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The Dimerization of Acrylonitrile to 2-Methyleneglutaronitrile with Metal Halide and Trialkylamine

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Acrylonitrile is dimerized to 2-methyleneglutaronitrile by the binary catalyst system of metal halide and trialkylamine. The catalytic activities of metals are in this order: Co(II)≥Zn(II)≫Fe(II)>Al(III)≫V(III)> Cd(II)>Ti(IV), while that of halogens is I>Br>Cl. Triethylamine is particularly effective for the reaction. The kinetic features are discussed, and a reaction mechanism for the catalyst system of zinc chloride and triethylamine is proposed.

The catalytic dimerization of acrylonitrile has been extensively investigated. When phosphines are used as the catalysts, 2-methyleneglutaronitrile is selectively obtained; a reaction mechanism has been proposed by Baizer *et al.*[1] It is generally acecpted that Lewis bases can catalyze the reaction; many catalysts such as trialkylstibine, trialkylarsine,[2] triethylenediamine,[3] and phosphine-coordinated metal carbonyls[4] have been reported. Saegusa has also reported metal-isocyanide complexes as a new type of catalyst.[5] These catalysts are, however, effective only in the presence of protic solvents.

We have found that acrylonitrile is readily dimerized to 2-methyleneglutaronitrile under mild conditions by the binary catalysts; metal halide and tertiary amine.[6] With these catalyst systems, a protic solvent is not necessary. On the contrary, its presence hinders the reaction. In the present work, various metal halides and amines have been examined; the kinetic features will be discussed in detail.

Results and Discussion

Catalytic Activity of Metal Halide and Amines. The dimerization reaction of acrylonitrile was investigated using various metal halides and amines. The results are shown in Table 1.

Acrylonitrile was catalytically converted to methyleneglutaronitrile; only a small amount of the trimeric product was formed as a by-product. Gas-chromatographic analysis showed that no other acrylonitrile oligomers were formed. The reaction products were isolated by fractional distillation. Two fractions, with bp's of 97°C/3 mmHg and 202°C/4 mmHg, were identified as 2-methyleneglutaronitrile and 2,4,6-tricyanohexene-1 respectively by the molecular weight measurement, infrared and NMR spectroscopy.

Table 1 shows that the order of the catalytic activity is Co(II)≥Zn(II)≫Fe(II)>Al(III)≫V(III)>Cd(II) >Ti(IV) for metals and I>Br>Cl for halogens. In our investigation, only metal halides could catalyze the reaction; all the other metal compounds, such as acetates, stearates, oxides, carbonates, sulfates and acetylacetonates of zinc, cobalt and iron, did not catalyze the dimerization reaction.

Primary and secondary amines showed no catalytic activity when coupled with various metal halides, but an addition reaction to the double bond of acrylonitrile occurred. Polyamines such as triethylenediamine and hexamethylenetetramine were also found to be undesirable since the chelation to the metal halide proceeded and inhibited the dimerization reaction. From these results, it is quite probable that only tertiary amines can be used as catalyst components. Especially it was found that only three amines, triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine, were effective. Triphenylamine, tribenzylamine, and tricyclohexylamine, when coupled with zinc chloride or cobaltous chloride, did not show any catalytic activity. Also, *N*,*N*-diethylaniline and diethylcyclohexylamine, which are quite

1) M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965).
2) U. S. 2675372 (1954) (Eastman Kodak Co.).
3) Japan. 13924 (1969) (I.C.I. Ltd.).
4) Fr. 1411003 (1965) (Shell Inter. Res.).
5) T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, This Bulletin, **43**, 877 (1970).
6) Japan. 6892 (1971), 15492 (1971) 8287 (1972), [Ger. Off. 1922017 (1969)] (Mitsubishi Photochemical Co.).

