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Studies on the Isomerization Esterification of Crotonyl Chloride to the Vinylacetic Acid Ester. II. The Effects of the Amine, the Alcohol, the Solvent, and the Reaction Temperature

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The effects of the amine, the alcohol, the solvent, and the reaction temperature on the isomerization esterification of crotonyl chloride to the vinylacetic acid ester were investigated. Amines can be divided into three groups. The first group includes the amines with pK_a-values as high as 10; they give the isomerized product, ethyl vinylacetate (I_{Et}), in a *ca.* 90% yield. The second includes the amines with pK_a-values lower than 7.2; they give the normal product, ethyl *trans*-crotonate (III_{Et}). The third includes the remaining amines with intermediate pK_a-values; they give various amounts of the two products. Ethyl *cis*-crotonate (II_{Et}) is always formed in only a small quantity. Alcohols favored the product ratio of I_{Et} in the order:

$$MeOH < EtOH < i\text{-}BuOH < i\text{-}PrOH < t\text{-}BuOH.$$

Various aliphatic and aromatic solvents gave almost identical product ratios, regardless of their polarities. Below room temperature, the formation of I_{Et} was predominant (*ca.* 95—97%), but above that temperature II_{Et} and III_{Et} increased. It was understood that the steric factors of amine and alcohol influenced the extent of the double-bond shift and that the reaction proceeded *via* the ketene intermediate. The course of the reaction has been discussed.

In the previous paper,[1] it was reported that, in the esterification reaction of crotonyl chloride with alcohol in the presence of a strong *t*-amine, a double-bond shift unusually took place from the α, β- to the β, γ-position, and that the vinylacetic acid ester was formed instead of the normal product of the crotonic acid ester (Eq. (1)).

$$\begin{aligned} CH_3CH{=}CHCOCl + ROH + R_3'N \rightarrow \\ CH_2{=}CHCH_2COOR + CH_3CH{=}CHCOOR \\ \text{(major)} \qquad\qquad \text{(minor)} \\ \text{I} \qquad\qquad \text{II } \textit{cis}\text{-isomer} \\ \qquad\qquad \text{III } \textit{trans}\text{-isomer} \\ + R_3'NHCl \end{aligned} \tag{1}$$

It was also suggested that the amine played some important role in this reaction because (a) no isomerization occurred in the Fischer or Schotten-Baumann esterification when no *t*-amine was used; and (b) the extent of isomerization was greatly changed with the sort of amine.

This work was undertaken in order to clarify the effects of the amine, the alcohol, the solvent, and the reaction temperature.

Experimental

Reagents. The amines and solvents, and all the alcohols except monodeuteromethanol and β-fluoroethanol, were available commercially and were purified by fractional distillation after treating them with drying agents. Monodeuteromethanol (CH_3OD) and triethylamine hydrochloride were available in a 99% purity and G. R. grade respectively; they were used without further purification. Crotonyl chloride (bp 120—123°C) was prepared from crotonic acid and thionyl chloride. β-Fluoroethanol (bp 103—105°C, n_D^{25} 1.3657) was prepared by Kitano's method.[2] Ethylenechlorohydrine (171 g) and anhydrous potassium fluoride (232 g) were placed in a 1000-cc stainless steel autoclave and heated at 140°C with stirring for 5 hr. The pressure rose to 14 kg/cm². After cooling, the solidified mixture was crushed and extracted with ether. The ether layer was distilled off after drying with anhydrous sodium sulfate and anhydrous potassium fluoride. A distillate (94—107°C) was redistilled after treatment with dry sodium hydrogen sulfite in order to remove the by-product, crotonaldehyde[3]; yield, 23 g.

Some of the esterification products were isolated by fractional gas chromatography (Shimadzu GC-11A; tricresyl phosphate column (20%) 4.5 m; He carrier; 100°C) and were purified by trap-to-trap distillation.

Esterification. The apparatus and procedure employed were essentially the same as those described in the previous paper.[1]

Thermal Isomerization. In a flask equipped with a refluxing condenser, a thermometer, and a magnetic

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

2) H. Kitano, K. Fukui and T. Osaka, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **58**, 119 (1955).

3) B. C. Saunders, G. J. Stacey and I. G. E. Wilding, *J. Chem. Soc.*, **1949**, 773.

stirrer, the reagents were placed and stirred at a constant temperature. The isomerization was followed by gas chromatographic analysis.

