THE PREPARATION AND STRUCTURE OF A DIMER OF PARABROMOSTYRENE: 1,3-DI-(PARABROMOPHENYL)-1-BUTENE

By

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The writer wishes to express his sincere gratefulness to Dr. Gordon L. Goerner whose tolerant and kind guidance made this work possible.

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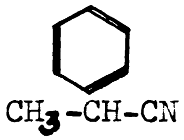
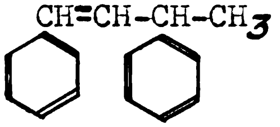
INTRODUCTION

In an attempt to prepare hydratroponitrile (α-phenylpropionitrile) I, Goerner and Hines (1)



I

heated α-chloroethylbenzene with cuprous cyanide to a temperature of 130°C. At this temperature a vigorous reaction ensued with the evolution of hydrogen cyanide. The product proved to be <u>cis</u>-1,3-diphenyl-1-butene, II.



II

A search of the literature showed no previous report of this reaction. The purpose of this investigation was to prepare α-chloro-α-(p-bromophenyl)-ethane, to attempt to react it with cuprous cyanide, and to determine the structure of any reaction products obtained.

A study of the paper mentioned above (1) together with the report submitted by Hines brings out the following points:

1. The reaction between α-chloroethylbenzene and cuprous cyanide proceeds quite vigorously at a temperature of about 130°C.

2. Lowering the temperature of reflux by the use of a solvent with a boiling point below 130° C. inhibits the reaction.

3. An anhydrous medium is necessary. If water is present, the hydrocarbon is not obtained, but rather, di-α-methylbenzyl ether C_6H_5-CH(CH_3)-O-CH(CH_3)-C_6H_5, III, (2).

4. The yield of <u>cis</u>-1,3-diphenyl-1-butene is about 40%.

5. The composition of the copper-containing residue has not been investigated.

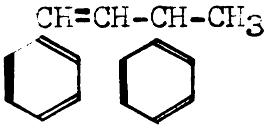
Later work (2) has shown that the reaction between the α-chloroethylbenzene and cuprous cyanide will proceed in a solvent if the boiling point of the latter is sufficiently high. Commercial xylene and styrene have been used as solvents. The use of styrene has brought about an increase in the yield of the product. By using a large excess of the latter, more <u>cis</u>-1,3-diphenyl-1-butene was obtained than could be obtained from the α-chloroethylbenzene alone. Obviously some of the styrene used as a solvent was entering into the formation of the <u>cis</u>-1,3-diphenyl-1-butene.

The structure of the hydrocarbon obtained by Goerner and Hines was easily proved because of the following facts.

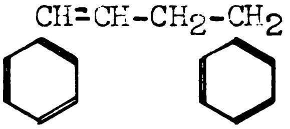
1. The physical properties of the hydrocarbon approximated those for the already described dimeric styrenes or distyrenes (3).

2. Hydroxylation and degradation of the hydro-

carbon gave benzaldehyde (characterized as its 2,4-dinitrophenylhydrazone). The position of the double bond in the hydrocarbon was thus determined, and on this basis it became apparent that formula IV or V represented the compound under consideration.



IV



V

No second degration product was isolated.

3. A dibromide of IV, m.p. 102°, was described in the literature (4).

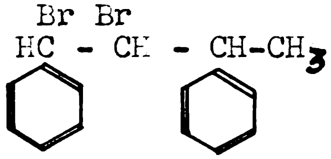
4. The compound under consideration formed a dibromide melting at 102° C. when alone or when mixed with an authentic sample of the already described dibromide.

5. Marion (5) had shown that the *trans* form of IV melted at 47°C., whereas the *cis* form was a liquid.

Erlenmeyer (7) prepared 1,3-diphenyl-1-butene (IV) by the action of HBr and cinnamic acid and Swartz (7) did the same using HCl. Fittig and Erdman (6) refluxed cinnamic acid with various concentrations of sulphuric acid, extracted the reaction mixture with ether and recovered the distyrene (IV) from the extraction.

Stobbe and Posnjak (9) repeated Erdman's work and proved the structure of the distyrene (IV) on the basis of the isolation of benzaldehyde and comparison of the ultra violet light absorption spectra data with other ethylenic compounds.

Stormer and Kootz (4) brominated IV without significant substitution in cold CS_2 solution to give 1,2-dibromo-1,3-diphenyl-butane (VI).



VI.

Three of four possible isomers were separated by crystallization from petroleum ether. Two of the isomers were shown on mixing to melt at 102° C., the reported melting point of the brominated <u>cis</u>-1,3-diphenyl-1-butene (IV). They further showed isomerization of 1,3-diphenyl-1-butene (IV) to 1,3-diphenyl-2-butene on long standing or heating with high concentrations of sulphuric acid.

Königs and Mai (10) have prepared the distyrene (IV) by the action of glacial acetic acid and sulphuric acid on styrene.

More recently 1,3-diphenyl-1-butene has been prepared by Marion (5). He prepared α,γ-diphenylbutyric acid by a Clemmensen reduction of α-phenyl-γ-benzoylpropionic acid. A Bouveault reduction of the substituted butyric ester gave α,γ-diphenylbutyl alcohol. A potassium bisulphate dehydration yielded 1,3-diphenyl-2-butene which isomerized upon standing to 1,3-diphenyl-1-butene (IV). He also observed that 1,3-diphenyl-1-butene, upon standing with sulphuric acid, isomerized to 1,3-diphenyl-2-butene.

Marion's product, a solid, melting at 47°C., was assigned the <u>trans</u> configuration. He further states that the <u>cis</u> and <u>trans</u> forms of 1,3-diphenyl-1-butene (IV) each have two possible dibromides, the four melting points being 79°, 86.5°, 122° and 129°C. The last two are those formed by the <u>cis</u>-distyrene, which is a liquid. Further, a mixture of the two <u>cis</u>-dibromides melts at 102°C. This is in agreement with the results of Stoermer and Kootz (4).

Barber et al. (11) prepared α-phenyl-α-chloroethane and condensed it to <u>meso</u>-2,3diphenyl-butane by means of magnesium in boiling ether. α-(p-Bromophenyl)-α-chloroethane was prepared from the corresponding carbinol by treatment with thionyl chloride but would not react with magnesium. A Wurtz type condensation was carried out by refluxing this chloride with sodium wire in anhydrous benzene for sixty hours. <u>Meso</u>-2,3-di(p-bromophenyl)-butane was obtained.

