



1-1963

Preparation and Properties of 3, 3' -disubstituted-2, 2' – Three-Carbon-Atom Bridged Biphenyls

Allan E. Nader

Follow this and additional works at: https://scholarworks.wmich.edu/masters_theses



Recommended Citation

Nader, Allan E., "Preparation and Properties of 3, 3' -disubstituted-2, 2' – Three-Carbon-Atom Bridged Biphenyls" (1963). *Master's Theses*. 4393.

https://scholarworks.wmich.edu/masters_theses/4393

This Masters Thesis-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Master's Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



PREPARATION AND PROPERTIES OF
3,3'-DISUBSTITUTED-2,2'-THREE-CARBON-ATOM
BRIDGED BIPHENYLS

by

Allan E. Nader

A thesis presented to the Faculty of the
School of Graduate Studies in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
January 1963

TABLE OF CONTENTS

	Page
Introduction	1
Experimental	3
Preparation of 6-chloro-2-iodotoluene	3
Preparation of 3,3'-dichloro-o,o'-bitolyl	3
Attempted preparation of 3,3'-dibromo-o,o'-bitolyl	3
Preparation of 2,6-dinitro-4-aminotoluene	7
Attempted preparation of 2-amino-6-nitrotoluene	7
Preparation of 2-amino-6-nitrotoluene	8
Preparation of 2-iodo-6-nitrotoluene	9
Preparation of 3,3'-dinitro-o,o'-bitolyl	10
Preparation of 3,3'-diamino-o,o'-bitolyl	10
Preparation of 3,3'-dibromo-o,o'-bitolyl	11
Preparation of α,α' -dibromo-3,3'-dibromo-o,o'-bitolyl	12
Preparation of diethyl 4,8-dibromo-5,7-dihydrodibenzo [a,c] cycloheptadiene-6,6-dicarboxylate	13
Discussion and Conclusion	15
Summary	24
Bibliography	25
Vita	27

CHARTS AND FIGURES

Charts	Page
I. Synthesis of Diethyl 4,8-dibromo-5,7-dihydrodibenzo [a,c] cycloheptadiene-6,6-dicarboxylate, Plan I	4
II. Synthesis of Diethyl 4,8-dibromo-5,7-dihydrodibenzo [a,c] cycloheptadiene-6,6-dicarboxylate, Plan II	4
 Figures	
I. Ultraviolet absorption spectra of 3,3'-dichloro-, 3,3'-dibromo-and 3,3'-diiodo-o,o'-bitolyl	22
II. Ultraviolet absorption spectra of diethyl 4,8-dichloro-, diethyl 4,8-dibromo-and diethyl 4,8-diiodo-5,7-dihydro dibenzo [a,c] cycloheptadiene-6,6-dicarboxylate.	23

INTRODUCTION

The configuration of biphenyl has been treated in numerous articles and reviews (1, 5, 6, 7, 8, 16, 22, 23). In particular the configuration of 2,2'-bridged biphenyl derivatives has obtained attention. The synthesis of an optically active 2,2'-three-carbon-atom-bridged biphenyl possessing an ultraviolet absorption maximum at 250 m μ has been reported by Iffland and Siegel (15). These properties require first, a non-planar configuration for the molecule and second, significant inter-ring conjugation as demonstrated by ultraviolet spectra.

Several 2,2'-three-atom-bridged biphenyls have been prepared by Ahmed and Hall (2, 3) in order to obtain some measure of their specific rotation. The use of various 6,6'-substituents, larger than hydrogen, were employed to increase optical stability of the compounds studied.

Another approach to the problem was undertaken by Iffland and Chiang who utilized bulky 3,3'-substituents as buttressing agents upon the three-atom bridge (11). The resulting change in configuration and twist angle could then be studied with gradual changes in the size of the substituents. With chlorine as the buttressing agent the molecule revealed a configuration not unlike the unsubstituted compound.

The material initially prepared and identified as the 3,3'-diiodo analog failed to exhibit an absorption maximum in the 250 m μ region; this was considered dramatic evidence for a buttressing effect (11). However, reexamination of the synthesis of the diiodo compound demonstrated an error in the assignment of structure to the two products

encountered (14). The ultraviolet spectrum of the true diiodo compound proved remarkably similar to that for the dichloro compound.

This work was undertaken before this assignment error was corrected and had as its objective the preparation of the analogous 3,3'-dibromo compound to complete the 3,3'-dihalo-2,2'-three-atom-bridged biphenyl series.

EXPERIMENTAL

In the following section, all boiling and melting points are in degrees Centigrade and are uncorrected. The micro-analytical data were obtained from the Galbraith Laboratories, Knoxville, Tennessee.

The ultraviolet absorption spectra were obtained on a Beckman Model DU spectrophotometer. The solvent for these measurements was 95% ethanol.

Preparation of 6-chloro-2-iodotoluene, II

Following the procedure described by Cohen and Miller (12), 1.0 moles of 3-chloro-2-methylaniline was converted to 6-chloro-2-iodotoluene in 75% yield: b.p. 99-100° at 5 mm; n_D^{25} 1.6255. Lit.: b.p. 132-133° at 25 mm.

Preparation of 3,3'-dichloro-o,o'-bitolyl, III

One mole of 6-chloro-2-iodotoluene was transformed into 3,3'-dichloro-o,o'-bitolyl according to the method of Chiang (11). A 75% yield of the bitolyl was obtained: m.p. 75-76°. The ultraviolet absorption spectrum is shown in Fig. I.