Results and Discussion

Effect of Amine. In the reaction of crotonyl chloride with ethyl alcohol in benzene, the effects of various amines on the product ratio was examined; the results are summarized in Table 1. The total ester yields were almost quantitative in all cases.

The product ratios are plotted against the pK_a-values of amines as an abscissa in Fig. 1. Although not regular, some trends may be noted.

(1) Amines can be divided into three groups.

(i) The first group includes tributylamine, triethylamine, dimethylcyclohexylamine, and *N*-ethylpiperidine, all with pK_a-values as high as 10. The isomerized product, ethyl vinylacetate (I_{Et}), was produced in a *ca.* 90% yield as the main product.

(ii) The second group includes the amines with pK_a-values lower than 7.2 (*N*, *N*-diethyl-*o*-toluidine), which give the normal product, ethyl *trans*-crotonate (III_{Et}), as the main product.

(iii) The third group includes *N*-methylmorpholine, *N*-ethylmorpholine, triallylamine, dimethylbenzylamine, and *N*-methylpiperidine with pK_a-values in the region of 7.4 to 10.1; they give various amounts of the two products, I_{Et} and III_{Et}.

Thermodynamically-unstable ethyl *cis*-crotonate (II_{Et}) was always formed in only a small quantity.

(2) The amines belonging to the second group not only have a lower pK_a; also, they are all aromatics. Hence, the lower yields of I_{Et} in the cases of 2, 4, 6-collidine and dimethylbenzylamine, which have relatively high pK_a-values, might be partly attributable to the influence of their aromatic nuclei. The inferior action of aromatic amines seems to be analogous to that in ketene formation from acyl halide with *t*-amine. It has been described how aliphatic *t*-amines are satisfactory for

Table 1. Effect of amine

t-Amine	pK_a of *1 amine	React. *2 temp., °C	Product ratio, %*3		
			I	II	III
Tributylamine*4	10.9	25—27	86.1	0.9	13.1
Triethylamine*4	10.7	22—28	96.1	0.6	3.3
Dimethylcyclohexylamine	10.7	25—30	83.6	1.7	14.6
N-Methylpyrrolidine	10.5	24—27	19.5	7.3	73.2
N-Ethylpiperidine	10.4	24—27	90.9	1.4	7.7
N-Methylpiperidine	10.1	23—26	44.8	8.8	46.3
2, 4, 6-Collidine	9.6	25—27	1.8	5.1	93.2
Dimethylbenzylamine	8.9	23—27	22.8	12.0	65.2
Triallylamine	8.3	24—26	59.6	5.7	34.7
N-Ethylmorpholine*4	7.7	24—26	74.6	3.5	21.9
N-Methylmorpholine	7.4	24—29	12.2	12.4	75.4
N, *N*-Diethyl-*o*-toluidine	7.2	24—26	0.3	6.3	93.3
N, *N*-Diethyl-*p*-toluidine	7.1	25—27	0.5	7.0	92.5
2, 6-Lutidine	6.8	24—28	0.8	5.9	93.3
N, *N*-Diethylaniline*4	6.6	25—27	0.1	7.1	92.7
N, *N*-Dimethyl-*o*-toluidine	5.9	25—26	0.4	6.8	92.8
N, *N*-Dimethyl-*p*-toluidine	5.6	24—27	0.5	15.0	84.5
Pyridine*4	5.2	25—27	0.9	5.9	93.2
Dimethylaniline	5.1	25—27	0.1	12.2	87.6
Quinoline	4.8	25—27	0.2	7.7	92.1
Tribenzylamine*5	—	24—27	0.4	5.2	94.4

*1 a) "Constants of Organic Compounds" in Series of Comprehensive Organic Chemistry, ed. by M. Kotake, Asakura, Tokyo (1963), p. 584.
b) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London (1965).

*2 Recipe: Ethyl alcohol (0.15 mol), amine (0.1 mol), crotonyl chloride (0.1 mol) and benzene (20 g) were used.

*3 I, II and III respectively mean vinylacetic acid ester, *cis*-crotonic acid ester and *trans*-crotonic acid ester throughout this paper.

*4 Previously reported data (see Ref. 1).

*5 Threefold quantity of benzene was used because of low solubility of tribenzylamine.

4) "Organic Reactions", Vol III, ed. by R. Adams, John Wiley & Sons, New York (1964), p. 124.

