# Oxidation of Alcohols with *t*-Butyl Chromate. III. The Oxidation of Alicyclic Alcohols*1

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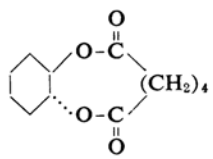
The previous papers[2,3] of this series have shown that the *t*-butyl chromate oxidation of the primary alcohol with an olefinic double bond or a phenyl group adjacent to a carbinol carbon gave the corresponding aldehyde, but did not produce the ester, and that the oxidation of the alcohol without these functional groups produced a mixture of the corresponding ester, aldehyde and acid. We have now attempted the *t*-butyl chromate oxidation of primary alicyclic alcohols, a secondary alicyclic alcohol and cyclic $\alpha$-glycols as an extension of our study of the oxidation of alcohols.[2,3]

**The Oxidation of Primary Alicyclic Alcohol.**—The oxidation of cyclohexylcarbinol (Exp. 1) at 1—2°C for 6 hr. with a benzene solution of *t*-butyl chromate prepared in the 1 : 1 mole ratio of the alcohol to this chromate gave the corresponding aldehyde (40% yield based on the alcohol), acid (28%) and ester, i. e., cyclohexylcarbinyl cyclohexanecarboxylate (19%). This oxidation is in contrast to that of benzyl alcohol,[3] which gave no ester but did give the corresponding aldehyde. The reason for the difference between these oxidations will be discussed in Part IV. The oxidation of myrtenol (Exp. 2) under the same conditions as in Exp. 1 produced no ester but did give the corresponding aldehyde (66%) and acid (5%). This finding agrees with those obtained in the oxidation of geraniol,[2] benzyl alcohol,[3] and *trans*-cinnamyl alcohol.[3]

**The Oxidation of Secondary Alicyclic Alcohol and Cyclic $\alpha$-Glycol.**—The oxidation of cyclohexanol at 35°C for 6 hr. with the oxidant solution prepared in the 1 : 3 mole ratio of the alcohol to the oxidant gave only the corresponding ketone (85%) (Exp. 3), but the oxidation for 48 hr. produced the cleavage product, adipic acid (7%), together with the ketone (68%) (Exp. 4). The oxidation of cyclohexane-*trans*-1, 2-diol*2 at 35°C for 3.5 hr. (Exp. 5) afforded no corresponding diketone, but it did afford adipic acid (57%) and a cyclic ester, *trans*-1, 2-adipoxycyclohexane (I) (7%).



(I)

*1 The oxidation of cyclohexanol and cyclohexane-*trans*-1, 2-diol, which composes a part of the present work, has been reported in Ref. 1 by one of the present authors. The other part was presented at the 4th Symposium on Perfume, Terpene and Essential Oil Chemistry of the Chemical Society of Japan, Sapporo, July, 1960.

1) T. Suga, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 918 (1959).

2) T. Suga, K. Kihara and T. Matsuura, This Bulletin, **38**, 893 (1959).

3) T. Suga, K. Kihara and T. Matsuura, ibid., **38**, 1141 (1965).

*2 L. P. Kuhn (Ref. 4) showed the two hydroxyl groups to be in the equatorial orientation.

4) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

That the corresponding diketone was not obtained may be explained as being because this diketone, produced transiently, was immediately subjected to an oxidative fission to yield adipic acid. The formation of the ester (I) has not yet been reported in the oxidation of this diol; the mechanism will be discussed in Part IV. The oxidation of *p*-menthane-*trans*-3, 4-diol*3 at 30°C for three different reaction times and with the oxidant prepared in the 1 : 1 mole ratio, as in Exps. 1 and 2, gave only the corresponding hydroxyketone (47, 60 and 63% in Exps. 6, 7 and 8 respectively). As regards the cyclic $\alpha$-glycol with a secondary and a tertiary hydroxyl group, a secondary hydroxyl group was oxidized to a ketone group, and only the corresponding hydroxyketone was formed, in contrast to the oxidation of cyclohexane-*trans*-1, 2-diol.

## Experimental

**Samples.** — Cyclohexylcarbinol was synthesized from cyclohexyl bromide and formaldehyde according to the known method[6]: b. p. 91.8°C/23.5 mmHg. Myrtenol was prepared by the oxidation of $\alpha$-pinene with selenium dioxide in a solvent of *t*-butyl alcohol according to the work[7] performed by one of the present authors: b. p. 96°C/9 mmHg. Cyclohexanol was obtained from a commercial source: b. p. 160—161°C. Cyclohexane-*trans*-1, 2-diol[8] (m. p. 103—104°C) and (+)-*p*-menthane-*trans*-3, 4-diol[5,9] (m. p. 76.5—77°C; $[\alpha]_D^{25}$ +27.5°, *c*, 1 in methanol) were prepared by the hydroxylation of cyclohexene and (+)-*p*-menth-3-ene respectively with performic acid. All the samples were purified by distillation or recrystallization just before use.

