The Reaction of Nitriles under High Pressure. II. The Catalytic Effects of Amines and Water on the Formation of Trisubstituted 1,3,5-Triazines from Nitriles[1]

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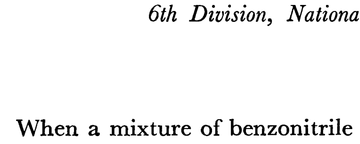
When a mixture of benzonitrile and methanol is kept under a high pressure of a few thousand atoms at an elevated temperature, methyl benziminoether is produced and trimerized to triphenyl-1,3,5-triazine.[1] In the present study it was confirmed that the addition of ammonium salts or some nucleophiles with an active hydrogen atom such as water, amines, and ammonia at several per cents in the molar fraction increases the rate of the formation of this triazine by several times. It was found that the nucleophilic benzamidines produced by the reaction of benziminoether with amines attacked the second molecule of the iminoether and successively took the third iminoether molecule to form a triazine ring. The addition of water to the nitrile–methanol mixture produced amidine, methyl ester, amide, and amidinium carboxylate, of which the carboxylate exhibited the highest promotive effect. Some benzamidines were obtained in fairly good yields from amines and benzonitrile under similar high-pressure conditions. It is thought that this could be useful for synthesizing amidines.

It was found in a previous study[1] that triphenyl-1,3,5-triazine (TPT) is formed under high pressures by the cyclotrimerization of the benziminoether produced from benzonitrile and alcohol and that the triazine formation proceeds through the following reactions:

$$C_6H_5CN + ROH \longrightarrow C_6H_5C(=NH)OR \qquad (1)$$

$$2\ C_6H_5C(=NH)OR \xrightarrow[\text{slow}]{-ROH} [C_6H_5C(OR)=NC(=NH)C_6H_5]$$



+ 2 ROH (2)

TPT

The formation was promoted by the addition of a dipolar aprotic substance such as dimethylformamide.[1] In the present investigation, the influence of protic substances other than alcohol on this reaction was examined under high pressures up to 10000 kg/cm^2.

It was revealed that the cyclotrimerization was intensely promoted by amidines or their salts, which were produced by the reaction of iminoether with substances such as water, ammonia, ammonium salts, and primary or secondary amines. These substances were added in catalytic amounts. The catalytic effects of these nucleophiles and salts were compared with the results obtained by Cairns, Larchar, and McKusick with ammonium acetate and concentrated aqueous ammonia as catalyzers[3] and with the results obtained by Kume and Moriyoshi with water.[4]

Results and Discussion

Influence of Amines. In contrast to the limited effect of tertiary amines with no active hydrogen atoms, ammonia, and primary or secondary amines showed a marked promotive effect on the production of TPT from benzonitrile in the presence of methanol, as is shown in Table 1. Methyl benziminoether (MBI),

Table 1. Effect of various amines on the formation of TPT in the mixture of benzonitrile and methanol[a]

Exp. No.	Amines	C_6H_5CN: CH_3OH: Amine[b] (molar ratio)	Yields (%)[c]			
			C_6H_5CN	MBI[f]	TPT[f]	$C_6H_5C(=NH)NR^1R^2$[d]
1	—	1 : 3.2 : 0	56.7	41.8	1.6	
2	NH_3	1 : 3.2 : 0.05	38.0	38.6	18.3	4.6
3	n-$C_4H_9NH_2$	1 : 3.2 : 0.14	52.1	9.5	14.0	14.3
4	$(C_2H_5)_2NH$	1 : 3.2 : 0.14	46.7	8.8	28.3	6.6
5	$(C_2H_5)_3N$[e]	1 : 2.5 : 0.20	82.9	6.9	1.0	
6	Pyridine[e]	1 : 2.7 : 0.20	74.2	19.9	3.4	
7	$(C_2H_5)_2NH$	1 : 0 : 1	100			

a) Reaction conditions: 6600 kg/cm^2, 100 °C, 10 hr.
b) Molar ratio in the initial mixtures.
c) Theoretical yield based on benzonitrile.
d) R^1, R^2: H or alkyl groups corresponding to those of the added amines.
e) Results of these two runs have already been reported.[1]
f) The abbreviations of methyl benzimino ether and triphenyl-1,3,5-triazine respectively.

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[1] Part I of this series: M. Kurabayashi, K. Yanagiya, and M. Yasumoto, This Bulletin, **44**, 3413 (1971).

