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Knoevenagel Reaction of Malononitrile with Acetone Followed by Double Cyclization Catalyzed by KF-Coated Alumina in Aqueous Solution

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The condensation reaction of malononitrile with acetone was catalyzed by variously pretreated alumina (1/4 equiv based on the amount of KF) to give a 2-azabicyclo[2.2.2]octane derivative in water (in more than 90% yield). With more catalyst (1 equiv), a potassium salt of the product was formed unexpectedly. Both products released isobutylene to give the corresponding pyridine derivatives.

In many industrial processes in chemical factories, solid phase catalysts are used skillfully in contrast to the laboratory. In such processes, reacting species are in gas or liquid phase which are different phases from that of catalysts.[1] Homogeneous reactions are usual in laboratory and heterogeneous reactions are carried out only rarely, but we sometimes experience unexpected chemical reactions on the surface of adsorbents in column chromatography. In fact, variously activated alumina was found to catalyze specific organic reactions.[2] Ando reported that KF-coated alumina catalyzed Knoevenagel reactions, aldol reactions, N- or O-alkylations, and Michael reactions.[3] Experiments using these solid phase catalysts generally have the following features; i) it is often easy to isolate the products and to separate the catalysts; ii) comparing the reaction conditions with those of related homogeneous reactions, they are so mild that a high yield of specific products and supression of by-product formation are expected; iii) selectivity and activity of the catalysts are often comparable to those of enzymes.

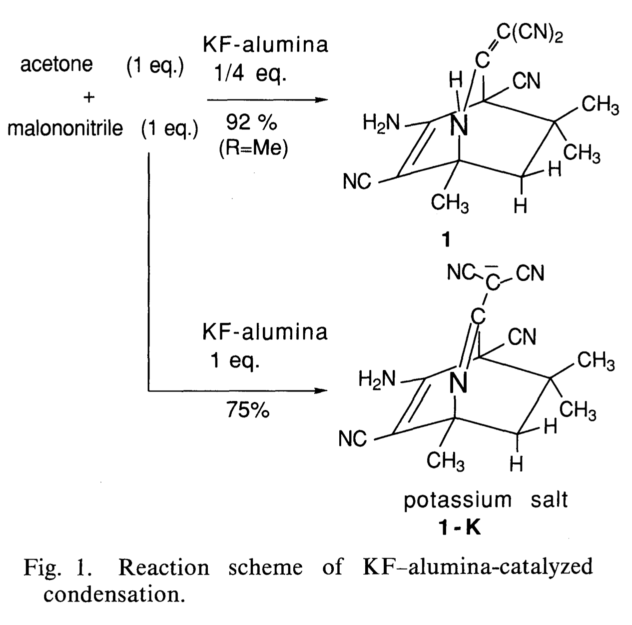

Fig. 1. Reaction scheme of KF-alumina-catalyzed condensation.

This report describes the efficient application of Ando's catalyst[4] and other pretreated alumina in a complex condensation reaction. The catalysts (1/4 equiv) were found to catalyze reaction of malononitrile with acetone to give 5-amino-4,6-dicyano-3-dicyanomethylene-1,8,8-trimethyl-2-azabicyclo[2.2.2]oct-5-ene (**1**) in a high yield (see Fig. 1). This reaction using the catalysts demonstrated the three advantages (i—iii) described above. With a large amount of catalyst (1 equiv), the potassium salt of the product was formed unexpectedly. The crystal structures of the products were determined by the X-ray diffraction method. Both the products undergo retro Diels–Alder reactions to give pyridine derivatives as expected from the structure.

Experimental

Apparatus. Infra red spectra (400—4000 cm^{-1}) were measured with a Hitachi 270-30 FT-IR spectrometer. Mass spectra were recorded on a JEOL JMS DX-300. NMR measurements and elemental analyses were carried out with a JEOL GSX-400 and a Yanaco MT-2, respectively. HPLC was performed on a Hitachi L6000.

Preparation of the Catalyst (KF-alumina). The catalyst was prepared according to Ando's method.[4] Thirty grams of alumina (Merck, neutral alumina 90) were suspended in an aqueous solution of KF (20 g) in 200 ml of water. The water was evaporated and the residue was heated to 100°C under vacum for 12 h.