TABLE 1. THE DIMERIZATION OF ACRYLONITRILE CATALYZED BY METAL HALIDES AND AMINES[a]

Metal[b] halide	Amine	(ml)	Reaction temp., °C	Reaction time, hr	Conv. %	Yield[c] MGN[d]	Yield[c] TCH[e]
CoI_2	$(C_2H_5)_3N$	(25)	20	6	76.9	73.5	3.4
$CoBr_2$	$(C_2H_5)_3N$	(25)	20	6	71.5	68.3	3.2
$CoCl_2$	$(C_2H_5)_3N$	(25)	20	6.5	59.3	56.0	3.2
$CoCl_2$	$(n\text{-}C_3H_7)_3N$	(34)	20	5	5.8	5.4	0.4
ZnI_2	$(C_2H_5)_3N$	(15.8)	20	4	72.4	68.5	3.9
$ZnBr_2$	$(C_2H_5)_3N$	(15.8)	20	6	67.1	63.7	3.4
$ZnCl_2$	$(C_2H_5)_3N$	(15.8)	20	6	50.8	48.5	2.3
$ZnCl_2$	$(n\text{-}C_3H_7)_3N$	(15.8)	30	6	8.5	8.1	0.4
$ZnCl_2$	$(n\text{-}C_4H_9)_3N$	(15.8)	30	6	3.6	3.4	0.2
$ZnCl_2$	$(C_6H_5CH_2)_3N$	(16.2)	30	6	—	—	—
$ZnCl_2$	$(C_6H_{11})_3N$	(15.8)	30	6	—	—	—
$ZnCl_2$	$(C_6H_5)_3N$	(15.8)	20	6	—	—	—
$ZnCl_2$	$(C_6H_5)_2(C_6H_{11})N$	(15.8)	20	6	—	—	—
$ZnCl_2$	$(C_2H_5)_2(C_6H_5)N$	(15.8)	20	6	—	—	—
$FeCl_2$	$(C_2H_5)_3N$	(25)	20	7	27.0	26.4	0.6
$AlCl_3$	$(C_2H_5)_3N$	(15.8)	30	6	17.1	14.9	2.2
VCl_3	$(C_2H_5)_3N$	(15.8)	30	6	2.7	2.5	0.2
$CdCl_2$	$(C_2H_5)_3N$	(15.8)	30	6	2.1	2.0	0.1
$TiCl_4$	$(C_2H_5)_3N$	(15.8)	30	6	1.7	1.6	0.1

a) In all the reactions, a 100 ml portion of acrylonitrile was employed. b) The same amount (2.77×10^{-2} mol) was employed. c) Based on the acrylonitrile originally fed in (%). d) 2-Methyleneglutaronitrile. e) 2,4,6-Tricyanohexene-1.

TABLE 2. DIMERIZATION OF VARIOUS ACRYLATES AND CO-DIMERIZATION OF ACRYLONITRILE AND ACRYLATES CATALYZED BY ZINC CHLORIDE AND TRIETHYLAMINE[a]

Monomer (ml)	Reaction time (hr)	Product (Yield,[b] %)	
CH_2=CH–CN (100)	6	NC–C(=CH_2)–CH_2–CH_2–CN (MGN)	(61.0)
CH_2=CH–CO_2Me (100)	50	MeOC–C(=CH_2)–CH_2–CH_2–C(=O)–OMe	(0.82)
CH_2=CH–CO_2Et (100)	50	EtOC–C(=CH_2)–CH_2–CH_2–C(=O)–OEt	(0.59)
CH_2=CH–CN (50)	50	NC–C(=CH_2)–CH_2–CH_2–C(=O)–OMe	(2.61)
CH_2=CH–CO_2Me (50)		MeO–C(=O)–C(=CH_2)–CH_2–CH_2–CN	(0.46)
		MGN	(4.32)
CH_2=CH–CN (50)	31	NC–C(=CH_2)–CH_2–CH_2–C(=O)–OEt	(1.51)
CH_2=CH–CO_2Et (50)		EtO–C(=O)–C(=CH_2)–CH_2–CH_2–CN	(0.23)
		MGN	(1.93)
CH_2=CH–CN (50)	50	NC–C(=CH_2)–CH_2–CH_2–C(=O)–OBu	(3.34)
CH_2=CH–CO_2Bu (50)		BuO–C(=O)–C(=CH_2)–CH_2–CH_2–CN	(0)
		MGN	(9.56)

a) Reaction condition: $ZnCl_2$; 2.77×10^{-2} mol, Et_3N; 11.4 $\times10^{-2}$mol, React. Temp.; 30°C.
b) Based on the monomers originally fed in (%).

analogous to triethylamine, did not catalyze the dimerization reaction. Many amines form complexes with halides of cobalt or zinc, and it has been reported[7,8] that acrylonitrile also forms complexes with halides of cobalt or zinc. It is probable that zinc halide forms a complex with triethylamine and acrylonitrile and that this complex catalyzes the dimerization reaction.

