The gas produced was analyzed in an Orsat–Williams apparatus, being collected over water previously saturated with the gas. The saturated hydrocarbon was calculated as methane.

Summary

The decomposition of acetic acid in the presence of silica gel at a temperature range of 400–500° has been studied.

Silica gel is an effective catalyst for the conversion of acetic acid to acetone. At least 85% of the acetic acid decomposed in the presence of silica gel produces acetone.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYLBENZENES. MESO AND RACEMIC 2,5-DI-(3-BROMO-2,4,6-TRIMETHYLPHENYL)-3,6-DIBROMOHYDROQUINONES AND THE CORRESPONDING QUINONES. XII.[1]

BY P. R. SHILDNECK[2] AND ROGER ADAMS

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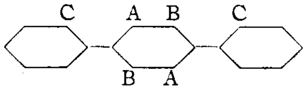
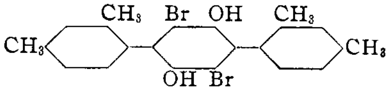
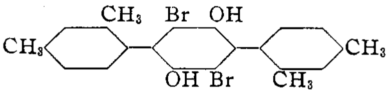
The possibility for the existence of a meso and a racemic modification of substituted 1,4-diphenylbenzenes of type (I) was demonstrated by isolation of two stereoisomeric 2,4-di-*m*-xylyl-3,6-dibromohydroquinones (IIa and IIb).[1b]



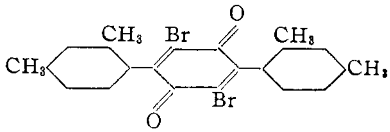
I



IIa



IIb



III

The two compounds formed two individual series of derivatives but oxidized to the same quinone (III). The quinone, in turn, upon reduction always gave a mixture of the two hydroquinones (IIa and IIb).

It was pointed out in the article describing these substances that on the basis of x-ray data and on the assumption that the quinone ring was essen-

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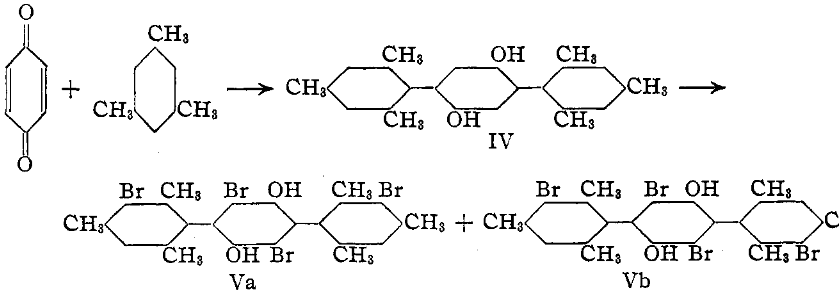
[1] The last three papers in this series are: (a) Stanley and Adams, THIS JOURNAL, **52**, 4471 (1930); (b) Steele and Adams, *ibid.*, **52**, 4528 (1930); (c) Browning and Adams, *ibid.*, **52**, 4098 (1930).

[2] This communication is a portion of a thesis submitted by P. R. Shildneck in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

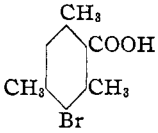
tially similar in character to the benzene ring, it might not be expected that two quinones would exist. The interference values indicated that in the quinone, although there would be collision between the methyl and the bromine groups, there would be none between the methyl and C=O groups and therefore free rotation would not be prevented.

In this investigation the study of diphenylbenzenes has been extended in order to demonstrate that isomerism of this type is general. Compounds have been selected which have at each of the linkages of the benzene rings, the four ortho positions substituted. Under these conditions not only should two stereoisomers exist as found in the trisubstituted compounds but if the proper groups are present, x-ray data lead to the conclusion that two stereoisomeric quinones are possible. Results have fully substantiated these predictions.

