Summary

1. The ultraviolet absorption spectra of uracil, dichloromethylpyrimidine, adenine, and thymus nucleic acid are presented. In each case, the effect of ultraviolet irradiation upon these absorption spectra has been followed.

2. Two effects of irradiation are noted. One, occurring early, consists chiefly in increased absorption in the regions of low absorption adjacent to the absorption band. A second, and later, effect consists in the gradual loss of all noteworthy selective absorption of these materials.

3. Possible explanations of the mechanism of these effects are critically discussed.

4. Possible biological implications of the changes described are alluded to briefly.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF PHENYLQUINONES. THE PREPARATION AND RESOLUTION OF 2-(3-BROMO-2,4,6-TRIMETHYLPHENYL)-5-METHYLBENZOQUINONE-3,6-DI-(ACETIC ACID). XVIII[1]

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The success in obtaining stereoisomeric diphenylbenzenes and diphenylquinones when properly substituted has led to the extension of the work to certain phenylquinones.

In this investigation 2-(3-bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6 di-(acetic acid) (XV) has been prepared and resolved through the morphine salt. This is the first phenylquinone that has been resolved into optical antipodes and thus the same conclusions may be drawn as from the study of the diphenylquinones[3] that a quinone and benzene ring when attached to each other and when each is properly substituted may have restricted rotation between them. Using the x-ray values previously discussed, this result might be anticipated. Assuming the CH_2COOH group to be essentially the same in hindering effect as the methyl group, the following conditions exist: CH_3, 1.73 Å. + C=O, 1.12 Å. $\longrightarrow$ 2.85 Å.; CH_3, 1.73 Å. + CH_2COOH, 1.73 Å. $\longrightarrow$ 3.46 Å. Thus on one side of the molecule after subtracting the vertical distance between the 2,2′ carbon

[1] For the two previous papers, see Stanley and Adams, THIS JOURNAL, **53**, 2364 (1931); Chang and Adams, *ibid.*, **53**, 2353 (1931). See also Stanley, *ibid.*, **53**, 3104 (1931).

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[3] Shildneck and Adams, THIS JOURNAL, **53**, 343 (1931).

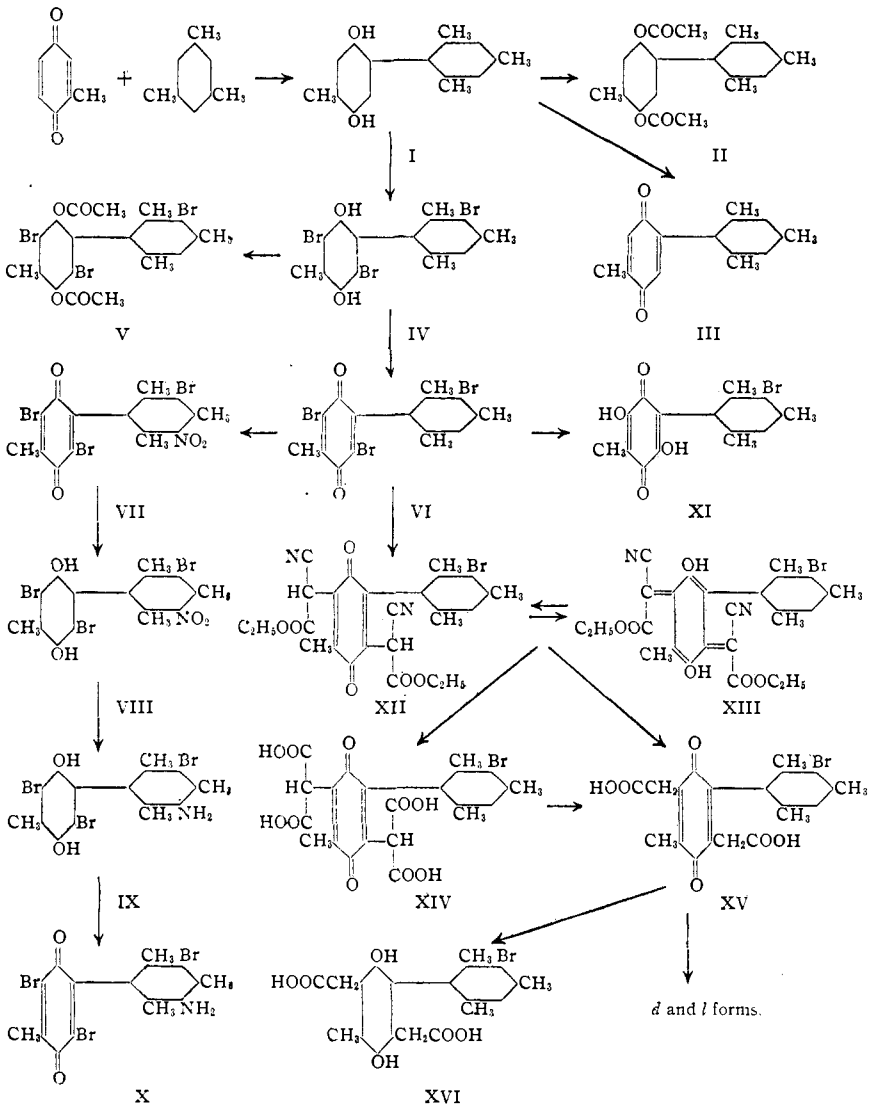
atoms of the two rings which in diphenyl is 2.90 Å., it is found that the groups on one side do not collide by −0.05 Å. but on the other side do collide by +0.56 Å. It is thus seen that such a molecule should probably be relatively stable to rotation between the rings. Even if more flexibility exists in the quinone ring so that the two rings may bend to or from each other readily, the average interference at the ideal point for rotation would be (+0.56 Å. − 0.05 Å.)/2 ⟶ +0.26 Å., an appreciably large value.

