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Condensation of olefins with p-Mercapto-Diphenyl

Raymond Michael Abrams

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CONDENSATION OF OLEFINS WITH
p-MERCAPTO-DIPHENYL

by

Raymond Michael Abrams, B.A.

A Thesis

Submitted in Partial Fulfillment
of the Requirements for the Degree of
Master of Science
in the Graduate School of the
University of Richmond
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Introduction

Markownikow's rule states that in the addition to unsaturates, negative groups add to the carbon atom having the least number of hydrogen atoms. It has been observed that mercaptans and hydrogen sulfide add to olefins contrary to Markownikow's rule in the presence of sodium alcolholates or sulfuric acid.

Pomer Ber. 58 666 (1905)

However, it was later noticed that sulfinic acids sometimes add to unsaturated ketones without the addition of such alcolholates.

Kohler and Reimer Am. Chem. J. 31 163 (1904)

In a corresponding experiment thiophenol and p-thiocresol condensed with $\alpha$-$\beta$ unsaturated ketones very readily at 100 degrees C without the aid of catalysts but similar additions occurred less readily in the presence of piperidime.

Nicolet J.A.C.S. 57, 1098 (1933)

Further results were then obtained showing that in the absence of catalysts thiophenol adds to olefins contrary to Markownikow's rule, but that in the presence of sulfuric acid.
acid (diluted with water or with acetic acid), which catalyzes the reaction, the normal alkylation product is obtained and not the abnormal one as erroneously reported by Posner.

Ipatieff, Fines and Friedman J.A.C.S. 60, 2731 (1938)

In this way, n-propyl, iso-propyl, n-butyl, n-amyl, and iso-amyl sulfides were prepared but these were not solids.

Ibid. J.A.C.S. 60, 2732 (1938)

About the same time it was found that sulfur takes hydrogen away even from unsaturates to form hydrogen sulfide, a part of which adds to double bonds producing a mercaptan which in turn adds to more of the unsaturate to give a sulfide. Furthermore, hydrogen sulfide adds to double bonds readily and follows Markownikow's rule, sulfur acting as an effective catalyst. Mercaptans, however, add to double bonds in accordance with Markownikow's rule if sulfur is present or if peroxides are eliminated. Otherwise, (i.e., if peroxides are present even in exceedingly small quantities) the abnormal addition takes place. As a result of this investigation, condensation of thiophenol with olefins of eleven to nineteen carbon atoms produce the corresponding sulfides which are solids. The melting points of these solids were checked by the preparation of the sulfides from the alkyl bromides and the potassium salt of the mercaptan.
The solid derivatives could then be used as a means of identification of the olefins. An attempt to obtain a general method for identification of olefins by

the condensation of thiocyanogen proved to be unsuccessful, because a number of the olefins would not condense with thiocyanogen to give crystalline compounds. Since thiophenol condensed with olefins of eleven carbon atoms or more to give solid derivatives whose melting points were high enough to be used practically for identification purposes, and since this was apparently not the case for olefins of less than eleven carbon atoms, it is reasonable to expect that if the molecular weight of the condensation products could be increased, solids of value for identification purposes should be obtained. Thus, the object of this investigation was to condense p-mercapto-diphenyl with olefins in the hope of learning more about the nature of the reaction of olefins with mercaptans and also in the hope of producing solid derivatives which could be used for the identification of olefins.
In 1871, Engelhardt and Latschinchow described for the first time the preparation of diphenyl-p-sulfonic acid.

Fifty grams of diphenyl and seventy grams of sulfuric acid were warmed together on a water bath until the odor of diphenyl was no longer noticeable. The mixture was diluted with water and filtered from unchanged diphenyl. The potassium salt was prepared by incompletely saturating the filtrate with potassium carbonate. The potassium salt was filtered and dried over sulfuric acid. From 1871 to 1880 apparently no further work was done on diphenyl-p-sulfonic acid.

