Acyl Cyanide. V. The Synthesis of 1-Cyano-1-alkenyl Esters by the Reaction of Acyl Cyanides with Acid Anhydrides and Isocyanates

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The reactions of enolizable acyl cyanides (acetyl, propionyl, and isobutyryl cyanide) with acid anhydrides (acetic, propionic, butyric, isobutyric, and benzoic anhydride) in the presence of a catalytic amount of tertiary amines (pyridine, lutidines, 4-(dimethylamino)pyridine) produced the corresponding 1-cyano-1-alkenyl carboxylates. In the reactions of propionyl cyanide, (*Z*)-1-cyano-1-propenyl carboxylates were formed predominantly over the (*E*)-isomers (isomer ratios *Z*/*E* were *ca.* 80/20). The reactions of the cyanides with isocyanates also gave the corresponding 1-cyano-1-alkenyl carbamates in moderate yields, and the acid-treatments of 1-cyano-2-methyl-1-propenyl phenylcarbamate induced its annelation into 3-phenyl-1,3-oxazolidine-2,4-dione derivatives.

Only a limited number of methods have been known for the synthesis of 1-cyano-1-alkenyl esters, known as versatile reagents for ring formations[1] and polymerizations,[2] and they are classified into two groups: dehydrohalogenation of 1-cyano-2-haloethyl acetate by tertiary amines,[3] and base-catalyzed addition of hydrogen cyanide to ketene.[4] However, these methods are limited to the preparation of 1-cyanovinyl esters. We therefore have tried to find a more general and convenient method for the synthesis of a variety of unsubstituted and substituted 1-cyano-1-alkenyl esters.

Related to the synthetic method of the cyanoalkenyl esters, it has been reported[5] that when the reaction of aliphatic acyl chloride with metal cyanide (Eq. 1) known as an authodox preparative method[6] of acyl cyanides was carried out in the presence of crown ether, acyl cyanide was not isolated. In addition, our analogous examination in the reaction of acetic anhydride with potassium cyanide in the presence of crown ether proved it unsuccessful in the synthesis of acetyl cyanide. However, 1-cyanovinyl acetate was obtained instead. The formation of the ester seems to be accountable by the base-catalyzed dimerization of acetyl cyanide followed by dehydrocyanation as was proposed by Tate[7] (Eq. 2). If this mechanism is correct, then the maximum yield of the ester, calculated upon the basis of inorganic cyanide consumed, should not exceed 50%. However, the ester was isolated in 52% from the reaction of isobutyric anhydride (two parts) and potassium cyanide (one part) in the presence of 18-crown-6 in 1,2-dimethoxyethane. Evidently, this fact implies that an alternative reaction path must (co)exist to produce the ester. We clarified this is the acylation of acyl cyanide intermediate by acetic anhydride (Eq. 3). We have extended this reaction to a variety of acyl cyanide–acid anhydride combinations and established its versatile characters. Also the carbamoylation of acyl cyanides with isocyanates was investigated to prepare 1-cyano-1-alkenyl carbamates (Eq. 4).

$$R^1R^2CHCOCl + Metal\text{–}CN \longrightarrow R^1R^2CHCOCN \quad (1)$$

$$R^1R^2CHCOCN + CN^- \longrightarrow R^1R^2CH\text{–}C(CN)_2O^-$$

$$\xrightarrow{R^1R^2CHCOCN} R^1R^2CH\text{–}C(CN)_2OCOCHR^1R^2$$

$$\xrightarrow{base} R^1R^2C{=}C(CN)OCOCHR^1R^2 \quad (2)$$

$$R^1R^2CHCOCN + (R^3CO)_2O \longrightarrow R^1R^2C{=}C(CN)OCOR^3 \quad (3)$$

$$R^1R^2CHCOCN + R^4\text{–}NCO \longrightarrow R^1R^2C{=}C(CN)OCONHR^4 \quad (4)$$

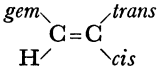
Results and Discussion

Both acyl cyanides and acid anhydrides are known as acylating reagents and they stay unchanged when mixed. However, a catalytic amount of tertiary amines, usually pyridine derivatives, induced a condensation reaction between these two reagents affording the corresponding 1-cyano-1-alkenyl esters in good yields.