Catalytic Dimerization of Other Olefinic Compounds by Zinc Chloride and Triethylamine. Many olefinic compounds, such as methacrylonitrile, crotononitrile, various acrylates, styrene, butadiene, and vinyl chloride, were examined, but no dimer was obtained except for acrylates. The rates of the dimerization of acrylates were smaller than that of acrylonitrile. The co-dimerizations of acrylonitrile and various acrylates were also attempted. These results are shown in Table 2.

In all the co-dimerization experiments, the dimer of acrylate was not detected and the dimerization of acrylonitrile was fairly much inhibited. This suggests that acrylates are more strongly coordinated to zinc chloride than to acrylonitrile.

Effect of Acrylonitrile Concentration. The relation of the 2-methyleneglutaronitrile obtained and the reaction time at various acrylonitrile concentrations is shown in Fig. 1.

The rate of 2-methyleneglutaronitrile formation was calculated from the initial gradient of the curves in Fig. 1. The result is plotted against the concentration of acrylonitrile in Fig. 2. A straight line with an inclination of +2 as observed in Fig. 2 suggests a second-order reaction with the acrylonitrile concen-

7) T. Ikegami and H. Hirai, *Chem. Commun.*, **1969**, 159.
8) M. F. Farona and G. R. Tompkin, *Spectrochim. Acta, A*, **24**, 788 (1968).

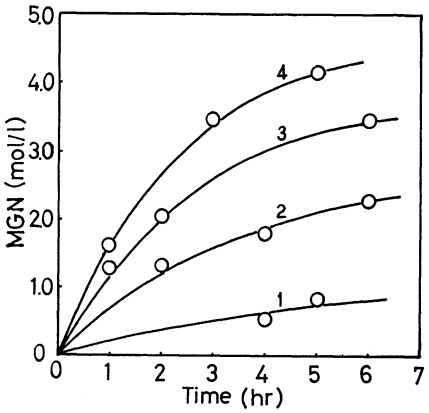


Fig. 1. The relation between amount of 2-methyleneglutaronitrile and reaction time at various acrylonitrille concentration.
Temperature: 20°C, $ZnCl_2$: 0.18 mol/l, Triethylamine: 2.40 mol/l, Acrylonitrile concentration: (1) 2.02 mol/l, (2) 4.05 mol/l, (3) 6.07 mol/l, (4) 8.09 mol/l.

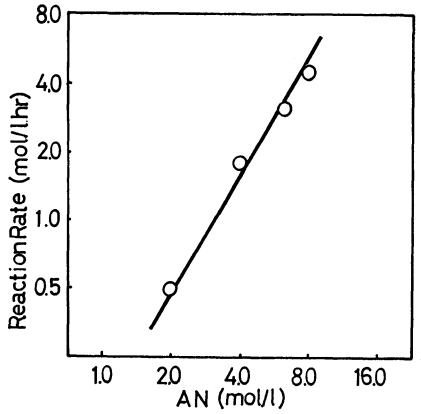


Fig. 2. Dependence of dimerization rate on concentration of acrylonitrile.
Temperature: 20°C, $ZnCl_2$: 0.18 mol/l, triethylamine: 2.40 mol/l.

tration.

The Reaction Paths of the Acrylonitrile Trimer. As is shown in Fig. 3, the trimeric product was found even in the very eary stages and exhibited a pattern of increase similar to that of the dimeric product. If the trimer is formed only from the dimer and the monomer by the consecutive reaction mechanism, its amount will be very small at first, but will show a rapid increase as the dimer increases. Such a pattern was not observed, however, even after more than half of the acrylonitrile was converted to the dimeric product. Therefore, two parallel paths for the trimeric product were postulated: one, a successive reaction of the dimer with the monomer, and the other, a simultaneous reaction from three molecules of acrylonitrile.

In order to confirm the assumption, the simulation of the rate process of the reaction was attempted by means of an analog computer (Melcom Model EA-716). The results of the simulation agree satisfactorily with the experimental results. An example is shown in Fig. 3; the results of the simulation are shown by solid lines, while the experimental values are illustrated symbols.

