Fraction 2 was analyzed with the following results.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.47; H, 10.20. Found: C, 73.0; H, 10.14.

These analytical figures, taken together with the density and refractive index of this fraction, supported the conclusion that it was mainly isopulegol acetate. It (4 g.) was therefore saponified by an alcoholic potassium hydroxide solution and the mixture distilled with steam. The volatile oil was extracted from the distillate with ether, the ether evaporated and the residual isopulegol oxidized by dichromate and sulfuric acid to the isopulegone, whose semicarbazone was prepared and melted at 183° (uncorr.). This product, when mixed with the inactive isopulegone semicarbazone obtained from citronellal itself, as already reported, showed no change in melting point.

Fraction 3 contained unchanged enol acetate.

Summary

1. Citronellal can be changed to isopulegol by the action of ultraviolet light, a fact which is of considerable significance to phytochemistry as well as to botany.

2. The mechanism of the reaction is believed to consist first in the rearrangement of the aldehyde into its enol formation, which then closes to the cyclic isopulegol, since it is shown that citronellal enol acetate also can be converted into isopulegol acetate by ultraviolet light.

NEW YORK, N. Y.

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

STEREOCHEMISTRY OF DIPHENYLBENZENES. PREPARATION OF STEREOISOMERIC 3,6-DI-(2,4-DIMETHYLPHENYL)-2,5-DIBROMOHYDROQUINONES AND THEIR DERIVATIVES. IX[1]

BY E. BROWNING[2] AND ROGER ADAMS

RECEIVED JULY 25, 1930 PUBLISHED OCTOBER 6, 1930

In a recent article[3] on the isomerism of diphenyl compounds it was pointed out that interesting possibilities for stereoisomerism existed in diphenylbenzene derivatives if the same conditions were found in these latter molecules that produced isomerism in diphenyl derivatives. Thus, for example, in a molecule of type (I) in which each of the two end benzene rings are asymmetric in themselves and similar to each other, meso and racemic modifications should exist. The meso form is of peculiar interest

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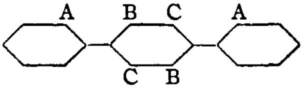
[1] For article No. VIII in this series see Stanley and Adams, THIS JOURNAL, 52, November, 1930.

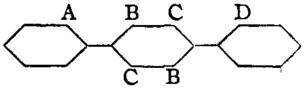
[2] This communication is the abstract of a thesis submitted by E. Browning in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Stanley and Adams, *Rec. trav. chim.*, **48,** 1035 (1929).

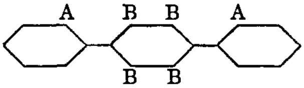
in that it contains a point of symmetry in distinction to a plane of symmetry found usually. If, on the other hand, the two end rings are dissimilar to each other (II), but still asymmetric in themselves, two racemic modifications should be possible. A third even more interesting type is that found in a formula of type (III) in which optical isomerism is not possible of existence but *cis–trans* isomers should occur whether the two end rings are similar or dissimilar, provided each is asymmetric in itself.



I



II



III

Investigations on these compounds are now under way in this Laboratory and the preliminary results are being presented in this communication on the study of compounds of type (I). In a recent article, Kögl and Erxleben,[4] who, apparently, had not read the communication from this Laboratory which contained a discussion of diphenylbenzene isomerism and a statement of the intention to undertake here a study of this problem experimentally, announced that they are planning to work on the resolution of terphenyl derivatives. The authors of this article, as they have established priority, desire to reserve this field for the next few years or until such a time, at least, as the predictions set forth by them in the article mentioned may be verified or disproved.

The specific compound which has been selected for study in this initial investigation is a derivative of 3,6-di-(2,4-dimethylphenyl)-hydroquinone (IV). This latter substance can, fortunately, be obtained with readiness following the general procedure of Pummerer.[5] A 50% yield of product was obtained by condensation of *m*-xylene with *p*-benzoquinone. This substance in itself has only two ortho substituents in each set of four positions existing adjacent to the linkages between the benzene rings. Past experience has shown that at least three groups are necessary in the adjacent positions before free rotation between the benzene rings is prevented. The compound, however, lends itself well to the satisfying of such conditions by the formation of a derivative which has these properties. Upon bromination with two moles of bromine in chloroform as a solvent, there is obtained a reaction mixture which, after reduction to remove traces of quinones which have been formed simultaneously, is found to contain two dibromo derivatives. That these two substances actually represent

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[4] Kögl and Erxleben, *Ann.*, **479**, 17, footnote (1930).

