[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

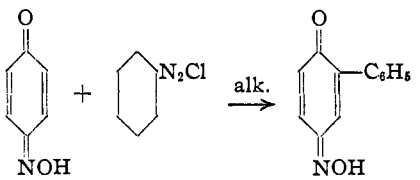
# An Optical Method for the Study of Reversible Organic Oxidation–Reduction Systems. IV. Arylquinones

BY D. E. KVALNES[1]

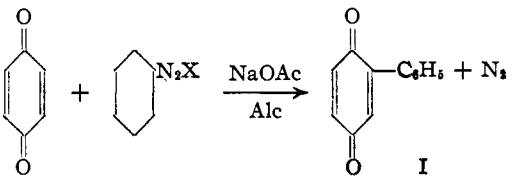
It is well known that the potential of the quinone–hydroquinone system is usually altered radically by substituents attached to the quinone nucleus, but there are as yet no data from which to determine whether the effect of a substituent can be transmitted through a phenyl group. It thus seemed of interest to study a series of phenylquinones with various substituents situated in the aryl group.

The methods known for preparing such compounds are not numerous. The Friedel–Crafts reaction affords a useful method of obtaining 2,5-diphenylquinone but it is applicable neither to the preparation of the monophenyl compound nor to aryl-substituted quinones of known structure. 2-Phenyl-1,4-naphthoquinone can be prepared by the oxidation of 2-phenylnaphthalene, but the hydrocarbon is not easily accessible and the method is of course not a general one. Other special methods have been reported by Fichter and Sulzberger[2a] and by Borsche and Schotten.[2b] Borsche[3] made the interesting discovery that benzene diazonium chloride reacts with *p*-nitrosophenol to give, instead of an azo compound, 2-phenyl-4-nitrosophenol, from which phenylbenzoquinone can be obtained by reduction and oxidation. The over-all yield, however, was only 8% of the theoretical.

Since *p*-nitrosophenol probably reacts in the quinone-oxime form, the reaction of Borsche may be represented as



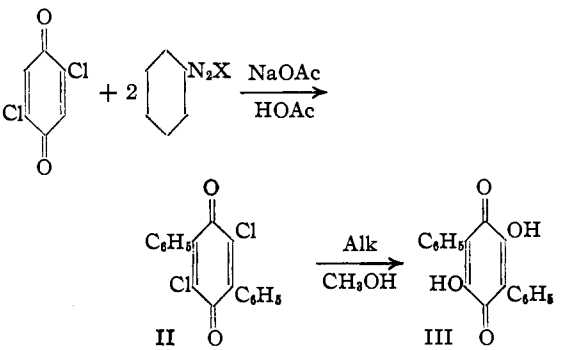

A reaction closely akin to this has been reported in the recent patent literature.[4] It is stated that an alcoholic solution of quinone reacts with aromatic diazo compounds, in the presence of sodium acetate, to give phenyl quinones




Since this appeared to offer a promising method of obtaining the aryl-substituted quinones desired, the reaction has been studied and applied to various benzo- and naphthoquinones.

The reaction cited in the equation proceeds smoothly and in 55–85% yields. The phenylquinone (I) can be caused to react further to give 2,5-diphenylquinone and tetraphenylquinone, although neither product has been obtained in good yield.

*p*-Xyloquinone, upon treatment with one mole of diazotized *m*-nitroaniline, gave the mono-substitution product and a small amount of the di-substitution product. The reaction between an acetic acid solution of 2,5-dichlorobenzoquinone and an excess of diazotized aniline gave the diphenyl substitution product (II), which was readily hydrolyzed with alcoholic alkali to give polyporic acid (III), a coloring matter in fungi.[5]




1,4-Naphthoquinone is not so reactive as benzoquinone but when treated with one mole of diazotized aniline besides unchanged 1,4-naphthoquinone, some 2-phenyl-1,4-naphthoquinone and a small amount of 2,3-diphenyl-1,4-naphthoquinone were formed. However, if a more reactive diazonium compound is used, such as diazotized *p*-aminobenzoic acid, a good yield of the mono substitution product can be obtained. 2,6-Di-

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(2) (a) Fichter and Sulzberger, *Ber.*, **37**, 878 (1904); (b) Borsche and Schotten, *ibid.*, **50**, 596 (1917).