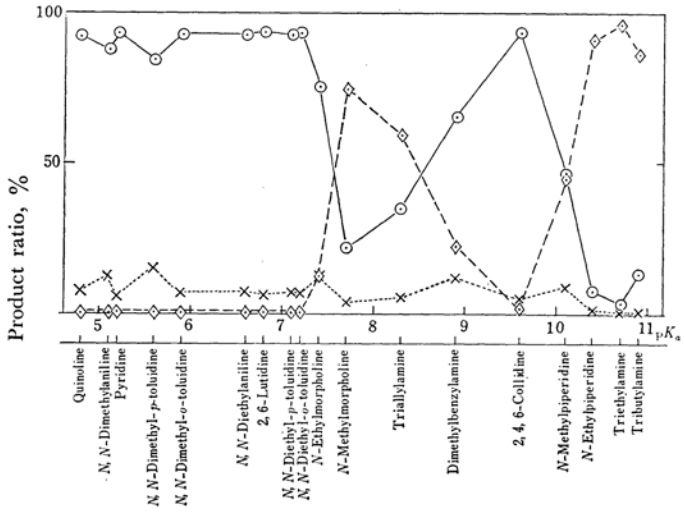


Fig. 1. Effect of amines.
—◇— Ethyl vinyl acetate, ···×··· Ethyl crotonate (*cis*)
—⊙— Ethyl crotonate (*trans*)

the preparation of ketoketenes, while aromatic amines are unsuccessful.[4]

(3) When the effects of the alkyl group are compared in the two sets, i) *N*-methylmorpholine and *N*-ethylmorpholine and ii) *N*-methylpiperidine and *N*-ethylpiperidine, the difference between methyl and ethyl groups is striking. The product ratios of I_{Et} were 90.9% for *N*-ethylpiperidine, 44.8% for *N*-methylpiperidine, 74.6% for *N*-ethylmorpholine, and 12.2% for *N*-methylmorpholine. Thus, although the differences in pK_a-values between methyl and ethyl derivatives are very small, the product ratios changed markedly. Methyl derivatives reduce the yield of I_{Et} considerably, and instead increase the yields of II_{Et} and III_{Et}. This should be understood as a steric effect.

(4) A comparison of the three series of amines with a similar bulkiness, *i. e.*,

i) triethylamine, *N*-ethylpiperidine and *N*-ethylmorpholine;

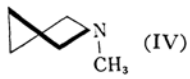
ii) *N*-methylpiperidine and *N*-methylmorpholine; and

iii) tributylamine and triallylamine;

shows that the greater the pK_a-value of the amine, the greater is the relative yield of I_{Et} within each series.

It should be understood from (3) and (4) that both the basicity and the steric effect of amine influence the product ratio.

(5) The low yield of I_{Et} in the case of *N*-methylpyrrolidine in spite of its higher pK_a might be attributed to its smaller steric requirement than in *N*-methylpiperidine, *etc.*, because of its half-chair conformation IV of the five-membered ring.[5]



(IV)

Effect of Alcohol. The effects of alcohols on the product ratios were investigated with nine amines. The results are shown in Table 2.

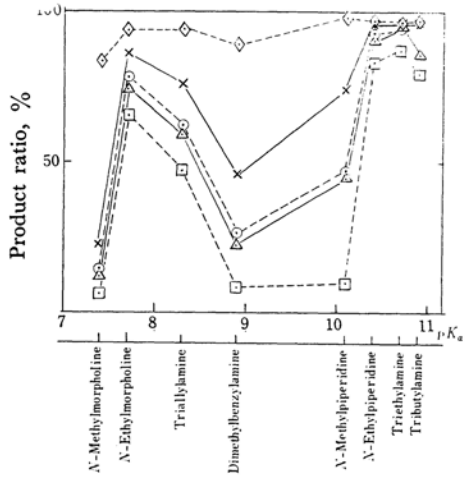


Fig. 2. Effect of alcohols.
--◇-- *t*-Bu ester —×— *i*-Pr ester
···⊙··· *i*-Bu ester —△— Et ester
—⊡— Me ester

The total ester yields were almost quantitative except for *t*-butyl alcohol. The product ratios are plotted against the pK_a-values of the amines used (see Fig. 2). It is understood that the product ratios also change with the sort of alcohol. The product ratios of I increased in the order:

5) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York (1962), p. 251.

