The Reaction of Nitriles under High Pressure. IV. The Replacement of the Substituents of Trialkyl-1,3,5-triazines[1]

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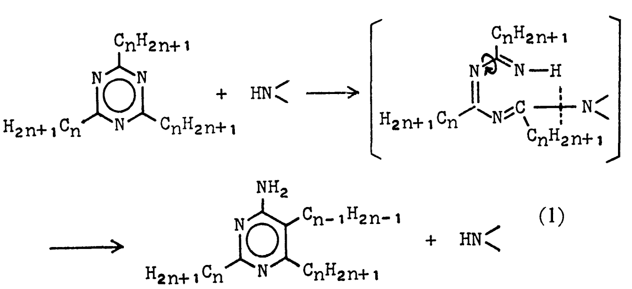
It was found that, when some symmetrically 2,4,6-tri-substituted 1,3,5-triazines are kept with an iminoether or an amidine under high pressures and at elevated temperatures, unsymmetrically 2,4,6-tri-substituted 1,3,5-triazines are produced by way of the replacement of one or two $\diagup N \diagdown \overset{|}{C} \diagup R$ groups of the triazines with the $-N{=}\overset{|}{C}{-}R'$ group of the iminoether or that of the amidine. Several mixtures of nitriles and methanol can be used for this replacement reaction in place of iminoethers or amidines at 4000—8000 atm and 100—150 °C. In these mixtures, equilibrium amounts of methyl iminoethers are rapidly formed. Increases in the size of the substituents of the original triazine and in their electron-releasing power inhibit this replacement reaction. Nitriles with an electron-releasing moiety give tri-substituted triazines replaced selectively by one of the original substituents.

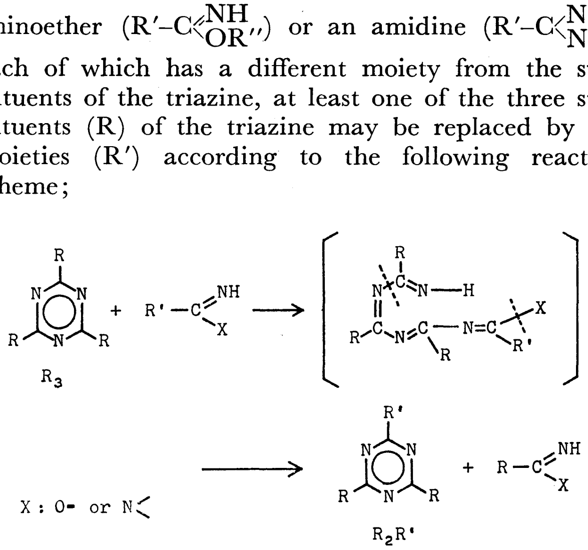
There have been reported no excellent method giving tri-substituted 1,3,5-triazines with two or three different kinds of substituents in a molecule. The stepwise method from cyanuric halide,[2] as one example, requires many synthetic steps and gives a poor yield. The co-trimerization of two kinds of nitriles[3,4] or iminoethers[5] or amidines,[6] and the co-trimerization of an iminoether and an amidine, each of which has a different moiety,[7] as a second example, gives a mixture of four kinds of tri-substituted 1,3,5-triazines, each of which has a different combination of the three substituents. The distribution among the yields of the four triazines was substantially governed by statistical laws, although some cases have been reported in which a triazine with a certain combination of substituents was selectively produced.[4,6,7] The method of substitution on the less available unsubstituted 1,3,5-triazine with iminoethers[8] or amidines,[9] as a third example, gives mono- and di-substituted 1,3,5-triazines, but no tri-substituted one.

