

Acyl Cyanide. VI. The Synthesis of 1-Cyano-1-alkenyl Esters by the Reaction of Acyl Cyanides with Acid Chlorides. Synthesis and Mechanism

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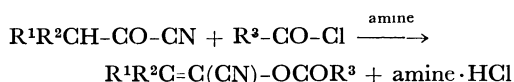
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The reactions of enolizable acyl cyanides (acetyl, propionyl, isobutyryl, and diphenylacetyl cyanide) with acid chlorides (acetyl, propionyl, benzoyl, *p*-nitrobenzoyl, diphenylcarbamoyl, and dimethylcarbamoyl chloride) in the presence of tertiary amines gave the corresponding 1-cyano-1-alkenyl carboxylates or carbamates in good yields. Among several solvents and amines examined in the reaction of acetyl cyanide with propionyl chloride, benzene and pyridine seem to be most appropriate. The maximum yield (98%) of the ester was attained in benzene when both the chloride and pyridine were used in excess amounts (1.2—1.4 times the amount of the cyanide). The rate of reaction depended little on the concentration of the chloride but on both the cyanide and the amine being of first order in each reactant; it was also influenced by the basicity of tertiary amines and, in the case of weak bases, additionally by their nucleophilic power.

In the preceding paper,¹⁾ we reported that 1-cyano-1-alkenyl esters can be easily synthesized by simply mixing acid anhydrides with primary or secondary acyl cyanides under the influence of amine catalysts. In the present study, we have extended the choice of acylating reagent from acid anhydride to acyl chloride including not only carboxylic acid chlorides but also carbamoyl chlorides, and have carried out their reactions with potentially enolizable acyl cyanides in the presence of stoichiometric amount of tertiary amines. In this report, solvent effects, base catalysis, and reaction mechanisms are discussed together with the synthesis.

Results and Discussion

The results of the reactions between four enolizable acyl cyanides and nine acid chlorides are listed in Table 1. Tertiary amines were adopted as the base, tetrahydrofuran (THF) and dichloromethane were used as solvents. The yields listed in this table are based upon the products isolated by fractional distillation and are not necessarily the best ones (as for improving product yields, see the following sections).



Although a stoichiometric amount of amine is required in this reaction in contrast to its catalytic amount in the reaction with acid anhydrides,¹⁾ the product esters were obtained in relatively high yields and in pure states not contaminated by such by-products as the dimer of acyl cyanide.

Solvents. In order to increase the reaction rates and also the product yields in this synthesis, the choice of appropriate solvents is important. As a model reaction, the reaction of acetyl cyanide with propionyl chloride in the presence of pyridine was chosen and the effect of solvents (acetonitrile, dichloromethane, benzene, and THF) were examined by plotting the product yields against reaction time (see Fig. 1). With this figure it becomes evident that the solvent effect on the rate of reaction is in the following order $\text{CH}_3\text{CN} \approx \text{CH}_2\text{Cl}_2 > \text{C}_6\text{H}_6 > \text{THF}$.²⁾ On the other hand, the yield was the highest in benzene (80%

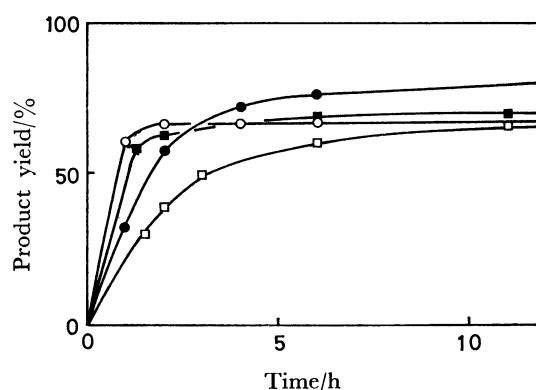


Fig. 1. The effect of solvent on the formation of 1-cyanovinyl propionate.^{a)}

CH_3CN (■), CH_2Cl_2 (○), C_6H_6 (●), THF (□).

a) Reactant ratio: cyanide/chloride/pyridine = 1/1/1, 0.02 mol/18 ml for each reagent, at 25 °C. Product yields were determined by VPC using the method of calibration curves.

when the reactant ratio was cyanide/chloride/amine = 1/1/1) but in CH_3CN or CH_2Cl_2 the yield hit a ceiling at ca. 60%, possibly due to the faster consumption of the chloride³⁾ than of the cyanide. Therefore, benzene seems to be most useful among the four solvents examined.