**The Oxidation, and the Treatment of a Reaction Mixture.**—A benzene solution of *t*-butyl chromate was prepared in the same manner as used in a preceding paper.[2] In Table I, the quantity of each component and the concentration of *t*-butyl chromate in this benzene solution are shown, together with the quantity of the sample alcohol and its solvent. After the oxidation was carried out under the conditions described above in a manner similar to that described in Ref. 2, the reaction mixture was treated with oxalic acid and water, as has also been shown in Ref. 2. The separated benzene solution containing a reaction product was subjected to the described examinations in each experiment. Each of the constituents of the reaction product 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 is shown above. Liquid-column chromatographic separation was made on a silica gel with a mixture of ethyl acetate and *n*-hexane.

**The Oxidation of Cyclohexylcarbinol (Exp. 1).** —The removal of the solvent from the separated benzene solution gave a reaction product (30.1 g.). The distillation of the reaction product gave cyclohexylaldehyde (b. p. 60—62°C/26.5 mmHg; $\nu_{aldehyde}^{liq.}$

Table I. The weights of the alcohol used and each component in the oxidant, and conditions of the oxidation

| Exp. | Sample | | | Oxidant[b] | | | Temp. | Time |
|---|---|---|---|---|---|---|---|---|
| | Alcohol[a] | | $C_6H_6$ | $CrO_3$ | *t*-BuOH | $C_6H_6$ | | |
| | | g. | g. | g. | g. | g. | °C | hr. |
| 1 | Cyclohexyl-carbinol | 30.0 | 58 | 26.3 | 52.6 | 99 | 1—2 | 6 |
| 2 | Myrtenol | 7.4 | 11 | 4.9 | 9.7 | 18 | 1—2 | 6 |
| 3 | Cyclohexanol | 20.0 | 20 | 60.0 | 111.0 | 600 | 35 | 6 |
| 4 | Cyclohexanol | 25.0 | 25 | 75.0 | 139.0 | 750 | 35 | 48 |
| 5 | Cyclohexane-*trans*-1, 2-diol | 30.0 | 26 | 77.4 | 143.4 | 774 | 35 | 3.5 |
| 6 | *p*-Menthane-*trans*-3, 4-diol | 3.0 | 13 | 1.75 | 3.5 | 18 | 30 | 2.5 |
| 7 | *p*-Menthane-*trans*-3, 4-diol | 20.0 | 88 | 11.7 | 23.3 | 132 | 30 | 4.5 |
| 8 | *p*-Menthane-*trans*-3, 4-diol | 3.0 | 13 | 1.75 | 3.5 | 18 | 30 | 8.5 |

a) The concentration of the alcohol in 1000 g. of benzene is 4.5 mol. in Exps. 1 and 2, 10 mol. in Exps. 3—5, and 1.3 mol. in Exps. 6—8.

b) The concentration of *t*-butyl chromate in the benzene solution is 35% in Exps. 1 and 2, 16% in Exp. 7, and 18% in the others.

*3 T. Suga et al. (Ref. 5) showed the two hydroxyl groups to be retained in the axial orientation.

5) T. Suga, T. Shishibori and T. Matsuura, This Bulletin, **37**, 310 (1964).

6) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, 182 (1948).

7) T. Matsuura, Y. Tokutomi and W. Shinoda, unpublished data obtained in our laboratory.

8) A. Roebuck and H. Adkins, "Organic Syntheses," Vol. 28, 35 (1948).

9) Y.-R. Naves, *Helv. Chim. Acta*, **42**, 1174 (1959).

2857, 2810, 2707, 1725, 955 $cm^{-1}$; 2,4-dinitrophenylhydrazone, m. p. 173—174°C), cyclohexanecarboxylic acid (b. p. 103—108°C/7 mmHg, m. p. 30.5—31.5°C, acid number, 436) and cyclohexylcarbinyl cyclohexanecarboxylate (b. p. 136—137°C/7 mmHg, $n_D^{25}$ 1.4727, $d_4^{25}$ 0.9763; $\nu_{ester}^{liq.}$ 1736, 1173 $cm^{-1}$); no original alcohol remained. The hydrolysis of the ester afforded cyclohexylcarbinol (its phenylurethane, m. p. 81.8—82.2°C) and cyclohexanecarboxylic acid (m. p. 30—31°C).