In 1880 Gabriel and Deutsch described the preparation of diphenyl-p-sulfonyl chloride.

by the reaction of the potassium salt of the diphenyl-p-sulfonic acid with an equivalent quantity of phosphorous pentachloride. The potassium p-diphenyl sulfonate was prepared in the manner described by Engelhardt and Latschinchow as previously stated. No conditions are mentioned in the article for the preparation of the diphenyl-p-sulfonyl chloride.
The reaction mixture was boiled with water and filtered. The residue was recrystallized several times from glacial acetic acid and yielded pale yellow crystals which melted at 115 degrees C uncorrected. In 1887, Obermeyer prepared the diphenyl-p-sulfonyl chloride from the description of Gabriel and Deutsch and by reacting it with a mixture of alcohol and ammonia at 100 degrees C obtained diphenyl-p-sulfonamide which was described as white crystals, melting at 227 degrees C uncorrected.

Obermeyer Ber. 20, 2027 (1887)

No further work on diphenyl-p-sulfonic acid or diphenyl-p-sulfonyl chloride has been reported in the literature.

The p-mercapto-diphenyl was first prepared by Gabriel and Deutsch by the reduction of diphenyl-p-sulfonyl chloride using tin and hydrochloric acid. The p-mercapto-diphenyl was steam distilled and melted at 110-111 degrees C uncorrected. The product was soluble in alkali, benzene and carbon disulfide and moderately soluble in alcohol and ether. With lead and mercury salts, a red lead salt of mercapto-diphenyl and a white mercuric salt of mercapto-diphenyl were reported. Diphenylthioglycollic acid was prepared from the mercapto-diphenyl by dissolving the mercaptan in alkali and adding chloroacetic acid. The precipitate was then filtered and dissolved in hot water. The diphenylthioglycollic acid was precipitated with hydrochloric acid and was described as white
priaps melting at 169-170 degrees C uncorrected. Biphenyl disulfide was prepared by the oxidation of the p-mercapto-diphenyl with nitric acid and the subsequent recrystallization from glacial acetic acid yielded white crystals which melted at 148-150 degrees C uncorrected. The biphenyl disulfide was also reported as being formed as a result of the oxidation by atmospheric oxygen of an alkaline solution of the mercapto-diphenyl. The lead salt of the diphenyl mercapten was prepared by the action of lead acetate on an alcoholic solution of the mercapto-diphenyl which gave red-brown, microscopic crystals. Upon the dry distillation of the red lead salt, diphenyl sulfide was formed as shiny leaflets melting at 171-172 degrees C uncorrected. Upon the oxidation of the diphenyl sulfide by potassium permanganate or potassium dichromate, diphenyl sulfone was formed.

Gabriel and Deutsch Ber. 15, 386 (1880)

Since 1887, apparently no further work has been reported on p-mercapto-diphenyl.

In 1888, Baeyer suggested the use of potassium permanganate as a means of detecting olefins and some other unsaturates. The unsaturates are oxidized and potassium permanganate is decolorized with the formation of manganese dioxide. Baeyer and Villiger suggested in 1900 the use of a solution of potassium persulfate in sulfuric acid tinted with permanganate. This gives no reaction with paraffin
hydrocarbons but attacks olefins and benzene and its homologues. Tetranitromethane has been suggested by Wernor as a reagent for double bonds since it gives a brown or yellow color with unsaturated compounds.

The principal reaction of unsaturated linkages, however, is the ability to combine additively with a large variety of substances. This results in the formation of saturated compounds. Seratier and Sanderens during the years 1899-1902 were largely responsible for the development of hydrogenation of olefins in the gaseous phase using finely divided nickel on a pumice base as a catalyst. In the period 1903-1922, the catalytic reduction of olefins in the liquid state by hydrogen was worked out. Later, reduction of the olefin using hydrogen formed by the reaction of an acid and a metal, or sodium on alcohol was worked out.

The reaction of olefins with sulfuric acid to form alkyl hydrogen sulfates and the consequent hydrolysis to yield the corresponding alcohol appears to have been observed by Kannel in 1823. Higher molecular weight olefins have a tendency to polymerize.

The oxidation of olefins with potassium permanganate to yield glycols has been described. When peracids are used the olefins are converted to ethylene oxides and thence by hydrolysis to the glycol. Braun, in 1909, used perbenzoic acid for this purpose. Harries, during the years 1905-1915, was the chief worker to describe methods for the ozonization of olefins and for their subsequent decomposition into pro-
ducts from which the positions of the double bonds may be determined.

