BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 148—152 (1971)

Studies on *s*-Triazines. VII. A New Method of Preparing 2-Methyl-4,6-bis(trichloromethyl)-*s*-triazine[1,2]

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(Received June 16, 1970)

During the liquid-phase chlorination of CH_3CN, a trimerization reaction occurred to yield four *s*-triazine derivatives, 2-methyl-4,6-bis(trichloromethyl)-*s*-triazine (I), 2-chloromethyl-4,6-bis(trichloromethyl)-*s*-triazine (II), 2-dichloromethyl-4,6-bis(trichloromethyl)-*s*-triazine (III), and 2,4,6-tris(trichloromethyl)-*s*-triazine (IV). The structure of each *s*-triazine derivative has been assigned on the basis of the results of elemental analysis and the spectral (particularly Mass and NMR) data after each derivative had been separated in a pure form using the gas-liquid chromatographic (GLC) method. The product composition was seen to depend upon the rate of the chrorination of CH_3CN and the presence of a catalyst. The *s*-triazine I was shown to be the precursor of the *s*-triazines II and III; the pathways for the formation of the *s*-triazine IV were also investigated. Then, the selective co-trimerization of CH_3CN with its chlorinated compounds was investigated; this yielded the *s*-triazine I, a useful intermediate of pesticides and resines. The reaction was found to provide a new method of preparing *s*-triazine I.

The *s*-triazine I is a valuable intermediate in the preparation of other substituted *s*-triazine derivatives, for example, the monoamino-[2,3] or diamino-*s*-triazines,[4,5] which are both extremely useful pesticides.[6–12] More-

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

[2] Previous paper of this series, K. Wakabayashi, M. Tsunoda and Y. Suzuki, *Yuki Gosei Kagaku Kyokai Shi*, **29**, in press (1971).

[3] K. Wakabayashi, M. Tsunoda, and Y. Suzuki, *ibid.*, **27**, 868 (1969).

[4] K. Wakabayashi, M. Tsunoda, and Y. Suzuki, *ibid.*, **28**, 252 (1970).

[5] K. Wakabayashi, M. Tsunoda, and Y. Suzuki, *ibid.*, **28**, 333 (1970).

[6] E. Knüsli, K. Rüfenacht, and H. Gysin, Ger. 1107448 (1961); U. S. 3086855 (1963).

[7] H. Gysin and E. Knüsli, "Advance in Pest Control Research," Vol. III, ed. by R. L. Metcalf, Interscience, New York (1960), p. 289.

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[10] M. Okuzu, K. Wakabayashi, and T. Okada, *Japanese Appl.* 30187 (1965).

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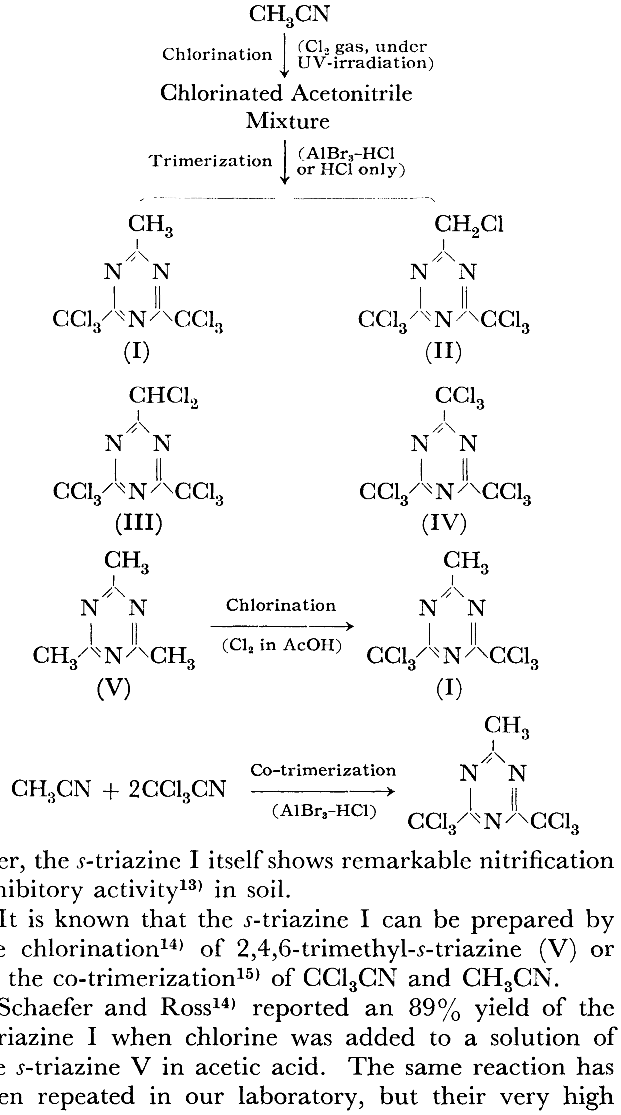
[12] K. Matsui, H. Kasugai, K. Wakabayashi, and S. Motojima, *ibid.*, 74210 (1967).



over, the *s*-triazine I itself shows remarkable nitrification inhibitory activity[13] in soil.

