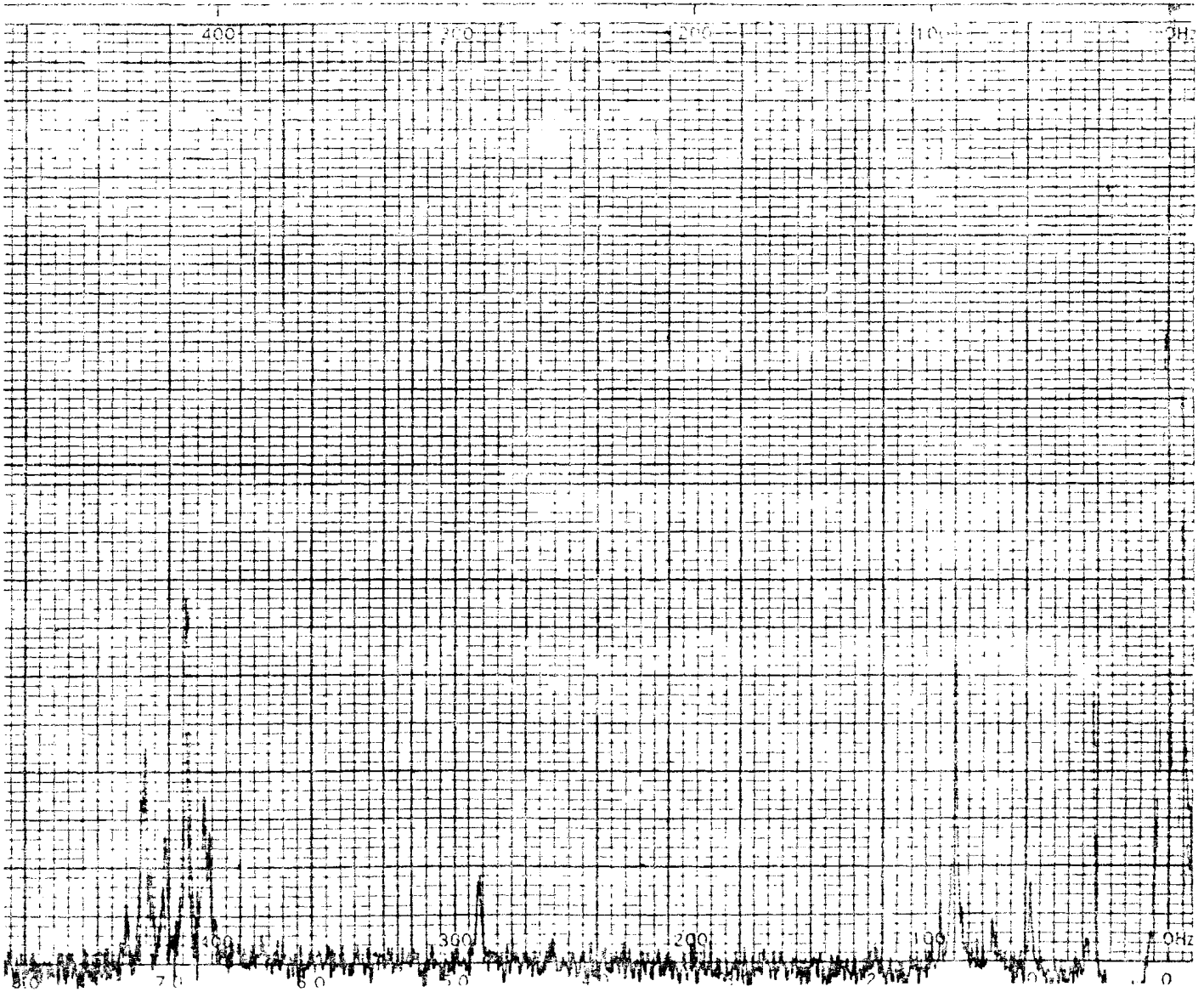
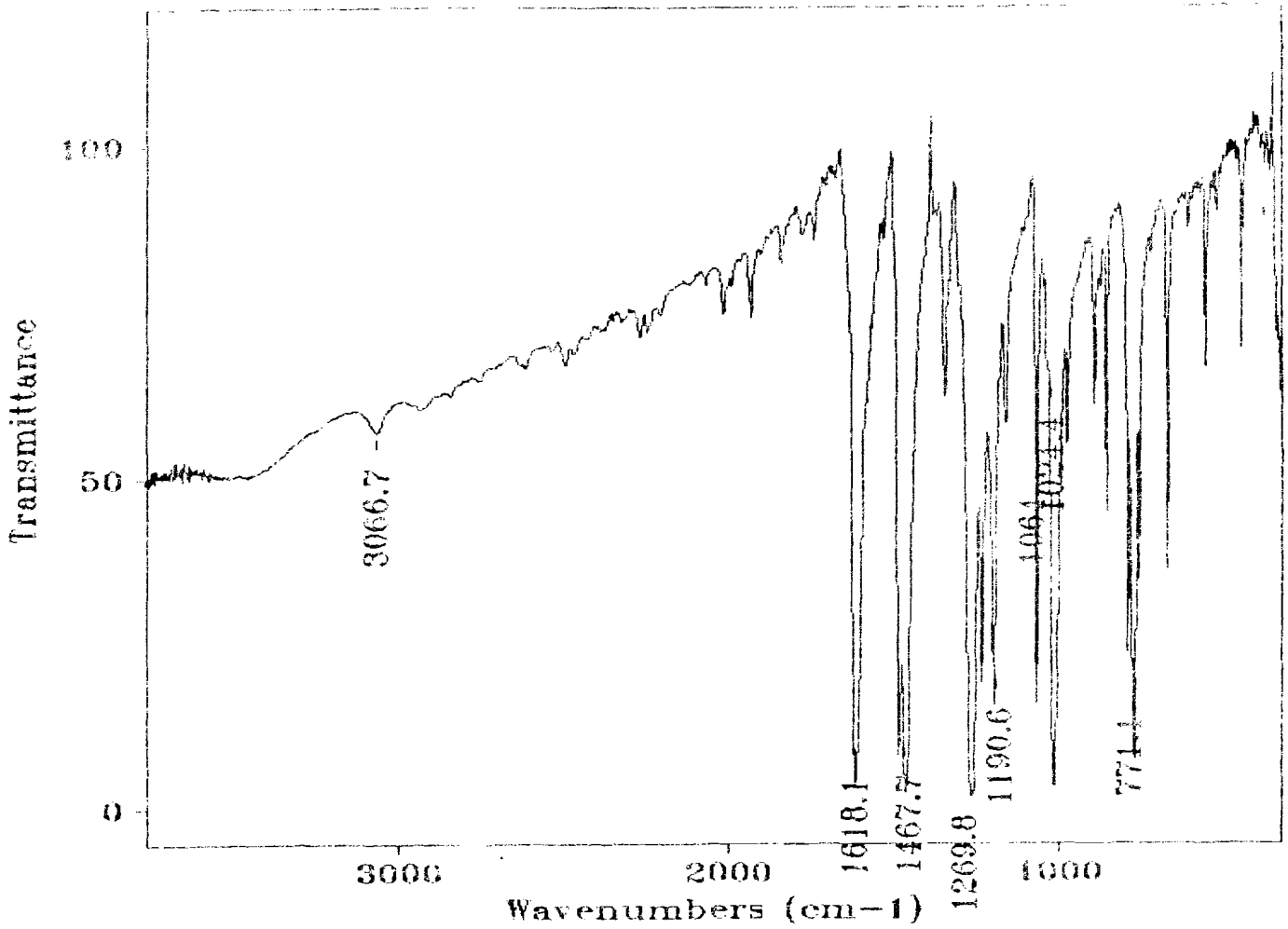

400
300
200
100
0Hz
400
300
200
100
0Hz
8.0
7.0
6.0
5.0
2
1
0
ppm

Figure 5: IR spectrum of sesquixanthene obtained from $LiAlH_4$ reduction, KBr pellet.