The procedure for obtaining the compound resolved is shown in the chart. The reaction between benzoquinone and various aromatic hydrocarbons in the presence of anhydrous aluminum chloride is difficult or perhaps impossible to control in such a way that merely a monophenyl hydroquinone is obtained. On the other hand, certain monosubstituted quinones such as toluquinone react readily to give a monoaryl methylhydroquinone. Toluquinone and mesitylene yielded 2-(2,4,6-trimethylphenyl)-5-methylhydroquinone (I), which may readily be converted to the corresponding diacetate (II) and quinone (III). The hydroquinone was brominated to 2-(3-bromo-2,4,6-trimethylphenyl)-2,6-dibromo-5-methylhydroquinone (IV) and this product acetylated to the diacetate (V). This hydroquinone in turn was readily oxidized to the corresponding quinone (VI). Several procedures were carried out on this compound in order to produce a quinone containing a salt-forming group.

The first procedure was to nitrate the quinone (VI) to give 2-(3-bromo-5-nitro-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylbenzoquinone (VII). Catalytic reduction of (VII) with platinum-oxide platinum black and hydrogen caused reduction merely of the quinone grouping and gave 2-(3-bromo-5-nitro-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylhydroquinone (VIII). By means of tin and hydrochloric acid (VIII) was reduced to the corresponding amino compound (IX), which in turn with benzoquinone gave the quinone 2-(3-bromo-5-amino-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylbenzoquinone (X). Unfortunately the amino group in this product was not sufficiently basic to give stable salts with camphorsulfonic acid or other active acids.

The second procedure followed depended on the ease with which the two bromines in the quinone nucleus of (VI) could be removed. By heating with aqueous sodium hydroxide, the substitution by hydroxyls was accomplished with the formation of 2-(3-bromo-2,4,6-trimethylphenyl)-3,6-dihydroxy-5-methylhydroquinone (XI). Due to the strongly acid character of the hydroxyls in (XI), deeply colored alkaloidal salts could be prepared. Preliminary experiments, however, indicated such difficulties in resolution that further attempts were abandoned.

The third and successful method for obtaining a resolvable compound by introducing salt forming groups also depended on the activity of the quinone halogens. They were replaced by cyanoacetic ester residues by



treating the halogen compound (VI) with the sodium derivative of ethyl cyanoacetate. Although an excellent yield of crude product was obtained in this reaction, only about a 20% yield of a single pure substance was secured upon purification. This may have been due to the presence of the several stereoisomers which are theoretically possible. The pure product which would presumably be 2-(3-bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(ethyl cyanoacetate) (XII) showed some unusual properties. It was cream-colored in solid form and hence very much lighter colored than any of the other quinones studied in this investigation.

On the other hand, it dissolved in solvents to give an orange solution from which it could be again obtained as a cream-colored solid. On this account it seems probable that the colorless solid has not the structural formula (XII) but (XIII) which would be expected to exhibit less color than (XII). In solution there is probably an equilibrium of the two forms (XII) and (XIII).

