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Studies on *s*-Triazines. I. Cotrimerization of Trichloroacetonitrile with Other Nitriles*[1]

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2-Substituted 4,6-bis(trichloromethyl)-*s*-triazines have been prepared by the cotrimerization of CCl_3CN with some nitriles. The reaction proceeds, in general, smoothly at ordinary pressure in the presence of hydrogen halide or Friedel-Crafts catalyst-hydrogen halide complex. An improved method was developed for the nitriles such as propionitrile with which CCl_3CN did not easily cotrimerize under above mentioned conditions.

2-Substituted 4,6-bis(trichloromethyl)-*s*-triazines and their derivatives, such as 2-substituted 4-amino-6-trichloromethyl-*s*-triazines, are highly effective as herbicides,[1,2] fungicides,[3,4] nitrification inhibitors,[5-10] in soil and antimalarials.[11]

Starting material, CCl_3CN, is easily obtained by the chlorination[12-16] of CH_3CN which is a by-product in SOHIO acrylonitrile process. This led us to investigate the cotrimerization of CCl_3CN with other nitriles.

*1 Taken in part from the dissertation presented by K. Wakabayashi to the University of Tokyo, 1969.

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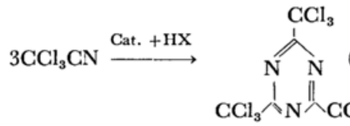
Table 1.* The effect of combined catalyst for trimerization of CCl_3CN

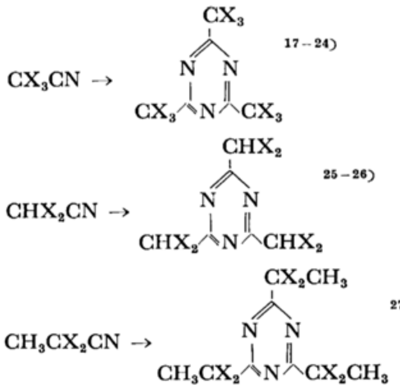


(I)

Combined catalyst		Starting material (g)	Product (I) (g)	Yield (%)	Mp °C
Catalyst	HX				
None	HCl	32.0	0.5	1.6	93
None	HBr	32.0	11.0	34.0	93
AlF_3	HCl	32.0	21.5	67.2	93
$AlCl_3$	HCl	32.0	11.5	35.9	92—93
$AlBr_3$	HCl	32.0	30.5	95.3	93
$AlBr_3$	HBr	32.0	30.5	95.3	92—93
BF_3-acetate	HCl	32.0	20.3	62.5	92—93
BF_3-etherate	HCl	32.0	30.1	93.8	93
$FeCl_3$	HCl	32.0	14.0	43.8	93
$ZnCl_2$	HCl	32.0	13.4	42.2	93
$SnCl_4$	HCl	32.0	16.4	51.6	92—93
$SbCl_3$	HCl	32.0	15.1	46.9	93
$TiCl_4$	HCl	40.0	16.2	40.5	92—93
$TiBr_4$	HCl	40.0	24.9	62.3	92—93

All samples in Table 1 were identified by a mixed melting point with an authentic sample[21] and IR spectra analyses.
* Reaction condition; See Experimental A).

Several authors[17-33] observed the formation of the *s*-triazines from α-chlorinated nitriles.



Scheme 1. (X: halogen)

Trimerization of nitriles has been effected with both basic and acidic catalysts. The basic catalysts, such as sodium,[34,35] potassium methoxide,[36] diethylzinc,[37,38] sodium hydride[38] and *N*-sodium methylaniline[38] give, in general, dimers[39] or pyrimidines[36] as main products. Acid catalyzed trimerization of nitriles [17-21,23-33] affords *s*-triazines in good yields. The reaction [19-21] was carried out in a closed system. $AlBr_3$-HCl (Norton's catalyst) is so effective that it can afford excellent yield under ordinary pressure in trimerization of CCl_3CN.[21]

The cotrimerization of CCl_3CN with other nitriles, RCN (R: methyl,[25,40-42,44] phenyl,[25,40,41] 2-

