UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

SYNTHETIC APPROACHES TO TRIS(1-B, 8-B'-NAPHTHYL)DIBORON

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

by William Karl Goerich MS 1970

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This Thesis

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Abstract

Goerich, William K. Synthetic Approaches to Tris(1-B, 8-B'-naphthyl)diboron. Department of Chemistry, May, 1970.

The purpose of this project was the synthesis of tris(1-B, 8-B'-naphthyl)diboron. The synthesis route attempted was the preparation of 1,8-dibromonaphthalene from 1,8-diaminonaphthalene by tetrazotization followed by a Sandmeyer reaction, treatment of the dibromo compound with n-butyllithium to give 1,8-dilithionaphthalene and subsequent addition of boron trifluoride to give the product.

When attempts to prepare the dibromonaphthalene by a tetrazotization reaction failed, an alternate procedure was followed and 1-bromo-8-iodonaphthalene was prepared from the diamine by way of the azimide. Reaction of this dihalonaphthalene with n-butyllithium and subsequent treatment with boron trifluoride diethyl ether adduct led to the formation of many by-products as shown by thin layer chromatography and mass spectra. The product was not isolated.

Acknowledgment

I wish to thank Dr. William B. Martin, Jr. of Union College for his aid and encouragement on this project. I wish to thank Dr. Jimmy L. Webb of the General Electric Company Research and Development Center for his helpful suggestions and encouragement. I express my grateful appreciation to the General Electric Research and Development Center, Schenectady, New York, for the use of laboratory, equipment, chemicals and analytical services.

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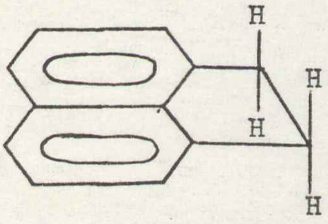
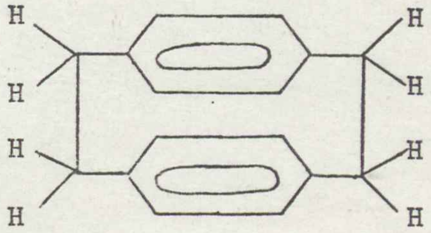
Introduction

Trinaphthobicycloundecanes and their bridgehead hetero analogs are of interest to Prof. William Martin for several reasons. The structures of these compounds are unique and are of interest in relation to similar structures such as triptycene (III) and the paracyclophanes.

Electron spin resonance (esr) has shown a high degree of hyperconjugation[1] in acenaphthalene (I) but a low degree in [2.2]paracyclophane (II).[2]



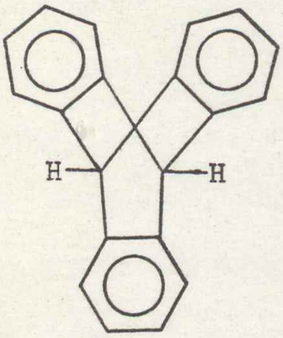
I



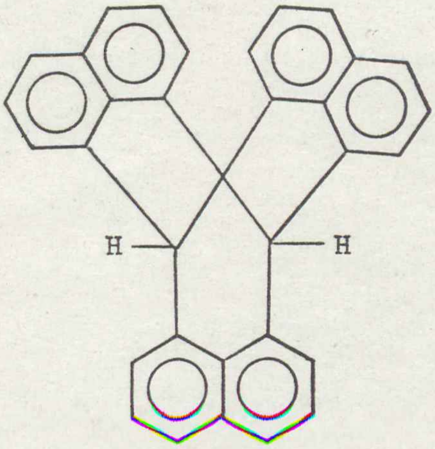
II

This is attributed to the lack of overlap of the sigma carbon-hydrogen bonds with the pi cloud of the aromatic ring in [2.2]paracyclophane, while in acenaphthalene a large amount of overlap can exist.

In triptycene (III) there should be little hyperconjugation due to the lack of overlap of the sigma carbon-hydrogen bonds and the pi cloud of the ring since the carbon-hydrogen bonds are parallel to the planar aromatic rings. Similarly, in the trinaphthobicycloundecane (IV), there should be minimal hyperconjugation unless steric hindrance due to the vicinal hydrogens on the naphthalene rings forces the bridgehead hydrogens out of the planes of the naphthalene rings.

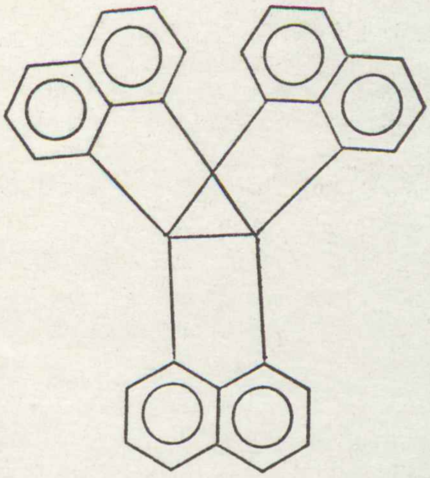


III



IV

A structure with sigma bonded bridgehead carbons such as V might be



V

prepared. If this compound were prepared, it would be most interesting because the carbon-carbon bond length of the central bond would be in the neighborhood of 2.3 Å compared to a normal bond length of 1.54 Å.

Some work has been started on V under the direction of Dr. Martin.[3] Certain analogues of V with hetero atoms at the bridgeheads would be interesting such as the nitrogen and boron analogues and the mixed nitrogen-boron analogue. The mixed nitrogen-boron analogue would be especially interesting with respect to a possible coordinate covalent bond between the boron and nitrogen held at a fixed distance by the rigid naphthalene structure. The catalytic properties of the diboron compound and other analogs should be carefully studied to relate with catalytic properties of simpler compounds.

Esr work mentioned earlier has shown that the radical anions of [2.2]- and [3.3]paracyclophane allow rapid intramolecular electron transfer between rings. The [4.4]paracyclophane anion does not allow rapid electron transfer, presumably because of greater ring separation and flexibility which allows nonparallel arrangement of the rings. The same work also showed that 4,4'-dimethylbibenzyl does not allow rapid transfer of the odd electron between the two aromatic rings. Yet, diphenyl methane, with but one carbon between the rings, does allow rapid transfer of the electron in its radical anion.

The question arises as to whether any single methylene or methine bridge between two benzenoid rings allows electron transfer in the radical anion. The diboron analog, whose synthesis was attempted in this project, will not answer this specific question. If it is assumed, however, that the empty P_z orbitals of the borons are improperly oriented to aid in transfer of electrons, then esr studies on the radical anion may answer the question of whether the nonparallel rings have enough pi cloud overlap to allow for rapid transfer of electrons.