[5] Pummerer and Huppmann, *Ber.*, **60**, 1445 (1927).

the meso (V) and the racemic (VI) modifications of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone has been quite definitely established.

The two substances thus obtained differ from each other quite widely in melting point, 190–191 and 236–237°. Mixed melting points where less than 10% of the high-melting form is present, show values lower than the lower melting. The two compounds have a different solubility in various solvents.

Each of the two dibromohydroquinones can be acetylated to give its own perfectly stable characteristic diacetate (VII and VIII), and each of the diacetates can, in turn, be nitrated to the corresponding individual tetranitro compound (IX and X).

That the substances are actually stereoisomers and not simple isomers due to different positions of the two bromine atoms in each of the molecules, was proved in more than one way. Each of the two dibromohydroquinones could be oxidized to give the same dibromoquinone (XI). It would thus appear either that diphenyl isomerism cannot exist in the molecule when the quinone ring is present, or that, if it does exist, one form is so much more stable than the other that only one isomer of the corresponding quinones is actually isolated.

It is of interest to apply calculations based on x-ray data to this quinone in order to determine whether interference might be expected. If the assumptions are made that the internuclear distance between the linked carbon atoms of the benzene ring and the quinone ring is essentially the same as the distance between the linked carbon atoms of the two rings in diphenyl, and that the angles in the quinone ring are the same as in benzene, then the sum of the x-ray values for the $-C{=}O$ and the $C-CH_3$ should indicate the possibility or impossibility of resolution.[6] If the $C-CH_3$ is 1.73 Å. and the $C{=}O$ value is 1.15 Å. (merely the volume of the oxygen atom is taken here), and from their sum, 2.88 Å., the value 2.90 Å. (the distance between the linked carbon atoms in diphenyl) is subtracted, there is obtained a value of -0.02 Å. Thus the quinone oxygen and the methyl group of the benzene ring may be assumed not to collide and free rotation of the rings should be possible. Regardless of the proper explanation, the fact that identically the same compound is obtained by the oxidation of these two quite different hydroquinones, demonstrates quite positively the stereoisomeric nature of the two products.

Further evidence that these two dibromo compounds are of the type presented, and that both bromines are ortho to the hydroxyls in each molecule, was obtained. (1) The dibromoquinone (XI) from oxidation of either of the two pure hydroquinones gives upon reduction always a mixture of the high- and low-melting hydroquinones (V and VI). (2) The 3,6-di-(2,4-dimethylphenyl)-quinone (XII) from the oxidation of 3,6-di-(2,4-