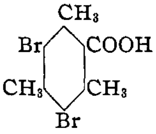
Mesitylene was added to *p*-benzoquinone and the resulting dimesitylhydroquinone (IV) was treated with four moles of bromine. Two isomeric tetrabromo compounds (Va and Vb) were readily isolated, each of which formed a characteristic diacetate. Although by the method of bromination (bromine in chloroform) it was very unlikely that two bromines could have entered a single mesitylene nucleus, nevertheless further information concerning the positions of the bromines in the two forms seemed desirable in order to be certain that two stereoisomeric compounds were in hand. Each of the two tetrabromo derivatives was oxidized with hydrogen peroxide and sodium hydroxide. There was formed first a deeply colored solution of quinone which gradually, after a long period of time, became nearly colorless. There was isolated as a result monobromomesitylcarboxylic acid (VI) in each instance. If the four bromines were not distributed with two in the inner ring and one in each of the outer rings in each molecule, part of the product should have been dibromomesitylcarboxylic acid (VII). No trace of this latter compound was found. Monobromomesitylcarboxylic acid and dibromomesitylcarboxylic acid were prepared by other methods and the latter was shown to be distinctly less soluble in water than the former. As a consequence the presence of any dibromo compound in a mixture of mono and dibromo should easily have been detected. The



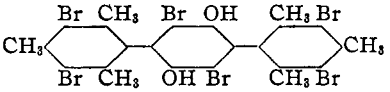
monobromo compound, however, was essentially pure as received from the reaction mixture, though the yield was low, as might be expected from an oxidation reaction of this type.



VI



VII

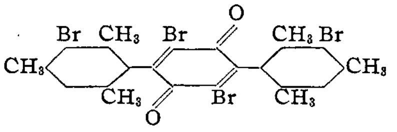


VIII

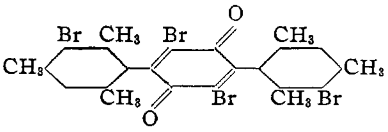
The two isomeric tetrabromohydroquinone derivatives (Va and Vb) upon treatment with liquid bromine yielded the same hexabromo derivative (VIII). This is of interest since it confirms the fact that the stereoisomers will exist only if each of the two end rings is asymmetrically substituted. The hexabromo derivative was then oxidized with hydrogen peroxide and sodium hydroxide. The reaction progressed in a fashion similar to the analogous oxidations of the two isomeric tetrabromo derivatives and pure dibromomesitylcarboxylic acid was isolated. Moreover, the hexabromo compound readily forms a diacetate and on oxidation the corresponding quinone.

All attempts to prepare the hexabromo derivative other than by the action of liquid bromine on the finely powdered tetrabromo derivatives failed. Likewise all attempts to prepare dibromomesitylcarboxylic acid by bromination of the monobromomesitylcarboxylic acid in solvents such as chloroform, carbon tetrachloride and glacial acetic acid failed. It was readily prepared by treating the solid monobromomesitylcarboxylic acid with liquid bromine. These facts indicate the unlikelihood of two bromines entering the mesitylene nucleus when the dimesitylhydroquinone was brominated in chloroform solution and further substantiate the contention that the two isomeric tetrabromo derivatives are stereoisomeric.

These two tetrabromodimesitylhydroquinones are of significance, not only because they represent a second example of stereoisomerism in the diphenylbenzene series, but because, unlike the two dibromodixylylhydroquinones which on oxidation give the same quinone, each upon oxidation yields an individual quinone (IXa and IXb). The two quinones differ from each other in solubility, melting point and other properties. The two quinones are, in turn, readily reduced back quantitatively each to its respective hydroquinone (Va and Vb). These two quinones, therefore, represent the first instance in which isomerism of the diphenyl type has been



IXa



IXb

discovered in molecules containing two rings one or the other of which is not a benzene nucleus. Which of the two quinones or hydroquinones is the meso and which the racemic is yet to be determined.