21) T. Norton, *J. Am. Chem. Soc.*, **72**, 3527 (1950).
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24) C. Broche, *ibid.*, (2), **50**, 97 (1894).
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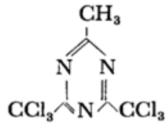
TABLE 2.* THE EFFECT OF COMBINED CATALYST FOR COTRIMERIZATION OF CCl_3CN WITH CH_3CN

$$2CCl_3CN + CH_3CN \xrightarrow{\text{Cat. }+HX}$$  (II)

Combined catalyst			Reaction time (hr)	Product (II) yield (%)	Mp °C
Catalyst (g)		HX			
AlF_3	3.0	HCl	8.0	95	96—97
$AlCl_3$	3.0	HCl	12.0	85	96—97
$AlBr_3$	3.0	HCl	3.0	95	96—97
$AlBr_3$	3.0		96.0	0	
BF_3-acetate	5.0	HCl	3.0	95	96—97
BF_3-etherate	5.0	HCl	4.0	95	96—97
BBr_3	3.0	HCl	5.0	88	96
$FeCl_3$	3.0	HCl	16.0	83	96
$ZnCl_2$	4.0	HCl	16.0	78	96
$SnCl_4$	4.0	HCl	16.0	83	96—97
$SbCl_5$	4.0	HCl	24.0	76	96—97
$TiCl_4$	3.0	HCl	3.0	90	96
$TiBr_4$	3.0	HCl	3.0	90	96
$CuCl_2$	10.0	HCl	48.0	58	96
$MgCl_2$	10.0	HCl	48.0	50	96—97
None		HBr	48.0	87	96
None		HCl	96.0	85	96—97

* Reaction condition; See experimental B-a).

naphthyl,[40] 2-chloroethyl[43] and 2-bromoethyl[43]), has also been reported, although the reaction is exceedingly slow.

We wish to report the results of reexamination and development of Norton's catalyst and also results of cotrimerization of CCl_3CN with other nitriles to give *s*-triazines.

Results and Discussion

Trimerization of CCl_3CN was undertaken to find out a new effective catalyst.

As shown in Table 1, it is clear that the use of combined catalysts to trimerize CCl_3CN (Friedel-Crafts catalysts-hydrogen halides) produces a good result, especially with $AlBr_3$-HCl, $AlBr_3$-HBr and BF_3 etherate-HCl. But the use of HCl only produces 1.6% yield of I.

Under a similar condition the use of combined catalysts to cotrimerize CCl_3CN with CH_3CN was investigated. These results are listed in Table 2. It is evident that the use of hydrogen halides only as well as that of the combined catalysts were effective, although the reaction was slow.

The parent peaks in mass spectrum of I and II are m/e 429(P_1) and m/e 327(P_2). Peaks at mass m/e 394(P_1-35), 292(P_2-35); 359($P_1-35\times2$), 257($P_2-35\times2$); 324($P_1-35\times3$), 222($P_2-35\times3$) are results from the loss of one, two and three chlorine atom(s) respectively. There are also large peaks at mass m/e 117($^+CCl_3$) and 108($^+CCl_2$-CN) in both spectra. Intensities of isotope peaks of I relative to the parent peak for chlorines (Cl_9) are as follows: P_1, 100% (100%), (Calcd (Found)); P_1+2, 287 (294); P_1+4, 366 (368); P_1+6, 273 (276); P_1+8, 130 (134); P_1+10, 42 (43). Similarly, intensities of isotope peaks of II relative to the parent peak for chlorines (Cl_6) are P_2, 100 (100); P_2+2, 190 (192); P_2+4, 153 (152); P_2+6, 65 (69).

The structure of all samples, (II), was identified by the consideration of Mass, IR, UV and NMR spectra with an authentic sample.[25,40]

The data in Table 2 indicate that the combined catalyst, $AlBr_3$-HCl, are most effective and economical.[44] This particular catalyst was used to investigate the distribution of the products by changing the molar ratio of CCl_3CN and CH_3CN. Table 3 shows the results.

We see that the best result was obtained in molar ratio, n: 1.5 or 2.0, in the cotrimerization of CCl_3CN with CH_3CN. GLC's relative R_t values are (I)=1.00, (II)=0.38 (based on (I)=1.00). These values were the same as those of authentic samples.

