Oxidation of Alcohols with *t*-Butyl Chromate. II. The Oxidation of Primary Aromatic Alcohols[*1]

By Takayuki SUGA, Keiichi KIHARA[*2] and Tamon MATSUURA

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The oxidation of benzyl alcohol with *t*-butyl chromate has been reported to give benzaldehyde in a quantitative yield[1] and to be accelerated by pyridine.[2] In the preceding paper of this series,[3] the *t*-butyl chromate oxidation of the primary aliphatic alcohols with the $-CH_2\cdot CH_2OH$, $>CH\cdot CH_2OH$, or $\rightarrow C\cdot CH_2OH$ groups was found to yield a mixture of the corresponding aldehyde, acid and ester in a comparable yield. On the other hand, the oxidation of the primary allylic alcohol was established as giving the corresponding aldehyde in a high yield, but not the ester. We have now tried the oxidation of benzyl alcohol and its *p*-substituted derivatives, β-phenylethyl alcohol, and *trans*-cinnamyl alcohol with *t*-butyl chromate.

[*1] The oxidation of benzyl alcohol has been recorded in *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 653 (1959), by one of the present authors. An other part of this work was presented at the 3rd Symposium on Perfume, Terpene and Essential Oil Chemistry of the Chemical Society of Japan, Tokyo, October, 1959.

[*2] Present address: The Tôyô Sôda Manufacturing Company, Ltd., Nanyô-chô, Tsuno-gun, Yamaguchi-ken.

1) R. V. Oppenauer and H. Oberrauch, *Anales asoc. quim. arg.*, **37**, 246 (1949).

2) A. Leo and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4383 (1952).

3) Part I: T. Suga, K. Kihara and T. Matsuura, This Bulletin, **38**, 893 (1965).

The re-examination of the oxidation of benzyl alcohol (Exp. 1) under conditions similar to those reported by Oppenauer et al.[1],[*3] gave benzaldehyde (81% yield based on the alcohol) and benzoic acid (17%). When this alcohol was oxidized (Exp. 2) at 1—2°C for 6 hr. with the oxidant solution prepared in the 1 : 1 mol. ratio of the alcohol to *t*-butyl chromate, as employed in many cases of a primary aliphatic alcohol,[3] the yield of benzaldehyde increased to 90% and the formation of benzoic acid was suppressed to 7%. No such ester as produced in the case of a saturated primary aliphatic alcohol[3] was formed in Exps. 1 and 2.

The effect of the para substituent on the formation of the aldehyde and the ester was checked with *p*-chlorobenzyl alcohol and *p*-isopropylbenzyl alcohol. The oxidation of *p*-chlorobenzyl alcohol (Exp. 3) under the same conditions as in Exp. 2 gave *p*-chlorobenzaldehyde (83%) and *p*-chlorobenzoic acid (10%), but it did not yield the ester. When this oxidation was repeated using a benzene solution with a lower concentration of the oxidant and the sample alcohol (Exp. 4), the yield of *p*-chlorobenzoic acid decreased to 5%, and *p*-chlorobenzaldehyde was obtained in a 91% yield. The oxidation of *p*-isopropylbenzyl alcohol (Exp. 5) under the same conditions as in Exp. 4 afforded *p*-isopropylbenzaldehyde (79%) and *p*-isopropylbenzoic acid (10%), but no ester was obtained. Thus, the electron-attractive or the electron-repulsive group in the para position was found neither to affect remarkably the yield of the aldehyde nor to cause the formation of the ester.

The oxidation of β-phenylethyl alcohol (Exp. 6) gave the corresponding ester, i. e., β-phenylethyl β-phenylacetate (46%), β-phenylacetaldehyde (3%) and β-phenylacetic acid (3%), accompanied by anomalous oxidation products, such as benzaldehyde (2%) and benzoic acid (7%). The formation of the anomalous products is probably due to the cleavage of the side chain. Besides, a resinous substance, probably a polymer of β-phenylacetaldehyde, was obtained in ca. 10% yield. The different oxidation mode between benzyl alcohol and β-phenylethyl alcohol will be discussed, together with the course of the formation of the ester, in Part IV of this series.

The oxidation of *trans*-cinnamyl alcohol (Exp. 7) under the same conditions as in Exp. 2 produced *trans*-cinnamaldehyde (61%) and *trans*-cinnamic acid (1%). In addition, benzaldehyde (6%) and benzoic acid (2%), presumably formed by the allylic double-bond fission, were obtained. Oxidation (Exp. 8) similar to that of Exp. 7, with a reaction time of 2 hr., gave the corresponding aldehyde (49%), the corresponding acid (1%), benzaldehyde (5%) and benzoic acid (3%). When *t*-butyl chromate dissolved in benzene containing glacial acetic acid and acetic anhydride was used as an oxidant (Exp. 9), *trans*-cinnamaldehyde was obtained in a 59% yield, even with a short oxidation time similar to that of Exp. 8, and the original alcohol was almost entirely exhausted. In this case, the yields of cinnamic acid, benzaldehyde and benzoic acid were 8, 10 and 1%. The oxidation (Exp. 10) with a neutral benzene solution of the oxidant under the same conditions as in Exp. 1 afforded cinnamaldehyde (52%), cinnamic acid (6%), benzaldehyde (6%) and benzoic acid (2%), but no original alcohol. The formation of the ester was not observed with cinnamyl alcohol (Exps. 7—10).

