Studies on the Isomerization Esterification of Crotonoyl Chloride to Vinylacetic Acid Ester. III. The Reactions of Branched Crotonoyl Chlorides

Toshitsugu OZEKI and Masakatsu KUSAKA

Yokkaichi Laboratory, Daikyowa Petrochemical Co., Ltd., Daikyo-cho, Yokkaichi, Mie

(Received February 17, 1967)

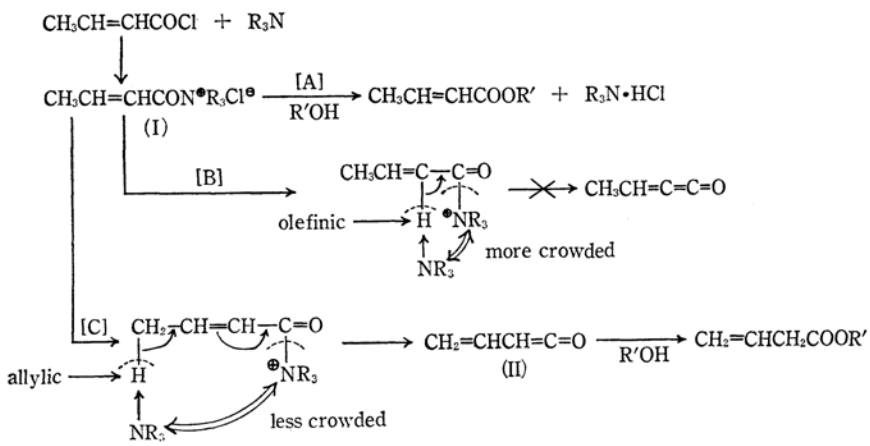
Previously the authors reported[1,2] that the double bond shift from the α, β- to the β, γ-position occurred in the alcoholysis of crotonoyl chloride in the presence of *t*-amine to afford vinylacetic acid ester as the main product. They found that the easiness of the double bond shift depended on the basicity of amines and the steric requirements of amines and alcohols as well as the reactivity of the proton to be abstracted, and proposed a mechanism *via* ketene intermediate (II).[3]

In this paper, the Einhorn reactions of branched crotonoyl chlorides, *i. e.* β, β-dimethylacryloyl chloride, 2-pentenoyl chloride, 2-hexenoyl chloride and 4-methyl-2-pentenoyl chloride were investigated. It was expected that in these branched crotonoyl chlorides, the isomerization may be favored because the alkyl substituent stabilize the β, γ-double bond newly formed.[4,5]

The Reaction of β, β-Dimethylacryloyl Chloride. It was discussed in the previous paper[2] that the product ratios varied with the basicity and the steric requirement of used amines. The methanolysis of β, β-dimethylacryloyl chloride was investigated using five amines with varieties of basicity. The results are shown in Table 1 with the results of crotonoyl chloride for comparison.

The yields of β, γ-unsaturated ester are roughly identical with both acyl chlorides.[6] This fact indicates that the product ratio is controlled by a primary proton abstraction step and the stability of the ketene is not important.

The Reactions of 2-Pentenoyl, 2-Hexenoyl and 4-Methyl-2-pentenoyl Chlorides. These acyl chlorides used were found to be contaminated with considerable amounts of β, γ-isomer as described in the experimental part. The contents of β, γ-isomer were 36%, 42% and 69% for 2-pentenoyl, 2-hexenoyl and 4-methyl-2-pentenoyl



1) T. Ozeki and M. Kusaka, This Bulletin, **39**, 1995 (1966).

2) T. Ozeki and M. Kusaka, *ibid.*, **40**, 1232 (1967).

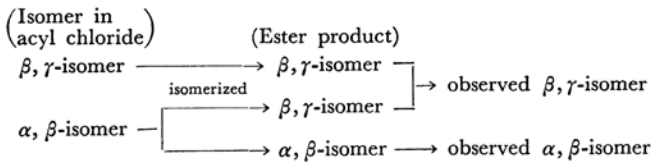
3) Very recently, W. E. Truce and R. W. Campbell (*J. Am. Chem. Soc.*, **88**, 3599 (1966)) reported an analogous isomerization in the alcoholysis of sulfonyl chloride, and assumed a sulfene intermediate.

$$CH_3CH{=}CHSO_2Cl \xrightarrow{Et_3N} [CH_2{=}CH{-}CH{=}SO_2] \xrightarrow{ROH} CH_2{=}CHCH_2SO_3R$$

4) G. B. Payne (*J. Org. Chem.*, **31**, 718 (1966)) proved the formation of ketene $CH_2{=}C(CH_3)CH{=}C{=}O$ in the reaction of β, β-dimethylacryloyl chloride and trimethylamine by trapping it with vinyl ether. However, he failed to trap ketene in the reaction of crotonoyl chloride, although amine hydrochloride and dark viscous polymeric product were obtained.

5) The equilibrium between α, β-unsaturated acid and its β, γ-isomer in the presence of alkali have been investigated (A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, **1928**, 2343). These authors reported the content of the β, γ-isomer as 0% (crotonic acid), 24.6% (2-pentenoic acid) and 94.4% (4-methyl-2-pentenoic acid).

6) In further esterifications in which *N*-methylpiperidine, dimethylbenzylamine and *N*-methylmorpholine were used, the increase of the yield of β, γ-unsaturated ester in contrast to the case of crotonoyl chloride was observed. The reason is not yet obvious.



chlorides, respectively, as determined by NMR spectra.

The absence of isomerization of β, γ-unsaturated ester to α, β-isomer in gas chromatographic analysis was ascertained with the isolated esters. The formation of 2-pentenoate was not observed in the reaction of authentic 3-pentenoyl chloride.[7] From these results, the above scheme is deduced.