It has been made clear[1] that some trialkyl-1,3,5-triazines are rearranged to 4-amino-2,5,6-trialkylpyrimidines by the attack of a nucleophile with an active hydrogen atom, such as primary and secondary amines and ammonia, under a pressure of a few thousand atm in the following manner:



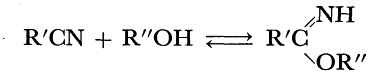
(1)

It was assumed from this rearrangement mechanism that, if a trialkyl-1,3,5-triazine (R_3) is treated with an iminoether ($R'-C\begin{smallmatrix}\diagup NH\\ \diagdown OR''\end{smallmatrix}$) or an amidine ($R'-C\begin{smallmatrix}\diagup NH\\ \diagdown N\langle\end{smallmatrix}$), each of which has a different moiety from the substituents of the triazine, at least one of the three substituents (R) of the triazine may be replaced by the moieties (R′) according to the following reaction scheme;



(2)

On the other hand, it is known[10] that an equilibrium amount of iminoether is quickly formed in a mixture of a nitrile and a lower alcohol by means of Eq. (3):



$$R'CN + R''OH \rightleftarrows R'C\begin{smallmatrix}\diagup NH\\ \diagdown OR''\end{smallmatrix} \qquad (3)$$

Therefore, a mixture of R_3, nitrile R′CN and methanol was kept at 6000—9000 kg/cm^2 and 100—150 °C. As a result, a mono-replaced triazine (R_2R') was obtained in a good yield. The reaction scheme of Eq. (2) was thus proved actually to take place.

Iminoethers and amidines are known to be synthesized from nitriles under atmospheric pressure. Therefore, many mixtures of nitriles and lower alcohols are thought to be better reagents than iminoethers or amidines for this reaction. This finding may offer a

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TABLE 1. EFFECT OF PRESSURE ON THE REACTION OF BENZONITRILE WITH Me_3[a] IN THE PRESENCE OF METHANOL[b]

Reaction pressure (kg/cm^2)	Yields (%)[c]								
	MeCN	PhCN	PhC(=NH)OMe	Me_3[a]	Me_2Ph[a]	$MePh_2$[a]	Ph_3[a]	Pyrimidine[d]	Amidine[d]
2000	11.9	65.9	3.66	81.5	18.1				
4000	40.8	24.9	4.52	41.5	65.7	1.39			
6000	40.4	1.13	0.70	15.8	94.7	2.97	0.43	3.04	1.11
7950	34.2	0.25	trace	16.8	91.6	3.85	0.44	6.30	2.68
8000[e]		72.9		87.4	6.12				

a) These symbols mean the tri-substituted 1,3,5-triazines with the substituents represented by the each symbol.

b) Reaction conditions: mixtures of Me_3, benzonitrile (the same molar amount with Me_3), and methanol (the same weight with Me_3) were kept at 100 °C for 30 hr under the various pressures.

c) Mole fraction based on Me_3.

d) Abbreviations of 4-amino-2,6-dimethylpyrimidine and *N*-2,6-dimethylpyrimidin-4-yl-acetamidine respectively.

e) Methanol was not added.

useful method for the preparation of unsymmetrically tri-substituted 1,3,5-triazines. Some electronic or steric properties of the original substituent and those of the introducing radical, and the relationship between the former and the latter, were shown to have a marked influence on this replacement reaction.

Results and Discussion

The trimethyl-1,3,5-triazine (Me_3), benzonitrile and methanol were kept at 100 °C and 2000—8000 kg/cm^2 as is shown in Table 1. Methanol was chosen from among the lower alcohols because of the highest equilibrium constant in Eq. (3) among those of the lower alcohols.[10] The reaction scheme proposed by Eq. (2) is supported by the fact that, in contrast to the good yield of Me_2Ph and the fair yields of acetonitrile and methyl benziminoether (MBI) in the presence of methanol at 6000—8000 kg/cm^2, only an inconsiderable amount of Me_2Ph was yielded without methanol at the same pressure. The progress of the reaction of Eq. (1) was negligibly slow in comparison with that of Eq. (2).

