

## Oxidation of Alcohols with *t*-Butyl Chromate. I. The Oxidation of Primary Aliphatic Alcohols<sup>\*1</sup>

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Oppenauer and Oberrauch<sup>1)</sup> have recorded that *t*-butyl chromate<sup>2)</sup> in a nonpolar solvent converts primary alcohols, such as cetyl alcohol, geraniol and benzyl alcohol, into the corresponding aldehydes in 80–94% yields, and also that this oxidant in a nonpolar solvent containing such an organic acid as acetic acid oxidizes to a ketone group a methylene group adjacent to a double bond. *t*-Butyl chromate has been employed for the preparation of  $\alpha, \beta$ -unsaturated ketones.<sup>3)</sup> Among primary alcohols, the *t*-butyl chromate oxidation of 2-isopropyl-5-methylhexanol and 3-isopropyl-1-heptanol<sup>4)</sup> has

been recorded to afford only the corresponding aldehyde in a low yield. However, the action of *t*-butyl chromate on alcohols appears not to have been examined in detail as yet. We have now attempted the oxidation of a variety of aliphatic alcohols with *t*-butyl chromate.

The oxidation was undertaken on a series of aliphatic alcohols, which are shown to have the general formula of  $R \cdot CH_2OH$ , where R is  $CH_3$ ,  $CH_3(CH_2)_2$ ,  $CH_3(CH_2)_3$ ,  $CH_3(CH_2)_4$ ,  $CH_3(CH_2)_{10}$ ,  $CH_3(CH_2)_{14}$  and  $CH_3(CH_2)_{16}$ . When cetyl alcohol (Exp. 1) was oxidized in benzene for a shorter time (see Table I) than that used by Oppenauer and Oberrauch,<sup>3)</sup> it gave palmitic acid (54%; based on the sample taken) and cetyl palmitate (39%), but not palmitaldehyde. Since Oppenauer et al. have used petroleum ether as a solvent in this oxidation, the oxidation of *n*-lauryl alcohol in petroleum ether (Exp. 2) for a shorter time than that in Exp. 1 was carried out, giving lauraldehyde (3%), lauric acid (52%) and *n*-lauryl laurate (28%); the results resemble those of Exp. 1. Even when *n*-lauryl alcohol was oxidized in benzene with ice-cooling for 6 hr. (Exp. 3), the reaction product consisted of the aldehyde (38%), the

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1) R. V. Oppenauer and H. Oberrauch, *Anales Asoc. Quim. Argentina*, **37**, 246 (1949).

2) H. Wienhaus, *Ber.*, **47**, 322 (1914); H. Wienhaus and W. Treibs, *ibid.*, **56**, 1648 (1923).

3) D. Ginsberg and R. Pappo, *J. Chem. Soc.*, **1951**, 516; T. Matsuura and K. Fujita, *J. Sci. Hiroshima Univ.*, **A16**, 173 (1952); G. Dupont, R. Dulou and O. Mondou, *Bull. soc. chim. France*, **1953**, 60; K. Fujita and T. Matsuura, *J. Sci. Hiroshima Univ.*, **A18**, 455 (1955); K. Fujita, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **78**, 1112 (1957); T. Matsuura and T. Suga, *ibid.*, **78**, 1117 (1957); T. Matsuura, T. Suga and K. Suga, *ibid.*, **78**, 1122 (1957); T. Suga, *This Bulletin*, **31**, 569 (1958); I. Alkony, *Chem. Ber.*, **94**, 2486 (1961); T. Matsuura, T. Suga and T. Sakao, *This Bulletin*, **35**, 1623 (1963).

4) R. Kitaoka, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **77**, 630 (1956); **78**, 1597 (1957).

<sup>\*3</sup> The oxidation recorded by Oppenauer et al. has been carried out at room temperature over a 14-day period, using a petroleum ether solution of *t*-butyl chromate prepared in the 1:2.5 mol. ratio of cetyl alcohol to this chromate and in a 28% concentration, and using a petroleum ether solution of cetyl alcohol in the same concentration as in Exp. 1.