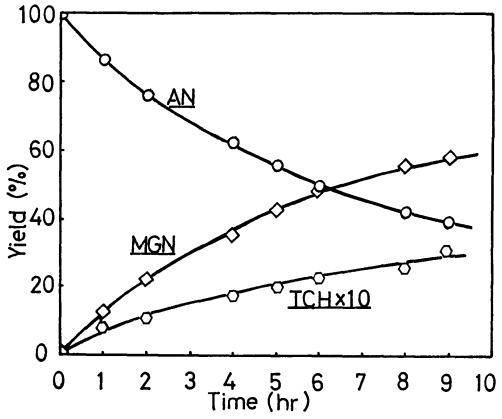


Fig. 3. Comparison of experimental yields with computer simulation. Solid lines are results of simulation (k_1: 0.180, k_2: 0.004, k_3: 0.009) and symbols are experimental values: ○ unreacted acrylonitrile, ◇ yield of methyleneglutaronitrile, ⬡ yield of 2,4,6-tricyanohexene-1. Temperature: 20°C, acrylonitrile: 13.1 mol/l, $ZnCl_2$: 0.18 mol/l, triethylamine: 0.98 mol/l.

We may conclude that the reaction of acrylonitrile catalyzed by zinc chloride and triethylamine is composed of the following reactions:

$$2CH_2{=}CH{-}CN \xrightarrow{k_1} CH_2{=}C(CH_2{-}CH_2{-}CN){-}CN \quad (1)$$

$$CH_2{=}CH{-}CN + NC{-}\overset{CH_2}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}CN \xrightarrow{k_2} CH_2{=}C(CH_2{-}CH(CH_2{-}CH_2{-}CN){-}CN){-}CN \quad (2)$$

$$3CH_2{=}CH{-}CN \xrightarrow{k_3} CH_2{=}C(CH_2{-}CH(CH_2{-}CH_2{-}CN){-}CN){-}CN \quad (3)$$

The rate expression of the above reaction is as follows. The concentration of the dimer and the trimer are reduced to those of the acrylonitrile consumed:

$$-d[A_1]/dt = k_1[A_1]^2 + k_2[A_1][A_2] + k_3[A_1]^3$$
$$d[A_2]/dt = k_1[A_1]^2 - k_2[A_1][A_2]$$
$$d[A_3]/dt = k_2[A_1][A_2] + k_3[A_1]^3$$

A_1=acrylonitrile unreacted, A_2=acrylonitrile converted to 2-methyleneglutaronitrile, A_3=acrylonitrile converted to 2,4,6-tricyanohexene-1.

Temparature Dependence on the Reaction Rate. The rate constants calculated by means of the analog computer will be used hereafter.

Figure 4 shows, the k_1, k_2, and k_3 logarithms *vs.* $1/T$. The apparent activation energies, as calculated from Fig. 4, are 3.4, 2.8, and 2.3 kcal/mol for Reactions (1), (2), and (3) respectively.

These unusually small activation energy values suggest the existence of an exothermal partial equilibrium prior to the rate-determining step. Therefore, it is assumed that the apparent activation energies can be observed as the differences in the real activation energies and the reaction heats of the equilibrium reaction.

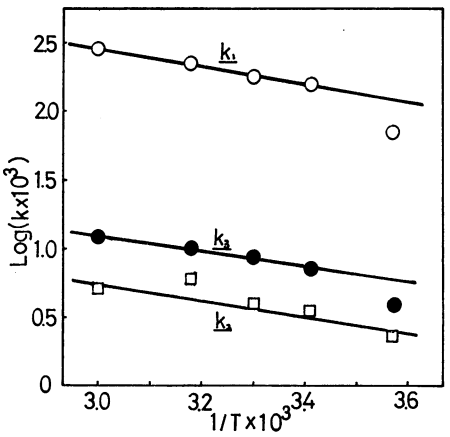


Fig. 4. Dependence of reaction rate on reaction temperature.
Acrylonitrile: 13.1 mol/l, $ZnCl_2$: 0.18 mol/l, triethylamine: 0.98 mol/l.