It is known that the *s*-triazine I can be prepared by the chlorination[14] of 2,4,6-trimethyl-*s*-triazine (V) or by the co-trimerization[15] of CCl_3CN and CH_3CN.

Schaefer and Ross[14] reported an 89% yield of the *s*-triazine I when chlorine was added to a solution of the *s*-triazine V in acetic acid. The same reaction has been repeated in our laboratory, but their very high yield was not always achieved and a complex mixture of all the possible *s*-triazines (I, II, III, IV, V, and other less chlorinated (Cl_{1-5}) 2,4,6-trimethyl-*s*-triazines) resulted.

In our earlier paper in this series,[15] we have reported that the co-trimerization of CCl_3CN with CH_3CN gave *s*-triazine I selectively in high yields. Therefore, we have investigated the preparation of CCl_3CN, the starting monomer, by the chlorination of CH_3CN, wherein the formation of a large amount of *s*-triazine derivatives as a by-product was observed. Gas-liquid chromatographic (GLC) and mass spectroscopic (Mass) analyses proved that the mixture contained *s*-triazines I, II, III, and IV.

Therefore we have investigated the preparation of the *s*-triazine I in a high yield and with a high selectivity by the co-trimerization of CH_3CN with its chlorinated mixture, without isolating them. It has now been found that the chlorinated mixture of CH_3CN can be co-trimerized with CH_3CN so as to selectively afford the *s*-triazine I. We wish here to report this first technical method for the preparation of the *s*-triazine I.

Results and Discussion

CH_3CN was chlorinated by chlorine in the presence of HCl under UV irradiation in order to prepare CCl_3CN. Table 1 shows some typical results of the chlorination experiments. CCl_3CN was the sole obtainable chlorinated nitrile; CH_2ClCN or $CHCl_2CN$ was detected to only a negligible extent in GLC. In addition, a large amount of a white solid was also obtained as a by-product. The GLC analysis of the solid revealed four peaks (A, B(minor), C(minor) and D); the relative R_t values were A=0.38, B=0.71, C=0.82, D=1.00 (based on D=1.00). The A and D relative R_t values were the same as those of the *s*-triazines I and IV respectively.[15] B, separated by GLC, was found to be the *s*-triazine II by Mass- (*m/e* 361(M^+, molecular peak), 326(M^+-Cl), 325(M^+-HCl) *etc.*); NMR-(τ 5.08 ppm(singlet, CH_2Cl)) and IR-data (1552, 1522, 1346 cm^{-1} (*s*-triazine ring)). C was found

Table 1. Chlorination of acetonitrile (Experimental A)

Chlorination time (hr)	Sp. gravity of chlorinated CH_3CN (D_4^{15})	Analysis of distillate				Analysis of residue				
		Total non-trimerized nitriles (mol)	Yield of CCl_3CN (%)	Selectivity of nitriles (%)		Total trimerized nitriles (mol)	Selectivity of *s*-triazines (%)			
				CH_3CN	CCl_3CN		I	II	III	IV
3	0.9010	100	8.7	91.3	8.7	0				
8	1.0004	100	18.2	81.8	18.2	0				
10	1.0512	100	24.4	76.5	24.4	0				
12	1.1004	100	30.6	69.4	30.6	0				
15	1.1502	99.4	36.8	63.0	37.0	0.6	100.0			
18	1.2010	97.9	43.6	55.5	44.5	2.0	100.0			
21	1.2504	82.6	40.3	51.2	48.8	17.3	94.8	3.4	1.8	
24	1.3006	68.5	38.8	43.4	56.6	31.5	85.7	5.7	6.7	1.9
29	1.3500	53.5	37.2	30.5	69.5	46.4	72.9	7.7	8.4	11.0
33	1.4020	42.7	36.8	13.8	86.2	57.3	62.8	8.5	9.9	18.8
38	1.4492	38.8	36.2	6.7	93.3	61.1	58.8	7.8	10.4	23.0

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[13] K. Wakabaysahi and M. Okuzu, *Nippon Dojo-Hiryogaku Zasshi*, **40**, 504 (1969).

[14] F. C. Schaefer and J. H. Ross, *J. Org. Chem.*, **29**, 1527 (1964).