Preparation of 5-Amino-4,6-dicyano-3-dicyanomethylene-1,8,8-trimethyl-2-azabicyclo[2.2.2]oct-5-ene (1). a) To a solution of malononitrile (0.66 g, 10 mmol) and acetone (0.58 g, 10 mmol) in water (40 ml), was added 0.36 g of KF-alumina which corresponded to 1/4 equiv of the substrate and the mixture was stirred at room temperature. A crystalline mass precipitated after 24 h. The precipitate was confirmed to be one componet by HPLC. The product was dissolved in hot methanol and the catalyst was removed. The product was recrystallized from methanol. The average yield was more

Table 1. Results of the Condensation Reaction of Malononitrile with Acetone$^{a)}$

Entry	Catalyst	Yield % of Compound **1**
1	KF–alumina	92
2	KOH–alumina$^{b)}$	54
	NaOH–alumina$^{b)}$	85
	Na_3PO_4–alumina$^{b)}$	65
3	KF–molecular sieves 3A$^{c)}$	90
	KF–molecular sieves 4A$^{c)}$	89
	Molecular sieves 3A$^{d)}$	68
	Molecular sieves 4A$^{d)}$	80
4	KF$^{e)}$	16
5	Alumina$^{d)}$	22
6	Silica gel$^{d)}$	0
	Florisil$^{d)}$	90
	Montmorillonite K-10$^{d)}$	0

a) All the reactions were carried out at room temperature for 24 h as described in the experimental section. b) An equimolar amount of inorganic salt was used and activated in the same manner as KF–alumina. c) The same weight of molecular sieves instead of alumina was used and activated in the same manner as KF–alumina. d) In these reactions, 0.44 g of materials were used as catalyst. e) In this reaction, only 0.3 g of KF was used.

than 90% on the basis of the necessary amount of malononitrile. IR (KBr), three peaks in the 3450—3100 region (νNH_2) and 2200 cm^{-1}; MS m/z, 278 (M^+, 9.9), 222 (100), and 56 (91); ^1H NMR (DMSO-d_6) δ=10.396 (1H, s, N-H), 7.224 (2H, s, NH_2), 1.727 (1H, d, J=12 Hz), 1.690 (1H, d, J=12 Hz), 1.533 (3H, s), 1.210 (3H, s), and 1.137 (3H, s); ^{13}C NMR (DMSO-d_6) δ=161.831, 153.719, 114.886, 114.712, 113.289, 112.119, 78.125, 56.668, 55.641, 49.585, 42.833, 26.674, 26.295, and 20.365. Found: C, 64.99; H, 4.85; N, 30.26%. Calcd for $C_{15}H_{14}N_6$: C, 64.73; H, 5.07; N, 30.20%. Various catalysts were examined in the same manner and the results are listed in Table 1.

The product popped actively at about 160 °C and decomposed gently to a pyridine derivative (**2**) (see Fig. 4). The popping behavior on heating was retro-Diels–Alder reaction releasing isobutylene which we experienced in analogous materials releasing isobutylene.[5] This degradation is probably responsible for the intense fragment peak in the mass spectrum of the product (mass number 56 and 222). The crystal structure of the product was determined as described below.

b) A mixture of acetone (0.58 g), malononitrile (0.66 g) and KF–alumina (0.36 g) in acetonitrile (30 ml) was stirred at room temperatue for 24 h (97% yield by HPLC). The catalyst was filtered and the acetonitrile was evaporated. The residual solid was recrystallized from methanol.

Preparation of 4-Amino-3,5-dicyano-3-dicyanomethyl-6-methylpyridine, 2 (Pyrolysis of the Product 1). When compound **1** was heated directly, isobutylene was released. Pyrolysis in organic solvents with boiling points higher than the isobutylene-releasing point was better than the method of simply heating the product **1**. A suspension of compound **1** (0.28 g, 10 mmol) in tetralin (30 ml) was refluxed until popping sounds ceased (about 2 h). The solid was then filtered. It decomposed at about 280 °C and did not show a clear mp. IR (KBr), a broad peak at 2500—3500 (highly-associated NH_2), and 2206 cm^{-1}; MS m/z 222 (M^+), and 195 (M^+ −HCN); ^{13}C NMR (DMSO-d_6), δ=160.457, 157.567, 154.915, 117.261, 113.658, 112.908, 86.226, 76.551, and 20.115. ^1H NMR, 8.066 (1H, it may be assigned to NH_2 and may be exchanged partially with DMSO-d_6). Methyl protons (singlet) were observed at 2.493 at a shoulder of DMSO. Since the proton, py-C$\underline{H}$(CN)$_2$, is acidic, it could not be observed probably due to exchange with DMSO-d_6. Found: C, 59.19; H, 2.30; N, 37.55%. Calcd for $C_{11}H_6N_6$: C, 59.45; ;H, 2.72; N, 37.82%.

