CHEMISTRY LETTERS, pp. 405-408, 1972. Published by the Chemical Society of Japan

THE STERIC EFFECT ON AN ADDITION REACTION OF α-HYDROXYALKYL RADICAL TO DIETHYL MALEATE AND DIETHYL FUMARATE

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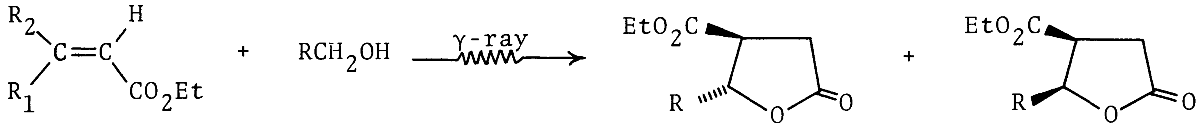
Radiation-induced addition reaction of ethanol and 1-propanol to diethyl maleate gives predominantly _cis_-γ-alkyl substituted paraconate, but the addition to diethyl fumarate produces _trans_- and _cis_-paraconates in almost the same yield. These results can be rationalized by the steric hindrance between α-hydroxyalkyl radical and maleate or fumarate ester.

It has been previously reported[1,2] that radiation and ultraviolet-induced addition reactions of various alcohols to α,β-unsaturated acids and esters give corresponding γ-butyrolactones, and proposed that the product ratio of _trans_- and _cis_-lactone may be effected by the degree of steric interaction in an addition step of an α-hydroxyalkyl radical to the carbon-carbon double bond. The present investigation was undertaken to substantiate the above proposal.

Irradiation of diethyl maleate (I) or diethyl fumarate (II) in a tenfold excess of alcohol with ^{60}Co γ-rays gives the isomeric 4-alkyl substituted paraconic acid esters (V, VI). The yield of lactones, conversion of maleate or fumarate esters and the isomer **ratio** of _trans_- and _cis_-lactone are listed in Table 1. G-Values in Table 2. are calculated from the low conversion linear part of the curve which is obtained from the plot of the yield of lactone and the conversion of ester against the irradiation time. The isomer ratio of _trans_- to _cis_-lactone is determined by glpc using several different columns. The product is identified mainly by spectral data. Nmr spectra[3,4] show that γ-alkyl proton of _cis_-isomer (VI) resonates in a higher **magnetic** field than that of _trans_-isomer (V). Nmr (CCl_4, τ) Va: γ-CH_3 8.53(d), VIa: γ-CH_3 8.71(d), Vb: γ-CH_2 8.25(qn), VIb: γ-CH_2 8.51(qn).



I, R_1=CO_2Et, R_2=H
II, R_1=H, R_2=CO_2Et

R=CH_3, C_2H_5

Va, R=CH_3
b, R=C_2H_5

VIa, R=CH_3
b, R=C_2H_5

Table 1.
Radiation-Induced Addition Reaction of Ethanol and 1-Propanol to Diethyl Maleate and Diethyl Fumarate[a)]

Alcohol	Irrad. Time (hr)	Diethyl Maleate (I)			Diethyl Fumarate (II)		
		Conversion[b)] of Ester(%)	Yield[b)] of Lactone(%)	$\frac{\text{trans(V)}}{\text{cis(VI)}}$	Conversion[b)] of Ester(%)	Yield[b)] of Lactone(%)	$\frac{\text{trans(V)}}{\text{cis(VI)}}$
EtOH	6	20	4	0.54	22	1	1.10
"	15	27	8	0.52	35	3	1.10
"	25	45	12	0.50	60	5	1.00
"	72	85	35	0.50	98	14	1.00
1-PrOH	6	8	5	0.48	10	0.5	1.00
"	15	22	12	0.44	25	2	1.00
"	25	28	20	0.44	49	3	0.96
"	72	70	46	0.44	98	9	1.00