Therefore, when a primary aromatic alcohol with a phenyl group or an ethylenic double bond adjacent to the hydroxymethyl group was oxidized with *t*-butyl chromate, the aldehyde corresponding to the sample alcohol was obtained as the main reaction product, but the corresponding ester was not formed. On the other hand, the oxidation of an aromatic alcohol with a methylene between the phenyl group and the hydroxymethyl group produced the aldehyde, the acid and the ester corresponding to the sample alcohol, as in the oxidation of a saturated primary aliphatic alcohol.[3]

Experimental

Sample Alcohols. — Benzyl alcohol and β-phenylethyl alcohol were obtained from a commercial source. Cinnamyl alcohol (m. p. 33—34°C; $\lambda_{infl.}^{\mathrm{EtOH}}$ 249 and λ_{max} 251 mμ, log ε 4.272 and 4.274) was supplied by the Takasago Perfumery Co., Ltd. Its melting point and ultraviolet absorption spectrum indicated this alcohol to be a trans-form.[4] *p*-Chlorobenzyl alcohol (m. p. 70.5—71°C) and *p*-isopropylbenzyl alcohol (b. p. 124—125°C/13 mmHg) were prepared from the corresponding benzoic acids by reduction with lithium aluminum hydride in ether.[5,6] All the sample alcohols were purified by distillation or recrystallization just before use.

[*3] The oxidation recorded by them has been carried out at room temperature over a 7-day period, using a benzene solution of *t*-butyl chromate prepared in the 1 : 1.3 mol. ratio of benzyl alcohol to this chromate.

[4] E. A. Braude, E. R. H. Jones and E. S. Stern, *J. Chem. Soc.*, **1946**, 396; E. B. Bates, E. R. H. Jones and M. C. Whiting, ibid., **1954**, 1854.

[5] Cf. R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

[6] Cf. C. C. Price and S.-T. Voong, *J. Org. Chem.*, **14**, 115 (1949).

TABLE I. THE WEIGHTS OF THE ALCOHOL USED AND EACH COMPONENT IN THE OXIDANT, AND CONDITIONS OF THE OXIDATION

Exp.	Sample				Oxidant				Time
	Alcohol		C_6H_6	Concn.[a]	CrO_3	*t*-BuOH	C_6H_6	Concn.	
		g.	g.	%	g.	g.	g.	%	
1[b]	Benzyl	16.2	70	2.4	20.0	44.0	70	37	7 days
2	Benzyl	30.0	90	4.5	28.0	56.0	110	35	6 hr.
3	*p*-Chlorobenzyl	40.0	63	4.5	28.1	55.9	100	35	6 hr.
4	*p*-Chlorobenzyl	40.0	280	1.0	28.1	55.9	339	15	6 hr.
5	*p*-Isopropylbenzyl	13.0	86.5	1.0	8.7	17.3	107	15	6 hr.
6	*β*-Phenylethyl	30.0	54.6	4.5	24.6	49.1	92	35	6 hr.
7	*trans*-Cinnamyl	30.0	49.8	4.5	22.4	44.8	84	35	6 hr.
8	*trans*-Cinnamyl	30.0	49.8	4.5	22.4	44.8	84	35	2 hr.
9[c]	*trans*-Cinnamyl	30.0	49.8	4.5	22.4	44.8	84	30[d]	2 hr.
10	*trans*-Cinnamyl	30.0	90	2.5	29.8	66.3	91	38	7 days

a) Mol. in 1000 g. of benzene.
b) The mol. ratio of the sample alcohol to *t*-butyl chromate was 1 : 1.3 and the oxidation was carried out at 22—25°C. Only benzene is represented by volume (ml.).
c) To the benzene solution of *t*-butyl chromate, 15 g. of glacial acetic acid and 10 g. of acetic anhydride were added.
d) The cocentration in the acidified benzene solution is shown.