By varying methods of saponification two different products were obtained. On mild saponification of (XII), a dimalonic acid (XIV) was produced or on vigorous saponification the desired diacetic acid derivative 2 - (3 - bromo - 2,4,6 - trimethylphenyl) - 5 - methylbenzoquinone - 3,6 - diacetic acid) (XV). The malonic acid (XIV) on heating also gave (XV). The quinone (XV) was readily reduced catalytically to the corresponding hydroquinone (XVI) which was colorless. The quinone (XV) readily formed salts with the alkaloids and the morphine derivative was especially suitable for resolution. Two salts distinctly different in solubility were readily separated from each other. Upon decomposition with mineral acid, the active acids were obtained $[\alpha]_D^{20}$ +34.7°, $[\alpha]_D^{20}$ −18.8°. The latter came from the more soluble salt and therefore does not represent the maximum rotation.

Experimental

2-(2,4,6-Trimethylphenyl)-5-methylhydroquinone (I).—In a 1500-cc. three-necked, round-bottomed flask fitted with a calcium chloride tube and well cooled in an ice–salt mixture was placed 750 cc. of mesitylene. To this was added 150 g. of aluminum chloride and the mixture well stirred. To this was added 50 g. of dry toluquinone in small quantities over the course of about two hours, care being taken that the temperature did not rise above 5°. Stirring was continued for three hours after the addition of the toluquinone and the mixture was then allowed to stand overnight. A thick oil separated from which the supernatant liquor was decanted and which was then decomposed by the addition of a mixture of 80 cc. of concentrated hydrochloric acid, 100 cc. of water and 100 g. of ice. The solid which separated was filtered and the filtrate added to the previously decanted mesitylene, the whole being steam distilled to recover the mesitylene. The residue in the flask was added to the solid filtered off above and the whole crystallized from petroleum ether (b. p. 65–110°). Four recrystallizations with the addition of norite were necessary to purify the product, which then appeared as colorless needles having m. p. 134–135° (corr.) in a yield of 60%.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.6. Found: C, 79.1; H, 7.4.

2-(2,4,6-Trimethylphenyl)-5-methylhydroquinone Diacetate (II).—A solution of 1.5 g. of 2-methyl-5-mesitylhydroquinone in 10 cc. of pyridine was treated with 10 cc. of acetic anhydride and the mixture boiled for fifteen minutes under a reflux condenser. It was then poured into hot water and maintained at the boiling point for half an hour to decompose the excess acetic anhydride. The solid product which separated was crystallized from 95% alcohol. It formed colorless needles of m. p. 138–139° (corr.) in a yield of 1 g.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.6; H, 6.7. Found: C, 73.4; H, 6.8.

2-(2,4,6-Trimethylphenyl)-5-methylbenzoquinone (III).—A solution of 5 g. of crude 2-(2,4,6-trimethylphenyl)-5-methylhydroquinone (I) in 30 cc. of 95% alcohol

was heated for five minutes with 3 g. of pure benzoquinone. The solution developed a deep red color and after cooling deposited a yellow solid which was purified by recrystallization three times from 95% alcohol. It was thus obtained as deep yellow needles of m. p. 129° (corr.) in a yield of 80%.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.8; H, 6.7.

2-(3-Bromo-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylhydroquinone (IV).—A solution of 3 g. of 2-(2,4,6-trimethylphenyl)-5-methylhydroquinone (I) in carbon tetrachloride was treated with a solution of 6 g. of bromine in 20 cc. of the same solvent in small portions on the steam-bath. Boiling was continued for one hour after the addition of the bromine and the solvent was then distilled off. Excess bromine was removed by two additions of chloroform and subsequent distillation. The dark colored product was dissolved in acetone and the color discharged by the addition of a small quantity of stannous chloride. Addition of water precipitated an oil which solidified on cooling in ice. This was recrystallized from a little 95% alcohol, then from 50% acetic acid and finally from 95% alcohol again. It was thus obtained as fine colorless needles of m. p. 148–149° (corr.) in a yield of 2 g.

Anal. (Parr bomb). Calcd. for $C_{16}H_{15}O_2Br_3$: Br, 50.1. Found: Br, 49.9.