Sesquixanthene, KBr pellet Res = 4 cm−1

e. Spectral details of the product obtained from the reaction with benzyl chloride.

The NMR spectrum of the product (Figure 6) had peaks around 7.0 ppm, 1.5 ppm, 1.2 ppm, 0.7 ppm , and 0.5 ppm.

The IR spectrum of the product (Figure 7) obtained form the reaction with benzyl chloride had peaks at 3061.7 cm^{-1}, 2922.1 cm^{-1}, 1608 cm^{-1}, 1468.4 cm^{-1}, 1263.1 cm^{-1} , and 1065.9 cm^{-1}.

f. Spectral details of the product obtained from the reaction with dry ice.

The product didn't give effervescence with $NaHCO_3$; hence, it is not a carboxylic acid.

The IR spectrum of the product (Figure 8) had peaks obtained from the reaction with dry ice at 3435.8 cm^{-1}, 3066 cm^{-1}, 2937 cm^{-1}, 1611.1 cm^{-1}, 1482.1 cm^{-1} , and 1267.1 cm^{-1}.

Figure 6: NMR spectrum of the product obtained from the reaction with benzyl chloride.
Solvent: $CDCl_3$
Reference: TMS

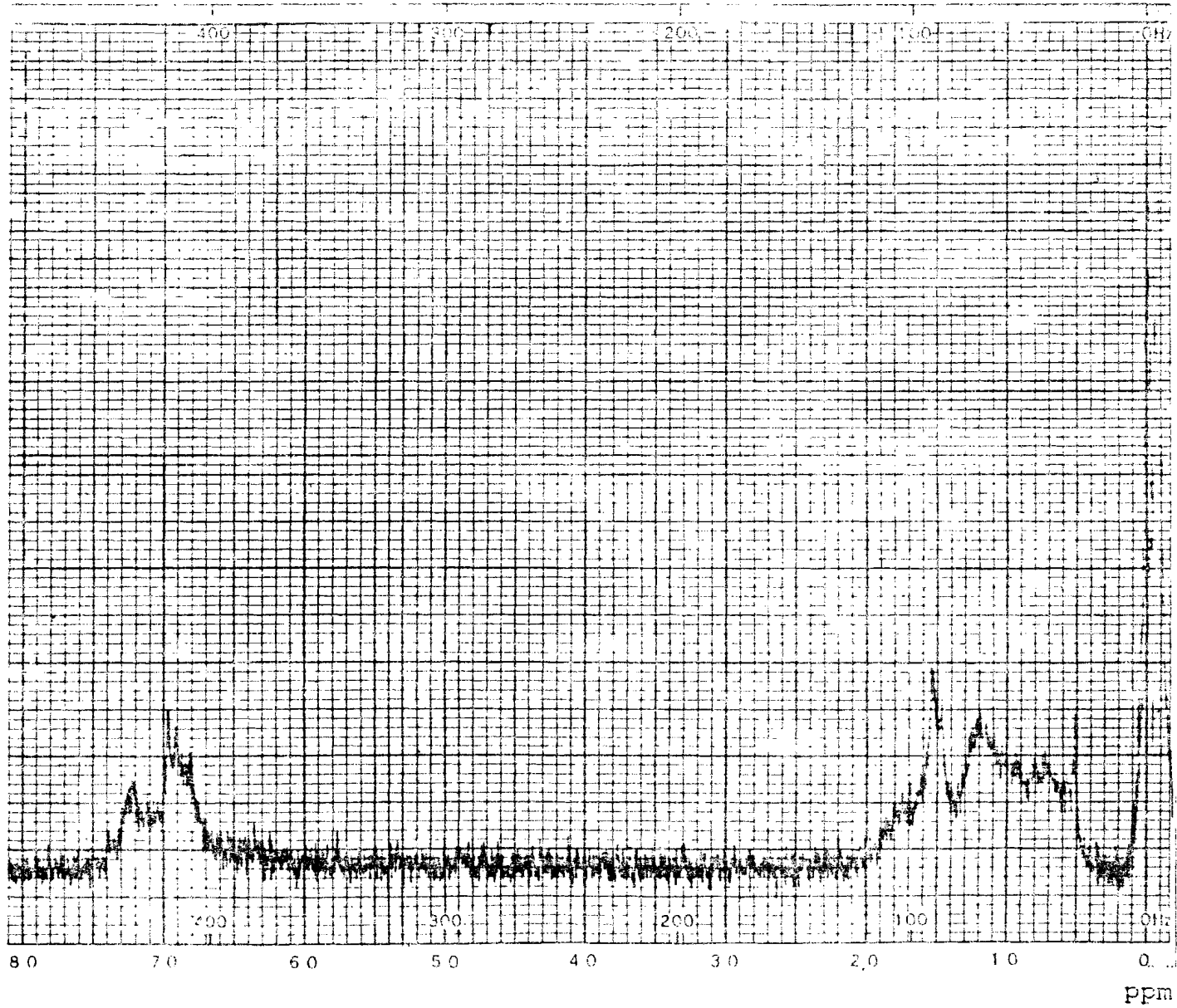
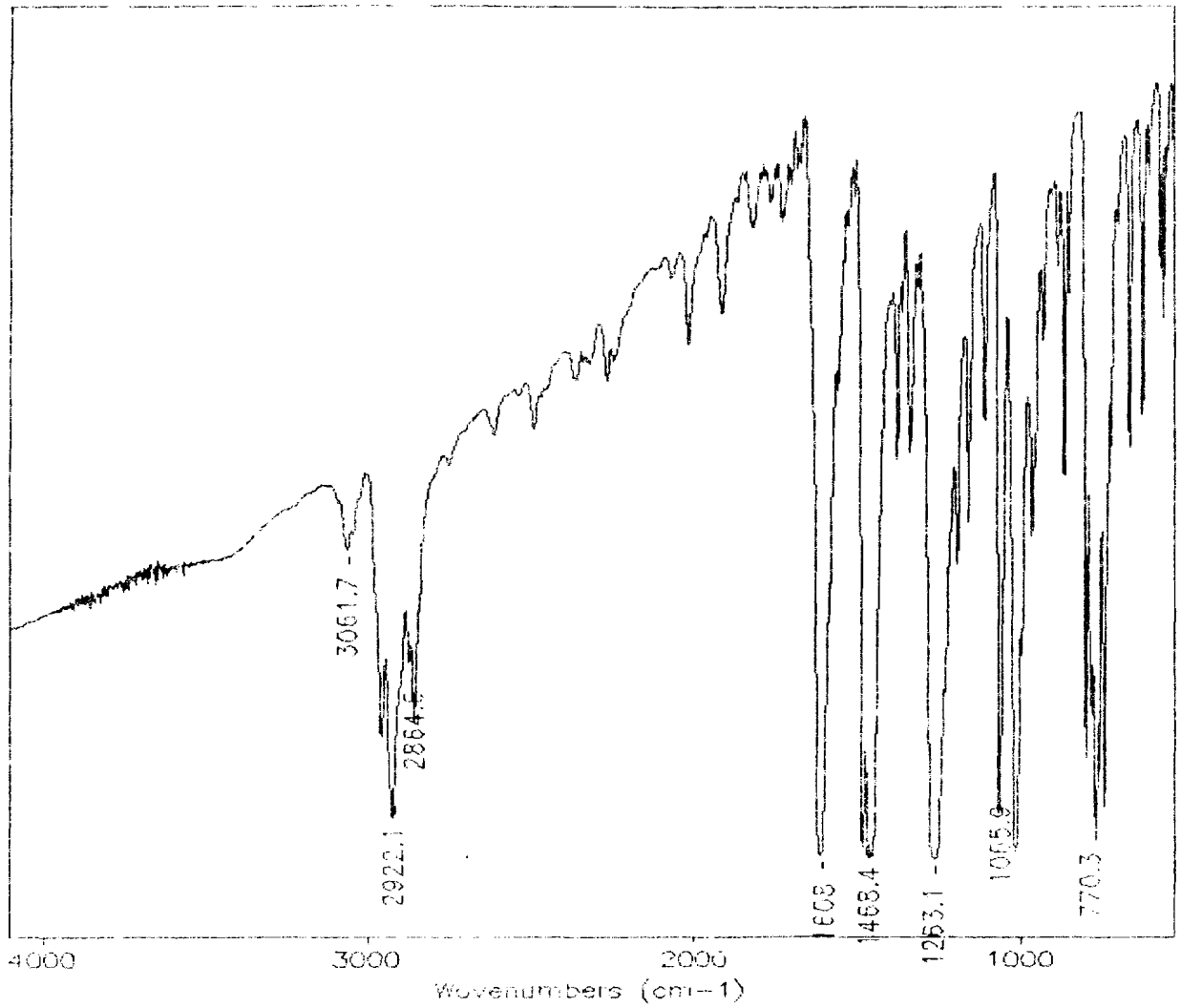
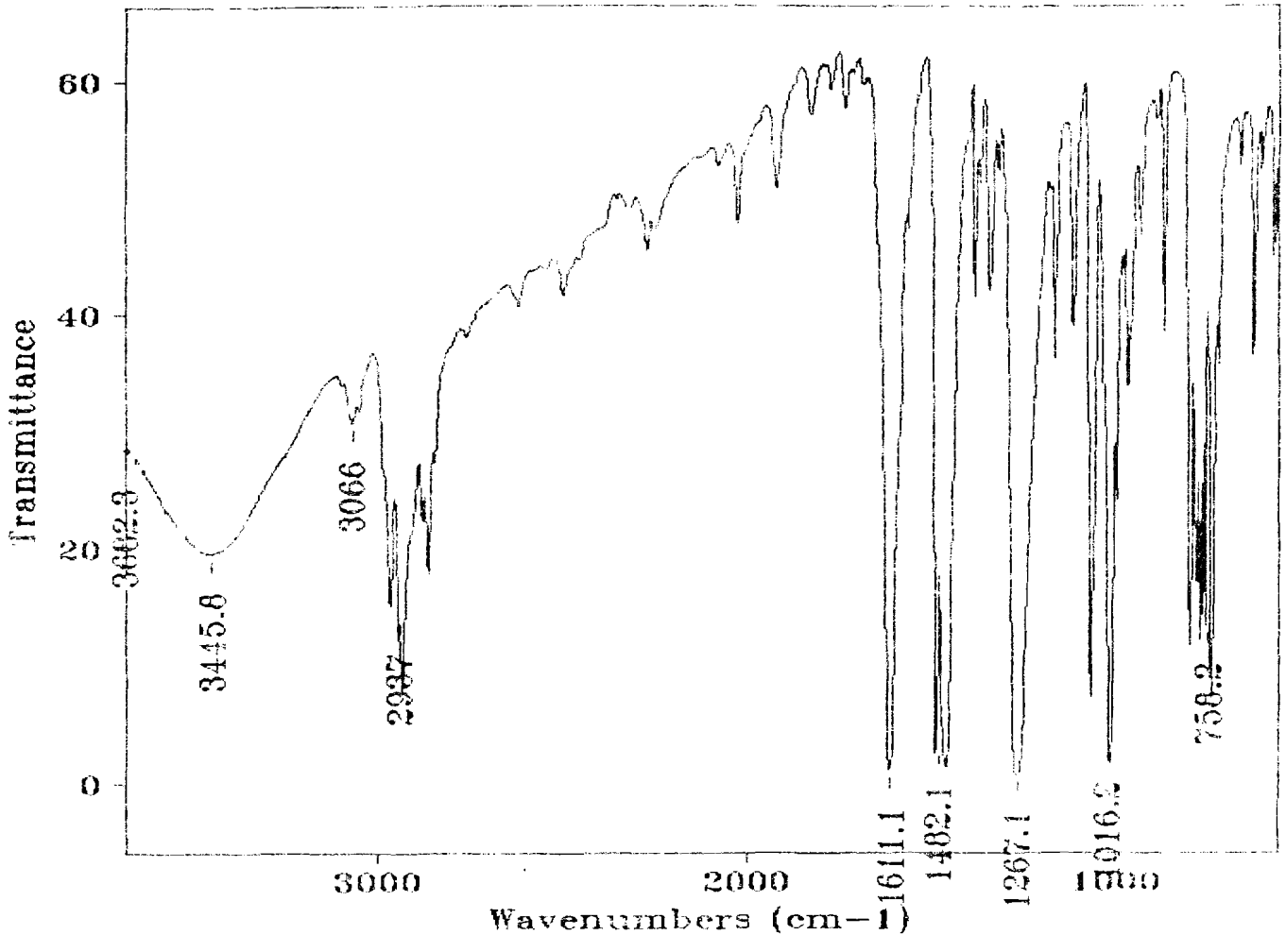

400
300
200
100
0Hz
300
200
100
0Hz
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.
ppm

Figure 7: IR spectrum of the product obtained from the reaction with benzyl chloride, KBr pellet.



Product from benzyl chloride reaction

Figure 8: IR spectrum of the product obtained from the reaction with dry ice, KBr pellet.



