[CONTRIBUTION FROM THE OHIO OIL CO. DENVER RESEARCH CENTER]

Chromate Oxidation of Alkylaromatic Compounds

R. H. REITSEMA[1] AND N. L. ALLPHIN

Received May 3, 1961

Controlled chromate oxidation of alkylaromatic compounds results in a new method of synthesis of aromatic substituted acids. While methyl-substituted aromatic compounds are converted to aromatic acids, ethyl-substituted aromatic compounds are converted to phenylacetic acids. Longer side chains similarly are converted to the corresponding acid. Under more severe conditions, the side chain is destroyed with production of the aromatic acid. The reaction appears to have many similarities to both the Willgerodt reaction and the conventional acidic chromate oxidation.

Oxidation of organic compounds with dichromate has been studied for a long time. The reaction has been applied generally to oxygenated compounds to produce ketones and acids or to polycyclic compounds to produce quinones. A unique application of the reaction was to toluene to give benzoic acid.[2] This application was not extended much further until recently when the successful oxidation of other methyl-substituted aromatic hydrocarbons to the corresponding aromatic acid was reported.[3] Aromatic hydrocarbons can be oxidized without destruction of the ring or formation of quinones through control of *p*H and use of high temperatures. The oxidation can be run with stoichiometric amounts of dichromate, and the solution becomes more basic as the reaction proceeds.

$$ArCH_3 + Na_2Cr_2O_7 \longrightarrow ArCOONa + Cr_2O_3 + NaOH + H_2O$$

The reported success in oxidizing the side chain methyl group was achieved through control of the *p*H of the reaction between 4 and 8 by use of an excess of dichromate or of a phosphate buffer.[3] Oxidation of alcohols to ketones is run in the presence of an acid such as sulfuric acid. This reaction results in ring attack during oxidation of alkyl-substituted aromatic hydrocarbons.

A new type of oxidation product of aromatic hydrocarbons with alkyl side chains larger than methyl has been found in the present study. Uniform reaction conditions involving one-hour heating at 275° with one equivalent of dichromate were established in this work as standard reference conditions to compare effects of different alkyl groups. Toluene, *p*-xylene, mesitylene, and durene all afforded high conversions of all methyl groups to carboxyl groups. Toluene still gave a 96% yield of benzoic acid even at a reaction temperature of 200°.

Oxidation of longer side chain substituents under the standard conditions gave unusual results. Ethylbenzene gave 89% phenylacetic acid rather than the expected benzoic acid. *n*-Propylbenzene, under the standard reaction conditions, gave benzoic acid. No phenylpropionic acid was detected. *n*-Butylbenzene gave a mixture consisting of 30% benzoic acid and 70% phenylbutyric acid. Styrene gave only benzoic acid, indicating that an olefinic bond promoted side chain shortening. Isopropylbenzene gave a mixture of benzoic and α-methylphenylacetic acids. The secondary alpha carbon structure thus led to more extensive side chain degradation. *tert*-Butylbenzene was found to be inert to oxidation under the standard conditions.

The nature of the final products could be modified by changing reaction conditions. Raising the temperature for oxidation of ethylbenzene to 300° gave some benzoic acid in addition to phenylacetic acid. Lowering the *n*-propylbenzene oxidation temperature to 200° made it possible to produce phenylpropionic acid. Use of insufficient dichromate for oxidation of all side chain carbon atoms led to isolation of longer chain acids such as phenylpropionic and phenylbutyric. These results are summarized in Table I.

TABLE I

OXIDATION OF ALKYLAROMATIC HYDROCARBONS

Compound	Acids Produced after 1 Hr. at 275°[a]	Acids Produced after 1 Hr. at Other Conditions
Ethylbenzene	Phenylacetic (96%)[b]	Benzoic (55%) Phenylacetic (12%) (at 300°)
n-Propylbenzene	Benzoic (100%)	3-Phenylpropionic (54%)[c] (at 200°)
Iso-propylbenzene	Benzoic (76%) 2-Phenylpropionic (24%)	Benzoic (<10%) 2-Phenylpropionic (70%)[d] (less Cr^{+6})
n-Butylbenzene	Benzoic (84%)[e] 4-Phenylbutyric (14%)	Benzoic (30%)[e] 4-Phenylbutyric (70%) (less Cr^{+6})
tert-Butylbenzene	None	
Styrene	Benzoic (56%)[f]	
α-Methylstyrene	Benzoic (100%)	

[a] Yields in parentheses as % of theory except as noted. [b] Based on recovery of 8% of feed. [c] Based on recovery of 70% of feed. [d] Based on recovery of 13% of feed. [e] Ratio of products, not actual yield. [f] Also 42% neutral polymer.