Reaction of Acetyl Cyanide with Acid Anhydrides. When a mixture of acetyl cyanide and an acid anhydride was treated with a catalytic amount of pyridine in tetrahydrofuran at ambient temperature, the corresponding 1-cyanovinyl carboxylate (**1**—**3**) was obtained. The results are tabulated in Table 1. All the product esters showed ν(C≡N) at 2210 cm^{-1} about 50 cm^{-1} lower than that of saturated nitriles, and the terminal methylene protons in NMR around δ 5.7 (J=3 Hz), thus demonstrating the product structures to be the expected ones.

Reaction of Propionyl Cyanide with Acid Anhydrides. As shown in Table 1, the product esters 1-cyano-1-propenyl carboxylates (**5**—**8**) consisted of two geometrical isomers (*Z*- and *E*-isomer). Their NMR assignment was carried out as follows.

First, we noticed that the major isomer shows higher chemical shifts of the terminal methylene protons than the minor one in any isomeric couple. If the Pascual's equation[8] which was proposed for the substituent effects in determining the chemical shifts of olefinic protons is applicable in our cases (Eq. 6), then the calculated chemical



$$\delta(H) = 5.28 + \sigma(gem) + \sigma(cis) + \sigma(trans) \quad (6)$$

shifts δ(H) are 5.90 for *E*-isomer and 5.83 for *Z*-isomer, thus indicating the major isomer should have a *Z*-configuration. Second, the greater deshielding effect of an acetoxyl group than a cyano group on a vicinal *cis* proton in β-substituted styrenes[9] also suggests that

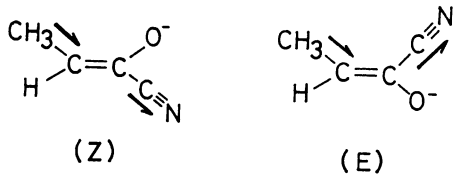
Table 1. Reaction of acyl cyanides with acid anhydrides

$$R^1R^2CH\text{-}CO\text{-}CN + (R^3CO)_2O \xrightarrow{\text{pyridine}} R^1R^2C{=}C(CN)OCOR^3$$

Compd	R^1	R^2	R^3	Solvent	Time h	Yield[b] %	Isomer ratio (Z/E)	PMR chemical shifts/ppm: $\Delta\delta$ between R^1 and R^2	PMR chemical shifts/ppm: $\Delta\delta$ ($\delta_Z-\delta_E$) of Olefin H	PMR chemical shifts/ppm: $\Delta\delta$ ($\delta_Z-\delta_E$) of Allylic Me
1	H	H	CH_3	THF	20	39		0.078		
2	H	H	C_2H_5	THF	24	44		0.080		
3	H	H	C_3H_7	THF	24	37		0.083		
4[c]	H	H	CH_3	THF	23	—[d]				
5	CH_3	H	CH_3	THF	24	65	77/23		−0.03	0.23
6	CH_3	H	C_2H_5	THF	24	80	80/20		−0.03	0.18
7	CH_3	H	iso-C_3H_7	THF	48	75	76/24		−0.03	0.20
8	CH_3	H	C_6H_5	THF	48	43[e]	69/31		−0.06	0.23
9	CH_3	CH_3	CH_3	DME	26	66		0.25		
10	CH_3	CH_3	C_2H_5	DME	22	40		0.26		
11	CH_3	CH_3	C_3H_7	DME	22	39		0.28		
12	CH_3	CH_3	C_6H_5	DME	48	61[f]		0.26		

a) Temperature 25 °C. Reactant ratios were 1:1:0.03 (cyanide/anhydride/pyridine). b) Isolated yields. c) 1.0 mol equiv of pyridine was added. d) 1,1-Dicyanoethyl acetate (**4**) was formed (76%). e) Determined by VPC, **6** was also formed (9%). f) Determined by VPC, 1-cyano-2-methyl-1-propenyl isobutyrate (**13**) was also formed (19%).

