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Studies on *s*-Triazines. II. Cotrimerization of Trichloroacetonitrile with Thiocyanates[1),*1]

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2-Substituted thio-4,6-bis(trichloromethyl)-*s*-triazines, a new class of *s*-triazine derivatives, were obtained by the cotrimerization of CCl_3CN with a wide variety of thiocyanates. Generally, the reaction proceeded smoothly at ordinary pressure in the presence of hydrogen chloride or the combined catalyst, Friedel-Crafts catalyst-hydrogen chloride.

Literature[2-4)] has revealed that attempts to prepare 2-substituted thio-4,6-bis(trichloromethyl)-*s*-triazines have mostly met with failure.

Kober[5)] reported that the reaction of 2,4,6-tris-(trichloromethyl)-*s*-triazine (I) with alcohols, in the presence of tertiary amines, led to the stepwise replacement of the CCl_3-groups with the alkoxyl groups, depending upon the reaction condition. Then Kober further attempted to determine whether the reaction of I with alkanethiols, instead of alcohols, would react in the presence of tertiary amines resulting in the formation of 2-alkylthio-4,6-bis(trichloromethyl)-*s*-triazines. His results, however, indicated that the reaction of I with

TABLE 1. ISOTOPE ABUNDANCES FOR CHLORINES AND SULFUR OF V

			P	P+2	P+4	P+6	P+8
M^+	387	Calcd	100	196	161	72	18
		Found	100	203	174	74	21
M^+-CH_3	372	Calcd	100	196	161	72	
		Found	100	199	150	75	
M^+-Cl	352	Calcd	100	164	109	37	
		Found	100	152	111	46	

Calculation based on $^{35}Cl : ^{37}Cl = 75.53 : 24.47$
$^{32}S : ^{34}S = 95.77 : 4.23$

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

[1)] Previous paper of this series, K. Wakabayashi, M. Tsunoda and Y. Suzuki, This Bulletin, **42**, 2924 (1969).

[2)] E. Kober, *J. Org. Chem.*, **26**, 2270 (1961).

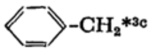
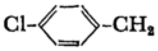
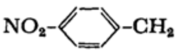
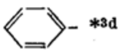
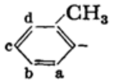
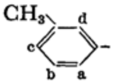
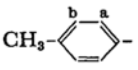
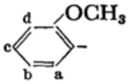
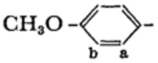
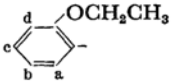
[3)] H. G. Schmelzer, G. Dankert, E. Degener and H. Holtschmidt, German Pat. 1200314 (1965); U.S. Pat. 3277091 (1966); Japanese Pat. 3178 (1966).

[4)] H. G. Schmelzer, E. Degener and H. Holtschmidt, *Angew. Chem.*, **78**, 982 (1966).

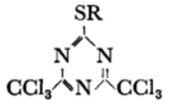
[5)] E. Kober, *J. Org. Chem.*, **25**, 1728 (1960).