Barber et al. brominated <u>meso</u>-2,3-diphenylbutane in a glacial acetic acid-water mixture under reflux. A 25% yield of a racemic 2,3-dibromo-2,3-di-(p-bromophenyl)-butane was obtained. This tetrabromo compound was partially debrominated with some difficulty by suspending it in glacial acetic acid under reflux and adding zinc dust. Predominately <u>cis</u>-$4,4^{1}$dibromo-α,β-dimethylstilbene was obtained. The <u>trans</u> isomer was obtained by refluxing the

<u>cis</u> isomer in nitrobenzene which contained a trace of iodine.

The reactivity of the aromatic bromine was demonstrated by conversion of <u>trans</u>-4,4'dibromo-α,β-dimethylstilbene to 4,4'dicyano-α,β-dimethylstilbene by treatment of the former with cuprous cyanide in boiling quinoline. Seventy-four percent conversion to the cyano derivative was obtained.

In spite of the scarcity of information about dimers of p-bromostyrene, it was hoped to proceed with the investigation in a manner similar to that used by Goerner and Hines. Because of the discovery of several discrepancies in the literature, it became necessary to prepare two reference aldehydes and their derivatives.

EXPERIMENTAL

CHEMICALS

The following chemicals were used in this investigation:

p-Dibromobenzene, Dow, m.p. 84 - 85°

Diethyl ether, C.p. dried over sodium wire

Magnesium turnings, for Grignard reagents

Ethyl bromide

Hydrogen chloride gas, anhydrous from a cylinder

Methyl alcohol, C.p. anhydrous Merck

Benzene, thiophene free, C.p. anhydrous

2,4-Dinitrophenylhydrazine, Eastman white label

Cuprous cyanide, J.T. Baker purified

Tertiary butyl alcohol, Eastman white label

Hydrogen peroxide, 30% C.p., Baker and Adamson

Osmium tetroxide, Eastman white label

p-Bromoacetophenone, Eastman white label

Ethyl chloroacetate, Eastman white label

Sodium metal, Merck, reagent

Ammonia, commercial grade from cylinder

p-Bromotoluene, Dow, commercial grade

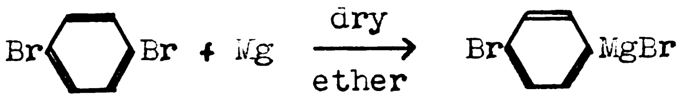
Bromine, Dow, N.F.

Acetaldehyde- acetaldehyde was prepared just before use by depolymerizing paraldehyde. Toluenesulfonic acid and concentrated sulfuric acid were used in small amounts as depolymerizing agents. Paraldehyde was heated with the depolymerizing agents and acetaldehyde distilled slowly from a 72 cm. Vigreux column at 20 - 21°. The receiver was chilled with crushed ice to prevent evaporation of acetaldehyde.

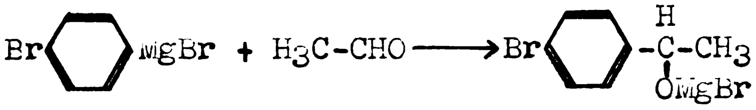
p-BROMOPHENYLMETHYLCARBINOL

Parabromophenylmethylcarbinol IX has been prepared previously by two different methods. Ziegler and Tiemann (12) and later Quelet (13) prepared the mono-Grignard reagent of p-dibromobenzene and treated this with acetaldehyde. Quelet reported yields of 45 to 50%. Overberger and co-workers (14) prepared the carbinol from p-bromobenzaldehyde and methylmagnesium bromide in yields of 64%.

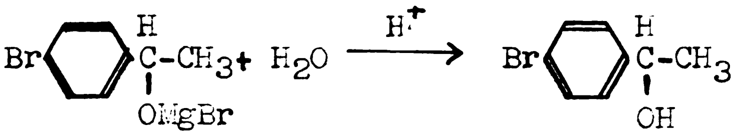
Because of the availability of p-dibromobenzene, the former method of preparation was used throughout this work. The following equations illustrate this preparation.



VII



VIII



IX

In a typical preparation, 108 gms. (4 moles) of magnesium were placed in a 5-l. three-necked flask equipped with mechanical glass stirrer, reflux condenser and an externally cooled Hershberg dropping funnel. To the flask was added 150 ml. of anhydrous ether followed by 5 ml. of ethyl bromide to serve as the "starter". To this, a saturated solution of 944 gms. (4 moles) of p-dibromobenzene in about 1500 ml. of anhydrous ether was added over a period of six hours. The upper surface of the flask was cooled from time to time with ice. After the Grignard reagent had been stirred for two hours, the flask was placed in an ice bath and a solution of 180 gms. of freshly distilled acetaldehyde in 700 ml. of anhydrous ether was added. The dropping funnel was chilled by an ice-salt mixture to prevent evaporation of the acetaldehyde. The time of addition was 2½ to 3 hours. Stirring was continued for one hour and the reaction mixture was then permitted to stand about thirty-six hours. During this time a dark green viscous layer separated from the ether.

Hydrolysis was accomplished by pouring the reaction mass upon crushed ice. The ether layer was decanted and the aqueous layer acidified to Congo paper with dilute H_2SO_4. The aqueous phase was extracted with three 500 ml. portions of ether. These latter ether extracts were washed with 10% sodium carbonate solution until alkaline and then added to the first ether decantate. The combined ether solution was dried over anhydrous potassium carbonate and the ether stripped from the solution.

The carbinol fraction was distilled under reduced pressure through a 62 cm. Vigreux column.

The following fractions were collected:

Fraction	Wt. Gms.	B.P., °C.	P., mm.	n_D^{18}
I	-	25- 74	13	-
II	28.3	75-106	2	1.5752
III	148.2	109-110.5	0.5	1.5728
IV	79.5	111-123	1.5	1.5730
V	180.0	residue	-	-

Dehydration of the p-bromophenylmethylcarbinol IX could be minimized by distillation through a shorter column. A reasonably pure product was obtained by distillation from a Claisen flask.

The following table of data summarizes the results of the preparation of p-bromophenylmethylcarbinol from dibromobenzene.