the olefinic proton of the *Z*-isomer should appear at higher field than the *E*-isomer. Third, on geometrical analysis of the shielding effect of the cyano group on the chemical shifts of allylic methyl group, it became evident that the methyl protons of the *E*-isomer should appear at a higher field than the *Z*-isomer, and this agreed with the observed results (see Table 1). Therefore, we concluded that the major isomers are (*Z*)-1-cyano-1-propenyl carboxylates. The demonstrated *Z*-configuration of the major product suggested us that this configuration is stabilized by a dipolar interaction rather than by steric factors in the structure determining step.



(Z) (E)

Reaction of Isobutyryl Cyanide with Acid Anhydrides. In the NMR spectra of the products, the differences in chemical shifts between the two allylic methyl groups ($\Delta\delta$) are analogous to those between *E* and *Z* isomers in the case of 1-cyano-1-propenyl esters (Table 1). The reaction with benzoic anhydride produced 1-cyano-2-methyl-1-propenyl isobutyrate (**13**) as a by-product. (Analogous side reaction was also observed in the reaction of propionyl cyanide with the same anhydride). Despite of the fact that isobutyryl cyanide undergoes dimer formation followed by the elimination of hydrogen cyanide to afford this ester, another reaction channel *via* acyl exchange between cyanide and benzoic anhydride seems also plausible (Eq. 7).

$$(CH_3)_2CHCOCN + (PhCO)_2O \rightleftharpoons (CH_3)_2CHCOOCOPh + PhCOCN \quad (7)$$

Tertiary Amine Catalysts. The presence of tertiary amine catalysts is essential in the present synthesis of cyanoalkenyl esters. Among several tertiary amines examined, pyridine derivatives with moderate basicity were found to be suitable for this purpose, *e.g.*, 4-(dimethylamino)pyridine, pyridine, lutidines, and picolines. Such strong bases as triethylamine and 1,7-diazabicyclo[4.3.0]non-6-ene were inadequate because they induced considerable degradation of the product esters. Solid-phase catalysts such as basic alumina and Amberlite IRA-400 were inactive in this reaction. Calcined anhydrous Hydrotalcite,[10] however,catalyzed the reaction to give the expected ester **5** (17%) in the reaction of propionyl cyanide with acetic anhydride besides 1,1-dicyanopropyl acetate **15** (22%) and 1,1-dicyanopropyl propionate **16** (13%) as by-products.

Reaction of Acyl Cyanides with Isocyanates. The above-mentioned reactions of acyl cyanides seemed to signify that acyl cyanide reacted in its enol (or enolate) form with acid anhydride. This prompted us to examine the reaction of acyl cyanides with isocyanates where the latter reacted as carbamoylating reagents to the former

Table 2. Reaction of acyl cyanides with isocyanates[a]

$$R^1R^2CH\text{-}COCN + R^3NCO \xrightarrow{\text{pyridine}} R^1R^2C{=}C(CN)OCONHR^3$$

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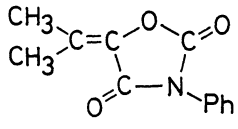
Compd	R^1	R^2	R^3	Solvent	Time h	Yield[a] %
17	CH_3	CH_3	C_6H_5	C_6H_6	20	62
18	CH_3	CH_3	C_2H_5	THF	20	25
19	CH_3	H	C_6H_5	THF	24	53[c]

a) Cyanide/isocyanate/pyridine=1:1:0.25 mole ratio. b) Isolated yields. c) Determined by NMR, not isolated. Isomer ratio *Z*/*E*=7/3.

giving rise to the formation of 1-cyano-1-alkenyl carbamates. Results are shown in Table 2. None of *C*-acylated products anticipated from the result of the reaction of carbamoyl cyanides with isocyanates[11] was detected in the reaction mixture. The rate of carbamate formation was relatively slow in this reaction that the formation of the acyl cyanide dimer became unnegligible, especially in the reactions with aliphatic isocyanate.