TABLE I. CONDITIONS OF THE OXIDATION

Exp.	Sample		Oxidant		Temp. °C	Time
	Alcohol	Concentration <sup>a)</sup> %	Sample to <i>t</i> -Bu. chrom. <sup>b)</sup> (mol. ratio)	Concentration %		
1	Cetyl	0.9	1 : 2.5	23	ca. 30	5 days
2 <sup>c)</sup>	<i>n</i> -Lauryl	1.2	1 : 2.5	28	ca. 25	2 days
3	<i>n</i> -Lauryl	4.5	1 : 1	36.5	1-2	6 hr.
4	<i>n</i> -Hexyl	4.5	1 : 1	36.5	1-2	6 hr.
5	<i>n</i> -Butyl	4.5	1 : 1	36.5	1-2	6 hr.
6	Ethyl	4.5	1 : 1	36.5	1-2	6 hr.
7	<i>n</i> -Amyl	2.3	1 : 1	23	1-2	6 hr.
8	Isoamyl	4.5	1 : 1	36.5	1-2	6 hr.
9	Isobutyl	4.5	1 : 1	36.5	1-2	6 hr.
10	Neopentyl	4.5	1 : 1	36.5	1-2	6 hr.
11	Geraniol	4.5	1 : 1	36.5	1-2	6 hr.
12	Isobutyl	6.8	1 : 1.5	38	ca. 15	66 hr.

a) Mole in 1000 g. of benzene or petroleum ether.

b) *t*-Bu. chrom. = *t*-Butyl chromate.

c) Petroleum ether was used as a solvent.

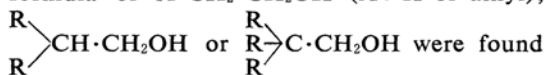
carboxylic acid (23%) and the ester (38%). The oxidation of *n*-hexyl alcohol (Exp. 4) under the same conditions as in Exp. 3 gave caproaldehyde (25%), caproic acid (37%) and *n*-hexyl caproate (34%); *n*-butyraldehyde (29%), *n*-butyric acid (32%) and *n*-butyl *n*-butyrate (35%) were also produced in the oxidation of *n*-butyl alcohol (Exp. 5). The oxidation of ethyl alcohol (Exp. 6) afforded acetaldehyde (17%), acetic acid (20%) and ethyl acetate (23%). In all these cases, only a small percentage of unchanged alcohol was recovered. Moreover, *n*-amyl alcohol (Exp. 7), diluted by a double quantity of benzene used in Exp. 3—6, was oxidized under the same conditions as above with a benzene solution of *t*-butyl chromate in a low concentration. The reaction product consisted of *n*-valeraldehyde (43%), *n*-valeric acid (17%) and *n*-amyl *n*-valerate (29%).

The oxidation was tried with alcohols with a variety of  $\alpha$ - or  $\beta$ -substituents. The oxidation of isoamyl alcohol (Exp. 8) under the same conditions as in Exp. 3 gave isovaleraldehyde (31%), isovaleric acid (29%) and isoamyl isovalerate (34%). When isobutyl alcohol (Exp. 9) was used, the products were isobutyraldehyde (17%), isobutyric acid (26%), isobutyl isobutyrate (29%) and acetone (4%). The formation of acetone was remarkable in Exp. 12 (17%); it is probably a result of the occurrence of the cleavage reaction. Furthermore, the oxidation of neopentyl alcohol (Exp. 10) yielded trimethylacetaldehyde (36%), trimethylacetic acid (5%) and neopentyl trimethylacetate (13%), and left unchanged the alcohol (38%). This is likely to have been the result of an attack of *t*-butyl chromate on

the hydroxymethyl group interrupted by the bulky *t*-butyl group around the hydroxyl group.

Oppenauer et al.<sup>13</sup> have obtained citral in a 80% yield on the *t*-butyl chromate oxidation of geraniol at 28°C for 3 days. A reexamination of the oxidation of geraniol under the same conditions as in Exp. 3 gave citral (77%), geranic acid (2%) and 2-methyl-2-hepten-6-one (3%), but the ester was not obtained. This methylheptenone is presumably produced by an ethylenic bond fission at the allylic position of the sample alcohol.

On oxidation with *t*-butyl chromate, the alcohol with an olefinic double bond on the carbon adjacent to the hydroxymethyl group afforded the corresponding aldehyde in a high yield, but not the ester. On the other hand, saturated primary alcohols with the formula of  $X-CH_2-CH_2OH$  ( $X$ : H or alkyl),



to produce aldehyde, carboxylic acid and ester corresponding to the alcohol in comparable yields. The formation of an ester was newly recognized in the *t*-butyl chromate oxidation of a saturated aliphatic primary alcohol. The course of the formation of the ester will be discussed in the near future in Part IV of this series.