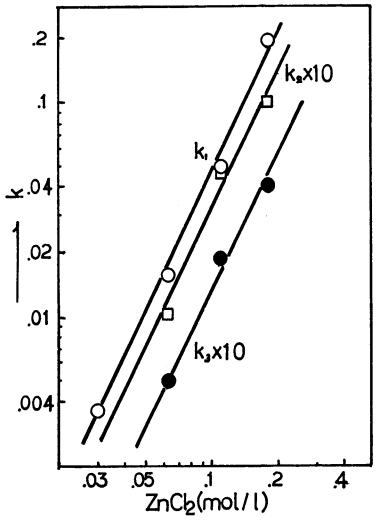


Fig. 5. Reaction rate as a function of $ZnCl_2$ concentration.
Temperature: 20°C, Acrylonitrile: 10.1 mol/l, Triethylamine: 2.40 mol/l.

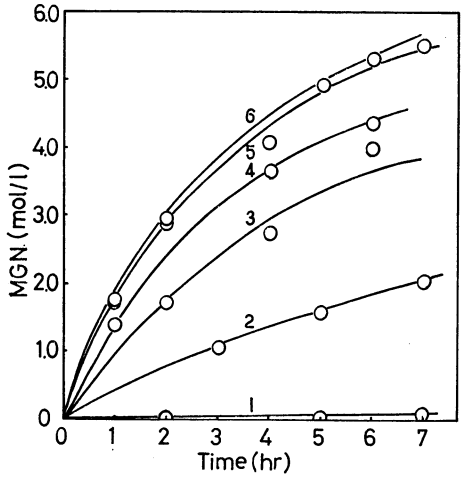


Fig. 6. The relation between amount of 2-methyleneglutaronitrile and reaction time at various triethylamine concentration.
Temperature: 20°C, Acrylonitrile: 10.1 mol/l, $ZnCl_2$: 0.18 mol/l, Triethylamine: (1) 0.19 mol/l, (2) 0.48 mol/l, (3) 0.96 mol/l, (4) 1.46 mol/l, (5) 1.94 mol/l, (6) 2.40 mol/l.

Effect of the Catalyst Concentration. The dependence of the zinc chloride concentration on the rate constants, k_1, k_2, and k_3, is shown in Fig. 5. The straight lines with the gradient of +2 for all the k's suggest that the reaction is of the second order with relation to the concentration of zinc chloride. This suggests that the zinc chloride complex exists in the dimeric form.

The relations of the 2-methyleneglutaronitrile and the reaction time obtained at various triethylamine concentrations are shown in Fig. 6. As is evident from Fig. 6, the catalytic activity is very small when the molar ratio of zinc chloride to triethylamine is less than unity, while it is almost constant when the ratio is over ten.

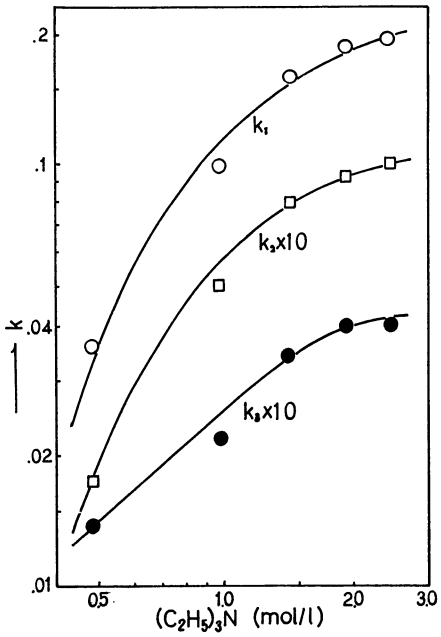


Fig. 7. Plots of reaction rates *vs.* concentration of triethylamine.
Temperature: 20°C, Acrylonitrile: 10.1 mol/l, $ZnCl_2$: 0.18 mol/l.

The logarithms of k_1, k_2, and k_3 are plotted against the logarithm of the triethylamine concentration in Fig. 7. The maximum gradient of each line was calculated as follows: about +2 for k_1 and k_2, and about +1 for k_3. In other words, the concentration of triethylamine influences Reactions (1) and (2) in the second order and Reaction (3) in the first order.