Experimental

2,5-Dimesitylhydroquinone (IV).[3]—In a 1-liter three-necked flask equipped with a mechanical stirrer and thermometer and surrounded with a freezing mixture of ice and salt was placed 700 cc. of mesitylene (b. p. 164–168°). Stirring was started and when the temperature reached 0°, 150 g. of finely powdered anhydrous aluminum chloride was added at once. The suspension developed a deep red color.

Thirty grams of finely pulverized dry *p*-benzoquinone (purified by steam distillation) was added in 1-g. portions as rapidly as possible without permitting the temperature to rise above 5°. The well-stirred mixture became noticeably viscous and the original red color changed to brown. Stirring was continued for fifteen minutes longer and then 20 g. more of quinone was added as before, keeping the temperature below 5°. The mixture then became so viscous that continued stirring soon rolled up balls of brown gummy material in the excess mesitylene. Stirring was continued for three hours thereafter and then the flask with its contents was permitted to come slowly to room temperature overnight.

The excess mesitylene was decanted and the semi-solid residue decomposed in a mixture of 300 cc. of concentrated hydrochloric acid, 500 cc. of water and 500 g. of ice. The nearly white product was filtered with suction and washed with 3 *N* hydrochloric acid followed by hot water. The weight of air-dried crude product amounted to 40 g. Two crystallizations (with norite) from benzene gave 30 g. of pure white crystalline material melting at 225–226° (corr.).

The mesitylene was separated from the filtrate, combined with that previously decanted and steam distilled. In this way 600 cc. of pure mesitylene boiling at 164–168° was recovered. A residue of 45 g. of tarry material from the mesitylene and the mother liquors from the crystallizations yielded an additional 12 g. of pure material, making a total yield of 42 g.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.19; H, 7.57. Found: C, 82.97; H, 7.63.

Stereoisomeric 2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinones (Va) and (Vb). Form (α).—In a 500-cc. three-necked flask equipped with a thermometer, reflux condenser and 250-cc. separatory funnel was placed 25 g. of 2,5-dimesitylhydroquinone and 75 cc. of chloroform. The mixture was heated to effect solution. The solution was allowed to cool to 50° and through the separatory funnel was then added a solution of 52 g. of bromine in 150 cc. of chloroform dropwise at such a rate that the temperature was maintained at 50–60°. At first the solution decolorized after each drop of bromine and heat was evolved. After about one-fourth of the bromine had been added the rate of absorption became slower and the temperature dropped. The reaction mixture was then gently refluxed and the remainder of the bromine added over a period of one hour. Refluxing was continued for one hour longer, during which time a heavy, crystalline precipitate appeared.

The reflux condenser was tilted downward and all but a few cc. of the chloroform distilled off; 250 cc. of fresh chloroform was added and distilled off as before, this time distilling to dryness on the steam-bath. The dry yellowish solid material in the flask was dissolved in 2 liters of acetone by refluxing for one-half hour. Then 2 g. of norite and 0.5 g. of powdered stannous chloride were added and refluxing was continued for

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[3] This compound was first made and analyzed by W. W. Moyer and described in his Ph.D. dissertation at the University of Illinois, June, 1929.

fifteen minutes longer. After a rapid filtration, the product separated on cooling. It was twice recrystallized from acetone, when it was obtained pure in the form of large rectangular prisms containing acetone of crystallization. The crystals effloresced to a white powder which when dry melted at 334–335° (corr.) with slight decomposition.

The filtrate from the original acetone crystallization was concentrated to 750 cc. and again cooled to room temperature. The crop of white prisms was filtered off (weight 2.5 g.) and the filtrate again concentrated to 250 cc. Upon cooling to room temperature and standing for several hours a third crop (1 g.) of white prisms was obtained. The two crops were combined and crystallized from 200 cc. of fresh acetone. About 2.8 g. of the α-form melting at 331–333° (corr.) was thus obtained.