[15] K. Wakabayashi, M. Tsunoda, and Y. Suzuki, This Bulletin, **42**, 2924 (1969).

Table 2. Trimerization of chlorinated acetonitrile mixture (Experimental B)

Chlorination time (hr)	Sp. gravity of chlorinated CH_3CN (D_4^{15})	AlBr$_3$-HCl catalyzed trimerization (Exp. B-1)					HCl catalylized trimerization (Exp. B-2)				
		Total yield of *s*-triazines (%)	Selectivity of *s*-triazines (%)				Total yield of *s*-triazines (%)	Selectivity of *s*-triazines (%)			
			I	II	III	IV		I	II	III	IV
12	1.1004	44.6	100.0				44.3	100.0			
15	1.1502	54.4	100.0				53.8	100.0			
18	1.2010	65.8	100.0				66.0	100.0			
21	1.2504	76.3	98.8	0.7	0.5		75.1	98.8	0.8	0.4	
24	1.3006	87.2	94.6	2.1	2.4	0.9	85.4	95.1	1.9	2.3	0.7
29	1.3500	92.3	81.4	3.8	4.1	10.7	90.5	86.6	4.0	4.1	5.3
33	1.4020	92.5	53.6	4.7	5.8	35.9	72.4	71.4	6.6	7.6	14.4
38	1.4492	94.0	43.5	4.7	6.4	45.4	64.3	63.5	7.3	8.8	20.4

to be the *s*-triazine III by Mass- (*m/e* 395 (M^+, molecular peak), 360(M^+—Cl), 359(M^+—HCl) *etc.*); NMR- (τ 3.12 ppm(singlet, $CHCl_2$)) and IR-data (1550, 1518, 1346 cm^{-1} (*s*-triazine ring)).

The following two pathways are possible for the formation of the *s*-triazine I:

1) by the chlorination of the *s*-triazine V or 2,4-dimethyl-6-trichloromethyl-*s*-triazine (VI), or

2) by the co-trimerization of 2 moles of CCl_3CN with 1 mole of CH_3CN.

The latter is more likely, since the *s*-triazines V[16] and VI were not detected during the chlorination of CH_3CN nor during the co-trimerization of CCl_3CN with CH_3CN,[15] whereas the *s*-triazine I was the sole product when the molar ratio,[17] CCl_3CN/CH_3CN, was less than two in the co-trimerization.[14]

The *s*-triazines II and III may be produced by the chlorination of the *s*-triazine I,[18] because CH_2ClCN and $CHCl_2CN$ were not detected in the chlorination mixture of CH_3CN and because neither CH_2ClCN nor $CHCl_2CN$ could co-trimerize with CCl_3CN.[19]

The trimerization of CCl_3CN does not proceed smoothly in the absence of a Friedel-Crafts catalyst-hydrogen halide complex under ordinary pressure.[15,20] The treatment of the chlorinated mixture of CH_3CN with $AlBr_3$-HCl or with HCl resulted in an increased formation of the *s*-triazine IV (*cf.* Table 2). Apparently a large part of the *s*-triazine IV could be formed by the chlorination of the *s*-triazine I,[18] while a small part of it could arise from the trimerization of CCl_3CN.

On the basis of this experimental result that a large amount of *s*-triazine derivatives was obtained during the chlorination of CH_3CN, we have tested to obtain the *s*-triazine I in a high yield and high selectivity by treating a chlorinated mixture of CH_3CN with a catalyst without isolating CCl_3CN. For this purpose several experiments were carried out under various reaction conditions (see Table 2).

When chlorine was introduced into CH_3CN for less than 15 hr, and when this chlorinated mixture was then treated with a catalyst, the total yield of the *s*-triazine I was lower, as is shown in Table 2, although the selectivity of the *s*-triazine I was higher. On the other hand, when chlorine was introduced into CH_3CN for more than 21 hr and it was then co-trimerized, the total yield was higher, although the selectivity was lower. The total yield of *s*-triazines in Exp. B-1 was higher when the chlorinated mixture was treated with the $AlBr_3$-HCl catalyst after a long chlorination time, since the CCl_3CN produced successively could be converted into the *s*-triazine I and IV smoothly by the aid of this catalyst. The total yield of *s*-triazines in Exp. B-2 was rather lower than that in Exp. B-1. This may have been because CCl_3CN could not be converted into the *s*-triazine I smoothly, because there was little CH_3CN over a long chlorination time, and also because it was hard to convert it into the *s*-triazine IV by means of the HCl catalyst alone.