As part of structure-determining experiments of the carbamates, the hydrogenation of 1-cyano-2-methyl-1-propenyl phenylcarbamate (**17**) over Pd/carbon catalyst was carried out in acetic acid. The carbamate slowly absorbed one mole of hydrogen to give not the expected acyclic carbamate but a cyclic iminourethane, *i.e.*, 3-phenyl-4-imino-5-isopropyl-1,3-oxazolidin-2-one (**21**). Analogous five-membered heterocyclic compound was obtained when carbamate **17** was hydrolyzed in aqueous sulfuric acid and its structure was attributed to 3-phenyl-5-isopropylidene-1,3-oxazolidine-2,4-dione (**20**).



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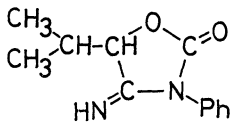

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Experimental

General. The NMR spectra were measured by Varian T-60A spectrometer in CCl_4 solutions unless otherwise stated and the chemical shifts are given in δ-units. The IR and MS spectra were taken on JASCO IRA-1 and Hitachi RMU-6L spectrometer respectively. Acyl cyanides were prepared from the corresponding carboxylic acids *via* the reaction of acyl bromides with copper(I) cyanide.[6a]

Reaction of Acyl Cyanides with Acid Anhydrides. A General Procedure: The mixture of an acyl cyanide (0.02 mol) and an acid anhydride (0.02 mol) dissolved in 10 ml of solvent (1,2-dimethoxyethane or tetrahydrofuran) was cooled at 0 °C, to which a solution of pyridine (0.001 mol) which was dissolved in 10 ml of the same solvent was added. The reaction mixture then was stirred at 25 °C for a certain period. After removing solvents, the residue was distilled in vacuum to give the corresponding 1-cyano-1-alkenyl carboxylate. For the product yields and reaction conditions, see Table 1. The spectroscopic data are as follows.

1-Cyanovinyl Acetate (1): Bp 48—52 °C/9 Torr. IR (liquid) 2220 and 1765 cm^{-1}. NMR 5.74 (2H, a pair of d, J=2.8 Hz), 2.27 (3H, s).

1-Cyanovinyl Propionate (2): Bp 34—38 °C/0.5 Torr. IR (liquid) 2240 and 1770 cm^{-1}. NMR 5.77 (2H, a pair of d, J=3 Hz), 2.54 (2H, q, J=7.3), 1.24 (3H, t, J=7.3).

1-Cyanovinyl Butyrate (3): Bp 55—58 °C/3 Torr. NMR 5.64 (2H, d, J=2.8 Hz), 2.40 (2H, t, J=6.8), 1.70 (2H, sext, J=7.2 and 6.8), 0.99 (3H, t, J=7.2).

1-Cyano-1-propenyl Acetate (5): Bp 95—98 °C/37 Torr. IR (liquid) 2220 and 1765 cm^{-1}. NMR: (*Z*)-isomer 6.15 (1H, q, J=7.3 Hz), 2.20 (3H, s), 1.75 (3H, d, J=7.3); (*E*)-isomer 6.18 (1H, q, J=7.3), 2.15 (3H, s), 1.98 (3H, d, J=7.3). *Z*/*E*=77/23.

1-Cyano-1-propenyl Propionate (6): Bp 108—110 °C/29 Torr. IR (liquid) 2220 and 1765 cm^{-1}. NMR: (*Z*)-isomer 6.25 (1H, q, J=7.2), 2.54 (2H, q, J=7.6), 1.75 (3H, d, J=7.2), 1.18 (3H, t, J=7.6); (*E*)-isomer 6.28 (1H, q, J=7.4), 2.55 (2H, q, J=7.6), 1.93 (3H, d, J=7.4), 1.15 (3H, t, J=7.6). *Z*/*E*=8/2.