Form (β).—The above filtrate of 250 cc. containing the more soluble material, was cooled to −10° in a freezing mixture. A white, fluffy precipitate appeared, quite different in appearance from the dense, granular less-soluble material. So soluble was this second material that it was found necessary to crystallize it from a mixture of acetone and water. For that purpose the acetone solution (250 cc.) was boiled for a few minutes with 1 g. of norite and 0.5 g. of powdered stannous chloride under the reflux, quickly filtered, heated again to boiling and hot water added a few cc. at a time until a permanent turbidity remained. Even from the hot solution a heavy precipitate of minute, shining flakes gradually appeared. The mixture was cooled to 0° and filtered. The crystalline precipitate was washed with 50% alcohol and dried. The yield amounted to 13 g. and the material melted at 292–294° (corr.).

The filtrate from this last crystallization was again heated to boiling and hot water added to the turbidity point as before. An additional 4.5 g. of product melting at 290–293° (corr.) was thus obtained. The last filtrate poured into an equal volume of water yielded 1.5 g. of less pure product.

The first two fractions were combined and recrystallized from a mixture of acetone and water as previously described, using, however, only 125 cc. of acetone. Thus 14.5 g. of pure material melting constant at 294–295° was obtained.

Wt. starting Material, g.	Less soluble product Yield, g.	M. p., °C.	More soluble product Yield, g.	M. p., °C.
25.0	27.5	334–335	17.5	294–295

Analysis of substance melting at 334–335°: α-form (Parr bomb). Calcd. for $C_{24}H_{22}O_2Br_4$: Br, 48.31. Found: Br, 48.16.

Analysis of substance melting at 294–295°: β-form (Parr bomb). Calcd. for $C_{24}H_{22}O_2Br_4$: Br, 48.31. Found: Br, 48.10.

The difference in solubility in acetone of the α-form and β-form is marked. A conservative estimate would place the ratio of solubilities in acetone at room temperature at fifty to one. There is also a similar difference in solubility in ethyl alcohol and toluene. Both of the forms crystallize from 95% ethyl alcohol in colorless flat prisms. From toluene the more soluble β-form crystallizes readily in long, slender needles, while the less soluble α-form dissolves with difficulty in boiling toluene and crystallizes with equal difficulty in very short needles.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone Diacetate (α-Form).—A solution of 5.0 g. of the higher-melting tetrabromohydroquinone (α-form) was made in 25 cc. of boiling pyridine. To this was added 25 cc. of acetic anhydride and the mixture was refluxed for thirty minutes. A white crystalline precipitate appeared during the refluxing. The mixture was then cooled, filtered, and washed with water. Upon purification from 85 cc. of pyridine a yield of 4.7 g. of small white prisms melting at 285–286° (corr.) without decomposition was obtained.

Anal. (Parr bomb). Calcd. for $C_{28}H_{26}O_4Br_4$: Br, 42.87. Found: Br, 42.70.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone Diacetate (β-Form).—This substance was made in the same way as the acetate of the α-form using 5 g. of the α-hydroquinone, 10 cc. of acetic anhydride and 5 cc. of boiling pyridine. Crystallization of the 5 g. of crude reaction product from 10 cc. of pyridine yielded a pure compound melting at 237–238° (corr.) without decomposition.

The solubility of this diacetate in boiling pyridine is from eight to ten times greater than that of the diacetate of the α-form.

Anal. (Parr bomb). Calcd. for $C_{28}H_{26}O_4Br_4$: Br, 42.87. Found: Br, 42.81.

Stereoisomeric 2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromoquinones (IXa) and (IXb). α-Form.—A solution of 5.0 g. of the α-form of the hydroquinone in 1-liter of boiling 95% ethyl alcohol was treated with 5 g. of benzoquinone and the mixture refluxed for one-half hour. During this time the orange, crystalline α-quinone appeared. After distilling 750 cc. of alcohol from the reaction mixture on the steam-bath, it was cooled and filtered. The product was washed free of benzoquinone with two 15-cc. portions of cold ethyl alcohol and dried in air. The yield amounted to 4.6 g. of product which melted at 295–296° with decomposition. Recrystallization from toluene did not alter the melting point. The quinone was readily soluble in cold pyridine, moderately soluble in hot toluene, sparingly in boiling ethyl alcohol and insoluble in boiling methyl alcohol.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_4$: Br, 48.44, Found: Br, 48.27.