Preparation of the Potassium Salt of 1 (represented as **1-K**). With more catalyst (1.46 g) under the same reaction conditions as the preparatin of **1**, the potassium salt of **1** precipitated (0.88 g (75%)). With K_2CO_3–alumina catalyst[6] also, the potassium salt (**1-K**) was obtained in more than 90% yield. The salt was recrystallized from methanol. It dissolved slightly in water. The isobutylene-releasing point was observed at about 120 °C. IR (KBr), broad peaks at 3000—3650, 2160, and 2190 cm^{-1} and three intense peaks at 1660, 1610, and 1510 cm^{-1}. ^1H NMR (DMSO-d_6) δ=6.612 (2H, s, NH_2), 1.408 (1H, d, J=11 Hz), 1.253 (1H, d, J=11 Hz), 1.330 (3H, s, CH_3), 1.109 (3H, s, CH_3), and 1.017 (3H, s, CH_3); ^{13}C NMR (DMSO-d_6) δ=159.910, 154.808, 116.312, 114.428, 78.675, 72.183, 57.260, 55.980, 49.195, 42.245, 27.030, 26.316, and 23.244. A significant mass spectrum could not be obtained. Found: C, 51.05; H, 4.64; N, 24.28%. Calcd for $C_{15}H_{13}N_6K \cdot 2H_2O$: C, 51.14; H, 4.83; N, 23.86%. This salt (**1-K**) was converted into **1** as follows. A solution of the potassium salt (0.2 g) in methanol (100 ml) was passed through a column of cellulose cation-exchanging resin (CM-type, Serva Co.). The methanolic eluted solution was evaporated. The infrared spectrum of the residual solid was identified as that of **1**.

Pyrolysis of 1-K. A suspension of **1-K** (0.4 g) in *o*-dichlorobenzene (30 ml) was refluxed for 4 h. The solid was filtered (0.30 g (quantitative)) and was recrystallized from methanol. IR (KBr)/cm^{-1}, broad intense peaks at 3100—3700 (νNH_2), 2200 cm^{-1}, and three strong peaks in the region of 1680—1440 cm^{-1}. ^1H NMR (DMSO-d_6) δ=6.539 (2H) and 2.270 (3H); ^{13}C NMR (DMSO-d_6) δ=162.487, 161.481, 157.933, 120.754, 116.639, 115.048, 95.443, 81.544, 75.271, 43.286, and 23.535. Found: C, 47.10; H, 2.28; N, 30.12%. Calcd for $C_{11}H_5N_6K \cdot H_2O$: C, 47.48; H, 2.52; N, 30.21%.

Crystal Structure Analysis of 1. Colorless plate crystals were obtained from ethanol after several days in the refrigerator. Crystals of approximate dimensions 0.3×0.5×0.6 mm were used. Accurate cell parameters were determined by a least squares fit for 25 reflections within the range of $26.7\,^\circ C < 2\theta < 37.5^\circ$ measured on a Rigaku AFC-5R diffractometer with Mo $K\alpha$ radiation (λ=0.71069 Å) monochromated by graphite.

Crystal data: Formula weight=278.31, $C_{15}H_{14}N_6$, monoclinic, $C2/c$, a=14.309(4), b=10.387(3), c=19.773(3) Å, β=94.88(2)°, V=2928(1) Å^3, Z=8, d_x=1.263, d_m=1.251 g cm^3 (measured by floatation in a mixture of xylene and carbon tetrachloride), μ=0.886 cm^{-1}, F(0 0 0)=1168.