DIPROD Res= 4 cm−1 06/25/90 13:05

Product from sesquixanthene and dry ice

g. Spectral details of the aqueous solution sesquixanthydryl tetrafluoro borate salt.

The visible spectrum of the aqueous solution of the sesquixanthydryl tetrafluoro borate salt is given in Figure 9.

h. Spectral details of the product obtained from the reaction with benzyl magnesium chloride.

The NMR spectrum of the product (Figure 10) had peaks around 7.0 ppm, 2.9 ppm, 1.5 ppm , and 0.5 ppm.

The IR spectrum of the product (Figure 11) obtained from the reaction with benzyl magnesium chloride had peaks at 3438.8 cm^{-1}, 3034 cm^{-1}, 2363.4 cm^{-1}, 1636 cm^{-1}, 1458.9 cm^{-1}, 1269.1 cm^{-1}, 1066.7 cm^{-1}, 1016.1 cm^{-1}, and 782.1 cm^{-1}.

i. Spectral details of the product obtained from the reduction using $NaBH_4/H_2O$.

The NMR spectrum of the product (Figure 12) had prominent peaks around 7 ppm, 4.8 ppm, 1.5 ppm, 1 ppm , and 0.5 ppm.

The IR spectrum of the product (Figure 13) had peaks at 3078.2 cm^{-1}, 2355.4 cm^{-1}, 1616.2 cm^{-1}, 1468.4 cm^{-1}, 1271.3 cm^{-1}, and 1008.5 cm^{-1}.

Figure 9: Visible spectrum of sesquixanthydryl tetrafluoro borate salt solution.
Solvent: water

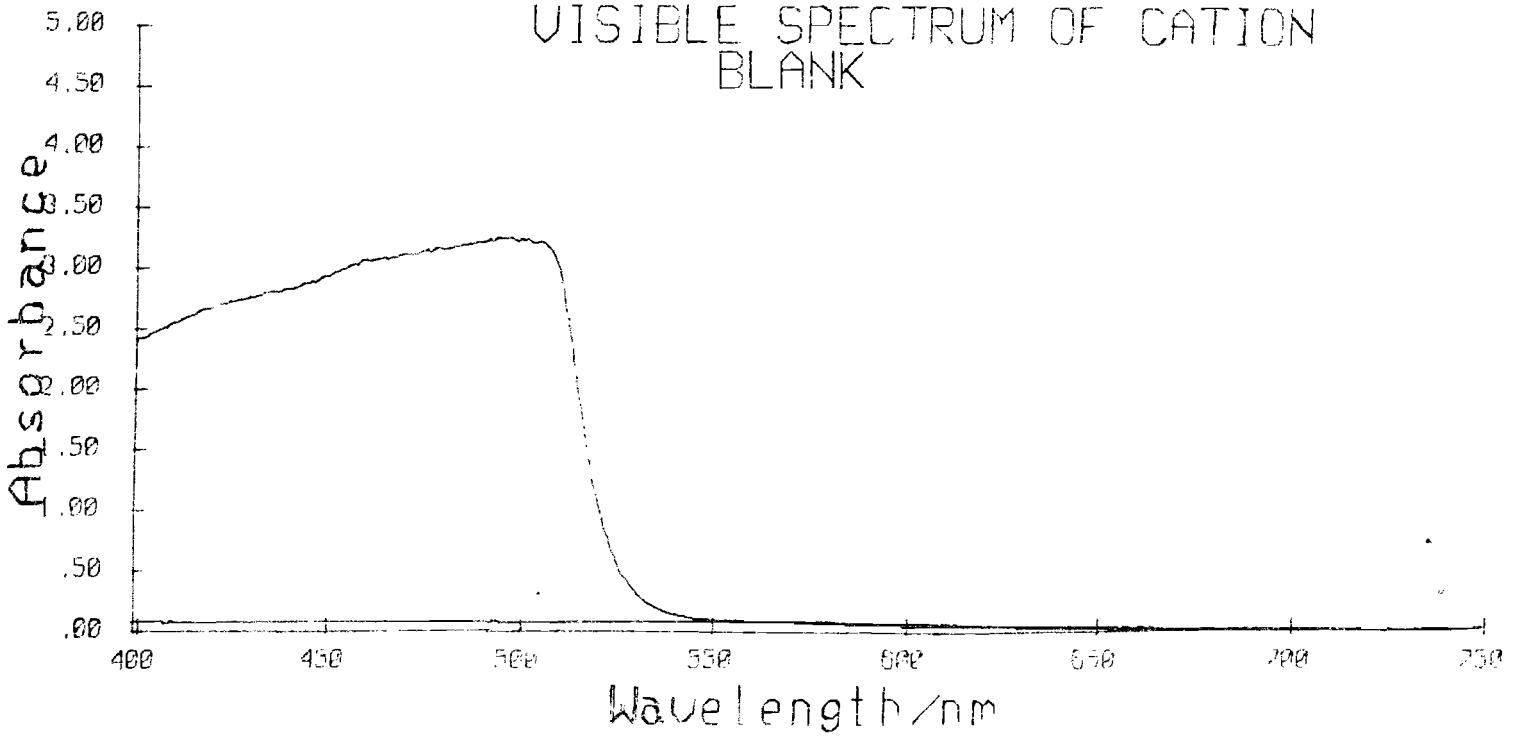

VISIBLE SPECTRUM OF CATION
BLANK
Absorbance
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
.50
.00
400
450
500
550
600
650
700
750
Wavelength/nm

Figure 10: NMR spectrum of product obtained from the reaction with benzyl magnesium chloride.
Solvent: $CDCl_3$
Reference: TMS