[2] The name of this Institute, Government Chemical Industrial Research Institute, Tokyo, was formally changed in April, 1972.

[3] T. L. Cairns, N. W. Larchar, and R. C. McKusick, US 2503979 (1950).

[4] Y. Kume and T. Moriyoshi, Presented at the 6th Meeting of the High-Pressure Symposium, Tokushima, Japan, 1964.

Table 2. Effect of benzamidine on the formation of TPT in relation to that of ammonia[a]

Exp. No.	Promoter	C_6H_5CN : CH_3OH : Promoter (molar ratio)	Yields (%)			
			C_6H_5CN	MBI	TPT	$C_6H_5C(NH)NH_2$
1	—	1 : 3.2 : 0	56.7	41.8	1.6	
2	NH_3	1 : 3.2 : 0.05	38.0	38.6	18.3	4.6
8	$C_6H_5C(NH)NH_2$	1 : 3.2 : 0.05	34.1	35.2	29.9	4.5

a) Reaction conditions were the same as those in Table 1.

which was found to be an intermediate[1] in the above scheme of Eq. (1), was detected again in every run of the present experiment. Benzamidines were formed when benzonitrile, methanol, and one of the following substances ammonia and primary and secondary amine, were employed. These experimental results, as well as the fact that amidines are synthesized from amines and iminoethers under atmospheric pressure,[5] indicate that the benzamidines were produced by the reaction of amines with the intermediate, MBI:

$$\underset{\text{MBI}}{C_6H_5C({=}NH)OCH_3} + RR'NH \longrightarrow C_6H_5C({=}NH)NRR' + CH_3OH \qquad (3)$$

R, R′: H or alkyl group

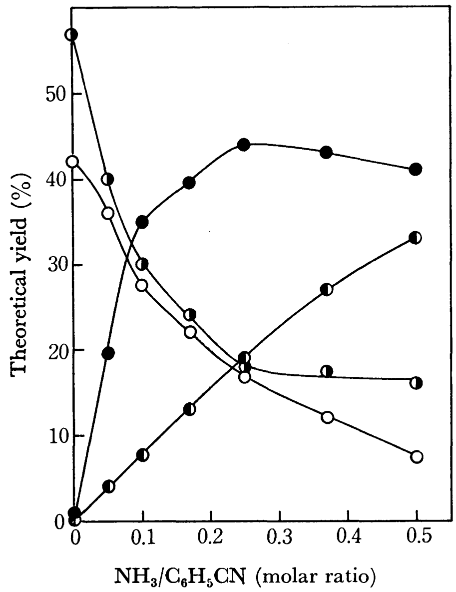

Fig. 1. Dependence of the yields of the reaction products on the amount of ammonia added to the mixture C_6H_5CN: $CH_3OH=1$: 3.2 in mol, at 6800 kg/cm² and 100 °C for 10 hr. ●: TPT, ◑: C_6H_5CN, ○: MBI, ◐: $C_6H_5C(=NH)NH_2$.

Figure 1 shows the relationship between the amount of ammonia added to the benzonitrile–methanol mixture and the amounts of the reaction products. The yield of benzamidine increased with the increase in the amount of ammonia added. The yield of TPT increased to a maximum when the amount of ammonia increased to 25 per cent in the molar fraction; above this fraction the yield decreased gradually, probably because of a decrease in [MBI]×[Benzamidine]. This may be evident from the mechanism described later. The increase in the rate of TPT formation by the addition of ammonia or amines may be assumed to be due to the catalytic effect of amidines derived from these additives. The assumption is supported by the experimental results listed in Table 2, which indicates that, in Exp. 8, the addition of benzamidine only 5 per cent of benzonitrile in the molar fraction yielded a large amount of TPT in the benzonitrile–methanol mixture in contrast to the small yield obtained without any additives in Exp. 1. On the other hand in Exp. 2 the addition of ammonia, the same molar fraction as the added benzamidine in Exp. 8, gave a fairly good yield of TPT amounting to 3/5 of that in Exp. 8 and yielded benzamidine in an amount nearly stoichiometrical to the added ammonia.[6]

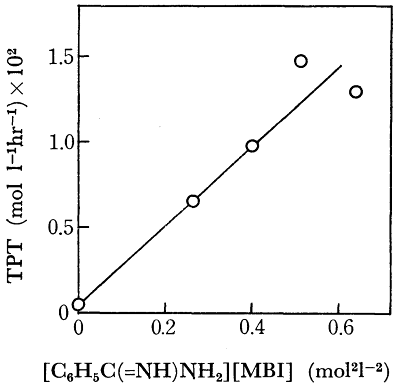

Fig. 2. Relation between the mean rate* of the formation of TPT and the concentrations of bemzamidine and MBI in the mixture C_6H_5CN: CH_3OH: $NH_3=1$: 3.2: 0—0.5 in mole, at 4500 kg/cm² and 100 °C for 10 hr.
* The mean rate of the formation of TPT (in mol $l^{-1}hr^{-1}$) is the value of the concentration of TPT divided by the reaction time. The volume of the reaction medium is assumed to be the sum of each volume of the initial material in the atmospheric pressure.

