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## Studies on *s*-Triazines. I. Cotrimerization of Trichloroacetonitrile with Other Nitriles\*<sup>1</sup>

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2-Substituted 4,6-bis(trichloromethyl)-*s*-triazines have been prepared by the cotrimerization of  $\text{CCl}_3\text{CN}$  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  $\text{CCl}_3\text{CN}$  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,<sup>1,2)</sup> fungicides,<sup>3,4)</sup> nitrification inhibitors,<sup>5-10)</sup> in soil and antimalarials.<sup>11)</sup>

Starting material,  $\text{CCl}_3\text{CN}$ , is easily obtained by the chlorination<sup>12-16)</sup> of  $\text{CH}_3\text{CN}$  which is a by-product in SOHIO acrylonitrile process. This led us to investigate the cotrimerization of  $\text{CCl}_3\text{CN}$  with other nitriles.

\*<sup>1</sup> Taken in part from the dissertation presented by K. Wakabayashi to the University of Tokyo, 1969.

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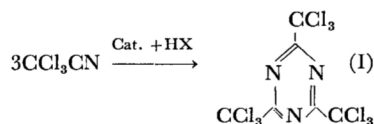
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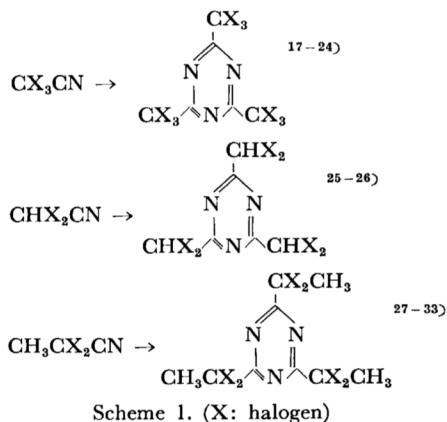
TABLE I.\* THE EFFECT OF COMBINED CATALYST FOR TRIMERIZATION OF  $\text{CCl}_3\text{CN}$ 

| 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    |
| $\text{AlF}_3$          | HCl | 32.0                  | 21.5            | 67.2      | 93    |
| $\text{AlCl}_3$         | HCl | 32.0                  | 11.5            | 35.9      | 92—93 |
| $\text{AlBr}_3$         | HCl | 32.0                  | 30.5            | 95.3      | 93    |
| $\text{AlBr}_3$         | HBr | 32.0                  | 30.5            | 95.3      | 92—93 |
| $\text{BF}_3$ -acetate  | HCl | 32.0                  | 20.3            | 62.5      | 92—93 |
| $\text{BF}_3$ -etherate | HCl | 32.0                  | 30.1            | 93.8      | 93    |
| $\text{FeCl}_3$         | HCl | 32.0                  | 14.0            | 43.8      | 93    |
| $\text{ZnCl}_2$         | HCl | 32.0                  | 13.4            | 42.2      | 93    |
| $\text{SnCl}_4$         | HCl | 32.0                  | 16.4            | 51.6      | 92—93 |
| $\text{SbCl}_3$         | HCl | 32.0                  | 15.1            | 46.9      | 93    |
| $\text{TiCl}_4$         | HCl | 40.0                  | 16.2            | 40.5      | 92—93 |
| $\text{TiBr}_4$         | HCl | 40.0                  | 24.9            | 62.3      | 92—93 |

All samples in Table I were identified by a mixed melting point with an authentic sample<sup>21)</sup> and IR spectra analyses.

\* Reaction condition; See Experimental A).

Several authors<sup>17-33)</sup> observed the formation of the *s*-triazines from  $\alpha$ -chlorinated nitriles.