TABLE 2. COTRIMERIZATION OF

$CCl_3CN + RSCN \rightarrow$

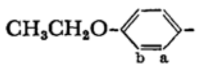
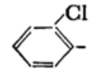
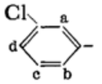
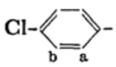
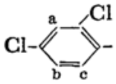
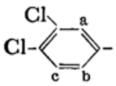
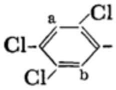
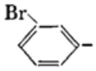
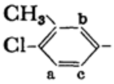
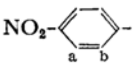
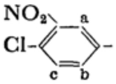
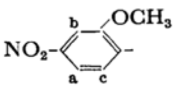
R	Yield (%)	Physical property		UV	IR*1	NMR τ*2)
		Bp, °C/mmHg	Mp, °C	$\lambda_{max}^{CH_3OH}$ mμ(ε)	cm^{-1}	(Sol. $CDCl_3$)
CH_3*3a,*4	93	160—165/0.65	71—72	217 (3340) 272 (15060)	1550 1498	7.27 (*s*, SCH_3)cf.)
C_2H_5*3b	94	170—171/1.0		221 (2850) 274 (13530)	1550 1505	8.51 (*t*, 3H, CH_3)cf.) 6.68 (*q*, 2H, SCH_2)
n-C_3H_7	88	188—190/2.0		215 (3500) 274 (13100)	1550 1503	8.88 (*t*, 3H, CH_3) 8.24 (*h*, 2H, CH_2) 6.73 (*t*, 2H, SCH_2)
i-C_3H_7	95	185—187/4.0	58—60	215 (3600) 274 (13840)	1548 1498	8.47 (*d*, 6H, CH_3) 5.88 (*m*, H, SCH)
n-C_4H_9	86	189—193/3.0		221 (2890) 275 (13690)	1550 1503	9.00 (*t*, 3H, CH_3) 7.92—8.73 (*m*, 4H, CH_2) 6.67 (*t*, 2H, SCH_2)
i-C_4H_9	95	180—183/2.0		220 (2960) 274 (14250)	1550 1505	8.87 (*t*, 6H, CH_3) 7.67—8.34 (*m*, H, CH) 6.77 (*d*, 2H, SCH_2)
n-C_5H_{11}	95	192—194/2.0		221 (2890) 275 (13690)	1550 1505	9.03 (*t*, 3H, CH_3) 7.98—8.82 (*m*, 6H, CH_2) 6.68 (*t*, 2H, SCH_2)
n-C_6H_{13}	90	195—200/1.0		218 (2590) 275 (14040)	1548 1504	9.05 (*t*, 3H, CH_3) 7.90—8.73 (*m*, 8H, CH_2) 6.68 (*t*, 2H, SCH_2)
n-$C_{12}H_{25}$*5	85	230—235/0.2		214 (2670) 274 (13490)	1542 1504	9.12 (*t*, 3H, CH_3) 8.04—8.96 (*m*, 20H, CH_2) 6.93 (*t*, 2H, SCH_2)
	72	186—189/1.0	84—85	231 (2420) 277 (13780)	1543 1504	5.43 (*s*, 2H, CH_2) 2.35—2.70 (*m*, 5H, Aro.)
	68		91—93	232 (3600) 279 (15200)	1542	
	74		121—122	295 (20400)	1535	
	95	210—214/2.0	65—67	271 (9710)	1537 1504	2.20—2.60 (*m*, 5H, Aro.)
	95	185—187/1.0	47—48	270 (9680)	1532 1503	7.56 (*s*, 3H, CH_3) 2.50—2.70 (*m*, 3H, b+c+d) 2.41 (*d*, H, a)
	93		74—75	270 (9720)	1545 1504	7.55 (*s*, 3H, CH_3) 2.69 (*m*, 2H, b+c) 2.41 (*m*, 2H, a+d)
	95		82—85	269 (10240)	1546 1504	7.53 (*s*, 3H, CH_3) 2.74 (*d*, 2H, b) 2.42 (d, 2H, a)
	83		98—101	272 (11020)	1542 1508	6.18 (*s*, 3H, CH_3) 2.50—3.10 (*m*, 3H, b+c+d) 2.40 (*d*, H, a)
	86		100—103	271 (11000)	1545 1508	6.23 (*s*, 3H, CH_3) 3.13 (*d*, 2H, b) 2.61 (*d*, 2H, a)
	88		45—48	213 (19000) 282 (9030)	1534 1504	8.56 (*t*, 3H, CH_3) 5.84 (*q*, 2H, CH_2) 2.60—3.10 (*m*, 3H, b+c+d) 2.45 (*d*, H, a)

