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Vinylacetic Acid Ester Formation in the Reaction of Crotonoyl Chloride with Alcohol in the Presence of *t*-Amine

By Toshitsugu OZEKI and Masakatsu KUSAKA

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

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In the esterification of crotonoyl chloride, vinylacetic acid ester was obtained predominantly, with an unusual double bond shift from the α, β- to the β, γ-position in the presence of a strong basic amine. In the case of ethyl alcohol, for example, the yields of ethyl vinylacetate were as follows (%): triethylamine (96.1), tributylamine (86.1), *N*-ethyl morpholine (74.6), *N*, *N*-diethyl aniline (0.1) and pyridine (0.9). The rest were *cis*- and *trans*-crotonic acid esters.

The interesting facts were found by the authors that, in the reaction of crotonoyl chloride with alcohol in the presence of a strong basic amine (the Einhorn reaction),[1] an unusual shifts of the double bond from the α, β- to the β, γ-position occurred and that vinylacetic acid ester was obtained predominantly (Eq. 1):

$$\begin{aligned} &CH_3CH{=}CHCOCl + ROH + R_3'N \longrightarrow \\ &CH_2{=}CHCH_2COOR + CH_3CH{=}CHCOOR \\ &\qquad \text{major product} \qquad\qquad \text{minor product} \\ &+ R_3'N^+HCl^- \qquad\qquad\qquad\qquad (1) \end{aligned}$$

Although the double bond shift from the α, β- to the β, γ-position has been reported in the hydroformylation of ethyl crotonate and crotonamide,[2-4] such a double bond shift has not ever been reported in relation to the Einhorn reaction; the occurrence of a double bond shift from a conjugated to an unconjugated system in such a reaction is very interesting.

Experimental

Reagents.—All the reagents used except crytonoyl chloride were obtained commercially. The alcohols, amines and benzene were purified by fractional distillation after they had been treated with a drying agent. Crotonic acid, sodium hydroxide and sulfuric acid (98%), each available in a G. R. grade, were used without further purification. Crotonoyl chloride (b. p. 120—123°C, n_D^{18} 1.4598), prepared from crotonic acid and thionyl chloride, was identified by means of its NMR[5] and IR (960 cm^{-1}, $^{H}\!\!>\!C{=}C\!<_{H}$ and 1768 cm^{-1}, C=CCOCl) spectra. The spectra are shown in Figs. 1 and 2.

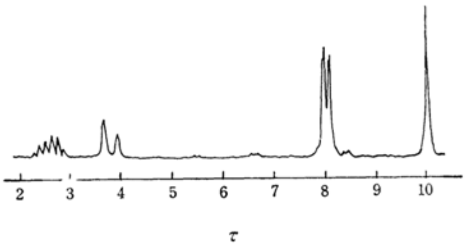

Fig. 1. NMR spectrum of crotonoyl chloride.
JNM-C-60
60 Mc., 20°C, Bulk
Stand. $(CH_3)_4Si$

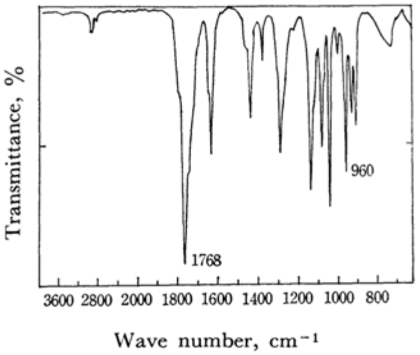

Fig. 2. IR spectrum of crotonoyl chloride.
Shimadzu IR-27
CCl_4 soln. (ca. 1.6%)
0.2 mm.

Procedure.—The alcohol, amine and solvent were placed in a flask fitted with a thermometer, a mechanical stirrer, a condenser, and a dropping funnel. Through the dropping funnel, crotonoyl chloride was then added slowly into the mixture with stirring at room temperature; after 15 min. the supernatant liquid of the reaction

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1) H. Krauch and W. Kunz, "Organic Name Reactions", John Wiley & Sons, New York (1964), 141.

2) J. Falbe and F. Korte, *Angew. Chem.*, **74**, 900 (1962).

3) J. Falbe and F. Korte, *Chem. Ber.*, **95**, 2680 (1962).

4) J. Falbe, N. Huppes and F. Korte, ibid., **97**, 863 (1964).

5) H. Kashiwagi and J. Niwa, This Bulletin, **36**, 405 (1963).