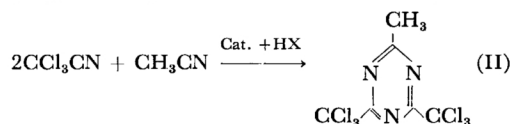


Trimerization of nitriles has been effected with both basic and acidic catalysts. The basic catalysts, such as sodium,<sup>34,35)</sup> potassium methoxide,<sup>36)</sup> diethylzinc,<sup>37,38)</sup> sodium hydride<sup>38)</sup> and *N*-sodium methylaniline<sup>38)</sup> give, in general, dimers<sup>39)</sup> or pyrimidines<sup>36)</sup> as main products. Acid catalyzed trimerization of nitriles<sup>17-21,23-33)</sup> affords *s*-triazines in good yields. The reaction<sup>19-21)</sup> was carried out in a closed system.  $\text{AlBr}_3$ -HCl (Norton's catalyst) is so effective that it can afford excellent yield under ordinary pressure in trimerization of  $\text{CCl}_3\text{CN}$ .<sup>21)</sup>

The cotrimerization of  $\text{CCl}_3\text{CN}$  with other nitriles,  $\text{RCN}$  (R: methyl,<sup>25,40-42,44)</sup> phenyl,<sup>25,40,41)</sup> 2-

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TABLE 2.\* THE EFFECT OF COMBINED CATALYST FOR COTRIMERIZATION OF  $\text{CCl}_3\text{CN}$  WITH  $\text{CH}_3\text{CN}$ 

| Combined catalyst       |      |     | Reaction time (hr) | Product yield (%) (II) | Mp °C |
|-------------------------|------|-----|--------------------|------------------------|-------|
| Catalyst (g)            |      | HX  |                    |                        |       |
| $\text{AlF}_3$          | 3.0  | HCl | 8.0                | 95                     | 96—97 |
| $\text{AlCl}_3$         | 3.0  | HCl | 12.0               | 85                     | 96—97 |
| $\text{AlBr}_3$         | 3.0  | HCl | 3.0                | 95                     | 96—97 |
| $\text{AlBr}_3$         | 3.0  |     | 96.0               | 0                      |       |
| $\text{BF}_3$ -acetate  | 5.0  | HCl | 3.0                | 95                     | 96—97 |
| $\text{BF}_3$ -etherate | 5.0  | HCl | 4.0                | 95                     | 96—97 |
| $\text{BBr}_3$          | 3.0  | HCl | 5.0                | 88                     | 96    |
| $\text{FeCl}_3$         | 3.0  | HCl | 16.0               | 83                     | 96    |
| $\text{ZnCl}_2$         | 4.0  | HCl | 16.0               | 78                     | 96    |
| $\text{SnCl}_4$         | 4.0  | HCl | 16.0               | 83                     | 96—97 |
| $\text{SbCl}_5$         | 4.0  | HCl | 24.0               | 76                     | 96—97 |
| $\text{TiCl}_4$         | 3.0  | HCl | 3.0                | 90                     | 96    |
| $\text{TiBr}_4$         | 3.0  | HCl | 3.0                | 90                     | 96    |
| $\text{CuCl}_2$         | 10.0 | HCl | 48.0               | 58                     | 96    |
| $\text{MgCl}_2$         | 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,<sup>40</sup> 2-chloroethyl<sup>43</sup>) and 2-bromoethyl<sup>43</sup>), 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  $\text{CCl}_3\text{CN}$  with other nitriles to give *s*-triazines.

### Results and Discussion

Trimerization of  $\text{CCl}_3\text{CN}$  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  $\text{CCl}_3\text{CN}$  (Friedel-Crafts catalysts-hydrogen halides) produces a good result, especially with  $\text{AlBr}_3$ -HCl,  $\text{AlBr}_3$ -HBr and  $\text{BF}_3$  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  $\text{CCl}_3\text{CN}$  with  $\text{CH}_3\text{CN}$  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( $P_1-35 \times 2$ ), 257( $P_2-35 \times 2$ ); 324( $P_1-35 \times 3$ ), 222( $P_2-35 \times 3$ )

are results from the loss of one, two and three chlorine atom(s) respectively. There are also large peaks at mass  $m/e$  117(+ $\text{CCl}_3$ ) and 108(+ $\text{CCl}_2\text{-CN}$ ) in both spectra. Intensities of isotope peaks of I relative to the parent peak for chlorines ( $\text{Cl}_6$ ) 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 ( $\text{Cl}_6$ ) 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.<sup>25,40</sup>