An approximately linear relationship was found between the rate of TPT formation and [MBI]×[Benzamidine] in Fig. 2. This suggests that TPT is produced *via* a rate-determining reaction in which an intermediate, *N*-benzimidoylbenzamidine(I), is formed by an attack of nucleophilic benzamidine on the carbon atom of MBI. This step is expected to proceed more favorably than the rate-determining reaction, Eq. (2), without a catalyzer. This is because benzamidine is a stronger nucleophile (base) than MBI. This step may be followed by the cyclic addition of another molecule

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[5] R. L. Schriner and F. W. Neumann, *Chem. Rev.*, **35**, 351 (1944); E. S. Hand and W. P. Tencks, *J. Amer. Chem. Soc.*, **84**, 3505 (1962); F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961).

[6] The existence of a benzamidine-rich equilibrium among methyl benziminoether, ammonia, benzamidine, and methanol under high pressures has been confirmed.

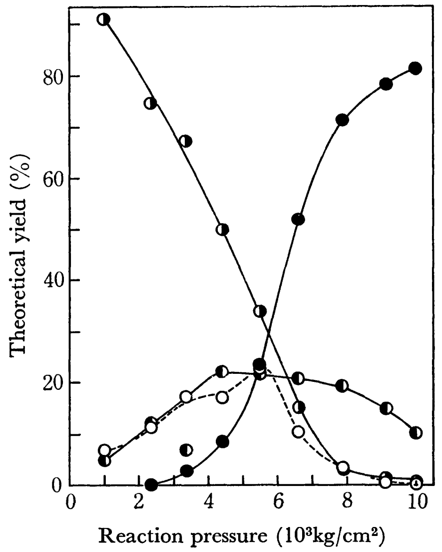
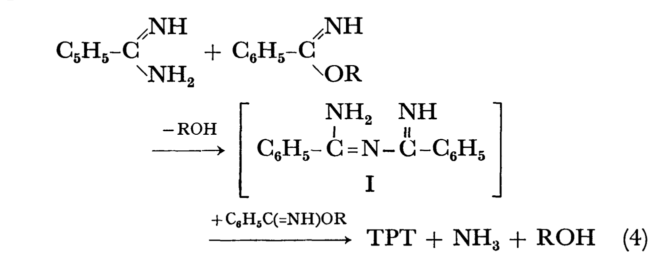


Fig. 3. Dependence of the yields of the reaction products in the mixture C_6H_5CN: CH_3OH: NH_3=1: 3.2: 0.25 in mole on the reaction pressure, at 110 °C for 10 hr.
●: TPT, ◑: C_6H_5CN, ○: MBI, ◐: $C_6H_5C(=NH)NH_2$.

of MBI to form TPT. This mechanism may be expressed as follows:



$$C_5H_5\text{-}C\begin{smallmatrix}{\nearrow}NH\\ {\searrow}NH_2\end{smallmatrix} + C_6H_5\text{-}C\begin{smallmatrix}{\nearrow}NH\\ {\searrow}OR\end{smallmatrix} \xrightarrow{-ROH} \left[C_6H_5\text{-}\overset{NH_2}{\overset{|}{C}}=N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}C_6H_5 \right]_{\text{I}} \xrightarrow{+C_6H_5C(=NH)OR} TPT + NH_3 + ROH \quad (4)$$

Figure 3 shows that the effect of the pressure on the formation of TPT in the presence of ammonia is as remarkable as in the absence of ammonia.[1]

Influence of Water. As is shown in Table 3 and Figs. 4 and 5, one of the remarkable effects of the water added to the benzonitrile–methanol mixture is the intense promotion of the TPT formation; another is the formation of benzamide, methyl benzoate, benzamidine, and benzamidinium benzoate. Some experiments were carried out in order to clarify the mechanism of the catalytic effect of water.