2-(3-Bromo-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylhydroquinone Diacetate (V).—A solution of 7 g. of crude 2-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylhydroquinone (IV) in a mixture of 50 cc. of pyridine and 25 cc. of acetic anhydride was boiled under a reflux condenser for half an hour. The reaction mixture was then poured into 300 cc. of water and heated to destroy the excess of acetic anhydride. The resulting solid was crystallized from 50 cc. of 95% alcohol and recrystallized from the same solvent with the addition of norite. Thus was obtained 4 g. of colorless needles with m. p. 137–138° (corr.).

Anal. (Parr bomb). Calcd. for $C_{20}H_{19}O_4Br_3$: Br, 42.6. Found: Br, 42.6.

2-(3-Bromo-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylbenzoquinone (VI).—A solution of 45 g. of 2-(2,4,6-trimethylphenyl)-5-methylhydroquinone (I) was brominated, as already described, in 400 cc. of carbon tetrachloride with 40 cc. of bromine dissolved in 250 cc. of the same solvent. The residue after removing the excess bromine with chloroform was dissolved in 500 cc. of hot 95% alcohol and the solution boiled for fifteen minutes with 25 g. of pure benzoquinone. The solution darkened and on cooling deposited orange-red needles which were twice recrystallized from 95% alcohol. By this means 75 g. of product was obtained with m. p. 137–138° (corr.).

Anal. (Parr bomb). Calcd. for $C_{16}H_{13}O_2Br_3$: Br, 50.2. Found: Br, 50.3.

2-(3-Bromo-5-nitro-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylbenzoquinone (VII).—To 30 cc. of well-cooled and well-stirred fuming nitric acid was added portionwise 4 g. of the brominated quinone (VI) at such a rate that the temperature did not rise above 5°. The solution developed a deep orange color and after the whole had been added, the reaction mixture was allowed to stand for five minutes and was then poured into 250 cc. of ice water. The yellow precipitate so obtained was crystallized from acetone, giving 3.5 g. of pale yellow needles of m. p. 205–206° (corr.)

Anal. (Parr bomb). Calcd. for $C_{16}H_{12}O_4NBr_3$: Br, 46.0. Found: Br, 45.9.

2-(3-Bromo-5-nitro-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylhydroquinone (VIII).—A suspension of 3 g. of the bromonitroquinone (VII) was made in 200 cc. of 95% ethyl alcohol and 0.1 g. of platinum oxide catalyst added. The mixture was shaken with hydrogen at 37 lb. pressure until the solid quinone had completely dissolved (about fifteen minutes). The solution was then filtered and evaporated to about 40 cc., when an equal volume of water was added. The nitrohydroquinone crystallized from this mixture as colorless rhombs of m. p. 178–179° in a yield of 1.8 g.

Anal. (Parr bomb). Calcd. for $C_{16}H_{14}O_4NBr_3 \cdot H_2O$: Br, 44.6. Found: Br, 44.6, 44.2.

2-(3-Bromo-5-amino-2,4,6-trimethylphenyl) - 3,6 - dibromo - 5-methylhydroquinone (IX).—The reduction of the nitrohydroquinone (VIII) was carried out by dissolving 3 g. in a mixture of 50 cc. of concentrated hydrochloric acid and sufficient alcohol to bring about complete solution. This solution was heated under a reflux condenser for twelve hours and 5 g. of granulated tin was added at intervals during the first three hours. The majority of the alcohol was then removed on the steam-bath and more concentrated hydrochloric acid added. The amine, which is insoluble in hydrochloric acid, was thus precipitated as a granular solid. It was crystallized from 50% alcohol from which it separated as small colorless needles having m. p. 223° (corr.). The yield was 1.7 g.

Anal. (Parr bomb). Calcd. for $C_{16}H_{16}O_2NBr_3$: Br, 48.6. Found: Br, 48.5.

Although insoluble in acids a suspension of the amine in hydrochloric acid could be diazotized and the diazo solution thus obtained couples with β-naphthol to give a red dye.

2-(3-Bromo-5-amino-2,4,6-trimethylphenyl)-3,6-dibromo - 5 - methylbenzoquinone (X).—A solution of 1 g. of the amino hydroquinone (IX) in 20 cc. of 95% alcohol was heated for five minutes with 0.3 g. of pure benzoquinone. Water was then added to the solution to bring the alcohol concentration to 60% and the solution was allowed to cool. The solid which separated was crystallized from 20 cc. of alcohol with the addition of norite. Thus was obtained 0.7 g. of a brick-red microcrystalline powder which commenced to decompose at 135–140° (corr.).