Reactant Ratios. At the last stage of average reactions where the initially charged reactant ratios were $[\text{cyanide}]/[\text{chloride}]/[\text{amine}] = 1/1/1$ as in the cases of the reactions of Table 1, usually the chloride was completely consumed while some amount of the cyanide remained unreacted. This implied that some side reactions were taking place competingly to consume the chloride.³⁾ Thus we thought that the increase in the initial amount of chloride relative to that of the cyanide would improve the yield. We inspected this effect in the reaction of acetyl cyanide with propionyl chloride in the presence of pyridine, and the results are shown in Table 2. This table clearly indicates that acetyl cyanide can be converted into 1-cyanovinyl propionate almost quantitatively when an excess amount of the chloride and amine (both 1.2—1.4 times more than the cyanide) are used. Proved also is the necessity of an equivalent amount of amine to that of chloride

TABLE 1. PREPARATION OF 1-CYANO-1-ALKENYL CARBOXYLATES BY THE REACTION OF ACYL CYANIDES WITH ACYL CHLORIDES
 $R^1R^2C=C(CN)OCOR^3$

Compd	R ¹	R ²	R ³	Amine ^{d)}	Solvent	Time/h	Yield/% ^{b)}
1	H	H	CH ₃	Pyr	CH ₂ Cl ₂	24	65
2	H	H	CH ₂ Cl	DMA	CH ₂ Cl ₂	21	76
3	H	H	C ₂ H ₅	Pyr	CH ₂ Cl ₂	24	56
4	H	H	OC ₂ H ₅	Pyr	CH ₂ Cl ₂	20	36
5	H	H	C ₆ H ₅	Pyr	CH ₂ Cl ₂	25	68
6	H	H	<i>p</i> -NO ₂ -C ₆ H ₄	Pyr	THF	24	49
7	H	H	N(CH ₃) ₂	Pyr	THF	24	c)
8	H	H	N(C ₆ H ₅) ₂	Pyr	THF	24	c)
9	CH ₃	H	CH ₃	Pyr	CH ₂ Cl ₂	24	70
	CH ₃	H	CH ₃	Dabco	CH ₂ Cl ₂	2	75
	CH ₃	H	CH ₃	DBU	CH ₂ Cl ₂	2	61
10	CH ₃	H	CH ₂ Cl	DMA	CH ₂ Cl ₂	28	77
11	CH ₃	H	OC ₂ H ₅	Pyr	CH ₂ Cl ₂	21	50
12	CH ₃	H	<i>p</i> -NO ₂ -C ₆ H ₄	Pyr	THF	24	60
13	CH ₃	H	N(CH ₃) ₂	Pyr	THF	24	33
14	CH ₃	H	N(C ₆ H ₅) ₂	Pyr	THF	24	25
15	CH ₃	CH ₃	CH ₃	Pyr	THF	21	78
16	CH ₃	CH ₃	<i>p</i> -NO ₂ -C ₆ H ₄	Pyr	THF	24	68
17	CH ₃	CH ₃	N(CH ₃) ₂	Pyr	THF	24	33
18	CH ₃	CH ₃	N(C ₆ H ₅) ₂	Pyr	THF	24	50
19	C ₆ H ₅	C ₆ H ₅	CH(C ₆ H ₅) ₂	Crown ^{e)}	DME	20	48

a) Reactant molar ratio: cyanide/chloride/amine = 1.0/1.0/1.0. b) Isolated yields after distillation or column chromatography. c) Only a trace amount of the corresponding cyanoalkenyl carbamate was formed whereas the major product was the dimer of the cyanide. d) Pyr = pyridine, DMA = *N,N*-dimethylaniline, Dabco = 1,4-diazabicyclo[2.2.2]octane, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, Crown = dicyclohexyl-18-crown-6. e) This ester was prepared directly by the reaction of diphenylacetyl chloride with potassium cyanide in the presence of crown ether catalyst.

