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Oxidation of Alcohols with *t*-Butyl Chromate. IV. The Course of the Formation of the Ester*

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The results obtained in the preceding papers (Parts I—III) of this series showed that, on oxidation with *t*-butyl chromate, the primary alcohol without a π-electron system on the carbon α to the hydroxymethyl group yields the corresponding ester in a comparable yield, together with the aldehyde and the acid, and also that the cyclic α-glycol with two secondary hydroxyl groups affords the corresponding cyclic ester, along with the glycol fission product. Chemical examination and infrared spectroscopic study have now proved that the course of the formation of these esters does not follow the direct esterification of the alcohol with the acid formed from it by oxidation, but rather involves the formation of a hemiacetal intermediate between the original alcohol and the aldehyde produced from the alcohol, and the subsequent oxidation of the hemiacetal. The oxidation of alcohols with *t*-butyl chromate has also been discussed generally on the basis of the results of our previous papers and of the present work.

Our previous papers[1-3] showed that, on oxidation with *t*-butyl chromate, saturated primary alcohols, such as aliphatic and β-phenylethyl alcohols and cyclohexylcarbinol, yielded mixtures of the corresponding aldehyde, acid and ester in comparable yields, while unsaturated primary alcohols, such as *trans*-cinnamyl and benzyl alcohols, geraniol and myrtenol, did not produce the ester, but yielded only the corresponding aldehyde and acid.

The ester might be formed in one of the following two courses: the direct esterification of the alcohol with the acid formed from it by oxidation,[4,5] or the hemiacetal formation between the original alcohol and the aldehyde produced from it by oxidation, and the subsequent oxidation to the ester.[6,7] We have now tried to clarify the course of the formation of the ester, together with the reason for the oxidation mode being different depending on the type of alcohol. In addition, generalizations as to the *t*-butyl chromate oxidation of alcohols have been given.

In the *t*-butyl chromate oxidation of *n*-butyl alcohol, *n*-butyric acid produced was removed by extracting the benzene solution with alkali before the solvent was removed (Exp. 1). The amount of *n*-butyl *n*-butyrate thus obtained was identical with that of the ester (Exp. 5 in Ref. 1) obtained without this treatment. A similar result (Exp. 2) was also observed in the oxidation of cyclohexane-*trans*-1, 2-diol, which yielded *trans*-1, 2-adipoxycyclohexane (II) as an ester (Exp. 5 in Ref. 3). Besides, *n*-butyl alcohol was not esterified (Exp. 3) by *n*-butyric acid during the agitation

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[1] T. Suga, K. Kihara and T. Matsuura, This Bulletin, **38**, 893 (1965).

[2] T. Suga, K. Kihara and T. Matsuura, ibid., **38**, 1141 (1965).

[3] T. Suga and T. Matsuura, ibid., **38**, 1503 (1965).

[4] L. Bouveaut, *Bull. Soc. Chim. France*, **1904**, 1306.

[5] G. R. Robertson, "Organic Syntheses," Coll. Vol. I, 138 (1941).

[6] W. A. Mosher and D. M. Preiss, *J. Am. Chem. Soc.*, **75**, 5605 (1953).

[7] J. C. Craig and E. G. Horning, *J. Org. Chem.*, **25**, 2098 (1960).

of a mixture of the alcohol and the acid in benzene under conditions similar to those in the oxidation. Moreover, if the ester were formed by direct esterification, *n*-hexyl acetate would be produced together with *n*-hexyl *n*-caproate when *n*-hexyl alcohol is oxidized in the presence of acetic acid. However, this oxidation (Exp. 4) did not give any *n*-hexyl acetate; it afforded only *n*-hexyl *n*-caparoate.

If another aldehyde ($R''-CHO$) is added to a mixture of an alcohol ($R'-CH_2OH$) and an aldehyde ($R'-CHO$) produced from it, two kinds of hemiacetals ($R'-CH(OH)\cdot O\cdot CH_2-R'$ and $R'-CH(OH)\cdot O\cdot CH_2-R''$) should be formed and then oxidized to two esters ($R'-CO\cdot O\cdot CH_2-R'$ and $R'-CO\cdot O\cdot CH_2-R''$ respectively). The oxidation of an equimolar mixture of *n*-hexyl alcohol and *n*-butyraldehyde (Exp. 5) showed the formation of *n*-hexyl *n*-butyrate and *n*-hexyl *n*-caproate; this was in agreement with the expectation. These results suggest that the course to the ester involves the hemiacetal oxidation.

