

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

OXIDATION IN THE BENZENE SERIES BY GASEOUS OXYGEN III. OXIDATION OF ALPHA PHENYL CARBINOLS

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In studying the oxidation of alkyl benzenes by gaseous oxygen,¹ the writer has found that methylbenzenes yield as the only identifiable products mono-aldehydes and the corresponding acids, while hydrocarbons containing two or more carbon atoms in the side chain were found to be attacked only at the alpha carbon atom, the products being ketones. In the case of hydrocarbons with secondary alkyl groups, for example, cumene, the reaction involves loss of a methyl group together with the alpha hydrogen. Although a careful search was made in many instances no trace of an alcohol was detected in the oxidation products.

The mere absence of alcohols in the products of oxidation does not, of course, preclude the possibility of their being formed in the reactions, as it might be expected that the oxidation of hydrocarbon to alcohol would require a higher potential than the oxidation of alcohol to aldehyde or ketone. In this event the alcohol would be destroyed as rapidly as it was formed. Preliminary to an attempt to find out whether or not the alcohol stage is an intermediate one in the production of aldehydes and ketones, it was considered desirable to study the oxidation of some α -phenylcarbinols under the same conditions that were employed in the oxidation of hydrocarbons. In this connection an investigation has been made of the oxidation of methyl-, ethyl-, dimethyl-, *n*-propyl- and *isopropyl*-phenylcarbinols.

In examining the products formed from the above alcohols, it was discovered, to our surprise, that no less than three concurrent reactions took place under the conditions employed. Only one of these is a direct oxidation while the other two appear to be thermal dehydrations. These latter will be reported on more fully at a later date, so it will be sufficient for our present purpose merely to mention that one of them involves the elimination of one molecule of water from two molecules of alcohol while the other involves the loss of a molecule of water from each molecule of alcohol. The structural nature of the products of the first type of dehydration is not yet fully established but in the second type unsaturated hydrocarbons are produced.

Oxidation Products

All the secondary alcohols employed, with the exception of *isopropyl*-phenylcarbinol, underwent direct oxidation to a very limited extent, yielding small amounts of the corresponding ketones. Ethylphenyl- and

¹ Stephens, *THIS JOURNAL*, **48**, 1824, 2920 (1926).

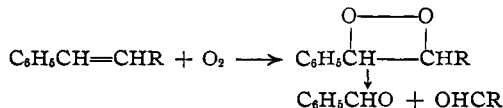
n-propylphenylcarbinols were found to be the most readily oxidized, methylphenylcarbinol was attacked very much less and, strange to say, *isopropylphenylcarbinol* was unaffected at the temperature used.

Although in the oxidation of the secondary alcohols a simple oxidation of the —CHOH— group to —CO— may take place, when tertiary alcohols are concerned (for example, dimethylphenylcarbinol) an alkyl group must be destroyed before a ketone can be formed. As acetophenone is a product in the oxidation of dimethylphenylcarbinol, this is probably what takes place, the oxidation being analogous to that of cumene,¹ the corresponding hydrocarbon, which also yields acetophenone. However, on account of there being another way (see below) in which acetophenone may be formed from dimethylphenylcarbinol, it is impossible to determine to what extent direct oxidation takes place or, indeed, whether it takes place at all.

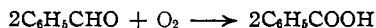
Secondary Oxidations

It has been mentioned that unsaturated hydrocarbons were produced by dehydration of the carbinols under the conditions employed. With the exception of one instance, that of the production of *isopropenylbenzene* from dimethylphenylcarbinol, no hydrocarbons were detected in the final products as they were destroyed by oxidation as rapidly as they were formed. The fact that they are actually formed from the secondary alcohols, as well as from dimethylphenylcarbinol, was demonstrated by heating a sample of ethylphenylcarbinol in an atmosphere of carbon dioxide at 102–104° for ten days, at the end of which time quite an appreciable amount of unsaturated hydrocarbon was detected. In the case of dimethylphenylcarbinol, the speed of dehydration was evidently much greater than the speed of oxidation of the product; consequently a considerable amount of hydrocarbon survived.