The data in Table 2 indicate that the combined catalyst,  $\text{AlBr}_3$ -HCl, are most effective and economical.<sup>44</sup> This particular catalyst was used to investigate the distribution of the products by changing the molar ratio of  $\text{CCl}_3\text{CN}$  and  $\text{CH}_3\text{CN}$ . 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  $\text{CCl}_3\text{CN}$  with  $\text{CH}_3\text{CN}$ . GLC's relative  $R_f$  values are (I)=1.00, (II)=0.38 (based on (I)=1.00). These values were the same as those of authentic samples.

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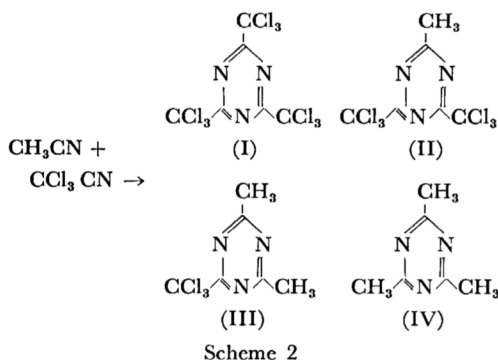
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TABLE 3.\* THE EFFECT OF MOLAR RATIO FOR  
COTRIMERIZATION OF  $\text{CCl}_3\text{CN}$  WITH  $\text{CH}_3\text{CN}$   
 $n \text{ CCl}_3\text{CN} + \text{CH}_3\text{CN} \rightarrow \text{I} + \text{II}$

| CCl <sub>3</sub> CN/CH <sub>3</sub> CN<br>Molar ratio<br>(n) | Yield**<br>of II<br>(%) | Selectivity |      |
|--|-------------------------|-------------|------|
|  |                         | I           | 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  $\text{AlBr}_3$  (3g), using 41 g (1 mol) of  $\text{CH}_3\text{CN}$ .

\*\* Based on  $\text{CCl}_3\text{CN}$ .



Although the values of relative  $R_i$  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  $\text{CCl}_3\text{CN}$  with  $\text{CH}_3\text{CN}$  was inspected.

Several other nitriles as well as  $\text{CH}_3\text{CN}$  were cotrimerized with  $\text{CCl}_3\text{CN}$ , using  $\text{HCl}$ -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<sup>45,46)</sup> was developed.

That is to say, 2-alkyl\*2,4,6-bis(trichloromethyl)-s-triazines were prepared from cotrimerization of 2 mol  $\text{CCl}_3\text{CN}$  and 1 mol aliphatic nitriles in good yield when anhydrous  $\text{HCl}$  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  $\text{HCl}$  only gave good results.

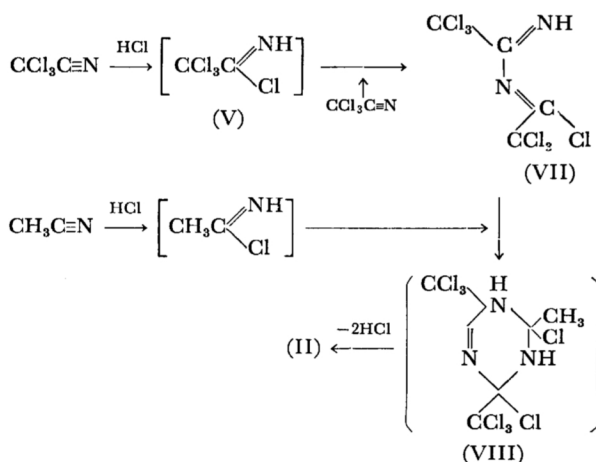
Table 5 shows the compounds obtained from the above mentioned method.