Table 1 shows the marked positive effect of the pressure on this replacement reaction. The ratio of the yield of Me_2Ph at 4000 kg/cm^2 to that at 2000 kg/cm^2 was 3.63: 1. This pressure effect is assumed to be due to two factors. One of them is an increase in the equilibrium concentration of iminoether in Eq. (3) with an increase in the pressure, and the other is an increase in the rate constant of Eq. (2) with an increase in the pressure. Here Eq. (2) is supposed to be the rate-determining step. The equilibrium concentrations at the initial point of the reactions at 4000 and 2000 kg/cm^2 are calculated on the bases of the experimental results reported in a previous paper.[10] These concentrations amount to 0.733 and 0.360 mol l^{-1} respectively.[11] The ratio of the former to the latter amounts to 2.04: 1.[12] This ratio is considerably smaller than the ratio in the yields of Me_2Ph, 3.67: 1 described above. It is clear from these examinations that the pressure effect depends not only upon the increase in the equilibrium constant with an increase in the pressure, but also partially upon the increase in the rate constant of Eq. (2) with that increase. The latter dependence is supported also by the experimental results listed on the first line of Table 2. On the line it is shown that hardly no substituent of Me_3 was replaced by MBI without an increase in the pressure, even at a high concentration of MBI. This high concentration was attained by starting the reaction with a mixture of benzonitrile, MBI, and methanol; it was kept over the equilibrium level throughout the reaction time. It is clear that this replacement reaction does not take place under a pressure of less than a few thousand atm; it starts either with a mixture of R_3 and iminoether or with a mixture of R_3, nitrile, and alcohol.

TABLE 2. REACTION OF METHYL BENZIMINOETHER WITH Me_3 WITHOUT INCREASING PRESSURE[a]

Additive	Yields (%)[b]					
	PhCN	PhC(=NH)OMe	Me_3	Me_2Ph	$MePh_2$	Ph_3
—	3.50	69.1	102.2	2.95		
Et_3N	24.7	47.2	101.8			
EtONa	54.8	7.23	99.1			
AcOH	36.5	6.07	97.5	5.78		13.0

a) Reaction conditions: Me_3: PhC (NH)OMe: MeOH=1: 1 (in mole): 1 (in weight to Me_3), 100 °C, 30 hr under the saturated pressure of methanol (≈3 kg/cm^2 gauge.). The lead capsules were filled with the mixtures and placed in an autoclave which was filled with methanol to protect the capsules from rupture.

b) Mole percent based on Me_3.

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11) It may be permissible to discuss the results at 100°C on the basis of the data calculated by means of the previously-obtained results at 110°C, because the difference between the pressure dependence of the equilibrium constant at 100°C and that at 110°C is negligible.

12) A smaller value than this can be expected when the calculation is done on the bases of the average concentration in the course of the reaction.

TABLE 3. INFLUENCE OF THE MOLAR RATIO OF Me_3 TO BENZONITRILE IN THE INITIAL MIXTURES ON THE YIELDS OF THE SUBSTITUENT-REPLACED TRIAZINES[a)]

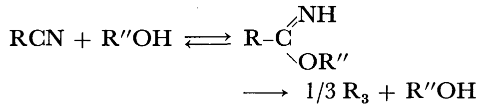
Me_3 (g)	Me_3:PhCN (mol)	PhCN (g)	MeOH (g)	Yields (%)[b]								
				MeCN	PhCN	PhC(=NH)OMe	Me_3	Me_2Ph	$MePh_2$	Ph_3	Pyrimidine	Amidine
0.512	1 : 1	0.430	0.648	24.89			10.2	84.0	7.88	0.24	19.6	4.86
0.465	1 : 1.5	0.586	0.468	26.00	7.33	1.31	3.70	103.6	18.7	1.63	9.05	0.70

a) Reaction conditions: 6000 kg/cm², 150 °C, 30 hr.
b) Mole percent based on Me_3.

Schaefer and Peters reported that, when 1,3,5-triazine was kept with some iminoethers[8)] or amidines,[9)] a substitution took place on the 2- or 2- and 4-position of the triazine through a scheme similar to Eq. (2). This difference in reactivity between substituted and unsubstituted 1,3,5-triazines may be caused by the difference in the electron-releasing power between the substituent and the hydrogen atom and by the difference in size between them (see below).