Attempted preparation of 3,3'-dibromo-o,o'-bitolyl, IV

Into a dry 500 ml. three neck flask, fitted with reflux condenser, addition funnel and stirrer, 4.9 g. (0.202 mole) of magnesium turnings and several iodine crystals were placed under a nitrogen atmosphere. After placing a solution of 25.2 g. (0.100 mole) of 3,3'-dichloro-o,o'-bitolyl in 200 ml. of dry tetrahydrofuran (THF) the entire mixture

CHART I

Plan I

Synthesis of Diethyl 4,8-dibromo-5,7-dihydrodibenzo [a,c] cycloheptadiene 6,6-dicarboxylate

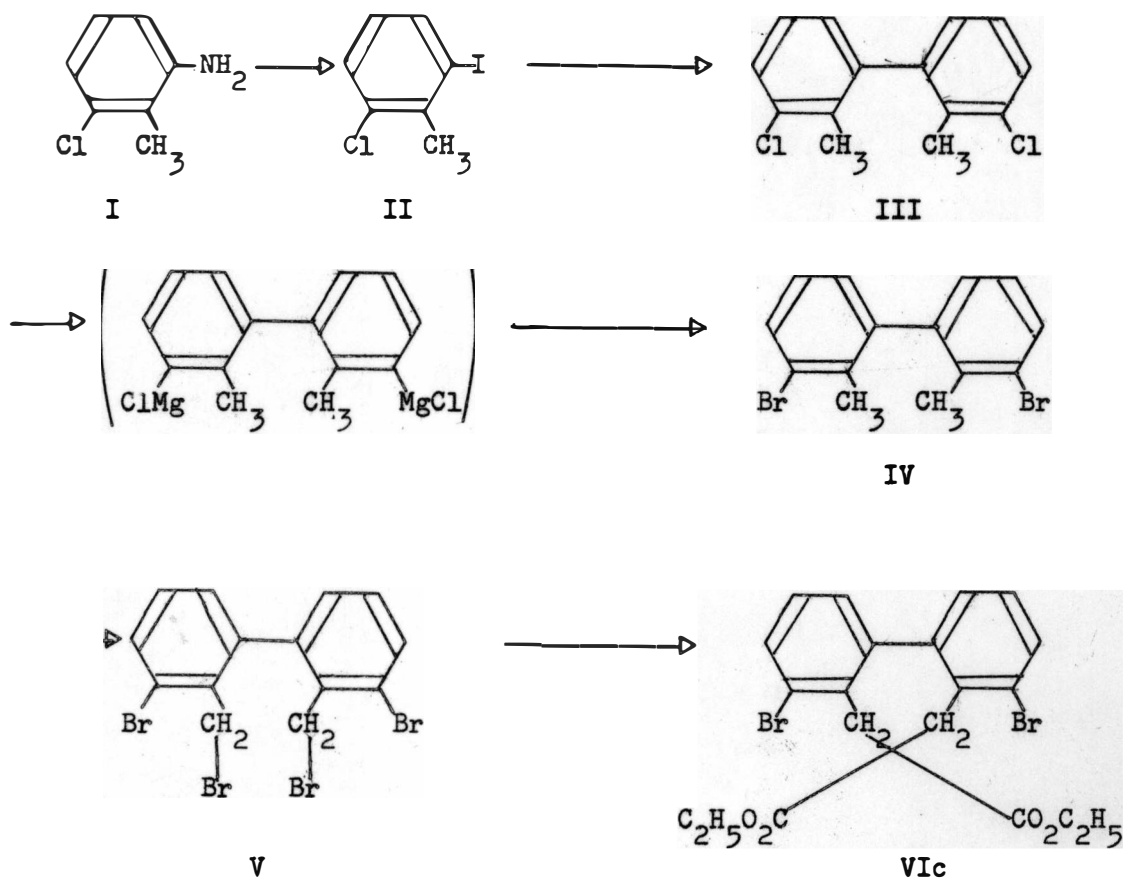
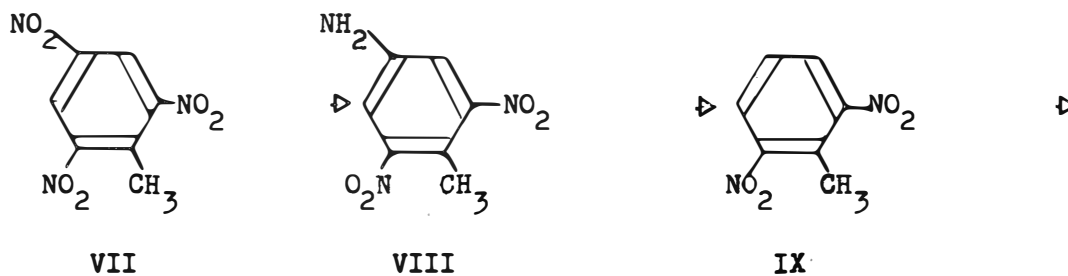
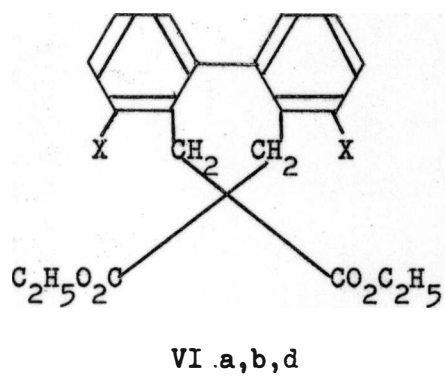
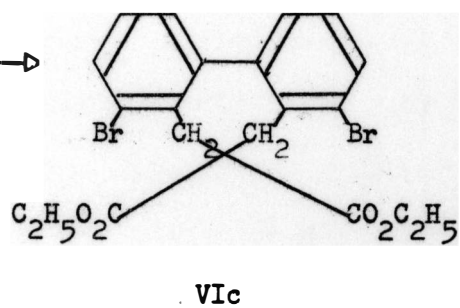
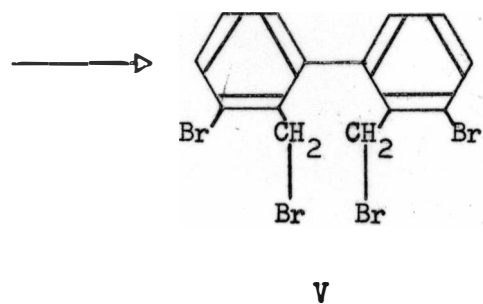
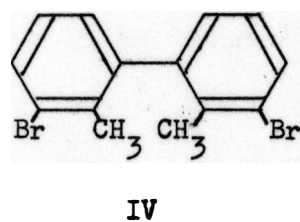
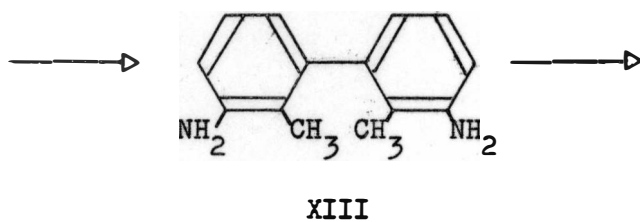
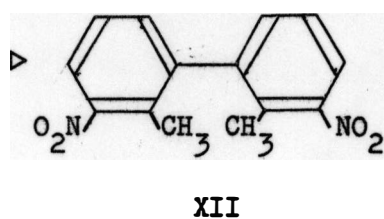
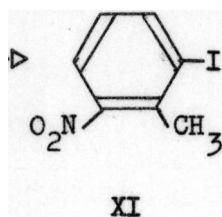
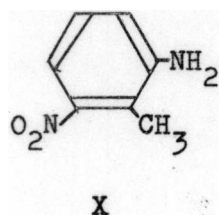