43) Z. N. Pazenko and T. N. Lebedeva, *Ukr. Khim. Zhur.*, **29**, 1192 (1963).

44) M. Okuzu, K. Wakabayashi and T. Okada, Japanese Pat. 11750 (1967).

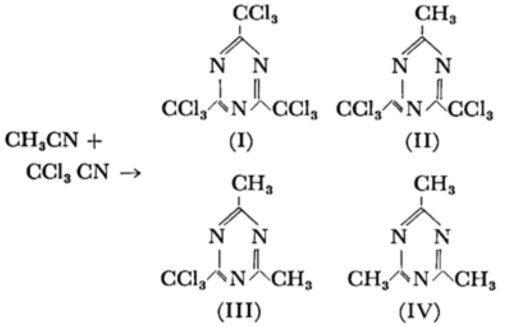
TABLE 3.* THE EFFECT OF MOLAR RATIO FOR COTRIMERIZATION OF CCl_3CN WITH CH_3CN

$n\,CCl_3CN + CH_3CN \rightarrow I + II$

CCl_3CN/CH_3CN Molar ratio (n)	Yield** of II (%)	Selectivity I	Selectivity II
1.0	97		100
1.5	97		100
2.0	95	0.5	99.5
3.0		23.5	76.5
4.0		38.8	61.2

* Experiment was carried out in the same reaction condition as Experimental B-a) in the presence of $AlBr_3$ (3g), using 41 g (1 mol) of CH_3CN.

** Based on CCl_3CN.



Scheme 2

Although the values of relative R_t of III and IV synthesized from another route were 0.16 and 0.08, no peak was found when the sample prepared from cotrimerization of CCl_3CN with CH_3CN was inspected.

Several other nitriles as well as CH_3CN were cotrimerized with CCl_3CN, using HCl-catalyst only. As shown in Table 4, several 2-substituted 4,6-bis(trichloromethyl)-*s*-triazines were obtained.

Some aliphatic nitriles which have more than 3 carbon atoms did not cotrimerize until a new improved method[45,46] was developed.

That is to say, 2-alkyl*[2]-4,6-bis(trichloromethyl)-*s*-triazines were prepared from cotrimerization of 2 mol CCl_3CN and 1 mol aliphatic nitriles in good yield when anhydrous HCl was introduced into the mixture and then heated strongly. The use of a combined catalyst also promoted this reaction. But it was not necessarily required, because the use of HCl only gave good results.

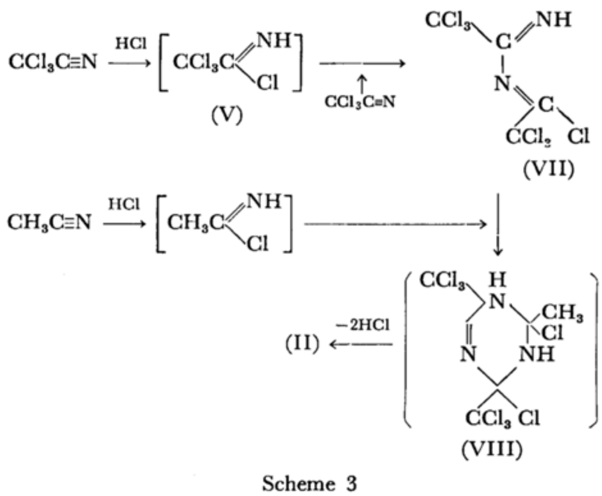
Table 5 shows the compounds obtained from the above mentioned method.

The following two experiments were carried out to observe some aspects of the mechanism about HCl-catalysed cotrimerization of CCl_3CN with CH_3CN. This mechanism may explain the cotrimerization of CCl_3CN with other nitriles also.

a) Addition of 1 mol CH_3CN to the adduct*[3] of 2 mol of CCl_3CN and 1 mol HCl.

b) Addition of 1 mol CH_3CN that has already absorbed 1 mol HCl to the adduct of 2 mol of CCl_3CN and 1 mol HCl.