The best way to obtain the *s*-triazine I is to co-trimerize both nitriles, CCl_3CN and CH_3CN, when the specific gravity of the chlorinated mixture of CH_3CN reaches *ca.* 1.2 — molar ratio, CCl_3CN/CH_3CN, 40/60. The detailed experimental conditions or techniques will be described in the experimental part. The results show that the *s*-triazine I can be prepared in high yields by a less costly and convenient method.

Experimental

All the boiling points and melting points are uncorrected. The gas-liquid chromatography was performed with a Shimadzu GC-2B apparatus fitted with a thermal conductivity detector, with 70 m*l*/min of helium, and using a ϕ 4 mm × 2 m column containing 20% DOP on Shimalite C at 100°C (GLC-1), or with such an apparatus fitted with a flame ionization detector, with 40 m*l*/min of nitrogen and using a ϕ 4 mm × 2 m column containing 5% SE-30 on Gaschrom P at 170°C (GLC-2). The IR* spectra were obtained with a JASCO model IR-G spectrometer. The NMR spectra were determined

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[16] *s*-Triazine V are obtainable from CH_3CN under high pressure using alkaline catalyst.[15]

[17] *s*-Triazine IV, beside *s*-triazine I, could be also obtained when the molar ratio is more than two and the co-trimerization is carried out in the presence of Friedel-Crafts catalyst.[14]

[18] To ascertain this chlorination pathway, *s*-triazine I was chlorinated under UV-irradiation and we obtained *s*-triazines II, III and IV besides the unreacted *s*-triazine I. (See Exp.-E).

[19] See Exp.-D.

[20] T. R. Norton, *J. Amer. Chem. Soc.*, **72**, 3527 (1950).

* Abbreviation: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

at 60 Mc/Mc with a Varian A-60 spectrometer, using TMS the internal standard. The mass spectra were obtained on as a Hitachi RMU-6C spectrometer, using a direct inlet, an ion-accelerating voltage of 1800 V, an electron accelerating voltage of 80 eV, a total emission current of 80 μA, a temperature of the ionization chamber of 200°C, a sample temperature of 100°C, and a vacuum of 1×10^{-6} mmHg.

Materials. The CH_3CN was supplied by Kasei Mizushima, Ltd. The CCl_3CN was prepared by the chlorination of CH_3CN.[21] Authentic 2-methyl-4,6-bis(trichloromethyl)-*s*-triazine (I) and 2,4,6-tris(trichloromethyl)-*s*-triazine (IV) were prepared by the (co-)trimerization of CCl_3CN according to the previously-presented procedures of the present authors.[15] 2-Chloromethyl-4,6-bis(trichloromethyl)-*s*-triazine (II) and 2-dichloromethyl-4,6-bis(trichloromethyl)-*s*-triazine (III) were separated in a pure form with GLC-2 from the trimerized product of the chlorinated mixture of CCl_3CN.

A) Chlorination of CH_3CN. A 10-*l*, five-necked flask was equipped with an efficient mechanical stirrer, a thermometer, a gas-inlet tube reaching nearly to the bottom of the flask, an efficient reflux condenser protected at the top with a calcium chloride tube, and an immersion-type mercury lamp (10—15 W, 2537 Å, Taika Kogyo Co.). The gas-inlet tube was connected to a container of chlorine through a flow meter and a 500 m*l* bottle containing about 200 m*l* of concentrated H_2SO_4. The outlet tube at the back of the calcium chloride tube was connected with a gas-absorption trap in which the evolved HCl was absorbed by running water. It was best to set the apparatus up under a good hood.

In the flask 4.1 kg (100 mol) of CH_3CN were placed and saturated with 1.5 kg of dry HCl at 35—40°C. Then, a current of chlorine (22 kg, 310 mol) was introduced into the reaction mixture under UV irradiation, the temperature of which was maitained at 45—50°C. The rate of the flow of the chlorine (*ca.* 9.9 g per minute) had to be regulated, care being taken that the liquid remain as colorless as possible. This chlorination required about 38 hr; at intervals samples of the chlorinating mixture were taken out. By distillation, the samples were divided into two parts, the distillate (bp 56—88°C) and the residue, each of which was separated by GLC and analysed by spectroscopic methods.

Analysis of the Distillate. Two components were separated in GLC-1; their relative R_t values, 1.00 and 0.70 (based on R_t of CH_3CN, 1.00), were in fair agreement with those of authentic CH_3CN and CCl_3CN.

The component of $R_t=1.00$ (CH_3CN): Bp 81—83°C, n_D^{25} 1.34430, D_4^{15} 0.7875 (lit,[22] bp 81.6°C/760 mmHg, n_D^{30} 1.33934, D_4^{15} 0.78745). NMR ($CDCl_3$): τ 8.04 ppm (singlet, CH_3).