 TABLE 2. THE INFLUENCE OF REACTANT RATIOS ON THE ESTER FORMATION^{a)}

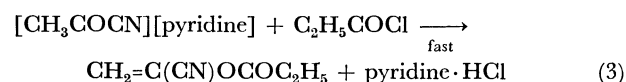
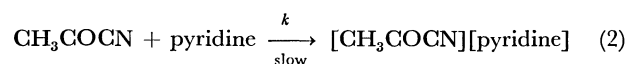
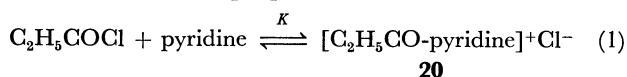
Run	Relative reactant ratio			Yield of ester ^{b)} %/Time (h)
	CH ₃ COCN	C ₂ H ₅ COCl	C ₆ H ₅ N	
1	1.0	1.0	1.0	80/10
2	1.0	1.4	1.0	81/10
3	1.0	1.4	1.4	96/10, 98/26
4	1.0	1.6	1.4	90/10, 97/24

a) In dry benzene at 25 °C. Standard reactant concentration for the cyanide was 0.02 mol in 16 ml of benzene. b) Determined by VPC analysis, calibrating with authentic compounds.

in this improved method.

Reaction Rate. In Table 3 are shown the effects of reactant ratios on the initial rates of reaction. Evidently, the rates seem to be dependent on the concentration of both the cyanide and the amine, being of first order in the concentration of each of these reactants, and hardly dependent on the concentration of the chloride.

Based on the above observations and subsidiarily on the fact that the chloride reacts rapidly with the amine to form a pyridinium salt **20**,^{4,5)} the following reaction channel is proposed.



Equation 1 means a rapidly established equilibrium prior to the condensation reaction. In Eq. 2 an intermediate (or a transition state) **21** consisting of the cyanide and pyridine is formed, whose structure will be discussed in the following section.

According to this mechanism, the initial rate of reaction R_0 is calculated and expressed by

$$R_0 = \frac{k}{2K} A_0 [- \{ 1 + K(E_0 - P_0) \} + \sqrt{ \{ 1 + K(E_0 - P_0) \}^2 + 4KP_0 }] \quad (4)$$

where E_0 , P_0 , A_0 are the initial concentration of the chloride, pyridine, and cyanide respectively. By substituting the observed values of Runs 1 and 4 in Table 3 for Eq. 4, $k = 3.06 \times 10^{-2}$ L/mol·s and $K = 0.10$ were obtained. With these two constants we calculated the initial rates $R_0(\text{calcd})$ which agreed well with the observed $R_0(\text{obsd})$, thus the reaction channel proposed above seems to be compatible with the experimental results.

Base Catalysis. In this reaction it must be noticed that the rate of reaction depends markedly upon the choice of amine catalysts. To find a general

TABLE 3. EFFECT OF THE MOLAR RATIOS OF REACTANTS ON THE INITIAL RATES OF REACTION R_0

Run	Reactant molar ratio			$R_0(\text{obsd})$ $\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$	Rel. rate	$R_0(\text{calcd})$
	Cyanide	Chloride	Pyridine			
1	0.396	0.396	0.396	4.7×10^{-3}	1.0	4.6×10^{-3}
2	0.770	0.385	0.385	8.2×10^{-3}	1.7	8.7×10^{-3}
3	0.382	0.764	0.382	4.5×10^{-3}	0.95	4.2×10^{-3}
4	0.384	0.384	0.762	8.5×10^{-3}	1.8	8.6×10^{-3}
5	0.371	0.742	0.742	9.3×10^{-3}	1.95	7.9×10^{-3}

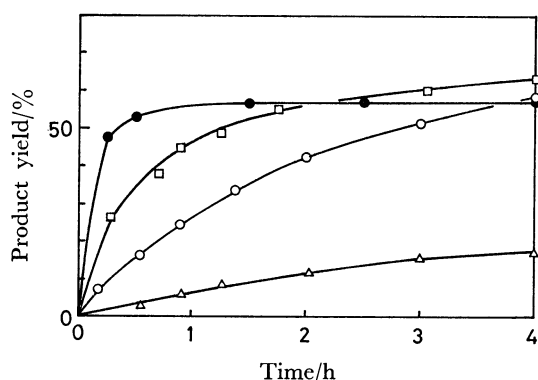


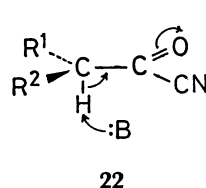
Fig. 2. The effect of tertiary amines on the rates of formation of 1-cyanovinyl propionate in benzene.^{a)} 2-Picoline (Δ), pyridine ($\circ$), 2,6-lutidine ($\square$), 1,4-diazabicyclo[2.2.2]octane ($\bullet$).
a) Reactant ratio: cyanide/chloride/amine = 1/1/1, 0.02 mol/18 mL for each reagent, at $25 \pm 0.5^\circ \text{C}$. Product yields were determined by VPC using the method of calibration curves.