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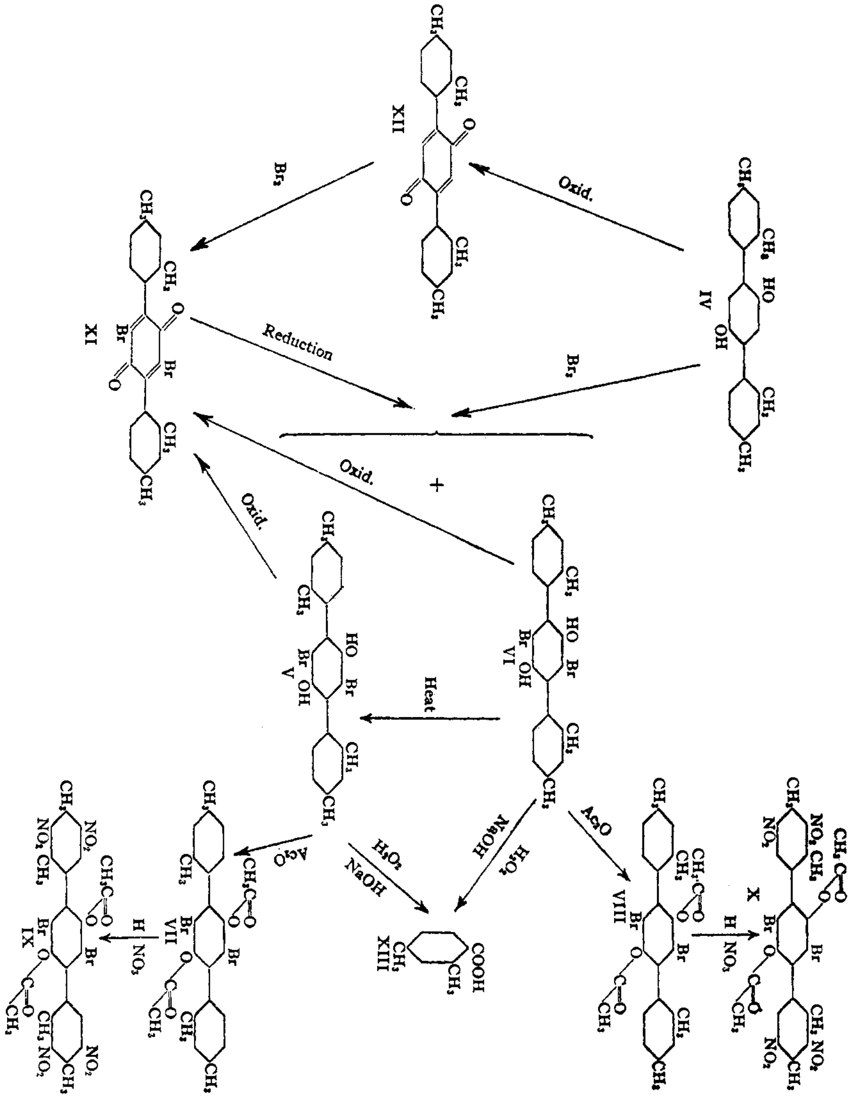
[6] Stanley and Adams, This Journal, 52, 1200 (1930).

dimethylphenyl)hydroquinone (IV) can be brominated in chloroform to give the same dibromoquinone (XI) that is obtained by oxidation of the dibromohydroquinones.



(3) Each of the two dibromohydroquinones (V and VI) is oxidized by means of strong sodium hydroxide solution and hydrogen peroxide, presumably with the primary formation of the corresponding quinone which is then oxidized further to a benzene derivative. The final compound obtained in each case is 2,4-dimethylbenzoic acid (XIII). Unfortunately the

yields are lower than might be desired (about one mole per mole of original hydroquinone, whereas, theoretically, two moles are possible). However, in an oxidation of this sort it is not to be unexpected that a quantitative yield of product is not obtained. It is pertinent, however, that the dimethylbenzoic acid which is produced is essentially pure as it comes from the reaction mixture and this is true in the oxidation of each of the two isomeric substances. If either of the two compounds had one or more bromine atoms in either of the two end rings, it is extremely likely that the corresponding bromodimethylbenzoic acid would appear in the reaction product, at least to an extent which would contaminate the dimethylbenzoic acid.

(4) By heating the lower-melting dibromohydroquinone (m. p. 190–191°) to a temperature 30° above its melting point and holding it there for several hours, a reaction product results which contains a proportion of the higher-melting compound.

Whether the higher-melting dibromohydroquinone is the meso or the racemic modification has not as yet been determined. It should be possible to introduce a salt-forming group into the molecule and then through a study of the resolution characterize each substance.

Experimental Part

3,6-Di-(2,4-dimethylphenyl)-hydroquinone.—In a 1-liter, three-necked, round-bottomed flask equipped with a thermometer and very efficient stirrer was placed 375 cc. of *m*-xylene of b. p. 138–139°. The *m*-xylene was cooled to 5° and 140 g. of aluminum chloride added with stirring, after which 70 g. of pure, dry, powdered benzoquinone (purified by steam distilling crude product and then drying over phosphorus pentoxide) was added in portions of about 0.5 g. The reaction mixture immediately turned dark brown and gradually became so viscous that stirring was difficult. In order to insure rapid mixing of the solid quinone it was added at such a rate that most of it had been incorporated before the mixture became thick (about forty-five minutes). Efficient cooling to keep the temperature below 20° is necessary since above this point the formation of tar seems to be considerably increased. After the addition the stirring was continued for two hours and the dark brown reaction mixture allowed to stand overnight in the refrigerator. It was then poured with vigorous stirring into a mixture of 100 cc. of concentrated hydrochloric acid and 400 cc. of water. The decomposition of the aluminum chloride complex was somewhat slow and the mixture was stirred until the solid which separated was dark gray in color and the excess of *m*-xylene had separated in a definite layer. The solid was filtered by suction and dried in a vacuum desiccator over phosphorus pentoxide. The dark gray powdery product was dissolved in benzene, boiled for one hour with decolorizing charcoal and filtered. Upon cooling with ice the product separated as an amorphous powder which, upon recrystallization from benzene, came down in white microscopic needles. The yield was 30 g. (43.7% of the theoretical) of a product melting at 188–189°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.97; H, 6.97. Found: C, 82.70; H, 6.76.