	REACTANTS		YIELD			
Run No.	$\frac{\text{Gms.}C_6H_4Br_2}{\text{Gms.}CH_3CHO}$	Gms.Mg.	Gms.	%	n_D^{18}	Gms. Residue
1.	944/180	108	451.6	56.4	1.5700	145
2.	708/135	81	227.7	37.8	1.5728	180
3.	708/135	81	115.7	17.5	1.5745	171.6
4.	785/167	90	278.0	41.7	1.5710	153.3
6.	944/180	108	247.7	30.8	1.5705	263.3
7.	944/180	108	368.2	45.8	1.5700[a]	90.0

a) temperature 20 C.

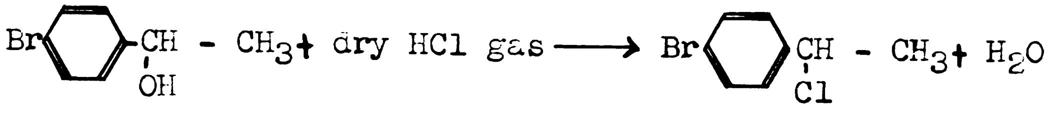
Run number 7 was refluxed one hour after the dibromobenzene had been added and the carbinol residue was distilled from a Claisen flask.

Numbers 6 and 7 were sampled before addition of acetaldehyde and an aliquot was titrated for yield of p-bromophenylmagnesium bromide using standard acid-base titration. Yield of p-bromophenylmagnesium bromide in run no. 6 was 89.9%, in no. 7, 91.6%.

α-CHLORO-α-(p-BROMOPHENYL)-ETHANE

Barber et al. (11) have prepared α-chloro-α-(p-bromophenyl)-ethane X in 81% yield by heating p-bromophenylmethylcarbinol IX and thionyl chloride on a steam bath. They reported the product to be a pinkish pungent oil boiling at 115-120°/ 11-12mm.

In this work, p-bromophenylmethylcarbinol IX was converted to α-chloro-α-(p-bromophenyl)-ethane X according to the following reaction:



IX X

This reaction was always carried out in a well ventilated hood. A typical run is as follows: One hundred to three hundred grams of p-bromophenylmethylcarbinol IX was placed in a 500 ml. three-necked round bottom flask equipped with a mechanical stirrer, an inlet tube which was submerged below the surface of the p-bromophenylmethylcarbinol, an outlet tube attached to a calcium chloride drying tube, and a thermometer. The flask and its contents were chilled to 0°C. by means of a sodium chloride-ice bath. HCl gas from a cylinder was passed first through a trap, through a concentrated sulphuric acid wash bottle, through a second trap and finally into the reaction flask at a slow, continuous rate so that bubbling could be detected. The reaction temperature was not permitted to change appreciably from 0° C. Introduction of HCl gas was continued until there was no appreciable increase in weight of the reaction flask. Two phases separated, the heavier, a dark red oil which was the crude product X, and the lighter, a transparent aqueous layer. The dark oil was separated and stored in a well-stoppered bottle over anhydrous calcium chloride for at least 24 hours in a refrigerator. At -10°C. this crude product was a solid.

The crude α-chloro-α-(p-bromophenyl)-ethane X was distilled in vacuo through an unpacked column of 31 cm. height. No forerun was collected. The fraction boiling 92 - 105° at 1.5 mm. was collected, n_D^{20} 1.5687 and represented 100% of theoretical yield.

The following table lists the results of a series of runs.

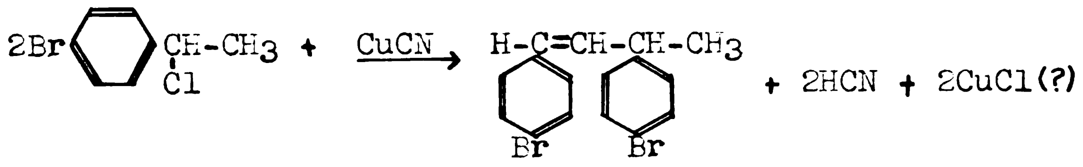
Run No.	Gms. of IX used	HCl gas	Gms. X	Yield,%	n_D^{20}	B.P.,°C.
A	100	14 hr.	87.8	80.4	1.5690	107-112/2mm.
B	100	13½ hr.	101.4	93.2	1.5681	91-104/1mm.
C	256.3	15½ hr.	223.6	80.0	1.5695	91-97/1mm.
D	113.3	14 hr.	123.8	100.0	1.5687	92-105/1.5mm.

In all cases the distilled α-chloro-α-(p-bromophenyl)-ethane was a water white oily liquid, stable at 20° C. when stored well-stoppered in a refrigerator for 6 months. HCl was not detected when the bottle was unstoppered occasionally during that period of time.

Using the procedure of Cheronis and Entrikin (15), the preparation of the S-alkylisothiourea picrate derivative of α-chloro-α-(p-bromophenyl)-ethane was attempted. All fractions of recrystallized material obtained were found to melt above 300° C. No further characterization was attempted.

1,3-DI-(p-BROMOPHENYL)-1-BUTENE

In the preparation of 1,3-di-(p-bromophenyl)-1-butene, the procedure of Goerner and Hines (1) was followed closely. The course of the reaction may be represented by the following equation:



X XI

In a typical preparation using no solvent, 58 gms. of CuCN was placed in a 500 ml., three-necked flask equipped with a reflux condenser, Hershberg stirrer and thermometer. A glass tube connected the top of the condenser to a coil and receiver packed in ice. A dropping funnel was fitted in the top of the reflux condenser and 142.5 gms. (0.65 moles) of α-chloro-α-(p-bromophenyl)-ethane X placed in the dropping funnel was allowed to drop slowly into the flask. An oil bath surrounding the flask was heated slowly and at 126° mild evolution of HCN began to take place. Approximately 10 minutes after completion of the addition of α-chloro-α-(p-bromophenyl)-ethane, HCN evolution ceased and the reaction subsided. The oil bath was removed and stirring continued for one hour. The cooled reaction mass was extracted with three

150 ml. portions of benzene.

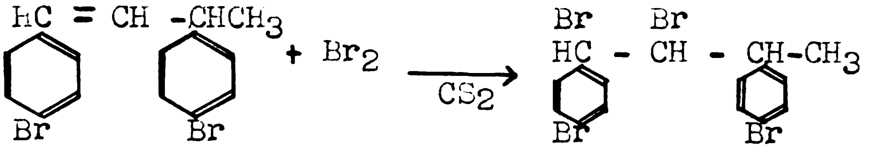
The benzene was removed under reduced pressure (aspirator) and the residue was distilled in vacuo through an unpacked column of 31 cm. The following fractions were collected.