TABLE I. COMPOSITION OF PRODUCTS

Exp. No.	Alcohol	Base	Solvent	Reaction temp., °C	Product ratio, %[*6] I	II	III
1[*1]	Methyl	TEA[*5]	Benzene	24—32	87.8	1.2	11.0
2[*1]	Ethyl	TEA	Benzene	24—28	96.1	0.6	3.3
3[*1]	Isopropyl	TEA	Benzene	26—30	96.6	0.8	2.7
4[*1]	*t*-Butyl	TEA	Benzene	23—28	96.9	1.2	1.9
5[*1]	*n*-Butyl	TEA	Benzene	24—28	95.4	0.7	3.8
6[*1]	Crotyl	TEA	Benzene	24—30	91.3	1.0	7.7
7[*2]	Isoamyl	TEA	Benzene	24—32	96.4	0.6	3.0
8[*2]	Methyl	TBA[*5]	Benzene	25—26	79.7	1.5	18.7
9[*2]	Ethyl	TBA	Benzene	25—27	86.1	0.9	13.1
10[*2]	Ethyl	EM[*5]	Benzene	24—26	74.6	3.5	21.9
11[*2]	Ethyl	Py[*5]	Benzene	25—27	0.9	5.9	93.2
12[*2]	Ethyl	DEA[*5]	Benzene	25—27	0.1	7.1	92.7
13[*2]	Ethyl	None	Benzene	23—26	3.2	9.5	87.3
14[*3]	Ethyl	NaOH	Benzene & Water	24—27	0.3	8.3	91.5
15[*4]	Ethyl	(H_2SO_4)	Benzene	Reflux	—	0.2	99.8

[*1] Alcohol 0.75 mol., amine 0.5 mol., crotonoyl chloride 0.5 mol. and solvent 100 g. were used.
[*2] Alcohol 0.35 mol., amine 0.25 mol., crotonoyl chloride 0.25 mol. and solvent 50 g. were used.
[*3] Alcohol 17.2 g., NaOH 10 g., crotonoyl chloride 26.1 g., water 40 g. and benzene 40 g. were used.
[*2] Alcohol 13.8 g., crotonic acid 8.6 g., benzene 20 g. and H_2SO_4 2 cc. were refluxed gently for 6 hr.
[*5] TEA: triethylamine, TBA: tri-*n*-butylamine, Py: pyridine, DEA: diethylaniline and EM: *N*-ethyl morpholine.
[*6] Total yields: 86—100% in Exp. 1—13 except Exp. 4, 65%.

TABLE II. CHARACTERISTIC BANDS OF IR (cm^{-1})*

	I_{Me}	I_{Et}	II_{Me}	II_{Et}	III_{Me}	III_{Et}
$\nu_{C=O}$	1742	1740	1720	1720	1727	1721
ν_{C-O-}	1170 1195	1177	1178 1200	1186	1179 1197	1184
$\nu_{C=C}$	1647	1646	1649	1652	1664	1666
$\nu_{=C-H}$	3085	3090	3030	3039	3062	3060
δ=C–H (in-plane)	1409	1407	1410	1414	—	—
δ=C–H (out-of-plane)	920 992	920 994	818	815	968	969

* Shimadzu IR-27, NaCl cell, liquid capillary.

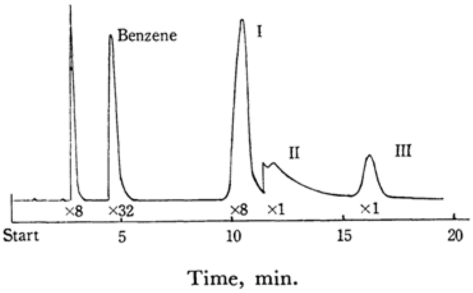


Fig. 3. Gas chromatogram for Exp. 2.

Shimadzu GC-2C
Tricresyl phosphate (10%, 5.25 m.)
100°C
H_2 10 cc./20 sec.

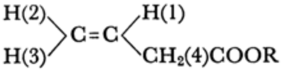
mixture was analyzed by gas chromatography in order to determine the product ratio. As amine hydrochlorides were soluble in benzene in Exp. 8, 9 and 12, an equal volume of *n*-hexane was added to the reaction mixture to precipitate them; thereafter an aliquot was withdrawn from the upper layer. In the Schotten-Baumann (Exp. 14) and Fisher (Exp. 15) methods, the benzene layer was submitted to analysis. A typical gas chromatogram for Exp. 2 is shown in Fig. 3. The results obtained are shown in Table I.

Identification

The products always consisted of three isomeric esters (denoted as I, II and III); they were isolated by fractional gas chromatography in some reactions (Shimadzu GC-11A; Tricresyl phosphate (20%) 4.5 m.; He; 100°C).