Another interesting compound related to these is the bicyclo undecane system with two naphthalenes and an anthracene. One could examine how this fixed geometry behaves with respect to energy transfer of electromagnetic energy absorbed uniquely by the naphthalene and emitted by the anthracene as fluorescence or phosphorescence. An excellent review of work to date in this area is given in a book by E. C. Lim.[4]

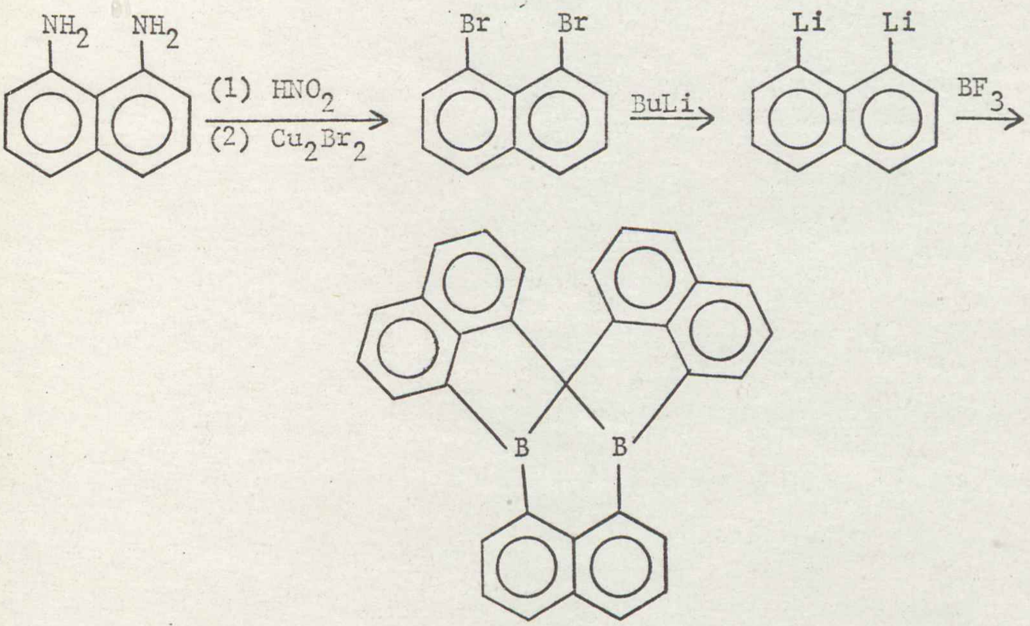
Historical

Aromatic organoboron compounds have been known for a relatively long time. Of particular interest to this project was the synthesis of tri-α-naphthyl borine by Krause and Nobbe[5] in 1930. The compound was prepared from the Grignard reagent of 1-bromonaphthalene and boron trifluoride. Significantly, the compound was reported to be stable in air and had a melting point of 203°C. Most aromatic boron compounds are sensitive to oxygen and this and their low volatility can make their separations from reaction mixtures difficult.[6] It is advisable to handle organoboron compounds in an inert atmosphere.

The synthesis of tris(1-B, 8-B'-naphthyl)diboron is not reported in the literature. However, certain 1,8-dihalonaphthalenes are known and these may be treated with n-butyllithium to give 1,8-dilithionaphthalene.

Discussion

The original proposal for this project involved the following synthesis scheme:

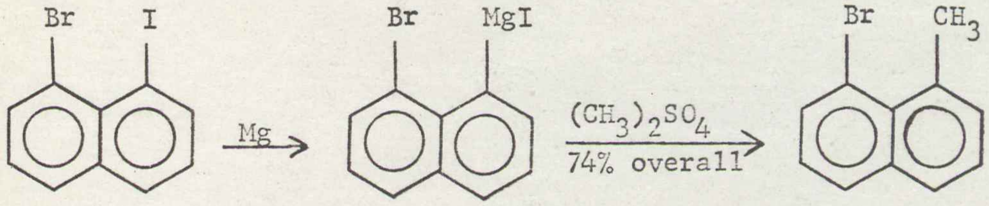


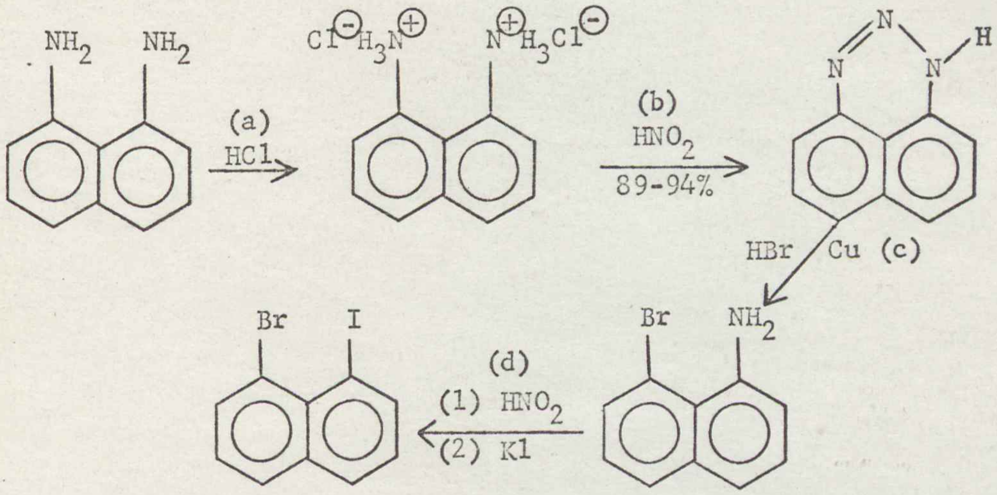
VI

This procedure presented two major difficulties. The first was the difficulty of preparing 1,8-dibromonaphthalene by a direct tetrazotization method. Prof. William B. Martin had pointed out the difficulties he had encountered in attempts of this reaction[7] and Letsinger, Gilpin and Vullo mention poor yields in their attempts to prepare the compound by this method.[8] The second major difficulty was the reaction of 1,8-dilithionaphthalene with boron trifluoride. The former is a difunctional molecule and the latter is a trifunctional molecule. The possibility of formation of polymeric material is evident.

