

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LEBANON VALLEY COLLEGE]

Oxidation of Some Secondary Aliphatic-aromatic Alcohols

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A tentative oxidation mechanism has been recently advanced by Mosher and Whitmore² to explain the formation of normal as well as anomalous oxidation products from the chromic acid oxidation of some secondary alcohols containing an alpha-neo carbon atom. This tentative oxidation mechanism involves the concept of an intermediate containing an electronically deficient oxygen atom whose stabilization involves the rupture of a carbon to carbon bond resulting in the formation of anomalous oxidation products or the loss of a proton resulting in the formation of normal oxidation products.

In the chromic acid oxidation of some secondary aliphatic alcohols, it has been reported that the amount of anomalous oxidation observed decreases as the electron attracting power of the group attached to the carbinol carbon atom increases and the steric strain decreases.³ It appeared advantageous to study the oxidation of a series of secondary alcohols with one radical held constant, and the other varied. By using alcohols containing the phenyl group as the constant radical and varying an aliphatic group, it should be possible to gain further information on electrostatic effects in anomalous oxidation. At the same time, the results should indicate whether the Mosher theory may be extended to include aliphatic-aromatic secondary alcohols.

A series of secondary alcohols with the general formula Ph-CHOH-R, where R is a *n*-butyl-, *i*-propyl-, *t*-butyl- and *t*-amyl group, were prepared and oxidized with chromic anhydride in acetic acid and potassium permanganate in acetic acid. Results of these oxidations are shown in Table I, where the normal oxidation product is the corresponding ketone and the anomalous oxidation product is benzaldehyde or benzoic acid.

TABLE I
OXIDATION PRODUCTS

Carbinol	Chromic anhydride in acetic acid, %		Potassium permanganate in acetic acid	
	Normal oxidation	Anoma- lous oxidation	Normal oxidation %	Anoma- lous oxidation %
<i>i</i> -Propylphenyl-	74.8	5.5	71.0	8.8
<i>n</i> -Butylphenyl-	93.1	..	96.0	..
<i>t</i> -Butylphenyl-	77.0	17.5	34.3	46.0
<i>t</i> -Amylphenyl-	73.6	14.4	33.2	55.7

In the chromic anhydride-acetic acid oxidation, the *n*-butyl-, *i*-propyl-, *t*-butyl- and *t*-amylphenyl-carbinols give the expected ketones and with the

latter three alcohols small amounts of benzaldehyde. The formation of benzaldehyde is of paramount importance in considering the electrostatic forces functioning in the molecule.

In applying the mechanism for the oxidation of secondary alcohols as advanced by Mosher and Langerak,³ the first step in the oxidation of Ph-CHOH-R would involve in effect the removal of a hydride ion from the hydroxyl group giving an intermediate containing an electronically-deficient oxygen atom. The stabilization of this intermediate could be accomplished by two different methods. First, the loss of a proton from the carbinol carbon atom would give the ketone, Ph-CO-R, the normal oxidation product. Second, the deficient oxygen atom could appropriate the electron pair involved in the bond joining the aliphatic group to the oxygenated carbon atom. The cleavage of this bond would result in the formation of a molecule of benzaldehyde and a new carboanion ion, which upon the addition of a hydroxy ion would form an aliphatic alcohol.

It is possible that the stabilization of the intermediate containing the electronically-deficient oxygen atom could occur by the aliphatic radical and a pair of electrons rearranging to the oxygen atom, which would then cleave to give the anomalous oxidation products. Rearrangements of this type have been suggested in the case of the oxidation of tertiary alcohols by Mosher, Langerak and Coleman.⁴

In the stabilization of the corresponding intermediate from the secondary alcohols here reported such a rearrangement might be possible. In the case of the aliphatic-aromatic secondary alcohols, the aromatic group, because of its greater migration aptitude, should rearrange. This would result in the eventual formation of phenols, and carbonyl compounds derived from the aliphatic portion of the molecule. Such compounds have not been found. The general formation of benzaldehyde and aliphatic alcohols indicate clearly that the electrons in the carbonyl group came from the aliphatic group. In view of the low electronegativity and low migration aptitude of these groups, it would appear, in this case at any rate, that the cleavage reaction involves only an electron shift and not group rearrangement.

When potassium permanganate in acetic acid was used as the oxidizing agent, a greater amount of cleavage took place with those carbinols containing a branched group in the alpha position. An explanation of the increase in anomalous oxidation might possibly be based on the fact that po-

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(2) W. A. Mosher and F. C. Whitmore, *THIS JOURNAL*, **70**, 2544 (1948).

(3) W. A. Mosher and E. O. Langerak, *ibid.*, **71**, 268 (1949).

(4) Presented before the Division of Organic Chemistry, American Chemical Society, New York, September 15, 1947.

tassium permanganate possesses a higher oxidizing potential than chromic acid. A very significant point is that the Mosher theory of oxidation can be applied not only to chromic acid oxidations but also to acid permanganate oxidation of secondary aliphatic-aromatic alcohols.

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Experimental

General.—*n*-Butyl-, *i*-propyl-, *t*-butyl- and *t*-amylphenylcarbinol were prepared by the action of the appropriate Grignard reagent on benzaldehyde according to the general procedure of Conant and Blatt.⁵ Identification of all products was by means of mixed melting points of both compound and a solid derivative.

