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CONVERSION OF TRI-*O*-BENZYLCELLULOSE TO BENZOYLCELLULOSE BY OZONIZATION

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ABSTRACT

Tri-*O*-benzylcellulose was oxidized to benzoylcellulose in good yields by ozonization. Degrees of substitution (DS) of benzoylcellulose thus prepared were higher than 2.5. A little depolymerization during the ozonization of tri-*O*-benzylcellulose was detected by gel permeation chromatography. In contrast, tri-*O*-*p*-methoxybenzylcellulose gave other reaction products than *p*-methoxybenzoylcellulose.

1. INTRODUCTION

The authors have developed the quantitative preparation method of tri-*O*-substituted cellulose ethers by using non-aqueous cellulose solvent systems^{1)–5)}. These new derivatives soluble in many organic solvents may be modified chemically to some reactive derivatives.

Ozone is an oxidizing agent reactive to functional groups having high electron densities. Carboxylic acids, ketones, aldehydes or alcohols are obtained by oxidation or reduction of ozonides produced by ozonization of aromatic rings or double bonds. Thus tri-*O*-benzylcellulose is expected to produce some new derivatives by oxidation or reduction treatments of ozonized products.

In this paper, tri-*O*-benzylcellulose and tri-*O*-*p*-methoxybenzylcellulose were ozonized under various conditions for introduction of some functional groups into both cellulose derivatives.

2. EXPERIMENTAL

2.1 Materials

Tri-*O*-benzylcellulose and tri-*O*-*p*-methoxybenzylcellulose were prepared from Avicel (commercial cellulose powder, DP_v=250) according to the previous method^{1),2)}.

2.2 Ozonization

Nippon Ozone O-3-2 type was used as an ozone

generator. Three grams of a sample was dissolved in 60 ml of dichloromethane-methanol (5:1 by vol). Ozone/oxygen gas containing 1.5% ozone was bubbled into the sample solution with the rate of 0.5 ml/min at –30 or 0°C. Fifteen ml of the ozonized solution was taken out at 5, 30, 60, and 180 min after the start of ozonization. Nitrogen gas was bubbled into them in order to remove the remaining ozone. Each solution was divided into four portions, and they were treated as described in the next paragraph. Acetic acid-methanol-water (8:1.5:0.5 by vol) system⁶⁾ was also used as an ozonization medium, which was a heterogeneous medium because benzylcellulose is insoluble in the system.

2.3 Post treatment

In order to degrade the ozonides produced by ozonization of tri-*O*-benzylcellulose, four types of following treatments were applied to the ozonized products.

1) One portion of the ozonized solution was evaporated to remove solvents, and the residue was dissolved in 2 ml of benzene or 2 ml of acetone. Twenty ml of glacial acetic acid, 1 ml of water, one drop of concentrated hydrochloric acid, and 2.5 ml of hydrogenperoxide solution (30%) were added to the solution, and the mixture was stirred for 1 day at room temperature⁷⁾. After neutralization with an aqueous saturated sodium hydrogen carbonate solution, the solution was

concentrated by evaporation. Precipitate was formed by the addition of methanol to the residue and separated by filtration.

2) Another portion of the ozonized solution was evaporated, and 5 ml of dioxane, 5 ml of water, and 0.1 g of sodium borohydride were added to the residue⁸⁾. After stirring the mixture for 1 day at room temperature, the reaction product was isolated by the addition of methanol and by subsequent filtration.

3) Another portion of the ozonized solution was treated with zinc powder under the usual condition⁷⁾.

4) The other portion was evaporated, and methanol was added to the residue. The precipitate was filtered, washed with methanol, and dried at 40°C in vacuo.

Yields after the above treatments (1)–(4) were 80–95 weight % of original tri-*O*-benzylcellulose.

2.4 General analyses

Infrared (IR) spectra were measured using the deposited film technique. ¹H- and ¹³C-NMR spectra were obtained using JEOL MH 100 and JEOL FX 100, respectively. Gel permeation chromatograms were collected using a Waters ALC/GPC 244 system with Styragel columns 10⁵, 10⁴, 10³, 10², 500, and 100 Å in the series.

3. RESULTS AND DISCUSSION

3.1 Analyses of Ozonized Products

As described in Experimental, tri-*O*-benzylcellulose was ozonized in homogeneous or heterogeneous media, and then was subjected to four kinds of treatments. However, contrary to our expectation, all final products thus obtained gave almost the same IR, UV, and ¹³C-NMR spectra, and they were soluble in organic solvents such as acetone and dioxane, and were insoluble in aqueous alkaline solutions even after the oxidative treatment. These results indicate that the ozonization of tri-*O*-benzylcellulose did not yield carboxyl groups.

Figures 1 shows the infrared spectra of reaction products prepared from tri-*O*-benzylcellulose by ozone at 0 and –30°C. Absorption bands around 1720 and 1260 cm^{–1} increased with the increase of ozonization time, and hydroxyl absorptions around 3400 cm^{–1} came to be detected. The bands around 690–760 cm^{–1} due to the out-of-

Fig. 1 IR spectra of products prepared by ozonization of tri-*O*-benzylcellulose at 0°C (A) and –30°C (B).

plane vibrations of C–H in aromatic rings of tri-*O*-benzylcellulose changed in their patterns by the advanced ozonization, and eventually a new sharp band appeared around 700 cm^{–1}. The bands around 3100–2800 cm^{–1} due to C–H stretching vibrations of aromatic rings of tri-*O*-benzylcellulose decreased with the increase of ozonization time. Changes in spectra by ozonization at –30°C were the same as those at 0°C, but the reaction rate for the former was lower than the latter. The absorption band around 1720 cm^{–1} is due to C=O groups of free carboxyls, esters or ketones, and that at 1260 cm^{–1} is due to carboxyls, esters, lactones or acid anhydrides. Since the reaction products were insoluble in aqueous alkaline solutions, they must be esters or ketones.