The same molar fractions of the by-products described above and some compounds related to the by-products were added to the benzonitrile–methanol mixture. The results of these experiments are listed in Table 4. Of these additives, benzamidinium benzoate and ammonium acetate promoted the TPT formation most. It is certain that the ammonium acetate added to the

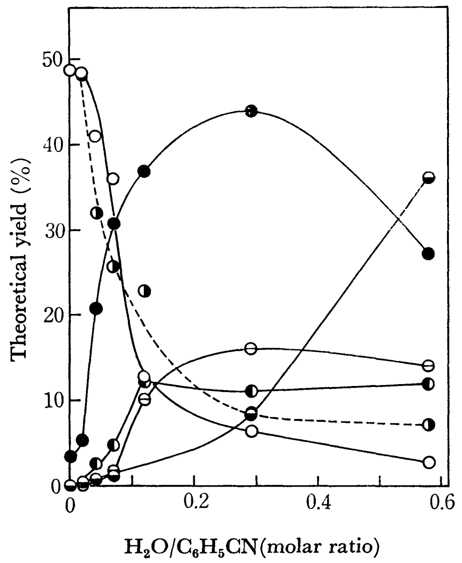


Fig. 4. Dependence of the yields of the reaction products on the amount of water added to the mixture C_6H_5CN: CH_3OH=1: 3.2 in mole, at 6800 kg/cm² and 100 °C for 10 hr.
●: TPT, ◑: C_6H_5CN, ○: MBI, ◒: $C_6H_5CONH_2$, ◐: $C_6H_5CO_2CH_3$, ⊖: $C_6H_5C(NH_2)_2\cdot C_6H_5CO_2$.

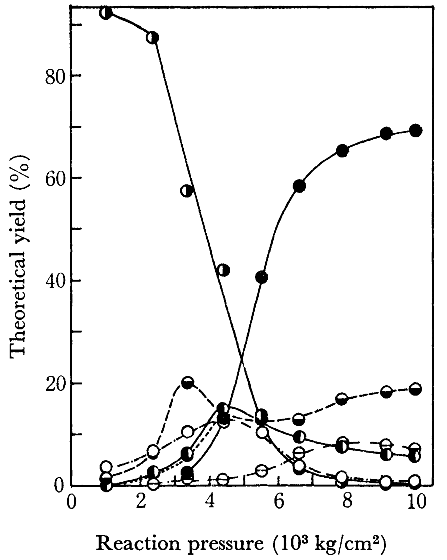


Fig. 5. Dependence of the yields of the reaction products in the mixture C_6H_5CN: CH_3OH: H_2O=1: 3.2: 0.25 in mole on the reaction pressure, at 110 °C for 10 hr.
●: TPT, ◑: C_6H_5CN, ○: MBI, ◒: $C_6H_5CONH_2$, ⊖: $C_6H_5C(NH_2)_2\cdot C_6H_5CO_2$, ◐: $C_6H_5CO_2CH_3$, ------: $C_6H_5C(NH)NH_2$*.
* Determination of benzamidine was done only when the reaction pressure was less than 4400 kg/cm².

TABLE 3. EFFECT OF WATER ON THE FORMATION OF TPT IN THE MIXUTRE OF BENZONITRILE AND METHANOL[a)]

Exp. No.	C_6H_5CN: CH_3OH: H_2O (molar artio)	Yields (%)						
		C_6H_5CN	MBI	TPT	$C_6H_5C(=NH)$ $-NH_2$	$C_6H_5C(NH_2)_2$ $\cdot C_6H_5CO_2$	$C_6H_5CONH_2$	$C_6H_5CO_2CH_3$
1	1 : 3.2 : 0	56.7	41.8	1.6				
9	1 : 3.2 : 0.04	32.4	41.0	20.6	+	1.5	1.1	2.6

a) Reaction conditions were the same as those in Table 1.