Oxidations: (a) **Chromic Anhydride in Acetic Acid.**—These oxidations were carried out in the following manner exemplified by the oxidation of *t*-amylphenylcarbinol: a solution of 9.5 g. of chromic anhydride (0.09 mole) dissolved in 125 ml. of water and 400 ml. of glacial acetic acid was added dropwise to a stirred solution of 25 g. of the carbinol (0.14 mole) over a period of three hours during which time the temperature was maintained between 25–30°. The reaction mixture was steamed distilled and from the distillate an oil layer was obtained (I) 18.2 g. (73.6%) *t*-amyl phenyl ketone, b. p. at 17 mm., 118–120° and *n*_D²⁰ 1.5128. The aqueous layer from the steam

distillation yielded (II) 1.8 g. (12%) benzaldehyde. From the steam distillation residue, (III) 0.4 g. (2.3%) benzoic acid was obtained.

The results of the oxidations of *t*-butyl-, *i*-propyl-, *t*-amyl- and *n*-butylphenylcarbinol are shown in Table II.

(b) **Potassium Permanganate in Acetic Acid.**—The same method of oxidation and isolation of products was employed as described in the chromic acid oxidations. The results of the oxidation of *t*-butyl-, *t*-amyl-, *i*-propyl- and *n*-butylphenylcarbinol are shown in Table III.

TABLE III
POTASSIUM PERMANGANATE OXIDATIONS

Ph- CHOH-R, where R is:	Molar relationships		Products			
	Alcohol	Oxi- dant	Ketone g.	%	Benzoic acid g.	<i>C</i> _T
<i>i</i> -Propyl-	0.046	0.06	4.9	71.0	0.5	8.8
<i>n</i> -Butyl-	.15	.06	23.2	96.3
<i>t</i> -Butyl-	.165	.14	9.2	34.3
<i>t</i> -Amyl-	.14	.05	8.2	33.2	0.8	4.7 ^b

^a 8.2 g. (46%) of benzaldehyde was isolated. ^b 7.6 g. (51.1%) of benzaldehyde was isolated.

Summary

1. The chromic acid oxidation of *n*-butyl-, *i*-propyl-, *t*-butyl- and *t*-amylphenylcarbinols gives the expected ketone and with the latter three carbinols small amounts of benzaldehyde and/or benzoic acid.

2. When using acid permanganate, *n*-butyl-, *i*-propyl-, *t*-butyl- and *t*-amylphenylcarbinols gives the corresponding ketones and with the latter three carbinols a significant amount of benzaldehyde and/or benzoic acid.

3. The Mosher theory of oxidation can be applied to the chromic acid and acid permanganate oxidations of secondary aliphatic-aromatic carbinols.

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TABLE II
CHROMIC OXIDE OXIDATIONS

Ph- CHOH-R, where R is:	Molar relationships		Products			
	Alcohol	Oxi- dant	Ketone g.	%	Benzoic acid g.	<i>C</i> _T
<i>i</i> -Propyl-	0.0665	0.04	7.4	74.8	0.45	5.5
<i>n</i> -Butyl-	.152	.05	23.0	93.1
<i>t</i> -Butyl-	.061	.05	7.6	77.0	1.3	17.5
<i>t</i> -Amyl-	.14	.08	18.2	73.6	0.4	2.3 ^a

^a 1.8 g. (12%) of benzaldehyde was also obtained.

(5) Conant and Blatt, *THIS JOURNAL*, **50**, 554 (1928).

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Acetylation of 3,2'-Nicotyrine

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As part of a research program on utilization of nicotine, a study has been made of the acetylation of 3,2'-nicotyrine (I), which is readily obtained from nicotine by catalytic dehydrogenation³ or oxidation.⁴ The acetylation of N-methylpyrrole⁵ with acetic anhydride and anhydrous sodium acetate has been reported to yield 1-methyl-2-acetylpyrrole. Use of these reagents at

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

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(3) (a) Wibaut and Overhoff, *Rec. trav. chim.*, **47**, 935 (1928); (b) Frank, Holley and Wikholm, *THIS JOURNAL*, **64**, 2835 (1942).

(4) Woodward, Badgett and Haines, U. S. Patent 2,432,642 (Dec. 16, 1947).

(5) Ciamician and Dennstedt, *Ber.*, **17**, 2944 (1884).

reflux temperature with I, however, gave only a negligible yield of any product. Hartough and Kosak⁶ acetylated thiophene and furan, with iodine and hydriodic acid as catalyst. The efficiency of this catalyst prompted its use in the acetylation of I.

The principal product obtained when (I) is acetylated with acetic anhydride containing small amounts of hydriodic acid and free iodine has been assigned the structure 1-methyl-2-(3-pyridyl)-5-acetylpyrrole (II) on the basis of a comparison of its absorption spectrum with that of the model compound. If anhydrous aluminum chloride is used as catalyst a small yield of an isomeric substance is obtained to which structure (III), 1-

(6) Hartough and Kosak *THIS JOURNAL*, **68**, 2639 (1946).