Hickinbottom and Ryder in 1931 established a process for the addition of halogens to olefins so that no substitution takes place. This was done by the addition of the halogen so that it never was in excess. Michael, Ipatieff, Smith and others have established the addition of halogen hydrides to olefins which react in general:

\[ \text{cis} + 
\text{< HAL} \rightarrow \text{cis} \text{HAL} \]

The addition of hypohalorous, hypobromous and hypiodous acids to olefins has been described by a number of workers during the years 1863-1907 according to the following scheme:

\[ \text{cis} + \text{HAL} \rightarrow \text{cis} \text{HAL} \]

Nitrosyl chloride was introduced by Tilden and Shenstone in 1877 as a reagent for the reaction with olefins to yield in many cases crystalline compounds useful for identification. Nitrogen trioxide and nitrogen tetroxide also add to olefins. These reactions may be demonstrated as follows:

\[ \text{cis} + \text{NOCl} \rightarrow \text{cis} \text{Cl} \]

\[ \text{cis} + \text{N}_2\text{O}_3 \rightarrow \text{cis} \text{NO} \text{NO}_2 \]

\[ \text{cis} + \text{N}_2\text{O}_4 \rightarrow \text{cis} \text{NO}_2 \text{NO}_2 \]
Wieland and Sakellarios demonstrated in 1920 that a mixture of nitric and sulfuric acids with ethylene yields 2-nitro-ethyl-alcohol in addition to ethyl-glycol-dinitrate which results, in general, from addition of nitric acid to olefins:

\[ \text{H}_2\text{C} = \text{C} \mathbf{\cdots} + \text{HNO}_3 \rightarrow \text{H}_2\text{C} - \text{C} \mathbf{\cdots} \]

Aromatic hydrocarbons were reported in 1890 to react with styrene to give diarylethanes; phenols react with olefins to give p-substituted phenols as reported in 1890 and aromatic amines react like phenols to give substituted aromatic amines as reported in 1932, by Hickinbottom.

Sulfurous acid in the presence of bisulphites and aryl sulfinic acids have been found by Kohler and Reimer to add to olefins on mixing the olefin and mercaptan in the presence of sulfuric acid or some other suitable catalyst and that these condensations are formed contrary to Markownikow's rule of addition.

This historical discussion of the reactions of olefins was condensed from "Reactions of Organic Compounds" Hickinbottom, published by Longman's, Green and Co. Feb., 1936.

Later it was noticed that sulfinic acids sometimes add to unsaturated ketones without the use of catalysts.

Kohler and Reimer Am. Chem. J. 51, 163 (1904)
Theophenol and thiocresol also condense with olefins in the absence of catalysts.

Nicolet J.A.C.S. 57, 1098 (1933)

Ipatieff, Pines, and Friedman J.A.C.S. 60, 2731 (1938)

showed that Pomer had erroneously reported abnormal addition of hydrogen sulfide to olefins in the presence of sulfuric acid. As a result of this confusion, Jonas and Reid

Jonas and Reid J.A.C.S. 60, 2452 (1938)

investigated the addition of hydrogen sulfide, sulfur, and mercaptans to olefins and found that hydrogen sulfide and sulfur added normally but that mercaptans added contrary to Markownikov's rule if peroxides even in exceedingly small amounts were present but added normally if they were absent or if sulfur was present.
Experimental

Preparation of Potassium p-Diphenylsulfonate

The method employed was to heat equivalent quantities of diphenyl and concentrated sulfuric acid at 160 degrees C for 15-20 minutes. Fifty grams (0.3 moles) of diphenyl and thirty-two grams (0.3 moles) of concentrated sulfuric acid were heated in a 500 cc. beaker on an open flame for 15-20 minutes. The reaction mixture was allowed to cool and 200 cc. of water was added. The precipitate was filtered by suction to separate the diphenylmonosulfonic acid from the unchanged diphenyl, which remained on the filter paper, and diluted to about one liter. A saturated solution of potassium carbonate was then added to the filtrate until effervescence no longer occurred. This takes place when the solution gives an alkaline reaction to litmus. The precipitate was filtered with suction and washed first with water and then with 95% alcohol. The potassium p-diphenyl sulfonate thus formed was placed in a beaker and dried in the oven at 120 degrees C until it was dry. The yield was 90 grams of potassium p-diphenyl sulfonate.