rule in this catalysis along the line of solving the reaction mechanism, the influence of five tertiary amines, *i.e.*, 1,4-diazabicyclo[2.2.2]octane (Dabco), 4-(dimethylamino)pyridine, 2,6-lutidine, 2-picoline, and pyridine, upon the reaction rate were examined by means of direct measurements by NMR and also by VPC analysis using the internal reference technique. The tendencies of the base catalysis obtained in triplicate experiments were reproducible and the same in both methods. Results are shown in Fig. 2. Amines with strong basicity (and possibly with strong nucleophilicity), *e.g.*, Dabco (pK_a 8.7) and 4-(dimethylamino)pyridine (pK_a 9.71),⁶⁾ showed the greatest rate-enhancement whereas the product yields were relatively low, probably due to some side reactions such as polymerization of the ester. In contrast, the best yield was attained when pyridine, a weaker base than the others, was adopted.

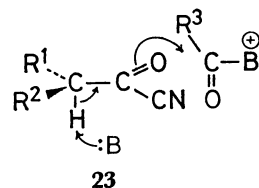
Looking at Figure 3, one notices that the effect of methyl-substituted pyridines on the rate acceleration is in the order of 2,6-lutidine (pK_a 6.75) > pyridine (5.27) > 2-picoline (5.97),⁶⁾ which is not in accord with the order of basicity nor nucleophilic power. Therefore, the rate is not solely dependent on either character of amines but seems to be controlled by both of them.

As a rational structure of the transition state which is compatible not only with the behavior of bases but also with the rate Eq. 4, a base-catalysis model **22** is

postulated where the proton-abstraction composes the rate-determining step. According to Eq. 1 the concentration of free amine must depend upon its nucleophilic power which, in the reaction of methyl-substituted pyridines toward acyl chloride, seems to be in the order of 2-picoline (steric factor is conformationally negligible with regard to its pyridinium structure) > pyridine > 2,6-lutidine. Therefore, the equilibrium constant K must be small for 2,6-lutidine, and large enough for 2-picoline to cancel out its higher basicity than pyridine's. As for strong bases above $pK_a \approx 8$, the nucleophilicity may not change so much as the pK_a does that the basicity plays an important role in the transition state.



22



23

Scheme 1.

As an alternative transition state, a push-pull model **23** seems to be proposable where the ionic character of the N-CO bond in pyridinium ion plays a part of the rate acceleration. In this, 2,6-lutidine acts as a strong base and simultaneously as a weak nucleophile that enhances the ionization of the N-CO bond, whereas 2-picoline acts in the opposite way. The nucleophilicity of pyridine, though being a weaker base than picoline, may lie in between the other two amines as explained above. Although, at a glance, the rate seems to be dependent on the concentration of the chloride in this sort of general acid-base catalysis, the possibility of rate acceleration by the increase in acyl chloride must be cancelled out by the decrease in free amine concentration at the other reacting terminus. Therefore, the rate may become almost insensitive to the change in the chloride concentration.

Experimental

General. NMR chemical shifts and coupling constants are expressed by δ and Hz unit respectively. Acyl cyanides (acetyl, propionyl, isobutyryl, and diphenylacetyl cyanide) were prepared according to the reported method.¹⁾ Other reagents were commercially available.

Reaction of Acyl Cyanide with Acyl Chloride; A General Synthetic Procedure. Under ice-cooling, tertiary amine (0.04 mol) dissolved in 10 mL of a solvent was added to a mixture of an acyl cyanide (0.04 mol) and an acyl chloride (0.04 mol)

both dissolved in 10 mL of the same solvent. Immediate formation of the pyridinium salt was observed. After stirring the mixture at ambient temperature for several hours, the solution was filtered, the filtrate was washed with water three times and dried over anhyd MgSO_4 . Fractional distillation of the solution gave the expected 1-cyano-1-alkenyl ester. The product yields and amines used are listed in Table 1. In the following paragraphs, the spectroscopic data of some 1-cyano-1-alkenyl esters are listed. For the other esters, see the preceding report.¹⁾

1-Cyanovinyl Chloroacetate (2): Bp 70–75 °C/4 Torr. IR 2240, 1780 cm^{-1} . NMR (CDCl_3) 5.93 (2H, a pair of d, $J=3.2$), 4.27 (2H, s).

