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Cyclotrimerisation of Cyano-compounds into 1,3,5-Triazines

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A survey is made of papers on the cyclotrimerisation of substituted monofunctional cyanides X.C:N differing in the structure of the substituent X = H, R, Ar, $\geqslant$N, HO, RO, ArO, HS, RS, Hal. This reaction has been widely used in recent years both in preparative organic chemistry and in large-tonnage industrial manufactures, by virtue of the availability of the initial compounds, the high yields of 1,3,5-triazines, and the simplicity of operation. Attention is paid mainly to recent work to elucidate the influence of substituents X on the reactivity of N : C-containing compounds; various mechanisms of cyclotrimerisation are discussed, as well as the effects of catalysts, pressure, and other factors. Consideration is given not only to homocyclotrimerisation but also to mixed cyclotrimerisation of cyanide derivatives and the influence of the reaction conditions on the structure of the resulting 1,3,5-triazines. A list of 247 references is included.

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I. INTRODUCTION

1,3,5-Triazines are important products of modern organic chemistry. They are widely used as intermediates in dye chemistry and in the paper, paint and varnish, and pharmaceutical industries, as herbicides and as monomers for the synthesis of thermostable polymers, and in several other branches of the national economy.

The most promising method for the industrial synthesis of 1,3,5-triazines is the cyclotrimerisation of compounds containing a nitrogen–carbon triple bond, since this reaction usually occurs selectively to give high yields of the final products. In industry cyclotrimerisation has been used to obtain such compounds as cyanuric acid, melamine, cyanuric chloride, etc. The cyclotrimerisation of several compounds containing an N$\vdots$C bond was known as early as the nineteenth century, but the largest amount of research has been conducted during recent years. Attention has been concentrated mainly on studying the mechanisms of cyclotrimerisation, the synthesis of new derivatives of 1,3,5-triazine, the selection of various catalytic systems, etc. Furthermore, a long series of papers has appeared on the synthesis of highly heat-resistant and thermostable polymers from N$\vdots$C-containing monomers.

In several of the earlier reviews and monographs[1-5] containing information on 1,3,5-triazines little attention was paid to cyclotrimerisation. Most of these surveys were published 15–20 years ago, and do not reflect advances made during recent years.

The present Review surveys published results on the cyclotrimerisation of cyanide derivatives in which the cyano-group is attached to various atoms and radicals (H, R, RO, RS, R_2N, Hal). Data on the conditions for the cyclotrimerisation of particular classes of compounds are summarised in tables. Attention is paid mainly to recent studies of mechanisms, the influence of the nature of substituents attached to cyano-groups on their electrophilic character, and the tendency to undergo this reaction. The cyclotrimerisation of compounds containing two or more functional groups to give polymers has been discussed in detail in several recent reviews[6-8], and therefore will not be considered here.

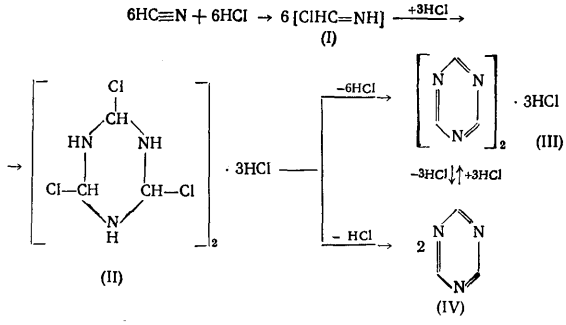
II. 1,3,5-TRIAZINE FROM HYDROGEN CYANIDE

Since 1,3,5-triazine, unlike most of its derivatives, is highly reactive towards nucleophiles, it could not be identified until 1954.[9,10] This compound was obtained by Nef[11] more than a half-century ago, but it was then regarded as a dimer of hydrogen cyanide.

The mechanism of the formation of 1,3,5-triazine by the action of hydrogen chloride on hydrogen cyanide was investigated by Grundmann and Kreutzberger[12]. They suggested that initial addition of equimolecular quantities of the reactants is followed by spontaneous trimerisation of the adduct (I)† to bis-(2,4,6-trichlorohexahydro-1,3,5-triazine) trihydrochloride (II); 1,3,5-triazine (IV)

†Kreutzberger has since[4] attributed the structure $[HC\vdots NH]^+Cl^-$ to the adduct (I).

was isolated by dehydrochlorination of (II) or of the intermediate (III) formed from (II):

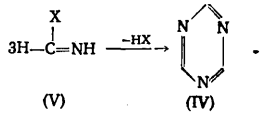


The yield of 1,3,5-triazine from the trimerisation of hydrogen cyanide in the presence of hydrogen chloride is 55–60%.[9,12,13]

Table 1. Synthesis of 1,3,5-triazine by the cyclocondensation of compounds (V).

X	Reaction conditions			Yield, wt.%	Ref.
	catalyst	T, °C	p, atm		
C_2H_5O	NaOH	—	—	10	11
HS	—	80	vacuum	20	15
H_2N	R_2N	150—250	0.02	3—72	12, 16, 17
$C_6H_5CH_2$—O	$C_5H_5N(C_2H_5)_2$	80	0.01	50	18

1,3,5-Triazine can also be obtained[10,14] by the thermal or base-catalysed (Table 1) cyclocondensation of compounds (V):

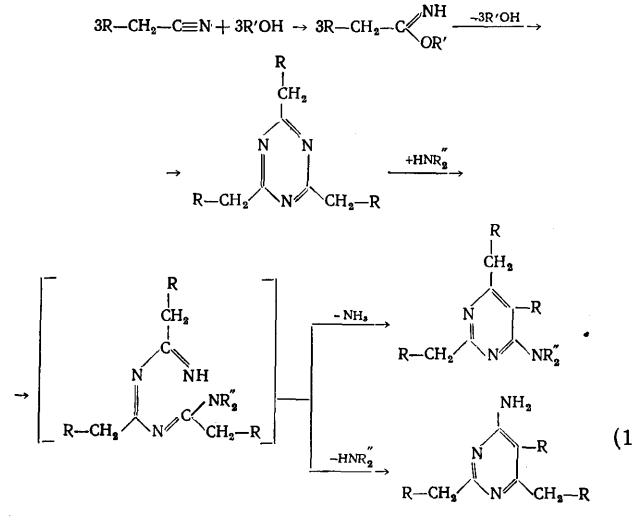


III. 2,4,6-TRIALKYL-1,3,5-TRIAZINES FROM ALKYL CYANIDES

1. 2,4,6-Trialkyl-1,3,5-triazines from Unsubstituted Alkyl Cyanides

Repeated attempts were made[19–29] to synthesise trialkyltriazines by the cyclotrimerisation of alkyl cyanides R.CN, but few successes were achieved. Thus the action of strong bases on alkyl cyanides involves deprotonation of the α-carbon–hydrogen bond followed by addition of the next cyanide molecules to form aminopyrimidine rings[19–29].