β-Form.—The oxidation was carried out in a manner similar to that of the α-form, except that for 5 g. of the lower-melting β-hydroquinone only 350 cc. of boiling 95% ethyl alcohol and 5 g. of benzoquinone were used. About 200 cc. of alcohol was removed as the orange product crystallized. The yield was 4.6 g. and melted at 284–285° with decomposition. Recrystallization from toluene did not alter the melting point.

In appearance this quinone resembles the other. The two have approximately equal solubilities in toluene and both crystallize readily from that solvent in small orange prisms. A difference in solubility was found in ethyl alcohol, the β-quinone being the more soluble. Likewise in methyl alcohol the β-quinone was found sparingly soluble in boiling solvent whereas the α-quinone was practically insoluble in boiling methyl alcohol.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_4$: Br, 48.44. Found: Br, 48.22.

Reduction of α- and β-Quinones.—A solution of 2.0 g. of the α- or β-quinone in 10 cc. of boiling pyridine was treated with finely powdered stannous chloride until the pyridine solution became colorless. The reaction mixture was then thrown into excess of 3 *N* hydrochloric acid, warmed and filtered. The product was washed free of acid with water and air-dried. The yield was quantitative and amounted to 2.0 g.

The crude product from the α-quinone reduction was dissolved in 200 cc. of boiling acetone, filtered and concentrated to 100 cc. The solution was rapidly chilled in a freezing mixture and allowed to stand for one hour; 1.8 g. of a fine, white crystalline material was filtered off and air-dried. The substance melted at 334–335° (corr.) with slight decomposition and showed no depression in melting point when mixed with the original α-hydroquinone. The filtrate from the crystallization yielded about 0.2 g. of product which melted about 5 to 7° lower.

The crude product from the β-quinone was recrystallized from acetone and water and gave white crystals melting at 294–295° with slight decomposition. A mixed melting point with the original β-hydroquinone showed no depression.

Oxidation of the α-Quinone with Hydrogen Peroxide and Sodium Hydroxide to Monobromomesitylcarboxylic Acid (VI).—The first step in the oxidation of the hydroquinones is the formation of quinones, consequently the complete oxidations were carried out with the quinones. To a solution of 5.0 g. of the α-quinone in 250 cc. of 95% ethyl alcohol was added a cold solution of 50 g. of sodium hydroxide in 125 cc. of water. The mixture was stirred mechanically and 125 cc. of 30% hydrogen peroxide was slowly added. The flask was surrounded with running water to maintain the temperature at 10–20°.

The quinone slowly went into a dark red solution, which changed to a light red in the course of six to eight hours. During the course of forty hours more the red color of the solution faded to a light pink and considerable sodium acetate crystallized out.

A cold solution of 25 g. of sodium hydroxide in 50 cc. of water was added, plus 50 cc. more of 30% hydrogen peroxide and the reaction mixture stirred for twenty-four hours longer at room temperature. More sodium acetate crystallized out but the solution did not completely decolorize.

The sodium acetate was filtered off. To the filtrate was added 1 liter of water and an equal volume distilled off in order to remove the alcohol. The remaining pink solution was acidified with concd. hydrochloric acid. The mixture, which at this point contains a yellow flocculent precipitate, was diluted to a volume of 2 liters with water, boiled for a few minutes, then quickly filtered. From the clear colorless filtrate long silky needles appeared upon cooling. The filtrate was chilled to 0° and the white needles were filtered and dried. The yield amounted to 0.75 g. The crude product after three recrystallizations from water melted constantly at 168° (corr.).