The following two experiments were carried out to observe some aspects of the mechanism about  $\text{HCl}$ -catalysed cotrimerization of  $\text{CCl}_3\text{CN}$  with  $\text{CH}_3\text{CN}$ . This mechanism may explain the cotrimerization of  $\text{CCl}_3\text{CN}$  with other nitriles also.

a) Addition of 1 mol  $\text{CH}_3\text{CN}$  to the adduct\*<sup>3</sup> of 2 mol of  $\text{CCl}_3\text{CN}$  and 1 mol  $\text{HCl}$ .

b) Addition of 1 mol  $\text{CH}_3\text{CN}$  that has already absorbed 1 mol  $\text{HCl}$  to the adduct of 2 mol of  $\text{CCl}_3\text{CN}$  and 1 mol  $\text{HCl}$ .

Like Grundmann *et al.*<sup>25)</sup> 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).

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79470 (1967).

\*<sup>2</sup> Alkyl having more than  $\text{C}_2$  in Table 5

\*<sup>3</sup> The adduct was identified in the form of  $(\text{CCl}_3\text{CO})_2\text{NH}$  (lit. 25).



TABLE 4.\*1 COTRIMERIZATION OF  $\text{CCl}_3\text{CN}$  WITH OTHER NITRILES

| R   | Yield<br>% | Mp**<br>°C | UV<br>$\lambda_{\text{CH}_3\text{OH}}$<br>$\lambda_{\text{max}}$ m $\mu$ ( $\epsilon$ ) | IR*<br>cm <sup>-1</sup> | Molecular<br>formula                                    | Anal., %                         |              |               |                  |
|---|------------|------------|---|-------------------------|---|----------------------------------|--------------|---------------|------------------|
|   |            |            |   |                         |   | C                                | H            | N             | Cl               |
| $\text{CH}_3$                                       | 95         | 96—97**4   | 219(1920)<br>280(950)   | 1543                    |   |                                  |              |               |                  |
| $\text{C}_6\text{H}_5$ †                            | 94         | 97—98**4   | 282(23210)  | 1514<br>1548            |   |                                  |              |               |                  |
| 2-ClC <sub>6</sub> H <sub>4</sub>                   | 91         | 120—122    |   | 1510<br>1548            | $\text{C}_{11}\text{H}_4\text{N}_3\text{Cl}_7$          | Calcd<br>30.99<br>Found<br>31.04 | 0.95<br>1.11 | 9.86<br>9.57  | 58.21<br>58.50   |
| 3-ClC <sub>6</sub> H <sub>4</sub>                   | 93         | 125—127    |   | 1548                    | $\text{C}_{11}\text{H}_4\text{N}_3\text{Cl}_7$          | Calcd<br>30.99<br>Found<br>30.86 | 0.95<br>0.99 | 9.86<br>10.03 | 58.21<br>58.19   |
| 4-ClC <sub>6</sub> H <sub>4</sub>                   | 92         | 158—159**5 |   | 1510<br>1548            |   |                                  |              |               |                  |
| 2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>   | 88         | 143—145    | 216(22690)<br>283(2600)   | 1510<br>1550            | $\text{C}_{11}\text{H}_3\text{N}_3\text{Cl}_8$          | Calcd<br>28.67<br>Found<br>28.34 | 0.66<br>0.87 | 9.12<br>9.36  | 61.55<br>61.38   |
| 3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>   | 90         | 139—140    |   | 1510<br>1548            | $\text{C}_{11}\text{H}_3\text{N}_3\text{Cl}_8$          | Calcd<br>28.67<br>Found<br>28.61 | 0.66<br>0.74 | 9.12<br>8.96  | 61.55<br>61.41   |
| 2,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> | 85         | 153—155    |   | 1510<br>1550            | $\text{C}_{11}\text{H}_2\text{N}_3\text{Cl}_9$          | Calcd<br>26.68<br>Found<br>26.52 | 0.41<br>0.53 | 8.49<br>8.50  | 64.43<br>64.72   |
| 4-BrC <sub>6</sub> H <sub>4</sub>                   | 92         | 161—163    |   | 1512<br>1548            | $\text{C}_{11}\text{H}_4\text{N}_3\text{Cl}_8\text{Br}$ | Calcd<br>28.06<br>Found<br>27.99 | 0.86<br>0.72 | 8.93<br>8.76  | 62.15**<br>62.22 |
| 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>     | 95         | 122—123**5 |   | 1512<br>1546            |   |                                  |              |               |                  |
| 3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>     | 74         | 103—104**5 |   | 1510<br>1538            |   |                                  |              |               |                  |
| 4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> †  | 90         | 144—145**5 | 240(7930)<br>328(22580)   | 1512<br>1546            |   |                                  |              |               |                  |
| 1-Naphthyl  | 83         | 216—218    |   | 1545                    | $\text{C}_{15}\text{H}_7\text{N}_3\text{Cl}_6$          | Calcd<br>40.76<br>Found<br>40.52 | 1.60<br>1.86 | 9.50<br>9.43  | 48.13<br>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  $\text{AlBr}_3$  (3 g), using 2 moles of  $\text{CCl}_3\text{CN}$  and 1 mole of  $\text{RCN}$ . \*\* 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 ( $\text{CDCl}_3$ )  $\tau$  1.38 (*d*, 2H), *a*; 2.41 (*q*, 3H), *b*.  $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-$   $\tau$  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<sub>3</sub>CN WITH ALIPHATIC NITRILES