1,3,5-Triazines have been obtained from aliphatic cyanides by conducting the reaction in solution in a primary alcohol under high pressure[30–33] (Table 2). The reaction involves intermediate formation of imidic esters. If a secondary amine is introduced into the reaction mixture, the main product is 4-aminopyrimidine resulting from rearrangement of 1,3,5-triazine[30]. A suggested[32] mechanism is



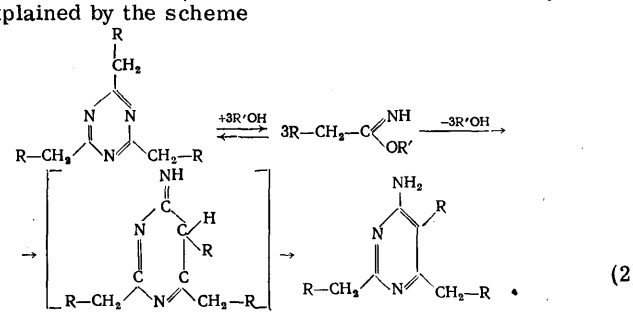
(1)

Table 2. 2,4,6-Trialkyl-1,3,5-triazines from unsubstituted alkyl cyanides RCN.

R	Reaction conditions				Yield, wt.%	Ref.
	10^3p, atm	T, °C	solvent	duration, h		
CH_3	7.9	120	methanol	10	29	32
	7.9	120	ethanol	10	6	32
	7.9	120	ethanol	24	11	32
C_2H_5	7.9	120	ethanol	24	7	32
	7—8	70	methanol	65	36	30, 31
C_3H_7	7.9	120	ethanol	24	1	32
n-C_4H_9	7—8	150	methanol	18	35	30, 31
	7—8	100	methanol	18	7	30, 31
t-C_4H_9*	10.5	130	thiolan *S*-dioxide	8	50	33
CH_2 / \ CH / CH_2	9	160	thiolan *S*-dioxide	6	90	33
	8—9	200—210	ethanol	10—15	90	33
	8—9	200—210	propan-1-ol	10—15	70	33

*Methanol used as catalyst.

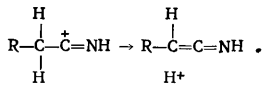
Such rearrangements have been observed[33] even in the absence of amines, under 9000 atm at 200°C. They were explained by the scheme



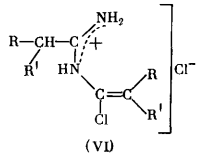
(2)

As evidence of the formation of an intermediate imidic ester 2-substituted benzimidazoles were isolated[33] on the addition of *o*-phenylenediamine to the reaction mixture. 4-Aminopyrimidines may be formed either through an intermediate stage from 1,3,5-triazines (schemes 1 and 2) or directly from the initial compounds. They were not observed[34] in the acid-catalysed formation of 1,3,5-triazines from imidic esters.

Several attempts have been made to synthesise 1,3,5-triazines by the cyclotrimerisation of unsubstituted alkyl cyanides in the presence of acids, but this has not yet been achieved. Ruske[35] explains the lack of success by the hyperconjugation effect of the alkyl radical, which diminishes the electrophilic character of the cyanide carbon atom and thus hinders addition of the next cyanide molecule:



Yanagida et al.[36] have also investigated the reaction between alkyl cyanides and hydrogen chloride, and have shown that stable hydrochlorides of *N*-substituted amidines



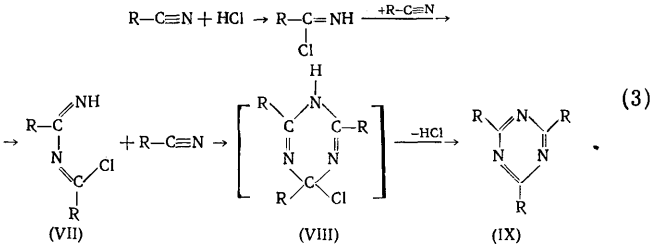
(VI)

are formed. The use of Lewis acids as catalysts for the cyclotrimerisation of acetonitrile also failed to yield the corresponding 1,3,5-triazine: 4-amino-2,6-dimethylpyrimidine was isolated[37].

2. 2,4,6-Trialkyl-1,3,5-triazines from Substituted Alkyl Cyanides

1,3,5-Triazines are formed from α-halogenated alkyl cyanides by acid catalysis, since the hyperconjugation effect of the α-carbon–hydrogen bond is counteracted by the effect of the substituent. Thus, whereas monohalogenated acetonitriles do not usually trimerise‡, and dihalogenated acetonitriles trimerise with insignificant yields§, trihalogenated acetonitriles readily yield the corresponding 2,4,6-tristrihalogenomethyl-1,3,5-triazines.

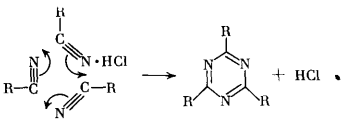
In the presence of hydrogen chloride the catalytic process leads to formation of a primary adduct[36,38,39] of the type 2RCN.3HCl. The electrophilicity of dimers of monohalogenoacetonitriles then becomes weaker in comparison with the monomer, and addition of another nitrile molecule impossible[40]. The mechanism first suggested[40] for this acid-catalysed cyclotrimerisation of αα-di- and ααα-tri-halogenated alkyl cyanides to the corresponding 1,3,5-triazines involved intermediate formation of the primary adduct (VII):



(VII) (VIII) (IX) (3)

This was followed[40] by cycloaddition of another cyanide molecule to give the 2,4,6-trialkyl-4-chloro-1,4-dihydro-1,3,5-triazine (VIII), which underwent spontaneous dehydrohalogenation to the 1,3,5-triazine (IX). However, treatment of $2CCl_3CN.HCl$ with acetonitrile does not yield the expected 1,3,5-triazine, although cyclotrimerisation of trichloroacetonitrile together with acetonitrile in the presence of hydrogen chloride gives the corresponding methylbistrichloromethyl-1,3,5-triazine[40].

Zil'berman[41,42] has suggested a different mechanism, in which the relatively easy formation of 1,3,5-triazines is due to a large gain in energy accompanying cyclisation, which may involve cyclic electron transfer:



On this view both free nitriles and their complexes with hydrogen halides take part in the formation of triazines.

