

Two Phase Oxidation of Aldehydes with Chromic Acid

by

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ABSTRACT

The possibility of the two-phase oxidation of an aldehyde to carboxylic acid was studied. Thus the ether solutions of representative aldehydes (2.0M) were treated with 1.5 mole equivalent of chromic acid solution (1.0M) for 30 minutes at room temperature. Of the ten aldehydes tested, butanal, benzaldehyde, tolualdehyde, o-, m-, p-nitrobenzaldehyde and cinnamaldehyde could be oxidized conveniently to the corresponding carboxylic acid giving an 80-90% yield. But furfural gave only a 30% yield of furoic acid and the oxidation of salicylaldehyde was unsuccessful.

Introduction

Among the variety of agents available for the oxidation of organic compounds, the most commonly used are the derivatives of hexavalent chromium or heptavalent manganese.¹⁾ Although many different reaction conditions were utilized for specific oxidations, it is rather difficult to find out the proper condition for the selective oxidation of an aldehyde group in the presence of other functional groups. For example, the existing condition for the permanganate oxidation of piperonal²⁾ is almost similar to those of the oxidation of o-chlorotoluene to o-chlorobenzoic acid³⁾ and the oxidation of naphthalene to phthalic acid.⁴⁾ Therefore, the milder reaction conditions suitable for the selective oxidation of an aldehyde bearing many functional groups should further be investigated. For this

purpose, we studied on the possibility of the two phase oxidation of aldehydes with chromic acid, the method already proved to be excellent for the oxidation of secondary alcohols to ketones.⁵⁾

Experiment

Materials

a) Aldehydes: All the aldehydes used were checked for their purity by their refractive index or melting points.

b) Chromic acid solution: The chromic acid solution was prepared by adding 297 gram of sodium dichromate dihydrate (1mole) to 225 ml of 98% sulfuric acid and diluted to 1 litre.

General Procedure for Two Phase Oxidation

In a 250 ml flask, fitted with a magnetic stirrer, a reflux condenser and a funnel, there was placed a 4.24 gr. of benzaldehyde (40 moles)

dissolved in 20 ml of ether. A 60 ml of the chromic acid solution (1M) was added to the stirred solution of benzaldehyde over 15 minutes through the funnel, maintaining the temperature at 25–35°C. After 30 minutes, the upper ether layer was separated and the aqueous layer was extracted with five 20 ml portions of ether. The combined ether extract was washed with water. The total volume of ether extract was 100 ml, and 5 ml of this solution was transferred into a 500 ml erlenmeyer flask. To this solution 30ml of standardized N/10 sodium hydroxide solution was added and titrated with standardized N/10 sulfuric acid solution, phenolphthalein being used as the indicator. N/10 sulfuric acid solution, 12.58 ml, was required.

The acid-alkalimetric analysis of this ether solution showed 87% yield of benzoic acid. The ether layer was extracted with several portions of 5% sodium hydroxide solution and the combined aqueous solution was decolorized and the benzoic acid was precipitated with 5% sulfuric acid, filtered and dried. There was obtained a 4.14 gr. of benzoic acid, mp 122°C (lit. 122°C) which corresponds to 85% yield. After two hours, the titration showed 90% yield and isolated yield was 88% (4.29 gr.) In the case of a water soluble acid, such as butanoic acid, separation was accomplished by distillation of the ether extract.

Furfural 2, 4-Dinitrophenylhydrazone

The combined ether extract was evaporated, dissolved in 95% ethanol and diluted to 100ml. Of this solution, 5ml, was transferred to a 250 ml. beaker and diluted with 50 ml. of 95% ethanol. A freshly prepared 2, 4-dinitrophenylhydrazine reagent was added to the ethanol solution, and the resulting mixture was allowed to stand at room temperature. The precipitate was filtered, washed with 50% ethanol and dried in a vacuum. There was obtained 0.38 gr. (70%) furfural-2, 4-dinitrophenylhydrazone, m. p., 201°C (lit., m. p., 202°C).⁶⁾

Results and Discussion

First, the possibility of two phase oxidation of an aldehyde was tested with benzaldehyde. Thus we dissolved 10 mmoles of benzaldehyde in 20 ml of ether and treated it with 30 ml of 1 M solution of chromic acid (30 mmoles) and obtained 8.6 mmoles of benzoic acid. This corresponds to an 86% yield. We repeated this experiment, changing the amount of benzaldehyde while keeping all of the other conditions constant. (Ether solution is 20 ml, 30 mmoles of chromic acid, at room temperature, and for 3 hours.)

The results are summarized in Table 1.

Table 1 Two Phase Oxidation of Benzaldehyde--Effect of the Aldehyde to Chromic Acid Ratio at Room Temperature.