The Component of $R_t=0.70$ *(CCl_3CN)*: Bp 84—86°C, n_D^{25} 1.43851, n_4^{15} 1.4418.

IR (liq. film, 0.05 mm): 2250 cm^{-1} (m, νC≡N), 1580(vw), 1374(vw), 1028(s), 971(m), 919(sh), 868(sh), 790(vs, νC–Cl), 648(w), 490(m).

NMR ($CDCl_3$): no signal.

Analysis of the Residue. Four components (A, B, C, D) were separated in GLC-2; their relative R_t values were A=0.38, B=0.71, C=0.82, D=1.00 (based on R_t of D, 1.00).

The Component A: The relative R_t value was same as authentic *s*-triazine I. Mp 96—97°C (lit,[15] mp 96—97°C).

Elemental analysis; Found: C, 21.95; H, 1.13; N, 12.70; Cl, 64.57%. Calcd for $C_6H_3N_3Cl_6$: C, 21.84; H, 0.92; N, 12.74; Cl, 64.49%.

IR (KBr): 2920 cm^{-1} (vw), 1570(s), 1551(vs), 1525(vs), 1490(sh), 1435(sh), 1406(s), 1350(m), 1341(s), 1048(m), 1011(sh), 1002(m), 992(m), 978(m), 852(m), 840(s), 828(vs), 818(sh), 790(vs), 771(vs), 746(sh), 722(sh), 696(vs), 600(m), 580(s), 500(m).

NMR ($CDCl_3$): τ 7.02 ppm (singlet, $C\underline{H}_3$).

Mass (relative intensity): *m/e* 335(0.8), 334(0.3), 333(2.8), 332(0.8), 331(6.2), 330(1.5), 329(7.7), 328(0.7), 327(4.0, M$^+$-peak), 300(3.8), 299(1.8), 298(20.5), 297(6.2), 296(64.2), 295(10.4), 294(100.0), 293(7.0), 292(61.8, M$^+$−Cl), 262(1.2), 261(6.5), 260(2.6), 259(15.0), 258(2.7), 257(12.1, M$^+$−Cl_2), 255(1.2), 253(1.8), 251(1.1), 220(1.5), 218(3.1), 216(2.4), 185(0.7), 183(1.5), 181(1.6), 173(0.7), 171(2.1), 169(2.1), 149(1.1), 147(0.6), 145(1.5), 143(1.7), 138(1.2), 137(0.8), 136(6.4), 135(0.9), 134(10.5), 133(0.3), 131.5(0.5), 131(1.5), 130.5(4.0), 130(1.1), 129.5(11.8), 129(1.5), 128.5(12.0), 123(0.8), 122(2.1), 121(5.3), 120(5.3), 119(16.5), 118(1.2), 117(17.3), 114(0.5), 113(0.6), 112(7.4), 111(2.1), 110(46.0), 109(2.8), 108(71.5, CCl_2CN), 102(1.2), 101(0.4), 100(3.0), 99(2.0), 98(1.8), 96(1.2), 94(2.0), 87(1.8), 86(2.0), 85(4.8), 84(10.8), 83(0.5), 82(15.1), 76(1.2), 75(3.8), 74(0.4), 73(12.0), 68(1.2), 67(14.7), 66(0.9), 64(0.8), 62(1.2), 61(0.7), 59(0.5), 57(1.0), 55(1.0), 53(1.0), 52(1.3), 51(1.2), 50(0.7), 49(5.2), 48(0.6), 47(15.8), 46(0.8), 45(1.2), 44(0.7), 43(1.1), 41(4.8), 40(4.8), 39(2.1), 38(3.2), 37(0.7), 36(10.2), 35(2.0), 31(0.7), 29(1.0), 28(1.6), 27(3.7), 26(2.5), 15(4.8).

The Component B: This compound was identified as *s*-triazine II on the basis of elemental analysis and spectroscopic data. Mp 62—64°C (from *n*-hexane), bp 175—180°C/2.0 mmHg (lit,[14] mp 63—64°C, bp 120—125°C/0.1 mmHg).

Elemental analysis; Found: C, 19.87; H, 0.55; N, 11.42; Cl, 68.29%. Calcd for $C_6H_2N_3Cl_7$: C, 19.78; H, 0.55; N, 11.54; Cl, 68.13%.

IR (KBr): 2961 cm^{-1} (vw), 1552(vs), 1522(vs), 1406(m), 1346(s), 1018(m), 990(w), 942(w), 850(m), 836(vs), 818(sh), 790(m), 768(vs), 746(sh), 730(sh), 696(vs), 578(w).

NMR ($CDCl_3$): τ 5.08 ppm (singlet, CH_2Cl).