Sulphuric acid[47], Lewis acids[47-49], and complexes of the latter with hydrogen halides[50-53] have also been used as acid catalysts, among which the complexes are the best for cyclotrimerisation. Zil'berman et al.[48] have described the preparation of 2,4,6-tristrichloromethyl-1,3,5-triazine from the complexes

$2Cl_3C—CN \cdot AlCl_3$ (X); $Cl_3C—CN \cdot AlCl_3$ (XI); $Cl_3C—CN \cdot 2AlCl_3$ (XII).

at 100°C (Table 3). They showed[48] that raising the temperature to 140–150°C leads to the formation of polymers, hexachloroethane, and cyanogen in various proportions. Polymeric products are also formed from dichloroacetonitrile in the presence of aluminium trichloride at 100°C.[49]

A large number of possible catalysts have been reported for the cyclotrimerisation of fluorinated nitriles to 1,3,5-triazines, including metal oxides[54,55]

(Al_2O_3, Bi_2O_3, CaO, Ag_2O, Co_2O_3, Fe_2O_3, HgO, PbO_2, Cu_2O, BaO, Sb_2O_3, TiO_2, V_2O_3, Y_2O_3, ZnO, Mn_2O_3, Tl_2O_3)

silver salts[56]

($AgCl$, $AgBr$, AgI, $AgClO_3$, $AgNO_3$, Ag_2SO_3, Ag_2SO_4, $AgClO_4$, $AgBF_4$

fluorides[56]

SnF_2, CdF_2, ThF_2, AgF, CoF_2, CoF_3, FeF_2, FeF_3, CrF_3, VF_5, CuF_2, ZnF_2, NaF, KF, NH_4F, NH_4BF_4, SnF_4, LiF, NiF_2);

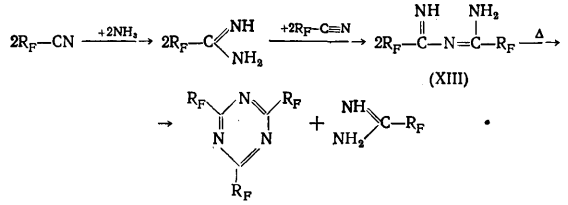
and organometallic compounds[57] [e.g. $(n\text{-}C_8H_9)_3SbO$ and $(CH_3)_3Sb(OH)_2$], as well as amine oxides[58]. Ammonia also catalyses the cyclotrimerisation of fluorinated

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‡Yanagida et al.[36] have obtained 2,4,6-trischloromethyl-1,3,5-triazine from the adduct $2CH_2ClCN.2HCl$.

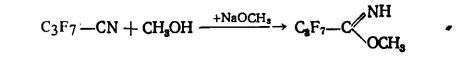
§It was assumed in the early work that dimers were formed[43-46].

nitriles $R_F.CN$¶, both at high[59] and at normal[59-62] pressures. At normal pressure the reaction is assumed to involve intermediate formation of imidoylamidines (XIII) [59,60]:



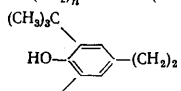
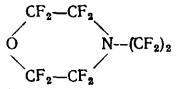
(XIII)

In the presence of alcohols at high pressures the formation of 1,3,5-triazines from fluorinated alkyl cyanides[63] and also from 1,1-dichloropropionitrile[30] may involve an imidic ester stage:



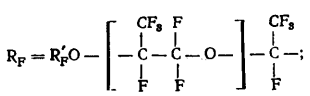
At 70–140 atm fluorinated alkyl cyanides trimerise even in the absence of a catalyst[62]. The uncatalysed cyclotrimerisation of pentafluoropropionitrile at normal pressure has been reported[62], providing additional

Table 3. 2,4,6-Trialkyl-1,3,5-triazines from substituted alkyl cyanides RCN.

R	Reaction conditions: catalyst	*p*, atm	*T*, °C	solvent	duration, h	Yield, wt.%	Ref.
$HO(CH_2)_n$ ($n = 3,4,5$)	Cu, Zn, Fe halides	—	0—50	—	—	—	69
$HO(CH_2)_n$ ($n = 3,4,5$)	—	500	0—50	—	—	—	69
$HO(CH_2)_n$ ($n = 3,4,5$)	*hv*	—	0—50	—	—	—	69
$HO(CH_2)_n$ ($n = 3,4,5$)	HCl	—	0	ethanol	8	73	70
	CH_3COOH	—	—	—	72	73	70
$C_2H_5—O—CO$ [a]	HCl	—	—	—	2-4 weeks	~96	71
Cl_2HC [b]	HCl; HBr	—	—	—	—	—	43,45,46
Cl_2HC	$AlCl_3$	—	50—70	—	6	20	49
F_3C	HCl	0—0.5	—	—	18—20	—	72
CF_3	—	42—70	300	—	16	31	62
$CF_3—CF_2$	—	—	300	—	120	48	62
$CF_3—(CF_2)_2$	—	117—139	350—400	—	130	8	62
$CF_2Cl—CFCl$	$AlCl_3$/HCl	—	22—60	—	20	~50	74
$CF_2Cl—CFCl$	$AlCl_3$/HCl	[c]	100	—	16	25	74
$CF_2H—CF_2—O—(CF_2)_3—O—(CF_2)_2$	NH_3	—	165—175	—	20	88	61
$HCFCl—CF_2—O—(CF_2)_2$	NH_3	—	150	—	19	80	61
	NH_3	—	150	—	14	88	61
$CH_3—CCl_2$	HCl	—	25	—	a few months	—	75
$CH_3—CCl_3$	—	7000—8000	100	methanol	18	74	30,31
$CH_3—CCl_3$	—	7000—8000	125	butan-1-ol	18	8	30,31
CCl_3	HCl [d]	—	—10—25	—	12	2	50
CCl_3	HCl	56	—	—	100	96	76
CCl_3	HBr [e]	—	—10—25	—	12	34	50
CCl_3	H_2SO_4	—	150[f]	—	4	—	47
CCl_3	$AlCl_3$	—	100	—	12	60	48
CCl_3	AlF_3/HCl	—	—10—25	—	12	~67	50
CCl_3	$AlCl_3$/HCl	—	—10—25	—	12	~36	50
CCl_3	$AlCl_3$/HCl	—	75	—	5	~93	51
CCl_3	$AlCl_3$/HCl; $AlBr_3$/HCl	—	—40—20	—	3—20	80—93	52
CCl_3	$AlBr_3$/HCl or HBr	—	—10—25	—	12	~95	50
CCl_3	$AlBr_3$/HCl	—	25—65	—	~4	95	51
CCl_3	BF_3-ether/HCl	—	—10—25	—	12	94	50
CCl_3	PCl_5/HCl	—	100—105	—	240	82	53
CCl_3	$FeCl_3$/HCl	—	—10—25	—	12	~44	50
CCl_3	$ZnCl_2$/HCl	—	—10—25	—	12	~42	50
CCl_3	$SnCl_4$/HCl	—	—10—25	—	12	~52	50
CCl_3	$SnCl_2$/HCl	—	—10—25	—	12	~47	50
CCl_3	$TiCl_4$/HCl	—	—10—25	—	12	~41	50
CCl_3	$TiBr_4$/HCl	—	—10—25	—	12	~62	50
CBr_3	HCl	—	—	—	a few days		76,77,80

[a] See also Refs. 40 and 73.
[b] Formation of polymers favoured by raising the temperature to 100–130°C and also by high concentration of aluminium chloride.
[c] Reaction conducted in an autoclave.
[d] See also Refs. 73, 77, and 78.
[e] See also Refs. 43, 77, and 79.
[f] Below 80°C the main reaction product is $(CCl_3CONH_2)_2SO_2$.

