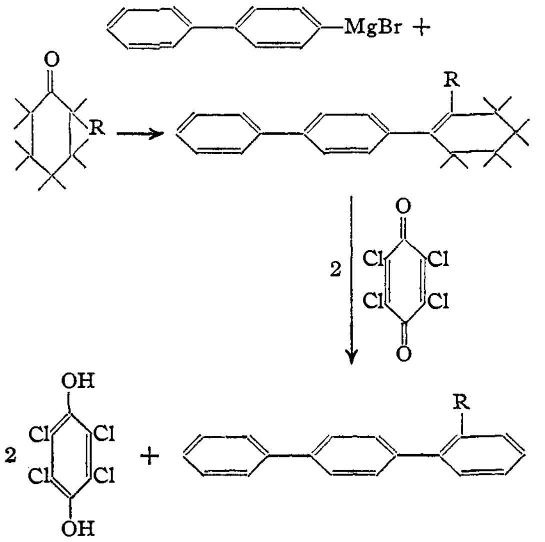
NOTES

Low Temperature Dehydrogenations. II

By Richard T. Arnold, Clair Collins and Wm. Zenk

In an introductory report[1] it was shown that several different types of hydroaromatic compounds can be dehydrogenated at comparatively low temperatures by making use of chloranil or other quinones with high oxidation potentials.

This method has now been extended to reactions leading to the preparation of unsymmetrical biphenyl, terphenyls, etc., according to the scheme



Of course, the synthesis of substituted cylohexenes in the first step here is limited to those molecules which do not have groupings present which will react rapidly with the Grignard reagent. However, these groups (—NO_2, etc.) are not affected in the dehydrogenation reaction with chloranil as they are when sulfur or selenium is used.

A convenient and cheap synthesis of chloranil has been described[2] and confirmed in this Laboratory. It makes use of the action of concentrated hydrochloric acid on benzoquinone in the presence of hydrogen peroxide (30%). This preparation practically eliminates the cost of these dehydrogenations, especially when it is realized that three-fourths of the hydroquinone which results can be recovered and converted quantitatively to the quinone by nitric acid.

It has been demonstrated recently[3] that sulfur can be used to prepare certain unsymmetrical biphenyls in satisfactory yields, but in the terphenyl and phenylnaphthalene series the classical dehydrogenations are disappointing.[4,5] The procedure described in this paper gives very satisfactory yields (50–70%) in all of these cases.

Thermal rearrangements have been found to be commonplace in alkyl and arylnaphthalenes in the region of 300.[6] The use of low temperature dehydrogenation here is obvious.

Recently, the classical synthesis of terphenyls by the reaction between nitrosoamines and hydrocarbons has been extended to new cases and the conditions of the synthesis greatly improved.[7] While this method is very general, the yields reported are not comparable with those obtained in our investigations. The results obtained are summarized in Table I.

Table I

Compound	Product	Yield, %
1-*p*-Biphenylcyclohexene	Terphenyl	47
1-*p*-Biphenyl-2-methylcyclohexene	2-Methylterphenyl	72
1-α-Naphthylcyclohexene	α-Phenylnaphthalene	67
1-β-Naphthylcyclohexene	β-Phenylnaphthalene	72
1-*o*-Tolylcyclohexene	2-Methylbiphenyl	72

At present we are investigating the efficacy of chloranil as a dehydrogenating agent for straight chain hydrocarbons.

Experimental

1-*p*-Biphenyl-2-methylcyclohexene.—Ninety-five cubic centimeters of a Grignard solution (prepared from 100 g. of 4-bromobiphenyl, in 500 cc. of ether) was treated with 12 cc. of 2-methylcyclohexanone in an equal volume of benzene. The reaction mixture was decomposed with dilute sulfuric acid. Dehydration was accomplished by heating for one hour with 20% oxalic acid. The benzene layer was fractionated and the residue distilled in a sausage flask; yield 6.75 g.

2-Methylterphenyl.—A solution containing 3.58 g. of the above cyclohexene derivative, 7.3 g. of chloranil and 25 cc. of commercial xylene was refluxed for ten hours, cooled, and filtered, giving 4.55 g. of chloranilhydroquinone. The filtrate was diluted with an equal quantity of ether,

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(1) Arnold and Collins, This Journal, **61**, 140 (1939).

(2) M. Gallatti, *Ann. chim. applicata*, **22**, 602 (1932).

(3) Sherwood, Short and Stansfield, *J. Chem. Soc.*, 1832 (1932).

(4) Von Braun, Irmisch and Nelles, *Ber.*, **66**, 1472 (1933).

(5) Fieser and Hershberg, This Journal, **60**, 940 (1938).

(6) Mayer and Schiffner, *Ber.*, **67**, 67 (1934).

(7) France, Heilbron and Hey, *J. Chem. Soc.*, 1283 (1939).

washed with dilute alkali, dried, and fractionated. The residue was distilled in a small sausage flask and yielded 2.53 g. of the methylterphenyl which melted at 91–92° after recrystallization from methanol.[7]

Anal. Calcd. for $C_{19}H_{16}$: C, 93.34; H, 6.60. Found: C, 92.97; H, 6.58.