Reaction Mechanism. Summing the experimental results, we get: (1) zinc chloride, triethylamine, and acrylonitrile form a complex, and this complex catalyzes the reaction; (2) the trimer is formed through two different paths; (3) an exothermal partial equilibrium exists prior to the rate-determining step, and (4) the kinetic order of each catalyst component was determined and the product distribution in the co-dimers of acrylonitrile and acrylates was investigated.

The following reaction scheme is proposed on the basis of the experimental results:

i) Formation of methyleneglutaronitrile:

$$2ZnCl_2 + 2Et_3N + AN \rightleftarrows [Zn_2Cl_4(Et_3N)_2(AN)] \quad (4)$$

$$[Zn_2Cl_4(Et_3N)_2(AN)] + AN \xrightarrow{\text{-A-}} [Zn_2Cl_4(Et_3N)_2(MGN)] \quad (5)$$

$$[Zn_2Cl_4(Et_3N)_2(MGN)] + AN \xrightarrow{\text{fast}} [Zn_2Cl_4(Et_3N)_2(AN)] + MGN \quad (6)$$

ii) Formation of 2,4,6-tricyanohexene-1:

a) Successive reaction from methyleneglutaronitrile:

$$2ZnCl_2 + 2Et_3N + AN \rightleftarrows [Zn_2Cl_4(Et_3N)_2(AN)]$$

$$[Zn_2Cl_4(Et_3N)_2(AN)] + MGN \xrightarrow{\text{-A-}} [Zn_2Cl_4(Et_3N)_2(TCH)] \quad (7)$$

$$[Zn_2Cl_4(Et_3N)_2(TCH)] + AN \xrightarrow{\text{fast}} [Zn_2Cl_4(Et_3N)_2(AN)] + TCH \quad (8)$$

b) Direct formation from acrylonitrile:

$$2ZnCl_2 + Et_3N + 2AN \rightleftarrows [Zn_2Cl_4(Et_3N)(AN)_2] \quad (9)$$

$$[Zn_2Cl_4(Et_3N)(AN)_2] \xrightarrow{\text{fast}} [Zn_2Cl_4(Et_3N)(MGN)] \quad (10)$$

$$[Zn_2Cl_4(Et_3N)(MGN)] + AN \xrightarrow{\text{-A-}} [Zn_2Cl_4(Et_3N)(TCH)] \quad (11)$$

$$[Zn_2Cl_4(Et_3N)(TCH)] + 2AN \xrightarrow{\text{fast}} [Zn_2Cl_4(Et_3N)(AN)_2] + TCH \quad (12)$$

or

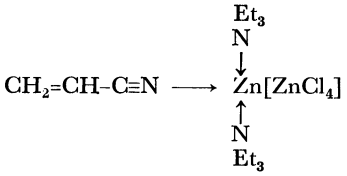
$$[Zn_2Cl_4(Et_3N)(TCH)] + AN + Et_3N \xrightarrow{\text{fast}} [Zn_2Cl_4(Et_3N)_2(AN)] + TCH \quad (13)$$

AN: acrylonitrile, MGN: 2-methyleneglutaronitrile, TCH: 2,4,6-tricyanohexene-1, Et_3N: triethylamine.

The above mechanism requires that zinc chloride be in the dimeric form and that the molar ratios of chlorine, acrylonitrile and triethylamine to zinc in the catalytic complex (Scheme 4) be 2, 1, and 1/2 respectively. We have tried to separate the catalytic complex and have succeeded in obtaining an orange precipitate by adding a small amount of toluene to the reactive solution.

The precipitate was examined by elemental analysis and by IR and NMR spectroscopy, and was shown to contain zinc, chlorine, acrylonitrile, triethylamine, and toluene as components. However, the integral stoichiometry was not determined (except that the ratio of chlorine to zinc is 2), since the complex was rather unstable in the air.

The dimeric form of zinc chloride may be supported by the fact that cadmium chloride forms an autocomplex like $Cd[CdCl_4]$, though the same structure has not been established for zinc chloride. Thus, according to the above mechanism, the structure of the catalytic complex may be postulated to be as follows:



However, the real stoichiometry and the autocomplex structure were not proved in our experiments; these problems are left to further investigations.