Reflection data were collected on a 2θ–ω scan mode up to $2\theta=60^\circ$ with a scan width of $\Delta\omega=(1.42+0.30\tan\theta)^\circ$. Three standard reflections were recorded before every 150 reflections. Decrement was not observed in the intensities of the standard reflections. A total of 4663 reflections were collected at a rate of 16° min^{-1} in ω of which 1942 were assumed to be significant ($|F_o|>3\sigma(|F_o|)$). The structure was solved by the direct method and refined by full matrix least squares with

TEXSAN.[7] The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=4|F_o|^2/\sigma^2(|F_o|^2)$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography. All the non-hydrogen atoms were refined anisortropically. Hydrogen atoms found in difference Fourier maps were refined isotropically. Max D/r and min D/r in the final difference map were 0.24 and -0.19 e/Å^{-3}, respectively. Final R (and R_w) was 0.047 (0.034). The final atomic parameters of non-hydrogen atoms (Table A), the anisotropic temperature factors for non-hydrogen atoms (Table B), the F_o-F_c (Table C), the atomic parameters for the hydrogen atoms (Table D), nonessential bond distances and angles (Table E) and packing along the *b* and *c* axes (Figs. A and B) are deposited as Document No. 9036 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Crystal Structure Analysis of 1-K. Colorless plate crystals were obtained from acetone after 2—3 d in the refrigerator. Crystals of approximate dimensions 0.65×0.25×0.10 mm were used. Accurate cell parameters were determined by a least squares fit for 14 reflections within the range of $30.6<2\theta<34.6°$ measured on a Rigaku AFC-5 diffractometer with Cu $K\alpha$ radiation (λ=1.5418 Å) monochromated by graphite.

Crystal data: Formula weight=352.44, $C_{15}H_{13}N_6K\cdot 2H_2O$, orthorhombic, $Pna2_1$, a=15.878(2), b=14.945(2), c=7.038(1) Å, V=1670.0(4) Å^3, Z=4, d_x=1.40, d_m=1.38 g cm^{-3} (measured by floatation in a mixture of 1,1,2,2-tetrachloroethane and tetralin), μ=29.5 (Cu $K\alpha$) cm^{-1}, F (0 0 0)=7 3 6.

Reflection data were collected on a 2θ-ω scan mode up to 2θ=110° with a scan width of $\Delta\omega$=(1.0+0.5 tanθ)°. Three standard reflections were recorded before every 200 reflections. No decrement was observed in the intensities of the standard reflections throughout the measurement. A total of 1188 reflections were collected at a rate of 3° min^{-1} in ω of which 1115 were assumed to be significant ($|F_o|>3\sigma(|F_o|)$). The structure was solved by the direct method using the program UNICS III[8] and refined by block-diagonal least-squares with FACOM 360. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=1\ (\sigma^2(|F_o|)+0.02\ (|F_o|)^2)^{-1}$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography. All the non-hydrogen atoms were refined anisotropically. The Z coordinate of the potassium ion was fixed at -0.0069. Hydrogen atoms found in difference Fourier maps and calculated geometricaly were refined isotropicaly. Positional and thermal parameters of all the hydrogen atoms were fixed at the later stage of refinement. Max D/r and min D/r in the final difference map were 0.53 and -0.81 e Å^{-3}, respectively. The final R (and R_w) was 0.068 (0.082). The final atomic parameters of non-hydrogen atoms (Table F), the anisotropic temperature factors for non-hydrogen atoms (Table G), the F_o-F_c (Table H), the atomic parametes for the hydrogen atoms (Table I), non-essential bond distances an angles (Table J) and packing along the *c* and *a* axes (Fig. C and D) are deposited as Document No. 9036 at the Office of the Editor of Bull. Chem. Soc. Jpn.

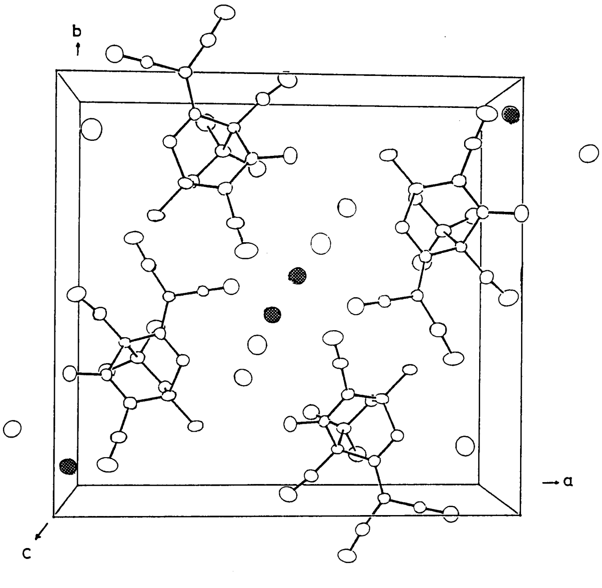

Fig. C. Shadowed particles indicate potassium ions.