(3) Borsche, *Ber.*, **32**, 2935 (1899); *Ann.*, **312**, 211 (1900).

(4) U. S. Patent 1,735,432, *C. A.*, **24**, 732 (1930); German Patent 508,395, *C. A.*, **25**, 712 (1931).

(5) (a) Kögl, *Ann.*, **447**, 78 (1926); (b) P. R. Shildneck and R. Adams, THIS JOURNAL, **53**, 2373 (1931).

methyl-1,4-naphthoquinone reacted with diazotized aniline to give a poor yield of 2,6-dimethyl-3-phenyl-1,4-naphthoquinone. An acetic acid solution of 1,2-naphthoquinone on treatment with diazotized *p*-aminobenzoic acid gave a good yield of crude reaction product from which the di-substitution product was isolated. The mono-substitution product or products were not obtained in a pure state. It should be noted that though benzoquinone reacted with diazotized *o*-nitroaniline, 2,6-dimethylaniline and α-naphthylamine only tars were obtained from which no pure reaction products were isolated. 2-Methoxy-1,4-naphthoquinone appeared to undergo no reaction at all with diazotized aniline.

Thus it appears that the reaction is quite general in scope and that almost any open position in the benzo- and naphthoquinones is subject to the introduction of an aryl group.

Kehrmann and Goldenberg[6] found that 2-hydroxy-1,4-naphthoquinone forms hydroxy azo compounds upon reaction with diazotized amines, and the observation has been confirmed in the present work. With a hydroxyl group attached to the quinoid nucleus normal coupling occurs.

**Oxidation–Reduction Potentials.**—The results of the comparative study of the various phenylated quinones are summarized in Table I. The $E_0'$ values are the relative potentials of the systems in benzene as determined by the optical method given in the preceding papers of this series.[7] The $E_0$ values are the electrometrically determined potentials in a 70% alcoholic buffer solution. The potentials as given are averages of several measurements in each case.

TABLE I

OXIDATION–REDUCTION POTENTIALS AT 25°

| Substituent on benzoquinone (system named as oxidant) | Relative potential in benzene; benzoquinone = 0.711 $E_0'$, v. | Normal potential by e. m. f. measurement;[a] benzoquinone = 0.722 $E_0$, v. |
|---|---|---|
| —$C_6H_4NO_2$ (*p*) | 0.721 | ... |
| —$C_6H_4NO_2$ (*m*) | .721 | ... |
| —$C_6H_4$—$C_6H_5$ (*p*) | .719 | 0.695 |
| —$C_6H_4COOC_2H_5$ (*p*) | .716 | ... |
| —$C_6H_4COOH$ (*p*) | ... | .715 |
| —$C_6H_4COCH_3$ (*p*) | .715 | .719 |
| —$C_{10}H_7$ (β) | .713 | .699 |
| —$C_6H_4CH_3$ (*p*) | .703 | .691 |
| —$C_6H_5$ | .698 | .694 |
| —$C_6H_4OCH_3$ (*p*) | .692 | .683 |
| —2,5-Diphenyl | .689 | .673 |

[a] 70 alcoholic solution, 0.2 *N* in HCl and 0.2 *N* in LiCl.

It may be noted that the potentials of the substituted quinones are lower with respect to that of benzoquinone in alcoholic solution than they are in benzene solution. This effect has been noted previously. It is clear from the figures that the phenyl group produces only a moderate lowering in the potential of the parent compound. The effect amounts to 13 mv. in benzene and 28 mv. in alcoholic solution, as compared with a lowering of 58 mv. in benzene or 55 mv. in alcohol, produced by the methyl group.[7c] Meta and para substituents in the aryl nucleus of phenylquinone have surprisingly little influence on the potential of the compound, particularly in benzene solution. In alcoholic solution the differences are slight but they appear to be insufficiently marked to be of significance. The unsaturated carboxyl and acetyl groups produce some increase in potential, while the potential is lowered by a methyl group and still more so by a methoxyl group. These effects are in the same direction as when the groups are joined directly to the quinoid nucleus, but they are of greatly decreased magnitude.