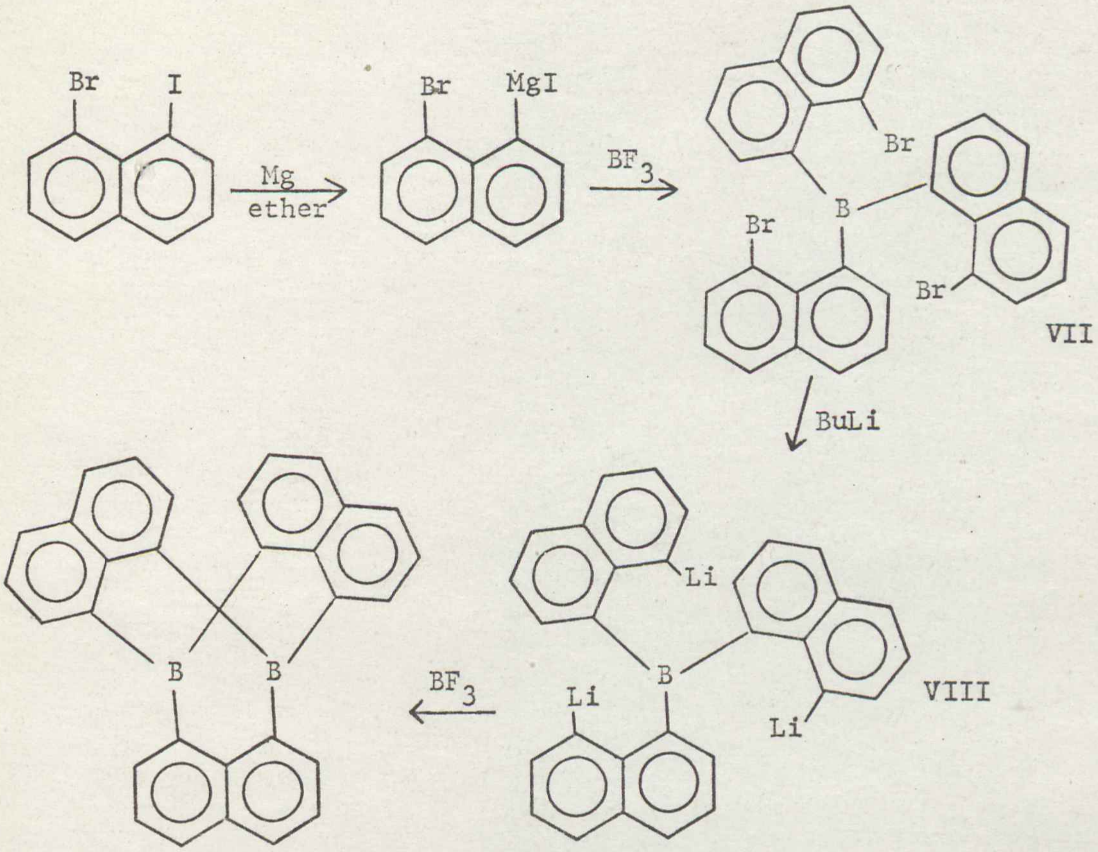
Despite known difficulties, the tetrazotization reaction was attempted using the procedure of Hodgson and Whitehurst[9] as a basis. One problem was the isolation of the product. The reference does not mention how the product was isolated. Attempts to use solvent extraction were unsuccessful. Perhaps a steam distillation would have isolated any 1,8-dibromonaphthalene formed, but this was not attempted because a new approach to the synthesis was decided upon.

A reaction of 1-bromo-8-iodonaphthalene is mentioned in Fieser and Fieser.[10] It was reasoned that this compound would undergo the exchange reaction with butyl lithium as readily as 1,8-dibromonaphthalene and perhaps a synthesis for this compound might be easier. Examination of the literature yielded a synthesis procedure developed by Fieser and Seligman.[11] The procedure involved preparation of an azimide, which could be converted to the bromo-amino compound and, through diazotization, to the bromo-iodo compound. The final step (d) could be modified to yield 1,8-dibromonaphthalene. The reaction shown for the bromo-iodo compound illustrates that the halogens on the naphthalene can react selectively. A new synthesis route to the diborine was proposed based





upon this observation.



This route avoids the difunctional dilithionaphthalene and would tend to lessen the formation of polymeric material.

The synthesis of 1-bromo-8-iodonaphthalene was attempted following the method of Fieser and Seligman. The difficult step in this synthesis is the conversion of the azimide to the bromo-amino compound. These workers used heat treated copper for the reaction. Klemm, Sprague and Mak[12] followed the procedure of Fieser and Seligman but were unsuccessful in the use of heat treated copper. They reported that the use of copper turnings in 48% HBr was effective. Fieser and Seligman mention that the coating of copper oxide produced in the heat treatment is important for catalysis of the desired reaction. Untreated copper gave poor yields.

Taking these findings into consideration, the reaction was tried using copper turnings and 48% HBr. This gave a poor yield. Another attempt was made using copper turnings and copper shot which had been heated in a Bunsen burner flame. This gave some product, but was still low in yield. In order to be sure that copper oxide was present, both cuprous and cupric oxide were added along with copper turnings and heat treated copper shot. This gave a yield in at least one attempt which was as high as that reported in the literature.

The bromo-iodo compound was prepared according to the procedure of Fieser and Seligman except that a saturated solution of potassium iodide was used.

The crude bromo-iodo compound was purified by use of column chromatography. This proved to be an effective method of purification because it was not necessary to use heat. Aromatic iodides may decompose on heating. The melting point was only three degrees below that reported in the literature after one recrystallization from methanol.

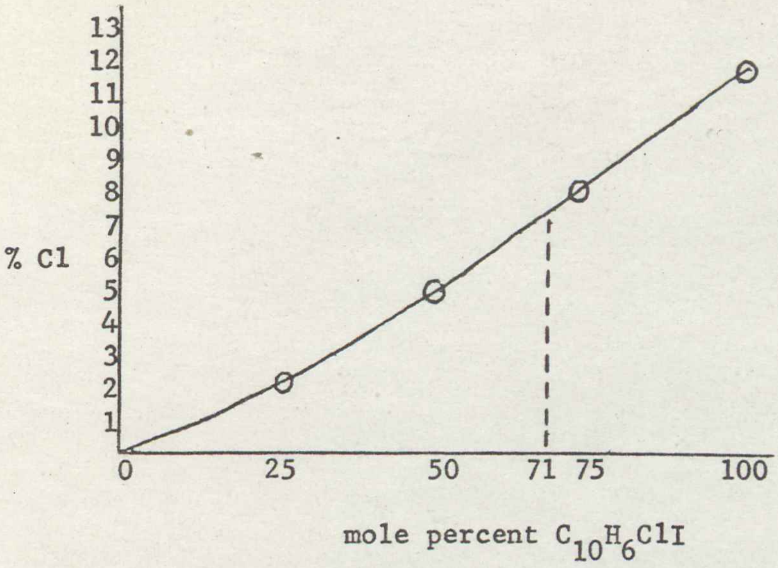
An elemental analysis on the compound indicated the presence of chlorine. This was very surprising. At first it was thought that there must have been an error in the analysis but a mass spectrum confirmed this. The mass spectrum showed a large parent peak at 332 m/e. There was a peak at 288 m/e indicating the presence of chloro-iodonaphthalene although this peak was less than one-tenth the intensity of 332 m/e. It should be noted that in the mass spectra of chloro and bromo derivatives, the appropriate doublets representing isotope distribution were observed. A peak at 166 m/e which was assigned to $C_{10}H_6BrI^{++}$ was also at least ten times larger than a peak at 144 due to $C_{10}H_6ICl^{++}$. Also the peak at 205 m/e, $C_{10}H_6Br^+$, was at least ten times larger than the peak at 161, $C_{10}H_6Cl^+$. However, mass spectroscopy is not an effective technique for quantitative study. The intensity of a peak depends in part upon the stability of the positive ion. Direct comparisons are thus invalid, although they may be somewhat indicative. Interestingly, there was no peak at 240 which would correspond to $C_{10}H_6BrCl^+$.