| R  | Yield % | Bp, °C/mmHg<br>Mp, °C<br>(From solvent) | UV<br>λ <sub>max</sub> <sup>CH<sub>3</sub>OH</sup> mμ (ε) | IR* <sup>1</sup><br>cm <sup>-1</sup> | NMR* <sup>2</sup><br>τ   | Molecular formula  | Anal., %       |                |              |                |                |
|--|---------|---|---|--------------------------------------|--|--|----------------|----------------|--------------|----------------|----------------|
|  |         |   |   |                                      |  |  | C              | H              | N            | Cl             |                |
| C <sub>2</sub> H <sub>5</sub>                                  | 92      | 165-166/11* <sup>3</sup><br>34-36       | 221(1770)<br>278(570)                                     | 1525<br>1543                         | 8.64( <i>t</i> , 3H)<br>6.79( <i>g</i> , 2H)   | C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> Cl <sub>6</sub>   | Calcd<br>Found | 26.85<br>26.70 | 1.97<br>1.82 | 11.74<br>11.75 | 59.44<br>59.62 |
| <i>n</i> -C <sub>3</sub> H <sub>7</sub>                        | 93      | 136-138/2                               | 220(1820)<br>278(660)                                     | 1528<br>1548                         | 8.92( <i>t</i> , 3H)<br>8.01( <i>h</i> , 2H)<br>6.82( <i>t</i> , 2H)                         | C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> Cl <sub>6</sub>   | Calcd<br>Found | 26.85<br>26.49 | 1.97<br>1.89 | 11.74<br>11.83 | 59.44<br>60.11 |
| <i>i</i> -C <sub>3</sub> H <sub>7</sub>                        | 87      | 170-175/14                              | 214(3220)<br>265(580)                                     | 1522<br>1545                         | 8.55( <i>d</i> , 6H)<br>6.60( <i>m</i> , H)  | C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> Cl <sub>6</sub>   | Calcd<br>Found | 26.85<br>26.49 | 1.97<br>1.89 | 11.74<br>11.83 | 59.44<br>60.11 |
| <i>n</i> -C <sub>4</sub> H <sub>9</sub>                        | 90      | 157-159/3                               | 216(3840)<br>281(730)                                     | 1528<br>1545                         | 8.97( <i>d</i> , 6H)<br>7.58( <i>m</i> , H)<br>6.94( <i>d</i> , 2H)                          | C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> Cl <sub>6</sub>   | Calcd<br>Found | 29.06<br>28.88 | 2.44<br>2.39 | 11.30<br>11.34 | 57.20<br>57.36 |
| <i>i</i> -C <sub>4</sub> H <sub>9</sub>                        | 82      | 154-156/3                               | 216(3840)<br>281(730)                                     | 1528<br>1545                         | 8.97( <i>d</i> , 6H)<br>7.58( <i>m</i> , H)<br>6.94( <i>d</i> , 2H)                          | C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> Cl <sub>6</sub>   | Calcd<br>Found | 29.06<br>28.96 | 2.44<br>2.34 | 11.30<br>11.48 | 57.20<br>57.43 |