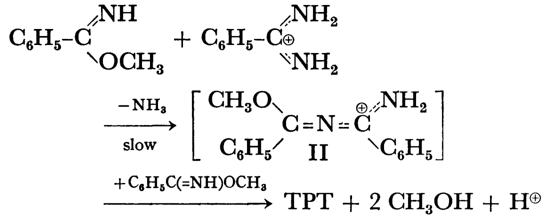
Table 4. Effects of both the by-products produced in the water-added mixture of benzonitrile and methanol and some reagents related to them on the formation of TPT in the benzonitrile and methanol mixture[a)]

Exp. No.	By-product and reagent	$C_6H_5CN : CH_3OH$: B&R (molar ratio)	Yields (%)						
			C_6H_5CN	MBI	TPT	C_6H_5C-(=NH)NH_2	$C_6H_5C(NH_2)_2\cdot C_6H_5CO_2$	C_6H_5-$CONH_2$	$C_6H_5CO_2$-CH_3
1	—	1 : 3.2 : 0	56.7	41.8	1.6				
8	$C_6H_5C(NH)NH_2$	1 : 3.2 : 0.05	34.1	35.2	29.9	4.5			
10	$C_6H_5C(NH_2)_2\cdot C_6H_5CO_2$	1 : 3.2 : 0.05	12.9	6.8	74.1	+	+		
11	$C_6H_5CONH_2$	1 : 3.2 : 0.05	30.9	41.1	20.2	+	+	−2.2[b)]	4.4
12	$C_6H_5CO_2CH_3$	1 : 3.2 : 0.05	53.4	36.5	7.4				+
13	$NH_4\cdot CH_3CO_2$	1 : 3.2 : 0.05	11.3	11.9	67.9	+	+		
14	$K\cdot CH_3CO_2$	1 : 3.2 : 0.05	18.5	15.1	1.0				

a) Reaction conditions were the same as those in Table 1.

b) Remainder of the substruction of the amount of the added benzamide from that of the observed benzamide in the reaction mixture.

benzonitrile–methanol mixture was converted to benzamidinium acetate, because several amidine salts are synthesized from iminoether salts and ammonia under atmospheric pressure. The fact that sodium acetate had no influence means that the formation of TPT is not influenced by a usual electrolyte. Therefore, the catalytic effects of those salts may be attributed merely to the benzamidinium cation. Figure 4 shows the noticeable yield of benzamidinium benzoate in the reaction with added water. Considering the strong effect of the amidinium cation as a catalyzer, it is likely that the greater part of the promotive effect of water is caused by the benzamidine benzoate derived from water. The rate-determining reaction is inferred to be the attack of the imino-nitrogen of MBI on the strongly positive carbon atom of the benzamidinium cation, which gives *N*-methoxybenzylidenebenzamidinium cation (II) as an intermediate. The whole reaction course is proposed to be as follows:



$$C_6H_5\text{-}C(=NH)OCH_3 + C_6H_5\text{-}C^{\oplus}(NH_2)_2 \xrightarrow[\text{slow}]{-NH_3} \left[\begin{matrix} CH_3O \\ C_6H_5 \end{matrix} \!\!>\! C{=}N{=}\overset{\oplus}{C}(NH_2)C_6H_5 \right]_{\text{II}} \xrightarrow{+C_6H_5C(=NH)OCH_3} \text{TPT} + 2\,CH_3OH + H^{\oplus} \qquad (5)$$

The structures of (I) and (II) are supported by the literature, in which similar compounds with a polyperhalogenomethylene group have been reported.[7)]

The route of the formation of methyl benzoate may be assumed to be Eq. (6), since the rapid hydrolysis of iminoether into the ester and ammonia under atmospheric pressure is well known:

$$C_6H_5C(=NH)OCH_3 + H_2O \longrightarrow C_6H_5COOCH_3 + NH_3 \qquad (6)$$

The ammonia thus liberated will attack MBI to give benzamidine by means of Eq. (3). The nearly equimolar yields of the ester and amidine in the low pressure range shown in Fig. 5 support this reaction scheme.

The experiments shown in Table 5 were carried out to determine the route of benzamide formation in the benzonitrile–methanol mixture. The results of Exp. 15 shows that benzamide is produced more or less by the direct hydration of benzonitrile:

$$C_6H_5CN + H_2O \longrightarrow C_6H_5CONH_2 \qquad (7)$$

However, when Exp. 15 is compared with Exp. 16, it appears that there is another route yielding benzamide with the aid of methanol. The hydrolysis of benzamidine is most likely, since this hydrolysis is known to take place smoothly under atmospheric conditions:

$$C_6H_5C(=NH)NH_2 + H_2O \longrightarrow C_6H_5CONH_2 + NH_3 \qquad (8)$$

The hydrolysis of MBI to benzamide has not been reported. The ammonolysis of methyl benzoate is unlikely, since the reverse reaction, the methanololysis of benzamide to methyl benzoate, proceeds (see Exp. 17):

$$C_6H_5CONH_2 + CH_3OH \longrightarrow C_6H_5COOCH_3 + NH_3 \qquad (9)$$

Benzamide promotes the TPT formation, as may be seen in Exp. 11 in Table 4. The promotion mechanism may be partially explained by Eq. (9).