Mass (relative intensity): *m/e* 369(0.6), 368(0.2), 367(1.9), 366(0.3), 365(3.8), 364(0.4), 363(3.9), 362(0.4), 361(1.7, M$^+$-peak), 360(0.2), 336(1.0), 335(0.5), 334(8.3), 333(1.0), 332(34.3), 331(4.5), 330(79.8), 329(11.0), 328(100.0), 327(12.6), 326(52.4, M$^+$−Cl), 325(6.5), 299(2.0), 298(0.6), 297(10.2), 296(3.0), 295(29.8), 294(9.5), 293(47.2), 292(15.0), 291(30.1, M$^+$−Cl_2), 290(9.0), 261(0.8), 260(2.0), 259(1.2), 258(3.7), 257(2.3), 256(2.9, M$^+$−Cl_3), 255(1.7), 220(0.7), 219(0.4), 218(1.4), 217(0.3), 216(1.1), 185(0.8), 184(0.9), 183(1.8), 182(0.8), 181(1.8), 173(0.6), 171(1.4), 169(1.4), 147(1.7), 146(1.5), 145(4.3), 144(6.7), 143(4.6), 138(1.2), 137(1.0), 136(5.1), 135(2.2), 134(8.4), 133(0.8), 130(1.5), 129.5(0.7), 129(1.0), 128.5(1.3), 128(2.1), 127.5(1.0), 127(1.0), 124(0.9), 123(0.7), 122(1.7), 121(4.5), 120(2.0), 119(13.8), 118(0.8), 117(14.1), 113(1.6), 112(5.0), 111(3.0), 110(31.8), 109(3.8), 108(48.2), 103(2.2), 102(1.1), 101(5.6), 100(1.9), 96(1.0), 95(0.9), 94(1.7), 88(0.7), 87(1.2), 86(1.3), 85(4.8), 84(6.8), 83(6.7), 82(10.9), 81(0.6), 79(0.7), 78(0.8), 77(1.2), 76(3.0), 75(4.3), 74(9.3), 73(7.2), 71(0.8), 69(0.7), 67(0.8), 66(2.4), 65(0.7), 64(1.0), 63(0.7), 62(1.0), 61(2.4), 60(1.1), 59(0.9), 57(0.5), 56(0.7), 55(1.0), 54(0.5), 53(0.8), 52(1.7), 51(4.2), 50(1.8), 49(8.3), 48(2.6), 47(10.3), 45(1.1), 44(3.2), 43(1.7), 42(0.6), 41(1.7), 40(2.9), 39(1.9), 38(2.9), 37(1.3), 36(8.8), 35(4.1), 31(0.8), 29(1.0), 28(1.8), 27(1.1), 26(1.1).

The Component C: This compound was identified as *s*-triazine III on the basis of elemental analysis and spectroscopic data. Mp 41—42°C (from *n*-hexane), bp 170—173°C/0.5 mmHg.

Elemental analysis; Found: C, 17.98; H, 0.32; N, 10.56;

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[21] K. Dachlauer, German 694479 (1942); *D. R. P. Org. Chem.*, **6**, 1384.

[22] "The Merck Index," eighth edition, ed. by P. G. Stecher, Merck & Co., Inc., New Jersey, U. S. A. (1968), p. 8.

Cl, 71.30%. Calcd for $C_6HN_3Cl_8$: C, 18.07; H, 0.25; N, 10.54; Cl, 71.13%.

IR (KBr): 2970 cm^{-1}(vw), 1550(vs), 1518(s), 1410(w), 1346 (s), 1018(m), 930(w), 846(sh), 833(s), 818(sh), 790(m), 761(vs), 746(sh), 730(sh), 695(vs).

NMR ($CDCl_3$): τ 3.12 ppm (singlet, $CHCl_2$).