CCl_3CN WITH THIOCYANATES



Method		Molecular formula		Anal., %				
A or B	Solvent			C	H	N	S	Cl
A		$C_6H_3N_3SCl_6$	Calcd	19.91	0.83	11.61	8.86	58.78
			Found	19.86	0.91	11.35	8.88	58.58
A		$C_7H_5N_3SCl_6$	Calcd	22.37	1.34	11.18	8.53	56.59
			Found	22.52	1.38	11.10	8.63	56.61
A		$C_8H_7N_3SCl_6$	Calcd	24.64	1.81	10.78	8.22	54.55
			Found	24.69	1.85	10.76	8.07	54.65
A		$C_8H_7N_3SCl_6$	Calcd	24.64	1.81	10.78	8.22	54.55
			Found	24.51	1.88	10.51	7.90	54.98
A		$C_9H_9N_3SCl_6$	Calcd	26.76	2.25	10.40	7.94	52.66
			Found	26.66	2.24	10.29	8.02	52.81
A		$C_9H_9N_3SCl_6$	Calcd	26.76	2.25	10.40	7.94	52.66
			Found	26.85	2.35	10.16	8.06	52.77
A		$C_{10}H_{11}N_3SCl_6$	Calcd	28.73	2.65	10.05	7.67	50.89
			Found	28.86	2.62	9.83	7.55	50.93
A	Ether	$C_{11}H_{13}N_3SCl_6$	Calcd	30.58	3.03	9.73	7.42	49.24
			Found	30.72	3.11	9.67	7.50	49.40
A	Ether	$C_{17}H_{25}N_3SCl_6$	Calcd	39.55	4.88	8.14	6.21	41.21
			Found	39.41	5.02	8.33	6.29	41.32
A	Ether	$C_{12}H_7N_3SCl_6$	Calcd	32.91	1.61	9.59	7.32	48.57
			Found	32.68	1.86	9.48	7.35	48.81
B	Ether	$C_{12}H_6N_3SCl_7$	Calcd	30.51	1.28	8.89	6.79	52.53
			Found	30.62	1.43	9.02	6.65	52.48
B	Ether	$C_{12}H_6N_4O_2SCl_6$	Calcd	29.84	1.25	11.60	6.64	44.04
			Found	30.01	1.36	11.45	6.55	44.12
A	Ether	$C_{11}H_5N_3SCl_6$	Calcd	31.16	1.19	9.91	7.56	50.17
			Found	31.38	1.41	9.73	7.48	49.97
A	Ether	$C_{12}H_7N_3SCl_6$	Calcd	32.91	1.61	9.59	7.32	48.57
			Found	32.88	1.81	9.63	7.53	48.67
B	Ether	$C_{12}H_7N_3SCl_6$	Calcd	32.91	1.61	9.59	7.32	48.57
			Found	32.76	1.58	9.72	7.47	48.49
B	Ether	$C_{12}H_7N_3SCl_6$	Calcd	32.91	1.61	9.59	7.32	48.57
			Found	33.19	1.77	9.31	7.31	48.66
B	Ether	$C_{12}H_7N_3OSCl_6$	Calcd	31.75	1.55	9.26	7.06	46.86
			Found	31.70	1.44	9.06	7.24	46.51
B	Ether	$C_{12}H_7N_3OSCl_6$	Calcd	31.75	1.55	9.26	7.06	46.86
			Found	31.65	1.61	9.33	7.16	46.53
B	Ether	$C_{13}H_9N_3OSCl_6$	Calcd	33.36	1.94	8.98	6.85	45.45
			Found	33.55	2.02	9.11	6.79	45.51

TABLE 2.

R	Yield (%)	Physical property		UV	IR[*1]	NMR τ[*2]
		Bp, °C/mmHg	Mp, °C	$\lambda_{max}^{CH_3OH}$ mμ(ε)	cm^{-1}	(Sol. $CDCl_3$)
	81		54—56	212 (15190) 283 (11830)	1542 1503	8.55 (*t*, 3H, CH_3) 5.92 (*q*, 2H, CH_2) 3.02 (*d*, 2H, b) 2.47 (*d*, 2H, a)
	92		58—60	210 (15680) 270 (10150)	1532 1510	2.18—2.80 (*m*, 4H, Aro.)
	93		57—58	213 (17780) 270 (10910)	1540 1510	2.50 (*m*, 3H, b+c+d) 2.27 (*s*, H, a)
	95	224—226/1.0	68—70	210 (19070) 268 (10900)	1548 1504	2.46 (*d*, 4H, a+b)
	86	230—240/2.0	68—70	213 (21090) 267 13090)	1545 1512	2.55 (*d*, H, c) 2.36 (*d*, H, b) 2.23 (*s*, H, a)
	90	245—248/2.0	85—87	212 (23840) 271 (9170)	1540 1512	2.47 (*d*, 2H, b+c) 2.18 (*s*, H, a)
	83		97—99	213 (23730) 266 (7070)	1538 1516	2.29 (*s*, H, b) 2.14 (*s*, H, a)
	83		60—62	215 (17500) 270 (10650)	1540 1510	
	87		75—76	270 (10770)	1540 1508	7.58 (*s*, 3H, CH_3) 2.52 (*m*, 2H, b+c) 2.45 (*d* H, a)
	61		93—95	288 (16320)	1520	2.30 (*d*, 2H, b) 1.66 (*d*, 2H, a)
	83		65—66	263 (11080)	1540 1512	2.25 (*d*, 2H, b+c) 1.75 (*s*, H, a)
	64		65—67	286 (9980)	1526	5.93 (*s*, 3H, CH_3) 2.20 (*m*, 2H, b+c) 2.08 (*d*, H, a)