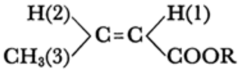
TABLE III. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF NMR[*1]

Ester	Chemical shift (τ-value)				Coupling constant (c.p.s.)[*2]					
	H_1	H_2	H_3	H_4	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}
$\mathrm{I_{Me}}$	4.1	4.9	4.9	7.0	9.5	17	6.4	—	1.3	1.3
$\mathrm{I_{Et}}$	4.1	4.9	4.9	7.0	9.4	17	6.7	—	1.4	1.4
(Lit.)[*3]	(4.10)	(4.92)	(4.89)	(6.96)	(10.3)	(17.3)	(6.9)	(1.8)	(−1.5)	(−1.6)
	H_1	H_2	H_3		J_{12}	J_{13}	J_{23}			
$\mathrm{II_{Me}}$	4.2	3.7	7.9		12	1.4	7.0			
$\mathrm{II_{Et}}$	4.3	3.8	7.9		12	1.8	7.3			
(Lit.)[*4]	(4.28)	(3.72)	(7.86)		(11.4)	(−1.82)	(7.27)			
	H_1	H_2	H_3		J_{12}	J_{13}	J_{23}			
$\mathrm{III_{Me}}$	4.2	3.1	8.1		17	1.7	6.7			
$\mathrm{III_{Et}}$	4.2	3.1	8.1		15	1.6	6.8			
(Lit.)[*4]	(4.24)	(3.10)	(8.12)		(15.5)	(−1.67)	(6.85)			



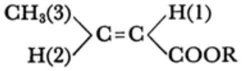
$$\begin{matrix}\mathrm{H(2)} & & \mathrm{H(1)} \\ & \mathrm{C{=}C} & \\ \mathrm{H(3)} & & \mathrm{CH_2(4)COOR}\end{matrix}$$

I



$$\begin{matrix}\mathrm{H(2)} & & \mathrm{H(1)} \\ & \mathrm{C{=}C} & \\ \mathrm{CH_3(3)} & & \mathrm{COOR}\end{matrix}$$

II



$$\begin{matrix}\mathrm{CH_3(3)} & & \mathrm{H(1)} \\ & \mathrm{C{=}C} & \\ \mathrm{H(2)} & & \mathrm{COOR}\end{matrix}$$

III

[*1] Varian HR-100, 100 Mc., 10% CCl_4 soln., room temp., stand. $(CH_3)_4Si$.

[*2] Absolute values. Not considered about the sign.

[*3] Ref. 8.

[*4] Ref. 5.

TABLE IV. PHYSICAL AND CHEMICAL CONSTANTS

Methyl esters	$\mathrm{I_{Me}}$	$\mathrm{II_{Me}}$	$\mathrm{III_{Me}}$
Purity, %[*1]	100	99.0	99.8
B. p., °C/mmHg	53.8—4.0/106	—	68.8—9.6/118
(Lit.)[*2]	(108/774)	—	(119/768)
$n_D^{(t)}$	$1.4085^{(20.2)}$	$1.4258^{(20.0)}$	$1.4254^{(20.2)}$
(Lit.)[*3]	(1.4083)	(1.4223)	(1.4248)
Iodine value (calcd. 254)	245	—	248
Sapon. value (calcd. 561)	563	—	562
UV[*4]			
λ_{max}(mμ), (log ε_{max})	208 (3.47)	—	206 (4.16)
(Lit.)	(225_s) ((2.0))[*5]	—	(212) ((4.16))[*6]
Ethyl esters	$\mathrm{I_{Et}}$	$\mathrm{II_{Et}}$	$\mathrm{III_{Et}}$
Purity, %[*1]	99.6	99.5	99.9
B. p., °C/mmHg	53.0—3.4/58	58.6—8.8/68	57.5—7.8/47
(Lit.)[*2]	(124/745)	—	(136.5/761)
$n_D^{(t)}$	$1.4109^{(19.8)}$	$1.4253^{(20.2)}$	$1.4251^{(19.8)}$
(Lit.)[*2]	(1.4110)	—	(1.4247)
Iodine value (calcd. 223)	221	216	216
Sapon. value (calcd. 492)	496	495	495

[*1] By gas chromatographic analysis.

[*2] Ref. 9.

[*3] Ref. 10.

[*4] Measured in 95% EtOH with ORD-UV-5 (JASCO).

[*5] Values for ethyl ester in *n*-hexane (s: shoulder). J. C. Crawford, *J. Chem. Soc.*, **1953**, 2658.

[*6] R. F. Rekker, P. J. Brombacher, H. Hamann and W. J. Nauta, *Rec. trav. chim.*, **73**, 410 (1954).