In the reaction without *t*-amine, the mixture of α, β- and β, γ-unsaturated acyl chlorides gave the mixture of esters with the roughly same isomer ratio.[8] Hence, it can be assumed that *β, γ-unsaturated ester resulted actually from α, β-unsaturated acyl chloride* is *the observed product ratio of β, γ-unsaturated ester* minus *the content of β, γ-isomer in acyl chloride*. The corrected product ratios are shown in Table 2.

The ratios of isomerized to non-isomerized products (the last column of Table 2) decrease in the order of crotonoyl>2-pentenoyl>2-hexenoyl>4-methyl-2-pentenoyl. This would probably be explained on the basis of increasing steric hindrance on the γ-proton.

Remarkably, the isomerization did occur in the presence of pyridine as well in sharp contrast to the cases of crotonoyl and β, β-dimethylacryloyl chlorides. The reason is not clear yet.

Experimental

Reagents. Commercially available alcohols, amines and benzene were purified by fractional distillation.

β, β-Dimethylacrylic acid was prepared according to Smith's method.[9] 2-Pentenoic acid, 2-hexenoic acid and 4-methyl-2-pentenoic acid were prepared from malonic acid and propionaldehyde, *n*-butyraldehyde and isobutyraldehyde, respectively, by the application of Johnson's method.[10] These acids were identified as pure *trans*-α, β-unsaturated acids from IR and NMR.

Acyl chlorides were prepared at room temperature with thionyl chloride as usual. IR and NMR analysis made it clear that these acyl chlorides except β, β-dimethylacryloyl chloride were mixtures of α, β- and β, γ-unsaturated acyl chlorides. The ratios are given in the text.

Esterification. The apparatus and procedure employed were essentially the same as those mentioned in the previous paper.[1] Acyl chloride (0.1 mol),

Table 1. Product ratios in the methanolysis of β, β-dimethylacryloyl chloride and crotonoyl chloride

Amine	pK_a	Product ratio of methyl ester (%)*			
		from β, β-Dimethylacryloyl		from Crotonoyl**	
		3-Methyl-3-butenoate	β, β-Dimethylacrylate	Vinylacetate	Crotonate***
Triethylamine	10.7	83.1	16.9	87.8	12.2
N-Ethylpiperidine	10.4	89.6	10.4	83.5	16.4
Triallylamine	8.3	44.1	55.9	47.4	52.6
N-Ethylmorpholine	7.7	69.1	30.9	65.3	34.8
Pyridine	5.2	0.6	99.4	1.6	98.4

* Total ester yield was almost quantitative in all cases.
** Data reported in Ref. 2.
*** Sum of cis- and trans-crotonates.

7) Prepared from pure 3-pentenoic acid which was synthesized according to Lane's method. Purity of the acyl chloride was determined by gas chromatographic analysis to be 99.2%. J. F. Lane, J. Fentress and L. T. Sherwood, Jr., *J. Am. Chem. Soc.*, **66**, 545 (1944).

8) The product ratios in the absence of *t*-amine were as follows:

Acyl chloride	(Isomer ratio)		Ester product		
	β, γ-	α, β-	β, γ-isomer	α, β-isomer	unidentified compound
2-Pentenoyl chloride	(36%	64%)	34.3%	57.2%	8.5%
2-Hexenoyl chloride	(42%	58%)	49.8%	46.1%	4.5%

9) L. I. Smith, W. W. Prichard and L. J. Spillane, "Organic Syntheses," Coll. Vol. III, p. 302 (1955).

10) J. R. Johnson in "Organic Reactions," ed. by R. Adams, Vol. 1, John Wiley & Sons., New York (1942), p. 252.

TABLE 2. PRODUCT RATIOS IN THE ALCOHOLYSIS OF 2-PENTENOYL, 2-HEXENOYL AND 4-METHYL-2-PENTENOYL CHLORIDES

Acyl chloride	Alcohol	Amine	Corrected product ratio(%)*		β,γ-/α,β-isomer
			β,γ-isomer	α,β-isomer	
Crotonoyl**	EtOH	TEA***	96.1	3.9	24.6
2-Pentenoyl	EtOH	TEA	90.5	9.5	9.5
2-Hexenoyl	EtOH	TEA	84.3	15.7	5.3
Crotonoyl**	MeOH	TEA	87.8	12.2	7.0
2-Pentenoyl	MeOH	TEA	70.7	29.2	2.4
2-Hexenoyl	MeOH	TEA	62.7	37.2	1.7
4-Methyl-2-pentenoyl	MeOH	TEA	42****	58****	0.7
Crotonoyl**	MeOH	Py***	1.6	98.4	0.02
2-Pentenoyl	MeOH	Py	31.3	68.8	0.5
2-Hexenoyl	MeOH	Py	39.3	60.7	0.6

* Total ester yield was almost quantitative in all cases except 2-pentenoyl chloride-pyridine system in which considerable amount of unidentified products was produced.
** Data reported in the previous paper.[2]
*** TEA: triethylamine; Py: pyridine.
**** Values obtained from the proton ratios of NMR spectrum because the sufficient separation of peaks required to determine the ratio on gas chromatogram was not obtained.

alcohol (0.15 mol), amine (0.1 mol) and benzene (20 g) were used. The esters were isolated with Shimadzu GC-11A preparative gas chromatograph (tricresyl phosphate (20%) 4.5 m, He, 120°C) and identified by means of IR and NMR.

IR spectra were measured with Shimadzu IR-27, and NMR spectra with Varian HA-100 at The Government Industrial Research Institute, Tokyo.