Like Grundmann *et al.*[25] we could hardly obtain the (co)trimerized product under the condition of a). However, the reaction proceeded readily to afford in a good yield under the condition of b).



Scheme 3

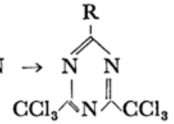
45) K. Matsui, K. Wakabayashi, M. Tsunoda, Y. Suzuki, M. Tsuda and M. Nakazawa, Japanese Appl. 79006 (1967).

46) K. Matsui, K. Wakabayashi, M. Tsunoda, Y. Suzuki, M. Tsuda and M. Nakazawa, Japanese Appl. 79470 (1967).

*[2] Alkyl having more than C_2 in Table 5

*[3] The adduct was identified in the form of $(CCl_3CO)_2NH$ (lit. 25).

Table 4.*1 Cotrimerization of CCl_3CN with other nitriles

$2CCl_3CN + RCN \rightarrow$ 

R	Yield %	Mp*2 °C	UV $\lambda_{max}^{CH_3OH}$ mμ(ε)	IR*3 cm^{-1}	Molecular formula		Anal., % C	H	N	Cl
CH_3	95	96—97*4	219(1920) 280(950)	1543						
C_6H_5†	94	97—98*4	282(23210)	1514 1548						
2-ClC_6H_4	91	120—122		1510 1548	$C_{11}H_4N_3Cl_7$	Calcd Found	30.99 31.04	0.95 1.11	9.86 9.57	58.21 58.50
3-ClC_6H_4	93	125—127		1512 1548	$C_{11}H_4N_3Cl_7$	Calcd Found	30.99 30.86	0.95 0.99	9.86 10.03	58.21 58.19
4-ClC_6H_4	92	158—159*5		1510 1548						
2,4-$Cl_2C_6H_3$	88	143—145	216(22690) 283(2600)	1510 1550	$C_{11}H_3N_3Cl_8$	Calcd Found	28.67 28.34	0.66 0.87	9.12 9.36	61.55 61.38
3,4-$Cl_2C_6H_3$	90	139—140		1510 1548	$C_{11}H_3N_3Cl_8$	Calcd Found	28.67 28.61	0.66 0.74	9.12 8.96	61.55 61.41
2,4,5-$Cl_3C_6H_2$	85	153—155		1510 1550	$C_{11}H_2N_3Cl_9$	Calcd Found	26.68 26.52	0.41 0.53	8.49 8.50	64.43 64.72
4-BrC_6H_4	92	161—163		1512 1548	$C_{11}H_4N_3Cl_6Br$	Calcd Found	28.06 27.99	0.86 0.72	8.93 8.76	62.15*6 62.22
4-$CH_3C_6H_4$	95	122—123*5		1512 1546						
3-$NO_2C_6H_4$	74	103—104*5		1510 1538						
4-$CH_3OC_6H_4$†	90	144—145*5	240(7930) 328(22580)	1512 1546						
1-Naphthyl	83	216—218		1545	$C_{15}H_7N_3Cl_6$	Calcd Found	40.76 40.52	1.60 1.86	9.50 9.43	48.13 48.46
2-Naphthyl	78	210—212*4		1545						

*1 Cotrimerization was carried out in the same reaction condition as Experimental B-a) in the presence of $AlBr_3$ (3 g), using 2 moles of CCl_3CN and 1 mole of RCN. *2 Recrystallized from ethanol. *3 Characteristic absorption of *s*-triazine system. *4 K. Dachlauer, German Pat. 682391 (1939). *5 H. G. Schmelzer *et al.*, U. S. Pat. 3277091 (1966); German Pat. 1200314 (1965). *6 Calcd Value: Cl+Br.