Table 2. Effect of alcohol

t-Amine	*t*-BuOH			*i*-PrOH			*i*-BuOH			EtOH			MeOH		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Tributylamine	97.3	1.5	1.2	96.2	0.9	2.8				86.1	0.9	13.1	79.7	1.5	18.7
Triethylamine	96.9	1.2	1.9	96.6	0.8	2.7	94.4	2.1	3.6	96.1	0.6	3.3	87.8	1.2	11.0
N-Ethyl-piperidine	97.1	1.1	1.8	96.7	1.0	2.3	93.4	0.9	5.7	90.9	1.4	7.7	83.5	1.6	14.8
N-Methyl-piperidine	98.1	1.9	trace	74.3	3.9	21.7	47.6	9.3	43.1	44.8	8.8	46.3	10.0	6.9	83.2
Dimethyl-benzylamine	89.5	2.6	7.9	46.1	7.7	46.2	26.5	13.8	59.7	22.8	12.0	65.2	8.4	9.2	82.4
Triallylamine	94.8	2.6	2.6	76.2	4.1	19.7	62.6	4.7	32.7	59.6	5.7	34.7	47.4	6.2	46.4
N-Ethyl-morpholine	94.0	2.2	3.8	86.3	2.2	11.4	78.9	2.9	18.2	74.6	3.5	21.9	65.3	3.6	31.2
N-Methyl-morpholine	83.8	3.6	12.6	22.5	8.0	69.5	14.6	12.1	73.3	12.2	12.4	75.4	6.3	14.1	79.6
Pyridine				0.5	5.1	94.5				0.9	5.9	93.2	1.6	5.9	92.5

Table 3. Product ratios with methyl cellosolve and β-fluoroethanol

Amine	Methyl cellosolve			β-Fluoroethanol		
	I	II	III	I	II	III
Tributylamine	90.8	trace	9.2			
Triethylamine	93.4	trace	6.6	90.8	0.5	8.7
N-Metylpiperidine	47.2	7.8	45.0			
Dimethylbenzylamine	27.4	8.7	63.9			
Triallylamine	75.3	4.4	20.3			
N-Ethylmorpholine	81.8	3.1	15.2	90.8	0.8	8.4

MeOH < EtOH < *i*-BuOH < *i*-PrOH < *t*-BuOH. This order shows that the steric effects of alkyl groups in alcohols have a considerable influence on the product ratios; bulkier groups cause more isomerization. At the same time, however, the inductive effects of these alkyl groups change with this order. To clarify this parallelism, experiments were made with methyl cellosolve and β-fluoroethanol, which have a bulkiness similar to that of isobutyl alcohol or ethyl alcohol, but differ in polar character. The results are in Table 3. In Fig. 3 the product ratios listed in Tables 2 and 3 are plotted against the σ* of R with ROH as abscissa. The results with methyl cellosolve and β-fluoroethanol suggest the greater importance of the steric factor.

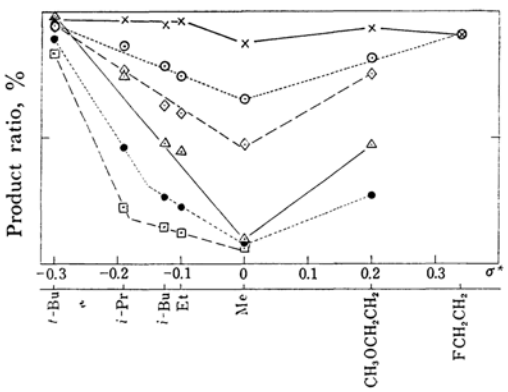


Fig. 3. Effect of alcohols.*
—×— Triethylamine, ···⊙··· *N*-Ethylmorpholine
--◇-- Triallylamine, —△— *N*-Methylpiperidine
···●··· Dimethylbenzylamine
--⊡-- *N*-Methylmorpholine
* σ*-value for CH_3OCH_2-CH_2- and FCH_2CH_2- were derived from CH_3OCH_2 (+0.6) and FCH_2- (+1.10) by postulating the shield by methylene group as 2/3.

Reaction with CH_3OD. It was pointed out above that the reaction under consideration was analogous to the ketene formation, for which aromatic amines were unsuccessful. If the reaction proceeds *via* a ketene intermediate, it would be expected that the ester containing a deuterium atom on α-carbon should be formed in the reaction with CH_3OD (Eq. (2)):

$$\rangle C{=}C{=}O + CH_3O\underline{D} \rightarrow \rangle \underline{C}D\text{-}C{=}O \quad (2)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O\text{-}CH_3$$

The product ratios of monodeuteromethanol esters in the presence of triethylamine or pyridine are shown in Table 4. No difference in product ratio is noticed between CH_3OD and CH_3OH. The main products in each reaction were isolated and subjected to mass spectroscopic analysis.