1-Cyanovinyl Ethyl Carbonate (4): Bp 46–50 °C/3 Torr. IR 2230, 1765 cm^{-1} . NMR (CDCl_3) 5.70 (2H, a pair of d, $J=3.0$), 4.25 (2H, q, $J=7.3$), 1.40 (3H, t, $J=7.3$).

1-Cyanovinyl p-Nitrobenzoate (6): Mp 132–135 °C. IR 1760 cm^{-1} . NMR (CDCl_3) 8.47 (4H, m), 6.03 (2H, a pair of d, $J=3.5$).

1-Cyanovinyl Benzoate (5): Mp 35.5–38 °C. Bp 88–95 °C/0.4 Torr. IR 2220, 1740 cm^{-1} . NMR (CDCl_3) 8.2–7.3 (5H, m), 5.87 (2H, a pair of d, $J=2.5$).

1-Cyano-1-propenyl Chloroacetate (10): Bp 75–84 °C/3 Torr. IR 2220, 1780 cm^{-1} . NMR (CDCl_3) Z-isomer 6.30 (1H, q, $J=7.3$), 4.27 (2H, s), 1.80 (3H, d, $J=7.3$); E-isomer 6.35 (1H, q, $J=7.4$), 4.23 (2H, s), 2.00 (3H, d, $J=7.4$). Z/E=5.

1-Cyano-1-propenyl Ethyl Carbonate (11): Bp 67–69 °C/5 Torr. NMR (CDCl_3) Z-isomer 6.20 (1H, q, $J=7.1$), 4.35 (2H, q, $J=7.0$), 1.85 (3H, d, $J=7.1$), 1.40 (3H, t, $J=7.0$); E-isomer 6.85 (1H, q, $J=7.1$), 4.32 (2H, q, $J=7.0$), 1.97 (3H, d, $J=7.1$), 1.37 (3H, t, $J=7.0$). Z/E=7.0.

1-Cyano-1-propenyl p-Nitrobenzoate (12): Mp 153–154 °C (Z-isomer). IR 2220, 1780 cm^{-1} . NMR (CDCl_3) Z-isomer 8.35 (4H, s), 6.38 (1H, q, $J=7.3$), 1.87 (3H, d, $J=7.3$); E-isomer 8.32 (4H, s), 6.47 (1H, q, $J=7.3$), 2.09 (3H, d, $J=7.3$). Z/E=6.7.

1-Cyano-1-propenyl Dimethylcarbamate (13): Bp 75–78 °C/0.6 Torr. IR 2230, 1725 cm^{-1} . NMR (CCl_4) Z-isomer 1.77 (3H, d, $J=7.1$), 3.01 (6H, bs), 6.08 (1H, q, $J=7.1$); E-isomer 1.99 (3H, d, $J=7.4$), 2.98 (6H, bs), 6.11 (1H, q, $J=7.4$). Z/E=2.4. 1,1-Dicyanopropyl dimethylcarbamate was also formed (8%), NMR (CCl_4) 1.30 (3H, t, $J=7.2$), 2.35 (2H, q, $J=7.2$), 3.00 (6H, bs), MS (m/e) 181 (M^+).

1-Cyano-1-propenyl Diphenylcarbamate (14): Mp 213–216 °C. IR 2220, 1720 cm^{-1} . NMR (CCl_4) Z-isomer 7.25 (10H, s), 5.92 (1H, q, $J=7.1$), 1.60 (3H, d, $J=7.1$); E-isomer 7.25 (10H, s), 6.04 (1H, q, $J=7.1$), 1.80 (3H, d, $J=7.1$). Z/E=2.8.

1-Cyano-2-methyl-1-propenyl Dimethylcarbamate (17): IR 2220, 1720 cm^{-1} . NMR (CDCl_3) 1.83 (3H, s), 2.05 (3H, s), 3.01 (6H, bs).

1-Cyano-2-methyl-1-propenyl Diphenylcarbamate (18): Mp 110–112 °C. IR 2230, 1730 cm^{-1} . NMR (CDCl_3) 7.27 (10H, s), 1.98 (3H, s), 1.73 (3H, s).