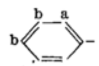
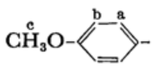
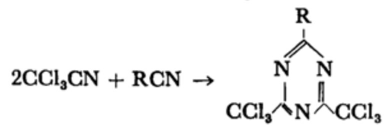
† NMR ($CDCl_3$)  τ 1.38 (*d*, 2H), a; 2.41 (*q*, 3H), b.  τ 6.10 (*s*, 3H), c; 2.97 (*d*, 2H), b; 1.36 (*d*, 2H), a.
(*s*, singlet; *d*, doublet; *q*, quartet)

TABLE 5.† COTRIMERIZATION OF CCl_3CN WITH ALIPHATIC NITRILES



R	Yield %	Bp, °C/mmHg Mp, °C (From solvent)	UV $\lambda_{max}^{CH_3OH}$ mμ (ε)	IR*1 cm^{-1}	NMR*2 τ	Molecular formula		Anal., % C	H	N	Cl
C_2H_5	92	165—166/11*3 34—36	221(1770) 278(570)	1525 1543	8.64(*t*, 3H) 6.79(*q*, 2H)						
n-C_3H_7	93	136—138/2	220(1820) 278(660)	1528 1548	8.92(*t*, 3H) 8.01(*h*, 2H) 6.82(*t*, 2H)	$C_8H_7N_3Cl_6$	Calcd Found	26.85 26.70	1.97 1.82	11.74 11.75	59.44 59.62
i-C_3H_7	87	170—175/14	214(3220) 265(580)	1522 1545	8.55(*d*, 6H) 6.60(*m*, H)	$C_8H_7N_3Cl_6$	Calcd Found	26.85 26.49	1.97 1.89	11.74 11.83	59.44 60.11
n-C_4H_9	90	157—159/3		1528 1545		$C_9H_9N_3Cl_6$	Calcd Found	29.06 28.88	2.44 2.39	11.30 11.34	57.20 57.36
i-C_4H_9	82	154—156/3	216(3840) 281(730)	1528 1545	8.97(*d*, 6H) 7.58(*m*, H) 6.94(*d*, 2H)	$C_9H_9N_3Cl_6$	Calcd Found	29.06 28.96	2.44 2.34	11.30 11.48	57.20 57.43
s-C_4H_9	81	142—146/3	222(1910) 276(600)	1528 1548	9.04(*t*, 3H) 8.56(*d*, 3H) 8.17(*qi* 2H) 6.80(*m*, H)	$C_9H_9N_3Cl_6$	Calcd Found	29.06 29.20	2.44 2.56	11.30 11.21	57.20 57.34
t-C_4H_9	56	154—157/8 68—70	224(2220) 283(610)	1525 1543	8.50(*s*)	$C_9H_9N_3Cl_6$	Calcd Found	29.06 29.17	2.44 2.62	11.30 11.42	57.20 57.08
n-C_5H_{11}	95	175—177/5	216(3500) 280(650)	1528 1548	9.08(*t*, 3H) 7.93—8.72(*m*, 6H) 6.83(*t*, 2H)	$C_{10}H_{11}N_3Cl_6$	Calcd Found	31.12 31.03	2.87 2.74	10.89 10.73	55.12 55.08
n-C_9H_{19}	78	192—194/5*4	216(2320) 262(450)	1525 1548	9.12(*t*, 3H) 7.42—8.46(*m*, 14H) 6.84(*t*, 2H)	$C_{14}H_{19}N_3Cl_6$	Calcd Found	38.04 37.95	4.33 4.18	9.50 9.55	48.12 48.34
n-$C_{17}H_{35}$	92	210—215/4*5		1520 1548		$C_{22}H_{35}N_3Cl_6$	Calcd Found	47.67 47.54	6.36 6.30	7.58 7.52	37.38 37.51
$\underset{a}{CH_2}Cl\underset{b}{CH_2}$	69	65—67*6 (EtOH)	244(3320)	1528	6.36(*t*, 2H),[b] 5.88(*t*, 2H),[a]						
CH_2ClCCl_2	87	47—48 (EtOH)	223(2330) 285(770)	1548	518(*s*)	$C_7H_2N_3Cl_9$	Calcd Found	18.10 18.72	0.45 0.38	9.40 9.43	71.35 71.54

† Reaction conditions; See Experimental B-b).

*1 Characteristic absorption of *s*-triazine system. *2 *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *qi*, quintet; *h*, heptet; *m*, multiplet. *3 H. G. Schmelzer *et al.*, German Pat. 1200314 (1965). *4 n_D^{28} 1.4746. *5 n_D^{28} 1.4850. *6 Z. H. Pazenko *et al.*, *Ukr. Khim. Zh.*, **29**, (11), 1192 (1963). It was reported that this compound was obtained without strong heating.