Examination of the mass spectrum for bromo-aminonaphthalene showed a parent peak at 221 m/e. A peak at 177 m/e (less than one-tenth the intensity of 221 m/e) indicated chloro-aminonaphthalene. This showed conclusively that chlorine had been introduced into the molecule before the diazotization reaction was performed. The only time chloride ion was present in the reaction scheme was in the initial reaction to form the azimide. The azimide was isolated by simply filtering the reaction mixture. Since the azimide is an amine, it could have formed a hydrochloride salt. Reaction of the azimide hydrochloride with copper in HBr may have produced the chloro-aminonaphthalene.

The chlorine analysis of 8.3% means that the compound is about 71 mole percent $C_{10}H_6ClI$. This was calculated by assuming some mole percents and calculating the percent chlorine.

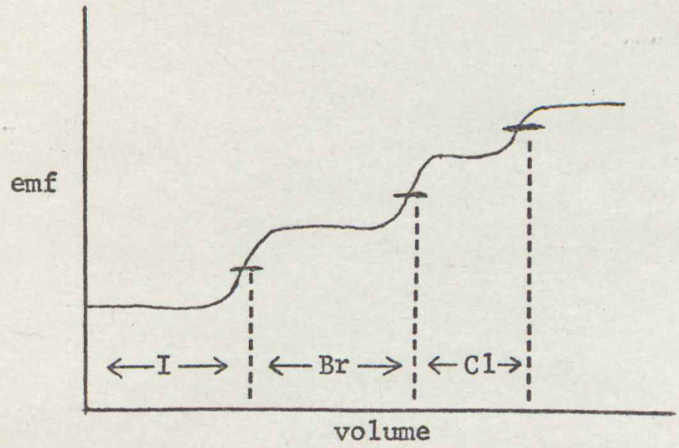
mole percent $C_{10}H_6ClI$	mole percent $C_{10}H_6BrI$	percent chlorine
0	100	0.0
25	75	2.7
50	50	5.7
75	25	8.9
100	0	12.3

The information was plotted and from the graph the actual mole percent can be found.



Such a high mole percent of the chloro-iodocompound did not seem reasonable because all relevant peaks in the mass spectrum indicated that 1-chloro-8-iodonaphthalene was a smaller component of the mixture than the bromo-iodocompound.

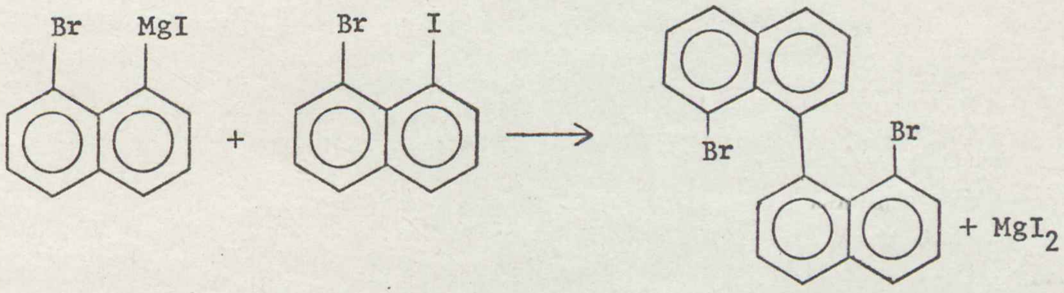
The chlorine analysis was done by burning the sample in an oxygen combustion chamber and the sample gases were absorbed in water. The solution was treated with hydrazine sulphate to reduce all halogens present to halide. The solution was then acidified and titrated with silver nitrate using an automatic potentiometric titrating device. The recorder plots emf versus volume of silver nitrate added.



From the amount of silver nitrate added, the elemental analyses can be calculated.

Although this method is theoretically sound, it is likely that an error was made in the halogen analysis. For one thing the total elemental analysis adds up to 103% which is an obvious error. The actual mole percent of 1-chloro-8-iodonaphthalene is probably 10%. This can be assumed from the mass spectrum and checked by the carbon analysis, which is done independently of the halogen analysis. The calculated percent carbon for a 10 mole percent mixture of $C_{10}H_6ClI$ in $C_{10}H_6BrI$ is 36.6%. This was the exact result of the carbon analysis. If it were assumed that the chlorine analysis were true and there were 71 mole percent $C_{10}H_6ClI$, then the carbon analysis would be expected to be 39.9% which is far from the actual analysis.

The reaction of the 1-bromo-8-iodonaphthalene with magnesium to give the mono-Grignard seemed to give some by-products. One of the by-products was fluorescent. This could have been formed by a coupling reaction of the Grignard since many aromatic hydrocarbons larger than naphthalene are fluorescent. Iodides couple rather easily with Grignards.[13] When Grignard compounds are hydrolyzed, the product is the hydrocarbon. Gas liquid chromatography showed 1-bromonaphthalene to be present when a sample from the reaction was quenched in water. This showed that the



Grignard had formed. Boron trifluoride was introduced to the reaction flask in the form of its diethyl ether adduct because this is far more convenient to work with and measure than the gas. A reddish brown color was quickly formed, indicating reaction was taking place. The product, believed to be VII, came out of solution as an oil.

Since the plan was to treat VII with n-butyllithium to give VIII, the fact that VII came out of solution was a detriment. Also, the formation of by-products showed that the reaction was not very clean.

An attempt was made to make the di-Grignard reasoning that this could be treated directly with boron trifluoride to give VI. The reaction was done in tetrahydrofuran which is sometimes effective in making di-Grignards.[14] This was a rather poor situation because of the presence of chlorine. Aromatic Grignards are difficult to form with chlorides.[15] Also, the iodide promotes coupling. Thus it was not too surprising that the di-Grignard was not formed to any appreciable extent. Gas liquid chromatography showed only a trace of naphthalene when a sample was hydrolyzed. Heating the reaction mixture produced a product that was very fluorescent.