Fraction	Boiling Range	Wt. Gms.	Pressure mm.
A	77 - 143°	21.5	3
B	178 - 216°	64.8	3
C	216 - 225°	5.5	3

Fraction B solidified on standing overnight at room temperature. The oily solids were recrystallized from methyl alcohol and 24.1 gms. of a white crystalline solid melting at 67.5 - 68.0° and 38 gms. of a material of lower melting point were isolated. Yield, calculated as XI, was 47.9% based on recrystallized solids.

Analysis of a sample of the solid melting at 67.5-68° for bromine by the Parr bomb method (16) gave 43.3%, 43.6% and 43.8%. Calculated for $C_{16}H_{14}Br_2$: Br, 43.6.

Stobbe and Posnjak (9) found that halogenation in CS_2 as a solvent almost completely eliminated side chain substitution reactions for compounds of type XI; for that reason their procedure was used in the addition of bromine to XI. Two and five tenths gms. (.0068 moles) of 1,3-di-(p-bromophenyl)-1-butene was dissolved in CS_2 in a test tube which was excluded from light by wrapping with a cloth and a 5% solution of Br_2 in CS_2 was added dropwise to the solution. Bromine discoloration was slow and only enough bromine was added to maintain a brown color in the reaction mixture. One half hour was necessary to reach the point of the persistent bromine color. The CS_2 mixture was poured on a watch glass and allowed to evaporate. The solid residue was taken up in C.P. benzene and the benzene volume reduced to approximate saturation. Petroleum ether was added and a solid separated. Recrystallization from benzene-petroleum ether yielded 3.1 gms. of a white solid melting point 154 - 160°. This corresponded to a yield of 83%. A bromine analysis by the Parr bomb method (16) gave 61.0% and 61.1% compared with a theoretical value of 60.8% for XII. It thus appears that the course of the bromination reaction may be represented by the following equation:



XI XII

Molecular weight determinations on 1,3-di(p-bromophenyl)-1-butene were attempted using the procedure of

Shriner and Fuson (17) based on the melting point depression of camphene and pinene hydrochloride. However, results were not reproducible for the depressed melting point of the mixture and so the procedure was abandoned. Freezing point depressions further in benzene as a means of determining molecular weight were attempted, using the procedure of Daniels, Mathews and Williams (18). It was found, however, that at the freezing point of benzene 1,3 di-(p-bromophenyl)-1-butene began to display an insolubility which would not permit its use for a reliable determination. No other solvents were tried.

1,3-Di-(p-bromophenyl)-1-butene when stored in a stoppered glass vial for a period of 6 months in a place where incidental sunlight struck it showed a continuous loss in melting point value. It finally became an oily semi-solid material. No investigation was made of this because of the lack of time. Two possible explanations may be offered, however.

1. Possible <u>cis</u>-<u>trans</u> isomerism is potentially existent. One of the isomers may be represented by this preparation and light may supply sufficient energy to convert it to the other. The oily mixture may represent some depressed melting range of mixtures of the two isomers.

2. Marion (5) and Stoermer and Kootz (4)

observed isomerization of 1,3-diphenyl-1-butene to 1,3-diphenyl-2-butene upon standing with H_2SO_4. Light may be sufficient to cause a slow isomerization of the double bond position of 1,3-di-(p-bromophenyl)-1-butene.

A dimerization of α-chloro-α-(p-bromophenyl)-ethane was run using redistilled tertiary amylbenzene as a solvent. Using the same conditions described in a typical preparation, 50 gms. of CuCN, 120 gms.(0.548 moles) of α-chloro-α-(p-bromophenyl)-ethane and 150 ml. of tertiary amybenzene were used. The reaction took place at 125°C., but practically no HCN was obtained. The reaction was maintained at 138° for two and one half hours. It was cooled and filtered. The filtrate was stripped of solvent using the reduced pressure of an aspirator. Distillation in vacuo gave the following fractions:

Fraction	Boiling Range	Wt. Gms.	Pressure, mm.
a	64 - 100°	28.6	6
b	100 - 150°*	15.4	4
c	150 - 205°	32.3	2

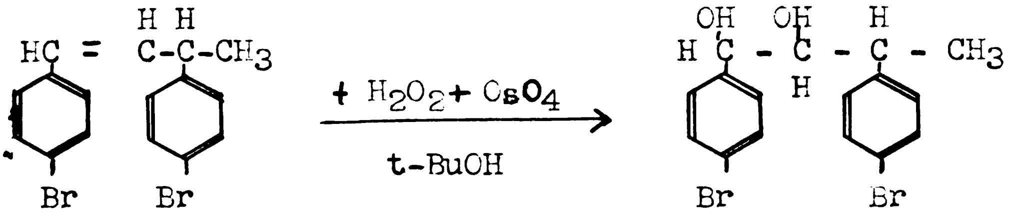
*Major portion received at 128°/ 4mm.

Fraction c represented the crude yield of dimer XI. Yield 29.6%. From this data the use of a solvent decreases the yield of dimer. Lack of time prevented a further investigation of this product.

DEGRADATION STUDIES ON 1,3-DI(p-BROMOPHENYL)-1-BUTENE

A. Hydroxylation.

The procedure of Milas and Sussman (19) was used in the hydroxylation of the double bond of 1,3-di-(p-bromophenyl)-1-butene XI. The course of the reaction may be represented by the following equation.



XI XII

Preparation of the hydrogen peroxide reagent was accomplished in the following manner (19). Four hundred milliliters of redistilled tertiary butyl alcohol was added to 100 ml. of 30% hydrogen peroxide and to the solution was added small portions of anhydrous sodium sulphate until two layers appeared. The tertiary butyl alcohol containing most of the hydrogen peroxide was separated and dried over anhydrous sodium sulphate and finally stored over anhydrous calcium sulphate (Drierite) in the cold at approximately 10° C. A solution of approximately 6-7% H_2O_2 was obtained. If all of the water were not separated properly, the H_2O_2 content decreased slowly on storage. If, however, all water was removed the solution of H_2O_2 in tertiary butyl alcohol was stable for periods up to six months.