The mechanism may be explained as follows. The dimer (VII) (formed from 2 molecules CCl_3CN and 1 molecule HCl) and acetimidoyl chloride (VI) (formed from 1 molecule CH_3CN and 1 molecule HCl) may produce the adduct (VIII) by Diels-Alder type reaction. VIII may be changed into resonance-stabilised *s*-triazine, II, by the loss of 2 molecules HCl.

It may be explained that the intermediates (VIII) from the nitriles in Table 4 are converted smoothly into *s*-triazine by the loss of 2 molecules HCl at room temperature, but the intermediates (VIII) from the nitriles in Table 5 are not converted without strong heating.

Experimental

All the boiling points and melting points are uncorrected. Gas-liquid chromatography was performed with a Shimadzu GC-2C fitted with a flame ionization detecter, with 25 ml/min of nitrogen, using a 2 m×4 mm column containing 4% SE-30 on Gaschrom. P. IR spectra were obtained with a JASCO model IR-S spectrometer. UV spectra were obtained with a Perkin-Elmer model 202 spectrometer. NMR spectra were determined at 60 Mc with a Varian A-60 spectrometer, using TMS as the internal standard. Mass spectra were obtained with a Hitachi RMU-6C spectrometer.

Materials. *Nitriles.* CH_2ClCH_2CN[47] was prepared from acrylonitrile. CCl_3CN[12] was prepared by the chlorination of acetonitrile and CH_2ClCCl_2CN[48] by the chlorination of acrylonitrile. *i*-C_4H_9CN, *s*-C_4H_9CN, *t*-C_4H_9CN, *n*-$C_9H_{19}CN$, 2-ClC_6H_4CN, 3-ClC_6H_4CN, 4-BrC_6H_4CN, 2,4-$Cl_2C_6H_3CN$, 3,4-$Cl_2C_6H_3CN$ and 2,4,5-$Cl_3C_6H_2CN$ were prepared by the dehydration of corresponding amide with P_2O_5. Acetonitrile and acrylonitrile were supplied from Kasei Mizushima Ltd. Other nitriles were obtained from Tokyo Kasei Kogyo Co., Ltd.

Metal Halides. All reagents were obtained from Wako Pure Chemical Industries Ltd.

A) Trimerization of CCl_3CN. *2,4,6-Tris-(trichloromethyl)-s-triazine (I).* 32 g (0.22 mol) of CCl_3CN and 0.5 g of a catalyst were placed into a 300 ml flask. The mixture was saturated with anhydrous HCl at −10—0°C with stirring. The reaction mixture was kept at room temperature for 12 hr to complete trimerization. The contents of the flask was melted by heating at 100—110°C and poured into a large quantity of water to wash out HCl and catalyst. The mixture was cooled to let the product solidify again. The solid product was filtered, dried in air and recrystallized from ethanol (Table 1). Analysis example; using $AlBr_3$-HCl as the catalyst.

Found: C, 16.60; N, 9.49; Cl, 73.90%. Calcd for $C_6N_3Cl_9$: C, 16.64; N, 9.70; Cl, 73.66%.

IR absorption; 1545, 1341 cm^{-1} (*s*-triazine ring).

UV absorption; $\lambda_{max}^{CH_3OH}$ 219 mμ (ε 2590); 287 mμ (ε 790).

B) Cotrimerization of CCl_3CN. *a) 2-Methyl-4,6-bis(trichloromethyl)-s-triazine (II).* 289 g (2 mol) of CCl_3CN and 50 g (1.2 mol) of CH_3CN and a catalyst were placed into a 500 ml flask. The mixture was saturated with anhydrous HCl at −20—0°C with stirring, which was continued at the same temperature for 2—3 hr. At the end of the reaction time the contents of the flask solidified. After the reaction mixture was kept at room temperature to complete cotrimerization, the product was melted by heating at 100—110°C and poured into a large quantity of water to wash out HCl and the catalyst. After being cooled to room temperature, the separated solid was collected, dried in air and then recrystallized from ethanol. (Table 2).