[*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.*, U. S. Pat. 3347859 (1967) a) mp 63°C; b) bp 154—157°C/0.4 mmHg; c) mp 83—84°C; d) mp 68—70°C.

[*4] H. G. Schmelzer *et al.*, German Pat. 1200314 (1965).

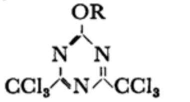
[*5] n_D^{28} 1.5710

Continued

Method		Molecular formula		Anal., %				
A or B	Solvent			C	H	N	S	Cl
B	Ether	$C_{13}H_9N_3OSCl_6$	Calcd	33.36	1.94	8.98	6.85	45.45
			Found	33.41	2.04	8.90	6.72	45.25
B	Ether	$C_{11}H_4N_3SCl_7$	Calcd	28.82	0.88	9.17	7.00	54.14
			Found	28.61	0.92	8.99	6.97	54.25
B	Ether	$C_{11}H_4N_3SCl_7$	Calcd	28.82	0.88	9.17	7.00	54.14
			Found	29.03	0.93	8.97	7.09	53.92
A	Ether	$C_{11}H_4N_3SCl_7$	Calcd	28.82	0.88	9.17	7.00	54.14
			Found	28.96	0.92	9.06	7.01	53.96
A	Ether	$C_{11}H_3N_3SCl_8$	Calcd	26.81	0.61	8.53	6.51	57.55
			Found	26.66	0.63	8.44	6.41	57.31
A	Ether	$C_{11}H_3N_3SCl_8$	Calcd	26.81	0.61	8.53	6.51	57.55
			Found	26.82	0.73	8.31	6.27	57.65
B	Ether	$C_{11}H_2N_3SCl_9$	Calcd	25.05	0.38	7.97	6.08	60.51
			Found	25.37	0.63	8.05	5.83	60.73
B	Ether	$C_{11}H_4N_3SBrCl_6$	Calcd	26.27	0.80	8.36	6.38	58.19[*6]
			Found	26.34	0.96	8.45	6.43	58.24
B	Ether	$C_{12}H_6N_3SCl_7$	Calcd	30.51	1.28	8.89	6.79	52.53
			Found	30.69	1.40	8.69	6.66	52.47
B	Ether	$C_{11}H_4N_4O_2SCl_6$	Calcd	28.17	0.86	11.95	6.84	45.36
			Found	28.34	1.01	12.13	6.76	45.51
B	Ether	$C_{11}H_3N_4O_2SCl_7$	Calcd	26.24	0.60	11.13	6.37	49.30
			Found	26.35	0.81	10.85	6.34	49.19
B	Ether	$C_{12}H_6N_4O_3SCl_6$	Calcd	28.88	1.21	11.23	6.43	42.63
			Found	29.01	1.45	11.36	6.53	42.55

[*6] Calcd value: Cl+Br

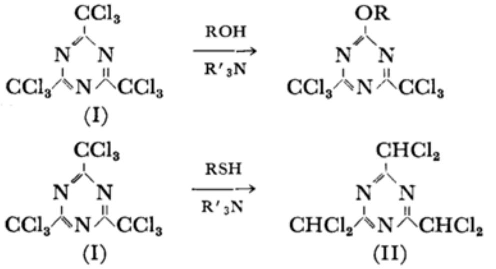
cf. NMR ($CDCl_3$)



