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

Oxidation in the Benzene Series by Gaseous Oxygen. V. The Oxidation of Tertiary Hydrocarbons

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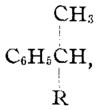
It has been shown by one of us[2] that alkyl benzenes are slowly oxidized at the α-carbon atom at 100°. If at least two hydrogen atoms are attached to this carbon atom an aldehyde or ketone is formed and the oxidation is completely inhibited by excess water. If two alkyl groups and only one hydrogen atom are attached to the α-carbon atom a ketone is formed, through the loss of one of the alkyl groups, and the oxidation is not inhibited by water. The absence of inhibition by water in the latter type of hydrocarbon was previously established only in the cases of cumene and cymene but in the present paper a similar behavior is shown for methylethylphenyl-, methylpropylphenyl-, methylbutylphenyl-, methyldiphenyl-, and triphenylmethane. One further example of a secondary hydrocarbon, diphenylmethane, was included as a control and in conformity with previous experience its oxidation was completely inhibited by water.

Inhibition by water has been ascribed to a reversible elimination of water in the decomposition of a primary oxidation product. The failure of water to inhibit the oxidation of tertiary hydrocarbons therefore implies that in this case there is no such reversible decomposition. This may find explanation in the fact that the formation of a molecule of water from one of a primary addition product of oxygen and tertiary hydrocarbon would require the contribution of one of the hydrogen atoms from an alkyl group. The resulting alkylene residue then must drop off if a ketone, which is always the observed product, is formed. The loss of a carbon atom attendant upon the elimination of water may so reduce the probability of reversal of this step by excess water that no observable inhibition results.

It has been found that hydrocarbons of the type  $C_6H_5\overset{CH_3}{\underset{R}{CH}}$, in which R is ethyl, n-propyl, or n-butyl, lose the larger group, and acetophenone was the only ketone that could be identified. The absence of the alternative ketone was checked very carefully in the case of methylethylphenylmethane by oxidizing 100 g. of the hydrocarbon at a temperature higher than usual (140°). In 7.5 g. of crude ketone obtained from the oxidation no propiophenone could be detected and it appears quite safe to say at least that acetophenone constitutes well over 90% of the total ketone formed. On the basis of the above mechanism this would indicate that the larger alkyl group is involved in the elimination of water from the primary oxidation product. Such behavior is strongly reminiscent of the dehydration of the phenyldialkylcarbinols, which apparently involves the larger alkyl group exclusively.[3] Triphenylmethane distinguishes itself from all other examples studied by having no alkyl group to participate in the elimination of water. The only products identified in this case were benzophenone and phenol.

Experimental Part

Materials and Apparatus.—The hydrocarbons listed below were oxidized in 15 to 25-g. samples for periods varying between fourteen and twenty-nine days in the absence of water and between thirty-one and thirty-four days in the presence of an equal weight of water. Oxidation was carried out in a specially constructed flask, by bubbling oxygen slowly through the hydrocarbon. The flask was sealed to a tall reflux condenser and enclosed in a vapor-bath for maintaining constant temperature. Boiling pentanol-2 (b. p. 119°) was used in this bath for oxidations in the absence of water and boiling water for oxidations in the presence of water. The following is a description of the hydrocarbons employed.

1. Methylethylphenylmethane, from Friedel and Crafts reaction; b. p. 173–174°, n^{25}D 1.4863.
2. Methyl-n-propylphenylmethane, from Friedel and Crafts reaction; b. p. 191–192°, n^{25}D 1.4902.
3. Methyl-n-butylphenylmethane, from Friedel and Crafts reaction; b. p. 206–207°, n^{25}D 1.4902.
4. Methyldiphenylmethane, from paraldehyde and concd. H_2SO_4; b. p. 267–269°, n^{25}D 1.5702.
5. Triphenylmethane, from Kahlbaum; m. p. 90°.
6. Diphenylmethane, from Friedel and Crafts reaction; b. p. 258–259°, n^{25}D 1.5649.

It has been emphasized in previous papers that oxidations of the alkyl benzenes proceed very slowly at temperatures of the order of 100°. It is desirable, however, to keep

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[1] This paper is based largely on the Master's Thesis of Roduta, Minnesota, 1931.