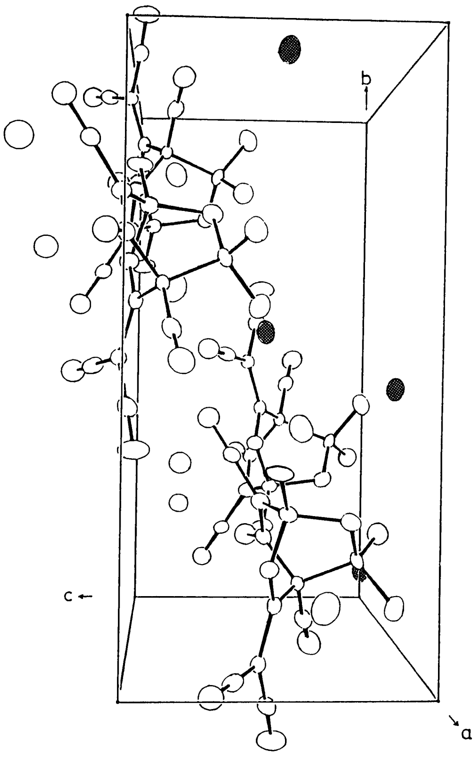

Fig. D. Shadowed particles indicate potassium ions.

Results and Discussion

Condensation Reaction. In contrast to our general experiences, a complex condensation reaction proceeded heterogeneously and smoothly in water in a high yield (see preparation of **1** in the experimental section). In such common organic solvents as methanol or acetonitrile, good results were obtained. But in methanol, a mixture of **1** and **1-K** was obtained. In acetone, four components incuding the present product were detected by HPLC. Since acetone itself is reactive on the surface of alumina, the other components may be self-condensation products. Apparently, **1-K** was formed via **1.** Indeed, **1** was converted to the potassium salt with 2 equiv of potassium fluoride or KF-alumina in acetonitrile.

The catalyst contributes a crucial effect to the reactions as shown in Table 1. A combination of KF and alumina (neutral, basic, or acidic alumina gave almost the same results) is the best. In this reaction, both KF and alumina are essential (see Entries 1, 4, and 5). Molecular sieves also worked well, but were slightly inferior to alumina (Entry 3). Among the silicate species, only Florisil was effective (Entry 6). Several other species also were moderately effective.

Crystal Structure of Compounds 1 and 1-K. We had already reported a 3-methoxy-2-azabicyclo[2.2.2]octane analogue.[5] The structue of the product **1** could also be elucidated from the fact that it released isobutylene on heating and on comparing the ^1H and ^{13}C NMR spectra with those of the 3-methoxy analogue. But the spectra gave us only limited sructural informations, because all the compounds in this series have so many quarternary carbons and isolated methyl groups that the ^1H and ^{13}C NMR spectra are difficult to assign. To our regret, we made a minor mistake in the analogous reaction products due to such limited knowledge.[9] To avoid such a mistake, we confirmed the structure of **1** by the X-ray diffraction method.

Until the X-ray structure analysis, we did not imagine that **1-K** was a simple potassium salt of **1**. The potassium ion is far from the anion in the unit cell as shown in Figure C and D. The crystal structure prompted us to ascertain this fact and it was confirmed also chemically. A methanolic solution of **1-K** was passed through a column of cation-exchanging resin (CM-type), and the material obtained from the methanolic eluent was identified as product **1** by its IR

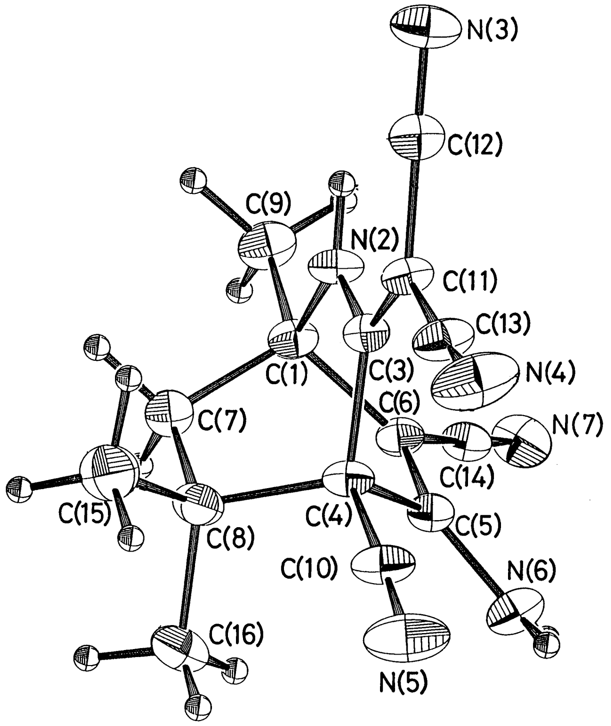

Fig. 2. ORTEP drawing of **1**.