Anal. (Parr bomb). Calcd. for $C_{16}H_{14}O_2NBr_3$: Br, 48.7. Found: Br, 48.5.

2-(3-Bromo-2,4,6-trimethylphenyl)-3,6-dihydroxy-5-methylbenzoquinone (XI).—A solution of 20 g. of sodium hydroxide in 200 cc. of water was added to a suspension of 10 g. of the tribromoquinone (VI) previously described, in 200 cc. of methyl alcohol. The solution immediately assumed a deep red color and on stirring for six hours and cautiously raising the temperature to about 50° all the solid dissolved. The solution was filtered to remove any unchanged tribromo compound and the hydroxyquinone was precipitated by acidifying with hydrochloric acid. The orange colored product was crystallized from amyl alcohol, whereby 6 g. of orange-yellow needles of m. p. 282° (decomp. corr.) was obtained.

Anal. (Parr bomb). Calcd. for $C_{16}H_{15}O_4Br$: Br, 22.8. Found: Br, 23.1.

Attempted Resolution of 2-(3-Bromo-2,4,6-trimethylphenyl)-3,6-dihydroxy-5-methylbenzoquinone. Brucine Salt.—To a solution of 12 g. of brucine in 300 cc. of hot dry ethyl acetate was added 10 g. of the dihydroxyquinone. A blood-red color was immediately produced and after five minutes' boiling, the whole of the salt was in solution. The solution was filtered and set to crystallize. A first crop of 8 g. separated with m. p. 166–175° (corr.) and $[\alpha]_D^{20}$ 0.0 in dry chloroform. This was recrystallized and yielded 5 g. of a deep red crystalline salt with a characteristic sheen. The salt had m. p. 185–190° (decomp. corr.) and $[\alpha]_D^{20}$ 0.0 in dry chloroform.

This crop was decomposed by the addition of ice cold 10% hydrochloric acid and the free dihydroxyquinone filtered off and washed with acid and water until completely free from brucine. It was dried in the air and showed no rotation.

Anal. (Parr bomb). Calcd. for $C_{16}H_{15}O_4Br \cdot C_{23}H_{26}N_2O_4$: Br, 10.8. Found: Br, 10.7.

Strychnine Salt.—A solution of 10 g. of hydroxyquinone in 400 cc. of hot dry ethyl acetate was added to a solution of 11 g. of strychnine in 600 cc. of the same solvent. The deep red solution was then evaporated to 400 cc., filtered and allowed to crystallize.

A first crop of dark red crystals was thus obtained, weighing 3.0 g., of m. p. 200° (decomp. corr.) and showing no rotation. The mother liquor was evaporated to 200 cc. and a second crop separated. This weighed 5.0 g., had m. p. 195° (decomp. corr.) and showed no rotation. The mother liquor was again evaporated, this time to 100 cc. The third crop weighed 3.0 g., had m. p. 195° (decomp. corr.) and showed no rotation. These three crops were combined and recrystallized from 200 cc. of ethyl acetate. The product, which had the same red color and characteristic sheen as the brucine salt, had m. p. 194–200° (decomp. corr.) and showed no rotation in dry chloroform.

Anal. (Parr bomb). Calcd. for $C_{16}H_{15}O_4Br.C_{21}H_{22}N_2O_2$: Br, 11.7. Found: Br, 11.8.

This salt was decomposed as described for the brucine salt and yielded the free quinone having no rotation.

2-(3-Bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(ethyl Cyanoacetate) (XII and XIII).—In a three-necked flask fitted with a calcium chloride tube and a stirrer was placed 1000 cc. of absolute alcohol and to this was added 2.5 g. of sodium. When all the sodium had dissolved, 12.5 g. of redistilled ethyl cyanoacetate was added. The solution was allowed to cool to room temperature and 20.0 g. of 2-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromo-5-methylbenzoquinone (VI) was then added. The solution, which was dark red, was stirred at room temperature for sixteen hours during which time it assumed a dark green color. The whole of the quinone had then dissolved. An equal volume of water was added and the solution filtered to remove any unchanged material. A further 1000 cc. of water was then added and a few drops of hydrochloric acid, whereby 20 g. of an orange-brown precipitate was obtained. Considerable difficulty was experienced in the purification of this compound. It was dissolved in 400 cc. of hot methyl alcohol and allowed to stand in the cold for twenty-four hours. About 5 g. of pale brown, fine needles separated and after six further crystallizations from methyl and ethyl alcohol, 3 g. of a cream-colored material having a m. p. of 205–206° (corr.) was obtained. The compound was soluble in the usual organic solvents, giving a deep orange-colored solution. It was also soluble in sodium hydroxide with a deep color.

