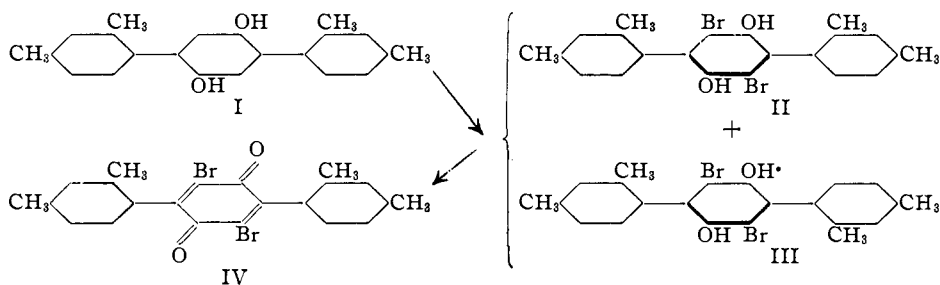


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Stereochemistry of Biphenyls. XLVII.¹ Certain 3,6-Di-(2,4-dimethylphenyl)-hydroquinones and their DerivativesBY ROGER ADAMS AND G. C. FINGER²

Browning and Adams³ condensed *m*-xylene with *p*-benzoquinone to give 3,6-di-(2,4-dimethylphenyl)-hydroquinone (I). Upon bromination of this compound, two diastereoisomeric 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinones (II and III) were readily formed and separated from each other by their different solubilities.



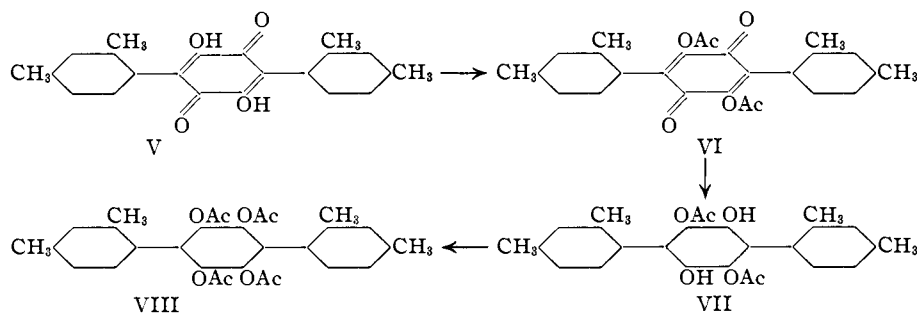
The two dibromohydroquinones (II and III) formed their own characteristic diacetates and tetranitrodiacetates. On the other hand, the oxidation of II or III gave the same 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone (IV). Reduction of IV gave a mixture of II and III. From this it is evident that a methyl, bromine, hydroxyl, and hydrogen in the 2,2',6,6'-positions of a biphenyl are sufficient to cause restricted rotation. However, in a phenylquinone, a bromine, methyl and hydrogen in addition to the carbonyl will not cause restricted rotation.

methylphenyl)-2,5-dihydroxyquinone (V) which formed the diacetyl derivative (VI). This in turn was reduced to the diacetoxy hydroquinone (VII) which upon acetylation gave 3,6-di-(2,4-dimethylphenyl)-1,2,4,5-tetraacetoxybenzene (VIII).

In none of these derivatives was the presence of diastereoisomeric forms observed. It may thus

be deduced that in a biphenyl, two acetoxy, a methyl and a hydrogen or one acetoxy, a hydroxyl, a methyl and a hydrogen in the 2,2',6,6'-positions will not cause restricted rotation.

On the basis of atomic radii, two hydroxyls, a methyl, and a hydrogen in the 2,2',6,6'-positions of a biphenyl should result in a slightly restricted rotation, provided a rather rigid coaxial formula is assumed. Since greater mobility is always observed in 2,2',6-trisubstituted biphenyls, to which group the products studied belong, than in 2,2',6,6'-tetrasubstituted compounds, it is not sur-



The investigation has now been extended to analogous derivatives. The dibromoquinone (IV) upon treatment with alkali gave 3,6-di-(2,4-di-

prising that the substances described show absence of restricted rotation. Apparently, the acetoxy groups are not sufficiently larger than the hydroxyl to modify the results.

Experimental

3,6-Di-(2,4-dimethylphenyl)-hydroquinone (I) and 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromo-

(1) For previous paper see Adams and Cairns, *THIS JOURNAL*, **61**, 2179 (1939).

(2) An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry.

(3) Browning and Adams, *THIS JOURNAL*, **52**, 4098 (1930).

hydroquinones (II and III).—The procedures used for the preparation of these compounds were those described by Browning and Adams.³ The preparation of the former was modified in that the original reaction mixture was not allowed to stand overnight but worked up after the addition of the quinone was complete and the mixture had been stirred for two hours. The yield by these former authors was miscalculated as it should have been about 15% as obtained in this investigation.