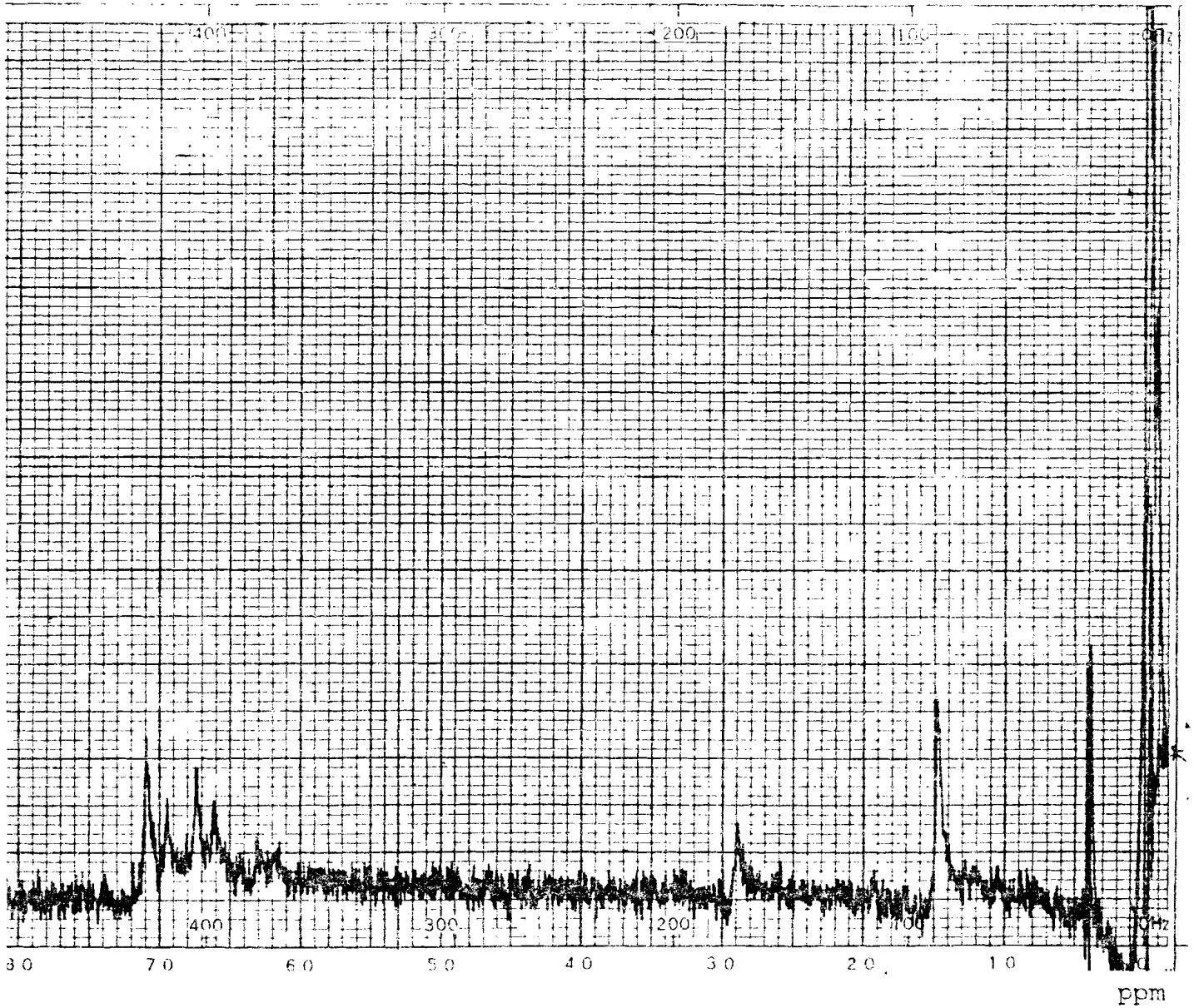

400
300
200
100
0Hz
400
300
200
100
0Hz
80
70
60
50
40
30
20
10
0
ppm

Figure 11: IR spectrum of the product obtained from the reaction with benzyl magnesium chloride, KBr pellet.

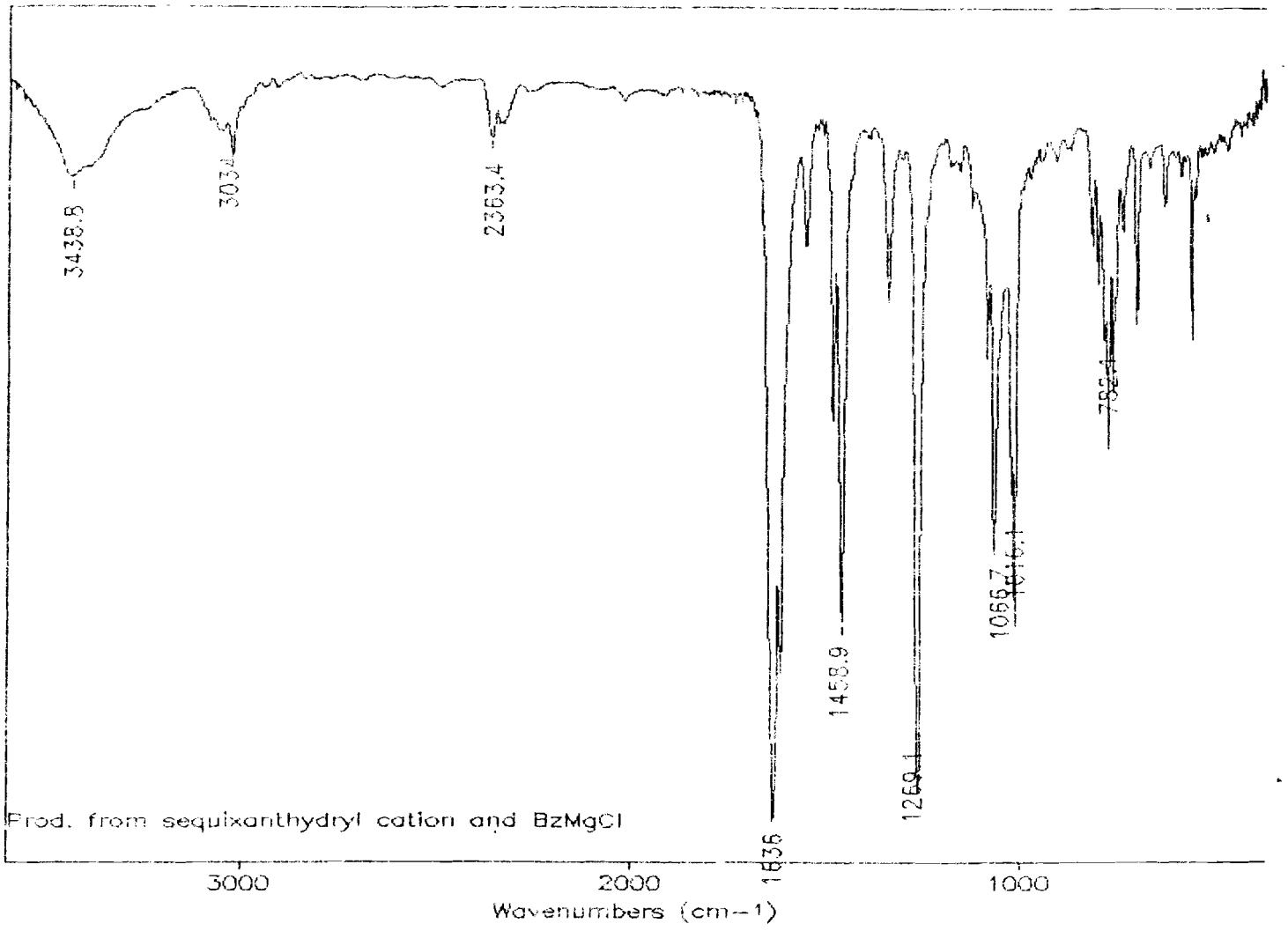

3438.8
303
2363.4
1636
1458.9
1269.1
1066.7
1016.1
784.1
Prod. from sequixanthydryl cation and BzMgCl
3000
2000
1000
Wavenumbers (cm-1)

Figure 12: NMR spectrum of sesquixanthene obtained from $NaBH_4/H_2O$ reduction reaction.
Solvent: $CDCl_3$
Reference: TMS