### Experimental

**Sample Alcohols.**—Neopentyl alcohol was prepared from *t*-butyl chloride and formaldehyde by Grignard reaction;<sup>5)</sup> it showed b. p. 110.5–111.5°C

5) S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, 510 (1948); A. Courtot, *Bull. soc. chim. France*, 1906, 985.

TABLE II. THE WEIGHT OF THE SAMPLE ALCOHOL, EACH COMPONENT IN THE OXIDANT AND THE REACTION PRODUCT PRODUCED

Exp.	Sample		Oxidant			Reaction Product				Unchanged Alc.
	Alcohol	C <sub>6</sub> H <sub>6</sub>	CrO <sub>3</sub>	<i>t</i> -BuOH	C <sub>6</sub> H <sub>6</sub>	Aldehyde	Acid	Ester	Cleavage product	
	g.	g.	g.	g.	g.	g.	g.	g.	g.	g.
1 <sup>a)</sup> Cetyl	50.0	275	50.8	102.0	412	—	27.2	19.6	—	1.9
2 <sup>b)</sup> <i>n</i> -Lauryl	15.0	107	19.8	39.6	161	0.4	7.8	4.2	—	0.3
3 <i>n</i> -Lauryl	30.0	36	16.1	32.2	60	9.6	7.0	11.4	—	1.5
4 <i>n</i> -Hexyl	30.0	65	29.3	59.0	110	7.6	11.0	10.1	—	—
5 <i>n</i> -Butyl	30.0	90	40.0	80.0	150	8.8	9.5	10.5	—	—
6 Ethyl	30.0	145	65.1	130.3	244	5.1	5.9	7.0	—	—
7 <i>n</i> -Amyl	25.0	127	28.4	56.8	214	10.7	4.2	7.2	—	2.7
8 Isoamyl	20.0	51	23.0	46.0	86	6.2	5.8	6.7	—	—
9 Isobutyl	20.0	60	27.0	54.0	100	3.4	5.2	5.8	0.7 <sup>c)</sup>	—
10 Neopentyl	30.0	76	34.0	68.0	128	10.9	1.6	4.0	—	11.3
11 Geraniol	40.0	58	25.9	51.8	97	30.9	0.8	—	1.1 <sup>d)</sup>	2.0
12 Isobutyl	10.0	20	20.0	44.0	60	0.5	1.8	4.3	1.7 <sup>c)</sup>	—

a) Only benzene is represented by volume (ml.).

b) Petroleum ether (ml.) was used as a solvent.

c) The product is acetone.

d) The product is 2-methyl-2-hepten-6-one.

and m. p. 55–56°C after it had been rectified. Geraniol supplied by the Takasago Perfumery Co., Ltd., was purified following the literature method<sup>6</sup>) and showed b. p. 111.8–112°C/11 mmHg,  $n_D^{25}$  1.4714 and  $d_4^{25}$  0.8760. The rest of the sample alcohols were obtained from a commercial source and were purified by distillation or recrystallization.

**Oxidant.**—*t*-Butyl chromate was prepared by adding chromium trioxide in small portions to *t*-butyl alcohol under ice-cooling, diluting the resultant with benzene or petroleum ether, and drying the resultant benzene or petroleum ether solution of *t*-butyl chromate over anhydrous sodium sulfate. The quantity of each component used is shown in Table II. The concentration of *t*-butyl chromate in this solution and the mole ratio of a sample alcohol to this chromate are shown in Table I.

**Oxidation and Treatment of a Reaction Mixture.**—Into the benzene or petroleum ether solution of a sample alcohol (the concentration of the alcohol is shown in Table I), the oxidant prepared as above was stirred over a period of 0.5 hr., keeping the internal temperature at 1–2°C; it was then stirred continuously at the same temperature or at room temperature for a further 5.5 hr. or for a period shown in Table I under an atmosphere of nitrogen. Then the whole reaction mixture was treated with water and oxalic acid, except in Exp. 10 (see below), in order to hydrolyze the residual oxidant. The mixture was separated into a benzene layer and an aqueous one, and the latter was repeatedly extracted with benzene or petroleum ether. The removal of the solvent from the combined benzene or petroleum ether solution, after drying over anhydrous sodium sulfate, left a reaction product. The constituents of the reaction product were examined in a manner shown in each

experiment. Each of the constituents was identified by a comparison of its infrared spectrum with that of an authentic sample and by a mixed melting point determination of a constituent or its crystalline derivatives. The yield of the constituents of the reaction product is shown in Table II.