3,6 - Di - (2,4 - dimethylphenyl) - 2,5 - dihydroxyquinone (V).—To a cold solution of 21 g. of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone (m. p. 192–193°) in 1200 cc. of ethanol was added with stirring a cold solution of 180 g. of sodium hydroxide in 720 cc. of water. The rate of addition was controlled so that no appreciable rise in temperature took place. The mixture was allowed to come to room temperature and stirred continuously for twenty-four hours. It was then poured with stirring into ice and concentrated hydrochloric acid was added until the mixture was just acid to litmus. During this neutralization the temperature was maintained at 25° by the addition of ice. The dihydroxyquinone separated as a red precipitate which was coagulated by heating on a steam-bath and allowing to stand for several hours. The crude product weighed 14.5 g. (94%). No satisfactory solvent was found for this product and the sample for analysis was obtained by hydrolysis of the pure diacetate. When obtained in this manner it recrystallized from hot benzene as small red needles (m. p. 282–284°).

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.82; H, 5.79. Found: C, 75.52; H, 5.86.

3,6 - Di - (2,4 - dimethylphenyl) - 2,5 - diacetoxyquinone (VI).—To a solution of 14.5 g. of crude 3,6-di-(2,4-dimethylphenyl)-2,5-dihydroxyquinone in 50 cc. of hot pyridine was added 50 cc. of acetic anhydride and the mixture was then refluxed for fifteen minutes. Upon cooling the diacetate precipitated. After filtering, washing with a little acetic anhydride, then with water containing a small amount of hydrochloric acid the crude product was dried and purified from ethanol or butanol. It crystallized in bright yellow needles, m. p. 186–188°.

Anal. Calcd. for $C_{26}H_{24}O_6$: C, 72.19; H, 5.59. Found: C, 72.57; H, 5.8.

The filtrate from the original reaction mixture of diacetate upon dilution with a liter of water resulted in the separation of unreacted dihydroxyquinone.

A solution of 0.52 g. of pure diacetoxyquinone in 10 cc. of hot glacial acetic acid and 2 cc. of dilute hydrochloric acid was refluxed for a few minutes. Hydrolysis took place rapidly and small red needles of the dihydroxyquinone separated which were readily purified from benzene, m. p. 282–284°.

3,6 - Di - (2,4 - dimethylphenyl) - 2,5 - diacetoxyhydroquinone (VII).—A solution of 2 g. of 3,6-di-(2,4-dimethylphenyl)-2,5-diacetoxyquinone (m. p. 186–188°) in 270 cc. of hot ethanol was heated with 1 g. of stannous chloride and the mixture refluxed for fifteen minutes. The deep color of the original solution changed to faint yellow. The mixture was poured into a liter of 4 *N* hydrochloric acid, stirred and allowed to stand until coagulation took place. The crude product weighed 1.5 g. (75%). It was purified best from hot butanol forming white crystals, m. p. 213–215°.

Anal. Calcd. for $C_{26}H_{26}O_6$: C, 71.85; H, 6.03. Found: C, 71.99; H, 5.73.

3,6 - Di - (2,4 - dimethylphenyl) - 1,2,4,5 - tetraacetoxybenzene (VIII).—Acetylation was carried out on crude diacetoxyhydroquinone, either in acetone or in pyridine; the latter proved to be the better procedure. A solution of 1.9 g. of diacetoxyhydroquinone in 20 cc. of hot acetic anhydride, 3–5 cc. of pyridine and a pinch of stannous chloride was refluxed. In the course of a few minutes a heavy precipitate of the tetraacetoxy compound formed. The reaction mixture was poured into 100 cc. of water and 20 cc. of concentrated hydrochloric acid. The crude product weighed 1.9 g. (84%). It was purified from butanol, forming large flake-like crystals, m. p. 276–278°.

Anal. Calcd. for $C_{30}H_{30}O_8$: C, 69.46; H, 5.83. Found: C, 69.26; H, 6.01.

The tetraacetoxy compound just described was taken in the crude state and crystallized from four different solvents, acetic anhydride, acetone, methanol, and butanol. In no case was it possible to obtain more than a single individual compound.

Summary

3,6 - Di - (2,4 - dimethylphenyl) - 2,5 - dibromoquinone was converted by the action of alkali to 3,6 - di - (2,4 - dimethylphenyl) - 2,5 - dihydroxyquinone. This was acetylated to the diacetoxyquinone which was reduced to 3,6-di-(2,4-dimethylphenyl) - 2,5 - diacetoxyhydroquinone. Acetylation of this last product gave 3,6-di-(2,4-dimethylphenyl)-1,2,4,5-tetraacetoxybenzene.

In no case were diastereoisomeric forms obtained. It is thus concluded that two acetoxy groups, a methyl, and a hydrogen or one acetoxy group, one hydroxyl, a methyl, and a hydrogen in the 2,2',-6,6'-positions of a biphenyl will not cause restricted rotation.

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