| <i>s</i> -C <sub>4</sub> H <sub>9</sub>                        | 81      | 142-146/3                               | 222(1910)<br>276(600)                                     | 1528<br>1548                         | 9.04( <i>t</i> , 3H)<br>8.56( <i>d</i> , 3H)<br>8.17( <i>qt</i> , 2H)<br>6.80( <i>m</i> , H) | C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> Cl <sub>6</sub>   | Calcd<br>Found | 29.06<br>29.20 | 2.44<br>2.56 | 11.30<br>11.21 | 57.20<br>57.34 |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub>                        | 56      | 154-157/8<br>68-70                      | 224(2220)<br>283(610)                                     | 1525<br>1543                         | 8.50( <i>s</i> )   | C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> Cl <sub>6</sub>   | Calcd<br>Found | 29.06<br>29.17 | 2.44<br>2.62 | 11.30<br>11.42 | 57.20<br>57.08 |
| <i>n</i> -C <sub>5</sub> H <sub>11</sub>                       | 95      | 175-177/5                               | 216(3500)<br>280(650)                                     | 1528<br>1548                         | 9.08( <i>t</i> , 3H)<br>7.93-8.72( <i>m</i> , 6H)<br>6.83( <i>t</i> , 2H)                    | C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> Cl <sub>6</sub> | Calcd<br>Found | 31.12<br>31.03 | 2.87<br>2.74 | 10.89<br>10.73 | 55.12<br>55.08 |
| <i>n</i> -C <sub>9</sub> H <sub>19</sub>                       | 78      | 192-194/5* <sup>4</sup>                 | 216(2320)<br>262(450)                                     | 1525<br>1548                         | 9.12( <i>t</i> , 3H)<br>7.42-8.46( <i>m</i> , 14H)<br>6.84( <i>t</i> , 2H)                   | C <sub>14</sub> H <sub>19</sub> N <sub>3</sub> Cl <sub>6</sub> | Calcd<br>Found | 38.04<br>37.95 | 4.33<br>4.18 | 9.50<br>9.55   | 48.12<br>48.34 |
| <i>n</i> -C <sub>17</sub> H <sub>35</sub>                      | 92      | 210-215/4* <sup>5</sup>                 | 244(3320)   | 1520<br>1548                         | 6.36( <i>t</i> , 2H) <sup>b</sup><br>5.88( <i>t</i> , 2H) <sup>a</sup>                       | C <sub>22</sub> H <sub>35</sub> N <sub>3</sub> Cl <sub>6</sub> | Calcd<br>Found | 47.67<br>47.54 | 6.36<br>6.30 | 7.58<br>7.52   | 37.38<br>37.51 |
| CH <sub>3</sub> ClCH <sub>2</sub><br><sup>a</sup> <sub>b</sub> | 69      | 65-67* <sup>6</sup><br>(EtOH)           | 223(2330)<br>285(770)                                     | 1528                                 | 518( <i>s</i> )  | C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> Cl <sub>9</sub>   | Calcd<br>Found | 18.10<br>18.72 | 0.45<br>0.38 | 9.40<br>9.43   | 71.35<br>71.54 |