1-Cyano-2,2-diphenylvinyl Diphenylacetate (19): Mp 126–126.5 °C. IR 2220, 1773 cm^{-1} . NMR (CDCl_3) 5.03 (1H, s), 7.1–7.4 (10H, m). Found: C, 84.03; H, 4.79; N, 3.17%. Calcd for $\text{C}_{28}\text{H}_{21}\text{NO}_2$: C, 83.83; H, 5.09; N, 3.37%.

Examination of Solvents. To a mixture of purified acetyl cyanide and propionyl chloride (0.02 mol each) in 10 mL of purified solvent (acetonitrile, THF, CH_2Cl_2 , or benzene) was added the solution of pyridine (0.02 mol) dissolved in the same solvent (8 mL), and successively isobutyl isobutyrate (0.02 mol, as the internal standard for VPC analysis). The reaction mixture was kept at 25 or 0 °C and an aliquot of the mixture was sucked up by a syringe

at specified time intervals and analyzed by VPC.

Kinetics. **Reagents:** Methyl benzoate (as the internal standard) and acetyl cyanide were dried over anhyd CaSO_4 and distilled. Propionyl chloride was purified according to Paul's method.⁷⁾ Pyridine was purified by the reported method.⁸⁾ Each of the reagents thus purified was divided into several 0.5 mL portions which were stored in ampule tubes. In each experimental run, reagents from new ampules were used.

Procedure: Into a NMR tube which was preliminarily flushed by dry N_2 and sealed with a septum cap, the specified amounts of benzene- d_6 , methyl benzoate, acetyl cyanide, and propionyl chloride were injected and mixed. Then pyridine was added, the solution was vigorously mixed for a few seconds at 25 °C, the tube was inserted into the NMR cavity whose temperature was controlled at 35 °C. The rates of formation of 1-cyanovinyl propionate (3) were measured at specified time intervals by integrating the relative intensity of the methylene protons to the internal standard. The number of data collections per reaction was more than eight in all cases.

Data Analysis: Molar change of 3 *vs.* reaction time was plotted and from this curve the fractions of yield per minute ($\Delta Y/\Delta t$) for the first 6 min were measured. These fractions were extrapolated to $t=0$ to obtain $\Delta[\text{product}]/\Delta t=R_0$, the initial rate of reaction. These $R_0(\text{obsd})$ values are listed in Table 3.

Derivation of $R_0(\text{calcd})$: Based on the reaction Eqs. 1, 2, and 3, the initial rate of reaction $R_0(\text{calcd})$ was derived as follows. Abbreviations: *E*, *P*, *A* are the concentrations of propionyl chloride, pyridine, and acetyl cyanide respectively, E_0 , P_0 , A_0 are the corresponding initial concentrations.

$$R_0 = \frac{d[\text{product}]}{dt} = kAP \quad (5)$$

Since the equilibrium (Eq. 1) is established at the initial stage of the reaction and the concentrations of 21, 3, and pyridine·HCl are negligible, P_0 , E_0 , and A_0 are expressed by

$$E_0 = E + KPE, P_0 = P + KPE, A_0 = A \quad (6)$$

From Eq. 6, *P* is expressed by the following equation

$$P = \frac{1}{2K} [-\{1 + K(E_0 - P_0)\} + \sqrt{\{1 + K(E_0 - P_0)\}^2 + 4KP_0}] \quad (7)$$

Substituting Eqs. 6 and 7 for Eq. 5, R_0 is obtained as expressed by Eq. 4.

Examination of the Effect of Amines. **Reagents:** Three amines (2,6-lutidine, 2-picoline, pyridine) were purified by the reported method.⁸⁾ Purified *o*-dichlorobenzene was used as the internal standard in VPC analysis. For the other reagents, see the preceding paragraph.

Procedure: In a 50 mL flask equipped with a septum cap, a 0.02 mol each of acetyl cyanide, propionyl chloride, and *o*-dichlorobenzene were mixed in 10 mL of dry benzene under dry N_2 atmosphere. The flask was held in a bath controlled at 20 ± 0.5 °C, and then the solution of a tertiary amine (0.02 mol in 8 mL of benzene) was added to the mixture at one time. An aliquot of the solution was then periodically analyzed by VPC by means of calibration curves independently prepared from authentic compounds.

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