CHART II

Plan II

Synthesis of Diethyl 4,8-dibromo-5,7-dihydrodibenzo [a,c] cycloheptadiene-6,6-dicarboxylate





$X \doteq H$ **VIa**
 $X = Cl$ **VIb**
 $X = I$ **VIId**

was heated. After refluxing for 100 hours, the mixture was cooled and the liquid portion decanted leaving 0.2 g. (0.00823 mole) of unreacted magnesium.

A mixture of 53.5 g. (0.20 mole) anhydrous aluminum bromide in 200 ml. of THF was prepared with cooling; 31.9 g. (0.20 mole) bromine was then slowly added. The Grignard reagent was added dropwise over a one-hour period and allowed to react until no further evolution of heat. An ice-water mixture was added and sufficient sodium bisulfite to insure removal of unreacted bromine. A sodium hydroxide solution (40%) was added to neutralize the mixture. The organic portion was separated and the remaining material dissolved in hydrochloric acid and extracted with benzene. Finally all organic portions were combined and dried over anhydrous potassium carbonate. The solvents were removed by distillation and the residual oil distilled under reduced pressure. Fractions were collected having the properties summarized below.

Fraction	Boiling Point	Pressure	Weight	n_D^{25}
1	up to 131°	6mm Hg.	1.3g.	1.5573
2	131-145°	6 " "	2.6g.	1.5702
3	145-155°	6 " "	3.3g.	1.5775
4	155-165°	6 " "	3.9g.	1.5883
5	165-175°	7 " "	6.2g.	1.6005
6	185-220°	6 " "	4.2g.	1.6102

Although no fractionation of a pure product was obtained, the infrared spectra (2000-1650 cm^{-1}) suggested ring poly-bromination

(tetra-substituted benzenes.)

A previous attempt to effect a halogen exchange in the absence of aluminum bromide failed (11). The use of N-bromosuccinimide, as a brominating agent, also proved worthless in the production of the dibromo compound.

Preparation of 2,6-dinitro-4-aminotoluene, VIII

Following in general the procedure of Parkes and Farthing (21) a reaction vessel was set up with a stirrer, gas inlet tube and containing 55.5 g. (0.220 mole) of 90% 2,4,6-trinitrotoluene dissolved in 125 ml. of dioxane. Six drops of concentrated ammonia solution were added and hydrogen sulfide gas introduced. Reaction set in after five minutes with evolution of heat, cooling was occasionally applied to maintain the temperature below 40°. Free sulfur precipitated and gas introduction was continued until the temperature dropped. Three additional drops of ammonia were added and passage of hydrogen sulfide continued till no further change in temperature was noted. The solution was cooled and the solid sulfur filtered (17.0 g., 0.53 mole) leaving a dark red filtrate. The solution was poured into two liters of water precipitating the organic material. The slurry was filtered yielding an orange amorphous solid, which upon recrystallization from acetic acid (40%), produced 13.5 g. of orange crystals in 31% yield: m.p. 169-172°. Lit.: m.p. 172°. In other attempts to prepare this compound, yields were variable and ranged as low as 0%.

Attempted preparation of 2-amino-6-nitrotoluene, X

Adapting the method of Lesslie and Mayer (18) 72.1 g. (0.3 mole)

of sodium sulfide mono-hydrate dissolved in 30 ml. of hot water was added over a ten minute period with vigorous stirring to a suspension of 18.2 g. (0.1 mole) of 2,6-dinitrotoluene (K & K Laboratories, m.p. 66°) in 200 ml. of water. The mixture was refluxed for an additional two-hour period, cooled and stored overnight in a refrigerator. The solution was filtered leaving a yellow-orange solid, which was dissolved in hot benzene, clarified with charcoal and dried over anhydrous sodium sulfate. The solution was concentrated and upon the addition of sufficient petroleum ether (40-60°) crystals formed. A recrystallization from hot water yielded a yellow unknown material m.p. about 135°. M.p. desired product 92° (10).

Preparation of 2-amino-6-nitrotoluene, X

One-tenth mole (18.2 g.) of 2,6-dinitrotoluene (K & K Laboratories) was dissolved in 150 ml. of hot ethanol (95%), 50 mg. of platinum oxide catalyst was added and reduction was completed in a Parr low pressure hydrogenation apparatus at 30 psi initial pressure. The reaction was stopped after the hydrogen uptake reached theoretical value for the reduction of one-tenth mole of nitro group. The solution was treated with Norite and filtered through a Celite filter pad. The same procedure was repeated for three additional batches giving a total of 0.4 mole of reduced nitro compound. The filtrates were combined and the solvent was removed on a vacuum evaporator leaving 65 g. of crude solid. The solid was extracted with 1000 ml. of hot hydrochloric acid (17%) leaving 11.5 g. of dark residue. The acid extract was cooled and poured into excess cold 25% aqueous sodium hydroxide to form a precipitate.

The solid was removed by filtration and dried under vacuum. The material was then continuously extracted with hot petroleum ether (60-110°), from which yellow crystals formed. Recrystallization from fresh petroleum ether gave 26.7 g. of 2-amino-6-nitrotoluene in 44% yield: m.p. 88-90°. Lit.: m.p. 92° (10).