Stereoisomeric 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinones.—In a 200-cc., three-necked, round-bottomed flask fitted with a dropping funnel, mercury-sealed stirrer and condenser with a trap for hydrogen bromide fumes were placed 13 g. (0.04

mole) of 3,6-di-(2,4-dimethylphenyl)-hydroquinone and 150 cc. of chloroform. The flask was warmed until the solid was completely dissolved, and the solution was then cooled to 40–50°. To this solution was added slowly with stirring 13 g. (0.08 mole) of bromine dissolved in 30 g. of chloroform (30% solution). The rate of addition was controlled so that the bromine was absorbed almost as rapidly as it entered the reaction mixture. After about three-fourths of the bromine had been added the temperature was raised to 70° to increase the rate of reaction. At this temperature fumes of hydrogen bromide were evolved for the first time; in experiments in which the entire bromination was carried out at 70°, however, the evolution of hydrogen bromide was continuous throughout the entire procedure.

The chloroform and slight amount of unreacted bromine were removed at once by distilling from a steam-bath under reduced pressure, adding more chloroform as required until the distillate was no longer colored with bromine. The chloroform was then distilled completely and to the dry, slightly yellow reaction product (amounting to 16–18 g.) was added 100 cc. of ethyl alcohol. If the bromination was properly controlled, the color was only slightly yellow (due to the presence of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone from oxidation of the hydroquinone). To the alcohol containing the partially dissolved product was added a few drops of hydrochloric acid and the minimum amount of stannous chloride required to decolorize the product. It is highly desirable to control the rate of addition of the bromine as indicated previously in the procedure so as to avoid oxidation and the use of stannous chloride as far as possible, since the latter seems to make the subsequent separation and purification of the two compounds in the product more difficult. The total yield of bromination product before crystallization was 16 g. (82% of the theoretical).

High-Melting Modification. α-Form.—The ethyl alcohol containing the partially dissolved bromination product and stannous chloride was boiled until completely decolorized, cooled somewhat and filtered by suction. The residue was recrystallized from acetone until it reached a constant melting point at 236–237°. The yield was 6 g. of white hexagonal prisms.

Anal. (Parr Bomb) Calcd. for $C_{22}H_{20}O_2Br_2$: Br, 33.61. Found: Br, 33.5.

Low-Melting Modification. β-Form.—The filtrate from the ethyl alcohol treatment of the bromination product of 3,6-di-(2,4-dimethylphenyl)-hydroquinone was cooled in an ice-bath for about two hours, during which time a small quantity of white crystals separated. This was filtered and 1.5 g. of a product was obtained melting without recrystallization at 130–131° which proved to be the high-melting modification contaminated with a small amount of the low-melting compound. The filtrate was evaporated to dryness at room temperature under reduced pressure. The slightly yellow product was recrystallized from acetone. Repeated crystallization from both acetone and methyl alcohol gave a product having a constant melting point of 190–191°. The yield was 4 g. of white tetragonal prisms.

Anal. Calcd. for $C_{22}H_{20}O_2Br_2$: Br, 33.61. Found: Br, 33.5.

The melting of a mixture of 5% 236–237° compound with 95% 190–191° compound showed softening at 181° and melting at 184–189°.

The solubility of the low- and high-melting compounds is markedly different. The compound melting at 236–237° is only slightly soluble in hot ethyl alcohol while the compound melting at 190–191° can be induced to crystallize from its solution in ethyl alcohol only by evaporation and cooling. A difference, though not so great, is found in methyl alcohol and acetone.