Characteristic infrared bands for methyl and ethyl esters are shown in Table II. These characteristic bands indicate the presence of the following functional groups⁶⁾;

in I nonconjugated carbonyl group
nonconjugated terminal vinyl group,
in II conjugated carbonyl group
conjugated cis-double bond,
and in III conjugated carbonyl group
conjugated trans-double bond.

NMR measurements for methyl and ethyl esters

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6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, New York (1958), Chap. 3 and Chap. 11.

were carried out at 100 Mc.⑦ The data are listed in Table III.

The spectra for II and III were analyzed and found to be of the ABX_3 type; their chemical shifts and coupling constants were consistent with the values given to *cis*- and *trans*-methyl crotonates in the literature.[5,8,9] It was reasonable to identify the spectra for I as the $ABCX_2$ type.[10] This result agreed well with the values for methyl vinylacetate.[11] These assignments were also supported by the proton ratios obtained by the integration of each signal.

The refractive index, the retention time in gas chromatography, and the infrared and ultraviolet spectra for I_{Me} were completely identical with those values for authentic methyl vinylacetate as prepared by Vogel's method.[12] Furthermore, the results of ozone oxidation, followed by the formaldehyde test using chromotropic acid, were positive, indicating the presence of a terminal vinyl group.

The physical and chemical constants for the isolated methyl and ethyl esters are shown in Table IV. Their iodine and saponification values were in agreement with the calculated values. The refractive indices were identical with the values in the literature.[12,13]

As to the other esters shown in Table I, analogous behavior in chemical and physical analysis was observed. Therefore, in all cases I, II and III were identified as the vinylacetic acid ester, the *cis*-crotonic acid ester and the *trans*-crotonic acid ester respectively.

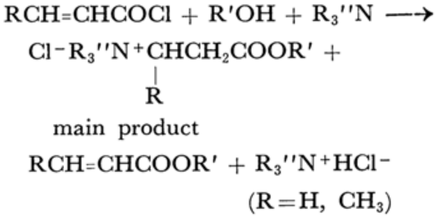
Discussion

The absence of vinylacetyl chloride in crotonoyl chloride was confirmed by the absence of peaks at 1800 cm^{-1} (unconjugated acyl halide), 910 and 990 cm^{-1} (terminal vinyl) in IR, and by the near 6.5 τ-value (substituted methylene, $C{=}CCH_2$-COX) in NMR.

Regarding gas chromatography, the same results were obtained with both tricresyl phosphate and diethyleneglycol succinate columns; no isomerization was observed in either column. Therefore, the composition of the products must be correct.

It may be understood from Table I that the vinylacetic acid ester was formed predominantly in the presence of a strong basic amine (Exp. 1—10), with little dependence on the sort of alcohol, but that the crotonic acid ester was predominant in the presence of a weak basic amine (Exp. 11—12). In the reaction without amine or in Schotten-Baumann and Fisher reactions, however, the crotonic acid ester was formed predominantly. These facts suggest that the amine plays an important role in the formation of the vinylacetic acid ester.

The occurrence of an unusual double bond shift from a conjugated to an unconjugated system is very interesting. Hickmott has reported the following reaction (Eq. 2)[14]:



$$\begin{gathered} RCH{=}CHCOCl + R'OH + R_3''N \longrightarrow \\ Cl^-R_3''N^+\underset{\displaystyle R}{\underset{|}{C}}HCH_2COOR' + \\ \text{main product} \\ RCH{=}CHCOOR' + R_3''N^+HCl^- \qquad (2) \\ (R=H,\ CH_3) \end{gathered}$$

This reaction may participate in the reaction mechanism of vinylacetic acid ester formation. Further investigation is now in progress and will be reported on at a later data.

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[7] NMR spectra at 100 Mc. were measured in The Government Chemical Industrial Research Institute, Tokyo. The NMR spectra at 60 Mc. were measured with a JNM 3H-60 (room temp.; bulk; stand. $(CH_3)_4$-Si) apparatus in the Japan Electron Optics Laboratory Co., Ltd.; the same results were obtained.

[8] R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961).

[9] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, **1960**, 2886.

[10] R. M. Silverstein and G. C. Bassler," Spectrometric Identification of Organic Compounds, "John Wiley & Sons, New York (1963), pp. 83—89.

[11] K. Hayamizu, unpublished data.

[12] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, **1948**, 658.

[13] D. E. McGreer. *J. Org. Chem.*, **25**, 852 (1960).

[14] P. W. Hickmott, *J. Chem. Soc.*, **1964**, 883.