Preparation of 2-iodo-6-nitrotoluene, XI

To a suspension of 22.8 g. (0.15 mole) of 2-amino-6-nitrotoluene in 200 ml. of water, 65.0 g. (4.4 mole) of concentrated hydrochloric acid was added forming an orange salt. The mixture was cooled to 0° and a solution of 10.4 g. (0.15 mole) of sodium nitrite, dissolved in 35 ml. of water was added dropwise forming a red mixture. Three grams of urea was added followed by a solution of 25.0 g. (0.15 mole) of potassium iodide dissolved in 30 ml. of water. The temperature was maintained at 0-5° throughout the addition. The mixture was then allowed to warm to room temperature. After nitrogen evolution ceased 100 ml. of benzene and solid sodium bisulfite were added and thoroughly mixed. The aqueous portion was separated and extracted with 100 ml. of additional benzene. The benzene extracts were combined and washed with 5% aqueous sodium hydroxide, water and finally dried over anhydrous sodium sulfate. The solvent was removed on a vacuum evaporator and the residue distilled under reduced pressure giving a viscous oil, b.p. 134-144° at 5 mm, which solidified on standing to a yellow solid m.p. 34-35°. Recrystallization from an ethanol-water mixture yielded 27.3 g. (69%) of yellow needles: m.p. 35-36°. Lit.: m.p. 35.5° (20).

The conversion of 2,6-dinitrotoluene to 2-iodo-6-nitrotoluene

could be improved to a 50% overall yield by diazotization of the crude reduction product.

Preparation of 3,3'-dinitro-o,o'-bitolyl, XII

Adapting the general procedure for conducting Ullman reactions in dimethylformamide solution, as described by Kornblum and Kendall (17), a solution of 26.3 g. (0.10 mole) of 2-iodo-6-nitrotoluene in 50 ml. of dry dimethylformamide was placed into a three neck flask fitted with reflux condenser and stirrer. The solution was heated to reflux and a mixture containing 19.1 g. (0.3 g. at. wt.) of electrolytic copper dust with an equal amount of sea sand was added. The reaction was stopped after 20 hours and 50 ml. of benzene was added and thoroughly mixed. The benzene was decanted and the copper extracted several times with additional hot benzene. The extracts were combined and filtered to remove suspended copper. The filtrate was washed with a large volume of water, 5% aqueous sodium bisulfite, again with water and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a viscous oil which solidified. Recrystallization from ethanol yielded 10.3 g. (74%) light yellow crystals: m.p. 120-121°. Anal. calculated for $C_{14}H_{12}N_2O_4$: N, 10.29. Found: N, 10.41.

In the absence of dimethylformamide solvent and at 200 to 210° this reaction produced principally o-nitrotoluene.

Preparation of 3,3'-diamino-o,o'-bitolyl, XIII

To a solution of 8.79 g. (0.0324 mole) of 3,3'-dinitro-o,o'-bitolyl dissolved in a hot mixture of 200 ml. of ethanol and 25 ml. of benzene, 0.10 g. of platinum oxide was added and the mixture reduced in a Parr

low pressure hydrogenation apparatus at 25.0 psi initial pressure. Upon completion of hydrogen absorption the mixture was filtered and concentrated on a vacuum evaporator. Removal of the solvent furnished a solid residue which was washed with pentane and dried. Recrystallization from aqueous methanol gave 6.05 g. (88%) of tan crystals melting 168-169°. Anal. calculated for $C_{14}H_{16}N_2$: N, 13.20. Found: N, 13.07.

Preparation of 3,3'-dibromo-o,o'-bitolyl, IV

Twenty three milliliters of 48 percent hydrobromic acid (0.20 mole) and 20 ml. of water were added to 8.29 (0.039 mole) of 3,3'-diamino-o,o'-bitolyl and the mixture heated to a boil and then cooled to 0°. The diamine salt was diazotized with a solution of 5.4 g. (0.078 mole) of sodium nitrite dissolved in 10 ml. of water. The temperature was maintained at 0-5°. The cold diazonium salt was added rapidly with vigorous stirring to a freshly prepared solution containing 23.8 g. (0.20 mole) of potassium bromide, 33.8 g. (0.17 mole) of cuprous bromide and 20 ml. of 50% aqueous hydrobromic acid dissolved in 100 ml. of water at room temperature. After addition of the diazonium salt the mixture remained at room temperature for about 10 minutes and then heated on a steam bath until the nitrogen evolution ceased. Upon completion of the reaction, 150 ml. of benzene was added and stirred. The liquid portion was decanted into a separatory funnel and the benzene extract separated. The benzene portion was filtered to remove suspended material and then washed with water, 20% aqueous sodium hydroxide, 20% aqueous sodium bisulfite solution and finally with water. The extract was dried over

anhydrous sodium sulfate and the solvent was removed under reduced pressure leaving a viscous oil which solidified on standing. The material was purified by chromatography on an acid alumina column and eluted with benzene. Seven and five-tenths grams of white product (57%) melting 74-76° was isolated. A sample for analysis was recrystallized from ethanol and melted 78-79°. The ultraviolet absorption spectra is shown in Fig. I. Anal. calculated for $C_{14}H_{12}Br_2$: C, 49.44; H, 3.56. Found: C, 49.39; H, 3.63.

Preparation of α,α' -dibromo-3,3'-dibromo-o,o'-bitolyl, V

One gram of benzoyl peroxide was added to a mixture of 6.2 g. (0.035 mole) of N-bromosuccinimide (NBS) and 4.73 g. (0.014 mole) of 3,3'-dibromo-o,o'-bitolyl in 170 ml. of carbon tetrachloride. The mixture was refluxed a total of 28 hours with 1.0 g. additional benzoyl peroxide added after 18 hours. After cooling the mixture was filtered, washed with 5% aqueous sodium bisulfite and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left 9.5 g. of oil. The residual oil was dissolved in a minimum amount of carbon tetrachloride and chromatographed on neutral alumina using the same solvent as eluent. Fractions were collected and two widely separated components were isolated. The more readily eluted material amounted to 5.13 g. (74%), which upon several recrystallizations from petroleum ether (60-110°) melted 138.5-140°. Anal. calculated for $C_{14}H_{10}Br_4$: C, 33.77; H, 2.03. Found: C, 33.95; H, 2.09.

