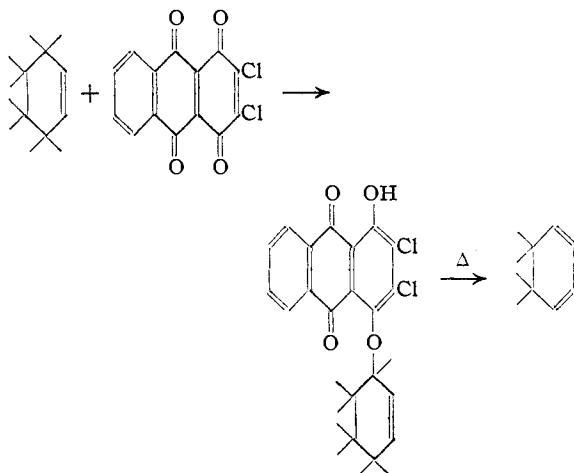


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

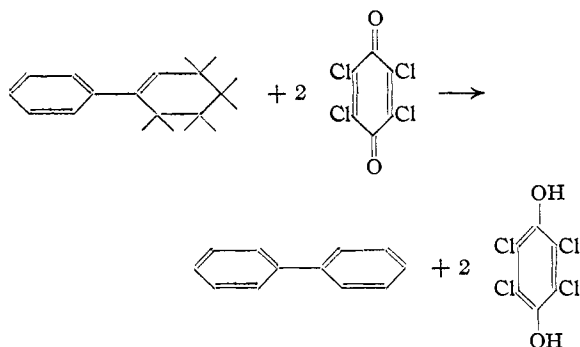
The Low Temperature Dehydrogenation of Hydroaromatic Rings

BY RICHARD T. ARNOLD AND CLAIR J. COLLINS

It has been shown¹ that certain hydrocarbons such as cyclohexene and tetralin will react with active quinones at elevated temperatures to form monoethers of a hydroquinone. These substances when pyrolyzed yield the hydroquinone and a hydrocarbon containing a new double bond, thus



In this Laboratory, we attempted to prepare phenylcyclohexadiene by this general procedure. Using chloranil as the oxidizing agent and commercial xylene (b. p. 140°) as the solvent we were unable to isolate any of the expected monoether and biphenyl was produced in good yields according to the equation



The generality of this oxidation has been studied in several cases. The negative result shown in Table I for methylcyclohexene probably is due to the fact that the reaction temperature is of necessity held at 80° unless a bomb is used. In all of the other cases, however, we found chloranil in

(1) Criegee, *Ber.*, **69B**, 2758-2761 (1936).

boiling xylene to be an effective oxidizing agent for hydroaromatic rings.

A slight oxidation of the solvent was noted over long periods of refluxing and for this reason a 5-10% excess of the quinone was used.

At the finish of the reaction a major portion of the hydroquinone can be precipitated by cooling in an ice-bath. This material after being filtered can be reoxidized to chloranil with nitric acid.

A summary of the results of this investigation is given in Table I.

TABLE I

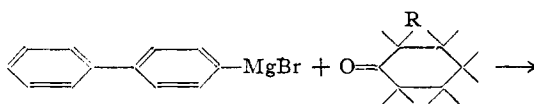
| Compound | Product | Time, hrs. | Yield, % |
|--------------------------------|------------------|------------|----------|
| 1,2,3,4-Tetrahydrophenanthrene | Phenanthrene | 22 | 56 |
| 9,10-Dihydroanthracene | Anthracene | 33 | 63 |
| Phenylcyclohexene | Biphenyl | 4 | 52 |
| 6-Methoxyflavanone | 6-Methoxyflavone | 15 | 60-70 |
| Methylcyclohexene | No reaction | .. | .. |
| Decalin | Complex mixture | .. | .. |
| Tetralin | Naphthalene | 14 | ° |

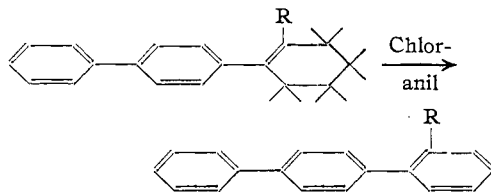
° This yield varied widely due to the ease of sublimation of naphthalene. The hydroquinone produced, however, indicated that the reaction was quite complete.