R=CH_3CH_2- τ: 8.44 (*t*, 3H, CH_3); 5.26 (*q*, 2H, CH_2)

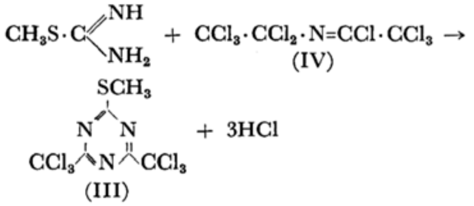
R=CH_3- τ: 5.72 (*s*, 3H, CH_3)

alkanethiols in the presence of tertiary amines took an entirely different course as compared with the reaction of I with alcohols. Instead of being replaced with the alkylthio groups, the CCl_3-groups were converted into $CHCl_2$-groups and resulted in 2,4,6-tris(dichloromethyl)-*s*-triazine (II).[2]



Scheme 1

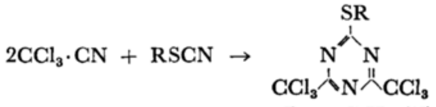
The only type of these *s*-triazines hitherto known, is 2-methylthio-4,6-bis(trichloromethyl)-*s*-triazine[3] (III) which was obtained from the reaction of *S*-methyl isothiourea with *N*-pentachloroethyl-trichloroacetimidoyl chloride (IV). The following Scheme 2 shows this method to be successful.



Scheme 2

While the *S*-methyl isothiourea is derived readily from thiourea,[6] IV has been only obtained by high temperature (250—300°C) chlorination reaction of $(C_2H_5)_2NH$[7] or of *N*-ethyl-trichloroacetimidoyl chloride[8] under UV irradiation. Many side reactions may occur, if the reaction is not carried out carefully in this chlorination process. Because of such conditions, the method mentioned above is not readily applicable to the preparation of the desired compounds.

The authors have also investigated the preparation of 2-substituted thio-4,6-bis(trichloromethyl)-*s*-triazines, in order to evaluate these *s*-triazines as fungicides[9] or nitrification inhibitors[10] in soil. Accordingly, the extention of the cotrimerization reaction[1] of CCl_3CN with other nitriles to that of CCl_3CN with RSCN, have been examined as a method in the preparation of these types of *s*-triazines. The results show that 2-substituted thio-4,6-bis(trichloromethyl)-*s*-triazines can be prepared in high yield by a less costly and moderate reaction condition involving the simple cotrimerization of CCl_3CN with RSCN at atmospheric pressure.



Scheme 3

Cotrimerization reaction was done by introducing HCl gas into the mixture of 2 mol of CCl_3CN and 1 mol of RSCN and a small amount of Friedel-Crafts catalyst.[11] The strong heating treatment was

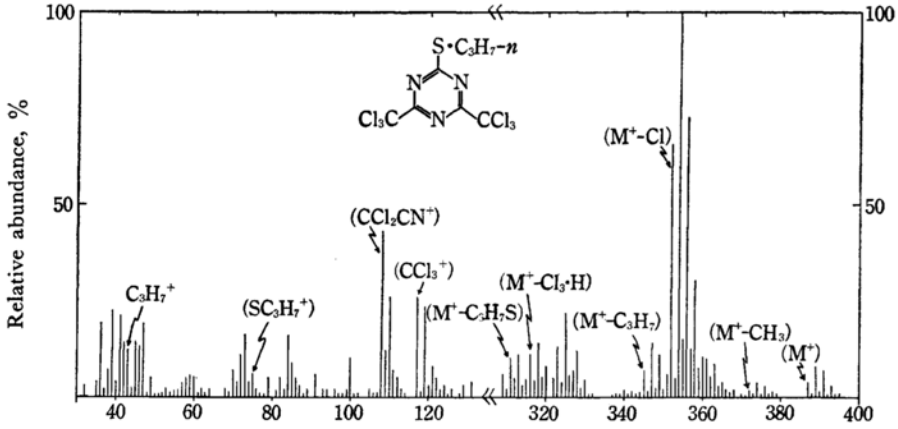


Fig. 1. Mass spectrum of V.