Figure 2 shows ¹³C-NMR spectra of tri-*O*-benzylcellulose and its reaction products after ozonization. A single peak due to carbonyl groups appeared at 166 ppm by ozonization, and on the contrary the peak at 73–75 ppm due to the benzyl carbon of tri-*O*-benzylcellulose became smaller by ozonization. Also the aromatic carbons of tri-*O*-benzylcellulose changed to give one small peak at 133 ppm and two peaks at 129 and 130 ppm. The peaks due to C2, C3 and C6 of glucose residues of tri-*O*-benzylcellulose moved to high magnetic fields by ozonization.

Fig. 2 ^{13}C -NMR spectra of products prepared by ozonization of tri-*O*-benzylcellulose at -30°C .

Fig. 3 UV spectra of products prepared by ozonization of tri-*O*-benzylcellulose at -30°C .

Figure 3 shows UV spectra of tri-*O*-benzylcellulose and its ozonized products. Tri-*O*-benzylcellulose has peaks at 252, 258 (maximum), 264 and 267 nm, whereas ozonized products have peaks at 272 (maximum) and 280 nm. The peak intensities of ozonized products increased by advanced ozonization and became more than 4 times as large as those for tri-*O*-benzylcellulose.

3.2 Chemical Structure of Ozonized Products

The previous results indicate that the ozonized product may be unexpectedly benzoylcellulose, because (a) carbonyl carbons was introduced in place of benzyl carbons and (b) the reaction product has still aromatic rings. Furthermore, all reaction products showed almost same spectra, independent of the post treatments of the ozo-

nized products. Then the previous data were examined from viewpoints of the conversion of tri-*O*-benzylcellulose to benzoylcellulose.

Benzylacetate has UV peaks at 257 ($\epsilon=194$) 261 and 268 nm, and ethylbenzoate has those at 272 ($\epsilon=794$) and 284 nm⁹⁾. ^{13}C -Chemical shifts of methylbenzoate are calculated¹⁰⁾ to be 130.6 ppm for aromatic C1, 129.7 ppm for aromatic C2 and C6, and 128.5 ppm for C3 and C5 and 132.9 ppm for aromatic C4. Etherified carbons have chemical shifts of approximately 6 ppm down fields compared to those of the corresponding esterified carbons¹¹⁾. These data coincide well with the previous results. Therefore, it is concluded that benzyl ethers of tri-*O*-benzylcellulose are efficiently oxidized to benzoyl esters by ozonization (Figure 4). Almost all benzyl ethers were converted to benzoyl esters after 3 hours reaction under the condition described in Experimental. Although at this point hydroxyls were detected in IR spectra of reaction products, judging from the absorptions due to hydroxyls, amounts of free hydroxyls produced during the reactions must be less than 0.5 per anhydroglucose unit. Cromic acids¹²⁾ is known to convert ethers to esters, but its effectiveness is less than that of the ozonization described here.

Fig. 4 Reaction during ozonization of tri-*O*-benzylcellulose.

Figure 5 shows gel permeation chromatograms of tri-*O*-benzylcellulose and its ozonized products at -30°C , and some depolymerizations of cellulose molecules were detected.

As to the reaction mechanism of the conversion of benzyl ethers to benzoyl esters, some radicals may probably participate in this reaction, but details are unknown. Ozonization of tri-*O*-p-methoxybenzylcellulose, on the contrary, gave

Fig. 5 Gel permeation chromatograms of tri-*O*-benzylcellulose and its ozonized products prepared at 0 and -30°C .

complicated products instead of *p*-methoxybenzylcellulose. The cleavage of aromatic rings of *p*-methoxybenzyl groups may occur to some extents. Thus the conversion of ethers to esters by ozonization is a specific reaction only for benzyl ethers. This specific reaction will be useful in carbohydrate chemistry for the conversion of stable benzyl ethers to benzoyl esters, which can be removed by alkaline treatments.

After finishing this work, the authors found that Hirama and Shimizu¹³⁾ had reported the conversion of benzyl ethers to benzoyl esters by ozonization, but they used some low molecular compounds.

オゾン酸化によるセルロースベンジルエーテルの ベンゾイルエステルへの転換

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三置換したベンジルセルロースを 0°C と -30°C でオゾン処理したところ、それだけで効率よくベンジルエーテルがベンゾイルエステルに酸化された。置換基の脱離による水酸基の出現があるが、その程度はグルコース単位あたり0.5以下に押えられた。また、重合度の低下もある程度検出された。一方、ベンジル基にメトキシル基を持

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つ3置換 p -メトキシベンジルセルロースのオゾン処理では、対応するエステルが得られず、複雑な反応生成物が得られた。このことは、オゾンによるエーテルのエステル化反応がベンジルエーテルに特有の反応であることを示している。