## Experimental Part

**1. Preparation of Materials. Monoarylbenzoquinones.**—0.05 Mole of the aromatic amine was diazotized in the ordinary way, a minimum of water being desirable. The clear diazonium solution was added to a well stirred solution of 0.055 to 0.06 mole of benzoquinone dissolved in 125 cc. of alcohol. An excess of sodium acetate was added to the diazonium solution either before addition or immediately afterward. The resulting mixture was stirred and not allowed to rise above room temperature. Nitrogen was evolved and the aryl quinone slowly separated from solution. The mixture was filtered in about 45 minutes; the filtrate was strongly diluted with water to yield an additional crop of the quinone. The yield of crude product varied from 55 to 85%. The quinones were reduced to the hydroquinones with stannous chloride or sodium hydrosulfite.

**Other Reactions.**—The other reactions were carried out in a similar manner except that more alcohol was necessary to keep the reacting quinone in solution. The 2,5-dichlorobenzoquinone and 1,2-naphthoquinone were dissolved in acetic acid, in which they are more soluble than in alcohol. In the case of 1,4-naphthoquinone the separation of the products was somewhat difficult because the solubilities of 1,4-naphthoquinone and 2-phenyl-1,4-naphthoquinone are much alike. Furthermore, decomposition products from the diazotized aniline must be separated. The best procedure found was to reduce the reaction product by warming in acetic acid and adding zinc dust and finally a little concd. hydrochloric acid. The 2,3-diphenyl-1,4-naphthohydroquinone is quite insoluble in cold acetic acid

(6) Kehrmann and Goldenberg, *Ber.*, **30**, 2125 (1897).

(7) (a) Hunter and Kvalnes, THIS JOURNAL, **54**, 2869 (1932); (b) Kvalnes, *ibid.*, **56**, 667 (1934); (c) **56**, 670 (1934).

and was filtered off. Dilution of the filtrate precipitated a mixture of the naphthohydroquinone and the monophenyl derivative, the by-products from the diazonium compound remained in solution. The naphthohydro-