The later eluted material (0.18 g.) melted 192-196° and gave a noticeably different infrared spectrum than the above product.

Preparation of diethyl 4,8-dibromo-5,9-dibromodibenzo
[a,c] cycloheptadiene-6,7-dicarboxylate, VIc

A solution of sodium ethoxide was prepared by adding 0.20 g. (0.0086 g. at. wt.) of sodium to 30 ml. of absolute ethanol. After cooling 0.69 g. (0.0043 mole) of diethyl malonate was added and thoroughly stirred for 10 minutes and the salt transferred to an addition funnel. The mixture was then added dropwise to a vigorously stirred solution of 2.04 g. (0.0041 mole) α,α' -dibromo-3,3'-dibromo-o,o'-bitolyl dissolved in 20 ml. warm dioxane. The addition was completed in one hour and the mixture was then refluxed on a steam bath for a 5 hour period. Excess ice-water was added and the product separated as a precipitate. The mixture was extracted with ethyl ether and dried over anhydrous sodium sulfate. Removal of the solvent left a white solid which melted 126-140°. Recrystallized material from ethanol still gave a wide melting range. The solid was then dissolved in a minimum amount of carbon tetrachloride and developed on a four foot neutral alumina column (0.5 in. dia.) using carbon tetrachloride eluent. There was initially obtained 0.5 g. of material melting about 180°. The infrared spectrum of this material failed to show a carbonyl stretching band and was identical to the anomalous material isolated in the preparation of α,α' -dibromo-3,3'-dibromo-o,o'-bitolyl (vide supra). Methanol was then employed as an eluent and 1.5 g. of material melting about 160° was isolated and gave an infrared spectrum rational for the desired product, (carbonyl stretching band, 1725 cm^{-1}). It was purified by recrystallization from ethanol to give 1.0 g. (50%) of white crystalline material m.p. 167-168°. The ultraviolet spectra is shown in Fig. II:

$\lambda_{\max}^{250 \text{ m}\mu}$: $\log \epsilon_{\max}$ 4.18. Anal. calculated for $\text{C}_{21}\text{H}_{20}\text{O}_4\text{Br}_2$: C, 50.83; H, 4.06. Found: C, 50.95; H, 4.17.

The anomalous material after recrystallization from ethanol melted 192-193°. Anal. Found: C, 47.58; H, 2.97. The absence of a carbonyl stretching band and the presence of strong bands in the 1100 cm^{-1} region suggested an ether structure. The elemental analysis is in acceptable agreement with the calculated values for 4,8-dibromodibenz [c,e] oxepin. Calculated for $\text{C}_{14}\text{H}_{10}\text{OBr}_2$: C, 47.49; H, 2.85. Found: C, 47.58; H, 2.97.

DISCUSSION AND CONCLUSION

Two synthetic routes to the desired 4,8-dibromo-5,7-dihydrodibenzo [a,c] cycloheptadiene-6,6-dicarboxylate, (VIc) were explored. Plan one, summarized in Chart I, was based upon reactions which proved successful in the conversion of the 3,3'-dichloro-o,o'-bitolyl to the corresponding iodo substituted bitolyl. This conversion involved a halogen exchange reaction via a di-Grignard reagent to form the desired product. Although a previous attempt to effect a bromine exchange failed (11) it was believed that a further investigation was warranted, since if successful the desired product might be readily obtained.

Precautions were taken to insure complete Grignard reagent formation. Secondly, aluminum bromide was employed to promote the desired reaction. This innovation was based on the reasoning that it would aid the formation of positive bromine species eg. Br^+ , which might prove more reactive to exchange than ordinary molecular bromine. It proved, however, instead to effect random nuclear bromination which resulted in an inseparable mixture of substances. Further exploratory reactions involving the conversion of chlorobenzene to a Grignard and subsequent attempted introduction of bromine using N-bromosuccinimide also proved unsuccessful.

Due to the failure to complete plan one, interest was turned to a second reaction sequence (Chart II). This route again was based upon analogy to reactions previously reported.

The starting material in this case was the readily available 2,4,6-trinitrotoluene (VII). The initial selective reduction to the

2,6-dinitro-4-aminotoluene (VIII) proceeded poorly despite the application of procedures reported as favorable in the literature. Three basic methods were attempted to accomplish this reduction. All of the references cited, employed sulfide reducing agents such as hydrogen sulfide or sodium hydrosulfide. The reductions attempted according to the procedures of Parkes and Farthing (21), Foster, Rosicky, and Niemann (13), and Lowe (19), provided little or no success. Only in the procedure of Parkes and Farthing, which employed hydrogen sulfide as the reducing agent, was a significant amount of desired product (VIII) isolated (31%). However, difficulties in controlling the extent of reaction and in the isolation and purification steps rendered this procedure synthetically impractical. As a result of the aforeto mentioned problems, 2,6-dinitrotoluene (IX) was investigated as a potential starting material. This compound had not been previously used due to its expense and the potential problem to develop a good selective reduction technique. Therefore, it was considered advisable to gain experience with the selective reduction using the less expensive trinitrotoluene.

A sodium sulfide reduction of the 2,6-dinitrotoluene initially attempted according to Lesslie and Mayer (18) yielded no isolatable amine. Reinvestigation of the literature showed that a selective hydrogen reduction over platinum black had been successfully performed on this material (24). An attempted similar reduction using platinum oxide gave a 44% yield of good quality 2-amino-6-nitrotoluene (X).

Using the 2-amino-6-nitrotoluene in the usual Sandmeyer procedure, 2-iodo-6-nitrotoluene (XI) was obtained in 69% yield with no difficulty. The amount of 2-iodo-6-nitrotoluene obtained could be further increased

by reduction of the starting material, removal of the solvent, and subsequent diazotization of the crude amine. In this manner the overall yield for the two reactions was raised to 53%.