Osmium tetroxide dissolves readily in tertiary butyl alcohol and is perfectly stable provided no isobutylene is present. Otherwise, it is reduced to an insoluble black oxide which can be oxidized by H_2O_2. When a 0.5% solution of osmium tetroxide in t-butyl alcohol was prepared and stored in the light, the characteristic black precipitate formed. It was found that the addition of a small amount of H_2O_2 in tertiary butyl alcohol caused the black precipitate to dissolve and restored the catalyst to an active condition.

In the actual hydroxylation of 1,3-di-(p-bromophenyl)-1-butene, an excess of OsO_4 was used in contrast to 1 ml. of catalyst solution recommended for each 0.1 mole of double bond. For a typical reaction, 2 ml. of 0.5% OsO_4 solution in tertiary butyl alcohol was used for 0.0274 moles of double bond. Further, nine-tenths of the theoretical amount of H_2O_2 was found to permit fragmentation of the glycol XII possibly by avoiding an excess of reagent which might cause extensive oxidation.

Ten grams (0.0274 moles) of 1,3-di-(p-bromophenyl)-

1-butene was dissolved in 175 ml. of tertiary butyl alcohol. Two ml. of 0.5% OsO_4 solution was added at room temperature. No temperature change was noted. Ten and eleven hundredths gms. (14.5 ml.), (0.0246 moles) of a 7.36% H_2O_2 solution was added in increments, first 5 ml., 15 minutes later, 5 ml., and ten minutes after the second addition, 4.5 ml. The reaction was very mildly exothermic with no more than a three degree temperature rise of the mixture noted in any run. The reaction was then allowed to stand until the next day with partial exclusion of light.

B. Distillation

Previous to distillation the hydroxylation reaction mixture was treated with 2 gms. of zinc dust and 3 ml. of water to destroy any H_2O_2 which might still have been present.

Distillation was carried out in vacuo in a 50 ml. 24/40 standard taper flask equipped with a finger condenser type distilling head. Solvents were first removed at room temperature with a water aspirator.

The following fractions were collected:

Fraction	Boiling Range	Pressure	n^{20}_{D}	Physical Appearance at Room Temperature
1	76 - 86°	2 mm.	-	solid
2	89 - 90°	2 mm.	-	"
3	97 -107°	1½ mm.	1.5760	green liquid
4	115°	2 mm.	1.5760	" "
5	125 -147°	1½ mm.	-	" "
6	160 -192°	2 mm.	-	liquid slowly solidfying

Fractions 1, 2, 3, 4 and 5 gave an orange precipitate with a 5% solution of 2,4-dinitrophenylhydrazine in 20% perchloric acid.

Previous runs which had been treated with ceric perchlorate to cleave the glycol gave results similar to those recorded above. Thus, because the heat of distillation appeared to be sufficient to cleave the glycol XII. it was felt unnecessary to continue the ceric perchlorate procedure.

C. Characterization of Fractions.

2,4-Dinitrophenylhydrazones were prepared for fractions 1 and 3. The procedure of Cheronis and Entrikin (20) was used.

A small quantity of fraction 1 was dissolved in 10 ml. of methyl alcohol and added to 250 ml. of methyl alcohol saturated with 2,4-dinitrophenylhydrazine. Mild reflux was allowed for about 3 minutes and several drops of concentrated HCl were added to the point of incipient precipitation. Refluxing was continued five minutes and 2 ml. of water was added. The insoluble hydrazone precipitated. After the solution stood overnight at room temperature, the derivative was filtered, washed with water and some methyl alcohol and dried, m.p. 253-254°. Recrystallization from methyl alcohol raised the melting point to 257-258°. A mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of p-bromobenzaldehyde, reported to melt at 260-261° (21), (see section on Reference Aldehydes), melted at 257°.

Fraction 3 was treated by the same procedure as described for fraction 1. After the first crop of crystals, A was filtered, water was added dropwise and a second crop B was obtained. Similar treatment gave C. The addition of excess water caused crop D to precipitate. The melting points of the fractions were:

A. 235 - 240°C.

B. 185 - 190°C.

C. 118 - 121°C.

D. 109 - 195°C.

PREPARATION OF REFERENCE ALDEHYDES

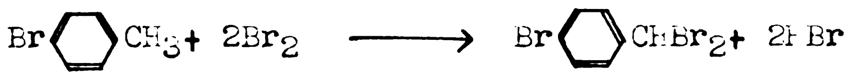
In the early phases of this investigation, the proof of structure of 1,3-di(p-bromophenyl)-1-butene XI was contemplated by the characterization of 2,4-dinitrophenylhydrazone derivatives of carbonyl components obtained by fragmentation of the hydroxylated butene XII.

p-Bromobenzaldehyde had been previously prepared (13) and Heilbron (19) reported the melting point of its 2,4-dinitrophenylhydrazone as 128°. This did not compare with the derivative isolated in our reaction and was later found to be in error (14). Further, an error of 10 degrees in the melting point of p-bromobenzaldehyde was found in Coleman and Honeywell's procedure (13) for its preparation. p-Bromohydratropaldehyde had not been reported or characterized in the literature previously.

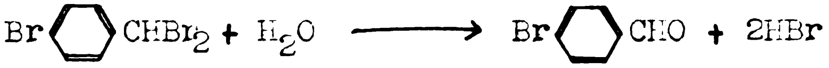
For these reasons, it was decided to prepare these aldehydes and characterize them in order that they might be used for comparison purposes with those isolated in the degradation studies of 1,3-di(p-bromophenyl)-1-butene.

PARA BROMOBENZALDEHYDE

p-Bromobenzaldehyde was prepared according to the procedure of Coleman and Honeywell (22). The course of the reaction may be represented by the following equations:



XIII XIV



XIV XV

In a 1-l. three-necked flask equipped with mechanical stirrer, reflux condenser, thermometer and dropping funnel was placed 200 gms. (1.16 moles) p-bromotoluene which was commercially available. Flask and contents were illuminated with an unfrosted 150 watt lamp and heating of the contents was commenced. Addition of 394 gms. (2.46 moles) of bromine was started at such a rate that there was not a large excess present at any time. The bromine was introduced under the surface of the reaction mixture. About one-half of the bromine was added in the first hour at 105-110°C. The rest was added over about 3 hours at a temperature of 135°C.