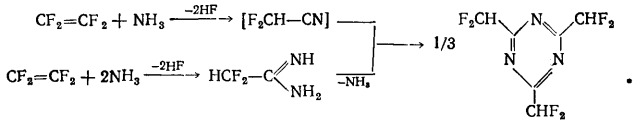
¶ Here



$R'_F = CF_3$, $Hal[CF_2]_m$, $H[CF_2]_m$, where $m = 1-8$, $n = 1-20$, $T = 300-350$°C, and $p = 49-63$ atm.

evidence of the highly electrophilic character of the nitrile group in perfluorinated alkyl cyanides.

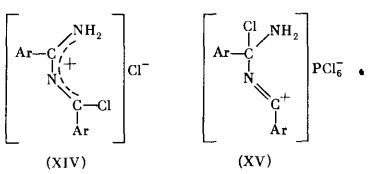
Syntheses of 1,3,5-triazines have also been described[63-67] in which halogenated nitriles are probably intermediate products. Thus the action of chlorine on acetonitrile and on propionitrile yields 2,4,6-tristrichloromethyl- and 2,4,6-trisdichloroethyl-1,3,5-triazine respectively[65-67]. A fluorinated triazine has been obtained[64] via an intermediate amidine stage:



The action of chlorine or bromine on 1,2,2,2-tetrafluoroethyl cyanide gives 2,4,6-tris-1'-chloro(or bromo)tetrafluoroethyl-1,3,5-triazine[68].

IV. 2,4,6-TRIARYL-1,3,5-TRIAZINES FROM ARYL CYANIDES

2,4,6-Triphenyl-1,3,5-triazine (cyaphenine) was first isolated[81] from the reaction between benzoyl chloride and potassium cyanide. It was first obtained by the cyclotrimerisation of benzonitrile in the presence of metallic sodium in 1868.[82] Later, in 1878, a method of synthesising 2,4,6-triaryl-1,3,5-triazines was developed[83] by the acid-catalysed cyclotrimerisation of aromatic nitriles, a process which has since been widely used. Good yields of 2,4,6-triphenyl-1,3,5-triazines are obtained by using as catalyst chlorosulphuric acid[84] in the molecular proportions $HSO_3Cl : C_6H_5CN = 3 : 1$ at 0°C. Increasing this ratio or lowering the temperature diminishes the yield. Raising the temperature by 10 deg also lowers the yield of trimer as a consequence of sulphonation of the benzonitrile. Hydrogen chloride is a weak cyclotrimerisation catalyst, since it forms a stable 2 : 2 adduct with benzonitrile[39], but when a Lewis acid is also present high yields of triaryltriazines are formed[53,85]. It was assumed[53] that the mechanism of formation of triphenyltriazine in this case consisted in weakening of the nucleophilic character of the chloride ion in the adduct (XIV) by formation of the complex (XV) with the Lewis acid (phosphorus pentachloride):

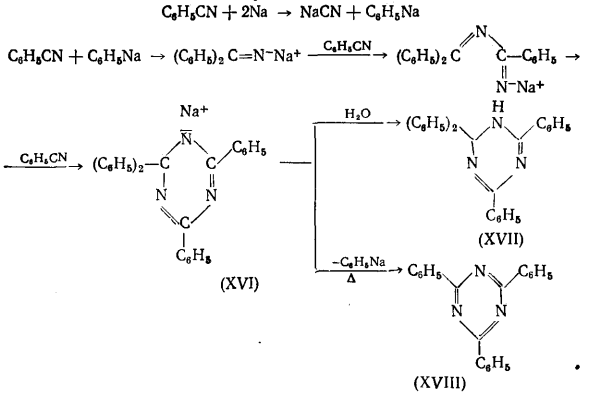


(XIV) (XV)

The hexachlorophosphate (XV) reacts further with another molecule of the aryl cyanide or with an adduct (1 : 1) of the nitrile and phosphorus pentachloride to give a 1,3,5,triazine, which may also be formed[39] by the pyrolysis of (XIV).

Lewis acids—aluminium, phosphorus(V), zinc, and titanium(IV) chlorides and boron trifluoride—have been used as catalysts for the cyclotrimerisation of aryl cyanides[50,53,86-91]. Their catalytic activity is considerably lower than that of corresponding mixtures of Lewis acids with various promoters—proton-containing compounds (mineral acids, water, amides, organic acids) and organic compounds containing mobile halogens—e.g. benzoyl chloride, etc.[87-89] Such a difference in catalytic activity is attributed to a change in the structure of the complexes† of the aryl cyanides with the Lewis acids[6,92-94]. When complexes of benzonitrile with Lewis acids are heated, either triphenyltriazine or a linear polymer of azomethine structure may be obtained depending on the conditions chosen (temperature, nature of complexes, additions of promoters, etc.)[87-89,92,95]. Pure Lewis acids have little catalytic effect on the cyclotrimerisation of nitriles[50], and only additions of cocatalysts (water, hydrogen chloride, etc.) produce a marked increase in their activity (see below).

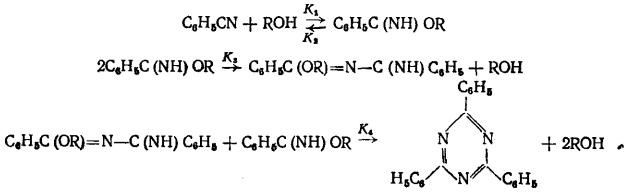
The reactions involved in the trimerisation of benzonitrile in the presence of bases have been studied in detail[97-100]. The action of sodium on benzonitrile forms initially phenylsodium‡, to which three molecules of benzonitrile then add successively to give the sodium salt of 1,2-dihydro-2,2,4,6-tetraphenyl-1,3,5-triazine (XVI):



(XVI) (XVII) (XVIII)

Hydrolysis of (XVI) gives the dihydro-1,3,5-triazine (XVII) in 85% yield[100]. When (XVI) was heated in a high-boiling solvent (xylene or nitrobenzene), 2,4,6-triphenyl-1,3,5-triazine (XVIII) was isolated[99]. The elimination of phenylsodium is accelerated by passing carbon or sulphur dioxide through the reaction mixture or by adding benzonitrile.

The cyclotrimerisation of aryl[30,31,33,43] and heterocyclic[33] cyanides catalysed by amines and alcohols under high pressures occurs similarly to that of alkyl cyanides described above. The trimerisation of benzonitrile in the presence of an alcohol under 2–10 kbar at 100–120°C involves initial formation of the benimidic ester[101]:



†For the structure of the complexes of nitriles with Lewis acids see also Ref. 96, pp. 571 and 583.

‡With organic compounds of alkali metals of the type RCH_2Na 2,4,6-triphenylpyrimidine is formed (with elimination of ammonia)[98].