Mass (relative intensity): *m/e* 405(0.4), 404(0.5), 403(1.0), 402(0.9), 401(2.0), 400(2.0), 399(3.4), 398(3.0), 397(2.7), 396(2.5), 395(1.2, M$^+$-peak), 394(1.1), 370(6.2), 369(4.9), 368(17.9), 367(8.7), 366(54.9), 365(13.1), 364(96.4), 363(14.6), 362(100.0), 361(9.0), 360(45.9, M^+-Cl), 333(4.7), 332(4.4), 331(20.3), 330(9.0), 329(42.1), 328(20.6), 327(52.2), 326(24.9), 325(27.4, M^+-Cl_2), 324(12.8), 296(1.6), 295(1.4), 294(4.7), 293(4.0), 292(7.3), 291(6.0), 290(4.6), 289(3.7), 255(0.8), 253(1.2), 251(0.7), 222(0.3), 221(0.5), 220(1.0), 219(1.0), 218(2.1), 217(0.8), 216(1.6), 186(0.9), 185(0.7), 184(3.6), 183 (1.8), 182(3.8), 181(1.9), 173(0.5), 172(0.6), 171(1.3), 170(0.8), 169(1.3), 166(0.7), 165(2.7), 164(6.3), 163(7.8), 162(4.2), 160 (0.4), 159(1.3), 158(0.4), 157(1.3), 149(0.8), 148(1.3), 147 (3.2), 146(5.2), 145(4.4), 144(0.8), 143(1.3), 139(0.5), 138 (0.9), 137(2.3), 136(5.5), 135(3.9), 134(8.4), 133(0.4), 132 (1.6), 131(1.0), 130(1.5), 129(0.9), 128(1.8), 127(1.2), 123(1.0), 122(2.2), 121(7.1), 120(2.8), 119(21.1), 118(0.7), 117(21.5), 113(0.6), 112(5.6), 111(3.1), 110(37.7), 109(4.1), 108(54.6, CCl_2CN), 105(0.7), 104(0.3), 103(0.5), 102(1.7), 101(0.9), 100(5.4), 99(1.0), 98(0.8), 97(1.1), 96(1.4), 95(1.7), 94(2.1), 92(2.4), 91(0.5), 89(0.8), 88(1.2), 87(4.7), 86(4.3), 85(11.2), 84(9.6), 83(17.9), 82(14.4), 78(0.5), 77(1.7), 76(6.7), 75(2.8), 74(20.4), 73(9.0), 72(0.5), 71(0.5), 70(0.4), 69(0.5), 68(0.5), 67(0.5), 66(0.5), 65(0.7), 64(0.5), 63(0.5), 62(1.8), 61(0.9), 60(2.1), 59(1.0), 57(0.8), 55(1.0), 53(1.1), 52(1.1), 51(3.2), 50(2.0), 49(4.8), 48(5.5), 47(15.3), 45(0.5), 44(3.6), 43(1.1), 42(0.8), 41(0.4), 40(0.8), 39(1.8), 38(5.5), 37(1.1), 36(17.2), 35(3.3), 31(0.9), 29(1.3), 28(1.7), 27(1.3).

The Component D: Its relative R_t value was same as authentic *s*-triazine IV. Mp 94—95°C (from ethanol) (lit,[15] mp 93°C), bp 175—177°C/10 mmHg (lit,[23] bp 176—178°C/12 mmHg).

Elemental analysis; Found: C, 16.72; N, 9.65; Cl, 73.53%. Calcd for $C_6N_3Cl_9$: C, 16.64; N, 9.70; Cl, 73.66%.

IR (KBr): 1540 cm^{-1}(vs), 1508(sh), 1341(s), 1017(m), 846 (sh), 832(s), 818(sh), 756(vs), 744(sh), 726(sh), 692(vs).

NMR ($CDCl_3$): no signal.

Mass (relative intensity): *m/e* 439(0.9), 437(2.7), 435(5.6), 433(7.4), 431(5.8), 429(2.0, M$^+$-peak), 406(0.9), 405(0.5), 404(6.9), 403(2.4), 402(25.8), 401(4.7), 400(64.0), 399(8.8), 398(100.0), 397(8.0), 396(89.2), 395(3.2), 394(35.4, M^+-Cl), 369(0.8), 368(0.6), 367(3.9), 366(2.4), 365(12.0), 364(4.7), 363(21.8), 362(4.0), 361(23.0), 360(1.6), 359(10.2, M^+-Cl_2), 331(0.2), 330(2.7), 329(0.4), 328(0.4), 327(0.6), 326(8.0), 325(0.4), 324(4.2, M^+-Cl_3), 255(1.7), 253(2.6), 251(1.6), 220(0.6), 219(0.1), 218(1.2), 216(0.9), 185(1.3), 184(0.5), 183.5(1.6), 183(3.8), 182.5(4.4), 182(1.3), 181.5(8.4), 181 (4.0), 180.5(9.0), 180(0.8), 179.5(4.1), 167(0.4), 166(1.5), 165(5.4), 164(12.3), 163(16.4), 162(8.0), 147(0.2), 145(0.7), 143(0.7), 136(9.8), 135(0.8), 134(13.2), 133(1.3), 132(0.5), 131(3.9), 130(0.4), 129(4.0), 123(1.0), 122(2.4), 121(10.6), 120(4.8), 119(32.8), 118(0.8), 117(34.2), 112(7.0), 111(2.4), 110(42.5), 109(1.0), 108(69.2), 96(1.6), 95(0.1), 94(2.4), 88 (2.5), 87(2.8), 86(2.8), 85(9.0), 84(15.9), 83(0.8), 82(26.1), 76(1.7), 75(3.8), 74(0.3), 73(12.0), 71(0.5), 70(0.7), 69(1.2), 62(0.8), 61(1.5), 59(2.0), 57(1.7), 56(0.9), 55(2.1), 50(0.6), 49(8.7), 48(0.4), 47(28.4), 44(2.5), 43(3.2), 42(0.7), 41(1.6), 38(5.9), 37(1.9), 36(18.2), 35(6.0), 29(0.6), 28(0.8), 27(0.7).