Mmoles of Benzaldehyde in 20 ml of Ether	10	20	30	40	60	80	100
Mmoles of Chromic acid	30	30	30	30	30	30	30
Mmoles of Benzoic acid obtained in 3 hrs.	8.6	17.2	24.9	31.2	43.2	52.8	58
Yield, %	86	86	83	78	72	66	58

The results show that the percentage yields are good when the ratio is smaller than one, but the low yield realized in the ratio of 100 to 30 is not pessimistic, since as much as 58 mmoles of aldehyde are oxidized in 3 hrs. This low yield would easily be overcome by recycling

the unreacted aldehyde especially if performed on the industrial scale. We further studied the effects of time, molar concentration of reactants and temperature on the reaction. The results are summarized in Table 2.

Table 2 Two Phase Oxidation of Benzaldehyde -- Effects of Time, Molar Concentration of Reactants, and Temperature on the Reaction.

Mmoles of Benzaldehyde in 20 ml of Ether	Amount of Chromic acid	Time, hrs. ^a						
		0.0	0.25	0.5	1.0	3.0	6.0	24.0
1. 40 (2.0M)	30 mmoles (30 ml of 1 M sol.)				72	75	79	86
2. 20 (1.0 M)	30 mmoles (")	82	86	87				
3. 40 (2.0 M)	60 mmoles (60 ml of 1 M sol.)	78	82	86 (82) ^b	87	90 (89) ^b		98

^a Yield of benzoic acid at room temperature. ^b At 0°C

The results show that the reaction took place rapidly (80% in the case of the mole ratio of 2:3 and 70% for the mole ratio of 4:3), but after that the reaction proceed very slowly and the molar concentration of reactants and temperature did not have much effect in so far as the mole ratio of aldehyde to chromic acid remained constant. (Entry 2 and 3). More detailed study would be necessary in order to understand

the mode of reaction completely; however, we are satisfied with the results of entry 3 of Table 2. Thus we could oxidize 40 mmoles of aldehyde in 20 ml of ether with 60 mmoles of chromic acid (60 ml of the 1.0 M solution) resulting in an 86% yield in 0.5 hr. and in a 90% yield in 2 hrs. Accordingly, we applied this method to ten representative aldehydes, and the results are summarized in Table 3.

Table 3 Two Phase Oxidation of Representative Aldehydes with Chromic acid at Room Temperature.

Aldehyde	Product	Yield, % obtained in 0.5 and 2.0 hrs., respectively		Physical const. of the product (°C)
		0.5	2.0	
Butyraldehyde	Butanoic acid	(85)	(88)	b. p., 161 (lit. 163)
Decaldehyde	Decanoic acid	88 ^a (84) ^b	92(87)	b. p., 272 (lit. 270)
Benzaldehyde	Benzoic acid	87(85)	90(87)	m. p., 122 (lit. 122)
Tolualdehyde	Toluic acid	86(83)	89(86)	m. p., 177 (lit. 176-178)
o-Nitrobenzaldehyde	o-Nitrobenzoic acid	83(80)	85(83)	m. p., 148 (lit. 147-148)
m-Nitrobenzaldehyde	m-Nitro benzoic acid	87(82)	91(86)	m. p., 43(lit. 43-44)
p-Nitrobenzaldehyde	p-Nitro-benzoic acid	86(82)	90(86)	m. p., 240 (lit. 242)
Cinnamaldehyde	Cinnamic acid	78(76)	81(78)	m. p., 134 (lit. 136-137)
Salicylaldehyde	Salicylic acid	0(0)	0(0)	
Furfural	Furoic acid	(27)	(30) ^c	m. p., 130 (lit. 133)

^a Yield estimated by alkali titration. ^b The data in parentheses are the isolated yields. ^c 70% of unreacted furfural was identified by 2, 4-dinitrophenylhydrazone.

As shown in Table 3, all aldehydes tested except salicylaldehyde and furfural, oxidized to the corresponding acids with 80-90% yields in 30 minutes, and the yields increased only slightly after two hours. As shown in the cases of butyraldehyde and decaldehyde, there is no difference in the reactivity between the water soluble aldehyde and the insoluble one. We believe there was no oxidation of the methyl group in tolualdehyde, since only the toluic acid was isolated by a simple separation scheme. (See the Experimental section) Nitrobenzaldehydes gave equally good results regardless of the position of the nitro group on the benzene ring. We obtained a little lower yield of cinnamic acid; however, there was no indication of the oxidation of the double bond. If it were attacked in this condition, a large difference between titration and isolated yield would take place and the yield would decrease rather than increase in proportion to the length of time. No salicylic acid and only 30% of the furoic acid was obtained from the corresponding aldehydes. In the case of furfural, the unreacted furfural amounted to 70% of the initial quantity by 2,4-dinitrophenylhydrazone, showing no side reaction.

Conclusion

Aldehydes, even if they contain a methyl group, a nitro group or a conjugated double bond, whether aliphatic or aromatic, can be

oxidized to the carboxylic acid conveniently by two phase oxidation with chromic acid. It failed in the case of salicylaldehyde, and seemed very slow in the case of furfural. Nevertheless this study opened up convenient possibilities of selective oxidation with this commonly used oxidizing agent.

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