Raising the pressure shifts the equilibrium towards formation of the trimer, whereas increasing the chain length and the degree of α-branching of the alcoholic radical hinders this reaction:

$CH_3OH > C_2H_5OH \approx n\text{-}iC_3H_7OH \approx n\text{-}C_4H_9OH > iso\text{-}C_3H_7OH \approx s\text{-}iC_4H_9OH$.

The reaction is second order with respect to the imidic ester: i.e. dimerisation (K_3) is the rate-determining stage. Polar solvents accelerate the reaction and increase the yield of trimer. The reaction is completely suppressed by acids; bases have hardly any effect. The effects of acid and basic catalysts on cyclotrimerisation are fundamentally different at high and normal pressures: in the latter case the reaction occurs in the presence of strong acids or bases. Raney nickel[102] and iron carbonyls[103] are relatively weak catalysts for the trimerisation of aryl cyanides.

Even in the absence of a catalyst aryl[30,31,104] and also heterocyclic[33] cyanides can be trimerised at high pressures. Formation of a dipolar intermediate form $R-C^{+}=N^{-}$ can be assumed, since in dipolar aprotic solvents[104], e.g. thiolan *S*-dioxide, trimerisation occurs under milder conditions than in the absence of a solvent[105].

Table 4. 2,4,6-Triaryl-1,3,5-triazines from aryl cyanides RCN.

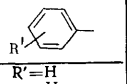
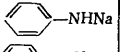
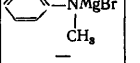
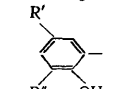
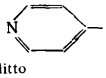
R	Reaction conditions: catalyst	$10^{-3}p$, atm	T, °C	solvent	duration, h	Yield, wt.%	Ref.
							
R′=H	HCl	—	100—105	—	—	trace	53
H	HCl	—	—	ethanol	24—48	—	106
H	H_2SO_4	—	—	—	24	—	83
H	HSO_3Cl	—	0	—	12	40	107
H	HSO_3Cl	—	0—5	—	12—24	~88	84
H	$AlCl_3$	—	140—160	—	6	—	86
H	PCl_5	—	~100	—	240	40	53
H	PCl_5/HCl; PBr_5/HCl; $SbCl_5$/HCl	—	100	—	24	98	85
H	PCl_5/HCl	—	100—105	—	24	98	53
H	$SbCl_5$/HCl *	—	100—105	—	24	62	53
H	PBr_5/HCl	—	100—105	—	24	20	53
H	$AlCl_3$/HCl	—	100—105	—	24	18	53
H	$SnCl_4$/HCl	—	100—105	—	24	21	53
H	$FeCl_3$/HCl; $ZnCl_2$/HCl	—	100—105	—	24	13	53
H	Na **, CO_2 or SO_2	—	80	benzene, xylene	27	~23	100
H	NaH	—	70—85	benzene, nitrobenzene, xylene	—	14	99
H	NaH	—	70—200	benzene, nitrobenzene	~6	14	99
H		—	35—190	ether	2	12	99
H		—	142	n-butyl ether	12	~21	99
H	—	—	285	pyrrolid-2-one	8	41	108
H	—	—	325	pyrrolid-2-one	8	44	108
H	—	7.5	100	methanol	18	76	30,31
H	—	7.5	125	methanol	18	82	30,31
H	—	7.5	100	ethanol	18	24	30,31
H	—	7.5	150	propan-2-ol	18	46	30,31
H	—	7.5	125	ethylhexanol	18	22	30,31
H	—	8—10	200	methanol	—	95	33
H	—	50	430	—	6***	~100	105
H	—	35	400	—	18***	~100	105
H	—	15.8	360	—	14	2.5	105
H	—	7.5	125	—	18	6	30,31
H	$Fe(CO)_5$; $Fe_2(CO)_9$	—	~190	—	a few hours	—	103
H	Ni, CH_3COOH	—	~190	—	48	3	
4-CH_3O	PCl_5/HCl	—	~100	nitrobenzene	120	8	53
2-CH_3	HSO_3Cl	—	0	—	48	—	107

Table 4. (contd.)

R	Reaction conditions: catalyst	$10^{-3}p$, atm	T, °C	solvent	duration, h	Yield, wt.%	Ref.
2-CH_3	H_3PO_4	37.5	350	—	16***	100	105
2-CH_3	—	50	480	—	6***	50	105
3-CH_3	HSO_3Cl	—	0	—	12	—	105
3-CH_3	PCl_5/HCl *	—	~100	—	120	63	53
3-CH_3	—	50	545	—	7***	100	105
4-CH_3	HSO_3Cl	—	0	—	12	—	107
4-CH_3	PCl_5/HCl	—	100—105	—	90	60	105
4-CH_3	—	50	500	—	6***	~100	105
4-CH_3	—	38.5	350	—	16***	30	105
4-Cl	HSO_3Cl	—	0	—	12	—	107
2-CN	acid	—	235	—	20	45	109
3-CN	$ZnCl_2$	—	360	—	25***	100	91
3-CN	$ZnCl_2$	—	420	—	2	89	91
3-CN	$ZnCl_2$	—	275	—	4	38	90
3-CN	PCl_5	—	250	—	9	—	90
3-CN	P_2O_5	—	250	—	5	52	90
3-CN	—	—	285	pyrrolid-2-one	24	46	108
4-CN	$AlCl_3$/HCl	—	100—105	nitrobenzene	120	26	53
4-CN	PCl_5/HCl	—	100—105	nitrobenzene	120	34	53
4-CN	$ZnCl_2$	—	270	—	5	64	90
4-CN	—	—	285	pyrrolid-2-one	24	50	108
4-NO_2	$AlCl_3$/HCl	—	100—105	nitrobenzene	120	16	53
4-NO_2	PCl_5/HCl	—	100—105	nitrobenzene	120	62	53
							
R′=H, Cl, Br; R″=H	—	—	160—180	—	2—3	—	110
R′=H, R″=CN; R′=CN, R″=H	—	—	153	*NN*-dimethylaniline	1	—	111
R′=NO_2, R″=H	—	—	melt	—	—	—	112
R′, R″=Br	—	—	melt	—	—	—	112
	PCl_5/HCl *	—	100—105	nitrobenzene	120	22	53
	—	8—10	200	piperidine	—	90	33
ditto	—	8—10	200	thiolan *S*-dioxide	—	50	33
»	—	8	180	methanol	5	90	33
	—	8.2	100	methanol	5	60	33
	NaOH	—	—	—	30***	—	113
	NaOH	—	—	—	30***	25	113
	NaOH	—	—	—	30***	25	113
ditto	$SnCl_4$	$1.3\cdot10^{-6}$ ****	320	—	—	15	114
»	$NaOC_2H_5$	****	220	ethanol	22	90	114

*Chlorinated 1,3,5-triazines formed as byproducts.

**Phenylsodium is an active catalyst, and has been used for the cyclotrimerisation of benzonitrile.[71,80,81]

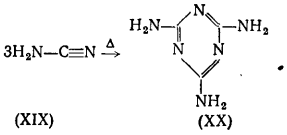
***Duration of reaction in minutes.