1-Cyano-1-propenyl Isobutyrate (7): Bp 115 °C/26 Torr. IR (liquid) 2220 and 1760 cm^{-1}. NMR: (*Z*)-isomer 6.23 (1H, q, J=7.2), 2.75 (1H, hept. J=7.2), 1.73 (3H, d, J=7.2), 1.24 (6H, d, J=7.2); (*E*)-isomer 6.26 (1H, q, J=7.5), 2.78 (1H, hept. J=7.2), 1.93 (3H, d, J=7.5), 1.20 (6H, d, J=7.2). *Z*/*E*=76/24.

1-Cyano-1-propenyl Benzoate (8): Separated by VPC. IR (liquid) 2220 and 1730 cm^{-1}. NMR: (*Z*)-isomer 8.2—7.95 (3H, m), 7.7—7.3 (2H, m), 6.22 (1H, q, J=7.2), 1.80 (3H, d, J=7.2); (*E*)-isomer 6.28 (1H, q, J=7.4), 2.03 (3H, d, J=7.4). *Z*/*E*=69/31.

1-Cyano-2-methyl-1-propenyl Acetate (9): Bp 90 °C/25 Torr. IR (liquid) 2210 and 1760 cm^{-1}. NMR 2.17 (3H, s), 2.02 (3H, s), 1.77 (3H, s).

1-Cyano-2-methyl-1-propenyl Propionate (10): Bp 125 °C/60 Torr. IR (liquid) 2220 and 1765 cm^{-1}. NMR 2.47 (2H, q, J=7.5), 2.04 (3H, s), 1.77 (3H, s), 1.20 (3H, t, J=7.5).

1-Cyano-2-methyl-1-propenyl Butyrate (11): Bp 125—130 °C/45 Torr. IR (liquid) 2200 and 1760 cm^{-1}. NMR 2.43 (2H, t, J=6.5), 1.70 (2H, sext. J=6.5 and 7.0), 1.00 (3H, t, J=7.0), 2.06 (3H, s), 1.77 (3H, s).

1-Cyano-2-methyl-1-propenyl Benzoate (12): Separated by VPC. IR (liquid) 2230 and 1750 cm^{-1}. 8.07 (2H, m), 7.6 (3H, m), 2.09 (3H, s), 1.83 (3H, s).

Reaction of Isobutyric Anhydride with KCN in the Presence of 18-Crown-6. A mixture of isobutyric anhydride (7.1 g, 0.04 mol), KCN (1.5 g, 0.02 mol), and 18-crown-6 (0.5 g, 2 mmol) in 30 ml of dimethoxyethane was stirred at 25 °C for 7 h. The mixture was poured into 60 ml of petroleum ether, filtered, and the filtrate was evaporated followed by fractional distillation to give 1-cyano-2-methyl-1-propenyl isobutyrate (**13**) 2.35 g (52%), bp 110—115 °C/20 Torr. IR (liquid) 2210 and 1760 cm^{-1}. NMR 2.60 (1H, hept, J=7.2), 2.01 (3H, bs), 1.75 (3H, bs), 1.25 (6H, d, J=7.2).

Reaction of Propionyl Cyanide with Acetic Anhydride in the Presence of Calcined Hydrotalcite. Propionyl cyanide (2.49 g, 0.03 mol) and acetic anhydride (3.09 g, 0.03 mol) were mixed in 20 ml of THF, to which was added 3.0 g of Hydrotalcite (calcined at 470 °C for 2 h under vacuum) under N_2-atmosphere. The reaction mixture was stirred at ambient temperature for 23 h, filtered, and the solvent was removed. The residue contained three products which were separated preparatively by VPC; 1-cyano-1-propenyl acetate (**5**) 17%, *Z*/*E*=7/3; 1,1-dicyanopropyl acetate (**15**) 22%, NMR 1.32 (3H, t, J=7.2), 2.25 (3H, s), 2.35 (2H, q, J=7.2), IR (nujol) 2260 and 1770 cm^{-1}; 1,1-dicyanopropyl propionate (**16**) 13%, NMR 1.27 (3H, t, J=7), 1.33 (3H, t, J=7), 2.17—2.77 (4H, a mixture of two q).