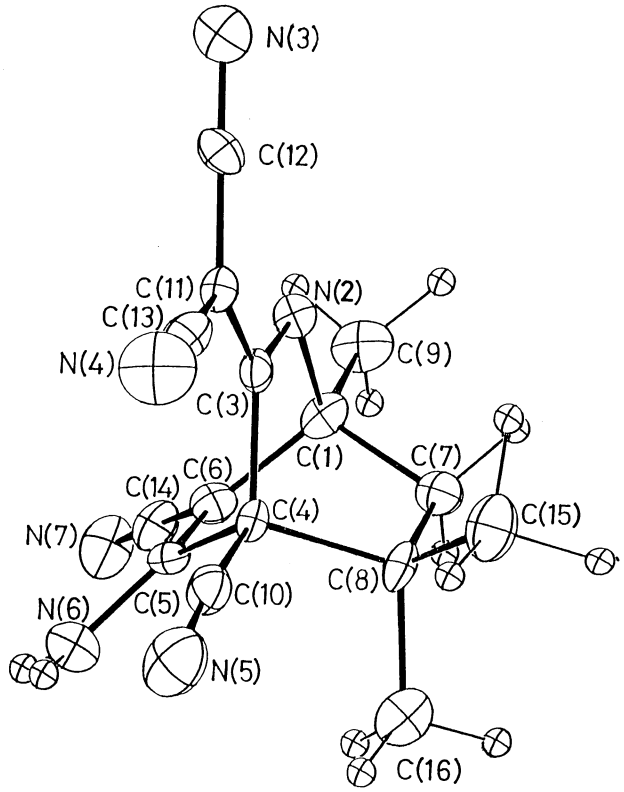

Fig. 3. ORTEP drawing of **1-K**.

Table 2. Selected Bond Distances and Angles of Product **1** within the Molecule[a)]

Atom–Atom	Distance	Atom–Atom	Distance	Atom–Atom–Atom	Angle	Atom–Atom–Atom	Angle
C(1)–N(2)	1.488(2)	N(2)–C(3)	1.326(2)	C(1)–N(2)–C(3)	117.9(2)	C(16)–C(8)–C(15)	109.1(2)
C(4)–C(8)	1.604(3)	N(2)–H(N2)	0.86(2)	C(5)–C(4)–C(8)	106.5(2)	C(3)–C(4)–C(5)	107.1(2)
N(3)–C(12)	1.140(3)	N(4)–C(13)	1.132(3)	N(6)–C(5)–C(6)	128.5(2)	C(3)–C(4)–C(8)	108.1(2)
C(3)–C(4)	1.533(3)	N(6)–C(5)	1.336(3)	N(6)–C(5)–C(4)	119.5(2)	C(6)–C(5)–C(4)	112.0(2)
C(3)–C(11)	1.385(3)	C(5)–C(6)	1.352(3)	C(1)–C(6)–C(5)	114.3(2)	C(5)–C(6)–C(14)	123.6(2)
C(5)–C(4)	1.535(3)	C(1)–C(6)	1.509(3)	N(2)–C(3)–C(4)	110.0(2)	C(1)–C(6)–C(14)	121.9(2)
C(6)–C(14)	1.415(3)	C(1)–C(7)	1.526(3)	N(2)–C(3)–C(11)	122.9(2)	N(2)–C(1)–C(6)	105.7(2)
C(7)–C(8)	1.549(3)	C(11)–C(12)	1.431(3)	C(4)–C(3)–C(11)	127.1(2)	N(2)–C(1)–C(7)	105.6(2)
C(11)–C(13)	1.422(3)			C(6)–C(1)–C(7)	108.4(2)	C(1)–C(7)–C(8)	110.9(2)
				C(7)–C(8)–C(4)	106.3(2)	C(3)–C(11)–C(12)	119.3(2)
				C(3)–C(11)–C(13)	126.7(2)	C(12)–C(11)–C(13)	114.0(2)

a) Distances and angles are in angstroms and degrees, respectively. Estimated standard deviations are given in parentheses.