****Reaction conducted in an autoclave.

Steric factors also exert a strong influence on cyclotrimerisation. With *ortho*-substituted aryl cyanides, in contrast to the *meta*- and *para*-derivatives, severe conditions are required, and 1,3,5-triazines are formed from them in lower yields. 9-Cyanophenanthrene, 9-cyanoanthracene, and adamant-1-yl cyanide do not trimerise[33] even under 8000–17 000 atm at 150–240°C (Table 4).

V. 1,3,5-TRIAZINE-2,4,6-TRIAMINES (MELAMINES) FROM CYANAMIDES

Few results have been published on the cyclotrimerisation of cyanamide (**XIX**) to form 1,3,5-triazine-2,4,6-triamine (**XX**):

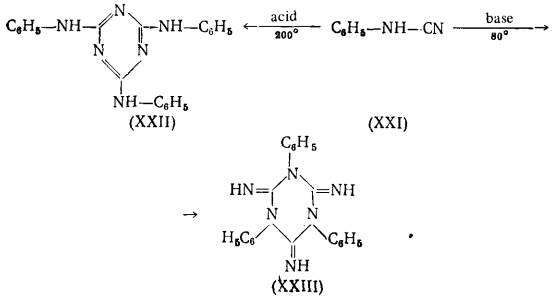


(XIX) (XX)

This synthesis is achieved either in molten cyanamide above 150°C (Ref. 1, p. 309) or by heating in a solvent of high boiling point [115].

The cyclotrimerisation of substituted cyanamides has been reported repeatedly (Ref. 1, p. 349), but until recently published results were contradictory [116-122]: in some cases the products were isomelamine derivatives [116, 117, 120], whereas in others substituted melamines of normal structure were obtained [118, 119, 121, 122]. From these results it may be concluded that 1,3,5-triazine-2,4,6-triamines are formed more readily if the substituting groups cause steric hindrance to attack on the NH group, as do tertiary alkyls [118, 119, 121], adamant-1-yl, [119] and *ortho*-substituted aryls [122].

A recent series of investigations [123-128] on the cyclotrimerisation of phenylcyanamide (**XXI**) has shown that either the normal triphenylmelamine (**XXII**) or triphenylisomelamine (**XXIII**) may be formed depending on the conditions:

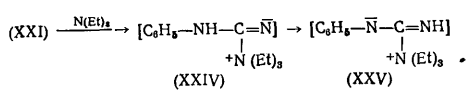


(XXII) (XXI) (XXIII)

Thus in the melt under mild conditions (20–80°C) the cyclotrimerisation of (**XXI**) yields (**XXIII**), whereas at 200°C the normal product (**XXII**) is mainly formed [123]. The structure of the final product is determined also by the nature of the catalyst: in the presence of Lewis acids—tin(II), zinc, titanium(IV) chlorides, etc.—(**XXII**) is formed, but basic catalysts—triethylamine, pyridine, triphenylphosphine, etc.—yield the iso-form (**XXIII**).

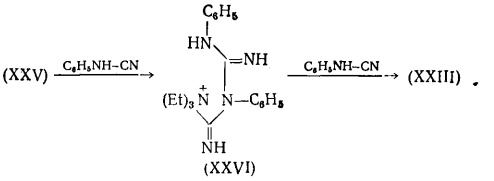
As in the catalytic cyclotrimerisation of nitriles, Lewis acids probably form with (**XXI**) adducts in which the electron pair of the π bond has been displaced to different extents, from molecular compounds of the type $C_6H_5.NH.C\equiv N, MX$ to ionic structures $C_6H_5.NH.C^+:N.M^-X$. Increasing the polarisation of the cyano-groups tends to accelerate the cyclotrimerisation of (**XXI**) to (**XXII**).

Catalysis by triethylamine probably involves formation of a complex with (**XXI**) by nucleophilic attack by the nitrogen atom of the tertiary amine on the electrophilic carbon atom of the nitrile group:



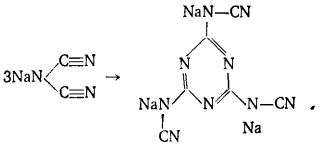
(XXIV) (XXV)

It is probable that (**XXV**) is more stable than the tautomeric structure (**XXIV**). This is supported by infrared spectroscopy, since addition of triethylamine to a toluene solution of (**XXI**) is accompanied by weakening in the spectrum of the mixture of the absorption band at 2230 cm^{-1} characteristic of vibrations of the N≡C bond in cyanamides, [129] with appearance of a band at 2130 cm^{-1} due to vibrations of the carbodi-imide group [129]. The complex (**XXV**) evidently then adds two more (**XXI**) molecules to form triphenylisomelamine (**XXIII**) via the transition state (**XXVI**) [125]:



(XXVI)

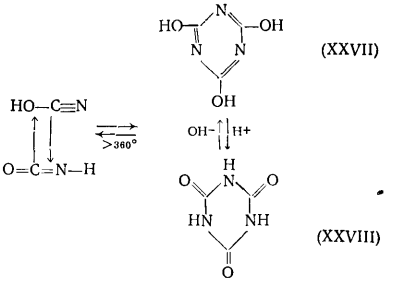
The trimerisation of disubstituted cyanamides was first described by Weith [130], who obtained hexaphenylmelamine by the action of cyanogen chloride on diphenylamine, which should involve intermediate formation of diphenylcyanamide. 2,4,6-Tripyrrol-1′-yl-1,3,5-triazine was also obtained by the action of cyanogen chloride on pyrrole. [131] Heating the sodium salt of dicyanamide gave the trisodium salt of 2,4,6-triscyanoamido-1,3,5-triazine [132]:



A kinetic study of the cyclotrimerisation of *N*-ethyl-*N*-phenylcyanamide has shown [126] that the presence of an aliphatic substituent α to the cyano-group diminishes the reactivity of the cyanamide group, so that this compound cyclotrimerises only in the presence of a cationic catalyst such as a Lewis acid to form 2,4,6-tris-(*N*-ethyl-*N*-phenylamino)-1,3,5-triazine. The presence of an isomelamine structure among the reaction products was not detected [126].

VI. CYANURIC ACID FROM CYANIC ACID

Cyanic acid exists in tautomeric equilibrium with isocyanic acid, and hence two forms of its trimers are possible—enolic (**XXVII**) and ketonic (**XXVIII**):



(XXVII) (XXVIII)

Polymerisation of cyanic acid yields not only cyanuric acid but also cyamelide, [133-135] a polymer (or trimer) of cyanic acid in which the carbonyl bond has been opened. Cyamelide is an amorphous white powder, insoluble in water and organic solvents, and readily depolymerised when heated (especially in the presence of acids). The polymerisation of cyanic acid vapour above 150°C results

in formation mainly of cyamelide, but below this temperature the chief product is cyanuric acid[135], which depolymerises at about 360°C.