**The Oxidation of Myrtenol (Exp. 2).** — The separated benzene solution was extracted with a sufficient volume of a 3% sodium bicarbonate solution, which then gave myrtenic acid ($\nu^{liq.}$ a broad band of 2700—3500, 1686, 1424, 1270, 949 (COOH), 1623, 841 (trisubstd. C=C) $cm^{-1}$) on acidification. The removal of the solvent from the neutral benzene solution gave a neutral product (6.3 g.). The liquid-column chromatography of the neutral product gave myrtenal (b. p. 84—87°C/9 mmHg; $\nu_{aldehyde}^{liq.}$ 2816, 2733, 1682 $cm^{-1}$; 2,4-dinitrophenylhydrazone, m. p. 217—218°C), unchanged alcohol ($\nu_{OH}^{liq.}$ 3374, 1014 $cm^{-1}$; 3% yield), and a resinous substance (9%), probably a polymer.

**The Oxidation of Cyclohexanol (Exps. 3 and 4).** —The separated benzene solution was treated as in Exp. 2. The product (b. p. 153—155°C) obtained from the neutral benzene solution was then examined by infrared spectroscopy and chromatostrip chromatography,[10] while cyclohexanone was estimated by the 2,4-dinitrophenylhydrazine method.[11] The sodium bicarbonate extracts were combined with the aqueous solution used for hydrolyzing the residual oxidant. Adipic acid (m. p. 151—152°C) was obtained by extracting the combined solution with ether after acidification. No original alcohol remained in either experiment.

**The Oxidation of Cyclohexane-*trans*-1,2-diol (Exp. 5).**—The removal of the solvent from the separated benzene solution gave a viscous, neutral product (6.1 g.) and adipic acid (m. p. 151—152°C), which was also obtained from the aqueous solution used for hydrolyzing the residual oxidant (cf. Exps. 3 and 4). The neutral product deposited a crystalline mass (2.2 g.; m. p. 125—125.5°C; $\nu_{ester}^{KBr}$ 1733, 1271, 1155 $cm^{-1}$).

Found: C, 63.44; H, 8.29; ester number, 247.8. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%; ester number, 248.0.

The hydrolysis of the crystalline ester gave, quantitatively, cyclohexane-*trans*-1,2-diol (m. p. 103—104°C) and adipic acid (m. p. 151—152°C). Therefore, the ester was confirmed to be *trans*-1,2-adipoxycyclohexane (I).

No cyclohexane-1,2-dione was detected, and the other, resinous part of the neutral product looked like a polymer.

**The Oxidation of (+)-*p*-Menthane-*trans*-3,4-diol (Exps. 6—8).**—The separated benzene solution was treated in the same manner as in Exp. 2. The sodium bicarbonate extracts did not give any reaction product. The liquid-column chromatography of the reaction product obtained from the neutral benzene solution gave (−)-4-hydroxymenthone (b. p. 104—105°C/13 mmHg; $[\alpha]_D^{25}$ −96.7° (neat); $\nu^{liq.}$ 3493, 1154 (OH), 1709 (C=O), 1430 ($-CH_2-CO-$) $cm^{-1}$; 2,4-dinitrophenylhydrazone, m. p. 102.5—103°C; Found: N, 15.73. $C_{16}H_{22}O_5N_4$ requires N, 15.99%). (−)-4-Hydroxymenthone 2,4-dinitrophenylhydrazone was produced on treating the keto alcohol with a 2 N hydrochloric acid solution of 2,4-dinitrophenylhydrazine. On the other hand, the treatment of the keto alcohol with an ethanol-sulfuric acid solution of 2,4-dinitrophenylhydrazine gave (±)-*p*-menth-3-en-5-one 2,4-dinitrophenylhydrazone (m. p. 147.5—148.5°C).

## Summary

1) The *t*-butyl chromate oxidation of myrtenol gave no ester, but it did give the corresponding aldehyde as the main product, while the oxidation of cyclohexylcarbinol gave a mixture of the corresponding aldehyde, acid and ester in comparable yields.

2) A similar oxidation of cyclohexanol afforded the corresponding ketone in a high yield, while the oxidation of cyclohexane-*trans*-1,2-diol produced no corresponding diketone, but it did produce the glycol fission product and a cyclic ester such as *trans*-1,2-adipoxycyclohexane (a new compound). On the other hand, *p*-menthane-*trans*-3,4-diol yielded only the corresponding hydroxyketone in a good yield.

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10) J. G. Kirchner, J. M. Miller and G. J. Keller, *Anal. Chem.*, **23**, 420 (1951); J. M. Miller and J. G. Kirchner, ibid., **25**, 1107 (1953).
11) H. A. Iddles, A. W. Low, B. D. Rosen and R. T. Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).