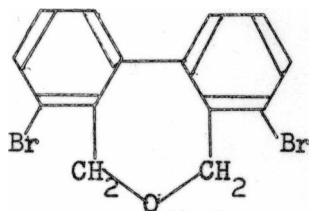
The third step in the synthetic scheme was to produce the 3,3'-dinitro-o,o'-bitolyl (XII). The usual method for symmetrical biphenyl preparation employs an Ullmann reaction at high temperatures (200-220°). An initial attempt to use this technique resulted in the production of a large amount of o-nitrotoluene and only 7% of the desired product. It was reasoned that some manner of decomposition and subsequent reduction had occurred and that a lower reaction temperature might minimize this result. The procedure of Kornblum and Kendall (17) employing dimethylformamide (b.p. 153°) as a solvent was adapted and produced 50-75% yield of the desired dinitro compound (XII).

The reduction of the 3,3'-dinitro-o,o'-bitolyl to the corresponding diamine (XIII) using platinum oxide as a catalyst proceeded well giving 80-90% of 3,3'-diamino-o,o'-bitolyl (XIII).

The next step was the conversion of the 3,3'-diamino-o,o'-bitolyl to 3,3'-dibromo-o,o'-bitolyl (IV) via a double Sandmeyer reaction. Adapting the procedure of Bigelow (9) the principal products were phenol-like in character and only a trace of the dibromo compound (7%) was isolated. The literature procedures for this reaction all involved the addition of the diazonium salt to a hot potassium bromide solution containing cuprous bromide as a catalyst. Due to the large amount of phenolic material formed, lower initial temperatures were tried. It was found that addition of the cold diazonium salt to the potassium bromide-catalyst mixture at room temperature, followed by decomposition

of the diazonium complex on a steam bath, resulted in a 59% yield of the dibromo-bitolyl (IV). The ultraviolet spectrum of the 3,3'-dibromo-o,o'-bitolyl is shown in Fig. I. It reveals the typical spectra of ortho substituted biphenyls and fits the general pattern of the chloro and iodo analogs.

The side chain bromination of the methyl groups employing N-bromo-succinimide followed the procedure of Chiang (11). A 75% yield of α,α' -dibromo-3,3'-dibromo-o,o'-bitolyl (V) was obtained. During the purification process of elution chromatography over neutral alumina, in addition to the desired product, a small amount of anomalous material was isolated melting much higher than the desired substance (192 vs. 138°). The identical material was isolated in greater amount from the reaction mixture of the final ring closure reaction. The elemental analysis of the by-product fits that for the cyclic ether 4,8-dibromo-dibenz [c,e] oxepin (XIV).



XIV

Since, rigorously dry reagents were not used, a trace of water may have been a factor in effecting this change. The fact that the material was also obtained in the ring closure reaction, which involves the use of sodium ethoxide, indicates that this compound can form under varied basic conditions. The presence of water in this reaction would reasonably form hydroxide ion which may initiate a series of

nucleophilic substitution reactions resulting in the formation of the ether.

The final reaction consisted of a malonic ester alkylation with (V) to give the desired bromo ring compound (VIc) in a 50% yield along with the aforeto mentioned oxepin derivative. The separation of these two compounds proved difficult and was finally accomplished by elution chromatography using a 48 in. x 0.5 in. acid-washed alumina column and carbon tetrachloride-methanol mixtures as eluents.

The non-planarity of diethyl 5,7-dihydro [a,c] cycloheptadiene-6,6-dicarboxylate (VIa), as evidenced by observed optical activity, was demonstrated by Iffland and Siegel (15). The observed facile racemization and 250 m μ biphenyl absorption band are reasonable only if the twist angle between the benzene rings is small.

The ultraviolet spectra of the diethyl 4,8-dichloro-5,7-dihydro-dibenzo [a,c] cycloheptadiene-6,6-dicarboxylate (VIb) prepared by Chiang (11) and the later prepared authentic diethyl 4,8-diiodo-5,7-dihydrodibenzo [a,c] cycloheptadiene-6,6-dicarboxylate (VIId) were found to be almost identical to that of compound (VIa). The diiodo compound revealed in addition to a 250 m μ maxima a shoulder at 230 m μ which has been assigned to the absorption by iodine atoms (4,7) and is also present in the ultraviolet spectrum of 3,3'-diiodo-o,o'-bitolyl.

The ultraviolet spectra of the diethyl 4,8-dibromo-5,7-dihydro-dibenzo [a,c] cycloheptadiene-6,6-dicarboxylate (VIc) synthesized in this study was found to approximate that of the chloro-ring compound (VIb) and iodo-ring compound (VIId). The 250 m μ maximum is still retained but the spectrum also reveals a broadening of the 230 m μ region with

a reduction in the trough present in the chloro (VIb) and unsubstituted (VIa) analogs. This alteration in the spectrum may suggest some buttressing effect in the 3,3'-dibromo-2,2'-three-atom-bridged biphenyl not exhibited in the spectrum of the dichloro analog. The absorption by iodine, however, obscures any similar effect in the diiodo compound and as a result makes exact assignment of this factor in the ultraviolet spectrum difficult.

These results are now interpreted as denoting a great similarity in the respective configurations of the 3,3'-dihalo-2,2'-three-atom-bridged biphenyls studied. Thus, a buttressing effect is shown to be either negligible or absent using ultraviolet spectra as criteria. Two reservations may be considered: First, the ultraviolet spectra may not be a satisfactory or sufficient criteria to measure buttressing effect or, second, buttressing effect of the chlorine atoms is sufficient to twist the biphenyl frame to the limit permitted by the three-atom-bridge and no further effect is observed in the change to the dibromo or diiodo compound.

Finally, the similarity of spectra also indicates there is no electronic interaction from variation of meta-halo substituents in these systems.

A more conclusive indication of a buttressing effect will be provided by successful resolution studies on the respective dichloro, dibromo and diiodo ring compounds. The stability of the respective optical enantiomers would yield evidence of any increase in buttressing effect with a corresponding increase in halogen size.

The results are summarized below.