Table 4. Product ratios in the reaction with CH_3OD

	CH_3OD			CH_3OH		
	I_{Me}	II_{Me}	III_{Me}	I_{Me}	II_{Me}	III_{Me}
Triethylamine	87.8	1.2	11.0	89.6	0.8	9.6
Pyridine	1.6	5.9	92.5	—	7.5	92.5

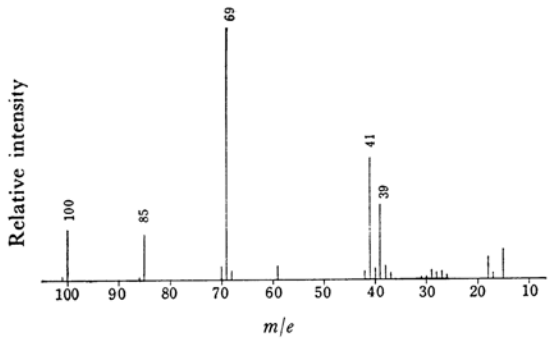


Fig. 4. Mass spectrum of Methyl crotonate.

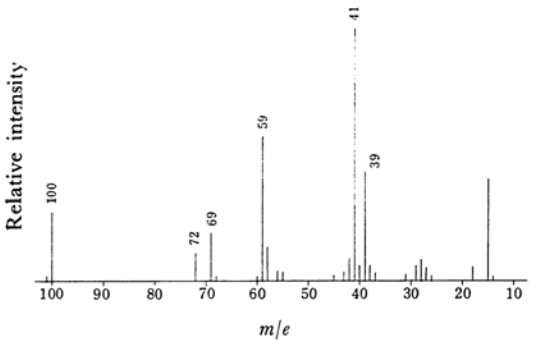


Fig. 5. Mass spectrum of Methyl vinylacetate from CH_3OH.

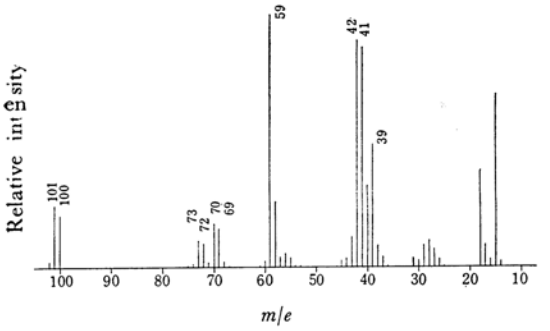
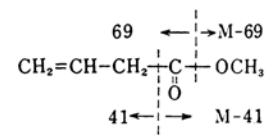


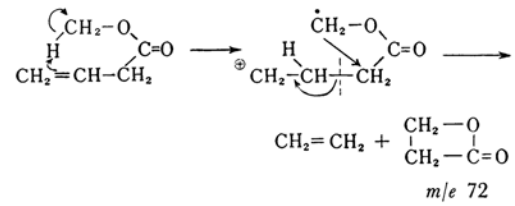
Fig. 6. Mass spectrum of methyl vinylacetate from CH_3OD.

Methyl *trans*-crotonates (III_{Me}) from CH_3OD-pyridine and CH_3OH-pyridine systems gave the same spectrum (see Fig. 4). It is obvious that deuterium was not found in methyl crotonate. Figures 5 and 6 show the spectra of methyl acetates (I_{Me}) from CH_3OH-triethylamine and CH_3OD-triethylamine systems respectively. In addition to fragments in Fig. 5, the appearance of fragments *m/e* 101, 73, 70 and 42 may be seen in Fig. 6; this indicates the existence of an ester containing deuterium. It may be understood from a comparison of their intensities that deuterium are present in only halfs of the esters.[6]

Fragments 69 and 41 in Figs. 5 and 6 are caused from the fragmentation as follows:



Therefore, fragments 70 and 42 in Fig. 6 indicate that one hydrogen atom in the CH_2=$CHCH_2$- group has been replaced by a deuterium atom. Although the mechanism of the formation of fragment 72 in Figs. 5 and 6 is not clear, a probable course may be the elimination of ethylene by the fragmentation as follows:



The presence of the fragment 73 in Fig. 6 strongly suggests that the deuterium atom is on the α-carbon. Furthermore, the presence of deuterium on the α-carbon is supported by NMR analysis (see Fig. 7). The observed proton ratios are consistent with the values calculated by assuming that equal amounts of CH_2=$CHCH_2COOCH_3$ and CH_2=$CHCHDCO$-OCH_3 are present in the esters.