The successful isolation of the high- and low-melting compounds in the pure state depends upon the initial separation by the use of ethyl alcohol as described in the above procedure. If too much alcohol is used, the low-melting compound is contaminated with the high-melting product and is purified by subsequent recrystallization only with great difficulty and loss of material in the filtrates. If too little alcohol is used the high-melting compound will be contaminated with the other form, but this product is more easily purified, at least to a point a few degrees below the correct melting point.

One attempt was made to carry out a fractional crystallization of the crude bromination product using methyl alcohol as the solvent and omitting the preliminary separation with ethyl alcohol. The different fractions obtained after several crystallizations seemed from their melting points to be mixtures of various proportions of the more and less soluble modifications.

3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone Diacetate. α-Form. A. (Derivative of Hydroquinone Melting at 236–237°.)—Six grams of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone was dissolved in 10 cc. of hot pyridine and 12 cc. of acetic anhydride added with stirring. The solution was heated almost to boiling for fifteen minutes, after which time the acetyl derivative began to separate from the hot solution. The reaction mixture was cooled with ice and allowed to stand for several hours, after which the product was filtered, recrystallized from acetic anhydride and left in a vacuum desiccator until the odor of acetic anhydride could no longer be detected. The yield was 6 g. of hard, white, orthorhombic crystals melting at 235–236°. Only a small amount of additional material was obtained by pouring the original pyridine–acetic anhydride filtrate into water. This acetyl derivative is only slightly soluble in hot acetone.

Anal. Calcd. for $C_{26}H_{24}O_4Br_2$: Br, 28.57. Found: Br, 28.29.

3,6-Di-(2,4-dimethyl-3,5-dinitrophenyl)-2,5-dibromohydroquinone Diacetate. α-Form.—To 40 cc. of fuming nitric acid (sp. gr. 1.48) cooled below −5° was added slowly with very rapid stirring 6 g. of the powdered diacetyl derivative just previously described and melting at 235–236°. A red coloration appeared momentarily as the solid came in contact with the acid but disappeared as the compound went into solution. After standing in the freezing mixture for 15 minutes a solid began to separate, and after one hour the nitration mixture was poured into ice water. The nitro derivative was filtered, washed free of acid with a 5% sodium carbonate solution, followed by water and dried. The product was washed with acetone until pure white and melted at 304–305° after drying. Crystallization from acetic anhydride yielded 4.8 g. of white needles melting sharply at 305–306° (decomposed after melting, with evolution of gas bubbles).

Anal. (Parr Bomb) Calcd. for $C_{26}H_{20}O_{12}N_4Br_2$: Br, 21.62. Found: Br, 21.78.

3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone Diacetate. β-Form. B. (Derivative of Hydroquinone Melting at 190–191°.)—The acetylation was carried out in the same way as for the acetylation of the high-melting hydroquinone using 4 g. of the substituted hydroquinone, 5 cc. of pyridine and 8 cc. of acetic anhydride. The acetyl derivative did not separate from the hot solution as in the previous case, but came out on cooling in an ice–salt mixture. It was allowed to stand overnight and the white powdery product filtered by suction. The amount thus obtained was 3.5 g. and 1 g. additional by pouring the filtrate into water. The product was readily soluble in acetone as contrasted with the preceding diacetyl derivative, and upon recrystallization from this solvent yielded 3 g. of white microscopic needles melting at 193–194° (with previous softening). A mixed melting point with the starting material showed a depression and melted over a range of 160–165°.

Anal. Calcd. for $C_{26}H_{24}O_4Br_2$: Br, 28.57. Found: Br, 28.42.

3,6-Di-(2,4-dimethyl-3,5-dinitrophenyl)-2,5-dibromohydroquinone Diacetate. β-Form.—The nitration of the diacetate just described was carried out as in the case of the higher-melting diacetate using 2 g. of the diacetyl derivative and 20 cc. of fuming nitric acid. The product in this case did not precipitate from the cold nitration mixture even after long standing, and it was found more satisfactory to pour the solution immediately into ice water in order to avoid excessive formation of a lemon-yellow by-product, presumably formed by hydrolysis of the acetyl groups, followed by oxidation. Recrystallization from acetone yielded 0.4 g. of microscopic white needles melting at 282–283° with slight decomposition and evolution of gas.

Anal. Calcd. for $C_{26}H_{20}O_{12}N_4Br_2$: Br, 21.62. Found: Br, 21.43.