**Oxidation of Cetyl Alcohol (Exp. 1).**—The removal of the solvent from the separated benzene solution gave the reaction product (m. p. 51–54°C), from which palmitic acid (m. p. 61–62°C) was then taken out as the lead salt.<sup>7</sup>) The neutral product free from the acid was subjected to liquid-column chromatography on silica gel with a mixture of *n*-hexane and ethyl acetate in order to separate cetyl palmitate (m. p. 51–52°C;  $\nu_{\text{max}}^{\text{KBr}}$  1735, 1186 cm<sup>-1</sup>) and unchanged cetyl alcohol. No isolated palmitaldehyde could be observed in spite of a careful examination.

**Oxidation of *n*-Lauryl Alcohol (Exp. 2 and 3).**—The distillation of the reaction product gave lauraldehyde (b. p. 103–110°C/3 mmHg), unchanged alcohol (b. p. 115–122°C/3 mmHg) and lauric acid (b. p. 150–151°C/3 mmHg) as the distillate, and *n*-lauryl laurate (m. p. 27–28°C;  $\nu_{\text{max}}^{\text{KBr}}$  1740, 1161 cm<sup>-1</sup>) as the residue.

**Oxidation of *n*-Hexyl Alcohol (Exp. 4).**—The distillation of the reaction product gave caproaldehyde (120–140°C), caproic acid (b. p. 111–112°C/20 mmHg) and *n*-hexyl caproate (b. p. 129–130.5°C/20 mmHg;  $\nu_{\text{max}}^{\text{KBr}}$  1736, 1171 cm<sup>-1</sup>). Caproaldehyde was also contained in removed benzene; it was estimated by the hydroxylamine method.<sup>8</sup>)

**Oxidation of *n*-Butyl Alcohol (Exp. 5).**—An ether solution of the reaction product (b. p. 99–102°C/81 mmHg) obtained by the removal of the

6) E. Guenther, "The Essential Oils," D. Van Nostrand Company, Inc., New York (1952), p. 171.

7) J. D. Piper, A. G. Fleiger, C. C. Smith and N. A. Kerstein, *Ind. Eng. Chem.*, **31**, 307 (1939); W. F. Whitmore and M. Lauro, *ibid.*, **22**, 646 (1930).

8) W. M. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, **57**, 57 (1935).

solvent from the separated benzene solution was extracted with a 10% sodium carbonate solution. The sodium carbonate extracts gave *n*-butyric acid (b. p. 161–163°C) on acidification, while the removal of the solvent from the neutral ether solution afforded *n*-butyl *n*-butyrate (b. p. 97–99°C/80.5 mmHg;  $\nu_{\text{max}}^{\text{liq.}}$  1737, 1183  $\text{cm}^{-1}$ ). *n*-Butyraldehyde was separated as the 2,4-dinitrophenylhydrazone<sup>9)</sup> from the solvent so removed; it was then estimated.

**Oxidation of Ethyl Alcohol (Exp. 6).**—After the reaction mixture had been treated with oxalic acid and water, acetaldehyde in the separated aqueous solution was estimated by the 2,4-dinitrophenylhydrazine method,<sup>9)</sup> while acetic acid was determined by titrating the steam-distillate of the aqueous solution with a standard solution of sodium hydroxide. The separated benzene solution was subjected to gas chromatographic analysis in order to estimate acetaldehyde and ethyl acetate.

**Oxidation of *n*-Amyl Alcohol (Exp. 7).**—The distillation of the reaction product gave *n*-valeraldehyde (b. p. 91–111°C), unchanged alcohol (b. p. 131–145°C), *n*-valeric acid (b. p. 101–103°C/30 mmHg) and *n*-amyl *n*-valerate (b. p. 106–108°C/29 mmHg;  $\nu_{\text{max}}^{\text{liq.}}$  1735, 1178  $\text{cm}^{-1}$ ).