The infrared spectra of mixtures of an aldehyde and an alcohol were examined in order to establish the formation of a hemiacetal as an intermediate. Two absorption cells, one filled with an aldehyde and the other with an alcohol, were placed in series so that the recorded spectrum was the sum of the spectra of two samples. On the other hand, an equimolar mixture of an aldehyde and an alcohol was placed in one cell and the spectrum was again recorded. A comparison was then made between the "separate" and "mixed" spectra. The spectra of the pair, *n*-butyraldehyde and *n*-hexyl alcohol (Fig. 1), showed considerable differences between the "separate" and "mixed" spectra. In the "mixed" spectrum the strong new bands were found at about 850, 1000—1015, 1090, 1115, and 1140 cm^{-1} and were assignable to an ether-linkage of a hemiacetal.[8,9] The same phenomena as above were also observed in the spectra of the other pairs, *n*-butyraldehyde and *n*-butyl alcohol, and β-phenylacetaldehyde and β-phenylethyl alcohol. The formation of the ester has been observed in the oxidation of these alcohols and is in harmony with the appearance of new bands which can be ascribed to the formation of an intermediate hemiacetal in the spectra of mixtures of the alcohols and the corresponding aldehydes. In contrast, a complete agreement was observed between the "separate" and "mixed" spectra of the two pairs, benzaldehyde and benzyl alcohol, and *trans*-cinnamaldehyde and *trans*-cinnamyl alcohol. This is coincident with the finding of our previous work[2)] that the *t*-butyl chromate oxidation of these alcohols does not produce the ester; this can be ascribed to the failure of these pairs to form a hemiacetal.

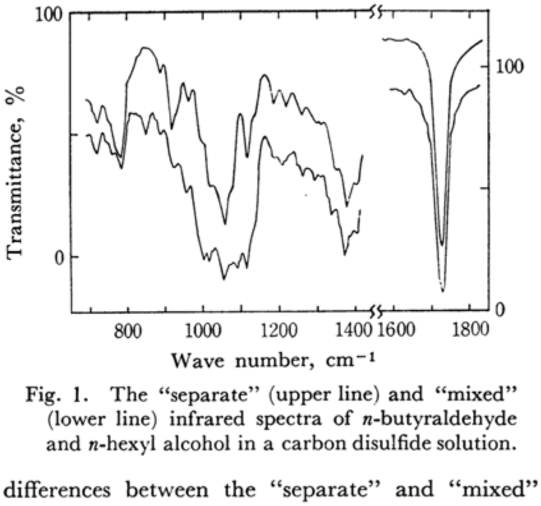
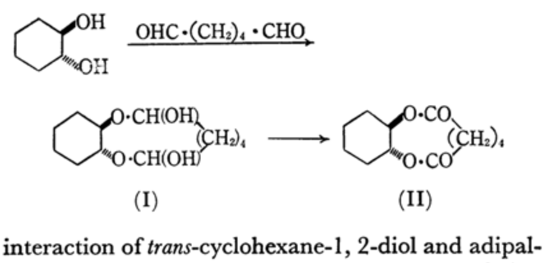


Fig. 1. The "separate" (upper line) and "mixed" (lower line) infrared spectra of *n*-butyraldehyde and *n*-hexyl alcohol in a carbon disulfide solution.

The agreement observed between the "separate" and "mixed" spectra of the two pairs, benzaldehyde and *n*-hexyl alcohol, and *trans*-cinnamaldehyde and *n*-butyl alcohol, also indicated no formation of a hemiacetal between these pairs, while the formation of a hemiacetal was shown by the differences observed between the spectra of two other pairs, caproaldehyde and benzyl alcohol, and *n*-butyraldehyde and *trans*-cinnamyl alcohol. Accordingly, it was found that the hemiacetal formation does not depend on the structure of the alcohol, but on that of the aldehyde, namely, on the substitution system on the carbon α to the carbonyl group.

A previous paper[3)] of this series showed that the *t*-butyl chromate oxidation of *trans*-cyclohexane-1, 2-diol produces *trans*-1, 2-adipoxycyclohexane (II), the formation of which has not yet been reported in the oxidation of this diol. Recently, Head[10)] has observed the reaction of *trans*-cyclohexane-1, 2-diol with glyoxal at room temperature to give a crystalline bishemiacetal, *trans*-hexahydro-2, 3-dihydroxy-1, 4-benzodioxane. The formation of II can, therefore, be explained by the process by which the hemiacetal (I) shown in the following equation is first formed by the interaction of *trans*-cyclohexane-1, 2-diol and adipaldehyde probably produced by the glycol-fission of the 1, 2-diol, and is subsequently oxidized.