The temperature was then raised slowly to 150°C.

The chilled crude p-bromobenzal bromide was transferred to a 5 l. round bottom flask and was mixed with 400 gms. of $CaCO_3$. Six hundred milliters of water was added and the mixture was heated under reflux for twenty-six hours to effect hydrolysis. The hydrolyzed mixture was then steam distilled, insuring complete agitation of the heavy solids, through a Hopkins still head to minimize bumping over into the condenser. The first 3 l. contained most of the product but an additional 3 l. of distillate was collected.

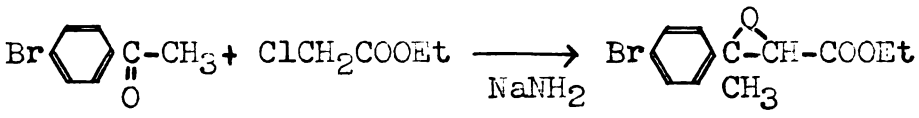
Yield:	148.5 gms.	M.P. 67-68°
	24.6 gms.	63-64°
total	173.1 gms.	78% yield

The 2,4-di-nitrophenylhydrazone (XVa) of p-bromobenzaldehyde XV was prepared by the method of Cheronis and Entrikin (20) previously described. The melting point was 257-258° after one recrystallization from methyl alcohol. Snyder and Handrick (21) report the melting point of the 2,4-dinitrophenylhydrazone of p-bromobenzaldehyde as 260-1°.

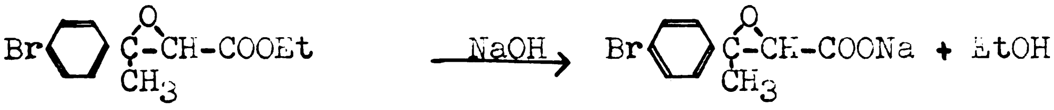
PARA BROMOHYDRATROPALDEHYDE

The Darzens glycidic ester condensation was used for the synthesis of p-bromohydratropaldehyde. p-Bromoacetophenone XVI and ethyl chloroacetate XVII are commercially available so this appeared to be the shortest route. Allen and Van Allen (23) had previously converted ethyl-β-methyl-β-phenyl-glycidate to hydratropaldehyde in 50% yield and Newman and Closson (24) had carried out the same reaction with minor modifications of conditions.

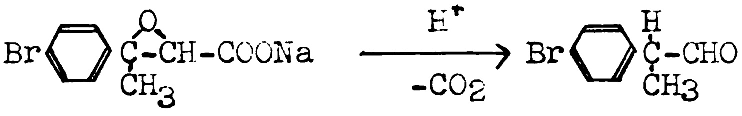
The course of the reaction may be represented by the following equations:



XVI XVII XVIII



XVIII XIX



XIX XX

Sodamide was prepared by the procedure of Hancock and

Cope (25). The preparation was carried out in a well ventilated hood. A 1-l. three-necked flask equipped with a reflux condenser, which was stoppered with a soda lime drying tube and a glass inlet tube, for introducing ammonia was chilled in an acetone-carbon dioxide bath. Ammonia from a cylinder was introduced slowly to allow liquifaction of the gas. When approximately 500 ml. of liquid NH_3had been collected the flask was removed, a crystal of $Fe(NO_3)_3$ added, followed by 92 gms. (4 moles) of sodium metal cut in small pieces. Stirring was continued throughout the addition. When the liquid NH_3 had evaporated the solid sodamide was removed and stored under dry nitrogen in wax sealed rubber stoppered bottles. Yield 138. gms., or 87.1%.

Ethyl β-(p-bromophenyl)-β-methylglycidate XVIII was next prepared using sodamide as the condensing agent. One hundred grams (0.5 moles) of p-bromoacetophenone XVI, 62 gms.(0.5 moles) of ethyl chloroacetate XVII and 150 ml. of anhydrous C.p. benzene were mixed in a 2 l. three-necked flask equipped with thermometer, mechanical stirrer and a reflux condenser carrying a soda lime drying tube. Twenty-three and six-tenths grams (0.6 moles) of sodamide, which was well powdered, was added in small increments over a two hour period maintaining a reaction temperature of 15-20° C. by means of a crushed ice bath. Stirring was continued two hours after completion of sodamide addition.

The contents of the flask were poured into 350 gms. of crushed ice and the benzene layer separated. The aqueous layer was extracted twice with 200 ml. of benzene. The combined extractions were washed three times with 100 ml. portions of water, the last portion containing 10 ml. of glacial acetic acid. The washed extract was dried over anhydrous sodium sulfate overnight.

The benzene solution was transferred to a 150 ml. 24/40 standard tapered, round bottom flask and the benzene evaporated at room temperature under the reduced pressure of an aspirator using a Claisen head. For the distillation of the glycidic ester XVIII a distilling head of the finger condenser type was used. Distillation was carried out in vacuo using a Cenco HiVac pump. The following fractions were obtained:

	DISTILLATE			
Fraction	Wt. Gms.	Boiling Range	Pressure	n_D^{20}
A	21.7[a]	38 -113° C.	3 mm.	solid
B	-	113°	$2\frac{1}{2}$ mm.	"
C	-	113-120°	$2\frac{1}{2}$ mm.	"
D	6.8	125-127°	$2\frac{1}{2}$ mm.	1.5530

E	10.7	130-136°	2 mm.	1.5400
F	18.0	137°	1½ mm.	1.5361
G	17.1	138-140°	1½ mm.	1.5360
H	7.6	140-140.5°	1½ mm.	1.5372
I	6.4	141-146°	2 mm.	1.5380
J	0.7	to 150°	2 mm.	1.5414

a)-combined weight of fractions A,B and C.

Analysis of fraction G using the Parr bomb method (16) gave 28.0% bromine compared with a theoretical value of 28.0% for ethyl β-(p-bromophenyl)-β-methylglycidate XVIII.

This glycidic ester XVIII appeared to be quite stable when stored in a well stoppered vial for periods of one to two months. It is a straw-colored, viscous oil, b.p. 139° C. at 1.5 mm n_D^{20} 1.5360. The yield was 30.6% based on fractions F through I.

Fractions A, B and C consist mostly of unreacted p-bromoacetophenone and ethyl chloroacetate. This is characteristic of previous reports of the condensation reaction for preparation of other glycidic esters.