	α-H	β-H	γ-H	$-OCH_3$
Observed	1.5	1.1	2.1	3
Calculated	1.5	1	2	3

Modification of the Reaction Procedure. It is known that methyl and ethyl ketene can exist

6) It would be expected from Eq. (2) that all the esters contain a deuterium atom, but only a half of the esters really contained deuterium. This may be attributed to the following equilibrium:

$$(C_2H_5)_3N\cdot HCl + CH_3OD \rightleftharpoons (C_2H_5)_3N\cdot DCl + CH_3OH$$

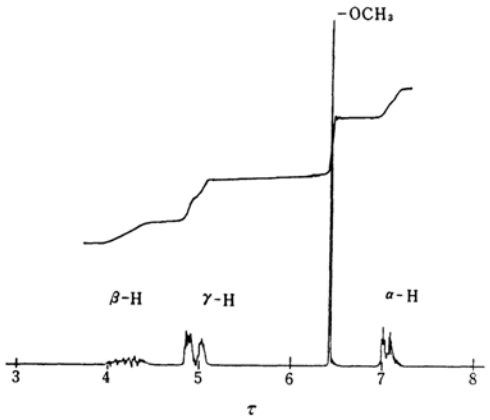
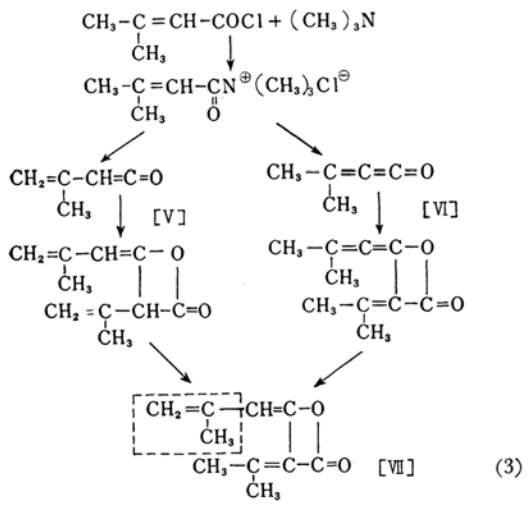


Fig. 7. NMR spectrum of methyl vinylacetate from CH_3OD.

only in an ether solution.[7] Recently, Payne isolated and identified a ketene dimer VII with an isopropenyl group from the reaction of α, β-unsaturated acid halide with *t*-amine, and postulated such ketenes as V and VI as intermediates (Eq. (3)).[8] To verify the formation of ketene as an intermediate in the reaction concerned experiments were carried out under the conditions of the ketene formation.[9] The reaction proceeded smoothly at −30°C.[10] The results are shown in Table 5.



(3)

7) "Chemistry of Carbon Compounds," Vol I, ed. by E. H. Rodd, Elsevier Publishing Co., Amsterdam (1951), p. 529.
8) G. B. Payne, *J. Org. Chem.*, **31**, 718 (1966).
9) Ref. 4, p. 138.
10) *t*-Amine (0.1 mol) was added to an ether solution of crotonyl chloride (0.1 mol) for 30 min at −30°C, after which the mixture was stirred for 20 min at the same temperature. Thereafter, the temperature was raised to 25°C, and ethyl alcohol was added to the reaction mixture for 25 min. In the experiment conducted at room temperature, the reaction mixture became dark, and no reaction with alcohol proceeded.

Table 5. Product ratios in the modified procedure

Amine	I_{Et}	II_{Et}	III_{Et}
Triethylamine	92.6	1.3	6.1
N-Ethylpiperidine	88.5	1.7	9.9
N-Ethylmorpholine	63.3	4.8	31.9

The main reaction was also the isomerization esterfication. The product ratios of I_{Et} were very similar to the values in Table 1, although the total ester yields were somewhat decreased. Unfortunately, neither the isolation nor the identification of ketene itself was successful.