The mixtures of Me_3, MBI, methanol, and a small amount of acids or bases were kept at 100 °C without increasing the pressure with a view to getting a promoter for this replacement reaction. Table 2 shows that this attempt resulted in failure. Acids and bases did not noticeably influence the replacement, but did promote the dissociation of MBI to benzonitrile and methanol.

It is certain that a nitrile eliminated by Eq. (2) is partly re-cyclized to the original triazine, since it is known that nitrile is cyclotrimerized with the help of a lower alcohol under high pressures by means of Eq. (4):[1,10,13)]



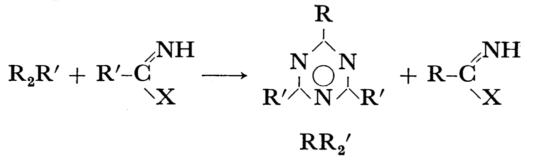
$$RCN + R''OH \rightleftharpoons R\text{-}C\begin{matrix}\nearrow NH\\ \searrow OR''\end{matrix} \longrightarrow 1/3\,R_3 + R''OH \qquad (4)$$

Equation (2) is then transformed as Eq. (5) to give the stoichiometrically maximum ratio of R_2R' to R_3:

$$R_3 + 3/2\,R'CN \longrightarrow 3/2\,R_2R' \qquad (5)$$

The results collected in Table 3 indicate that the employment of more than the equimolar amount of benzonitrile to Me_3 was effective in increaseing the yield of Me_2Ph based on Me_3, although nearly quantitative yield by means of Eq. (5) was less possible because of the progress of such side reaction as Eqs. (1), (4), (6), and (7).

The influence of the property of the nitrile moiety on the replacement reaction was examined by keeping equimolar mixtures of Me_3 and various nitriles in methanol under high pressures. The results are shown in Table 4. In the cases of aromatic nitriles, nearly theoretical yields of Me_2R' were obtained. In the case of propionitrile, the only case of an aliphatic nitrile, not only the yield of Me_2R', but also the sum of the yields of Me_2R' and MeR'_2, was far less than the theoretical yields, while the ratio of the yield of MeR'_2 to that of Me_2R' was larger than those in the cases of aromatic nitriles. From these experimental results, the following considerations may be derived. Aromatic iminoether is more basic than aliphatic iminoether[14)] probably because of the highly resonating structure of the iminium cation with the aromatic moiety. Therefore, aromatic iminoether may be more active in the replacement reaction, but the resulting mono-replaced triazine may be protected from the next replacement by the increasing density of the π-electron on the carbon atoms of the triazine ring. The increase in the density is caused by the strong electron-releasing power of the newly-introduced aromatic substituent. While aliphatic iminoether is less active in the replacement, the resulting mono-replaced triazine is subject to the next replacement, because the next attack of the iminoether may be less inhibited because of the less electron-releasing property of the newly introduced aliphatic substituent;



(6)

TABLE 4. INFLUENCE OF THE MOIETIES OF NITRILES ON THE SUBSTITUENT-REPLACEMENT OF Me_3[a)]

R'-CN R'	Me_3 : R'-CN (mol)	Reaction pressure (kg/cm²)	Yields (%)			
			Me_3	Me_2R'	MeR'_2	R'_3
Et	1 : 1	6000	27.7	28.0	9.17	1.04
Ph	1 : 1	6000	15.8	94.7	2.97	0.43
p-$CH_3C_6H_4$	1 : 1	6000	10.8	95.2	1.71	
	1 : 1	8000	22.7	104.6		
p-ClC_6H_4	1 : 1	6000	12.0	92.0	2.20	0.88
β-Naphthyl	1 : 0.70	8000	34.9	70.6		
γ-Pyridyl	1 : 1	8000	39.5	75.1	4.52	4.84

a) Reaction conditions: Me_3: MeOH=1: 1 by weight, 100 °C, 30 hr.
b) Mole percent based on Me_3.