Hydrolysis and decarboxylation of the glycidic ester XVIII essentially followed the procedure of Allen and Van Allen (23). The p-bromohydratropaldehyde XX was distilled in vacuo, however, because of its probable liquid character.

To 25.6 gms. (.0885 moles) of ethyl β-(p-bromophenyl)-β-methylglycidate (from vials F and H), contained in 1-l. three-necked flask equipped with mechanical stirrer, reflux condenser and thermometer, was added a solution of 8.4 gms. (.210 moles) of sodium hydroxide in 24 ml. of water. Almost immediately an exothermic reaction set in and the temperature of the reaction mixture rose to 65°C. The flask was chilled and the temperature maintained at 45-50°C. by means of a water-ice bath. An insoluble white solid precipitated.

After stirring for five hours, the reaction mixture was acidified with 6 N. HCl until blue to Congo paper. External cooling of the flask was necessary. The acidified mixture was refluxed for two and one half hours and upon cooling, an oily layer separated. The water layer was extracted with two 30 ml. benzene portions and the combined oily layer and extracts placed under the reduced pressure of an aspirator to remove the benzene. The residue was distilled in vacuo using a finger condenser type distilling head.

The following fractions were collected:

Fraction	Wt. Gms.	Boiling Range	Pressure	n_D^{20}
1	2.2	90- 96°C.	2 mm.	1.5604
2	6.2	98-100°C.	2 mm.	1.5602
3	2.3	104-110°C.	2 mm.	1.5602
4	1.3	117-127°C.	2 mm.	1.5605
5	1.2	130-146°C.[a]	2 mm.	1.5623
6	1.8	147-165°C.[a]	2 mm.	1.5701

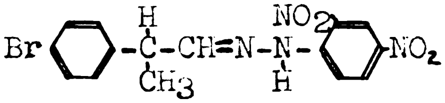
a) Decomposition noted during distillation

Fractions 1-4 represent a 65.7% yield of aldehyde XX from the glycidic ester XVIII. The distillate was a green-white liquid in the first four fractions. A drop of fractions 1 and 3 gave precipitates when mixed with 5 ml. of a 5% phenylhydrazine solution in 20% perchloric acid.

Bromine analysis of fractions 1 and 3 by the Parr bomb method (16) gave respectively, 39.6% and 39.1% as compared with a theoretical value of 43.2% bromine for p-bromohydratropaldehyde XX. If XX may be compared with hydratropaldehyde, its stability would be expected to be very poor because of susceptibility to oxidative influences. This would explain the poor comparison of halogen analysis with the theoretical.

A 2,4-dinitrophenylhydrazone XXa of p-bromohydratropaldehyde was prepared by the method of Cheronis and Entrikin (20) and recrystallized from glacial acetic acid to remove excess 2,4-dinitrophenylhydrazine. A bromine analysis of this phenylhydrazone (XXa) (16) indicated 20.1 and 20.5% bromine compared with 20.3% theoretical bromine.

p-Bromohydratropaldehyde-2,4-dinitrophenylhydrazone (XXa)



XXa

is a yellow crystalline solid melting 123-124° C. It crystallizes as needles from methyl alcohol and prisms from glacial acetic acid. Its comparative solubility in methyl alcohol is greater than p-bromobenzaldehyde-2,4-dinitrophenylhydrazone (XVa).

XXa was mixed with the 2,4-dinitrophenylhydrazone of crop (C) (see page 26) and a melting point of 118-119° was observed. A bit of crop (C) was seeded in a saturated solution of XXa in glacial acetic acid and crystallization took place. The dried crystals melted at 123-124°. Thus crop (C) and XXa must be identical and the second component of the hydroxylation degradation is p-bromohydratropaldehyde.

DISCUSSION

The work of Goerner and Hines (1) has been extended to α-chloro-α-(p-bromophenyl)-ethane X which was prepared from p-bromophenylmethylcarbinol IX (see Experimental for preparation). It is interesting to note, that α-chloro-α-(p-bromophenyl)-ethane, prepared in the manner described (page 14) gave average yields of 10% higher than that reported by Barber et al. (11) who used thionyl chloride instead of HCl for converting the alcohol to the chloride. Further, Barber reported α-chloro-α-(p-bromophenyl)-ethane in what would seem to be its more crude state. We have found it to be a pinkish pungent oil in the crude state, whereas upon distillation, this crude product gave a water white oil of physical properties comparable to those described by Barber (11).

It seems highly probable that analysis of the aliphatic chlorine in α-chloro-α-(p-bromophenyl)-ethane is feasible by a sodium hydroxide reflux technique. We were able to titrate an aliquot which had been refluxed for twenty-six hours in 6 molar excess of 6N. alcoholic aqueous NaOH and obtained results only within 1% of the calculated values. It was felt that questionable purity of the original sample might add to the explanation of low results.

The reaction of α-chloro-α-(p-bromophenyl)-ethane with cuprous cyanide can be compared favorably with the reaction of α-chloroethylbenzene. Goerner and Hines reported yields of 40% for their dimer. In this investigation we have obtained yields of dimer of the same order of magnitude. It would appear that this dimerization reaction is characteristic of α-halo-ethylbenzenes. The reaction does not, however, seem to be as violent in this case as that observed by Goerner and Hines (1). It starts at approximately the same temperature but there is not the violence of filling the condenser with HCN or its rapid generation noted in the previous instance. This may be partially explained through the fact that molecular ratios of CuCN and α-chloro-α-(p-bromophenyl)-ethane do not require as much CuCN as was needed in the case of α-chloro-α-phenyl ethane. Thus the actual generation of HCN on a weight basis would be much less in the preparation of 1,3-di(p-bromophenyl)-1-butene.

The structure of 1,3-di(p-bromophenyl)-1-butene seems to be reasonably well established. When sharply melting crystals were hydroxylated and cleaved either by heat or ceric perchlorate and heat, the carbonyl components were isolated and characterized as their

2,4-dinitrophenylhydrazones.

p-Bromobenzaldehyde had previously been prepared and characterized as the 2,4-dinitrophenylhydrazone. It was easily isolated in the distillate of a hydroxylation degradation and precipitated as the 2,4-dinitrophenylhydrazone. On comparison with an authentic sample of p-bromobenzaldehyde-2,4-dinitrophenylhydrazone there was no melting point depression.