X	Radius (\AA)	λ_{max} ($m\mu$)	ϵ	$\log \epsilon$
H	0.92	249	16,980	4.228
Cl	1.89	250	14,970	4.176
Br	2.11	250	15,155	4.180
I	2.22	252	14,680	4.167

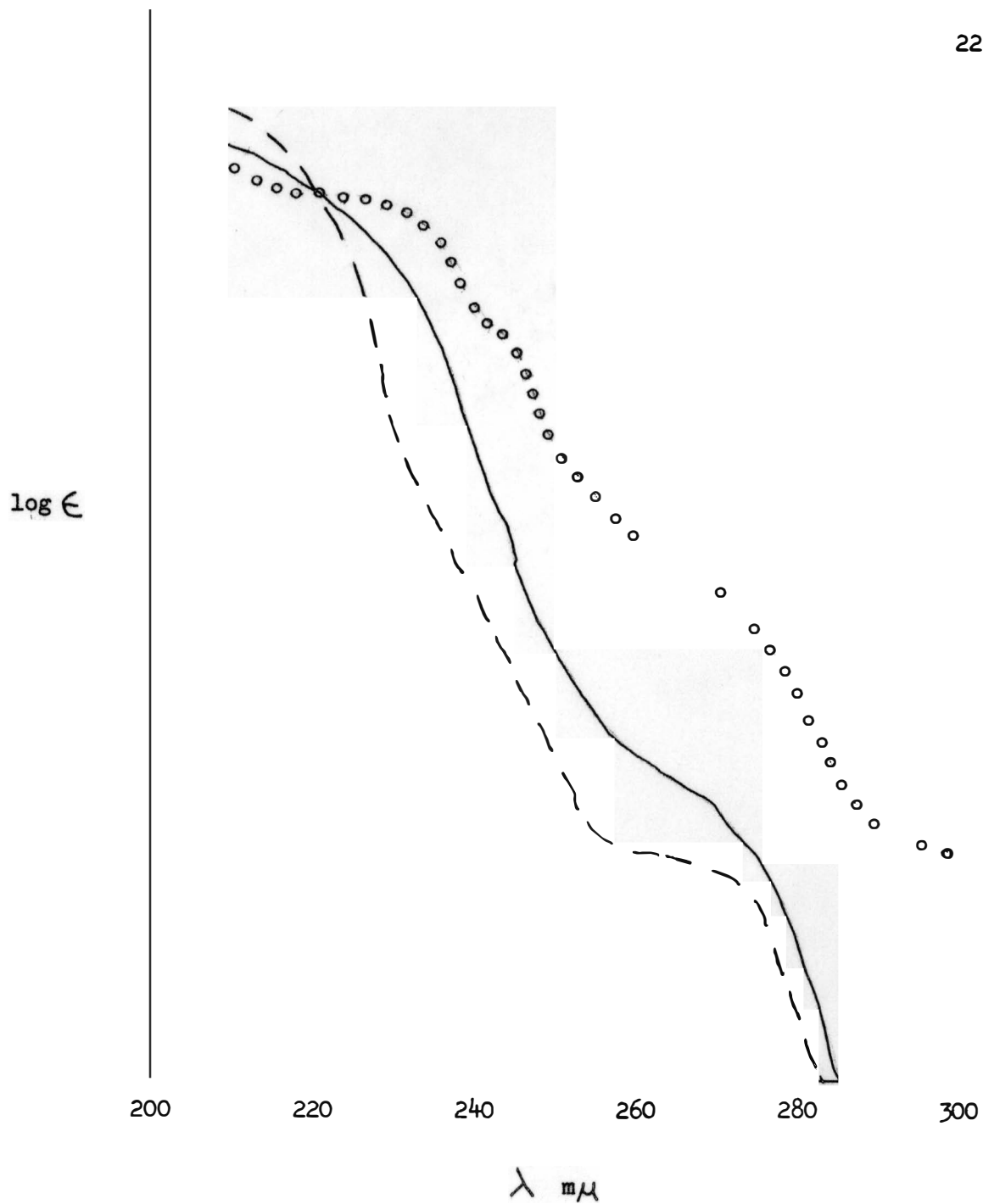


Fig. I Ultraviolet Absorption Spectra

- — — 3,3'-dichloro-o,o'-bitolyl
- — — 3,3'-dibromo-o,o'-bitolyl
- • • • • 3,3'-diiodo-o,o'-bitolyl