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TABLE 5. INFLUENCE OF THE SUBSTITUENTS ON THE SUBSTITUENT-REPLACEMENT OF TRI-SUBSTITUTED 1,3,5-TRIAZINES WITH NITRILES (R'-CN)[a]

Substituents of original 1,3,5-triazine	R'-CN	Reaction conditions			Yields (%)[b]					
	R'	(kg/cm²)	(°C)	(hr)	R'-CN	R'C(=NH)OMe	R_3	R_2R'	RR'_2	R'_3
Me_3	Ph	6000	100	30	0.91	0.58	15.8	94.7	2.97	0.43
Et_3	Ph	6000	100	30	49.0	21.7	75.2	29.7	1.10	0.73
n-Pr_3	Ph	6000	100	30	52.1	24.4	82—96	19.8		1.73
Me_2Ph	Ph	6000	100	30	56.6	29.4		100.4		3.56
		6000	150	30	19.9	8.3		90.1	17.4	11.2
Ph_3[c]	Me	6000	100	30	+		97.1			+

a) Reaction mixtures: triazine: R'-CN: MeOH=1: 1 (in mol): 1 (in weight to the triazine).

b) Mole per cent based on the trisubstituted triazines.

c) Ph_3 0.103 g, MeCN 0.979 g (1: 72 in mol), and MeOH 3.82 g were mixed to make into a solution.

TABLE 6. CO-TRIMERIZATION OF TWO KINDS OF NITRILES (R^1-CN AND R^2-CN) UNDER HIGH PRESSURE IN THE PRESENCE OF METHANOL, INDICATING THE DISTRIBUTION OF THE RESULTING FOUR TRISUBSTITUTED 1,3,5-TRIAZINES[a]

R^1-CN		R^2-CN		R'-CN: R^2-CN (mol)	MeOH (g)	Yields							
						R^1_3		$R^1_2R^2$		$R^1R^2_2$		R^2_3	
R^1	(g)	R^2	(g)			(g)	(%)[b]	(g)	(%)[b]	(g)	(%)[b]	(g)	(%)[b]
MeCN	1.050	PhCN	1.315	2 : 1	2.366	0.104	8.27	1.123	59.2	0.814	32.1	0.016	0.49
MeCN	0.372	PhCN	1.857	1 : 2	2.230	0.0062	0.60	0.209	13.5	1.323	64.3	0.556	21.6
MeCN	2.026	EtCN	2.716	1 : 1	4.744	0.161	9.51	0.665	35.2	0.835	40.1	0.345	15.2

a) Reaction conditions: 9150 kg/cm², 120 °C, 24 hr.

b) Mole per cent among the four triazines.

TABLE 7. REACTION OF BENZAMIDINE WITH Me_3 AT 6000 kg/cm AND 100 °C FOR 30 hr

Me_3 (g)	PhC(=NH)-NH_2 (g)	Me_3: PhC(NH)NH_2 (mol)	Dioxane (g)	Yields (%)[a]								
				MeCN	PhCN	PhC(NH)-NH_2	Me_3	Me_2Ph	$MePh_2$	Ph_3	Pyrimidine	Amidine
1.573	1.490	1 : 1	2.369	8.54	3.56	6.50	42.6	41.9	6.52	1.18	4.53	10.9

a) Mole percent based on Me_3.

The influence of the chain length of the original substituents on this replacement reaction is shown in Table 5. The fact that the yields of the mono-replaced triazines decreased with an increase in the length of the original aliphatic substituents suggests that this replacement is hindered by the bulk of the original substituents. The suppressive effect resulting from the electron-releasing power of an aromatic substituent described above is indicated again in this table. The replacement of a substituent of Me_2Ph with a phenyl radical was particularly difficult in comparison with the replacement of a substituent of R_3, such as Me_3, Et_3, and n-Pr_3, by the same radical. These facts suggest that the formation of the small amounts of $MePh_2$ shown in Tables 1, 3, and 4 was due largely to the co-trimerization of the added benzonitrile and the acetonitrile liberated by Eq. (2), and less to the second replacement by Eq. (6).

$$RCN + R'CN \xrightarrow{R''OH} R_3 + R_2R' + RR_2' + R_3' \quad (7)$$

In order to demonstrate the excellent applicability of this replacement reaction to the synthesis of unsymmetrically tri-substituted 1,3,5-triazines, R_2R' in particular, the co-trimerization of nitriles under high pressure by means of Eq. (7) was examined as a comparative method. Table 6 indicates that this co-trimerization is not suitable for the selective preparation of a triazine with a desired combination of the three substituents.