**Oxidation of Isoamyl Alcohol (Exp. 8).**—The reaction product obtained by the evaporation of the solvent was examined in the same manner as that in Exp. 5; it was seen to consist of isovaleric acid (b. p. 97–99°C/38.5 mmHg) and isoamyl isovalerate (b. p. 100–102°C/39 mmHg;  $\nu_{\text{max}}^{\text{liq.}}$  1735, 1188  $\text{cm}^{-1}$ ). Isovaleraldehyde contained in the distilled solvent was estimated by the 2,4-dinitrophenylhydrazine method.

**Oxidation of Isobutyl Alcohol (Exp. 9 and 12).**—The reaction product obtained by the removal of the solvent was found, by the same manner as in Exp. 5, to consist of isobutyric acid (b. p. 152–153°C) and isobutyl isobutyrate (b. p. 146–148°C;  $\nu_{\text{max}}^{\text{liq.}}$  1156 and 1198 (doublet), 1739  $\text{cm}^{-1}$ ). Acetone and isobutyraldehyde were caught as a mixture of the corresponding 2,4-dinitrophenylhydrazone from the solvent removed, and then the dinitrophenylhydrazone was separated by chromatography on a silica gel column.<sup>10)</sup>

**Oxidation of Neopentyl Alcohol (Exp. 10).**—After the oxidation, the reaction mixture was treated with hydrazine sulfate (40 g.) and dilute sulfuric acid in order to hydrolyze the residual oxidant. The distillation of the reaction product gave unchanged alcohol (b. p. 110.5–115°C), trimethyl-

acetic acid (m. p. 34–35°C) and neopentyl trimethylacetate (b. p. 165°C;  $\nu_{\text{max}}^{\text{liq.}}$  1723, 1154  $\text{cm}^{-1}$ ). The acid and the ester were separated from each other by extracting a fraction (b. p. 161–166°C) of the distillate with a sodium carbonate solution. Trimethylacetaldehyde and also a small amount of unchanged alcohol contained in removed benzene were estimated by gas chromatographic analysis.

**Oxidation of Geraniol (Exp. 11).**—The separated benzene solution was extracted with a 3% sodium bicarbonate solution. Geranic acid was obtained from this alkaline solution on acidification. The distillation of the neutral product obtained from the neutral benzene solution gave 2-methyl-2-hepten-6-one (b. p. 60.2–65°C/11.5 mmHg) and citral (b. p. 107–112°C/11.5 mmHg). No ester could be detected, even by thin layer chromatography and gas chromatography of the distillate and the residue.

## Summary

Oxidation with *t*-butyl chromate has been carried out on the straight-chain alcohols with the general formula of  $\text{R}\cdot\text{CH}_2\text{OH}$ , where R is  $\text{CH}_3$ ,  $\text{CH}_3(\text{CH}_2)_2$ ,  $\text{CH}_3(\text{CH}_2)_3$ ,  $\text{CH}_3(\text{CH}_2)_4$ ,  $\text{CH}_3(\text{CH}_2)_5$ ,  $\text{CH}_3(\text{CH}_2)_6$ ,  $\text{CH}_3(\text{CH}_2)_7$ ,  $\text{CH}_3(\text{CH}_2)_8$ ,  $\text{CH}_3(\text{CH}_2)_9$ ,  $\text{CH}_3(\text{CH}_2)_{10}$ ,  $\text{CH}_3(\text{CH}_2)_{11}$  and  $\text{CH}_3(\text{CH}_2)_{12}$ , on branched-chain alcohols with a variety of substituents at the carbon alpha or beta to the hydroxymethyl group, and on unsaturated alcohol with an allylic hydroxymethyl group. Thus, a saturated primary alcohol containing the grouping of  $-\text{CH}_2\cdot\text{CH}_2\text{OH}$ ,  $>\text{CH}\cdot\text{CH}_2\text{OH}$  or  $>\text{C}\cdot\text{CH}_2\text{OH}$  has been found to produce mixtures of the corresponding aldehyde, acid and ester in comparable yields. On the other hand, an unsaturated primary alcohol with an olefinic double bond on the carbon adjacent to the hydroxymethyl group produces the corresponding aldehyde in a high yield, but not the ester.

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9) H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

10) Cf., J. Roberts and C. Green, *ibid.*, **18**, 335 (1946).