Isolation of p-bromohydratropaldehyde as a component of the hydroxylation fragmentation was more difficult. It had not been previously reported in the literature. Preparation through the Darzens glycidic ester condensation was accomplished during this investigation. It was characterized as the 2,4-dinitrophenylhydrazone.

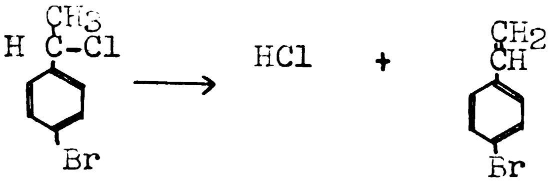
Once p-bromohydratropaldehyde had been prepared and characterized, sufficient information was available to choose distillate fractions of the hydroxylation fragmentation which were richer in this component. By precipitation as the 2,4-dinitrophenylhydrazone and fractional crystallization from methyl alcohol p-bromobenzaldehyde-2,4-dinitrophenylhydrazone was isolated from the hydroxylation fragmentation mixture and compared by mixed melting point with the prepared sample. No depression was noted.

Having established the structure of 1,3-di(p-bromophenyl)-1-butene, bromination in CS_2, which is an accepted method of adding to the double bond, undoubtedly yields 1,2-dibromo-1,3-di(p-bromophenyl)-butane. Halogen analysis compared with calculated values for the brominated butane derivative seems to bear this out.

Little accurate information is actually known about the mechanism of this dimerization reaction. Goerner (2) has observed that the use of styrene as a solvent in the dimerization of α-chloro-α-phenylethane greatly increases the yield of dimer. If sufficient styrene were present, yields greater than 100% of theoretical based on dimerization (eq. see p. 16) were obtained. Further, p-bromostyrene must be present in the dimerization reaction of α-chloro-α-(p-bromophenyl) ethane. When a forerun of the distillation was refluxed with a saturated solution of maleic anhydride in benzene and a trace of benzoylperoxide, in about ten minutes a polymeric precipitate formed.

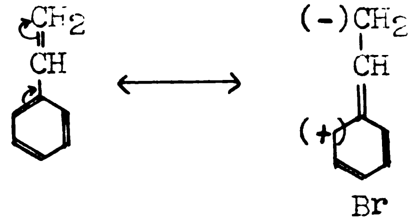
It is a well known fact that α-chloroethylbenzene decomposes to form styrene. By analogy we could expect the following reaction:

a.)



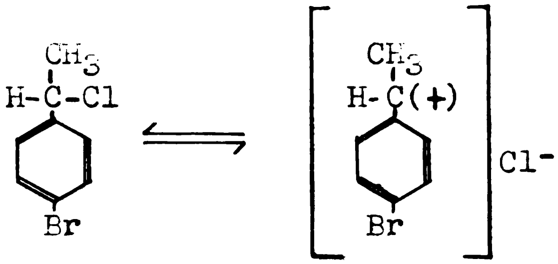
p-Bromostyrene may exist in at least the indicated possible resonance forms.

b.)



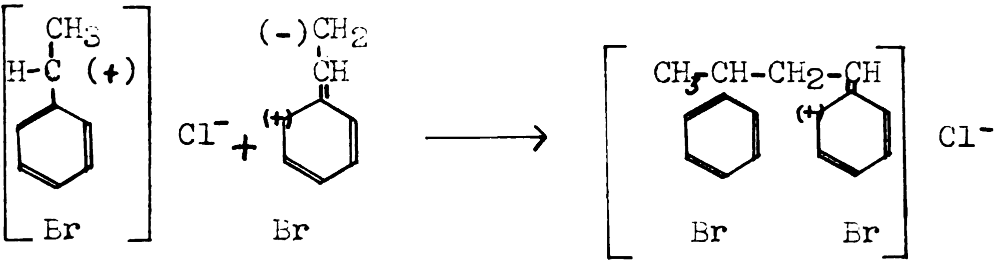
If reaction (a.) takes place a possible intermediate step in the formation of p-bromostyrene might be the formation of a carbonium ion.

c.)



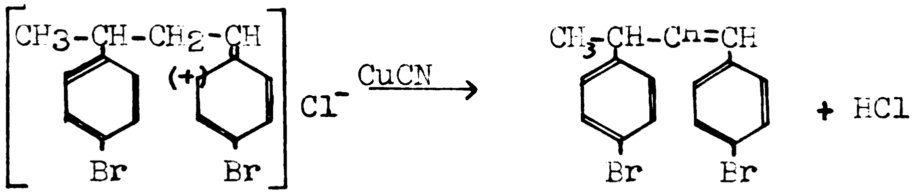
Reaction of the carbonium ion in (c.) and the resonance structure given in (b.) would give a dimer

d.)



In the presence of a molecule of CuCN a molecule of HCl would tend to split out of the ionic form of the dimer accompanied by rearrangement.

e.)



In an attempt to convert the dimer from the <u>cis</u> to the <u>trans</u> forms or the reverse, 1 gram of 1,3di(p-bromophenyl)-1-butene was dissolved in 25 ml. of nitrobenzene and refluxed for twenty-six hours with a trace of iodine (11). A polymeric material was obtained. This would further help to explain the tendency of the double bond in the dimer to undergo addition type of polymerization.

SUMMARY

1. α- Chloro-α-(p-bromophenyl)-ethane has been prepared and compares favorably with the preparation reported by Barber et al.(11).

2. α-Chloro-α-(p-bromophenyl)-ethane has been dimerized to 1,3-di(p-bromophenyl)-1-butene by the treatment with CuCN in yields of the order of 47%.

3. The structure of 1,3-di(p-bromophenyl)-1-butene has been established by hydroxylation and fragmentation of the aliphatic double bond to carbonyl components.

4. The carbonyl components, p-bromobenzaldehyde and p-bromohydratropaldehyde, were characterized as their 2,4-dinitrophenylhydrazones and compared with prepared samples of each.

5. p-Bromobenzaldehyde was prepared and characterized as previously reported in the literature (20) (22).

6. p-Bromohydratropaldehyde had not been previously reported in the literature. It was prepared through a Darzens glycidic ester condensation and characterized as the 2,4-dinitrophenylhydrazone.

7. 1,3-Di(p-bromophenyl)-1-butene was brominated to 1,2 dibromo-1,3-di(p-bromophenyl)-butane.

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