Anal. Calcd. for $C_{26}H_{25}O_6N_2Br$: C, 57.7; H, 4.6; N, 5.17; Br, 14.8. Found: (micro) C, 57.6; H, 4.4; N, 5.39; Br (Parr bomb), 15.0, 14.8.

2-(3-Bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(malonic Acid) (XIV).—A solution of 1 g. of the di-(cyanoacetic ester) quinone (XII) in 150 cc. of 2% potassium hydroxide solution was stirred at room temperature for twelve hours. The dark brown solution was then acidified with 2% hydrochloric acid and the solution heated. The hot solution was filtered and allowed to crystallize. A pale orange-colored product was obtained with m. p. 160–165° (decomp. corr.) in a yield of 0.5 g.

Anal. (Parr bomb). Calcd. for $C_{22}H_{19}O_{10}Br$: Br, 15.3. Found: Br, 15.1.

2-(3-Bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(acetic Acid) (XV).—A solution of 1 g. of the di-(cyanoacetic ester) quinone (XII) in 50 cc. of 5% aqueous potassium hydroxide was heated under a reflux condenser for two hours. A deep brown solution resulted, which after cooling was diluted with 50 cc. of water and acidified with 2% hydrochloric acid. The precipitate was redissolved by heating and the solution filtered and allowed to crystallize. The product, which was obtained in a yield of 0.4 g., was an orange-colored micro-crystalline powder of m. p. 220–223° (corr.).

Anal. Calcd. for $C_{20}H_{19}O_6Br$: C, 55.1; H, 4.4; Br, 18.4. Found: (micro) C, 55.0; H, 4.55; Br (Parr bomb), 18.4.

Conversion of the Dimalonic Acid to the Diacetic Acid.—A small quantity of the dimalonic acid (XIV) was heated in an oil-bath to 160°. Considerable evolution of

carbon dioxide occurred and some decomposition of the final product. After cooling, the solid was treated with dilute aqueous potassium hydroxide and the alkaline solution filtered and acidified with dilute hydrochloric acid. The precipitate was redissolved by heating, the hot solution filtered and the diacetic acid (XV) allowed to crystallize as before. The orange-colored product had m. p. 210–212° (corr.) and a mixed m. p. with the pure diacetic acid was 215–218° (corr.).

Resolution of 2-(3-Bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(acetic Acid) (XV).—To a solution of 1.5 g. of the diacid (XV) in 10 cc. of hot absolute alcohol was added a solution of 2.4 g. of morphine in 25 cc. of hot dry ethyl acetate. An immediate separation of a brown salt occurred which was redissolved by the addition of 15 cc. of absolute alcohol and the solution was set aside to crystallize. By this means 0.35 g. of a brown crystalline material of m. p. 199–204° (decomp. corr.) separated.

Rotation. 0.0670 g. made up to 15 cc. with methyl alcohol at 20° gave α_D −0.10°; l = 1; $[\alpha]_D^{20}$ −31.4°.

The mother liquor from this crop was heated to boiling, 65 cc. of dry ethyl acetate added and the solution again allowed to crystallize. A further 0.35 g. of brown crystalline material of m. p. 199–204° (decomp. corr.) separated.

Rotation. 0.0800 g. made up to 15 cc. with methyl alcohol at 20° gave α_D −0.16°; l = 1; $[\alpha]_D^{20}$ −32.0°.

The mother liquor was then evaporated to 50 cc. and again set aside to crystallize. Thus was obtained 0.55 g. of brown crystalline material of m. p. 198–200° (decomp. corr.).

Rotation. 0.0950 g. made up to 15 cc. with methyl alcohol at 20° gave α_D −0.27°; l = 1; $[\alpha]_D^{20}$ −45.7°.

These three crops, the latter of which obviously contained some free morphine, were combined and crystallized from a mixture of 15 cc. of methyl alcohol and 15 cc. of dry ethyl acetate. Thus 0.75 g. of brown crystalline material of m. p. 201–205° (decomp. corr.) was obtained.