It is well known that in some cases auto-oxidation of substances containing the ethylenic linkage involves scission of the molecule at the double bond and by assuming this type of reaction to take place, all oxidation products isolated in the oxidation of carbinols can be satisfactorily accounted for. Considering the hydrocarbons that would result from the dehydration of the secondary carbinols, the following general equations would represent the oxidations that could take place



and



Benzaldehyde was actually isolated in only one oxidation, that of ethylphenylcarbinol, but its oxidation product, benzoic acid, was isolated in the oxidation of ethylphenyl-, *n*-propylphenyl- and *isopropylphenyl*-

carbinols. A small amount of solid acid was also obtained from methylphenylcarbinol but this was insufficient for purification. The second aldehyde which would be expected from scission of the peroxide was never isolated, as it was probably lost by volatilization or, in the case of formaldehyde, by oxidation,² under the conditions of the experiments.

On the above basis *isopropenylbenzene* (from dimethylphenylcarbinol) would be expected to yield, as oxidation products, acetophenone and formaldehyde. On oxidation of the hydrocarbon alone at 102–104°, acetophenone was formed, while the formaldehyde was lost by volatilization. On account of the fact that acetophenone is formed from the dehydration product of dimethylphenylcarbinol and is also probably a product of the direct oxidation of the alcohol, it is impossible to determine the extent of direct oxidation, if it takes place at all.

The Inhibitory Action of Water

In the presence of excess water all three reactions mentioned above are completely inhibited. In view of the fact that each reaction involves the elimination of water, the most obvious explanation of this surprising inhibitory effect might lie in the assumption that all are reversible. In the two dehydrations which take place, it is not difficult to understand how the elimination of water might be a strictly reversible reaction, but in the case of direct oxidation of the alcohol, the way is not so clear. In the earlier papers on the oxidation of hydrocarbons to aldehydes or ketones, it has been assumed that oxidation consists of more than one stage, one of these being a reversible reaction involving the elimination of the elements of water. In the oxidation of carbinols it seems necessary to make a similar assumption.

Further work on the mechanism of these reactions is in progress and an investigation of the reversibility of the two dehydrations of carbinols is also planned.

Experimental Part

Materials.—The carbinols employed in the research were all synthesized by means of the Grignard reaction. The secondary carbinols were prepared from benzaldehyde with methylmagnesium iodide, ethylmagnesium bromide and *n*-propyl- and *isopropyl*magnesium chlorides. Dimethylphenylcarbinol was prepared from phenylmagnesium bromide and acetone.

In purifying the secondary carbinols the unchanged benzaldehyde was first carefully removed by allowing the product to stand over saturated bisulfite solution. This was repeated with fresh portions of bisulfite until no precipitate formed on standing for twenty-four hours. After washing the residual liquid with several small portions of the solution and finally

² Ref. 1, p. 2921.

with potassium carbonate solution, it was dried over anhydrous potassium carbonate and fractionated under reduced pressure. Distillations were repeated until a product was obtained which boiled within 1° . The first two or three drops of each final distillate gave no test for carbonyl compounds with semicarbazide hydrochloride and potassium acetate in aqueous alcohol solution.

Procedure.—The crude product of oxidation was in each case examined for benzaldehyde, benzoic acid and a ketone. The benzaldehyde was removed by allowing the liquid to stand for at least forty-eight hours over a small portion of saturated sodium bisulfite solution. Only in the case of ethylphenylcarbinol was a precipitate of addition compound obtained and this was decomposed with sodium carbonate and the aldehyde characterized as the semicarbazone. When no precipitate was obtained the bisulfite was neutralized with sodium carbonate, partially distilled and the distillate treated with semicarbazide hydrochloride and potassium acetate, but no semicarbazone was detected in any of these instances.

Benzoic acid was removed by treating the residue from the bisulfite treatment with sodium bicarbonate solution and later acidifying with dilute hydrochloric acid. Finally, the liquid was dried over anhydrous potassium carbonate and submitted to fractional distillation under reduced pressure. As ketones always boil at a lower temperature than the corresponding alcohols, the lower fractions were collected and these treated with semicarbazide hydrochloride and potassium acetate in aqueous alcohol solution.

Methylphenylcarbinol

I. Twenty-five g. of methylcarbinol, b. p. $85-86^{\circ}$ (7 mm.), treated with dry oxygen for ten days at $102-104^{\circ}$ yielded 2.1 g. of a liquid, b. p. $132-136^{\circ}$ (7 mm.), and a very small amount of acetophenone, isolated as the semicarbazone (m. p. 201^{*3}), m. p. 201° .