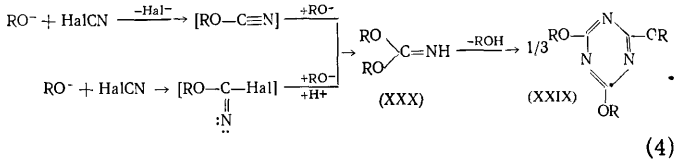
The Raman spectra show that solid cyanuric acid is present in the keto-form[136], which is confirmed by numerous investigations of the infrared spectra[137-140]. In solution the content of a particular form is determined by the pH: thus in saturated aqueous solution[141] at 20°C the content of the enolic form is 5.6%, in strongly alkaline medium the trimer is present in the enolic form, but in acid medium (pH < 6) the keto-form predominates[142-144]. An explanation of the predominance of the keto-form of cyanuric acid in neutral solution and in the solid state is that the loss of $\pi-\pi$ conjugation is largely balanced by strong $n-\pi$ conjugation, which makes this form the energetically more favourable structure.

Several syntheses of cyanuric acid other than the cyclotrimerisation of cyanic acid have been described[1,135] (see Ref. 2, p. 26). The principal industrial method is the pyrolysis of urea:

$$3NH_2CONH_2 \rightarrow (HOCN)_3 + 3NH_3 .$$

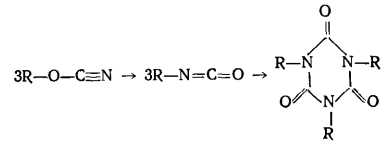
VII. 2,4,6-TRIALKOXY-1,3,5-TRIAZINES (TRIALKYL CYANURATES) FROM ALKYL CYANATES

Trialkyl cyanurates (**XXIX**) were first obtained in attempts to prepare alkyl cyanates from alkoxides and cyanogen halides[145-148]. A carbonimidic ester (**XXX**) is an intermediate product, which Nef[149] assumed to be formed directly from the anion of the chloroformidic ester, whereas other workers[150] assumed initial formation of the alkyl cyanate:



(4)

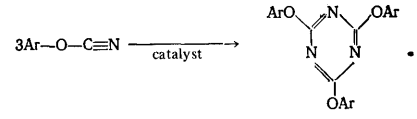
An obstacle to direct trimerisation of alkyl cyanates is the lability of the alkyl–oxygen bond, which results in side reactions. Thus the nucleophilic catalysts and anions of Brønsted acids used for trimerisation undergo alkylation[151,152], whereas Lewis acids and exposure to light of wavelength ≤250 nm promote their isomerisation into alkyl isocyanates[153]. Even on attempted distillation at normal pressure or on heating in solvents alkyl cyanates are isomerised into isocyanates[154-157], which in turn partly trimerise to form isocyanurates:



The rate of this isomerisation depends on the polarity of the solvent and on its ability to solvate cations. Solvents investigated in relation to this reaction form the sequence toluene < nitrobenzene ≈ acetonitrile < dimethylformamide ≪ dimethyl sulphoxide according to their tendency to isomerise alkyl cyanates[158]. Steric hindrance or strongly electron-accepting substituents enhance the stability of alkyl cyanates[7,158-164]. Thus 2,2,3,3-tetrafluoropropyl cyanate has been cyclotrimerised in theoretical yield to the corresponding cyanurate[159,160]. Carbaborane-containing cyanic esters $CB_{10}H_{10}CCH_2.O.C\vdots N$ resistant to isomerisation have been obtained[7,161-163], which also undergo selective trimerisation to the corresponding cyanurate structures[7,162,164].

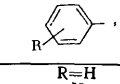
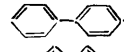
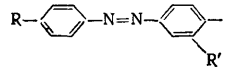
VIII. 2,4,6-TRIARYLOXY-1,3,5-TRIAZINES (TRIARYL CYANURATES) FROM ARYL CYANATES

In the presence of catalysts aryl cyanates readily undergo trimerisation to 2,4,6-triaryloxy-1,3,5-triazines (Table 5):



In contrast to alkyl cyanates, aryl cyanates do not isomerise into isocyanates: resonance interaction occurs between the cyanato-oxygen atom and the aromatic ring[165] ($\sigma^0_R = -0.27$), which stabilises the carbon–oxygen bond.

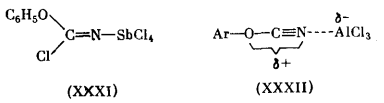
Table 5. 2,4,6-Triaryloxy-1,3,5-triazines from aryl cyanates ArOCN.

Ar	Reaction conditions: catalyst	T, °C	solvent	duration, h	Yield, wt.%	Ref.
						
R=H	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	85	157
H	PCl_5	20	CCl_4	~2	95	165
2-CH_3	PCl_5	20	CCl_4	~2	95	165
3-CH_3	PCl_5	20	CCl_4	~2	15	165
4-CH_3	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	84	157
4-CH_3	$AlCl_3$	50—60	—	~5*	100	158
4-CH_3	HCl(gas)	—	ether	—	100	158
4-CH_3O	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	98	157
4-Cl	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	80	157
4-Cl	PCl_5	20	CCl_4	~2	35	165
2-Br; 4-Br	PCl_5	20	CCl_4	~2	30	165
	$AlCl_3$	150	—	—	80	159
	PCl_5	20	CCl_4	~2	65	165
	PCl_5	20	CCl_4	~2	95	165
	$AlCl_3$	—	—	—	—	166
R=H, NO_2, R'=H; R=H, NO_2, R'=$CO_2C_2H_5$						

*Duration of reaction in minutes (Ed.of Translation).

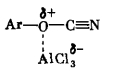
Active catalysts for the trimerisation of aryl cyanates include protic and aprotic acids[7,158,166-180] and bases[157,166-168,173,175-181], mixtures thereof[176], transition-metal complexes[176-178,182-190], and others[176]. Several hypotheses on the mechanism of catalysis of this reaction by Lewis

acids [antimony(V), tin(IV) and aluminium(III) chlorides, the ether complex of boron trifluoride] were made by Martin and Weiss [172] in an infrared spectroscopic investigation of complexes of aryl cyanates with Lewis acids. But, whereas the boron trifluoride–ether complex produces no change in the structure of phenyl cyanate, antimony pentachloride forms in dichloromethane solution the complex (**XXXI**). From the shift in the infrared absorption band of the cyanato-group and the appearance of a few new bands in the range 1700–700 cm^{-1} it was suggested that structures such as (**XXXII**)–(**XXXVI**) might be formed. Structure (**XXXVII**) was assumed for the complex $ArOCN{-}SnCl_4$. The way in which the complexes (**XXXII**)–(**XXXVII**) are involved in trimerisation has not yet been ascertained [172].

