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Formation of 3-Butenoates from Crotonyl Chloride in the Presence of Amines

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The reaction of acyl halides with alcohols is a conventional method of preparing esters.[1] In the course of applying this method to *trans*-crotonyl chloride in order to obtain unsaturated esters, which are used as monomers in vinyl polymerization, it was found that hydrogen abstraction from the β-methyl group of *trans*-crotonyl chloride occurred and that esters of vinylacetic acid (3-butenoates) were formed, possibly as a result of elimination-addition. In connection with this work, Payne has reported[2] that the dehydrochlorination of 3,3-dimethylacrylyl chloride through the use of tertiary amine occurs by 1,4-elimination to give the intermediate isopropenylketene, which is trapped in a dimeric form. The thermal isomerization of methyl *trans*-crotonate has also been investigated by Butler *et al.*[3]

The dependence of the formation of isomerized esters on various factors, such as the reaction conditions and the kinds of starting materials, was studied by determining by gas chromatography (GC) the ratio of crotonate and 3-butenoate existing in the products. The experimental results are summarized in Table 1. The structural assignment of each ester rests on the infrared and NMR spectra. The experimental results thus far examined show that the product ratio is influenced chiefly by the method of the reaction and by the kinds of reactants, such as alcohols and amines, while it is not so much influenced by the reaction time, the temperature, and the solvents. There was little difference in products ratios between the two methods of addition: 1) the simultaneous addition of acid chloride and amine into alcohol,

TABLE 1. REACTION OF *trans*-CROTONYL CHLORIDE WITH ALCOHOL

Run	Alcohol	Amine	Temp. °C	Solvent	3-Butenoate %	*trans*-Crotonate %	Method of reaction
1	MeOH	TEA	20	THF	76.7	23.3	Amine and acid chloride were added into alcohol.
2	MeOH	TEA	20	THF	74.2	25.8	Amine and acid chloride were added into alcohol, allowed to stand for 18 hr.
3	MeOH	Pyridine	20	THF	8.7	91.3	Amine and acid chloride were added into alcohol.
4	MeOH	DABCO*	20	THF	14.3	85.7	Amine and acid chloride were added into alcohol.
5	MeOH	TEA	20	THF	92.2	7.8	Acid chloride was added into amine and alcohol.
6	MeOH	TEA	−30	THF	92.2	7.8	Acid chloride was added into amine and alcohol.
7	MeOH	TEA	20	Benzene	93.9	6.1	Acid chloride was added into amine and alcohol.
8	MeOH	TEA	20	THF	79.6	20.4	Amine was added into acid chloride and alcohol.
9	*i*-BuOH	TEA	20	THF	98.3	1.7	Acid chloride was added into amine and alcohol.

TEA: Triethylamine THF: Tetrahydrofuran DABCO: Diazabicyclooctane

* On the contrary to our expectation, amount of 3-butenoate in product was small, presumably due to low solubility and basicity of its half-protonated form.

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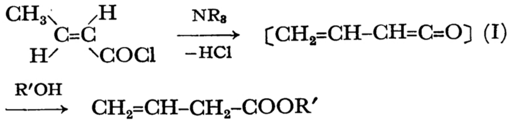
[1] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, Inc., New York (1961), p. 481.

[2] G. B. Payne, *J. Org. Chem.*, **31**, 718 (1966).

[3] J. N. Butler and G. J. Small, *Can. J. Chem.*, **41**, 2492 (1963).

and 2) the addition of amine to a mixture of alcohol and acid chloride. However, by the addition of acid chloride to a mixture of amine and alcohol, that is, by a reaction under amine excess conditions, 3-butenoate was predominantly obtained possibly because of elimination-addition. It was noteworthy that a strong base such as triethylamine favored the formation of 3-butenoate, while *trans*-crotonate was mainly given by pyridine under the same reaction conditions. Isobutanol, which is rather bulky, gave a larger amount of isomerized ester than did methanol.



Several mechanisms are possible for the formation of 3-butenoate. The most probable explanation of the reaction scheme is that *trans*-crotonyl chloride is converted to an unstable vinylketene intermediate (I), which then reacts very rapidly with alcohol to give the isomerized ester. This assumption is well in accordance with the description of Payne.[2] The influence of the carbonyl group of α,β-unsaturated acid chlorides on the mobility of β-methyl hydrogen would be extended by conjugation, which has been established in the deuterium exchange reaction of such carboxylic acids as tiglic acid.[4]

Finally, 3-butenoate once formed was stable enough and had little tendency to isomerize to crotonate when the reaction mixture was kept standing at room temperature as long as amine salt did not exist in the system and *vice versa*. However, small amounts of such amines as *n*-butylamine and benzylamine assisted the migration of the double bond of isolated 3-butenoates to the stable conjugated form at elevated temperatures.

Experimental

Synthesis of Standard Materials. The methyl *trans*-crotonate and methyl 3-butenoate (methyl vinylacetate) were synthesized by the esterification of the corresponding acids in excess methanol with a small amount of a *p*-toluenesulfonic acid catalyst: bp; methyl *trans*-crotonate,[5] 120—122°C; methyl 3-butenoate,[6] 111—113°C. The methyl *cis*-crotonate[7] was obtained by courtesy of Professor T. Tsuruta of The University of Tokyo, bp 119°C.

Reaction Conditions. Equimolar amounts (0.1 mol) of alcohol, amine, and *trans*-crotonyl chloride which had been diluted appropriately were allowed to react in a solvent (40 m*l*) for 30 min at a constant temperature. The amine hydrochloride thus precipitated was removed by filtration, and the resultant filtrate was sabjected to GC measurement.

Gas chromatography was carried out under the following conditions:

Column PEG 1500, 2 m; He 40 m*l*/min; Column Temperature 129°C; Sample 1—4 μ*l*.

The retention times of the esters are shown in Table 2. The amounts of the esters were determined from the areas of the peaks in the GC charts. Although they were not measured, the absolute yields were thought to be good enough, since the reactions were carried out under mild conditions.

TABLE 2. RETENTION TIMES OF EACH ESTER IN GC

Ester	Retention time	
	min	temp. °C
Methyl *trans*-crotonate	3.08	129
Methyl *cis*-crotonate	2.43	129
Methyl 3-butenoate	2.42	129
Isobutyl 3-butenoate	2.94	155
Isobutyl *trans*-crotonate	3.40	155

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[6] E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2251 (1953).

[7] F. Bürki, *Helv. Chim. Acta*, **1**, 231 (1918).