Anal. (Parr bomb.) Calcd. for $C_{10}H_{11}O_2Br$: Br, 32.89. Found: Br, 32.81. Calcd. for $C_6H(CH_3)_3BrCOOH$: neut. equiv., 243. Found: 245.

Oxidation of the β-Quinone with Hydrogen Peroxide and Sodium Hydroxide to Monobromomesitylcarboxylic Acid, (VI).—Five grams of the β-quinone was oxidized in exactly the same manner as the α-quinone. The product was worked up in the same manner. There was isolated 0.80 g. of long silky needles which after three recrystallizations from water melted constantly at 168° (corr.). A mixed melting point with the acid obtained from the oxidation of the α-quinone showed no depression.

Anal. (Parr bomb). Calcd. for $C_{10}H_{11}O_2Br$: Br, 32.89. Found: Br, 33.02. Calcd. for $C_6H(CH_3)_3BrCOOH$: neut. equiv., 243. Found: 245.

Monobromomesitylcarboxylic Acid, (VI).—In a 1-liter, 3-necked flask equipped with a mercury-sealed mechanical stirrer, a dropping funnel and a reflux condenser, were placed 130.5 g. of mesitylcarboxylic acid,[4] 1 g. of iron filings and 250 cc. of carbon tetrachloride. One hundred thirty-five grams of bromine was placed in the dropping funnel, the stirrer started, the flask heated to an oil-bath temperature of 120–130°, and the bromine run in over a period of one-half hour. Stirring and heating were continued for an additional half hour, then the mixture was cooled and filtered. The product was treated with a solution of 200 cc. of hydrochloric acid in 300 cc. of water, again filtered, dissolved in an excess of 5% sodium hydroxide, filtered and the free acid obtained by acidifying this solution with hydrochloric acid. The product was recrystallized from carbon tetrachloride or better 50% alcohol and melted when pure at 168°. The yield was 112 g.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: Br, 32.88. Found: Br, 32.40. Calcd. for $C_{10}H_{11}O_2Br$: neut. equiv., 243. Found: 244.

2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone, (VIII).—Efforts were made to brominate further the α- and β-forms of the tetrabromohydroquinones (Va) and (Vb) in chloroform, carbon tetrachloride and glacial acetic acid solutions without success. Liquid bromine gave the desired results.

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[4] Made according to the method of Bamford and Simonsen, *J. Chem. Soc.*, 97, 1906 (1910).

(A) **Bromination of the α-Hydroquinone.**—Five grams of the finely powdered α-hydroquinone was placed in a 500-cc. Kjeldahl flask and 15 cc. of liquid bromine added. After standing for six hours the excess bromine was removed with air and the light yellow solid residue in the flask was washed with 5% sodium bisulfite solution, filtered and washed with water. The air-dried product (6.2 g.) was then dissolved in 60 cc. of hot pyridine and refluxed for a few minutes with 1 g. of norite and 0.25 g. of powdered stannous chloride. White granular crystalline material was obtained which was recrystallized from 50 cc. of fresh pyridine. The yield of product from this second crystallization amounted to 4.0 g. and the substance melted constantly at 395–398° (obs.) on the Bloc Maquenne.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_6$: Br, 58.51. Found: Br, 58.24.

(B) **Bromination of the β-Hydroquinone.**—Five grams of the β-hydroquinone was brominated in exactly the same manner as the α-hydroquinone. The reaction product was purified in the same way; 4.1 g. of purified product melting at 395–398° (obs.) on the Bloc Maquenne was obtained. A mixed melting point with the brominated α-hydroquinone showed no depression.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_6$: Br, 58.51. Found: Br, 58.19.

In order to make certain of no mistake, the bromination products of both the α- and β-hydroquinones were kept separate and converted independently to the diacetates and quinones. In each case identical products resulted.