The use of n-butyllithium to form 1,8-dilithionaphthalene was far more successful than attempts to prepare the di-Grignard. It has been reported[16] that 1-bromonaphthalene gives a 95% yield of 1-lithionaphthalene upon treatment with n-butyllithium. The reaction is an equilibrium reaction; the lithium will tend to bond to the more nucleophilic species. Since the phenyl group is more nucleophilic than the butyl group, exchange is favored. Reaction of 1,8-dibromonaphthalene with n-butyllithium is reported to give an 85% yield.[17] It is interesting to note that, whereas the 1,8-dibromonaphthalene gives a high yield, 5,6-dibromoacenaphthene exchanges only one bromine. The 1,8-positions seem to stabilize the two positive lithiums better than the 5,6-positions.[18]

The first reactions were done by adding n-butyllithium to a solution of the 1-bromo-8-iodonaphthalene at room temperature. Gas liquid chromatography indicated that a large amount of naphthalene was formed when a sample from the reaction flask was quenched in water. A small amount of what appeared to be 1-bromonaphthalene still remained. This indicated that although the exchange had gone to high yield (~ 90% by glc) the stoichiometric amount of butyllithium did not give complete exchange. Thin layer chromatography showed three spots. The one of highest r.f. value corresponded to naphthalene. The middle spot was fluorescent and the third spot was at the origin. The fluorescent spot was probably due to a coupling reaction, similar to that postulated for the Grignard coupling reaction. Additional ether was added to dilute the dilithionaphthalene solution and the boron trifluoride was added in dilute concentration and with slow addition. It was hoped that high dilution would tend to favor intramolecular reactions, giving the reactants a chance to form the desired product and hindering formation of polymeric material. The reaction seemed to be rapid, because as the dilute boron trifluoride ethyl ether adduct was added, a reddish brown color formed. A mass spectrum on the precipitate formed showed a huge number of peaks. There was only a small peak at 400 m/e which is the molecular weight of the desired product VI. There did not seem to be much high molecular weight material formed because the highest peak was at 516 m/e. Most of the peaks formed seemed to be of intermediates leading up to the desired product. A peak at 515 m/e may be $C_{40}H_{24}B^+$. Such a species could form in the reaction flask if an excess of the dilithionaphthalene were present.[19] Since the boron trifluoride was added to the dilithionaphthalene, this is quite possible. A salt of formula $(C_{10}H_6)_4B^-Li^+$ could have formed. To limit this possibility, subsequent additions of boron trifluoride were done rapidly. A peak at 389 m/e was probably $C_{30}H_{18}B^+$. A peak at 310 m/e was unexplained, although $C_{20}H_{12}B_2F_2^+$ would be 312 m/e. A peak at 264 m/e was probably $C_{20}H_{13}B^+$. A peak at 252 m/e was probably $C_{20}H_{12}^+$. A peak at 202 m/e was unexplained. A peak at 200 m/e may have been $C_{30}H_{18}B_2^{++}$. The last major peak was at 128 which was naphthalene.

The final experiment was done at low temperature to minimize any coupling reactions. Also, the 1-bromo-8-iodonaphthalene was added to the n-butyllithium to further reduce the possibility of coupling. An excess of butyl lithium was used to force the equilibrium over toward dilithionaphthalene. This introduced the problem of forming mixed borines of naphthalene and butyl groups. However, it is unlikely that these would be formed because they tend to disproportionate, especially in the presence of butyllithium.[20] The boron addition was done at room temperature and addition was rapid to prevent formation of boron salts as previously explained. The mixture was refluxed to improve solubility of intermediates. A mass spectrum done on the product of this reaction did show higher molecular weight material. A mass recorded as 529 m/e may be $C_{40}H_{26}B_2^+$ which has a molecular weight of 528. It is difficult to count the m/e peaks at such high molecular weight. This spectrum also showed very little 400 m/e indicating that the desired reaction is not taking place. Judging from thin layer chromatography which showed a large number of products and from the mass spectrum, it is difficult to decide if the tris(1-B, 8-B'-naphthyl)diboron could be formed.

Some suggestions for future experiments can be made. A co-solvent such as benzene might be added to help keep reaction intermediates in solution until they react to give the final product. Dilithionaphthalene should probably be added to a solution of the boron trifluoride diethyl ether adduct to prevent salt formation.

All nmr spectra were recorded on a Varian T-60. Other analyses were done by the Analytical Branch of the General Electric Research and Development Center.

Experimental

Attempted Tetrazotization of 1,8-Diaminonaphthalene. - A solution of 3.0 g of the diamine in 25 ml of glacial acetic acid was stirred into a solution of 3.0 g of sodium nitrite in 25 ml of concentrated sulphuric acid. After stirring for thirty minutes at 0-5°C the mixture was poured into 75 ml of water and ice and 0.5 g of urea was added to remove excess nitrous acid. The solution was filtered and then added, with stirring, to a solution of 7.5 g of cuprous bromide in 100 ml of concentrated hydrobromic acid and 100 ml of water at 80°C. The mixture was allowed to cool and was neutralized with ammonia solution. Chloroform was added to extract the product, but phase separation did not occur. Addition of sodium chloride did not aid in the separation. There did not seem to be an emulsion. It was a dark brown inseparable mixture. The reaction was attempted adding the sodium nitrite and sulphuric acid solution to a solution of the diamine in acetic acid at 0°C, but this was impossible because acetic acid melts at 16.6°C. Trifluoroacetic acid which melts at -15.3°C was substituted for acetic acid. This acid is quite strong and no sulphuric acid was used. After addition of sodium nitrite to the solution of the diamine at -5°C and treatment similar to the first reaction, the same results were obtained. The phases could not be separated. Probably the mixture should have been steam distilled.

Preparation of 1-Amino-8-bromonaphthalene. - To a solution of 110 ml of concentrated hydrochloric acid in three liters of water was added 45.0 g of 1,8-diaminonaphthalene (Baker, m.p. 64-65°C). The mixture was heated to 70-80°C for thirty minutes, filtered and cooled to 0°C with a dry ice, acetone, water bath. To the cooled solution was added 20.1 g of sodium nitrite dissolved in 500 ml of water over a period of fifty minutes.

During the addition a brown sludge was formed. After stirring for an additional twenty minutes, the solution was filtered and the crude azimide compound was dried in a vacuum oven at 40°C and used without further purification. The dried weight was 45.6 g. A Bunsen burner was used to heat 3.0 g of copper shot to red heat and after cooling the copper was added to 300 ml of 48% hydrobromic acid along with 6.0 g of copper turnings, 2.0 g of cupric oxide and 1.0 g of cuprous oxide. The mixture was heated to boiling and after most of the copper had dissolved, the powdered azimide was added at a rate which controlled the frothing. The mixture was then diluted with one liter of water, heated to boiling and filtered. The residue was extracted twice with 300 ml portions of boiling water. The total aqueous extract was cooled, made basic with ammonia solution and extracted three times with ether. The ether solution was washed with water, dried over anhydrous sodium sulphate, filtered and evaporated. The residue was distilled under reduced pressure to yield 20.1 g (31%) of nearly white 1-amino-8-bromonaphthalene, m.p. 86-88°C; nmr (CCl_4), 6.43-7.66 (m, 6), and 5.00 ppm (s, 2); D_2O exchange: 6.43-7.66 ppm (m, 6) only; mol wt (mass spectrum) 221.