† Reaction conditions; See Experimental B-b).  
<sup>\*1</sup> Characteristic absorption of *s*-triazine system. <sup>\*2</sup> *s*, singlet; *d*, doublet; *t*, triplet; *g*, quartet; *q*, quintet; *h*, heptet; *m*, multiplet. <sup>\*3</sup> H. G. Schmelzer *et al.*, German Pat. 1200314 (1965). <sup>\*4</sup> *n*<sub>2</sub><sup>D</sup> 1.4746. <sup>\*5</sup> *n*<sub>D</sub><sup>20</sup> 1.4850. <sup>\*6</sup> 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  $\text{CCl}_3\text{CN}$  and 1 molecule  $\text{HCl}$ ) and acetimidoyl chloride (VI) (formed from 1 molecule  $\text{CH}_3\text{CN}$  and 1 molecule  $\text{HCl}$ ) 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  $\text{HCl}$ .

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  $\text{HCl}$  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 detector, with 25 ml/min of nitrogen, using a  $2\text{ m} \times 4\text{ mm}$  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.  $\text{CH}_2\text{ClCH}_2\text{CN}$ <sup>47)</sup> was prepared from acrylonitrile.  $\text{CCl}_3\text{CN}$ <sup>12)</sup> was prepared by the chlorination of acetonitrile and  $\text{CH}_2\text{ClCCl}_2\text{CN}$ <sup>48)</sup> by the chlorination of acrylonitrile. *i*- $\text{C}_4\text{H}_9\text{CN}$ , *s*- $\text{C}_4\text{H}_9\text{CN}$ , *t*- $\text{C}_4\text{H}_9\text{CN}$ , *n*- $\text{C}_6\text{H}_{13}\text{CN}$ , 2- $\text{ClC}_6\text{H}_4\text{CN}$ , 3- $\text{ClC}_6\text{H}_4\text{CN}$ , 4- $\text{BrC}_6\text{H}_4\text{CN}$ , 2,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{CN}$ , 3,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{CN}$  and 2,4,5- $\text{Cl}_3\text{C}_6\text{H}_2\text{CN}$  were prepared by the dehydration of corresponding amide with  $\text{P}_2\text{O}_5$ . 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  $\text{CCl}_3\text{CN}$ .** 2,4,6-Tris(trichloromethyl)-*s*-triazine (I). 32 g (0.22 mol) of  $\text{CCl}_3\text{CN}$  and 0.5 g of a catalyst were placed into a 300 ml flask. The mixture was saturated with anhydrous  $\text{HCl}$  at  $-10$ – $0^\circ\text{C}$  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  $100$ – $110^\circ\text{C}$  and poured into a large quantity of water to wash out  $\text{HCl}$  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  $\text{AlBr}_3\text{-HCl}$  as the catalyst.

Found: C, 16.60; N, 9.49; Cl, 73.90%. Calcd for  $\text{C}_6\text{N}_3\text{Cl}_3$ : C, 16.64; N, 9.70; Cl, 73.66%.

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

UV absorption;  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  219  $\mu$  ( $\epsilon$  2590); 287  $\mu$  ( $\epsilon$  790).

**B) Cotrimerization of  $\text{CCl}_3\text{CN}$ .** a) 2-Methyl-4,6-bis(trichloromethyl)-*s*-triazine (II). 289 g (2 mol) of  $\text{CCl}_3\text{CN}$  and 50 g (1.2 mol) of  $\text{CH}_3\text{CN}$  and a catalyst were placed into a 500 ml flask. The mixture was saturated with anhydrous  $\text{HCl}$  at  $-20$ – $0^\circ\text{C}$  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  $100$ – $110^\circ\text{C}$  and poured into a large quantity of water to wash out  $\text{HCl}$  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  $\text{AlBr}_3\text{-HCl}$  as the catalyst.

Found: C, 21.99; H, 1.00; N, 12.69; Cl, 64.48%. Calcd for  $\text{C}_6\text{H}_3\text{N}_3\text{Cl}_3$ : C, 21.84; H, 0.92; N, 12.74; Cl, 64.49%.