Oxidation, and the Treatment of a Reaction Mixture.—A benzene solution of *t*-butyl chromate was prepared in the same manner as that in the preceding paper.[3] The quantity of each component and the concentration of *t*-butyl chromate in this solution are shown in Table I, which also lists the quantities of the sample alcohol and its solvent. The oxidation was carried out under the conditions described above in a manner similar to that described in Ref. 3. After the oxidation, the reaction mixture was treated with oxalic acid and water, except in Exp. 1, and then separated into a benzene solution and an aqueous one (see Ref. 3). The separated benzene solution containing a reaction product was subjected to the examinations described in each experiment. Each of the constituents of the reaction product was identified by the same method as used in the preceding study;[3] the yield of the constituents has been shown above.

The Oxidation of Benzyl Alcohol (Exp. 1).—After the oxidation, the reaction mixture was treated with hydrazine sulfate and 20% sulfuric acid instead of oxalic acid and water. An ether solution of the reaction product, obtained by the removal of the solvent from the separated benzene solution, was extracted with a 5% sodium carbonate solution, which gave benzoic acid on acidification. The removal of the solvent from the ether solution gave a neutral reaction product, which consisted of benzaldehyde (15%) and dibenzalhydrazine (85%). The steam distillation of this dibenzalhydrazine in the presence of dilute sulfuric acid gave benzaldehyde quantitatively. The formation of dibenzalhydrazine is considered to result from the reaction of hydrazine sulfate with benzaldehyde while the residual oxidant was hydrolyzed with this reagent.

(Exp. 2).—The reaction mixture was treated with oxalic acid and water, and then the separated benzene solution was repeatedly extracted with a 5% sodium carbonate solution, which gave benzoic acid on acidification. The neutral reaction product was obtained from the neutral benzene solution by the removal of the solvent. Thin-layer chromatographic analysis (silica gel) as well as infrared and ultraviolet spectroscopic analyses indicated the neutral product to be only benzaldehyde.

The Oxidation of *p*-Chlorobenzyl Alcohol (Exps. 3 and 4).—The separated benzene solution was treated in the same manner as in Exp. 2. *p*-Chlorobenzoic acid (m. p. 234—235°C) was obtained from the sodium carbonate extracts. Thin-layer chromatography (silica gel) indicated that the neutral product consisted of *p*-chlorobenzaldehyde (m. p. 45—46°C) and unchanged alcohol (0.2 and 4% in Exps. 3 and 4 respectively). The aldehyde was estimated by the 2,4-dinitrophenylhydrazine method.[7]

The Oxidation of *p*-Isopropylbenzyl Alcohol (Exp. 5).—The reaction product was examined in a manner similar to that used in Exps. 2—4. The boiling point of *p*-isopropylbenzaldehyde isolated was 98—100°C/8 mmHg, and *p*-isopropylbenzoic acid melted at 115—116°C. The unchanged alcohol amounted to 8.5%.

The Oxidation of *β*-Phenylethyl Alcohol (Exp. 6).—The distillation of a reaction product obtained from the separated benzene solution gave benzaldehyde (b. p. 73—78°C/22 mmHg), *β*-phenylacetaldehyde (b. p. 90—95°C/22 mmHg), unchanged alcohol (21% yield; b. p. 110—113°C/22 mmHg) and a residue (20.5 g.). Liquid-column chromatography on silica gel with a mixture of ethyl ether and

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[7] H. A. Iddles, A. W. Low, B. D. Rosen and R. T. Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).

n-hexane indicated that this residue contained benzoic acid (m. p. 120—121°C), β-phenylacetic acid (m. p. 76—76.5°C), β-phenylethyl β-phenylacetate (b. p. 180—182°C/5 mmHg; $\nu_{max}^{liq.}$ 1730, 1150 cm^{-1}), and a resinous substance, probably a polymer of β-phenylacetaldehyde.

The Oxidation of *trans*-Cinnamyl Alcohol (Exps. 7—10).—The reaction product was distilled to separate as five fractions, and then some fractions and the residue were individually subjected to liquid-column chromatography on silica gel with a mixture of ethyl acetate and *n*-hexane. The reaction product consisted of *trans*-cinnamaldehyde[8] (b. p. 96—100°C/3.5 mmHg; λ_{max}^{EtOH} 287 mμ, log ε 4.36), *trans*-cinnamic acid (m. p. 132—132.5°C), benzaldehyde, benzoic acid and unchanged alcohol (2, 19 and 2% in Exps. 7, 8 and 9 respectively).

Summary

The oxidation with *t*-butyl chromate has been carried out with benzyl alcohol, its *p*-substituted derivatives and *trans*-cinnamyl alcohol, and also with β-phenylethyl alcohol. In the former alcohols, the corresponding aldehyde was obtained as the main product, but the corresponding ester was not formed. On the other hand, the latter alcohol, containing a methylene group adjacent to the hydroxymethyl group, produced the corresponding ester, aldehyde and acid, as in the case of a saturated primary aliphatic alcohol.

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Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima

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[8] G. Gamboni, V. Theus and H. Schinz, *Helv. Chim. Acta*, 38, 255 (1955).