From these facts, it is reasonable to consider that the double bond shift in the reaction under consideration proceeds *via* a ketene intermediate.

Effect of Solvent. The effect of solvents were tested through the reaction with ethyl alcohol using five amines (triethylamine, *N*-methylpiperidine, dimethylbenzylamine, triallylamine, and *N*-ethylmorpholine). The results with aliphatic and aromatic solvents with different dielectric constants are shown in Table 6. Regardless of the polarity of the solvents, almost identical product ratios were obtained. In the acetonitrile-triethylamine system, considerable amounts of high-boiling-point products were produced. Although not identified, one of these materials exhibited the same retention time on a gas chromatogram as that of an authentic sample of $CH_3CHClCH_2COOR$. Therefore, it may be supposed that considerable addition reaction occurred. In the case of dimethylsulfoxide, the reaction mixture turned brown-black, and hardly any formation of ester was detected.

Effect of Reaction Temperature. The effect of the reaction temperature was investigated through the reaction with ethyl alcohol in benzene or toluene. The results are shown in Fig. 8. The product ratios of I_{Et} were almost the same (95—97%) below room temperature, but above it II_{E},

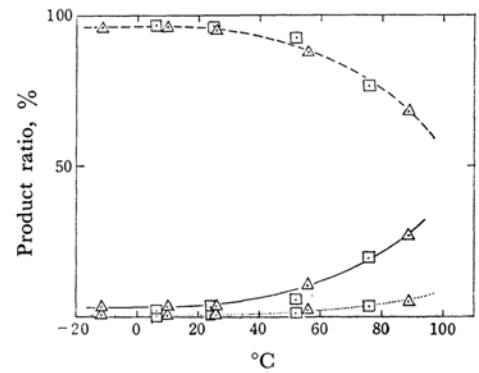


Fig. 8. Effect of temperature.
⊡ In benzene △ In toluene
—— Ethyl vinylacetate
····· Ethyl crotonate (*cis*)
—— Ethyl crotonate (*trans*)

Table 6. Effect of solvent

Solvent	(Dielect.) const.	Triethylamine			*N*-Methyl-piperidine			Dimethylbenzyl-amine			Triallylamine			*N*-Ethyl-morpholine		
		I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Hexane	(1.9)	91.9	1.0	7.1	34.6	10.0	55.4							75.4	3.2	21.4
CTC*	(2.2)	90.9	1.1	8.0	42.9	8.8	48.2							74.9	3.4	21.7
Dioxane	(2.2)	96.2	0.9	2.9												
Benzene	(2.3)	96.1	0.6	3.3	44.8	8.8	46.3	22.8	12.0	65.2	59.6	5.7	34.7	74.6	3.5	21.9
Toluene	(2.4)	95.5	0.8	3.7												
Chloro-from	(4.6)	94.8	0.9	4.3												
THF*	(7.4)	94.6	0.8	4.6	46.0	8.2	45.8	24.4	11.3	64.3	54.0	7.1	39.0	72.9	3.4	23.7
Acetone	(21.3)	96.6	0.7	2.6	55.6	7.4	37.0	29.4	11.5	59.2	63.3	5.6	31.2	83.0	2.4	14.6
Ethanol	(25.8)	87.9	1.0	11.1	29.9	13.4	56.7	18.4	13.8	67.8	66.2	5.0	28.8	75.9	3.2	20.9
Aceto-nitrile	(37.5)	83.3	1.4	15.2	61.0	5.6	33.4									

* CTC: Carbon tetrachloride; THF: Tetrahydrofuran.

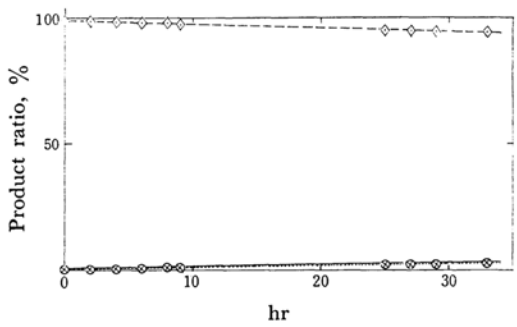


Fig. 9. Isomerization of ethyl vinylacetate.
Temp. 50°C. Et_3N 5.3 mol%
--◈-- Ethyl vinylacetate
···×··· Ethyl crotonate (*cis*)
—◉— Ethyl crotonate (*trans*)