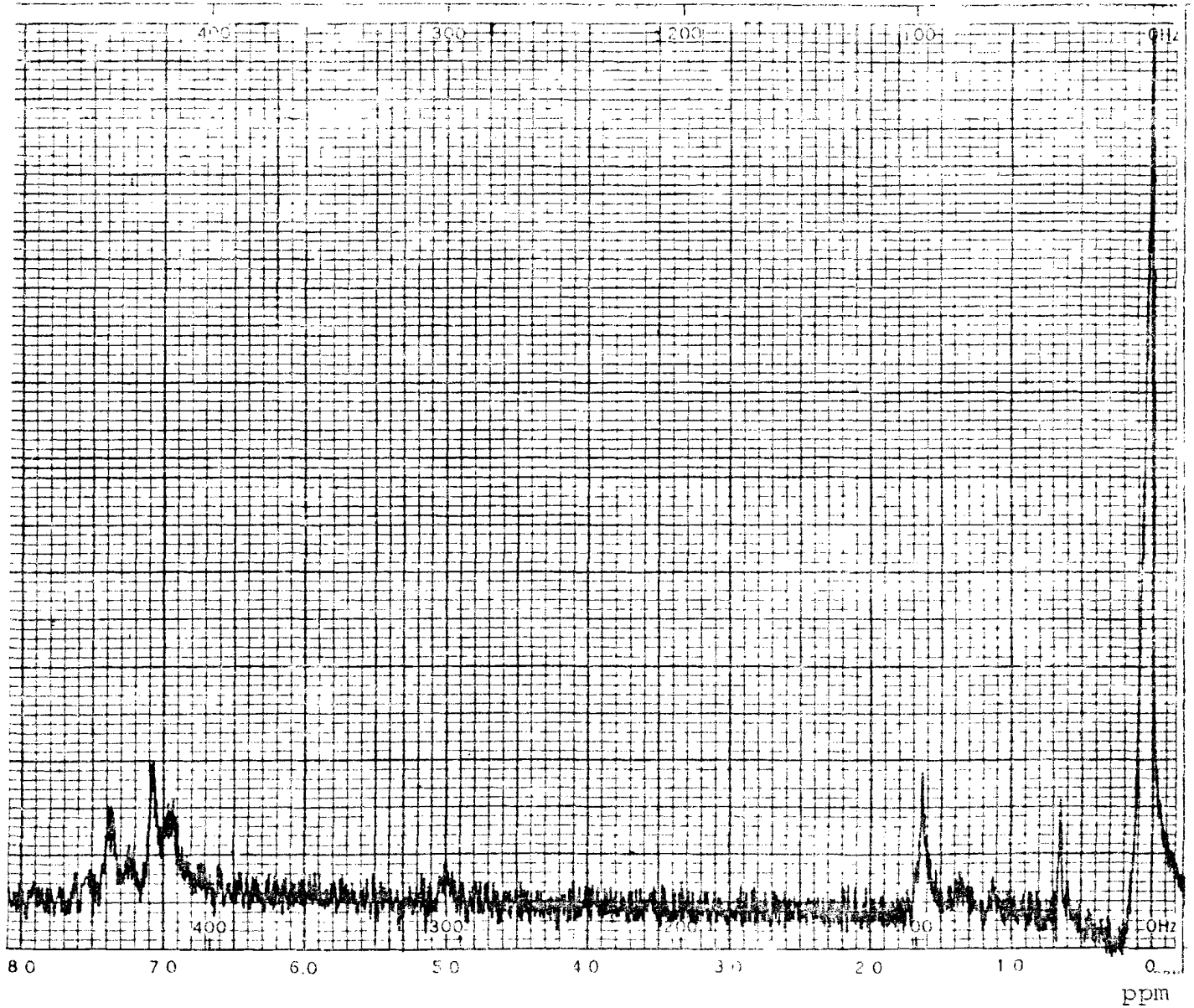
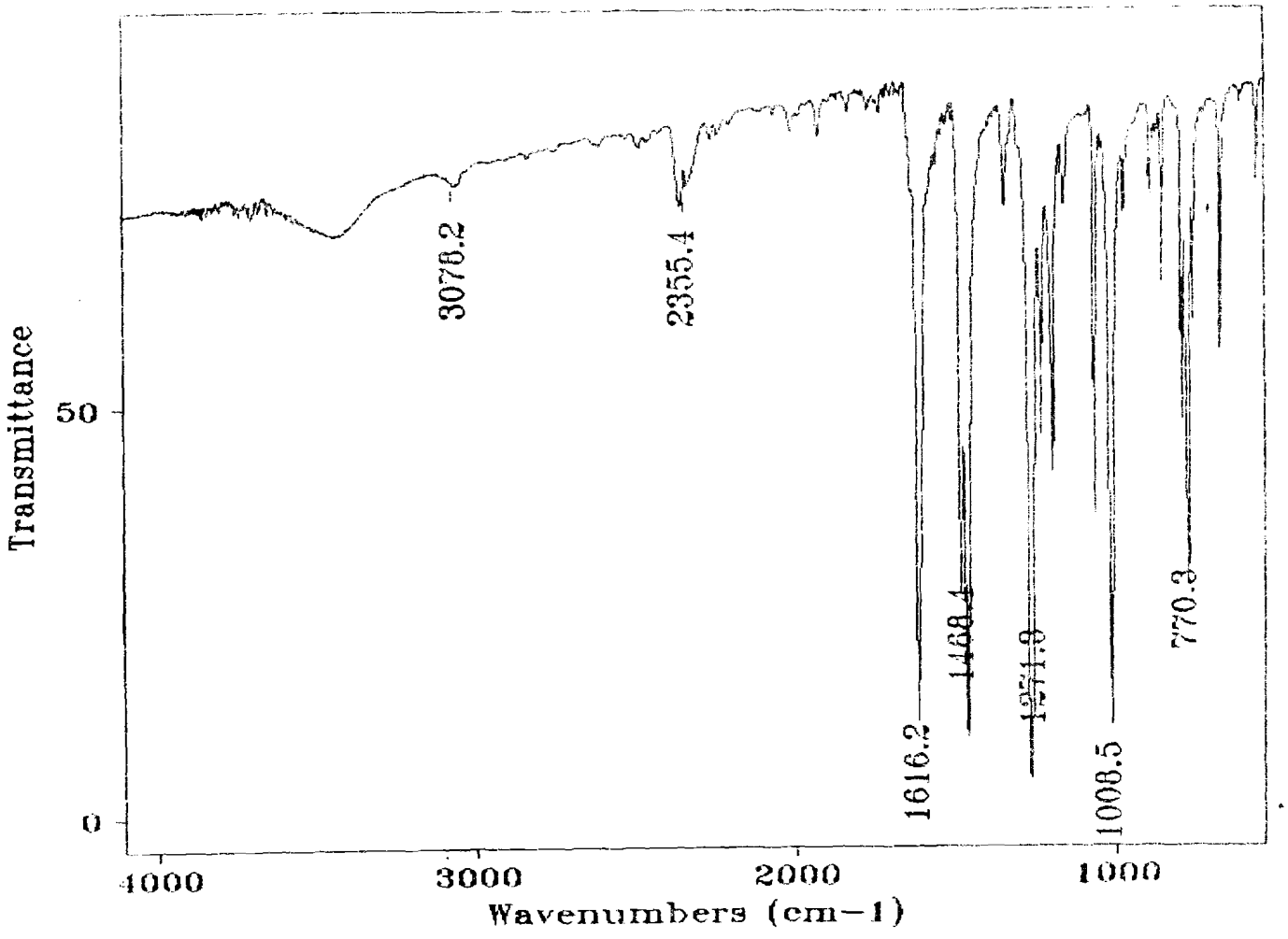

400
300
200
100
0Hz
400
300
100
0Hz
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

Figure 13: IR spectrum of sesquixanthene obtained from $NaBH_4/H_2O$ reduction reaction, KBr pellet.