TABLE II

ARYLQUINONES AND RELATED COMPOUNDS

| Quinone | M. p., °C. | Recryst. solvents | Color and cryst. form | Formula | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|---|
| Phenylbenzoquinone | 114 | Ligroin | Yellow plates | $C_{12}H_8O_2$ | | | | |
| *p*-Biphenylbenzo- | 199 | $CHCl_3$–ligroin | Orange-yellow plates | $C_{18}H_{12}O_2$ | 83.08 | 4.62 | 82.67 | 4.67 |
| β-Naphthylbenzo- | 173–174 | $C_6H_6$–ligroin | Orange needles | $C_{16}H_{10}O_2$ | 82.05 | 4.27 | 82.26 | 4.56 |
| *p*-Tolylbenzoquinone | 138–139 | $C_6H_6$–ligroin | Orange yellow plates | $C_{13}H_{10}O_2$ | 78.79 | 5.05 | 78.52 | 5.23 |
| *p*-Anisylbenzo-quinone[a] | 120–121 | Aq. alc., then $C_6H_6$–ligroin | Red rods and yellow plates | $C_{13}H_{10}O_3$ | | | | |
| *p*-Acetylphenylbenzo- | 152–153 | $CHCl_3$–ligroin | Yellow micro crystals | $C_{14}H_{10}O_3$ | 74.34 | 4.43 | 74.11 | 4.52 |
| *p*-Carboxyphenyl-benzoquinone | 220–221 dep. | Acetic acid | Orange yellow needles | $C_{13}H_8O_4$ | 68.42 | 3.53 | 68.58 | 3.72 |
| *p*-Carbethoxyphenyl-benzoquinone | 123–124 | $C_6H_6$–ligroin | Yellow micro crystals | $C_{15}H_{12}O_4$ | 70.31 | 4.69 | 70.00 | 4.74 |
| *p*-Nitrophenylbenzo- | 137 | Alcohol | Yellow plates and needles | $C_{12}H_7O_4N$ | 62.88 | 3.08 | 63.14 | 3.19 |
| *m*-Nitrophenylbenzo- | 105–107 | Alcohol | Yellow micro crystals | $C_{12}H_7O_4N$ | 62.88 | 3.08 | 62.85 | 3.31 |
| 2,5-Diphenylbenzo- | 214 | Acetic acid | Yellow plates | | | | | |
| Tetraphenylbenzo- | 311–315 | Acetic acid | Fine orange needles | $C_{30}H_{20}O_2$ | 87.34 | 4.89 | 87.13 | 5.13 |
| 2,5-Dichloro-3,6-diphenylbenzoquinone | 208–209 | Alcohol | Large golden plates | $C_{18}H_{10}O_2Cl_2$ | 65.65 | 3.06 | 65.70 | 3.24 |
| 2,5-Dihydroxy-3,6-diphenylbenzoquinone | 305 | Toluene | Bronze plates | ..... | | | | |
| 2,5-Dimethyl-3-(*m*-nitrophenyl)-benzo- | 123–124 | Alcohol | Yellow micro crystals | $C_{14}H_{11}O_4N$ | 65.37 | 4.28 | 65.39 | 4.42 |
| 2,5-Dimethyl-3,6-di-(*m*-nitrophenyl)-benzoquinone | 241–242 | Dioxane + $H_2O$ | Yellow micro cryst. | $C_{20}H_{14}O_6N_2$ | 63.49 | 3.70 | 63.12 | 3.86 |
| *p*-Biphenylhydro- | 177–178 | $CHCl_3$ | White plates | $C_{18}H_{14}O_2$ | 82.41 | 5.38 | 82.13 | 5.41 |
| β-Naphthylhydro- | 172–174 | Aq. alc. | Small white needles | $C_{18}H_{12}O_2$ | 81.32 | 5.13 | 80.97 | 5.35 |
| *p*-Tolylhydroquinone | 123 | $H_2O$ | Small white crystals | $C_{13}H_{12}O_2$ | 77.96 | 6.05 | 77.79 | 6.24 |
| *p*-Anisylhydroquinone | 111–112 | $C_6H_6$–ligroin | White micro crystals | $C_{13}H_{12}O_3$ | 72.19 | 5.60 | 72.33 | 5.81 |
| *p*-Acetylphenylhydro- | 192–193 | $H_2O$ then $CHCl_3$ | Small white crystals | $C_{14}H_{12}O_3$ | 73.65 | 5.31 | 73.61 | 5.55 |
| *p*-Carboxyphenylhydroquinone-hydrate | 230–231 | $H_2O$ | White needles | $C_{13}H_{12}O_5$ | 62.88 | 4.87 | 62.93 | 5.03 |
| *p*-Carboxyphenyl hydroquinone | 230–231 | Hydrate dried at 100° in vac. | | $C_{13}H_{10}O_4$ | 67.80 | 4.38 | 67.77 | 4.56 |
| 2-Phenyl-1,4-naphthoquinone | 110 | Alcohol | Fine yellow needles | | | | | |
| 2,3-Diphenyl-1,4-naphthoquinone | 135–136 | Ligroin | Bright yellow cryst. | $C_{22}H_{14}O_2$ | | | | |
| 2-(*p*-Carboxyphenyl)-1,4-naphthoquinone | 303–305 dep. | Acetic acid | Fine yellow needles | $C_{17}H_{10}O_4$ | 73.35 | 3.63 | 73.32 | 3.82 |
| 2,6-Dimethyl-3-phenyl-1,4-naphthoquinone | 114–115 | Alcohol | Pale yellow needles | $C_{17}H_{14}O_2$ | 81.57 | 5.64 | 81.99 | 5.58 |
| 2-Hydroxy-3-(phenylazo)-1,4-naphtho- | 225–226 dep. | Acetic acid | Bright red plates | $C_{16}H_{10}O_3N_2$ | 69.06 | 3.60 | 68.89 | 3.88 |
| 3,4-Di-(*p*-carboxyphenyl)-1,2-naphthoquinone | 260–262 | Acetic acid | Bright red crystals | $C_{24}H_{14}O_6$ | 72.36 | 3.54 | 72.18 | 3.77 |
| 1,4-Diacetoxy-2-(*p*-carboxyphenyl)-naphthalene[b] | 200–201 | Aq–acetic acid | Fine white needles | $C_{21}H_{16}O_6$ | 69.21 | 4.43 | 68.80 | 4.63 |
| 1,2,4-Triacetoxy-2,5-diphenylbenzene[c] | 191–192 | Alcohol | Small white crystals | $C_{24}H_{20}O_6$ | 71.26 | 4.99 | 70.92 | 5.15 |

[a] *Ann.*, **482**, 105 (1930). [b] From the reductive acetylation of 2-(*p*-carboxyphenyl)-1,4-naphthoquinone. [c] 2,5-Diphenylbenzoquinone underwent the Thiele reaction with acetic anhydride and sulfuric acid to give the triacetate of the hydroxyhydroquinone.

quinones were then oxidized by dissolving in cold acetic acid and treating with chromic oxide dissolved in a little water. Strong dilution with water precipitated the quinones which were fractionally crystallized from alcohol.