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6) P. R. Shildneck and Wallace Windus, "Organic Syntheses," Coll. Vol. II, p. 411 (1943).

7) W. Zecher, H. Tarnow and H. Holtschmidt, German Pat. 1222918 (1966); Netherland Appl. 6516622 (1966).

8) H. Holtschmidt, E. Degener and H. G. Schmelzer, *Liebigs Ann. Chem.*, **701**, 107 (1967).

9) K. Matsui, H. Kasugai, K. Wakabayashi, S. Motojima and M. Tsuda, Japanese Appl. 67973 (1968).

10) M. Okuzu, K. Wakabayashi, M. Tsunoda, S. Fujita and M. Tsuda, Japanese Appl. 86933 (1968).

11) H. G. Schmelzer and E. Degener, U. S. Pat. 3347859 (1967).

We came across this patent a few days after we carried out our experiment. $ZnCl_2$-HCl is used in the patented reaction instead of our combined catalyst, $AlBr_3$-HCl.

necessary to cotrimerize completely CCl_3CN with RSCN as well as the cotrimerization of CCl_3CN with aliphatic nitriles.[1] The reaction time was shortened by using Friedel-Crafts catalyst, which was not necessarily required to achieve this reaction.

In several cases the authors did not use solvents. When RSCN was not dissolved completely in CCl_3CN, suitable solvents such as ether, chloroform, carbon tetrachloride, *etc.*, could be used.

The following information shows that the product from CCl_3CN and n-C_3H_7SCN was to be a 2 : 1 cotrimer of them. The product has a strong infrared absorption at 1550 and 1503 cm^{-1} (*s*-triazine ring). Figure 1 shows the result of mass spectrum analysis.

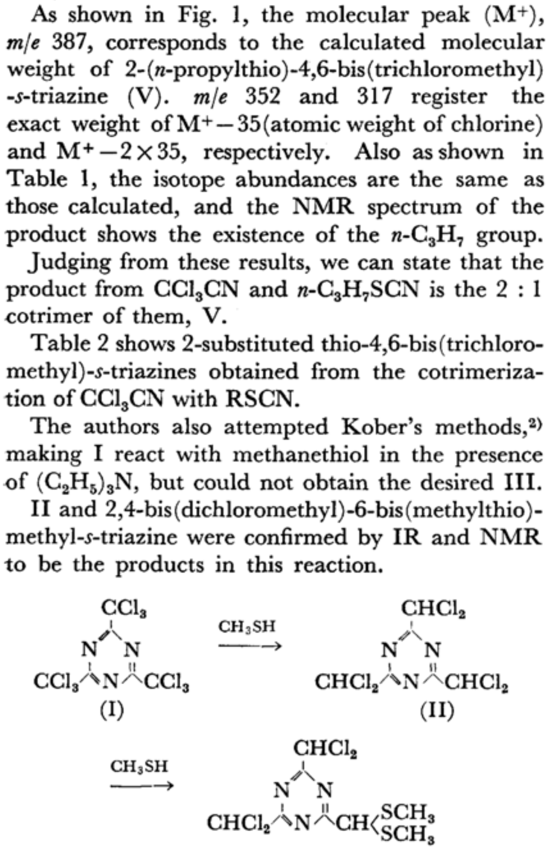
As shown in Fig. 1, the molecular peak (M^+), *m/e* 387, corresponds to the calculated molecular weight of 2-(*n*-propylthio)-4,6-bis(trichloromethyl)-*s*-triazine (V). *m/e* 352 and 317 register the exact weight of $M^+ - 35$(atomic weight of chlorine) and $M^+ - 2 \times 35$, respectively. Also as shown in Table 1, the isotope abundances are the same as those calculated, and the NMR spectrum of the product shows the existence of the n-C_3H_7 group.

Judging from these results, we can state that the product from CCl_3CN and n-C_3H_7SCN is the 2 : 1 cotrimer of them, V.