<u>Preparation of 1-Bromo-8-iodonaphthalene.</u> - A solution of 10 g of the bromo-amino compound dissolved in 100 ml of water containing 4 ml of concentrated sulphuric acid was cooled to 0°C and diazotized with 3.25 g of sodium nitrite in 10 ml of water. After stirring for twenty minutes the solution was added to 50 ml of a saturated solution of potassium iodide in water with stirring and the stirred solution was heated to 70-80°C and a dark oil was formed. The mixture was allowed to cool and the oil solidified. The mixture was bleached with sodium bisulfite and filtered. The crude product was dried, dissolved in hexane and the hexane solution

was run through a column of acidic alumina. A dark colored band remained at the top of the column and a clear solution came through. The hexane was evaporated off to yield a pale yellow, crystalline solid. In an attempt to remove the yellow color, the product was run through a second alumina column with hexane, but the color remained. The yield was 10.1 g (67%). A sample recrystallized from methanol gave yellow plates, m.p. 96-97°C; ir (KBr) no amine bands; nmr (CCl_4), 6.80-8.45 (complex); mol wt (mass spectrum) 332.

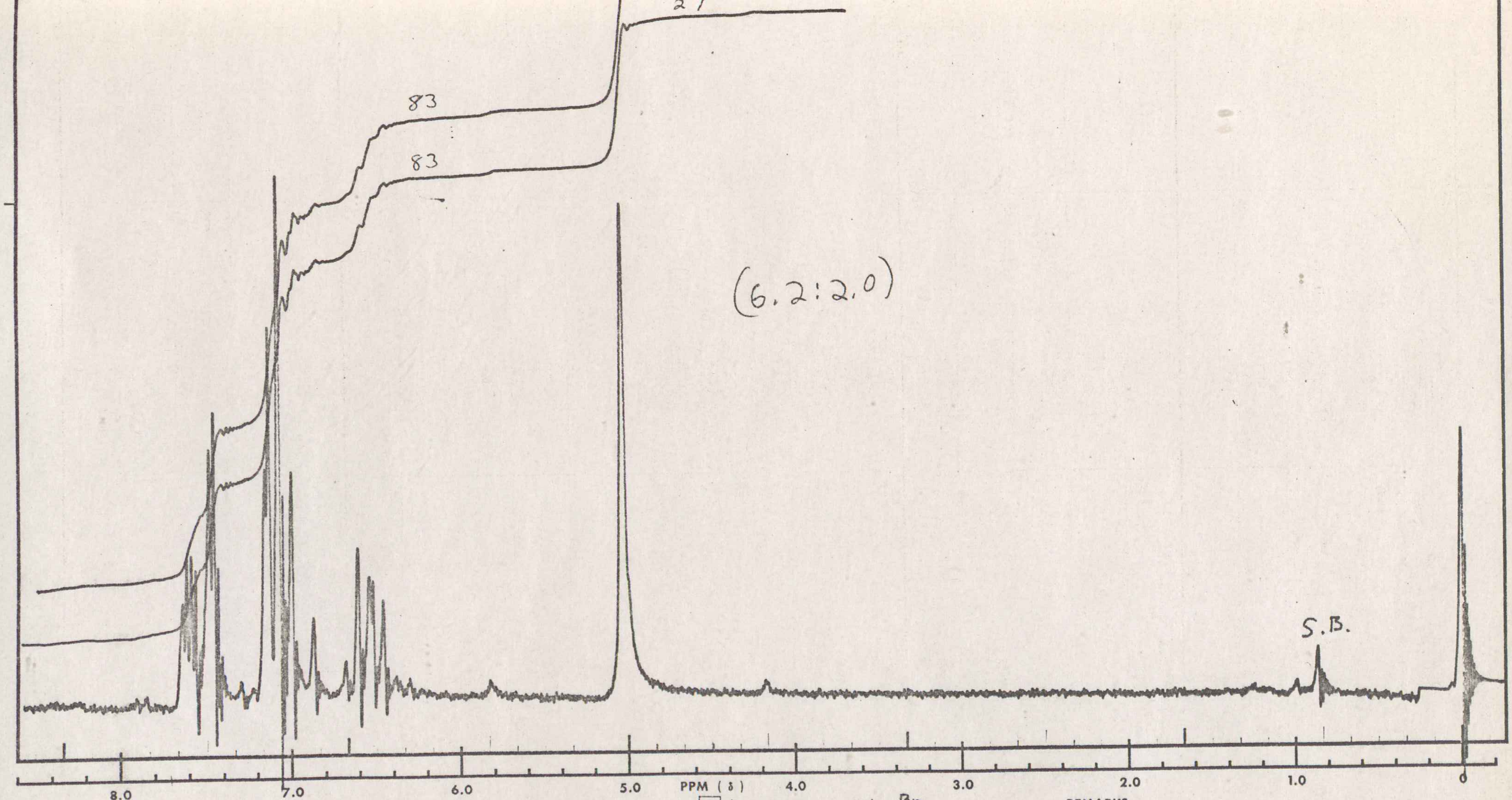
Anal. Calcd for $C_{10}H_6BrI$: C, 36.07; H, 1.82; Br, 24.00; I, 38.11. Found: C, 36.6; H, 1.8; Br, 22.2; I, 34.4; Cl, 8.3.

Grignard Reagents of 1-Bromo-8-iodonaphthalene. - All Grignard reactions were done in a nitrogen atmosphere; equipment was dried in an oven, and the ether was distilled from lithium aluminum hydride. To a solution of 2.0 g (0.006 mol) of 1-bromo-8-iodonaphthalene in 20 ml of diethyl ether was added 0.146 g (0.006 mol) of magnesium. This molar ratio was calculated to give the mono Grignard compound. After stirring for one day at room temperature, most of the magnesium had dissolved. A sample of the Grignard reaction was quenched in water and a thin layer chromatogram (hexane) was done. Thin layer showed three spots. The upper spot had an r.f. value corresponding to that of 1-bromonaphthalene. The middle spot was fluorescent under ultraviolet light. The lower spot was at the origin. Despite the probable impurities, 0.12 ml of boron trifluoride ethyl ether adduct (Eastman, purified) dissolved in 25 ml of ether was slowly added with stirring. Even at such low boron trifluoride concentrations, a brownish red color developed. A brownish red oil came out of solution. This was believed to be compound VII although it was not isolated.

Attempts were made to prepare the double Grignard compound. Due to the presence of chlorine, the reaction was done in dry, distilled tetrahydrofuran. To a solution of 2.0 g of 1-bromo-8-iodonaphthalene in 20 ml of THF was added 0.292 g of magnesium. The mixture was stirred for one day. Much of the magnesium had not dissolved. Gas liquid chromatography (4' polyphenylene ether column) was done on a sample which had been quenched in water. Glc showed almost no naphthalene and a peak with a retention time similar to bromonaphthalene. The reaction mixture was heated to reflux. This produced a greenish color. Under UV light there was tremendous fluorescence whereas before heating there had been none. The double Grignard evidently did not form.