Rotation. 0.0675 g. made up to 15 cc. with methyl alcohol at 20° gave α_D −0.14°; l = 1; $[\alpha]_D^{20}$ −32.6°.

Anal. (micro). Calcd. for $C_{20}H_{19}O_6Br \cdot 2C_{14}H_{19}O_3N$: Br, 7.95. Found: Br, 8.00.

The final mother liquor from the salt fractions above was slowly evaporated in the air to 7 cc. but no separation of the more soluble salt occurred. A certain amount of morphine began to separate, however, and in view of the small quantity and the presence of morphine no attempt was made to purify the remaining salt but it was decomposed directly to obtain the active acid.

***d*-2-(3-Bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(acetic Acid).**—To 0.7 g. of the less soluble salt was added 40 cc. of cold 5% hydrochloric acid and the product extracted with ether. The ether was well washed with further quantities of acid and then with water and was dried over anhydrous magnesium sulfate. The majority of the ether was then removed on the steam-bath and petroleum ether (65–110°) was added until a faint cloudiness appeared. The solution was set to crystallize overnight and yielded 0.2 g. of an orange-colored microcrystalline material of m. p. 198–200° (corr.).

Rotation. 0.0450 g. made up to 15 cc. with methyl alcohol at 20° gave α_D −0.10°; l = 1; $[\alpha]_D^{20}$ −34.7°.

Anal. (micro). Calcd. for $C_{20}H_{19}O_6Br$: Br, 18.4. Found: Br, 18.3.

***l*-2-(3-Bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(acetic Acid).**—The remaining more soluble salt was decomposed as described for the less soluble salt above. Thus 0.4 g. of an orange-colored powder was obtained, with m. p. 205–207° (corr.).

Rotation. 0.0624 g. made up to 25 cc. with methyl alcohol at 20° gave α_D −0.04°; $l = 1$; $[\alpha]_D^{20}$ −16.8°.

Anal. (micro). Calcd. for $C_{20}H_{19}O_6Br$: Br, 18.4. Found: Br, 18.35.

This material was recrystallized from ether or petroleum ether as before and 0.1 g. of product with m. p. 205–207 (corr.) was obtained.

Rotation. 0.0480 g. made up to 20 cc. with methyl alcohol at 20° gave α_D −0.045°; $l = 1$; $[\alpha]_D^{20}$ −18.8°.

2-(3-Bromo-2,4,6-trimethylphenyl)-5-methylhydroquinone-3,6-di-(acetic Acid) (XVI).—A solution of 0.4 g. of the quinone diacetic acid (XV) in 60 cc. of absolute alcohol was reduced by hydrogen at 33 lb. pressure for twenty minutes in the presence of 0.1 g. of platinum oxide catalyst. The pale yellow solution was filtered and concentrated to 15 cc. During the concentration a small quantity of stannous chloride was added to prevent oxidation to the quinone. Water and a little hydrochloric acid were added to the concentrated solution and the product allowed to crystallize. It was recrystallized from 40% ethyl alcohol being obtained as a colorless crystalline powder of m. p. 242–245° (decomp. corr.) in a yield of 0.2 g.

Anal. (micro). Calcd. for $C_{20}H_{21}O_6Br$: Br, 18.4. Found: Br, 17.9.

Summary

1. A phenylquinone has been prepared and resolved into optical enantiomorphs due presumably to restricted rotation between the rings.

2. The compound 2-(3-bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(acetic acid) (XV) was formed by the following series of reactions: mesitylene and toluquinone to 2-(2,4,6-trimethylphenyl)-5-methylhydroquinone (I); bromination of (I) to 2-(3-bromo-2,4,6-trimethylphenyl)-2,6-dibromo-5-methylhydroquinone (IV); oxidation of (IV) to the corresponding quinone (VI); reaction of (VI) with sodium cyanoacetic ester to give 2-(3-bromo-2,4,6-trimethylphenyl)-5-methylbenzoquinone-3,6-di-(ethyl cyanoacetate) (XII); saponification of (XII) to the compound desired (XV). Resolution of (XV) was accomplished through the morphine salt.

3. A discussion is also given of (a) the peculiar properties of (XV); (b) other attempted methods of obtaining resolvable phenylquinones; (c) expected results from a consideration of x-ray values.

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