Table 3. Selected Bond Distances and Angles of the Potassium Salt (**1-K**)[a]

Atom 1–Atom 2	Distance	Atom 1–Atom 2	Distance	Atom 2–Atom 1–Atom 3	Angle	Atom 2–Atom 1–Atom 3	Angle
C(1)–N(2)	1.502(10)	C(1)–C(6)	1.500(10)	N(2)–C(1)–C(6)	108.7(6)	N(2)–C(1)–C(7)	103.8(6)
C(1)–C(7)	1.565(13)	N(2)–C(3)	1.299(9)	C(6)–C(1)–C(7)	108.4(7)	C(1)–N(2)–C(3)	112.6(6)
N(2)–H(N2)	1.30(10)	C(3)–C(4)	1.524(10)	N(2)–C(3)–C(4)	116.1(6)	N(2)–C(3)–C(11)	121.0(7)
C(3)–C(11)	1.440(10)	C(4)–C(5)	1.535(11)	C(4)–C(3)–C(11)	122.9(6)	C(3)–C(4)–C(5)	106.5(7)
C(4)–C(8)	1.631(12)	C(5)–C(6)	1.348(9)	C(3)–C(4)–C(8)	106.1(6)	C(5)–C(4)–C(8)	107.2(6)
C(5)–N(6)	1.332(10)	C(6)–C(14)	1.412(11)	C(4)–C(5)–C(6)	110.9(6)	C(4)–C(5)–N(6)	120.5(6)
C(7)–C(8)	1.544(11)	C(8)–C(15)	1.543(12)	C(6)–C(5)–N(6)	128.5(7)	C(1)–C(6)–C(5)	115.6(7)
C(8)–C(16)	1.513(12)	C(11)–C(13)	1.413(10)	C(1)–C(6)–C(14)	123.4(7)	C(1)–C(7)–C(8)	110.8(7)
				C(4)–C(8)–C(7)	105.6(7)	C(4)–C(8)–C(15)	108.4(6)
				C(4)–C(8)–C(16)	110.4(7)	C(3)–C(11)–C(12)	117.6(7)
				C(3)–C(11)–C(13)	126.5(7)	C(12)–C(11)–C(13)	115.9(7)

a) Bond distances and angles are in angstroms and degrees, respectively. Estimated standard deviations are given in parentheses.

spectra.

The ORTEP drawings and numbering schemes of **1** and **1-K** are shown in Figs. 2 and 3. Although the perspective structures of both materials are almost the same, several significant differences in bond lengths are observed around atoms C(1), N(2), C(3), C(4), and C(11), probably due to resonance as listed in Table 2 and 3. The interatomic distances of N(2)–C(3) and C(3)–C(11) showed double bond character in **1**. Although the anion in **1-K** delocalized around atoms N(2), C(3), C(11), and two cyano groups, C(3)–C(11) showed a rather long distance in **1-K**. Other apparent differences between **1** and **1-K** were observed in IR spectra. A cyano group at 2210 cm^{-1} in **1** shifted to 2160 cm^{-1} in **1-K** was assigned to two cyano groups adjacent to the anion, while another peak at 2190 cm^{-1} did not move. An intense peak at 1572 cm^{-1} assigned to the double bond C(3)–C(11) in **1** shifted to 1510 cm^{-1} in **1-K**.

The seven atoms N(2), C(3), C(11), and two cyano groups in both materials are almost coplanar. Since deprotonation occurs from this system in **1-K**, the anion is assumed to be delocalized within the system. The electron density of amino group (N(6)) seemed to shift to the cyano group (C(11)–N(7)) through the double bond (C(5)–C(6)). C(6) of **1** and **1-K** was obseved at a rather high field in ^{13}C NMR (about 78 ppm).