Reaction of Acyl Cyanide with Isocyanate. A mixture of phenyl isocyanate (6.1 g, 0.05 mol), isobutyryl cyanide (5.0 g, 0.05 mol) and pyridine (1.0 g) in 50 ml of dry benzene was warmed at 33 °C for 20 h. After removing solvent, the residue was washed with petroleum ether and the obtained solid (7.6 g) was then chromatographed (silica gel, chloroform) to give 1-cyano-2-methyl-1-propenyl phenylcarbamate (**17**) 6.9 g (62 %), mp 129 °C (benzene). NMR ($CDCl_3$) 1.83 (3H, s), 2.06 (3H, s), 6.95 (1H, bs), 7.1—7.4 (5H, m). IR (Nujol) 3300, 2240, 1740, and 1550 cm^{-1}. MS (*m*/*e*) 216 (M^+). Found: C, 66.90; H, 5.79; N, 12.70%. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96%.

1-Cyano-2-methyl-1-propenyl ethylcarbamate (18): Yield 25%, mp 53.5—54 °C, recrystallized from cyclohexane/benzene= 10/2. NMR ($CDCl_3$) 1.20 (3H, t, J=7.5), 1.81 (3H, s), 2.05

(3H, s), 3.23 (2H, quintet, J=7.5 and 6), 5.97 (1H, bt, J=6). MS (*m/e*) 168 (M^+). Found: C, 57.53; H, 7.29; N, 16.43%. Calcd for $C_8H_{12}N_2O_2$: C, 57.23; H, 7.19; N, 16.66%.

*1-Cyano-1-propenyl phenylcarbamate (**19**)*: Yield 53% (by NMR), not isolated. NMR (*Z*)-isomer 7.30 (5H, m), 5.76 (1H, q, J=7.5), 1.78 (3H, d, J=7.5). (*E*)-isomer 7.30 (5H, m), 6.15 (1H, q, J=7.2), 1.72 (3H, d, J=7.2). Z/E=7/3.

*Hydrolysis of **17** in 25% Sulfuric Acid*: The mixture of **17** (0.945 g, 4.4 mmol, in 5 ml of dioxane) and 5 ml of 50% H_2SO_4 was heated at 100 °C for 17 h. After cooling the solution, water (50 ml) was added to separate colorless solids, which was filtered, dried, and chromatographed (silica gel, chloroform). The fraction eluting faster than the unreacted **17** was collected and recrystallized from cyclohexane to give 3-phenyl-5-isopropylidene-1,3-oxazolidine-2,4-dione **20**, 95 mg (10%), mp 93—94 °C. NMR ($CDCl_3$) 2.03 (3H, s), 2.27 (3H, s), 7.43 (5H, m). IR (Nujol) 1800, 1720, and 1185 cm^{-1}. MS (*m/e*) 217 (M^+). Found: C, 66.51; H, 5.14; N, 6.42%. Calcd for $C_{12}H_{11}O_3N$: C, 66.36; H, 5.07; N, 6.45%.

*Hydrogenation of **17***: A solution of **17** (1 mmol) dissolved in a mixture of acetic acid and methanol (5 ml+30 ml) absorbed *ca.* 25 ml of H_2 (1 mmol) over 5% Pd–carbon (100 mg) during 10 days. Evaporation of solvents separated a half-solidified material, which was then washed with CCl_4 and the residue was chromatographed (silica gel, chloroform) to give colorless solids of 3-phenyl-4-imino-5-isopropyl-1,3-oxazolidin-2-one (**21**), 175 mg (80%), mp 219—220 °C. MS (*m/e*) 218 (M^+). NMR (acetone-d_6) 0.80 (3H, d, J=7 Hz), 1.15 (3H, d, J=7), 2.48 (1H, m, probably a pair of splitted heptets, J=2.2 and 7), 5.02 (1H, d, J=2.2), 7.2—7.55 (3H, m), 7.7—7.9 (2H, m). IR (Nujol) 3250, 3070, 1740, 1625, and 1560 cm^{-1}. Found: C, 65.80; H, 6.41; N, 12.68%. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.83%.

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