---

[1] Present address: The Ohio Oil Co., Findlay, Ohio.

[2] *Soc. Industrielle de Products Chem.*, French Patent 714,701 (Aug. 5, 1930).

[3] Friedman, L., Fishel, D. L., and Shechter, H., Abstracts from the 136th Meeting of the American Chemical Society, Atlantic City, September 1959, p. 22.

The initial reaction in chromate oxidation may be on the alpha methylene group of the side chain as suggested by Waters.[4] The attack was suggested as occurring by a cation $(HCrO_3)^+$ with formation of an ester. This is in agreement with the relatively greater ease of attack on the isopropyl side chain than on the ethyl side chain. The unreactivity of *tert*-butylbenzene also indicates that the initial attack occurs on the alpha carbon. One may postulate that the terminal substitution results from migration of the ester group down the chain or from formation of successive formal olefin bonds. Destruction of the side chain could then occur under the severe reaction conditions by subsequent attack by additional chromate on the alpha carbon. Activation of the alpha carbon would promote this secondary attack. Benzoic acid is the favored product from isopropylbenzene in which the carbon alpha to the ring is secondary. Propylbenzene undergoes secondary reactions since any intermediate arising through migration of the charge or double bond down the side chain would give an allylic activation of the alpha carbon. This activation occurs to a lesser degree with butyl and longer chains. This is in accord with the isolation of acid with intact side chain from *n*-butylbenzene and not with *n*-propylbenzene under standard conditions. Ethylbenzene lacking either a secondary alpha carbon or possibility of allylic activation is converted in very high yields to phenylacetic acid. Benzoic acid is obtained from ethylbenzene only under reaction conditions more severe than normal. Conversely, mild conditions or a deficiency of chromate minimize secondary reactions, and phenylpropionic acid, for instance, can be obtained from propylbenzene at a reaction temperature of 200°.

This reaction presents a new method for production of aromatic-substituted acids with carboxylic groups at the end of the side chains. This type of product also is formed in the Willgerodt reaction, and mechanisms of the two reactions may be similar. This comparison is supported further by the report that in a study of the Willgerodt reaction itself, ethyl and propylbenzenes were found to give differing ratios of benzoic acid and of the corresponding phenylacetic or phenylpropionic acids depending upon reaction severity.[5,6]

Phenethyl alcohol could be a formal intermediate in the reaction scheme. Oxidation of this alcohol readily gave benzoic acid as the only reaction product. Acetophenone was converted to benzoic acid in nearly quantitative yield. These reactions were both run under conditions which had given phenylacetic acid from ethylbenzene. The alpha oxygen function promoted further reaction comparable to more severe reaction conditions on hydrocarbons. These results also make the ester mechanism of chromate attack, followed by Willgerodt type migration, appear likely.

EXPERIMENTAL

A mixture of 0.025 mole of alkylbenzene, 0.025 mole of sodium dichromate dihydrate per each side chain carbon atom, and 100 ml. of water was heated rapidly in a 300 ml. autoclave to 275° and shaken at this temperature for 1 hr. The autoclave was cooled rapidly, and the mixture was filtered to remove the green inorganic precipitate. The filtrate was extracted with ether to separate unreacted hydrocarbon and the aqueous layer was acidified with 6*N* sulfuric acid. Dibasic acids were separated by filtration. Monobasic acids were isolated by ether extraction of the acidified solution. Products were identified by melting points, mixed melting points with authentic acids, neutral equivalents, and infrared spectra for acids other than benzoic.

The above "standard" conditions were modified as suggested in Table I by changing the reaction temperature or by using less dichromate. Only enough dichromate to oxidize two side chain carbons was used for the second isopropylbenzene oxidation, and only enough dichromate to oxidize one side chain carbon was used for the second *n*-butylbenzene oxidation.

DENVER, COLO.

---

(4) Waters, W. A., *Trans. Faraday Soc.*, 42, 184 (1946).

(5) Naylor, M. A., U. S. Patent 2,610,980 (Sept. 16, 1952).

(6) Naylor, M. A., and Anderson, A. W., *J. Am. Chem. Soc.*, 75, 5395 (1953).