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SYNTHESIS OF γ-LACTONES BY THE CONDENSATION OF 2-ALKENE-1,4-DIOLS WITH ORTHOCARBOXYLIC ESTERS

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Various γ-lactones bearing vinylic substituent on β-position were obtained directly by the thermal condensation of trans-2-alkene-1,4-diols with orthocarboxylic esters in the presence of a catalytic amount of hydroquinone or phenol.

Johnson and his associates demonstrated that the condensation of allylic alcohols with ethyl orthoacetate in the presence of a trace amount of propionic acid gave γ,δ-unsaturated esters in excellent yields.[1)] The reaction was supposed to go through Claisen rearrangement of the intermediately formed ketene acetals. In an attempt to extend the reaction to various types of functionalized allylic alcohols, we have found that the use of 2-alkene-1,4-diols resulted in the direct formation of β-vinyl-γ-lactones.

Following procedure illustrates the new reaction. A mixture of trans-2-butene-1,4-diol 1 (0.1 mol) and ethyl orthoacetate (0.2 mol) was heated at 140-150°C for 24 hrs in the presence of hydroquinone (10 wt% against 1) under continuous removal of by-produced ethanol. Fractional distillation of the reaction mixture under reduced pressure afforded pure β-vinyl-γ-butyrolactone in 89% yield. Similarly, various γ-lactones bearing vinylic substituent on β-position were obtained from the corresponding trans-2-alkene-1,4-diols in fair to excellent yields. The results are summarized in Table I. The structures of all new γ-lactones were confirmed on the bases of spectroscopic data and combustion analyses.

The direct formation of the γ-lactones can be rationalized as follows. The exchange reaction of the alkoxy group of orthoester with the diol 1 followed by elimination of alcohol under acidic condition will produce mixed ketene acetal 2. Claisen rearrangement of 2 to β-vinyl-γ-hydroxycarboxylic ester 3 and lactonization of 3 to 4 under the reaction condition will complete the whole series of transformation.[2)]

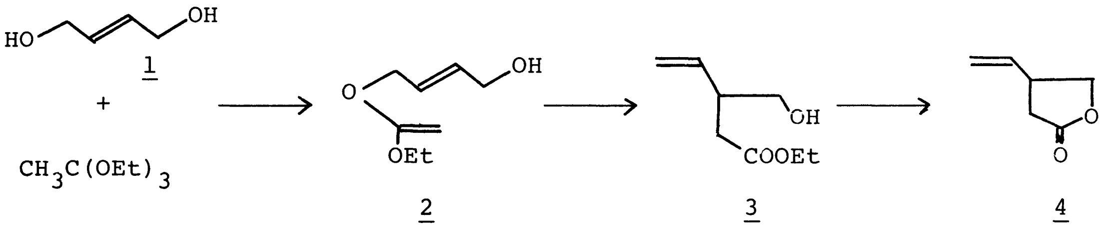
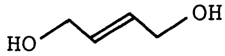
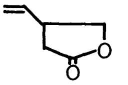
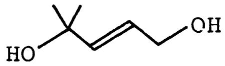
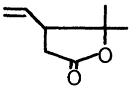
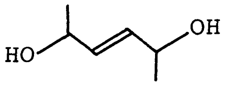
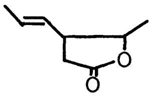
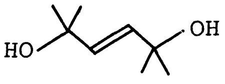
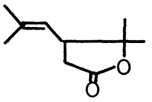
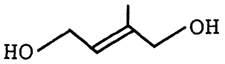
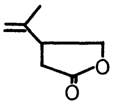
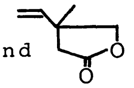
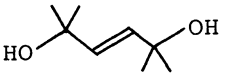
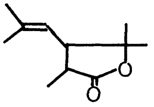


Table I. γ-Lactones from 2-alkene-1,4-diols and orthocarboxylic esters[a]

Starting trans-Diol	$RCH_2C(OEt)_3$ R	Product	Yield[b] (%)	B.p. (°C/mmHg)
	H	 4	89	96-98/14
	H		91	77-80/2.0
	H		52[c]	58-60/0.15
	H	 5	70[d]	128-130/14 m.p. 58.5-59°C[e]
	H	 and 	81[f]	103-104/14
	CH_3		60[c]	76-78/0.22

a) Condensation was performed at 140-150°C for 24 hrs, using hydroquinone (10 wt% against diol) as catalyst unless otherwise noted. b) Isolated yield. c) A mixture of cis and trans isomers. d) Phenol catalyst. e) Lit., m.p. 57-58°C (ref 3). f) The ratio of the products was determined to be ca. 6:4 from NMR spectrum.

When the condensation was performed using the cis-isomer of 2-butene-1,4-diol, the γ-lactone 4 and a cyclic orthoester, i.e. 2-methyl-2-ethoxy-1,3-dioxacyclohept-5-ene, were obtained in ca. 45 and 20% yields, respectively. Substituted cis-2-alkene-1,4-diols also afforded γ-lactones in decreased yields. Thus we feel that trans-diols are the prefered starting materials for the synthesis. The γ-lactone 5 shown in Table I is known as pyrocin, which was found in the pyrolysate of pyrethrin and shown to have strong insecticidal activity.[3,4,5] The present method may offer an easy entry to this type of biologically interesting γ-lactones.

References and Notes

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2) The formation of 5 by the reaction of cis-2,5-dimethyl-3-hexene-2,5-diol with dimethyl-(1-ethoxyvinyl)amine without details on the reaction condition and yield has recently been reported. Cf. W. Sucrow and W. Richter, Tetrahedron Lett., 1970, 3675.
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