Experimental

Materials and Reagents. As the reaction was strikingly hindered by the presence of water, it was carefully removed from all the reagents. The acrylonitrile and amines were dried over molecular sieves (4A) and distilled under nitrogen. The water content of the acrylonitrile after the purification was less than 10 ppm, while that of triethylamine was less than 20 ppm.

All the commercially-obtained metal halides except titanium tetrachloride were dried by heating them under nitrogen or gaseous hydrogen chloride.

The Reaction of Acrylonitrile. The following procedure was carried out under a nitrogen atmosphere.

About 3.6 g of zinc chloride were dissolved in 100 ml of acrylonitrile in a 200 ml three-necked flask provided with a stirrer, and then 16 ml of triethylamine were added. The flask was set in a water bath, and the temperature was controlled by means of a "Coolnics circulator" (Yamato Kagaku Co. Ltd.). The mixture was kept at the prescribed temperature for a certain number of hours. During the reaction, if desired, a portion of the reaction mixture was sampled by operating a micro syringe through the serum cap and was analyzed by gas chromatography.

NMR and IR Spectra of Reaction Products.

$NC-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-CN$: NMR (in CCl_4) τ 3.98 and 4.18 (s, 2H, CH_2=), 7.38 (s, 4H, $-C\underline{H}_2-C\underline{H}_2-$); IR (neat) 2265 and 2245 ($-C\equiv N$), 1625 and 953 cm^{-1} ($C=C$).

$CH_2=\underset{\underset{CN}{|}}{C}-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-CH_2-CN$: NMR (in CCl_4) τ 3.82 and 3.92 (s, 2H, $C\underline{H}_2$=), 6.87 (m, 1H, $-C\underline{H}-$), 7.29 (t, J= 6 Hz, 2H, $-C\underline{H}_2-CN$), 7.38 (d, J=7.2 Hz, 2H, $CH_2=\underset{\underset{CN}{|}}{C}-C\underline{H}_2-$), 7.59, (q, J=6.6 Hz, 2H, $-\underset{\underset{CN}{|}}{CH}-C\underline{H}_2-CH_2-$); IR (neat) 2250 and 2230 ($-C\equiv N$), 1620 and 955 cm^{-1} ($C=C$).

$CH_3O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OCH_3$: NMR (in CCl_4) τ 3.86 and 4.40 (s, 2H, $C\underline{H}_2$=), 6.24 and 6.35 (s, 6H, $-COOC\underline{H}_3$), 7.46 (s, 4H, $-C\underline{H}_2-C\underline{H}_2-$); IR (neat) 1735 ($C=O$), 1630 cm^{-1} ($C=C$).

$C_2H_5O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5$: NMR (in CCl_4) τ 3.83 and 4.36 (s, 2H, $C\underline{H}_2$=), 5.80 (m, J=7 Hz, 4H, $CH_3-C\underline{H}_2-O-$), 7.46 (m, 4H, $-C\underline{H}_2-C\underline{H}_2-$), 8.70 (m, J=7 Hz, 6H, $C\underline{H}_3-CH_2-O-$); IR (neat) 1720 ($C=O$), 1625 cm^{-1} ($C=C$).

$CH_3O-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_2}{\|}}{C}-CN$: NMR (in CCl_4) τ 3.69 and 3.78 (s, 2H, $C\underline{H}_2$=), 6.06 (s, 3H, $-COOC\underline{H}_3$), 7.24 (s, 4H, $-C\underline{H}_2-C\underline{H}_2-$); IR (neat) 2230 ($-C\equiv N$), 1740 ($C=O$), 1621 and 945 cm^{-1} ($C=C$).

$CH_3O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-CN$: NMR (in CCl_4) τ 3.23 and 3.77 (s, 2H, $C\underline{H}_2$=), 5.94 (s, 3H, $-COOCH_3$), 7.25 (s, 4H, $-C\underline{H}_2-C\underline{H}_2-$); IR (neat) 2255 ($-C\equiv N$), 1721 ($C=O$), 1630 and 955 cm^{-1} ($C=C$).

Gas-chromatographic Analysis of the Products. For the analysis of acrylonitrile, methyleneglutaronitrile and 2,4,6-tricyanohexene-1, a column of 1-m Triton-x-305 (5% on Chamelite F.K.) was used.

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