3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquinone.—Oxidation of the substituted hydroquinones to the corresponding quinones was carried out most readily by the method of Pummerer,[5] using benzoquinone as the oxidizing agent.

One gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone was dissolved in the minimum amount of hot methyl alcohol and 0.1 g. of benzoquinone added. The solution turned orange almost at once, and was boiled for ten minutes, during which time the less soluble substituted quinone began to precipitate. Another 0.1-g. portion of benzoquinone was added, the reaction mixture boiled for ten minutes and then cooled with ice. The product was filtered, recrystallized from methyl alcohol and dried in a vacuum desiccator; yield, 0.7 g. of microscopic orange needles melting at 197–198°.

Anal. Calcd. for $C_{22}H_{18}O_2Br_2$: Br, 33.75. Found: Br, 33.60.

One gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. 236–237°) was oxidized as in the preceding experiment, and yielded 0.8 g. of orange needles melting at 198° after one recrystallization from methyl alcohol. Repeated crystallization failed to raise the melting point.

A mixed melting point of the quinones obtained from the 190–191° and 236–237° compounds showed no depression.

3,6-Di-(2,4-dimethylphenyl)-quinone and 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquine.—3,6-Di-(2,4-dimethylphenyl)-quinone was prepared from the corresponding hydroquinone by the oxidation procedure given in the preceding experiment. The product, after crystallization from methyl alcohol, from 2 g. of hydroquinone was 1.8 g. of reddish-brown crystals melting at 180°.

The 1.8 g. of 3,6-di-(2,4-dimethylphenyl)-quinone was dissolved in 50 cc. of chloroform and a 30% solution of 2 g. of bromine in chloroform was added slowly with stirring at room temperature. The bromine was absorbed instantly but no hydrogen bromide was evolved until the solution was warmed. The chloroform was distilled, leaving 4 g. of an orange, crystalline product. Upon dissolving the material in methyl alcohol it was observed that some white crystalline substance was present, possibly some substituted hydroquinone formed by the addition of hydrogen bromide to the quinone. The solution was, therefore, treated with benzoquinone and boiled, after which an orange product separated which resembled in appearance the dibromoquinones previously prepared. After repeated crystallization from methyl alcohol, there was obtained 2 g. of an orange product melting sharply at 198°. A mixed melting point with 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone prepared by the other method described showed no depression.

Reduction of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquinone.—A solution of 3.8 g. of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone in acetone was reduced by means of 1.5 g. of stannous chloride and 2 cc. of concentrated hydrochloric acid. Decolorization of the orange solution was almost immediate after slight warming. The solution was poured into four times its amount of water and the precipitated reduction product filtered, washed several times with water and dried. To the product was added 40 cc. of ethyl alcohol; the mixture was heated for five minutes and filtered while warm. The insoluble part amounting to 1.2 g. was recrystallized from acetone to constant melting point and yielded 1.1 g. of a compound melting at 236–237°. The filtrate was cooled and permitted to stand for one hour, after which the crystals that had separated were filtered. Four-tenths of a gram of high-melting compound contaminated with some of the low-melting modification was thus obtained. It melted at 230–232° (softens at 225°). The acetone filtrate was evaporated to dryness at ordinary temperature and under reduced pressure and yielded 1.3 g. of substance melting at 190–192° (softens at 187°). This, after recrystallization from acetone, yielded 0.8 g. of a compound melting constantly at 190–191°. The compounds have also been purified in other experiments by crystallization from methyl alcohol.

Stability to Heat of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone, m. p. 190–191°.—In a small bomb tube was placed one gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. 190–191°) and the tube evacuated to 10 mm. The tube was then filled with nitrogen, again evacuated and the process repeated several times to insure complete removal of oxygen. The bomb tube was then sealed off while filled with nitrogen and immersed in an oil-bath at 220°, whereupon the substance melted to a clear liquid. After one hour (longer heating is not possible because of decomposition) the tube was allowed to cool to room temperature, after which it was opened and the white solidified product heated with 15 cc. of ethyl alcohol. The residue insoluble in alcohol was filtered and crystallized from acetone. There was thus obtained 0.05 g. of white crystals melting at 235–236°. A mixed melting point with the high-melting modification showed no depression.