(I)　(II)

In conclusion, our previous findings[1-3)] and the present work on the *t*-butyl chromate oxidation of alcohols permit us to generalize the oxidation

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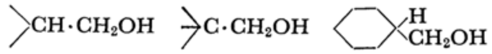
[8)] A. Ashdown and T. A. Kletz, *J. Chem. Soc.*, **1948**, 1454.

[9)] E. D. Bergmann and S. Pinchas, *Rec. Trav. Chim.*, **71**, 161 (1952).

[10)] F. S. H. Head, *J. Chem. Soc.*, **1960**, 1778.

as follows. The oxidation of the primary alcohol without a π-electron system on the carbon α to the carbinol carbon, such as the alcohol which contains the group shown below:

$R-CH_2\cdot CH_2OH$ (R=H, Alkyl, or Phenyl)



yields a mixture of the corresponding aldehyde, acid and ester in a comparable yield. On the other hand, the oxidation of the primary alcohol with a π-electron system on the carbon α to the hydroxymethyl group, such as the following system:

$-CR{=}CR\cdot CH_2OH$ (R=H or Alkyl)

$C_6H_5\cdot CH_2OH$

produces not the ester, but the corresponding aldehyde in a high yield and acid in a low yield. A secondary alicyclic alcohol and a cyclic α-glycol with a secondary and a tertiary hydroxyl groups are selectively oxidized to the corresponding ketone and α-hydroxyketone respectively, while the oxidation of a cyclic α-glycol with two secondary hydroxyl groups does not give the corresponding α-diketone, but the glycol fission product and the cyclic ester.

Moreover, there was evidence that the course of the formation of the ester did not involve direct esterification, but hemiacetal oxidation.

Experimental

Samples.—The alcohols were the same ones as were used in the previous papers[1-3] of this series; the aldehydes were obtained from a commercial source. All the samples were purified repeatedly by distillation or recrystallization just before use.

Oxidation or Reaction.—A benzene solution of *t*-butyl chromate was prepared in the manner used in a preceding paper.[1] The quantity of each component in this solution is shown in Table I, which also lists the quantity of the sample and its solvent. After the oxidation or the reaction was carried out at 1—2°C for 6 hr. (except in Exp. 2, which had a reaction time of 3 hr. at 35°C), the reaction mixture was treated with oxalic acid and water, as has been shown in Ref. 1. The separated benzene solution 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 the authentic sample and by a mixed melting point determination; the yield of the constituents is shown below.

The Oxidation of *n*-Butyl Alcohol (Exp. 1).—After the oxidation, the reaction mixture was treated with oxalic acid and water, and then the separated benzene solution was repeatedly extracted with a sufficient amount of a 5% sodium carbonate solution; this alkaline solution gave *n*-butyric acid (31.5% yield based on the alcohol; b. p. 99—100°C/79 mmHg, n_D^{25} 1.3957, d_4^{25} 0.9614) on acidification. The removal of the solvent from the neutral benzene solution afforded *n*-butyl *n*-butyrate (34.3%; b. p. 94—95°C/77 mmHg, n_D^{25} 1.4059, d_4^{25} 0.8663; $\nu_{\text{ester}}^{\text{liq.}}$ 1741, 1187 cm^{-1}).

The Oxidation of Cyclohexane-*trans*-1, 2-diol (Exp. 2).—The reaction mixture was treated in the manner described in Exp. 1. The neutral product obtained was subjected to examinations similar to those used in Exp. 5 in Ref. 3; *trans*-1, 2-adipoxycyclohexane (m.p. and mixed m.p. 103—104°C; $\nu_{\text{ester}}^{\text{KBr}}$ 1733, 1270, 1154 cm^{-1}) was thus obtained in a 7% yield.

The Agitation of a Mixture of *n*-Butyl Alcohol and *n*-Butyric Acid in Benzene (Exp. 3).—After a mixture of *n*-butyl alcohol and *n*-butyric acid in benzene had been stirred under the conditions shown above, the solvent was removed from the solution under an atmospheric pressure without previous treatment by an alkaline solution. The remaining liquid was analyzed by gas chromatography (column: silicone DC-550 on Celite, 130°C, 50 ml. helium/min.) and infrared spectroscopy. Not even a trace of *n*-butyl *n*-butyrate was detected; the liquid consisted of only the original samples.