Terphenyl.—A sample (1.46 g.) of *p*-biphenylcyclohexene, 3.3 g. of chloranil and 18 cc. of dry xylene were refluxed and the reaction worked up as described in the preceding section; yield of terphenyl 0.63 g. The product melted at 210–211.5°. The identity of the substance was checked by preparing the nitro derivative; melting point 275°.[7]

α-Phenylnaphthalene.—Five grams of α-naphthylcyclohexene prepared as described in the literature[8] was refluxed with 11.8 g. of chloranil in 20 cc. of xylene for five hours. The reaction mixture was cooled, diluted with an equal volume of petroleum ether (30–60°) and filtered, yielding 8.4 g. of chloranil hydroquinone. The remainder was removed by basic extraction. The resulting fractionation yielded 3.33 g. of α-phenylnaphthalene. The structure was checked by the formation of its nitro derivative which melted at 129–130°. The literature reports 132°.[8]

β-Phenylnaphthalene.[5]—Following the same procedure as given above, β-naphthylcyclohexene was dehydrogenated to give β-phenylnaphthalene in a yield of 72%. The constitution of this molecule was proved by direct oxidation to β-phenyl 1,4-naphthoquinone; melting point 108–109°.[9]

2-Methylbiphenyl.—This substance was obtained by refluxing a solution containing 12 g. of *o*-tolylcyclohexene, 36 g. of chloranil, and 115 cc. of xylene. The yield of pure product obtained by fractionation was 8.5 g. (72.6%).[3]

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[8] Weiss and Waidich, *Monatsh.*, **46**, 456 (1925).

[9] Chattaway and Lewis, *J. Chem. Soc.*, **65**, 873 (1894).

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Catalytic Action of 8-Hydroxyquinoline on the Oxidation of *p*-Phenylenediamine

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8-Hydroxyquinoline can, under certain conditions, catalyze the oxidation of cysteine to cystine.[2] It has now been shown that it has a catalytic effect on the oxidation of *p*-phenylenediamine and certain related substances. Figure 1 shows this effect on *p*-phenylenediamine recrystallized from water and from alcohol. The oxygen uptake was measured at 37° in the Warburg apparatus. Successive recrystallizations of the diamine have no effect on the catalysis, showing that the 8-hydroxyquinoline is not simply removing an antioxidant. Addition of metal ions such as the cupric, ferric and vanadate does not enhance the catalytic effect which is, therefore, probably not due to a metal-8-hydroxyquinoline complex. The catalysis is not affected by 0.02 *M* cyanide or pyrophosphate. It has an optimum *p*H at about 6.5 and the rate falls off rapidly in alkaline solutions. The oxidation product is deeply colored, which is characteristic of the polymer of the quinone diamine and which can be reduced by hydrosulfite. On isolation and hydrolysis with acid it gives free ammonia. From the oxygen uptake figures a small percentage of further oxidation products must be formed which have not been isolated.

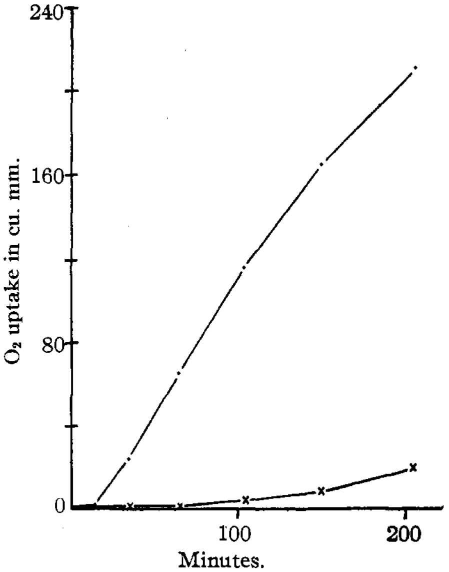

Fig. 1.—The oxygen uptake of 3.0 mg. of *p*-phenylenediamine in 2.0 cc. of water at *p*H 6.7: ×—×, control; ·—·, with 0.05 mg. of 8-hydroxyquinoline. The short latent period is characteristic.

8-Hydroxyquinoline has no effect on the oxidation of *o*-phenylenediamine, catechol or hydroquinone in acid or alkaline solutions. It has a comparatively small effect on the oxidation of *p*- and *o*-aminophenols in alkaline solutions (*p*H 7.8). 2-Hydroxyquinoline and certain other quinoline derivatives are without catalytic action.

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[1] One of us (P. H.) is indebted to the Markle Foundation for its support during this work.

[2] F. Bernheim and M. L. C. Bernheim, "Symposia on Quantitative Biology," Vol. VII, 1939, in press.

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The Mechanism of Plant Respiration

BY HAROLD HIBBERT

The discovery (see following note) in the ethanolysis products from spruce wood of methyl guaiacyl diketone alongside the previously re-