B) Trimerization of Chlorinated Mixture. Each sample in Experimental-A) was also trimerized in the presence of $AlBr_3$-HCl (Exp. B-1) or HCl only (Exp. B-2). Dry HCl gas (*ca.* 100 g) was introduced into a mixture of the sampling solution (100 m*l*) and $AlBr_3$ (2 g) or the sampling solution (100 m*l*) only at −20—0°C with stirring. The reaction mixture was kept at room temperature for 12 hr to complete trimerization. After HCl gas was removed under reduced pressure by water pump, each residue was analized by GLC-2 (see Table 2).

C) Preparation of the s-Triazine I. In the manner similar to Exp.-A, 4.1 kg of CH_3CN was chlorinated by the use of 10.6 kg of chlorine. Thus, a chlorinated CH_3CN mixture (*ca.* 10 kg; D_4^{45} 1.1945, $CCl_3CN/CH_3CN=43.3/56.7$ by GLC-1) was obtained. Then 30 g of $AlBr_3$ was added to this mixture with stirring. The resultant mixture was saturated with anhydrous HCl (1 kg) at −20—0°C for 2 hr, and kept at room temperature for 12 hr to complete co-trimerization. The obtained solid was melted by heating at 100—110°C and poured into a large quantity of water to wash out HCl and catalyst. After being cooled to room temperature, the resolidified product was collected, dried in air and then analyzed by GLC-2. Yield 7.0 kg (63.6%). Mp 93—96°C (if a purer product is desired, it may be recrystallized from ethanol. mp 96—97°C).

Analysis of the Crude Product, Mp 93—96°C, by GLC-2. *Ca.* 100% purity of the *s*-triazine I, and trace of *s*-triazines II and III was indicated.

Elemental Analysis of the Recrystallized Product, Mp 96—97°C. Found: C, 21.96; H, 1.04; N, 12.62; Cl, 64.35%. Calcd for $C_6H_3N_3Cl_6$: C, 21.84; H, 0.92; N, 12.74; Cl, 64.49%.

D) Attempted Co-trimerization of CH_2ClCN or $CHCl_2CN$ with CCl_3CN. The mixture of CCl_3CN (2 mol), CH_2ClCN or $CHCl_2CN$ (1 mol), and $AlBr_3$ (5 g) was saturated with anhydrous HCl at −20—−10°C by cooling with a dry ice-methanol bath for 2 hr under stirring. The reaction mixture was then kept for 48 hr at room temperature. After a severe strong heating treatment[15] such as was used in the preparation of 2-alkyl-4,6-bis(trichloromethyl)-*s*-triazines, the *s*-triazine IV became the only trimerized product, while CH_2ClCN or $CHCl_2CN$ was recovered in every case.

E) Chlorination of the s-Triazine I. Chlorine (25 g, 3.5 mol) was passed into a solution of 330 g (1 mol) of the *s*-triazine I in 1000 m*l* of CH_3CN (or CH_3COOH) at 45—50°C under illumination from the same UV lamp as was used in Exp.-A for a 7 hr period. Then the reaction mixture was evaporated at ordinary pressure as completely as possible, leaving a semisolid residue of 354 g (or 375 g in the case of CH_3COOH solution). This residue, containing a small amount of the solvent, was then analyzed by GLC-2, Mass, and NMR.

NMR ($CDCl_3$): three singlets at τ 7.02 (CH_3), 5.08 (CH_2Cl), and 3.12 ppm ($CHCl_3$).

The Composition of the Product Mixture from the Chlorination of the s-Triazine I: GLC and Mass data showed the selectivity of the *s*-triazines to be as follows; I, 56.5; II, 8.7, III, 10.8, and IV, 24.0 mol%. (In the case of the CH_3COOH solution; I, 32.2; II, 14.1; III, 17.2, and IV, 36.5 mol%).

The authors are indebted to the Mitsubishi Chemical Industries Ltd. for their generous support of this publication. They also wish to express their thanks to Mr. Y. Takigawa, Mr. Y. Ihashi and Mr. T. Sato for obtaining and interpreting the spectra which were of great assistance in this work. Valuable technical assistance was also provided by Mr. M. Tsuda and Mr. M. Nakazawa.

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