Benzamidine, being similar in many cases, to benziminoether in its reacting manner was kept with Me_3 in dioxane at 6000 kg/cm² and 100 °C for 30 hr; this gave the expected triazine, Me_2Ph.

Experimental

Reaction Apparatus and Procedure. The reaction mixtures for these experiments were placed in a collapsible lead capsule and kept under the desired conditions of pressure and temperature for the desired time by means of a high-pressure assembly and procedure described previously.[10)]

Materials. The drying and distillation of the reagents (all graded EP) supplied this experiment with benzonitrile, p-tolunitrile, methanol, triethylamine, and glacial acetic acid. The sodium ethylate was prepared in the usual manner in the form of a concentrated ethanolic solution. The β-naphthonitrile (Tokyo Chem. Ind.) and isonicotinonitrile (Koei Chem. Ltd)[10)] were used without further purification. The Me_3, Et_3, and n-Pr_3 were the same as have been previously reported.[1)] The Me_2Ph was prepared by the reaction of Me_3 with benzonitrile (see below).

Preparation of Authentic Samples, Identification of Reaction Products, and Analysis. Nitriles, Iminoethers, and Benzamidine: The procedures for the preparation, identification, and analysis of these substances have been described in previous reports.[10,15]

Me_3 and Ph_3: The identification and analysis of these substances were similar in a manner to those previously reported.[15]

Me_2Et, $MeEt_2$, and Et_3: A mixture of equimolar amounts of ethyl acetiminoether and ethyl propioiminoether[1] was added to glacial acetic acid (15 per cent of the total iminoether in the molar fraction), and the resulting mixture was kept at room temperature for 24 hr. The weight ratio of the four triazines produced in the mixture was determined by means of gas-liquid phase chromatography (glc) glc-a[16] to be Me_3: Me_2Et: $MeEt_2$: Et_3 = 1: 0.9: 0.8: 3.1. The mixture was gradually warmed to 100 °C in 10 hr to complete the co-trimerization. This procedure was carried out with reference to the methods of Schaefer and Peters[17] and Yakubovich *et al.*[5] The reaction mixture was separated from a majority of Me_3 by filtration and was fractionated into the four triazines by glc-A.[18] On the other hand, the reaction product of the mixture of Me_3, propionitrile, and methanol listed in Table 4 was fractionated by glc-A. The first fraction, at 142—148 °C amounted to 0.03 g. Found: bp 175.6 °C; C, 61.96; H, 8.17; N, 29.71%; mol wt (from the parent peak of mass spectroscopy (MS)), 137. Calcd for $C_7H_{11}N_3$: C, 61.29; N, 8.09; N, 30.63%; mol wt, 137.18. The results of the glc-a and infrared (IR) spectrometry of this fraction agreed with those of the 2,4-dimethyl-6-ethyl-1,3,5-triazine described above. The second fraction, at 149—154 °C amounted to 0.02 g. Found: bp 190.8 °C; C, 63.53; H, 8.85; N, 27.48%. Calcd for $C_8H_{13}N_3$: C, 63.55; H, 8.67; N, 27.79%. The data of the glc-a and IR spectrometry agreed with those of the 2,4-diethyl-6-methyl-1,3,5-triazine described above. The third fraction, at 155—160 °C, was a minute amount. The retention time of the glc-a and the IR spectrum (2960, 1540, 1460, 1425, 1390, 1070, 890, 840 cm^{-1}) agreed with those of the authentic sample of triethyl-1,3,5-triazine described above.