II. Twenty-five g. of methylphenylcarbinol, oxidized for eleven days at $122-124^{\circ}$, yielded about 8 g. of liquid, b. p. $132-136^{\circ}$ (7 mm.), 0.85 g. of acetophenone and a trace of a solid acid, presumably benzoic.

Action of Water.—Twenty-five g. of methylphenylcarbinol and 25 g. of water, treated at the boiling point with oxygen for twelve days, yielded no reaction product.

Ethylphenylcarbinol

Twenty-five g. of ethylphenylcarbinol, b. p. $105-106^{\circ}$ (17 mm.) oxidized for ten days at $102-104^{\circ}$, yielded 10 g. of a liquid, b. p. $158-160^{\circ}$ (12 mm.), 0.21 g. of benzoic acid, m. p. 121° , 0.34 g. of ethylphenyl ketone, isolated as semicarbazone,⁴ and a very small amount of benzaldehyde, identified as its semicarbazone by the mixed melting point method.

Action of Heat in an Inert Atmosphere.—Twenty-five g. of ethylphenylcarbinol heated to $102-104^{\circ}$ in an atmosphere of carbon dioxide, yielded a considerable amount of

³ Klages, *Ber.*, **37**, 2306 (1904).

⁴ The melting points given in the literature for the semicarbazone of ethylphenyl ketone vary from $173-175^{\circ}$ to 182° . The writer has found that rate of heating influences the melting point considerably. The highest melting point obtained was 179° .

unsaturated hydrocarbon and 9.5 g. of an oil, b. p. 158–160° (12 mm.). Assuming the hydrocarbon to be propenylbenzene, the absorption of bromine in carbon tetrachloride solution would indicate its presence to the extent of approximately 0.25 g.

Action of Water.—Forty g. of ethylphenylcarbinol plus 40 g. of water yielded no reaction product in detectable quantity.

Dimethylphenylcarbinol

Forty g. of dimethylphenylcarbinol, b. p. 79–80° (7 mm.), oxidized for ten days at 102–104° yielded 3.2 g. of an unsaturated hydrocarbon, b. p. 159–161°, 12 g. of a high-boiling liquid, b. p. 158–162° (8 mm.), and a very small amount of acetophenone, identified as semicarbazone, m. p. 201°. The unsaturated hydrocarbon, oxidized alone at 102–104°, yielded acetophenone as a product. It is, therefore, *isopropenylbenzene*, b. p. 161–162°.⁵ The other product, formaldehyde, which would be expected from the oxidation of this hydrocarbon, could not be detected, as it would be volatilized under the conditions employed.

Action of Water.—Twenty-two g. of dimethylphenylcarbinol plus 22 g. of water, treated with oxygen for twelve days at the boiling point, yielded no reaction product.

n-Propylphenylcarbinol

Twenty-five g. of *n*-propylphenylcarbinol, b. p. 107–108° (8.5 mm.), oxidized for ten days at 102–104° yielded 10.5 g. of a liquid b. p. 173–175° (12 mm.), a small amount of benzoic acid, m. p. 120–120.5°, and 0.76 g. of *n*-propylphenyl ketone, isolated as semicarbazone (m. p. 188.5°⁶), m. p. 188°.

Action of Water.—Fifteen g. of *n*-propylphenylcarbinol plus 15 g. of water, treated with oxygen for ten days at the boiling point, yielded no product.

*iso*Propylphenylcarbinol

Twenty-five g. of *isopropylphenylcarbinol*, b. p. 97.5–98.5° (9 mm.), oxidized for ten days at 102–104° yielded 9 g. of a liquid, b. p. 163–164° (12 mm.), and a very small amount of benzoic acid, m. p. 119–120° (recrystallized once), but no ketone.

Summary

The oxidation by gaseous oxygen of several α -phenylcarbinols has been studied and it has been found that only a very small proportion of the substances undergo direct oxidation to ketones.

Two other reactions take place under the conditions employed, both of which appear to be thermal dehydrations. One of these results in the formation of high-boiling liquids, which correspond to two molecules of carbinol minus one molecule of water. This latter is the main type of reaction that takes place. The other dehydration yields unsaturated hydrocarbons.

All three types of reactions are completely inhibited in the presence of excess water.

Work on the mechanism of these reactions is being continued in this Laboratory.

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⁵ Tiffeneau, *Ann. chim.*, [8] 10, 157 (1907).

⁶ Sorge, *Ber.*, 35, 1074 (1902).