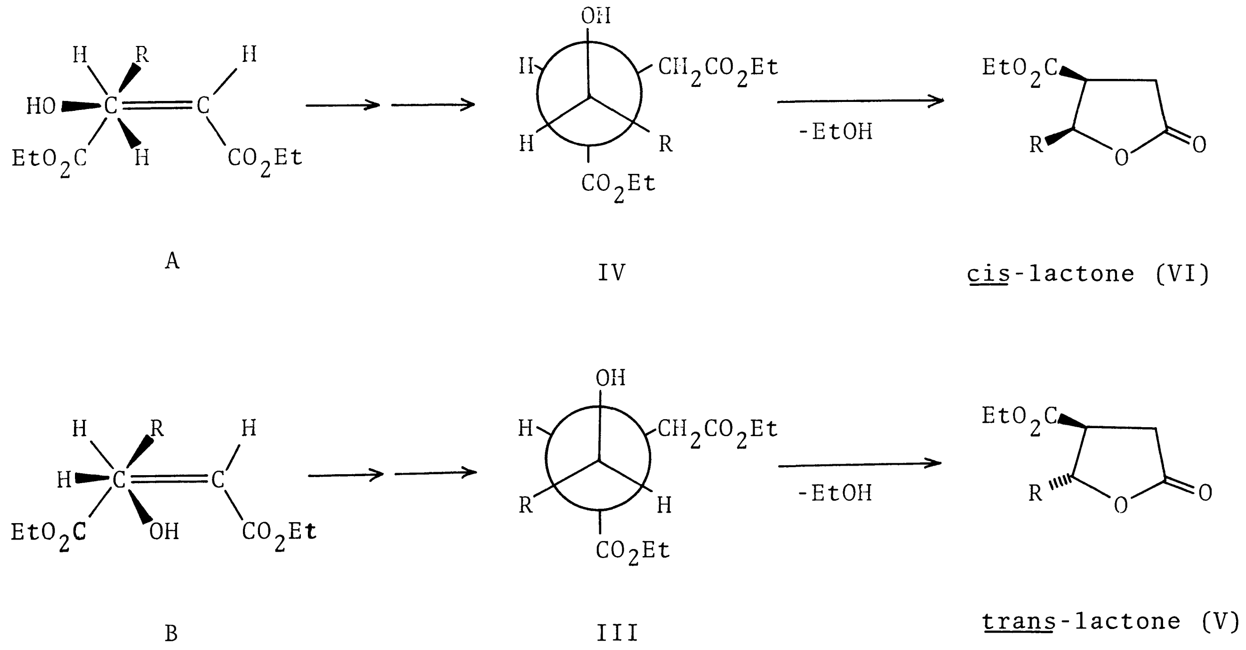
a) Dose rate: 8×10^5r/hr, reaction temperature: 15°C

b) Based on ester employed.

Table 2.
G-Value of Lactone Formation and Ester Consumption

Alcohol	Diethyl Maleate		Diethyl Fumarate	
	G(lactone)	G(-ester)	G(lactone)	G(-ester)
EtOH	9	35	4	44
1-PrOH	10	16	2	27

The formation reaction of γ-butyrolactone seems to proceed through a radical mechanism initiated by α-hydroxyalkyl radical (RCHOH). This might be supported by the fact that the reaction is retarded by the addition of a radical scavenger. The formation of two isomeric lactones may well be caused by an attacking course of α-hydroxyalkyl radical to the double bond of α,β-unsaturated esters. For example if an α-hydroxyalkyl radical attacks the carbon-carbon double bond in a steric course A and then the produced intermediate radical abstracts a hydrogen from alcohol, a cis-isomer (VI) would be obtained[5)]. The attacking of α-hydroxyalkyl radical as revealed in B would form a trans-isomer (V). The addition reaction of ethanol to diethyl maleate proceeds in a steric course A, which must be sterically less hindered than B, and produces predominantly cis-lactone as indicated in Table 1. This tendency is more pronounced when 1-propanol which has a more bulky R group is employed. On the other hand, the addition reaction to diethyl fumarate gives almost an equal amount of trans- and cis-lactone, probably because several steric courses have the same degree of steric hindrance. The same steric courses such



as A and B are also reported by Fukunishi et al.[6) in a radical initiated addition reaction of alcohols to maleic acid esters.

No other effects are found to influence the isomer ratio of _trans_- to _cis_-lactone. Firstly, isomerization of maleate-fumarate ester does not take place. If such a fast isomerization should occur prior to a radical addition, the same isomer ratio would be obtained from both maleate and fumarate ester. When diethyl maleate or fumarate in t-butyl alcohol or benzene solution is irradiated with γ-rays for 15 hr, a 10 to 40 % conversion reaction occurs while no isomerization in the recovered ester is observed. Although a reversible addition of a radical to olefin causes _cis_-_trans_ isomerization[7), such an isomerization did not occur in the present experiments. This may be deduced from the fact that no isomer is involved in the recovered ester when diethyl maleate or fumarate is irradiated in ethanol or 1-propanol. Secondly, no γ-hydroxyester (III or IV) not lactonyzed is found to remain in the reaction mixture. When the irradiation mixture is heated in an autoclave at 200° C for 2 hr, no change was observed in the yield of lactone and the isomer ratio of _trans_- to _cis_-lactone. This fact shows that no steric interaction exists in the lactonization step (III→V, or IV→VI). Thirdly, isomerization or decomposition of the produced lactone did not take take place under the present experimental conditions. Irradiation of the isolated _cis_- or _trans_-lactone in ethanol for 60 hr gave no isomeric lactone, but produced an unknown product with a higher retention time on glpc. This decomposed product did not appear in gas-chromatograms of the irradiation product of diethyl maleate or fumarate in ethanol or 1-propanol. It was suggested that a prolonged irradiation may cause decomposition of the produced lactones.

As indicated in Table 2, the G-value of ester consumption is larger in diethyl fumarate than the corresponding maleate but the G-value of lactone formation is larger in diethyl maleate. This is probably due to the larger reactivity of trans-unsaturated ester towards the radical addition.[2,8) A reactive ester such as diethyl fumarate is consumed predominantly in a polymerization step to give a telomer and polymer with a small amount of lactone.

Consequently, the isomer ratio of trans- to cis-lactone was found to be determined in the attacking step of α-hydroxyalkyl radical to the carbon-carbon double bond. It was also found that the steric course such as A and B is important for the radical addition reaction.

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(Received March 10, 1972)