These unsaturated systems favorably release

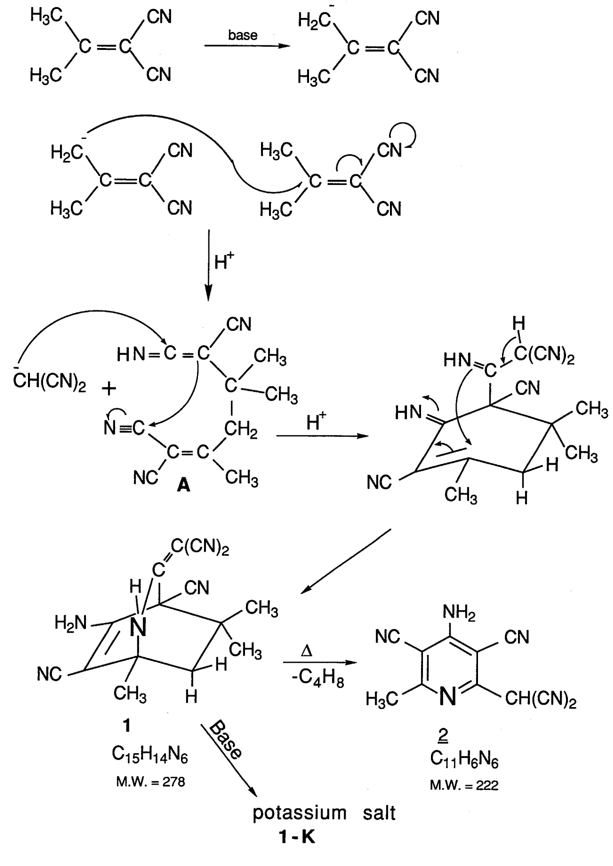

Fig. 4. A possible reaction mechanism for the condensation reaction.

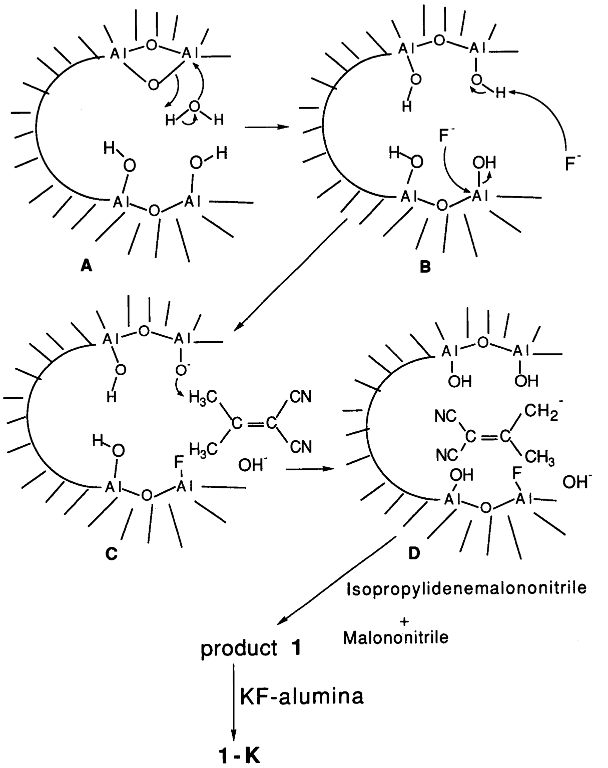

Fig. 5. A possible model of the alumina cluster.

isobutylene to give an aromatic ring. Compounds **1** and **1-K** release isobutylene at 160 °C and 120 °C, respectively. Two single bonds, C(1)–C(7) and C(4)–C(8), in **1-K** are longer than those in **1**. These rather long bond distances were reflected to the releasing point of isobutylene.

Mechanism of the Condensation Reactions. The structures of the two products enabled us to propose the reaction mechanism shown in Fig. 4. At the initial stage of the condensation reaction, the usual Knoevenagel reaction occurred, since the oil separated from the reaction mixture after 3 h was found to be isopropylidenemalononitrile. Posner proposed a model of the inner space in a well calcined alumina cluster.[2] On the other hand, Clark recognized the effects of a trace amount of water on the well-dried alumina in such condensation reactions.[10] Ando proposed similar models and some active species in KF-alumina clusters, and furthermore confirmed the release of OH^- ion.[11] Considering both models and our results, a possible model was proposed in aqueous system as shown in Fig. 5. Active species remove protons from isopropylidenemalononitrile to form an anion. The isopropylidenemalononitrile anion in the cluster can react with one more isopropylidenemalononitrile molecule and finally with a malononitrile anion. Within such a cluster, the entropy of activation will decrease, only if requisit species enter into the cluster. When a large amount of catalyst is used, the product may encounter the active site of the catalyst so many times that H(N2) may dissociate to form **1-K**. Since the potassium salt (**1-K**) was formed with K_2CO_3–alumina more than the reaction with KF–alumina, K_2CO_3–alumina seems to be more basic than KF–alumina.

Reactions with other ketones will be reported later.

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