Benzoquinone has been used previously to oxidize certain dihydroaromatic compounds^{2,3} but these oxidations could even be carried out by air in basic solutions. By many comparative experiments we have been able to show that chloranil acts more quickly than benzoquinone and will function in many cases where the latter is completely ineffective. These results are in agreement with recent oxidation reduction studies in non-aqueous solutions.⁴

The disadvantages of selenium dehydrogenations are well known. It is hoped that many rearrangements caused by the high temperatures required by this reagent can be avoided by using this low temperature method.

This mild and effective dehydrogenation method opens a way to a simple procedure for the introduction of aryl groups into aromatic compounds as outlined below

(2) Koelsch and Rosenwald, *J. Org. Chem.*, **3**, 462 (1938).(3) Allen and Overbaugh, *THIS JOURNAL*, **57**, 740 (1935).(4) Kvalues, *ibid.*, **56**, 667 (1934).



A detailed report of this will be published later.

Experimental

Preparation of Phenylcyclohexene.—This compound was prepared according to Haworth.⁵

Oxidation of Phenylcyclohexene.—Fourteen cubic centimeters of xylene containing 4.57 g. of chloranil and 1.463 g. of phenylcyclohexene was refluxed for four hours. The reaction mixture was cooled and 2.9 g. of chloranil hydroquinone was separated by filtration. The mixture was diluted with an equal volume of ether, washed

(5) Haworth, *J. Chem. Soc.*, **103**, 1246 (1913).

with 4% potassium hydroxide, dried and fractionated; yield of biphenyl, 0.755 g. The structure of this sample was determined by mixed melting with an authentic sample and the preparation of 4-nitrobiphenyl as a derivative.

Other Oxidations.—The other examples listed in Table I were run in a similar fashion to that described above. The last step of course depends on the nature of the product. In each of these cases the materials were identified in the usual manner.

Summary

A low temperature procedure for the dehydrogenation of hydroaromatic rings by chloranil has been discussed.

The advantage of this method over that of selenium dehydrogenation has been pointed out.

MINNEAPOLIS, MINN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Behavior of the Dimethyl Acetals of Glucose and Galactose Under Hydrolytic and Glycoside-forming Conditions

BY M. L. WOLFROM AND S. W. WAISBROT

Hudson and co-workers¹ have prepared the dimethyl acetal of *d*-arabinose by a series of reactions discovered by them for the arabinose structure. The synthesis of the crystalline dimethyl acetals of *d*-glucose² and of *d*-galactose³ has been reported from this Laboratory. Practically simultaneously, Campbell and Link⁴ reported the synthesis of galactose dimethyl acetal. As these compounds are postulated intermediates in the Fischer glycoside synthesis,⁵ with methanol-hydrogen chloride, their behavior under such conditions is of interest. When these acetals are placed in methanol containing hydrogen chloride, a very rapid initial reaction takes place. This initial reaction is so rapid that it is necessary to use a very small amount of hydrogen chloride (0.05%) in order to follow it polarimetrically at 25°. Campbell and Link employed a methanol solution containing 0.5% hydrogen chloride at

25° with galactose dimethyl acetal and their data do not show this initial change, although their first observed specific rotation was +40°, while that of the acetal in pure methanol was recorded by them as +20°. The polarimetric data that we have obtained under glycoside-forming conditions are tabulated in Tables I and II and are diagrammed on a logarithmic time scale in Figs. 1 and 2. Following the rapid attainment of this initial maximum, the polarimetric curve for the glucose compound moves very slowly downward to a minimum and then rises very slowly. In the case of the galactose compound, the minimum in the curve is not shown with our very low concentration of hydrogen chloride but it is observable distinctly in the data of Campbell and Link at the higher concentration of hydrogen chloride.

We have investigated the reaction mixtures at the maximum and final points in the curves for their content of easily acid-hydrolyzable material (Table V) according to the procedure of Levene, Raymond and Dillon.⁶ The procedure employed by these authors was to determine the amount of

(1) Edna M. Montgomery, R. M. Hann and C. S. Hudson, *This Journal*, **59**, 1124 (1937).

(2) M. L. Wolfrom and S. W. Waisbrot, *ibid.*, **60**, 854 (1938).

(3) M. L. Wolfrom, L. J. Tanghe, R. W. George and S. W. Waisbrot, *ibid.*, **60**, 132 (1938).

(4) H. A. Campbell and K. P. Link, *J. Biol. Chem.*, **122**, 635 (1938).

(5) E. Fischer, *Ber.*, **26**, 2400 (1893).

(6) P. A. Levene, A. L. Raymond and R. T. Dillon, *J. Biol. Chem.*, **95**, 699 (1932).