The Oxidation of *n*-Hexyl Alcohol in the Presence of Acetic Acid (Exp. 4).—After the oxidation had been carried out in benzene containing acetic acid corresponding to about a 5% concentration in the whole reaction mixture, the reaction mixture was treated as in Exp. 1. The sodium carbonate extracts afforded *n*-caproic acid (26.0%; b. p. 195—200°C, n_D^{25} 1.4129, d_4^{25} 0.9284) on acidification, while the removal of the solvent from the neutral benzene solution gave a neutral product; this was then fractionated by distillation and subjected to gas chromatographic analysis (column: silicone DC-550 on Celite, 140°C, 60 ml. helium/min.). The reaction product did not contain even a trace of *n*-hexyl acetate; it consisted of caproaldehyde (12.3%; b. p. 128—135°C, n_D^{25} 1.4070, d_4^{25}

TABLE I. THE WEIGHTS OF THE SAMPLE USED AND EACH COMPONENT IN THE OXIDANT

Exp.	Sample			Oxidant		
	Material	g.	C_6H_6 g.	CrO_3 g.	*t*-BuOH g.	C_6H_6 g.
1	*n*-Butyl alcohol	20.0	60	27.0	54.0	100
2	Cyclohexane-*trans*-1, 2-diol	30.0	26	77.4	143.4	774
3	*n*-Butyl alcohol *n*-Butyric acid	20.0 10.0	140	—	—	—
4[a]	*n*-Hexyl alcohol	40.0	87	39.1	66.6	159
5	*n*-Hexyl alcohol *n*-Butyraldehyde	51.1 36.1	111	50.0	100.0	195

a) To the benzene solution of *t*-butyl chromate, 20 g. of glacial acetic acid was added.

0.8238; $\nu_{\text{CHO}}^{\text{liq.}}$ 1724, 2723 cm^{-1}), *n*-hexyl *n*-caproate (46.5%; b. p. 110—113°C/8 mmHg; n_D^{25} 1.4226, d_4^{25} 0.8573; $\nu_{\text{ester}}^{\text{liq.}}$ 1738, 1168 cm^{-1}) and unchanged alcohol (3.3%; b. p. 93—100°C/49 mmHg).

The Oxidation of a Mixture of *n*-Hexyl Alcohol and *n*-Butyraldehyde (Exp. 5).—As soon as a benzene solution of an equimolar mixture of *n*-hexyl alcohol and *n*-butyraldehyde had been prepared under ice-cooling, the oxidation was conducted under the conditions shown above; then the reaction mixture was worked up as has been described above. The distillation of the acidic product gave *n*-butyric acid (10.5%; b. p. 83.5—84°C/40 mmHg, n_D^{25} 1.3958, d_4^{25} 0.9535) and *n*-caproic acid (8.4%; b. p. 121°C/40 mmHg, n_D^{25} 1.4136, d_4^{25} 0.9236). On the other hand, a combination of fractional distillation, gas chromatography and infrared spectroscopy indicated that the neutral product consisted of caproaldehyde (6.5%; b. p. 125—132°C, n_D^{25} 1.4041, d_4^{25} 0.8290), *n*-hexyl *n*-butyrate (18.6%; b.p. 97—98°C/19 mmHg, n_D^{25} 1.4142, d_4^{25} 0.8612; $\nu_{\text{ester}}^{\text{liq.}}$ 1734, 1184 cm^{-1}; ester number 331), *n*-hexyl *n*-caproate (5.4%; b. p. 127°C/19 mmHg, n_D^{25} 1.4224, d_4^{25} 0.8601; $\nu_{\text{ester}}^{\text{liq.}}$ 1741, 1170 cm^{-1}; ester number 280), unchanged alcohol (9.2%), and unchanged aldehyde (14.7%). The hydrolysis of the esters gave the corresponding alcohol and acid respectively.

The Measurement of the "Separate" and "Mixed" Infrared Spectra of the Aldehydes and the Alcohols.—The spectrometer used was a Hilger H-800 double-beam spectrophotometer fitted with a sodium chloride prism. Each of the cells used for the "separate" spectra measurements was 0.1 mm. thick, and the aldehyde and the alcohol were each a carbon disulfide solution of 1 molar concentration. In the "mixed" spectra measurements, the cell was 0.2 mm. long, and a carbon disulfide solution of an equimolar mixture of an aldehyde and an alcohol was prepared in a 1-molar concentration of each sample.

Summary

1) The formation of the ester which is produced when the alcohol without a π-electron system on the carbon α to the carbinol carbon and the cyclic α-glycol with two secondary hydroxyl groups are oxidized with *t*-butyl chromate, has been found to follow the course of the formation of an intermediate hemiacetal between the original alcohol and the aldehyde produced from it by oxidation, and subsequent oxidation.

2) The oxidation of alcohols with *t*-butyl chromate has been generally described on the basis of results obtained in our previous papers (Parts I—III) and in the present work.

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