[Contribution from the Chemical Laboratory of the University of Minnesota]

OXIDATIONS IN THE BENZENE SERIES BY GASEOUS OXYGEN
II. ALKYL BENZENES WITH TWO OR MORE CARBON ATOMS IN THE SIDE CHAIN

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In a previous paper[1] it was shown that the methylbenzenes are oxidized by gaseous oxygen at temperatures in the neighborhood of 100°. Aldehydes and the corresponding acids were identified as products. In extending this work to include hydrocarbons containing two or more carbon atoms in the side chain, there have been studied examples of normal, secondary and tertiary alkyl benzenes.

The oxidation of normal alkyl groups was studied by using ethylbenzene and *n*-propylbenzene. In each case the hydrogen attached to the carbon atom in the alpha position to the ring was removed, the products identified being, respectively, acetophenone and propiophenone. It is interesting to note that oxygen apparently tends to substitute in the same position as do the halogens.[2]

As examples of hydrocarbons containing secondary alkyl groups, cumene and *p*-cymene were chosen. In each case the *iso*propyl group lost one methyl group, together with the hydrogen attached to the alpha carbon atom, and a ketone was formed. Thus cumene yielded acetophenone, and cymene, *p*-tolylmethyl ketone. (In the case of cymene, as has been reported,[1] there were also formed cumic aldehyde and cumic acid, by oxidation of the methyl group.) The methyl group lost by the *iso*propyl group during oxidation is apparently oxidized to formic acid and at higher temperatures, to carbon dioxide and water. Formic acid was identified when oxidation took place at 80° but not when higher temperatures were attained.

tert.-Butylbenzene was the only tertiary alkyl benzene studied and no appreciable oxidation took place at 102–104° over a period of 25 days. It seems, then, that in order that oxidation may take place there must be at least one hydrogen atom attached directly to the carbon atom in the alpha position to the ring.

The Action of Water.—The inhibitory action of water in the oxidation of methylbenzenes has already been reported.[1] In the case of ethylbenzene and of *n*-propylbenzene it has also been found that the presence of water in large amounts entirely inhibits oxidation. In the case of the oxidation of the *iso*propyl group, however, water has the opposite effect, favoring instead of inhibiting the reaction. An interesting example of the opera-

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[1] Stephens, This Journal, **48**, 1824 (1926).

[2] Radziewanowski and Schramm, *Chem. Centr.*, [1] **69**, 1019 (1898). Schramm, *Ber.*, **18**, 1275 (1885).

tion of both of these effects was afforded in the case of cymene, the *iso*propyl group alone being oxidized. In this case, *p*-tolylmethyl ketone was the sole identifiable product.

It has been suggested[1] that the inhibitory action of water in oxidations of this type is due to the existence of a reversible stage in the reactions, in which water is eliminated. In the case of the oxidation of the *iso*propyl group, if we assume that the elements of methyl alcohol instead of the elements of water tend to be eliminated, the absence of retarding effect may be explained.

Experimental Part

In carrying out the oxidation of the hydrocarbons mentioned below, no attempt was made to carry the reactions to completion. The crude products contained large amounts of unchanged hydrocarbons from which the oxidation products were separated by fractional distillation under reduced pressure. No attempt was made to recover the unchanged hydrocarbon quantitatively on account of the somewhat variable loss by evaporation during oxidation. In cases where water inhibited the oxidation, the unchanged hydrocarbon was the only substance detected.

Ethylbenzene.—Fifty g. of ethylbenzene oxidized for 24 days at a bath temperature of 110–115° yielded 9.5 g. of acetophenone, identified by means of the oxime (m. p. 58°) and the phenylhydrazone (m. p., 101–103°). In addition, there was produced a very small amount of an unidentified oil which reduced Tollens' reagent but did not affect Fehling's solution or the fuchsin aldehyde reagent.

Action of Water.—Fifty g. of ethylbenzene and 50 g. of water treated with oxygen at the boiling point for 31 days yielded no acetophenone but a trace of non-volatile residue.

***n*-Propylbenzene.**—(I) Twenty-five g. of propylbenzene oxidized for 25 days at a bath temperature of 102–104° yielded no identifiable product, but a considerable quantity of black resin.

(II) Twenty g. of propylbenzene oxidized for 36 days at 78° (temperature of boiling alcohol) yielded a few drops of a liquid whose semicarbazone melted at 174–175°, and no resin. (The semicarbazone of propiophenone melts at 175°.)

Action of Water.—Twenty g. of propylbenzene and 20 g. of water, treated with oxygen at the boiling point for 27 days, yielded neither propiophenone nor resin, but a very small amount of oily residue.

Cumene.—(I) Twenty-five g. of cumene oxidized at 102–104° for 23 days yielded 1.02 g. of acetophenone and a very small amount of an oil which reduced Tollens' reagent but did not affect Fehling's solution or the fuchsin aldehyde reagent.

(II) A sample of cumene oxidized at 80° for 32 days yielded formic acid, identified by shaking the aqueous solution with mercuric oxide and warming the filtered solution, when a precipitate of mercury was obtained.

Action of Water.—Twenty-five g. of cumene and 25 g. of water oxidized for 20 days gave 4.65 g. of acetophenone, identified as described above.

***p*-Cymene.**—(I) Fifty g. of *p*-cymene oxidized at 102–104° for 14 days gave 0.96 g. of *p*-tolylmethyl ketone, identified as the semicarbazone (m. p., 204.5–205°)[3] in addition to cumic acid and aldehyde.

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[3] Auwers, *Ber.*, **38,** 1711 (1905).

(II) A sample of cymene oxidized at 80° for 14 days yielded formic acid, identified by the mercuric oxide test above.

Action of Water.—Fifty g. of *p*-cymene and 25 g. of water oxidized at the boiling point for 18 days gave 1.8 g. of *p*-tolylmethyl ketone, but no aldehyde and no acid.

tert.-**Butylbenzene.**—Twenty-five g. of *tert.*-butylbenzene treated with oxygen for 25 days at 102–104° gave only a trace of non-volatile residue.

Summary

1. The action of gaseous oxygen on aromatic hydrocarbons containing normal, secondary and tertiary alkyl groups has been studied and it has been found that oxidation takes place only at the carbon atom in the alpha position to the ring.

2. At least one hydrogen atom must be attached to the alpha carbon atom in order that oxidation may take place.

3. The presence of water inhibits the oxidation when at least two hydrogen atoms are attached to the alpha carbon atom, but favors it when only one hydrogen atom occupies that position. An explanation of this fact is suggested.

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THE ALKYLATION OF HYDROXYNAPHTHOQUINONE

I. ORTHO-ETHERS

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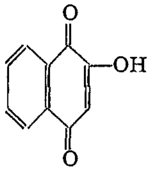
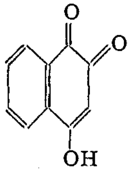
Although it has been known for some time that hydroxynaphthoquinone ("naphthalenic acid") may be prepared from derivatives of both α-naphthoquinone and of β-naphthoquinone, there is little evidence of a conclusive nature to indicate to which class of naphthoquinone derivatives the hydroxy compound belongs. In solution, the substance may consist of a tautomeric mixture of the two possible forms, and the possibility of the occurrence of a tautomeric change during the course of almost any reaction renders a solution of the problem by purely chemical means somewhat difficult.



p-Quinone form



o-Quinone form

O. Miller[1] sought to overcome this difficulty by preparing the silver

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[1] Miller, *J. Russ. Phys.-Chem. Soc.*, **43**, 440 (1911); **47**, 1536 (1915).