\[
\text{C}_6\text{H}_5\text{C}_6\text{H}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}
\]

\[
2\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{SO}_3\text{H} + \text{K}_2\text{CO}_3 \rightarrow 2\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{SO}_3\text{K} + \text{H}_2\text{O} + \text{CO}_2
\]

Preparation of Diphenyl-p-Sulfonyl Chloride

Gabriel and Deutsch's procedure for the synthesis of
diphenyl-p-sulfonyl chloride by the reaction of phosphorous pentachloride with potassium-p-diphenyl sulfonate was followed. The potassium p-diphenyl sulfonate was treated with slightly more than an equivalent quantity of phosphorous pentachloride. 90 grams (0.5 mole) of dry potassium p-diphenyl sulfonate was ground up finely in a heated mortar with 55 grams (0.4 moles) of phosphorous pentachloride so that intimate contact could be established. The mixture was then placed in a 500 cc. round bottom flask to which an air condenser having a calcium chloride tube attached to its top was connected and heated in a water bath for 12-15 hours. Every three hours the round bottom flask was cooled down and the mixture was stirred. After the fifteen hours of heating on the water bath had elapsed, the reaction mixture was boiled with water and filtered with suction. The precipitate was recrystallised four times from glacial acetic acid and pale yellow crystals of diphenyl-p-sulfonyl chloride melting at 115 degrees C were obtained. The yield was 25 grams. The diphenyl-p-sulfonylimide was prepared as a derivative by heating a solution containing 5 cc. of ammonia and 5 cc. of alcohol at 100 degrees C in a sealed tube with 22 grams of diphenyl-p-sulfonyl chloride. Twelve hours were allowed for reaction to take place. Upon cooling, a mass of white crystals melting at 220-225 degrees C was obtained. The literature reports the melting point of diphenyl-p-sulfonylimide to be 225-227 degrees C.

\[
\text{O-O-SO}_3\text{K} + \text{PCl}_3 \rightarrow \text{O-O-CL} + \text{POCl}_3 + \text{KCl}
\]
Preparation of p-narcapto-diphenyl

The 25 grams of diphenyl-p-sulfonyl chloride were reduced with tin and hydrochloric acid according to the method of Gabriel and Dautrech. 25 grams of diphenyl-p-sulfonyl chloride were placed in a 500 cc. round bottom flask and 100 cc. of 10% hydrochloric acid and 50 grams of tin were added. The mixture was refluxed, using a Liebig condenser, for five hours and then steam distilled. The compound from the steam distillation was not pure and so the product was dissolved in sodium hydroxide and acidified with hydrochloric acid. It was filtered with suction and placed on a porous plate to dry. It had a slight yellowish tinge. The melting point was found to be 109-111 degrees C uncorrected. The diphenylthioglycollic acid was prepared by taking a small sample of the p-narcapto-diphenyl and dissolving it in sodium hydroxide. Chloroacetic acid was added to the solution and the white precipitate formed was filtered with suction. The precipitate was then dissolved in 25 cc. of hot water and 10% hydrochloric acid was added to precipitate diphenylthioglycollic acid which was filtered and dried on a porous plate. The melting point was found to be 167-170 degrees C uncorrected. The literature reports the melting point of diphenyl thioglycollic acid to be 169-170 degrees C. The biphenyl disulfide was prepared by passing air through an alkaline solution of the mercaptan. The white precipitate was filtered and dried on a porous plate and was found to melt at 148-150 degrees C uncorrected.
The literature reports the melting point of biphenyl disulfide to be 148-150 degrees C.

\[
\text{C}_6\text{H}_4\text{SO}_2\text{Cl} + 6 [\text{H}] \rightarrow \text{C}_6\text{H}_4\text{SH} + 2\text{H}_2\text{O} + \text{HCl}
\]

**Condensation with Styrene**

4 drops of styrene containing hydroquinone to stabilize it from polymerization and 0.1 gram of the p-mercapto-diphenyl prepared were sealed in a small pyrex test-tube and placed in the combustion furnace. A temperature of 155 degrees C was maintained for 5 hours. The tube was opened, water was added and the reaction mixture boiled to steam distill off the styrene. The resulting product was recrystallized from ethyl alcohol. White crystals were formed. The melting point was found to be 65-67 degrees C uncorrected.