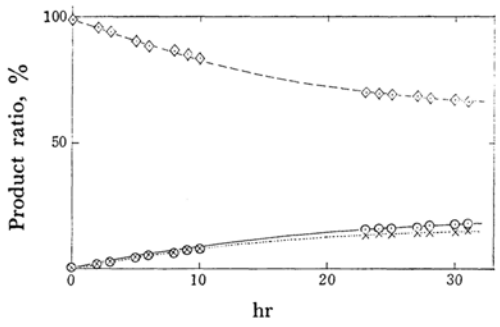


Fig. 10. Isomerization of ethyl vinylacetate.
Temp. 100°C Et_3N 6.1 mol%
--◇-- Ethyl vinylacetate
···×··· Ethyl crotonate (*cis*)
—○— Ethyl crotonate (*trans*)

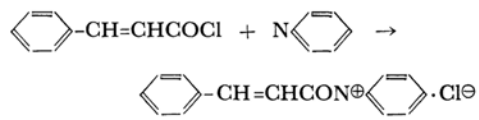
and III_{Et} increased progressively. At high temperatures, thermal isomerization has to be expected, because an α,β-isomer is thermodynamically more stable than a β,γ-isomer. Therefore, the thermal isomerization of ethyl vinylacetate and ethyl *trans*-crotonate was checked. Isomerization was observed neither with the ester alone nor in the presence of triethylamine hydrochloride at room temperature, 50°C, or 100°C. Only in the presence of free triethylamine was the slow isomerization of ethyl vinylacetate to ethyl crotonate observed; a 10% isomerization was observed only after 30 hr at 50°C or after 6 hr at 100°C (see Figs. 9 and 10).

These results rule out the possibility of such an isomerization between product esters under the conditions of esterification. The results in Fig. 8 must be explained only in terms of the stability of the reaction intermediate, probably ketene.

A Consideration of the Reaction Mechanism. From the discussion thus far, it may be understood that (1) the steric factors of amine and alcohol influence the extent of double-bond shift; (2) the reaction proceeds *via* a ketene intermediate, and (3) the amines with pK_a-values lower than 7.2 do not cause the double-bond shift. It has been described how the acyl ammonium salt resulting from acyl halide and *t*-amine is an acylating agent in the Einhorn reaction.[11] Payne[8] and Baumgarten[12] isolated and identified such acyl ammonium salts as VIII and IX respectively.

$$(CH_3)_2C{=}CHCOCl + (CH_3)_3N \rightarrow (CH_3)_2C{=}CHCON^{\oplus}(CH_3)_3\cdot Cl^{\ominus}$$

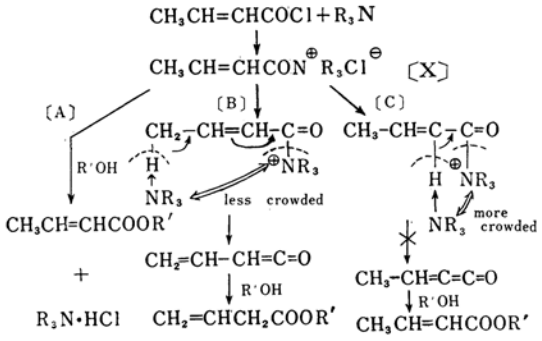
(VIII)



(IX)

11) H. Krauch and W. Kunz, "Organic Name Reactions," John Wiley & Sons, New York (1964), p. 141.
12) H. E. Baumgarten, *J. Am. Chem. Soc.*, **75**, 1239 (1953).

Judging from these results, the following mechanism may be proposed. Although the exact nature of the isomerization is not obvious, the authors prefer steric control in the proton abstraction by *t*-amine.



The first step is the formation of the acyl ammonium salt X. Less basic amines are not enough to abstract a proton, so the reactions in which they participate may proceed *via* course A. It has been described that a ketene intermediate was formed in the reaction in which the isomerization esterification was observed. Two courses for the ketene formation, B and C, are considered in this reaction, as Payne postulated (Eq. (3)). The α-proton abstraction in course C, however, is difficult because the system is more crowded sterically, because the proton to be abstracted is olefinic, and because the structure of the ketene formed may be less stable. Therefore, the γ-proton abstraction in course B would proceed with more ease. Furthermore, bulky alcohols would repress course A because of the crowding in the neighborhood of the reaction center; this also favors course B.

The kinetic analysis of the reaction is, unfortunately, not available because of the extreme rapidity of the reaction.

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