2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone Diacetate.—One gram of the hexabromo compound from the α- or β-tetrabromo compound was acetylated by refluxing with 10 cc. of pyridine and 10 cc. of acetic anhydride for thirty minutes. During the refluxing period the product crystallized from the boiling reaction solvent. The mixture was cooled and the crystalline precipitate filtered, washed with a few cc. of cold acetone and air-dried. The yield amounted to 1.05 g. After recrystallization from 15 cc. of boiling pyridine, 0.85 g. of pure white crystalline material melting sharply at 297° (corr.) was obtained.

Anal. (Parr bomb). Calcd. for $C_{28}H_{24}O_4Br_6$: Br, 53.06. Found: Br, 52.91.

2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromoquinone.—One-half gram of the hexabromohydroquinone (produced either from the α- or β-tetrabromo compound) and 1250 cc. of 95% ethyl alcohol were refluxed until all was dissolved. Then 2.0 g. of benzoquinone was added, refluxing continued for one-half hour, and 1 liter of alcohol distilled off on the steam-bath.

The light orange-colored quinone crystallized during the distillation. The mixture remaining in the distilling flask was cooled and filtered. The product was washed free of benzoquinone with two 10-cc. portions of cold ethyl alcohol. The yield of air-dried product amounted to 0.48 g.

The quinone crystallized in the pure state from the alcohol reaction mixture and melted constantly at 390–393° (obs.) on the Bloc Maquenne. It was found to be soluble in hot pyridine and hot toluene and could be recrystallized readily from the latter.

Anal. (Parr bomb). Calcd. for $C_{24}H_{18}O_2Br_6$: Br, 58.64. Found: Br, 58.36.

Stannous chloride immediately decolorized the yellow pyridine solution, which after pouring into excess 3 *N* hydrochloric acid and crystallizing the white product from pyridine yielded the original hydroquinone melting at 395–398° on the Bloc Maquenne.

Oxidation of 2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone with Hydrogen Peroxide and Sodium Hydroxide to Dibromomesitylcarboxylic Acid, (VII).—In a 1-liter round-bottomed flask were placed 2.0 g. of the hexabromohydroquinone, 150 cc. of 95% ethyl alcohol and a cold solution of 20 g. of sodium hydroxide in 50 cc. of water. The mixture was stirred mechanically and immediately acquired a deep red color. After thirty minutes stirring, 100 cc. of water was added and the mixture stirred for two hours at 50°. It was then cooled to 20° and 50 cc. of 30% hydrogen peroxide stirred in. The flask was kept cooled to 10–20°.

Upon addition of the hydrogen peroxide the original dark red color of the mixture changed to a light red over a period of four to six hours. Stirring was continued at the same temperature for forty-eight hours. Sodium acetate crystallized out and the color of the reaction mixture changed to a pink. At this point a solution of 10 g. of sodium hydroxide in 25 cc. of water and 25 cc. more of 30% hydrogen peroxide were added.

After an additional twenty-four hours of stirring at room temperature the sodium acetate was filtered from the pale pink solution and 500 cc. of water added to the filtrate. An equal volume (500 cc.) of water was distilled off to remove the excess ethyl alcohol. The residual solution was acidified with hydrochloric acid. The mixture, which at this point contained a yellowish flocculent precipitate, was diluted with water to a volume of 4 liters, brought to a boil and held there for a few minutes. It was then quickly filtered. Upon cooling the filtrate deposited a small crop of short white needles. The yield was 0.18 g. The melting point of this material, after recrystallization from 5 cc. of 50% ethyl alcohol, was constant at 210–211° (corr.). The yield was 0.11 g. of minute shining plates.

The substance was found to be soluble in 5% sodium bicarbonate solution, from which it was precipitated with hydrochloric acid as a white solid.

Anal. (Parr bomb). Calcd. for $C_{10}H_{10}O_2Br_2$: Br, 49.68. Found: Br, 49.50.