Me_2Ph and $MePh_2$: The reaction mixture of the experiment conducted at 7950 kg/cm^2 listed in Table 1, when it was treated by means of preparative glc glc-B,[19] yielded 0.32 g at 190—200 °C (mp 38 °C (34,[7] 35—37[2])); C, 71.16 (71.33 Calcd); H, 5.84 (5.99); N, 23.26% (22.69); mol wt (MS), 185 (185.23); IR, 3070, 2970, 2940, 1540, 1435, 1375, 750, and 690 cm^{-1} for the alkyl, phenyl, and triazinyl groups). It was identified with 2,4-dimethyl-6-phenyl-1,3,5-triazine. The preparative glc gave another fraction (0.11 g) at 230—260 °C (mp 105 °C (110[2])); C, 76.36 (77.71); H, 5.34 (5.30); N, 18.09% (16.99); mol wt (MS), 247 (247.31); IR, 3050, 2950, 1535, 1525, 1425, 1380, 1365, 740, and 680 cm^{-1} for alkyl, phenyl, and triazinyl group). It was determined to be 2,4-diphenyl-6-methyl-1,3,5-triazine.

Et_2Ph and $EtPh_2$: The preparative glc-C[20] of the reaction products in the mixture of Et_3, benzonitrile, and methanol, which are shown in Table 5, gave two fractions. The first amounted to 0.02 g at 196—226 °C. Found: C, 73.48; H, 7.47; N, 19.51%; IR, 3050, 2950, 1590, 1530, 1450, 1420, 1385, 790, and 690 cm^{-1} for the alkyl, phenyl, and triazinyl groups. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.71%. This fraction was determined to be 2,4-diethyl-6-phenyl-1,3,5-triazine. The second amounted to 0.005 g at 226—243 °C (IR, 3050, 2950, 1520, 1440, 1380, 740, and 680 cm^{-1}). This fraction is assumed to be 2,4-diphenyl-6-ethyl-1,3,5-triazine.

n-*Pr_2Ph*: The fractionation by glc-C of the reaction products in the mixture of *n*-Pr_3, benzonitrile, and methanol listed in Table 5, gave a fraction of 0.04 g at 193—217 °C. Found: C, 74.84; H, 7.44; N, 17.39%; IR, 3050, 2950, 1590, 1530, 1450, 1380, 760, and 690 cm^{-1} for the alkyl, phenyl, and triazinyl groups. Calcd for $C_{15}H_{19}N_3$: C, 74.66; H, 7.94; N, 17.42%. This fraction was determined to be 2,4-di-*n*-propyl-6-phenyl-1,3,5-triazine.

Me_2 p-$CH_3C_6H_5$: The reaction products in the mixture of Me_3 and methanol (each 1.66 g) and *p*-tolunitrile (1.58 g) at 8000 kg/cm^2, listed in Table 4, were filtered. The residue was then recrystallized from ethanol to give 0.19 g. Found: mp 78.4 °C; C, 71.68; H, 6.60; N, 21.73%; mol wt (MS), 199; IR, 2920, 1610, 1530, 1430, 1405, 1370, and 790 cm^{-1} for the alkyl, phenyl, and triazinyl groups. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.57; N, 21.09%; mol wt, 199.25. This crystal was determined to be 2,4-dimethyl-6-*p*-tolyl-1,3,5-triazine.

Me_2 p-ClC_6H_4 and (p-$ClC_6H_4)_3$: The reaction mixture from Me_3 and methanol (each 0.51 g) and *p*-chlorobenzonitrile (0.57 g), listed in Table 4, was separated from the precipitate by filtration, was separated from the volatile matter *in vacuo* and was then recrystallized from ethanol to give 0.55 g. Found: mp 133.1 °C; C, 60.20; H, 4.51; N, 19.24; Cl, 16.43%; mol wt (MS), 219; IR, 3030, 2900, 1570, 1530, 1430, 1400, 1380, 1370, 860, 850, and 790 cm^{-1} for the alkyl, *p*-chlorophenyl, and triazinyl groups. Calcd for $C_{11}H_{10}N_3Cl$: C, 60.14; H, 4.59; N, 19.13; Cl, 16.14%; mol wt, 219.67. It was determined to be 2,4-dimethyl-6-*p*-chlorophenyl-1,3,5-triazine. The precipitate was washed with methanol and amounted to 0.015 g. Found: mp 323 °C; C, 61.34; H, 3.06; N, 10.86; Cl, 24.73%; mol wt (MS), 412; IR, 3050, 1580, 1520, 1400, 1365, 1350, 840, and 800 cm^{-1} for the *p*-chlorophenyl and triazinyl groups. Calcd for $C_{21}H_{12}N_3Cl_3$: C, 61.12; H, 2.93; N, 10.18; Cl, 25.77%; mol wt, 412.71. It was determined to be tris(*p*-chlorophenyl)-1,3,5-triazine.

