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THE STEREOSELECTIVE SYNTHESIS OF 2,3-CIS-DIHYDROXY-γ-BUTYROLACTONES BY THE OXIDATION OF γ-BUTENOLIDES WITH $KMnO_4$-CROWN ETHER

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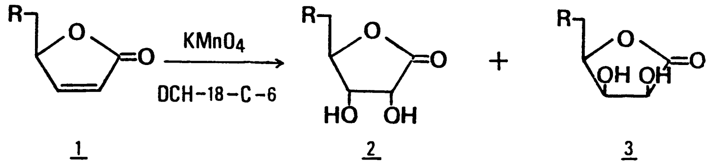
Oxidation of γ-butenolides was effected by $KMnO_4$-crown ether to afford the corresponding 2,3-cis-dihydroxy-γ-butyrolactones in high yields. High stereoselectivity was observed in cases when bulky substituents were introduced at the γ-position of the butenolides.

Stereoselective introduction of oxygen functionalities onto double bonds opens up wide possibilities in the synthesis of polyoxygenated natural products such as macrolides, carbohydrates and so on. Therefore, much efforts have recently been done along this line and resulted in the development of successful enantio-1a) and diastereo-1b) selective epoxidation reactions. However, utilization of the unsaturated lactones as substrates has been almost completely ignored because of the lack of general and reliable oxidation methods.2) In connection with our efforts in the field of carbohydrate synthesis, the development of the stereoselective oxidation of γ-butenolides was considered to be important. It was expected that the rigid structure of γ-butenolide 1 exhibits a sufficient sterical bias3) to stereoselective oxidations. In this communication, we wish to report i) the successful oxidation of γ-butenolides with $KMnO_4$-crown ether and ii) the effects of the substituents at the γ-position of these butenolides on the stereoselectivity.

In the first place, several oxidants were screened in the oxidation of γ-butenolide 1e, and the chemical yield of cis-diols (2e + 3e) and the ratio of 2e to 3e were as follows; OsO_4 (10%), $KMnO_4$-aq. acetone/0°C (38%, 8:1), $KMnO_4$-AcOH/r.t. (35%), $Et_3(Bn)N^+$ MnO_4^-/-42°C (65%,3:1),4) $KMnO_4$-10 mol% DCH-18-crown-6/r.t. (70%, 5:1),5) $KMnO_4$-10 mol% DCH-18-crown-6/-42°C (80%, 12:1). Thus, utilization of $KMnO_4$-crown ether gave the best result.

In the next place, the effect of the substituent at the γ-position of butenolides6) on the stereoselectivity was studied under the conditions described above (Table 1), and the ratio of stereoisomeric products was determined by HPLC and/or ^1H NMR analysis. The results show that the effective stereoselection is achieved in case of γ-alkoxymethyl or γ-siloxymethyl substituted butenolides. Especially, high stereoselectivities were observed in cases of 1f, 1g which are bearing bulky substituents. On the other hand, in the cases of alkyl or acyloxy substituents the stereoselectivity turned out to be low. The sturcture of the major product was determined as follows. The diol 2e was treated with Ac_2O-pyr to

Table 1. Substituent effect on the stereoselectivity



R	Yield a)	selectivity (2 : 3) b)
a) n-C_4H_9	56%	3 : 1 c)
b) n-$C_{10}H_{21}$	47%	3 : 1 c)
c) $PhCH_2COO$	27%	5 : 1 c)
d) PhCOO	60%	7 : 1 c)
e) $PhCH_2O$	66%	12 : 1 d)
f) $Ph_2(Me)SiO$	51%	> 30 : 1 d)
g) Ph_3CO	61%	> 50 : 1 d)

a) Yields of isolated diacetates[7] of 2 and 3.
b) The ratio of stereoisomers of diacetates of 2 and 3.
c) Determined by ^1H NMR integration.
d) Determined by the HPLC analysis——Merck SI 60 (AcOEt-hexane).

afford diacetyl derivative which was in full accordance with the authentic 2,3-di-O-acetyl-5-O-benzylribono-1,4-lactone derived from D-ribose.[8]

A typical procedure for the preparation of 2g is as follows: To a CH_2Cl_2 (2 ml) solution of 5-triphenylmethoxymethyl-2(5H)-furanone (1g)(150 mg, 0.4 mmol) and dicyclohexano-18-crown-6-ether (15 mg, 0.04 mmol) was added $KMnO_4$ (80 mg, 0.5 mmol) in several protions at -42°C and the reaction mixture was kept standing for 2 h at the temperature. Then sodium sulfite solution was added to the reaction mixture and neutralized by gradual addition of 5% H_2SO_4 at 0°C until the color of permanganate disappeared, and the products were extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. After evaporation,the resulting residue was treated with Ac_2O-pyr in a conventional manner, and the products were purified on silica-gel TLC (AcOEt-hexane) to give 2,3-di-O-acetyl-5-O-tritylribono-1,4-lactone (122 mg, 61%).

It is noted that the present method opens a new entry into the synthesis of sugar derivatives possessing 2,3-cis-dihydroxyl groups starting from the optically active γ-butenolides. Further investigation on the synthesis of monosaccharides by utilizing the present highly stereoselective oxidation is now under way.

References

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