Preparation of 1,8-Dilithionaphthalene and Reaction with Boron Trifluoride. - To a solution of 2.0 g of 1,8-di-halonaphthalene in 20 ml of ether was added 5.0 ml of 23.1% (weight-weight) n-butyllithium. The yellow solution became a darker yellow. A thin layer chromatogram (hexane) of a sample quenched in water showed a spot corresponding to naphthalene, a fluorescent spot of lower r.f. value and a spot at the origin. Gas liquid chromatography showed a peak of retention time equal to naphthalene strongly indicating formation of the dilithio compound. A second peak, although small, corresponded to bromonaphthalene. An additional 60 ml of ether was added to dilute the mixture and 0.25 ml of the boron trifluoride ether adduct was dissolved in 50 ml of ether and slowly dripped into the reaction mixture. The color turned from yellow to reddish brown as the solution was added. The reaction mixture was stirred for one hour. A precipitate formed. The reaction mixture was filtered and a dark reddish brown material was isolated. The material was washed two times with ether. A thin layer chromatogram (chloroform-hexane, 1:1) showed a string of spots. The highest spots had an r.f. value about that of naphthalene and there was a streak down to the origin. A mass spectrum on the material showed almost no peak at 400 m/e. There were small peaks at almost every m/e from 420 m/e down.

To limit the possibility of coupling, a reaction was done at low temperature. To a solution of 34 ml of 14% n-butyllithium in hexane at -40°C, kept cold by a dry ice, acetone, water bath, was added 8.0 g of 1-bromo-8-iodonaphthalene in 100 ml of ether. This was about a 10% excess of n-butyllithium. Fifteen minutes after addition was complete, a thin layer chromatogram (hexane) done on a sample quenched in water showed the typical three spots. The sample itself was very fluorescent under UV light. However, when the UV light was shined on the reaction flask, no fluorescence was noted. The reaction flask did not shield out this wavelength of light. Thirty minutes after addition was complete, 110 ml of ether were added. The reaction mixture was allowed to come to room temperature and a solution of 1 ml of the boron trifluoride ether adduct in 100 ml of ether was added in one minute and the reaction was refluxed for two hours. A precipitate again formed. The reaction was filtered and an amorphous solid was isolated. The solid was washed with ether. A thin layer chromatogram was similar to the preceding reaction.

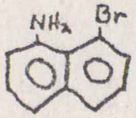


SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 20
INTEGRAL AMPLITUDE: 10
SPINNING RATE (RPS): 48

MANUAL
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: .06

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:



SOLVENT: CCl_4

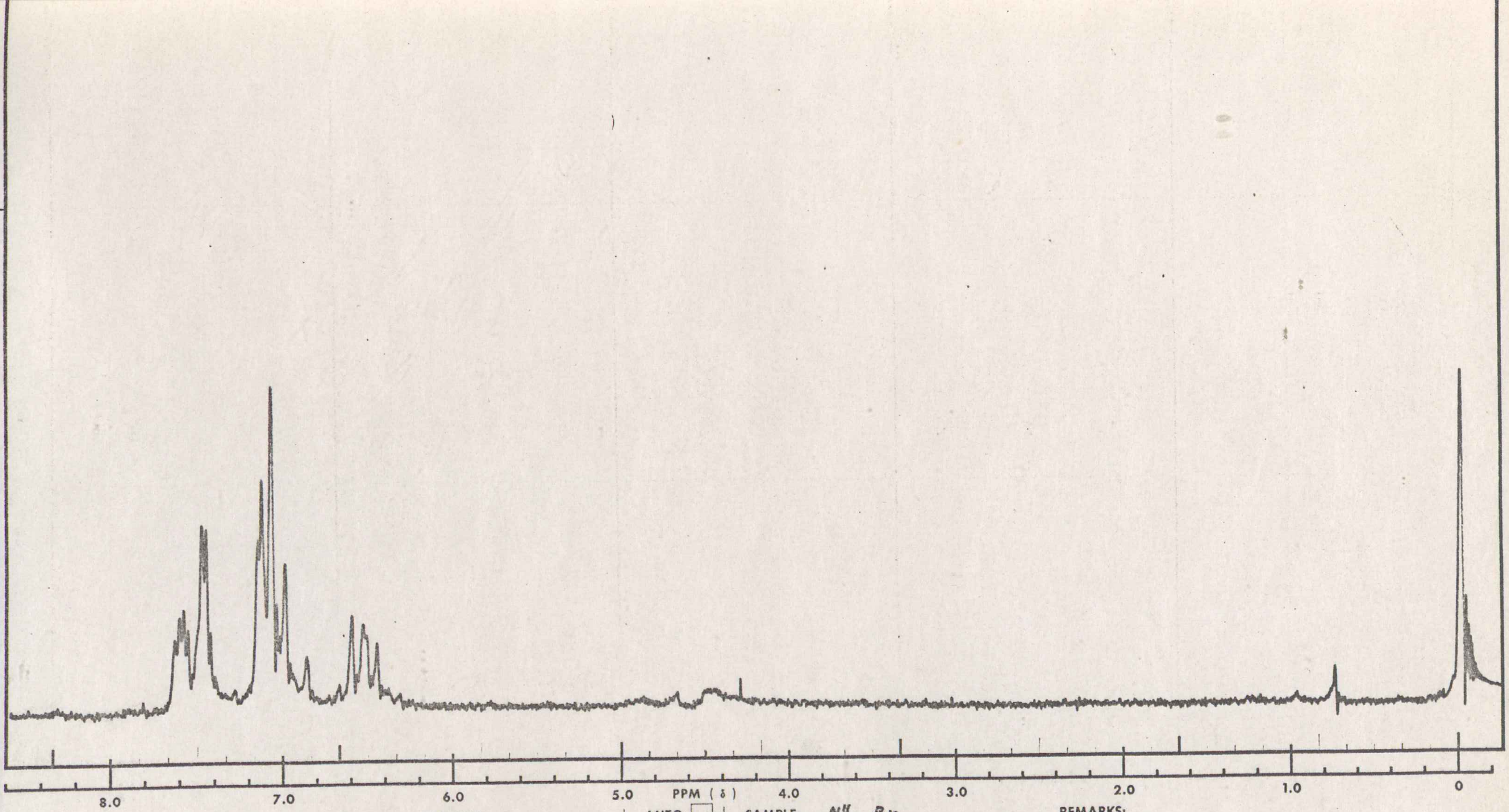
REMARKS:

varian
analytical instrument division

DATE: 12/21/69

OPERATOR: WKG

60 MHz NMR
SPECTRUM NO.



MANUAL

AUTO ☐

SWEEP OFFSET (Hz): 0

SPECTRUM AMPLITUDE: 20

INTEGRAL AMPLITUDE: –

SPINNING RATE (RPS): 45

SWEEP TIME (SEC): 50 [✓ 250] (250)

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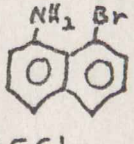
FILTER: [✓ 1] 2 3 4 5 6 7 8 (2)

RF POWER LEVEL: .06 (.05)

SAMPLE:



+ D_2O

SOLVENT: CCl_4

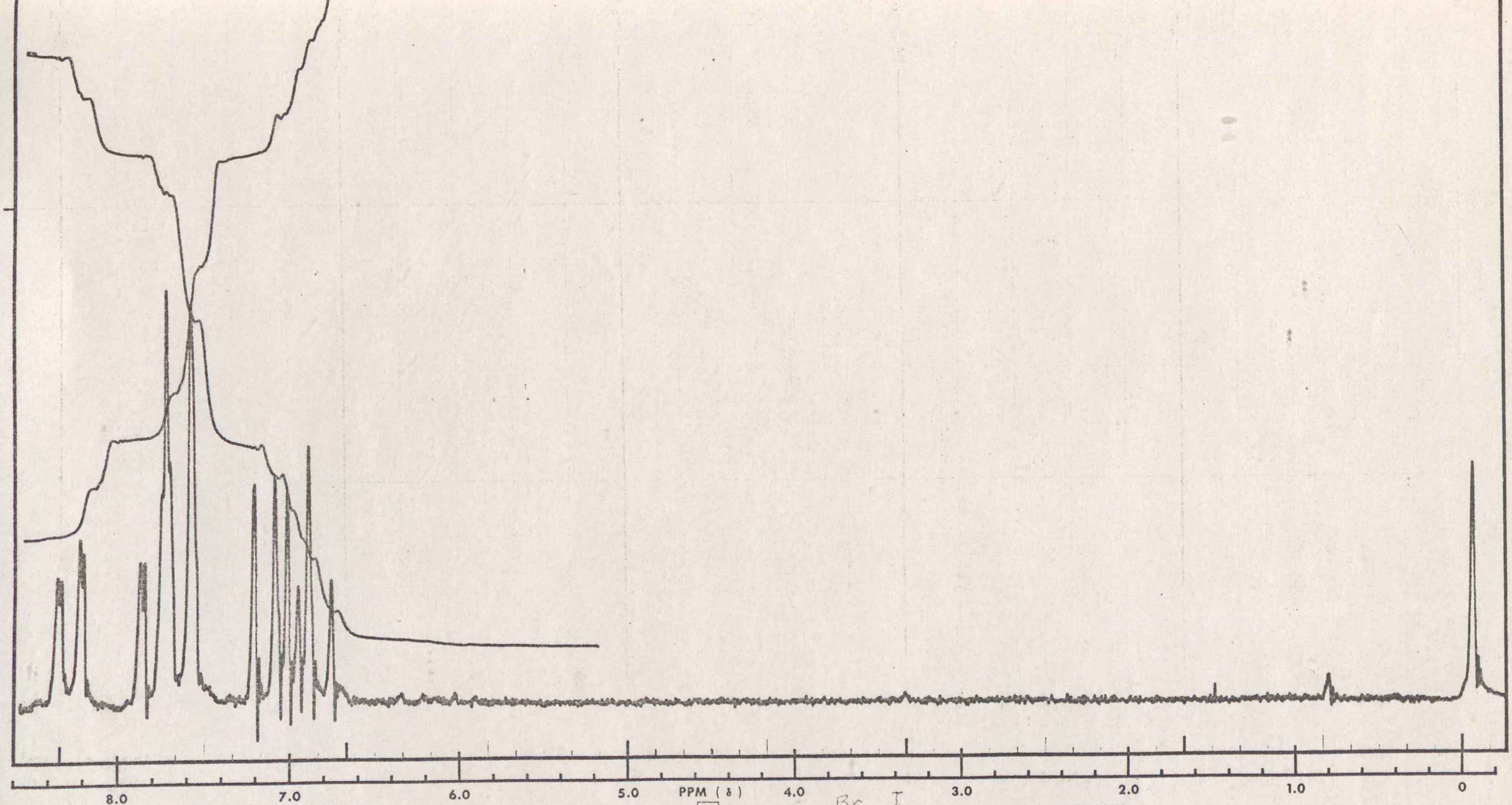
REMARKS:

varian
analytical instrument division

DATE: 12/21/69

OPERATOR: WKG

60 MHz NMR
SPECTRUM NO.



MANUAL

AUTO ☐

SWEEP OFFSET (Hz): 0

SPECTRUM AMPLITUDE: 20

INTEGRAL AMPLITUDE: 7

SPINNING RATE (RPS): 51

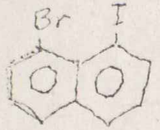
SWEEP TIME (SEC): 50 [✓ 250] (250)

SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500] (500)

FILTER: [✓ 1] 2 3 4 5 6 7 8 (2)

RF POWER LEVEL: .06 (.05)

SAMPLE:



SOLVENT: CCl4

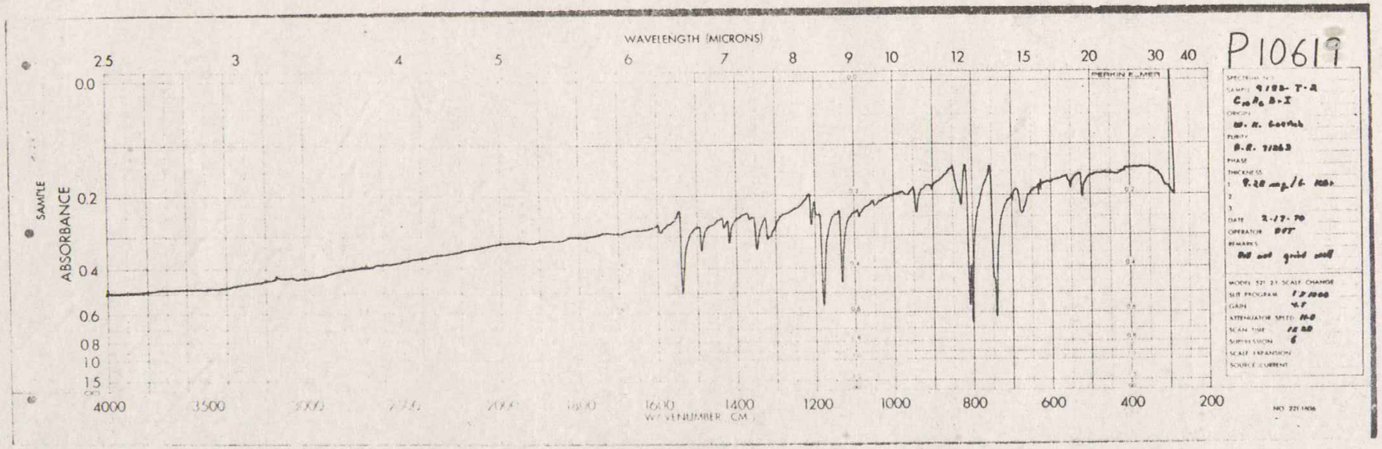
REMARKS:

varian
analytical instrument division

DATE: 1/29/70

OPERATOR: WKD

60 MHz NMR
SPECTRUM NO.



Infrared Spectrum of 1-Bromo-8-iodonaphthalene.

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