[2] Stephens, THIS JOURNAL, **48**, 1824, 2920 (1926); **50**, 2523 (1928).

[3] Tiffeneau, *Ann. chim. phys.*, [8] **10**, 362 (1907); Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82**, 96 (1910).

the temperature as low as possible in order to avoid excessive secondary reactions. Therefore, it follows that, within a reasonable time, only small amounts of oxidation products will be obtained. In the present investigation, as in previous ones, no attempt was made (except in one case) to carry the oxidation any further than was necessary to yield readily identifiable amounts of products. When the dry hydrocarbons were used the yields of ketones were approximately 0.5 to 1.5 g. In the presence of water the amounts were smaller, due to the lower temperature. Although the yields of ketone are of no particular significance it was considered very important to establish the presence or absence of other early oxidation products. To this end we made a careful search in each case for alcohols, but with consistently negative results.

The ketone was identified in each case as the dinitrophenylhydrazone and the identity of these derivatives with specimens prepared from pure ketones was established by mixed melting points. In addition to ketone there was always formed an appreciable amount of soft reddish-brown or dark brown resin with no simple empirical composition. These obviously arise essentially from further oxidation of the ketones, as the oxidation of acetophenone itself yields a product similar to those from hydrocarbons which give acetophenone.

The ketones obtained from the respective hydrocarbons were

Methylethylphenylmethane—acetophenone
Methyl-*n*-propylphenylmethane—acetophenone
Methyl-*n*-butylphenylmethane—acetophenone
Methyldiphenylmethane—benzophenone
Triphenylmethane—benzophenone
Diphenylmethane—benzophenone (no oxidation in the presence of water).

In order to make sure that we had not missed the alternative ketones, propio-, butyro- and valerophenone which might have been formed from the first three hydrocarbons, we oxidized 100 g. of methylethylphenylmethane for ninety days at 140°. On fractional distillation we obtained 7.5 g. of crude ketone which was cut into 4 fractions of 1.7, 4.1, 0.6 and 0.8 g. (residue). The dinitrophenylhydrazones of fractions 1, 2 and 3, without recrystallization, melted at 230–238, 235–238 and 234–238°, respectively. The derivative from acetophenone melts at 237.5–238.5°. The whole of the last fraction was treated with dinitrophenylhydrazine and yielded 0.2 g. of derivative which, after extracting with boiling ligroin and recrystallizing from a mixture of alcohol and chloroform, melted at 174–180°. A mixture of this material with the dinitrophenylhydrazone of propiophenone (m. p. 190–191.5°) melted at 169–172°. From these facts it is obvious that propiophenone was present, if at all, in only very small amount. It might be mentioned that 4.2 g. of benzoic acid was obtained in this particular experiment. This arises from further oxidation of acetophenone, as it was found that 198 g. of the latter, oxidized at the same temperature (140°) for six days, yelded 1.9 g. of benzoic acid. Benzoic acid had not previously been detected in the oxidations at lower temperatures.

Accompanying the ketone there ought to appear in each case some product corresponding to the alkyl radical which has been eliminated. It has been shown that cumene and cymene yield formic acid if oxidation is carried out at 80°. Similarly 12 g. of methyldiphenylmethane, oxidized at 80–85° in the presence of water for thirty days, gave a strongly acid water layer in which formic acid was recognized by the mercuric oxide test. In oxidations involving elimination of alkyl radical with two or more carbon atoms we have had great difficulty in obtaining a satisfactory identification of the corresponding acids. In the oxidation of methyl-*n*-butylphenylmethane, for example, the presence of butyric acid was indicated by the odor but we were unable to obtain a pure derivative. The second oxidation product of triphenylmethane, however, was readily identified as phenol. The crude product from 15 g. of hydrocarbon, oxidized at 119° for twenty-one days, was extracted with 80% alcohol, and on distilling the residue from this solution under reduced pressure a mass of colorless crystals collected in the condenser. On dissolving a few of these crystals in dilute acetic acid and adding bromine water a copious precipitate of tribromophenol (m. p. 92°) was obtained. Triphenylcarbinol was searched for with negative results.

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Summary

Results obtained from a study of the oxidation of several tertiary hydrocarbons show that oxidation always takes place at the α-carbon atom and that the reactions are not inhibited by water.

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