Dibromomesitylcarboxylic Acid, (VII).—In a test-tube 3.0 g. of monobromomesitylcarboxylic acid was treated with 5 cc. of liquid bromine at room temperature. The contents of the tube were then washed out with saturated sodium bisulfite solution and the collected light yellow solid residue washed with cold water. The yield of crude product amounted to 4.2 g. (air-dried).

The crude material was dissolved in 20 cc. of 95% ethyl alcohol and water added at the boil until a permanent turbidity appeared. Shining colorless plates appeared upon cooling. After one recrystallization from dilute (about 50%) ethyl alcohol the yield was 3.0 g. of shining flakes melting constantly at 211° (corr.).

A mixed melting point with the acid obtained from the alkaline hydrogen peroxide oxidation of the hexabromohydroquinone showed no depression.

Anal. (Parr bomb). Calcd. for $C_{10}H_{10}O_2Br_2$: Br, 49.68. Found: Br, 49.83. Calcd. for $C_6(CH_3)_3Br_2COOH$: neut. equiv., 322. Found: 321.

Summary

1. Meso and racemic forms of 2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinones have been prepared. These were synthesized by brominating 2,5-dimesitylhydroquinone which in turn is readily formed by the addition of mesitylene to *p*-benzoquinone.

2. The two stereoisomeric compounds form characteristic diacetates and quinones. These latter compounds represent the first examples of the diphenyl type of isomers in compounds which have one of the rings not a benzene nucleus.

3. Each of the two 2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinones may be oxidized with hydrogen peroxide and sodium hydroxide to monobromomesitylcarboxylic acid.

4. The two hydroquinones may be brominated to the same hexabromo derivative, 2,5-di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone, thus indicating that symmetry in the end rings eliminates the stereoisomerism.

5. The hexabromo compound just mentioned forms a characteristic diacetate and quinone. Moreover, it is oxidized by sodium hydroxide and hydrogen peroxide to dibromomesitylcarboxylic acid.

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THE REACTION BETWEEN CERTAIN ORGANIC SULFUR COMPOUNDS AND SODIUM IN LIQUID AMMONIA[1]

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In connection with certain investigations on the sulfur compounds in crude untreated petroleum, it was found necessary to determine the effect of sodium on some simple organic sulfur compounds. Sulfides, disulfides and mercaptans were chosen for this study, since they are representative of divalent sulfur compounds which are supposed to exist in crude petroleum.

Very little work has been done on the effect of sodium on these types of sulfur compounds. Moses and Reid[2] found that organic sulfides are unattacked by sodium in ether even after standing for three months. Disulfides are converted into the corresponding mercaptans.

Kraus and White,[3] using a solution of sodium in liquid ammonia, converted diphenyl sulfide into benzene and sodium sulfide. No other reaction products were isolated. Apparently, the solution of sodium in liquid ammonia is more reactive than the ether–sodium system. We found this idea borne out in the present investigation.

With the three types of compounds studied, sulfides, disulfides and mercaptans, sodium might be expected to react in liquid ammonia, at least in two ways: first, it might carry the reduction to completion, yielding as

[1] The investigation was carried out in 1928–1929 under a grant from the American Petroleum Institute, and specified as Project 17.

[2] Moses and Reid, THIS JOURNAL, **48**, 776 (1926).

[3] Kraus and White, *ibid.*, **45**, 775 (1923). We repeated Kraus' work on the reaction between diphenyl sulfide and sodium in liquid ammonia. Four experiments were made, two in which the procedure was identical with that described in the experimental part, and two in which the diphenyl sulfide was dropped into a solution of sodium in liquid ammonia as Kraus carried out the reaction. Our results were the same in all four experiments. A deep red solution was obtained when reaction was complete. The solid reaction product was a brown powder which ignited when exposed to moist air for a few minutes. Thiophenol and aniline were the only products identified. Benzene and sodium sulfide were watched for closely, since Kraus reported these, but we were unable to detect either compound.