Transmittance
50
0
3078.2
2355.4
1616.2
1468.4
1371.0
1008.5
770.3
4000
3000
2000
1000
Wavenumbers (cm-1)
SESE1
Res= 4 cm-1
07/17/90 11:18
Sesquixanthene from NaBH4/H20

Discussion

A thorough study of the spectra of the compound sesquixanthene and the products formed after reactions was done to confirm that a reaction had taken place. The spectra of sesquixanthydrol and sesquixanthene were compared to know whether reduction had taken place. For each reaction the spectra of the starting material and final product were compared to find whether expected results were obtained.

All of the NMR spectra peaks around 1.5 ppm and 0.5 ppm are due to the impurity present in $CDCl_3$ as shown by the spectrum of the solvent. If the spectrum of sesquixanthydrol is compared with sesquixanthene, it is determined that the broad peak around 2.2 ppm of sesquixanthydrol, which is an indication of an alcohol, is absent in sesquixanthene. The sharp peak in the spectrum of sesquixanthene around 4.8 ppm shows that the -OH group is replaced by -H and the chemical shift of this hydrogen is almost the same as expected. This shows that the reduction was successful.

Considering the product obtained from benzyl chloride reaction, the IR spectrum indicates absorption above 3000 cm^{-1} showing the presence of aromatic hydrogens. The absorption around 2900 cm^{-1} can be due to benzylic hydrogens. The latter peak can also be due to benzyl chloride which was added in excess. In the NMR spectrum

there also is no clear evidence for the presence of an additional benzyl group, namely, there is no different set of peaks for the hydrogens attached to the benzene ring forming the benzyl group and also for the $-CH_2-$ hydrogens. Additional evidence for the product expected is the color change in the formation of the carbanion, which was not observed.

The fact that the product formed from dry ice reaction didn't give effervescence with $NaHCO_3$ indicates that it is not a carboxylic acid. Absorption at 3445.8 cm^{-1} in the IR spectrum may be due to the presence of moisture in the compound. Moreover the carbonyl stretch is expected around 1725 cm^{-1} since it is not conjugated to the three benzene rings. Thus, the IR spectrum, which is very characteristic in the case of a carboxylic acid, indicates that carboxylic acid is not the product obtained.

In the reaction involving the cationic form of sesquixanthydrol, spectroscopic examination shows that the attempt to introduce a protecting group on the central carbon was successful. The most intense peak at 7.1 ppm in the NMR spectrum shows that the benzyl group is attached to the central carbon as a result of the reaction. The sharp peak at 2.9 ppm indicates the methylene hydrogens of benzylic substituent. The IR spectrum has absorption at 3034 cm^{-1} which is intense when compared to that of sesquixanthydrol or sesquixanthene. This shows that the

benzyl group is attached to the central carbon. The absorption peak at 1636 cm^{-1} is due to C-C stretch and the absorption peak at 1269 cm^{-1} is due to C-O stretch.

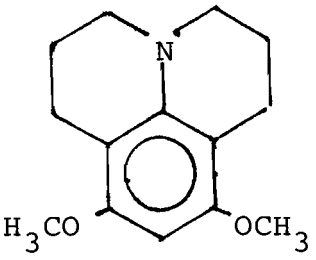
Reduction of the cation using $NaBH_4/H_2O$ was successful. That sesquixanthene was the product is confirmed by the IR and NMR spectra. The product decomposed at 240 - 252°C. This difference from the expected value may be due to the presence of impurities.

Since the reactions of anionic form of sesquixanthene with benzyl chloride and dry ice didn't yield as expected when n-butyl lithium was used, an attempt was made to generate the anion using methyl lithium. This also proved to be unsuccessful.

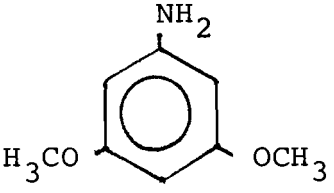
The purpose of this research project was to prepare a triarylmethane dye and introduce protecting groups on the central carbon. Only one of the methods to introduce a protecting group on the central carbon was successful. The need to protect the central carbon arises from the fact that sesquixanthene is easily converted to the cation with the aliphatic carbon as the center which is highly resonance stabilized and which won't undergo electrophilic substitution reaction readily.

To advance the state-of-the-art in this field, one could try the preparation of the dye from