\[
\text{C}_6\text{H}_4\text{Cl} + \text{C}_6\text{H}_4\text{SH} \rightarrow \text{C}_6\text{H}_4\text{CSH}
\]

**Condensation with Ethylene**

Ethylene was prepared by reacting ethyl alcohol with sulfuric acid at 130 degrees C and caught in a two liter bottle by displacing water from it. The outlets were closed by pinching the rubber tubing with pinch-clamps. 0.1 gram of p-mercapto-diphenyl was placed in a test tube and heated in an oil bath at 150-160 degrees C for three and one-half hours while the ethylene was passed into the
test tube at a constant rate. The ethylene was displaced by running water back into the two liter flask. Yellow colored prisms melting at 118-121 degrees C uncorrected were obtained. The product was insoluble in alkali.

\[
\text{CH}_2=\text{CH}_2 + \text{S} - \text{SH} \rightarrow \text{CH}_3-\text{CH}_2-\text{S}-\bigcirc-\bigcirc
\]
Discussion

Since the preparation of diphenylmonosulfonic acid was described only by Engelhardt and Latschinow and since this article did not include exact details for this preparation it became necessary to attempt other methods. At first, a commercial diphenylmonosulfonic acid made by Eastman and Co. was used, but this product was found to be so crude that it was decided to make the diphenylmonosulfonic acid in the laboratory. One of the methods attempted was to use equimolar quantities of diphenyl and fuming sulfuric acid at 100 degrees C, but this attempt failed to yield a product which had the properties assigned to the diphenylmonosulfonic acid. A second method attempted was to use a large excess of concentrated sulfuric acid at 100 degrees C until the odor of diphenyl was no longer noticeable. This was the method of Latschinow and Engelhardt. The product prepared in this manner was also found to be unsatisfactory. The last method attempted was to use equimolar concentrations of diphenyl and concentrated sulfuric acid maintained at a temperature of 150-160 degrees C for 15-20 minutes. The product made in this manner proved to be satisfactory because when the potassium salt was made it reacted with the phosphorus pentachloride to give the diphenyl-p-sulfonyl chloride.

There are at least two factors that ought to be considered in the sulfonation of diphenyl:
(1) the optimum conditions of temperature and concentration for the introduction of only one sulfonic acid group into the ring.

(2) the conditions that favor the substitution of the sulfonic acid group in the para position.

Engelhardt and Letschinow used a large excess of concentrated sulfuric acid at 100 degrees C until the odor of diphenyl no longer was noticeable. These investigators found that even at 100 degrees C the large excess of sulfuric acid tends to form, along with the diphenylmonosulfonic acid, appreciable amounts of the diphenyl-disulfonic acid. The use of equimolar concentrations of concentrated sulfuric acid and diphenyl at 150 degrees C for 15-20 minutes has given the best results in this laboratory. The probable reason for this is that elevated temperatures usually favors substitution in the para position. Moreover, equimolar concentrations at 150 degrees C ought not to allow an appreciable amount of diphenyl-disulfonic acid to be formed.

The articles by Gabriel and Deutsch and Obermeyer did not state the conditions at which the reaction between the potassium salt of the diphenylmonosulfonic acid and phosphorous pentachloride occurred best. Consequently, some difficulty was experienced in an attempt to prepare the diphenyl-p-sulfonyl chloride. At first, the same conditions as were used by Roger Adams and C.S. Marvel for the preparation of benzene sulfonyl chloride (from the reaction between the sodium salt of the benzene sulfonic acid and phosphorous
pentachloride) were applied to the reaction of the potassium p-diphenyl sulfonate and the phosphorous pentachloride.