Analysis example; using $AlBr_3$-HCl as the catalyst.

Found: C, 21.99; H, 1.00; N, 12.69; Cl, 64.48%. Calcd for $C_6H_3N_3Cl_6$: C, 21.84; H, 0.92; N, 12.74; Cl, 64.49%.

IR absorption; 1543, 1339 cm^{-1} (*s*-triazine ring).

UV absorption; $\lambda_{max}^{CH_3OH}$ 219 mμ (ε 1920); 280 mμ (ε 950).

NMR spectrum ($CDCl_3$); τ 7.02 (CH_3).

*b) 2-Alkyl*2-4,6-bis(trichloromethyl)-s-triazine.* The mixed solution of 289 g (2 mol) of CCl_3CN and 1.2 mol of RCN was saturated with anhydrous HCl at −30—−15°C by cooling with dry ice-methanol bath for 2 hr with stirring, which was continued at −10—0°C for 2—3 hr. The reaction mixture was kept overnight at room temperature. Then HCl gas was removed under reduced pressure by a water pump, gradually heating the reaction mixture at 150—200°C to complete cotrimerization. The residue is fractionated under reduced pressure. Thus 2-alkyl-4,6-bis(trichloromethyl)-*s*-triazine was obtained (Table 5).

C) The Preparation of Authentic Samples. *a) 2,4-Dimethyl-6-trichloromethyl-s-triazine (III).* III was prepared from acetic anhydride and *N*-(acetimidoyl) trichloroacetamidine which was prepared from CCl_3CN and acetamidine.[49] Yield 55%. Mp 72—73°C (lit[49] mp 69—71°C).

IR absorption; 1540 cm^{-1} (*s*-triazine ring).

UV absorption; $\lambda_{max}^{CH_3OH}$ 234 mμ (ε 2020); 260 mμ (ε 890).

NMR spectrum ($CDCl_3$); τ 7.26 (CH_3).

b) 2,4,6-Trimethyl-s-triazine (IV). IV was prepared by the method of Schaefer[50] from ethyl acetimidate. Yield 90%. Mp 60°C. Bp 150—155°C (lit[50] bp 155°C). IR absorption; 1536 cm^{-1} (*s*-triazine ring).

UV absorption; $\lambda_{max}^{CH_3OH}$ 228 mμ (ε 270); 257 mμ (ε 390).

NMR spectrum ($CDCl_3$); τ 7.42 (CH_3).

D) Experiments to Elucidate HCl-catalysed Cotrimerization of CCl_3CN with CH_3CN. *a) The Reaction of CH_3CN and the Adduct (VII) of CCl_3CN and HCl.* 18 g (0.5 mol) of anhydrous HCl was absorbed into 144.5 g (1 mol) of CCl_3CN at −10—0°C for 0.5 hr. Then 20.5 g (0.5 mol) of CH_3CN was added to this solution with stirring. The mixture was allowed to stand for 90 hr at room temperature. The product was distilled under reduced pressure by a water pump.

47) R. Stewart and R. H. Clark, *J. Am. Chem. Soc.*, **69**, 714 (1947).

48) N. B. Lorette, *J. Org. Chem.*, **26**, 2324 (1961).

49) American Cyanamid Co., Brit. Pat. 912112 (1962).

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

The distillate was a mixture of CH_3CN and CCl_3CN. A small amount of residue was obtained. This compound was found out to be a mixture of II and unidentified substance by GLC and IR analyses.

b) The Reaction of the Adduct (VI) of CH_3CN and HCl, and the Adduct (VII) of CCl_3CN and HCl. 18 g (0.5 mol) of anhydrous HCl was absorbed into 144.5 g (1 mol) of CCl_3CN at -10—0°C for 0.5 hr. 18 g of anhydrous HCl was also absorbed into 20 .5g (0.5 mol) of CH_3CN under the same condition. Then two solutions were mixed at 0—10°C with stirring. The mixture was allowed to stand for 90 hr at room temperature. At the end of the reaction, the reaction mixture almost solidified which was then poured into water. The crude product was filtered and air-dried to yield 140 g (85%). Mp 90—93°C. This compound was identified II by GLC and IR analyses.

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