Me_2 β-Naph: The reaction products from Me_3 and methanol (each 1.55 g) and *β*-naphthonitrile (1.36 g), listed in Table 4, gave a fraction (0.07 g) at 210—240 °C by glc-C. Found: mp 133.4 °C; C, 75.99; H, 5.43; N, 17.85%; mlo wt (MS), 235; IR, 2950, 1600, 1530, 1470, 1390, 800, 795, and 750 cm^{-1} for the alkyl, naphthyl, and triazinyl groups. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86%; mol wt, 235.27. 2,4-Dimethyl-6-naphth-2-yl-1,3,5-triazine was identical with this fraction.

Me_2 γ-Py, Me γ-Py_2, and γ-Py_3: The reaction products in the mixture of Me_3 and methanol (each 1.73 g) and isonicotinonitrile (1.46 g) listed in Table 4, were separated from the solid product and were then fractionated by glc-C. The fraction at 185—196 °C amounted to 0.48 g. Found: mp 71.8 °C; C, 64.42; H, 5.56; N, 29.93%; mol wt (MS), 186; IR, 3030, 2950, 1600, 1530, 1430, 1390, 1370, 850, 790, and 660 cm^{-1} for the alkyl and heteroaromatic groups. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09%; mol wt, 186.22. This fraction was determined to be 2,4-dimethyl-6-pyrid-4-yl-1,3,5-triazine. The fraction at 228—250 °C amounted to 0.08 g. Found: mp 127.5 °C; C, 66.69; H, 4.76; N, 28.56%; mol wt (MS), 249; IR, 3030, 2950, 1600, 1525, 1430, 1380, 1370, 820, 790, and 670 cm^{-1}. Calcd for $C_{14}H_{11}N_5$: C,

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15) M. Yasumoto, K. Yanagiya, and M. Kurabayashi, This Bulletin, **46**, 2798 (1973).

16) Glc-a: Reoplex 400, 3×750 mm, 50°C—, 4°C/min, He 25 ml/min.

17) S. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 2778 (1961).

18) Glc-A: DNP, 9×750 mm, 120°C, 2°C/min, He 125 ml/min.

19) Glc-B Thermol-3, 9×750 mm, 100°C—, 4°C/min, He 125 ml/min.

20) Glc-C SE-30, 9×750 mm, 140°C—, 6°C/min, He 125 ml/min.

67.46; H, 4.45; N, 28.09%; mol wt, 249.28. 2,4-Bis(4-pyridyl)-6-methyl-1,3,5-triazine is identical with this fraction. The solid product amounted to 0.21 g and was recrystallized from pyridine. The melting point (362 °C) of this crystal was not reduced by mixing it with the authentic tris(4-pyridyl)-1,3,5-triazine (mp 374 °C) previouslyreported.[10] The IR spectra of the two substances agreed.

4-Amino-2,6-dimethylpyrimidine and N-*2,6-Dimethylpyrimidin-4-yl-acetamidine*: These were identified and analysed by the methods described in the previous report.[1]

The gas-liquid-phase chromatographies, glc-a and glc-b,[21] were employed for the determination of the yields of the products in the reaction mixtures.

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[21] Glc-b: SE-30, 3×750 mm, 50°C—, 6°C min, He 35 ml/min.