The route of the formation of benzamidinium benzoate has not yet been clarified, although the overall reaction may be expressed as follows:

$$C_6H_5C(=NH)NH_2 + C_6H_5COOCH_3 + H_2O \longrightarrow C_6H_5C(=NH)NH_2\cdot C_6H_5COOH + CH_3OH \qquad (10)$$

Figures 4 and 5 show that the total amount of benzamide, methyl benzoate, and benzamidinium benzoate was nearly stoichiometrical to the added water. This indicates the fair stability of these by-products. Of these by-products, benzamide amounted to the largest part when much water was added. The addition of a small amount of water may be effective to obtain TPT in a good yield. The marked positive effect of pressure on the production of TPT as well as on the production of the by-products is shown in Fig. 5.

[7)] The polymer of perfluorogultaric acid (H. C. Brown, *J. Polymer Sci.*, **44**, 9 (1960)) and $CCl_3C(=NH)NHC(=NH)CCl_3$ (F. C. Schaefer, G. A. Peters, and V. P. Wystrach, *J. Amer. Chem. Soc.*, **81**, 1466 (1959)) correspond to (I). The hydrochloride of the dimer of perfluoroadipo(or glutaro-)iminoether (A. Ya. Yakubovcih, *et al.*, *J. General Chem. USSR*, **36**, 878 (1966)) corresponds to (II).

Table 5. Action of water on benzonitrile in the presence or absence of methanol, and the reaction of the resulting benzamide with methanol[a)]

Exp. No.	C_6H_5CN:CH_3OH:H_2O:$C_6H_5CONH_2$ (molar ratio)	Yield (%)						
		C_6H_5CN	MBI	TPT	C_6H_5C-(=NH)NH_2	$C_6H_5C(NH_2)_2$ $\cdot C_6H_5CO_2$	C_6H_5-$CONH_2$	$C_6H_5CO_2$-CH_3
15	1 : 0 : 1.15 : 0	86.1					11.2	
16	1 : 0.4 : 1 : 0	9.0		1.7			89.6	1.0
17	0 : 1 : 0 : 0.16						81.2[b)]	19.2[b)]

a) Reaction conditions were the same those as in Table 1.
b) These were calculated based on benzamide.

Table 6. Effect of water on the trimerization of acetonitrile in the methanol solution[a)]

Exp. No.	CH_3CN:CH_3OH:H_2O (molar ratio)	Yield (%)			
		CH_3CN	TMT[c)]	CH_3CONH_3	$CH_3CO_2CH_3$
18	1 : 1.28 : 0	92.1	6.3		
19	1 : 1.22 : 0.12	48.0	38.9	5.4	3.8
20	1 : 1.15 : 0.23	28.7	39.9	13.2	5.2

a) Reaction conditions were similar to those in Table 1.
b) Theoretical yield based on acetonitrile.
c) The abbreviation of trimethyl-1,3,5-triazine.

Table 7. Preparation of benzamidines under high pressure[a)]

Exp. No.	Amine	C_6H_5CN:CH_3OH: Amine (molar ratio)	Yield (%)[b)]			
			C_6H_5CN	MBI	Amidine	TPT
21	NH_3	1 : 3.2 : 0.5	16.3	7.4	33.0 (65.7)	41.1
22	n-$C_4H_9NH_2$	1 : 1.5 : 0.7	16.6	3.2	69.1 (98.7)	4.8
23	$(C_2H_5)_2NH$	1 : 1.5 : 0.7	40.0	7.6	32.0 (44.6)	11.8

a) Reaction conditions were similar to those in Table 1.
b) Theoretical yield based on benzonitrile.
c) Theoretical yield based on the amine.

The reaction products in the mixtures of several combinations of acetonitrile, methanol, water, and acetamide under high pressures are listed in Table 6; the table indicates that the behavior of water in the acetonitrile–methanol mixture is similar to that in the benzonitrile–methanol mixture.