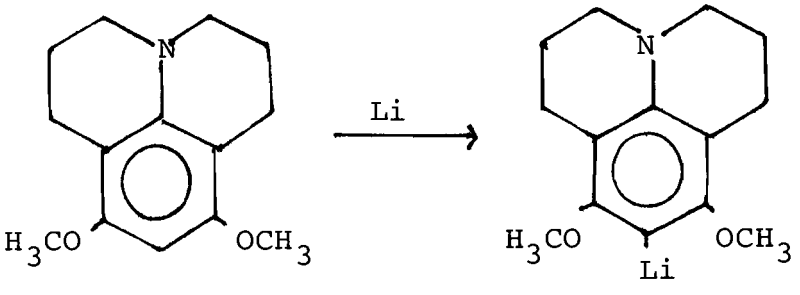
1,9 dimethoxy julolidine,

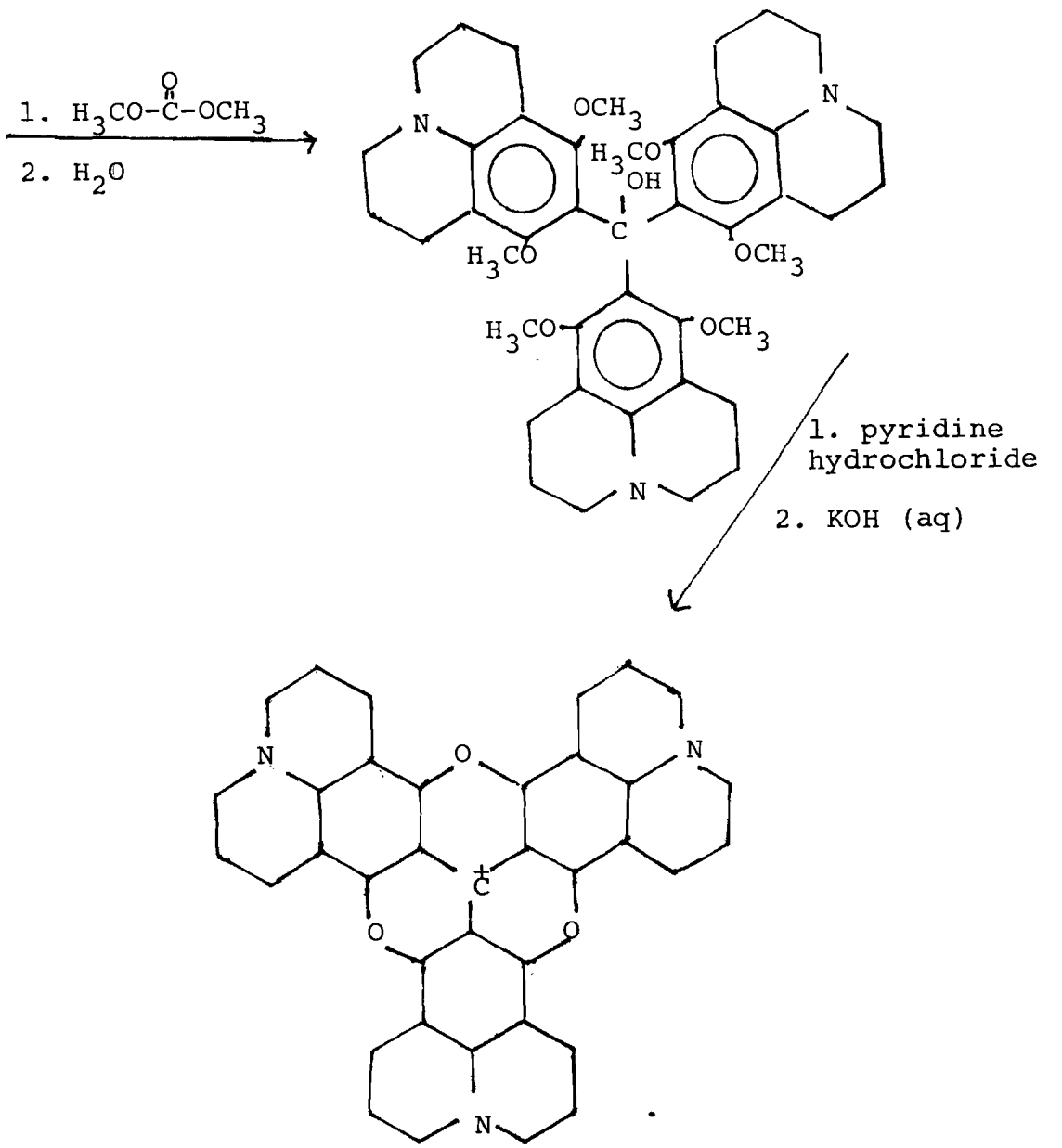


instead of preparing it from 3,5 dimethoxy aniline,



In the latter there are controversies regarding the position occupied by lithium. Dye prepared from the former one is expected to be more fluorescent and stable because the lone pair of electrons on nitrogen is coplanar with the three pi orbitals on the benzene rings. One of the methods to prepare it is as follows:




1. $H_3CO-\overset{O}{\overset{\|}{C}}-OCH_3$
2. H_2O
OCH_3
H_3CO
OH
C
H_3CO
OCH_3
H_3CO
OCH_3
N
N
N
N
1. pyridine hydrochloride
2. KOH (aq)
O
O
O
O
C
N
N
N

Bibliography

1. Lund, H. J. Am. Chem. Soc. 1927, 49, 1346.

2. Bunikiene, L.; Ramanauskas, E. Zh. Anal. Khim. 1968, 23 (9), 1364; Chem. Abstr. 1968, 69, 113233 w.

3. Bunikiene, L.; Ramanauskas, E.; Karpavieierie, V; Busilaite, E. Zh. Anal. Khim. 1968, 23 (11), 1679; Chem. Abstr. 1969, 70, 43815 g.

4. Yampol'skii, M. Z.; Khokhlov, L. M. Uch. Zap. Katedry Obshch. Khim. 1967, 35, 61; Chem. Abstr. 1969, 71, 18524 z.

5. Ganago, L. I.; Prostak, I. A. Zh. Anal. Khim. 1971, 26 (1), 104; Chem. Abstr. 1971, 74, 119702 y.

6. Kuznetsov, V. I.; Kleschel's Kaya, E. I. Agrokhimiya. 1970, (2), 148; Chem. Abstr. 1970, 73, 41531 z.

7. Badischi, Anilin & Soda-Fabrik A.-G. (by H. Finkenauer; H. Otterbach) British Patent. 1972, 902, 110, Chem. Abstr. 1962, 57, 12664 b.

8. Antropov, L. Z.; Kozlov, E. I.; Barmashenko, I. B. Tr. Ukr. Respub. Kone. Elecktrokhim, 1st. 1973, 2, 110; Chem. Abstr. 1975, 82, 46714 g.

9. Brazier, J. N.; Stephen, W. I. Analytica Chimica Acta. 1965, 33, 625.

10. Rao, N. V.; Dutt, V. V. S. E. Fresenius Z. Anal. Chem. 1971, 254 (2), 110, 128; Chem. Abstr. 1971, 74, 150686 v, 150688 x.

11. Coulter, A. K.; Schuster, I. I.; Kurland, R. J. J. Am. Chem. Soc. 1965, 87, 2278.

12. Ohla, G. A. Angew. Chem. Int. Ed. 1973, 12, 173.

13. Bowden, K.; Stewart, R. Tetrahedron. 1965, 21, 261.

14. Streitwieser, A. Jr.; Brauman, J. R.; Hammons, J. H.; Pudjaatmaka, A. H. J. Am. Chem. Soc. 1965, 87, 835.

15. Gold, V.; Hawes, B. W. V. J. Chem. Soc. 1951, 2102.

16. H. Gilman and J. W. Morton, J. Org. Reaction. 1954, 8.1, 286.

17. Slocum and Jennings. J. Org. Chem. 1976, 14, 3653.

18. Zakis, G.; Neiberte, B; Melke, A. Khim. Drev. 1973, 14, 98-108. Chem. Abstr. 1973, 65459 y.

21. Rene, L.; Busson, J. P.; Royer, R. Bull. Soc. Chem. Fr. 1974, (3-4, pt.2), 475-6 (Fr), Chem. Abst. 1974, 63416 h.

19. Williamson, K. L. Macroscale and Microscale organic experiments. D. C. Heath and Co., Lexington, 1989. Pages 354, 355.

20. Williamson, K. L. Macroscale and Microscale organic experiments. D. C. Heath and Co., Lexington, 1989. Pages 374, 375.

21. Rene, L.; Busson, J. P.; Royer, R. Bull. Soc. Chem. Fr. 1974, (3-4, pt.2), 475-6 (Fr), Chem. Abst. 1974, 63416 h.

22. Williamson, K. L. Macroscale and Microscale organic experiments. D. C. Heath and Co., Lexington, 1989. Pages 372, 373.