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

UV absorption;  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  219  $\mu$  ( $\epsilon$  1920); 280  $\mu$  ( $\epsilon$  950).

NMR spectrum ( $\text{CDCl}_3$ );  $\tau$  7.02 ( $\text{CH}_3$ ).

b) 2-Alkyl-4,6-bis(trichloromethyl)-*s*-triazine. The mixed solution of 289 g (2 mol) of  $\text{CCl}_3\text{CN}$  and 1.2 mol of  $\text{RCN}$  was saturated with anhydrous  $\text{HCl}$  at  $-30$ – $-15^\circ\text{C}$  by cooling with dry ice-methanol bath for 2 hr with stirring, which was continued at  $-10$ – $0^\circ\text{C}$  for 2–3 hr. The reaction mixture was kept overnight at room temperature. Then  $\text{HCl}$  gas was removed under reduced pressure by a water pump, gradually heating the reaction mixture at  $150$ – $200^\circ\text{C}$  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) trichloroacetamide which was prepared from  $\text{CCl}_3\text{CN}$  and acetamide.<sup>49)</sup> Yield 55%. Mp  $72$ – $73^\circ\text{C}$  (lit<sup>49)</sup> mp  $69$ – $71^\circ\text{C}$ ).

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

UV absorption;  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  234  $\mu$  ( $\epsilon$  2020); 260  $\mu$  ( $\epsilon$  890).

NMR spectrum ( $\text{CDCl}_3$ );  $\tau$  7.26 ( $\text{CH}_3$ ).

b) 2,4,6-Trimethyl-*s*-triazine (IV). IV was prepared by the method of Schaefer<sup>50)</sup> from ethyl acetimidate. Yield 90%. Mp  $60^\circ\text{C}$ . Bp  $150$ – $155^\circ\text{C}$  (lit<sup>50)</sup> bp  $155^\circ\text{C}$ . IR absorption; 1536  $\text{cm}^{-1}$  (*s*-triazine ring).

UV absorption;  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  228  $\mu$  ( $\epsilon$  270); 257  $\mu$  ( $\epsilon$  390).

NMR spectrum ( $\text{CDCl}_3$ );  $\tau$  7.42 ( $\text{CH}_3$ ).

**D) Experiments to Elucidate  $\text{HCl}$ -catalysed Cotrimerization of  $\text{CCl}_3\text{CN}$  with  $\text{CH}_3\text{CN}$ .** a)

The Reaction of  $\text{CH}_3\text{CN}$  and the Adduct (VII) of  $\text{CCl}_3\text{CN}$  and  $\text{HCl}$ . 18 g (0.5 mol) of anhydrous  $\text{HCl}$  was absorbed into 144.5 g (1 mol) of  $\text{CCl}_3\text{CN}$  at  $-10$ – $0^\circ\text{C}$  for 0.5 hr. Then 20.5 g (0.5 mol) of  $\text{CH}_3\text{CN}$  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.

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

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

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

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

The distillate was a mixture of  $\text{CH}_3\text{CN}$  and  $\text{CCl}_3\text{CN}$ . 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  $\text{CH}_3\text{CN}$  and  $\text{HCl}$ , and the Adduct (VII) of  $\text{CCl}_3\text{CN}$  and  $\text{HCl}$ .* 18 g (0.5 mol) of anhydrous  $\text{HCl}$  was absorbed into 144.5 g (1 mol) of  $\text{CCl}_3\text{CN}$  at  $-10-0^\circ\text{C}$  for 0.5 hr. 18 g of anhydrous  $\text{HCl}$  was also absorbed into 20.5 g (0.5 mol) of  $\text{CH}_3\text{CN}$  under the same condition. Then two solutions were mixed at  $0-10^\circ\text{C}$  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  $90-93^\circ\text{C}$ . This compound was identified II by GLC and IR analyses.

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