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ELIMINATION REACTION IN D-GLUCURONOLACTONE AND D-MANNURONOLACTONE

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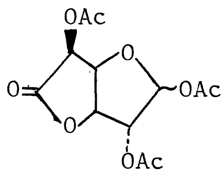
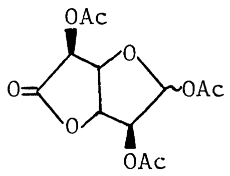
Triacetate of D-glucuronolactone (1) or D-mannuronolactone (2) is converted to 3-acetoxy-6-diacetoxymethylpyrane-2-one (3) and 2,5, 6 6-tetraacetoxy-2,4-hexadienoic acid (4) respectively by treatment with acetic anhydride-potassium acetate-18-crown-6 or acetic anhydride-triethylamine.

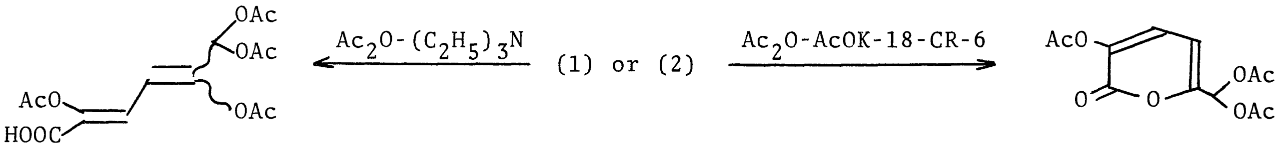
It has recently been shown that aldono lactone derivatives readily undergo β-elimination reaction to give unsaturated lactones.[1,2,3] From these results butenolide derivatives are assumed to be obtained as the elimination reaction products from D-glucuronolactone or D-mannuronolactone. We now report the elimination reactions in triacetates of D-glucuronolactone (1) and D-mannuronolactone (2) by using potassium acetate-18-crown-6 or triethylamine as a base in acetic anhydride. However, in our investigations, a butenolide derivative was not detected and an α-pyrone derivative (3) or a sorbic acid derivative (4) was obtained as a main product by changing the base.



(1)



(2)



(4)

(3)

At first, (1) or (2) was treated with potassium acetate-18-crown-6 in acetic anhydride. In this case 3-acetoxy-6-diacetoxymethylpyrane-2-one (3) was obtained from both lactones, (1) and (2). A typical example of the reaction was carried out in the following way. To a solution of 0.154 g (0.51 mmole) of (1) in 3 ml of acetic anhydride were added 0.049 g (0.50 mmole) of potassium acetate and 0.020 g (0.076 mmole) of 18-crown-6. After heating the mixture at 60°C for 16 hr, (3) was isolated by means of TLC and purified by recrystallization from benzene-petroleum ether (67 %, mp. 96-96.5°C). IR : 3090, 2920, 1740, 1660 cm^{-1}. NMR ($CDCl_3$) : δ 2.16 (s, 6H), 2.32 (s, 3H), 6.38 (d, J=7.2Hz, 1H), 7.10 (d, J=7.2Hz, 1H), 7.38 (s, 1H). Anal. Found : C, 50.67 %, H, 4.25 %, Calcd. for $C_{12}H_{12}O_8$: C, 50.71 %, H, 4.26 %.

On the other hand, when triethylamine was used instead of potassium acetate-18-crown-6, (3) was obtained only in small amounts from (1) or (2). The main product in this case was 2,5,6,6-tetraacetoxy-2,4-hexadienoic acid (4) as shown in Table. The reaction procedure was as follows. To a mixture of 5 ml of acetic anhydride and 0.5 ml of triethylamine was added 0.329 g of (2) which was obtained from alginic acid.[4] The solution was stirred for 16 hr at room temperature and then the reagents were distilled off under reduced pressure. The residue was extracted with benzene-water, and the aqueous layer was treated with ion exchange resin (Dowex 50WX2 H^+-form). After evaporation of water, (4) was obtained (46 %, mp. 132-132.5°C). IR : 3100, 1775, 1705, 1660, 1630 cm^{-1}. NMR ($CDCl_3$) : δ 2.12 (s, 6H), 2.28 (s, 6H), 6.45 (d, J=9.6Hz, 1H), 7.02 (d, J=9.6Hz, 1H), 7.27 (s, 1H), 9.52 (s,1H). Anal. Found : C, 48.77 %, H, 4.66 %, Calcd. for $C_{14}H_{16}O_{10}$: C, 48.84 %, H, 4.68 %. From the benzene layer, (3) was obtained in 4 % yield. All the results are listed in Table.

Table

Base	Starting Material	Temp. (°C)	Time (hr)	Yield (%)	
				(3)	(4)
AcOK-18-CR-6	(1)	60	16	67	0
"	(2)	"	"	60	0
$(C_2H_5)_3N$	(1)	R.T.	25	trace	44
"	(2)	"	15	4	46

In these investigations, two isomers, (1) and (2), afforded similar results both in the reactions with acetic anhydride-potassium acetate-18-crown-6 or acetic anhydride-triethylamine, and no significant differences were observed. The detailed studies on the mechanisms and the scope of these reactions are under investigation.

References

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