2. **Potential Determination.**—(a) The relative potentials in benzene were measured according to the directions previously outlined.[7] (b) The potentiometric determinations were made by titrating a solution of the phenyl hydroquinone in the 70% alcoholic solution with tetrabromo-*o*-benzoquinone. The reaction cell was connected to a hydrogen electrode by a bridge containing the same solvent. Good agreement was observed among the titration curves for each substance.

The author wishes to express his sincere appreciation for the interest and advice of Professor L. F. Fieser during the course of this research.

## Summary

An investigation was made of the reaction between a series of quinones and aromatic diazonium compounds to give arylquinones. The reaction can be utilized to give polyarylquinones. Potential measurements were made with a number of the quinone–hydroquinone systems and the effects of substitution and solvent upon the potentials have been discussed.

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[CONTRIBUTION FROM KENT AND JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

# The Preparation of Aldonic and Saccharinic Acid Amides in Liquid Ammonia

BY J. W. E. GLATTFELD AND DUNCAN MACMILLAN*

The desirability of obtaining erythrose in its optically active as well as inactive forms has been mentioned recently.[1] These tetroses are needed in order to make possible certain plans for a study of the conversion of the tetroses into the $C_4$-saccharinic acids. At the present time these sugars are not available in pure condition and efforts are being made in this Laboratory to produce *dl*-erythrose by the reduction of *dl*-erythronic lactone. The methods of reduction so far tried, when applied to *dl*-erythronic lactone, have not produced the tetrose. These experiments were carried out practically entirely in aqueous solution. It seemed desirable to try the reduction of the lactone also in other media, and liquid ammonia was therefore used. These reduction experiments in liquid ammonia led at once to the new procedure for the preparation of the amides that is reported below.

Very little work has been done so far with the carbohydrates or their derivatives in liquid ammonia. The most recent work reported in the literature along this line is that of Muskat.[2] This author apparently did not work with the sugar acids, however, and was interested especially in the alkylation of the sugars.

Amides of aldonic and saccharinic acids have been prepared in a number of ways, such as the solution of the lactones in aqueous ammonia,[3] the treatment of alcoholic solutions with ammonia gas,[4] and the hydrolysis of nitriles.[5] As amide formation in liquid ammonia proceeds rapidly, and requires little apparatus, the new method has some advantages over those previously employed. Thus several attempts to obtain *dl*-erythronamide by the procedure described by Weerman[4] were made. In each case the product was a gum which would not crystallize even when subjected to scratching, cooling, evacuation or trituration. The liquid ammonia technique was then used, and the resulting gum crystallized on standing in a vacuum desiccator. Also in the preparation of certain amides, in which it is otherwise necessary to work with absolute alcohol in anhydrous systems, the liquid ammonia technique is far more convenient.

While all aldonic and saccharinic acid lactones used so far have yielded amides at liquid ammonia temperatures, this is not true of some other lactones. For example, it is found that coumarin may be recovered from liquid ammonia unchanged. The lactone of γ-hydroxybutyric acid is not affected by liquid ammonia at its boiling point, although it is ammonolyzed at room temperature when sealed in a bomb with liquid ammonia. An extended study of ammonolysis of lactones is under way, and it is hoped that it may lead to a further understanding of the lactone bond.

*The material n this article will be used by Duncan Macmillan as part of his dissertation for the degree of Doctor of Philosophy in the University of Chicago.

(1) Glattfeld and Forbrich, THIS JOURNAL, **56**, 1209 (1934).

(2) Muskat, *ibid.*, **56**, 693 (1934).

(3) Hudson and Komatsu, *ibid.*, **41**, 1141 (1919).

(4) Weerman, *Rec. trav. chim.*, **37**, 24 (1918).

(5) Kiliani, *Ber.*, **19**, 3033 (1886).