Oxidation of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquinone to 2,4-Dimethylbenzoic Acid.—One gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone was suspended in 50 cc. of 20% sodium hydroxide solution and 25 cc. of 30% hydrogen peroxide added with stirring. The quinone gradually dissolved and the original deep red color of the solution changed to pink in the course of six hours. The addition of 25 cc. more of hydrogen peroxide and longer stirring failed to effect further change. The solution, in which the odor characteristic of aromatic aldehydes was noticeable, was acidified and the yellow solid which precipitated was filtered and dried. It was redissolved in very dilute sodium hydroxide and the pink color reappeared. Upon addition of 10 cc. of hydrogen peroxide to this faintly alkaline solution, a vigorous reaction occurred and the solution became decolorized in a few minutes. Acidification with hydrochloric acid caused the precipitation of a fairly white product. This was extracted with ether, the ether solution shaken out with a saturated sodium bicarbonate solution, and this alkaline solution acidified with hydrochloric acid. The product precipitated and was filtered and recrystallized from dilute ethyl alcohol. The yield was 0.2 g. of a compound melting sharply at 125–126°. A mixed melting point with 2,4-dimethylbenzoic acid showed no depression.

Neut. Equiv. Subs., 0.0788 g.: 0.1015 *N* NaOH, 5.07 cc. Calcd. for C_8H_9COOH: mol. wt., 150. Found: mol. wt. 153.

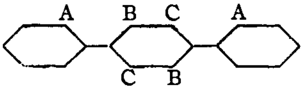
Oxidation of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. **190–191°**) **to 2,4-Dimethylbenzoic Acid.**—The oxidation was carried out in the same way as in the preceding experiment using 0.25 g. of the substituted hydroquinone, 30 cc. of 20% sodium hydroxide and 25 cc. of 30% hydrogen peroxide. The yield after the various extractions and purification was 0.06 g. (*i. e.*, 0.7 mole of acid from 1 mole of the compound) of 2,4-dimethylbenzoic acid melting at 125–126°.

Oxidation of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. **236–237°**) **to 2,4-Dimethylbenzoic Acid.**—The oxidation was accomplished as before, using 0.47 g. of substance, 50 cc. of 20% sodium hydroxide solution, and 50 cc. of 30% hydrogen peroxide. The 2,4-dimethylbenzoic acid was isolated and purified as before, and amounted to 0.13 g. (0.8 mole of acid from 1 mole of substance). The melting point was 125–126°.

Summary

1. Two stereoisomeric 3,6-di-(2,4-dimethylphenyl)-2,5-dibromodihydroquinones and some derivatives have been prepared.

2. These substances are the racemic and the meso modifications of a molecule of the following type



3. It may be concluded that the same conditions which cause optical isomerism in the diphenyl series also exist in the terphenyl series.

Urbana, Illinois

[Contribution from the Experimental Research Laboratories, Burroughs Wellcome and Company]

MIXED BENZOINS. II

By Johannes S. Buck and Walter S. Ide

Received July 26, 1930 Published October 6, 1930

In continuation of the work described in Part I,[1] six new benzoins, together with their benzils and desoxy compounds have been prepared. The work described cannot be said to support, or detract from, the theoretical conclusions advanced in Part I, as data on the reactivity of the aldehydes are lacking. The benzoins described in the present paper were all prepared in the usual manner, by mixing the reactants and refluxing, as it was found that the technique earlier described gave little, if any, better yields in the present cases. The results described in Part I and Part II represent the best that can be obtained by fractionation methods, and it is evident that further knowledge can only be attained by complete analysis of the reaction mixtures. It is hoped to carry this out in some cases.

Attention was given to the possibility of the occurrence of isomeric mixed benzoins, but no examples were found. Their occurrence, however, is not excluded, as in general only about one-half of the reactants was accounted for. The mixed benzoins described are very probably individuals and not mixtures or addition compounds, as in each case only one desoxy compound was obtained on reduction.

The mixed benzoins described are not specifically named, as it is not possible to assign either of the two alternative structures with any degree of probability.

Experimental

Benzoin from *p*-Dimethylaminobenzaldehyde and Anisaldehyde, (A).—Seven and one-half grams of *p*-dimethylaminobenzaldehyde, and 7.0 g. of anisaldehyde, dis-

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[1] Buck and Ide, This Journal, 52, 220 (1930).