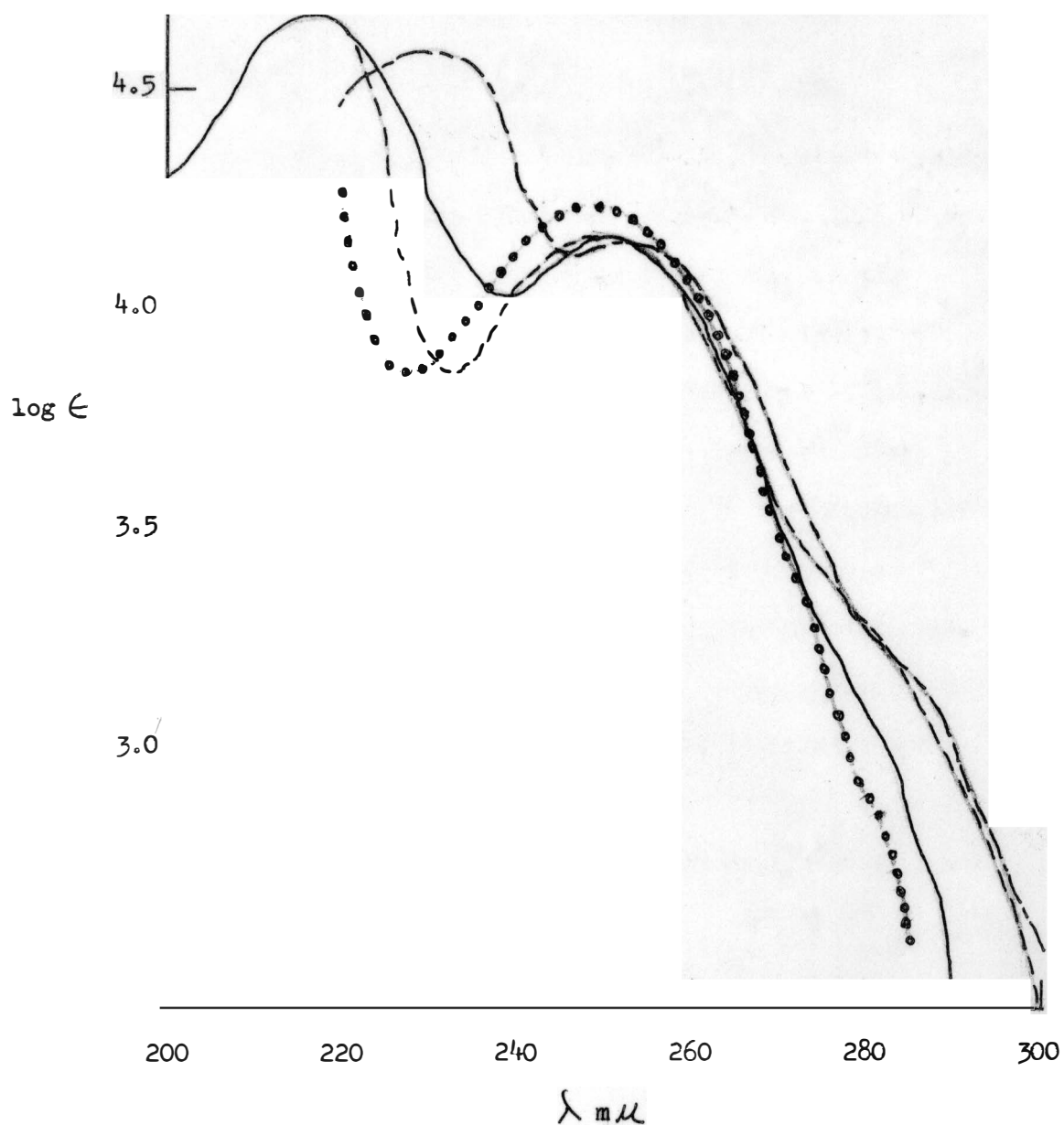


Fig. II. Ultraviolet Absorption Spectra

Diethyl 4,8-dibromo-5,7-dihydrodibenzo [a,c]
cycloheptadiene-6,6-dicarboxylate

Diethyl 4,8-dichloro-5,7-dihydrodibenzo [a,c]
cycloheptadiene-6,6-dicarboxylate.

Diethyl 4,8-diiodo-5,7-dihydrodibenzo [a,c]
cycloheptadiene-6,6-dicarboxylate.

..... Diethyl 5,7-dihydrodibenzo [a,c] cyclo-
heptadiene-6,6-dicarboxylate.

SUMMARY

The preparation of diethyl 4,8-dibromo-5,7-dihydrodibenzo [a,c] cycloheptadiene-6,6-dicarboxylate (VIc) was accomplished. The ultraviolet spectrum of compound (VIc) proved similar to that of the dichloro and diiodo analogs. The similarity of spectra indicates no marked electronic effect in the series of 3,3'-dihalo-2,2'-three-atom-bridged biphenyls. The spectral likeness is also interpreted as denoting a basic similarity in the configurations of the bridged biphenyls studied and thus indicates either the absence of or only an insignificant buttressing effect as measured by ultraviolet spectra. These observations may also raise reservation as to the validity of ultraviolet spectra as a sufficient criteria of buttressing effect. Finally, successful resolution studies are desired to furnish an unequivocal indication of a buttressing effect in these systems, if one does exist.

BIBLIOGRAPHY

1. Adams, R. and Yuan, H.C., Chem. Rev., 12, 261 (1933).
2. Ahmed, S. R. and Hall, D. M., J. Chem. Soc., 3043 (1953).
3. Ahmed, S. R. and Hall, D. M., ibid., 3383 (1952).
4. Ahmed, S. R. and Hall, D. M., ibid., 4156 (1960).
5. Beaven, G. H., Hall, D. M., Lesslie, M. S. and Turner, E. E., ibid., 854 (1952).
6. Beaven, G. H., Bird, G. R., Hall, D. M., Johnson, E. A., Ladbury, J. E., Lesslie, M.S. and Turner, E. E., ibid., 2708 (1955).
7. Beaven, G. H. and Hall, D. M., ibid., 4637 (1956).
8. Bell, F., ibid., 1527 (1952).
9. Bigelow, L. A., "Organic Synthesis", John Wiley and Sons, New York, 2nd ed. Collected Vol. I, 1961, p. 136.
10. Brand, K. and Steiner, J., Ber., 55, 884 (1922).
11. Chiang, Y. H., M.A. Thesis Western Michigan University (1961).
12. Cohen, J. B. and Miller, J., J. Chem. Soc., 85, 1627 (1904).
13. Foster, R. J., Rosicky, F. G. and Niemann, G., J. Am. Chem. Soc., 72, 3959 (1950).
14. Iffland, D. C. and Anderson, B., private communication.
15. Iffland, D. C. and Siegel, H., J. Am. Chem. Soc., 80, 1947 (1958).
16. Klyne, W., ed., "Progress in Stereochemistry", Academic Press, New York, 1954, Chapter 4.
17. Kornblum, N. and Kendall, D. L., J. Am. Chem. Soc., 74, 5782 (1952).
18. Lesslie, M. S. and Mayer, U. J. H., J. Chem. Soc., 611 (1961).
19. Lowe, E., U. S. Pat. 2,669,584 (Feb. 16, 1954).
20. Noelting, E., Ber., 37, 1024 (1904).

21. Parkes, G. D. and Farthing, A. C., J. Chem. Soc., 1275 (1948).
22. Suzuki, H., Bull. Chem. Soc. Japan. 27, 597-601 (1954).
23. Suzuki, H., ibid., 32, 1340 (1959).
24. Vesely, V. and Rein, E., Collection Czechoslov. Chem. Comm., 1, 360 (1929).

VITA

The author was born in Chicago, Illinois, on December 24, 1937. He received his elementary and secondary education in the schools of that city. He entered the Illinois Institute of Technology in January, 1956 and obtained a B.S. in Chemistry in 1960. In January, 1961 he received a teaching assistantship from Western Michigan University and from September, 1961 to June, 1962 was a research fellow sponsored by the Research Corporation.

APPROVAL OF EXAMINING COMMITTEE

DATE _____