Table 2 shows 2-substituted thio-4,6-bis(trichloromethyl)-*s*-triazines obtained from the cotrimerization of CCl_3CN with RSCN.

The authors also attempted Kober's methods,[2] making I react with methanethiol in the presence of $(C_2H_5)_3N$, but could not obtain the desired III.

II and 2,4-bis(dichloromethyl)-6-bis(methylthio)-methyl-*s*-triazine were confirmed by IR and NMR to be the products in this reaction.



Scheme 4

Experimental

All boiling points and melting points are uncorrected. 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.

Procedure of the Method. *2-Substituted Thio-4,6-bis(trichloromethyl)-s-triazine.* 290 g (2 mol) of CCl_3CN and thiocyanate*[2] (1 mol) and 3 g of $AlBr_3$ were placed in a 500 m*l* flask (if necessary, the solvent should be added). Anhydrous hydrogen chloride (*ca.* 150 g) was introduced into the mixed solution at −40—−20°C with stirring. The reaction mixture was kept at −10—0°C for 12 hr and then at room temperature for the next 24 hr. Hydrogen chloride gas was then removed under reduced pressure (20—30 mmHg) by use of a water pump from the reaction mixture, gradually heating it to 150—200°C to complete cotrimerization. The residue was fractionated under reduced pressure (Method A) or recrystallized from ethyl acetate (Method B). 2-Substituted thio-4,6-bis(trichloromethyl)-*s*-triazines obtained were shown in Table 2.

2,4,6-Tris(dichloromethyl)-s-triazine[2] *(II)*. To the mixed solution of 21 g (0.2 mol) of $(C_2H_5)_3N$ and 96 g (2 mol) of CH_3SH was added 43.3 g (0.1 mol) of 2,4,6-tris(trichloromethyl)-*s*-triazine by small portion at −20—−30°C with stirring. After adding, 200 m*l* of ether was added to this solution and the excess CH_3SH was removed below room temperature. The separated $(C_2H_5)_3N$-HCl salt was filtered and the filtrate was concentrated to remove ether and CH_3SSCH_3. The resulting oily residue was fractionated to give 24.7 g (75% yield) of 2,4,6-tris(dichloromethyl)-*s*-triazine, bp 150—60°C/0.5 mmHg, mp 62—65°C. Recrystallization from petroleum ether raised the melting point to 67—70°C. Found: C, 21.95; H, 1.03; N, 12.66; Cl, 64.52%. Calcd for $C_6H_3N_3Cl_6$: C, 21.84; H, 0.92; N, 12.74; Cl, 64.49%. IR absorption (KBr): 1552 cm^{-1} (characteristic absorption of *s*-triazine system). NMR spectrum ($CDCl_3$): τ 3.27 (singlet, $CHCl_2$).

2,4-Bis(dichloromethyl)-6-bis(methylthio)methyl-s-triazine. Using 50 g (0.5 mol) of $(C_2H_5)_3N$ and 96 g (2 mol) of CH_3SH and 43.3 g (0.1 mol) of 2,4,6-tris(trichloromethyl)-*s*-triazine, the reaction was carried out in the same way as in the preparation of II. The major product, 23 g (65% yield), bp 125—128°C/0.01 mmHg, n_D^{23} 1.5572, was 2,4-bis(dichloromethyl)-6-bis(methylthio)methyl-*s*-triazine.

Found: C, 27.35; H, 2.46; N, 12.01; Cl, 39.96; S, 18.34%. Calcd for $C_8H_9N_3Cl_4S_2$: C, 27.21; H, 2.57; N, 11.90; Cl, 40.16; S, 18.16%.

IR absorption (Film): 1548 cm^{-1} (characteristic absorption of *s*-triazine system).

NMR spectrum ($CDCl_3$): τ 7.73 (singlet, 6H, SCH_3); 6.12 (singlet, H, $-CH\langle{}^{S}_{S}$); 3.35 (singlet, 2H, $CHCl_2$).

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*[2] Materials. Alkyl thiocyanates were prepared from KSCN and the corresponding alkyl halides and aryl thiocyanates from the corresponding anilines.