Reaction Conditions for Synthesizing Trisubstituted 1,3,5-Triazines. It is known that noticeable amounts of trisubstituted 1,3,5-triazines are produced in nitrile–alcohol mixtures without a catalyzer under pressures of more than 4000 kg/cm^2 and at temperatures of more than 100 °C.[1,2)] The rate of the triazine formation increases with an increase in the pressure or with an increase in the equilibrium concentration of iminoether.[1)] This concentration is altered parallel with the pressure and is dependent on the choice of nitrile and alcohol.[1)] The elevation of temperature increases the rate.[1)] However, at temperatures above 140 °C the formation of a by-product, *N*-methylbenzamidine,[8)] was remarkable in the benzonitrile–methanol mixture. The employment of the catalyzers described above may give rise to a rapid progress of the triazine formation, even in somewhat low ranges of the temperature and the pressure.

New Preparative Method of Amidines. Figure 3 shows that the yield of benzamidine increased, until it was nearly stoichiometrical to the added ammonia when the reaction pressure increased to about 5000 kg/cm^2, above that pressure range it gradually decreased. Those facts suggest the usefulness of this high-pressure reaction for preparing amidines by means of a good selection of reaction conditions. This usefulness is supported by the results listed in Table 7. This procedure is thought to be an excellent method for preparing amidines from nitriles because it does not need any catalyzer. The known one-step methods all require the keeping of nitriles at fairly elevated temperatures with more drastic agents than methanol, such as, ammonium halide, ammonium salts in ammonia,[9)] mixtures of amines and Lewis acids,[10)] and metal amides in benzene or ammonia.[11)]

Experimental

Reaction Apparatus and Procedure. An initial mixture for a reaction was placed in a collapsible lead capsule and was then kept in the desired conditions of pressure and tempera-

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[8)] The route of the formation of the *N*-substituted amide is still unsolved, although one conceivable route is the Chapman rearrangement of the iminoether. The formation of *N*-methyl-2,3,3-tricyanoacrylamide from tetracyanoethylene and methanol at 5000 kg/cm^2 has been reported (M. Price and J. Horniak, *Chem. Commun.*, **1966**, 455).

[9)] E. F. Cornell, *J. Amer. Chem. Soc.*, **50**, 3311 (1928).

[10)] F. C. Schaefer and A. P. Krapcho, *J. Org. Chem.*, **27**, 1255 (1962).

[11)] P. Oxley, M. W. Partridge, and W. F. Short, *J. Chem. Soc.*, **1947**, 1110.

ture for the desired time, as has been described previously.[1]

Material Supply. The drying and distillation of EP-grade reagents, such as acetonitrile, benzonitrile, methanol, *n*-butylamine, diethylamine, and methyl benzoate, supplied this experiment with the samples of these substances. The water contents of benzonitrile and methanol were less than 0.017 per cent. Ammonia of a chemical grade was evaporated, dried on sodium hydroxide, and absorbed in methanol. The benzamide, ammonium acetate, and potassium acetate were of an EP-grade. The benzamidine was prepared from ethyl benziminoether hydrochloride[1] and ammonia[12] (mp 68.3 °C (80[13])). The melting point of the picrate was 228.5 °C. The benzamidinium benzoate was obtained by mixing an ethereal solution of benzoic acid with a stoichiometric amount of the benzamidine in a benzene solution and by recrystallizing the resulting raw product from water (mp 234.0 °C). Trimethyl-1,3,5-triazine (TMT) was prepared as follows: ethyl acetiminoether hydrochloride was prepared from acetonitrile and ethanol by Pinner's method. The iminoether was liberated by neutralization, fractionated at 87—90.5 °C, mixed with acetic acid (8 mol per cent of the iminoether), and kept at room temperature overnight.[14] The resulting TMT was extracted and distilled. The yield was 50.7 per cent (based on the iminoether) (bp 155 °C (155[14])); C, 58.38 (Calcd 58.52); H, 7.64 (7.37); N, 34.44% (34.12)).

Identification of Reaction Products. *MBI and TPT*: These substances were identified in a manner described previously.[1]