Heating at 170-180 degrees C for 15 hours was used. This method was found to be unsatisfactory for the synthesis of diphenyl-p-sulfonfyl chloride since crystals which melted at different temperatures in different runs were obtained. Melting points of 129-134 degrees C, 136-138 degrees C, and 144-147 degrees C were obtained for the products prepared in this manner. It is possible that, since phosphorous pentachloride dissociates to form phosphorous trichloride and chlorine at higher temperatures and since the diphenyl used had probably been prepared by using iron as a catalyst, chlorination may have taken place. In addition, at high temperatures, such as 170-180 degrees C, the tendency for the SO2 to slip out of the molecule (if any of the diphenyl-p-sulfonfyl chloride is formed) is greatly increased. Since it is very convenient to use a water bath the reaction was attempted at 100 degrees C for 15 hours. After three recrystallizations from glacial acetic acid, pale yellow crystals which melted at 115 degrees C were obtained. The diphenyl-p-sulfonamide was prepared in the manner described and the melting point checked with that recorded in the literature, showing quite conclusively that the diphenyl-p-sulfonfyl
chloride had been synthesized. It is probable that the yield can be increased if a temperature around 125 degrees C is used, although this reaction has not been attempted at 125 degrees C in this laboratory. In addition an attempt will be made to see whether the diphenyl-p-sulfonyl chloride will not recrystallize better from carbon tetrachloride or chloroform since acetic acid seems to recrystallize some of the impurity as well as the compound in question and since an advantage in the use of either of these solvents will be their greater volatility.

Neither of the two investigators who have reported the preparation of the mercapto-diphenyl in the literature have given the details of preparation. Gabriel and Deutsch mention that the p-mercapto-diphenyl may be prepared by the reduction of diphenyl-p-sulfonyl chloride using hydrochloric acid and tin, and after the reduction the diphenyl mercaptan is distilled over with steam. Little difficulty has been experienced with the reduction, but it is possible that the distillation with steam is perhaps not the best method of isolation because it is frequently the case that impurities present prevent the substance from being steam distilled. The steam distillate of the mercaptan prepared in the laboratory was very impure and so it was dissolved in sodium hydroxide and immediately reprecipitated with hydrochloric acid. It still contains a small amount of impurity which gives it a yellow tinge, but the melting point that has been taken is 109-111 degrees C and the value as given in the
literature is 110-111 degrees C. In addition, the biphenyl
disulfide and the diphenythioglycollic acid which were pre-
pared from the mercaptan as derivatives gave melting points
of 148-150 degrees C and 167-170 degrees C respectively.
The literature reports melting points of 148-150 degrees C
and 169-170 degrees C respectively.

Condensations of the p-diphenyl mercaptan are to be
carried out very shortly with ethylene, propylene, styrene,
and two other olefins which will be submitted by Dr. E.
Emmet Reid. Dr. Reid is to prepare condensation products
from alkyl bromides and p-mercaptodiphenyl to compare with
the products obtained in this laboratory with olefins and
p-mercaptodiphenyl.
Summary

1. The following compounds have been prepared and described:
   - potassium p-diphenyl sulphonate
   - diphenyl-p-sulfonyl chloride
   - p-mercaptodiphenyl

2. The condensation of p-mercaptodiphenyl with styrene has been described and other condensations are to be carried out.

3. Conditions for the formation of diphenyl-p-sulphonic acid have been described.

4. The reaction between phosphorous pentachloride and potassium p-diphenyl sulphonate has been carried out.

5. The following derivatives for identification of compounds prepared have been described:
   - diphenyl-p-sulphonamide
   - diphenylthioglycollic acid
   - biphenyl disulfide

6. The condensation of p-mercaptodiphenyl with ethylene was accomplished and crystals of high melting point, valuable for identification purposes, were obtained.
Acknowledgement

I wish to express to Dr. E. Emmet Reid and to Dr. J. Stanton Pierce my sincere appreciation for their guidance and suggestions during the pursuance of this work.
Autobiography

I, Raymond Michael Abrams, was born on December 12, 1911 in Brooklyn, New York. I attended the public schools of Brooklyn and Long Island and graduated from Grover Cleveland High School in June 1934. I attended New York University for one year and University of Michigan for three years, receiving the degree of Bachelor of Arts in June, 1938. In September, 1939, I matriculated as a graduate student in the Graduate Department of the University of Richmond.
Autobiography

I, Raymond Michael Abrams, was born on December 12, 1917 in Brooklyn, New York. I attended the public schools of Brooklyn and Long Island and graduated from Grover Cleveland High School in June 1934. I attended New York University for one year and University of Michigan for three years, receiving the degree of Bachelor of Arts in June, 1939. In September, 1939, I matriculated as a graduate student in the Graduate Department of the University of Richmond.

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