Amidines: A mixture of benzonitrile, ammonia, and methanol (1: 0.25: 3.2 in mole) was kept at 5500 kg/cm^2 and 110 °C for 10 hr. The reaction mixture was then separated from a volatile matter *in vacuo* and from TPT by extraction with toluene. A methanolic solution of picric acid was added to this mixture. Benzamidine picrate was precipitated and recrystallized from water to give yellow needles (mp 229 °C (232[15])); C, 44.73 (44.71); H, 3.01 (3.18); N, 20.51% (20.05); Infrared (IR) spectrum, 3400, 3200, 1675, and 1610 cm^{-1} for the amidinium group). The melting point was not decreased by mixing this picrate with the authentic sample described above. *N*-*n*-butylbenzamidine was collected at 170 °C by the fractionation of the reaction mixture of Exp. 22 by means of preparative gas-liquid phase chromatography (glc) (Reoplex-400, 9×750 mm, 70—200 °C, 4 °C/min, He 150 ml/min) (C, 74.52 (74.96); H, 9.22 (9.15); N, 15.42% (15.89); IR, 3250, 3050, 2930, 1645, 1600, 1570, 1360, 1190, 775, and 690 cm^{-1}). *N*,*N*-diethylbenzamidine was collected at 146 °C by the fractionation of the reaction mixture of Exp. 23 by the same procedure (C, 74.92 (74.96); H, 9.02 (9.15); N, 15.65% (15.89); IR, 3320, 3050, 2980, 1585, 1570, 1445, 1380, 1225, 1175, 775, and 700 cm^{-1}).

Benzamidinium Benzoate: A mixture of benzonitrile (2.39 g), methanol (2.29 g), and water (0.105 g) (1: 3.2: 0.25 in mol) was kept at 8000 kg/cm^2 and 110 °C for 10 hr. TPT was removed from the reaction mixture by filtration, and the volatile products were evaporated. The remaining crude benzoate, which amounted to 0.22 g (mp 210 °C; yield, 7.9% based on benzonitrile), was washed with toluene and recrystallized from water (mp 222.8 °C (230[16])); C, 69.53 (69.40); H. 5.91 (5.82); N, 11.65% (11.56); IR, 3200, 3000, 1710, 1610, 1570, 1520, 1490, 1390, 1035, 840, 720, and 690 cm^{-1}). The melting point was not decreased by mixing this crystal with the sample described above. The IR spectrum agreed with that of the sample as well.

Benzamide and N-*Methylbenzamide*: A mixture of benzonitrile (2.3 g), methanol (2.3 g), and water (0.10 g) (1: 3.2: 0.25 in mol) was kept at 4400 kg/cm^2 and 170 °C for 10 hr. The reaction mixture was fractionated by preparative glc (Reoplex-400, 9×750 mm, 100—205 °C, 4 °C/min, He 125 ml/min). *N*-Methylbenzamide (0.1 g) (4% based on the benzonitrile) was collected at 190—205 °C (mp 62.5 °C(75[17]); C, 71.33(71.09); H, 6.51(6.71); N, 10.27%(10.36); mol wt (from a parent peak of mass spectroscopy (MS)), 135(135.16); IR, 3350, 3050, 2950, 1640, 1550, 1490, and 1410 cm^{-1}). Benzamide was collected at 250 °C to give (0.8 g) (29% based on the benzonitrile). The melting point, 122 °C (128[13]), and the IR spectrum agreed with those of the authentic sample.

Methyl Benzoate and Acetate: Their presence in the reaction mixtures was assured by the agreement with the authentic samples on glc.

TMT: The reaction mixture of Exp. 19 was fractionated by preparative glc (DNP, 9×750 mm, 100 °C—, 2 °C/min, He 125 ml/min) to give 0.4 g at 121—127 °C (mp 58 °C (59—60[3])); C, 58.21(58.52); H, 7.48(7.37); N, 32.42%(34.12); mol wt (MS), 123 (123.15); IR, 2930, 1560, 1540, 1390, 1020, 925, and 765 cm^{-1}). The melting point, the retention time of glc, and the IR spectrum agreed with those of the authentic sample described above.

Acetamide: The reaction mixture of Exp. 20 gave 0.07 g at 150—174 °C by prepartive glc (Versamide, 9×750 mm, 60 °C—, 6 °C/min, He 125 ml/min) mp 73.5 °C(82.0[13]); C, 40.65(40.67); H, 8.59(8.53); N, 23.31%(23.71). The melting point, the retention time of glc, and the IR spectrum agreed with those of the authentic sample.

Methyl Acetate: This substance was identified from the agreement of the retention time in the glc of the reaction product of Exp. 20 with that of the authentic sample.

Analysis of Reaction Products. The yields of TPT in the reaction products were determined in a manner previously described.[1] The benazmidine was determined as the picrate. The benzamidinium benzoate was determined as a non-volatile and toluene-insoluble matter. The yields of the reaction products other than the above-mentioned substances were determined by two kinds of glc, Reoplex-400, 3×750 mm, 50—200 °C, 4 °C/min, He 25 ml/min and THEED+TEP, 3×2000 mm, 40—110 °C, 2° C/min, He 25 ml/min.

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