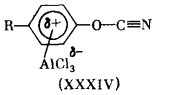


(XXXI)

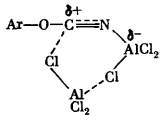
(XXXII)



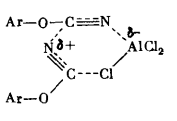
(XXXIII)



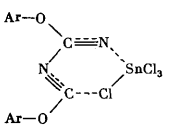
(XXXIV)



(XXXV)

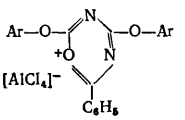


(XXXVI)



(XXXVII)

The complex of aluminium and benzoyl chlorides [174] causes especially rapid trimerisation of aryl cyanates, probably with intermediate formation of 2,4-diaryloxy-6-phenyl-3,5-diazapyrylium tetrachloroaluminate [191]



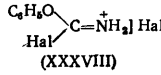
This intermediate can be isolated by replacing aluminium(III) by antimony(V) chloride.

Shevchenko et al. [170] trimerised aryl cyanates in the presence of phosphorus pentachloride, and showed that the reactions

$$ArO{-}C{\equiv}N + PCl_5 \rightarrow ArO{-}C(Cl){=}N(PCl_4) \xrightarrow{+PCl_5} \rightarrow [ArO{-}C(Cl){=}N(PCl_3)]^+PCl_6^- \xrightarrow{+ArO{-}C{\equiv}N} [(ArOC(Cl){=}N)_2PCl_2]^+PCl_6^-$$

occurred between −20 and −40°C.

Gaseous hydrogen chloride is a very good catalyst for the trimerisation of aryl cyanates [158,173–175]. On cooling in inert solvents phenyl cyanate forms with excess of anhydrous hydrogen chloride or bromide the complex



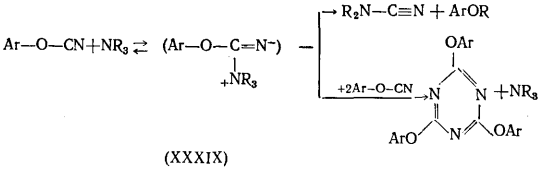
(XXXVIII) a: Hal=Cl b: Hal=Br

which separates from solution (in almost theoretical yield). The complex (**XXXVIIIa**) is more stable than (**XXXVIIIb**), comparable in stability with the cyanamide complex $H_2NCN.2HCl$, [192] whereas the corresponding complexes of acetonitrile [173] and thiocyanates [193] decompose at room temperature§. Mesomeric interaction of the aryloxy-group with the C_{sp^2} atom obviously enhances the activity of the imino-nitrogen atom.

There are hints in the literature [176–178] that the rate of the catalytic cyclotrimerisation of aryl cyanates by Lewis acids is appreciably increased by the addition of water.

Monohydric and dihydric phenols of varying acidity have also been examined as catalysts for the trimerisation of aromatic cyanic esters. The reaction velocity increases in proportion to the decrease in the pK_a of the phenols, and appropriate correlations have been derived [176,177].

High yields of aryl cyanurates have been obtained in the presence of bases. In addition to the catalysts listed in Table 5 alkoxides [166–168], aliphatic and heterocyclic tertiary amines [166,175–178,180], and sodium hydroxide [166,175] have been used. Several suggestions have been made concerning the mechanism of trimerisation catalysed by tertiary amines [166,173,176,177,181]. Thus it has been assumed [181] that the complex (**XXXIX**) is formed, and then may either take part in trimerisation or break down into a cyanamide and an ether by the van Braun reaction:



(XXXIX)

Pankratov et al. have shown [195] that the substituted cyanamide is not the active catalyst in the cyclotrimerisation of aryl cyanates. With tertiary amines of type NR_3 weakening their basicity produces some decrease in rate of cyclisation [176,177]. Pyridine and isoquinoline, however, despite their weak basicity, possess catalytic activity exceeding severalfold that of the considerably more basic aliphatic tertiary amines. This phenomenon is attributed [176,177] to the greater steric accessibility of the nitrogen atom in heterocyclic amines. It is noteworthy that mixtures of trihexylamine both with diphenylpropanediol and with tin dichloride exhibit a synergistic effect when used as catalysts [176,177].

Complexes of transition metals have also been used as trimerisation catalysts [176–178,182–190]. The kinetics and the heat of cyclotrimerisation of various aryl cyanates in the presence of chromium(III) acetylacetonate have been investigated by means of a double calorimeter [182–189]. The heat of reaction, the rate, and the effective activation energy were shown to be largely determined by the nature of the solvent, and the role of specific solvation in various solvents is discussed [186]. The nature of ring substituents in phenyl cyanates also has a great influence on the heat of reaction and the kinetic parameters: electron-donor substituents diminish, whereas electron-acceptor substituents increase, the rate of cyclotrimerisation, which correlates well with the σ_R^0 constants of the substituents [187].

The trimerisation of aryl cyanates by chromium(III) acetylacetonate is autocatalytic. Investigation of the nature of the active centre has shown [185] that the presence of water accelerates cyclotrimerisation, whereas the

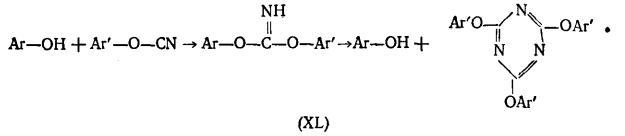
§ Phenyl thiocyanate in ether does not form complexes with hydrogen chloride even at −78°C. [194]

introduction of pentane-2,4-dione considerably retards it. It was suggested that water was involved in producing the active form of the catalyst, which was in equilibrium with the main form:

$$Cr(acac)_3 + H_2O \rightleftarrows [Cr(acac)_2]^+OH^- + acacH\ .$$

The 1,3,5-triazine ring is stabilised both by delocalisation of electrons to form an analogue to the π system of the benzene ring and by partial polarisation of the cyclic nitrogen–carbon bond [182,196]. The experimental heat of cyclotrimerisation of phenyl cyanate to triphenyl cyanurate was compared with the heat of reaction in the gaseous state (ΔH = −84.3 ± 1.0 and −58.2 kcal mole^{-1}). The latter value was calculated from the heats of formation of the two compounds computed additively from the contributions by the appropriate groups (ΔH°_{form} = 29.7 and 30.9 kcal mole^{-1}). The difference of 26 kcal mole^{-1} between experimental and theoretical heats of trimerisation was regarded as the energy of stabilisation of the 1,3,5-triazine ring (that of the benzene molecule is ~36 kcal mole^{-1}). [182,196]

Phenols add readily to aryl cyanates in the presence of bases [175] to form carbonimidic esters (XL) that decompose when heated, with separation of the more acidic phenol ($pK_{ArOH} < pK_{Ar'OH}$) and the 2,4,6-triaryloxy-1,3,5-triazine [175]:



(XL)

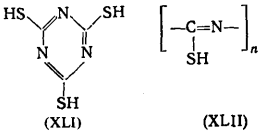
Formation of carbonimidic esters as intermediate products has been observed also in the trimerisation of aryl cyanates catalysed by alkoxides [197-201].

2,4,6-Triaryloxy-1,3,5-triazines can be formed also from aryl thiocarbamates by elimination of hydrogen sulphide followed by rapid trimerisation of the resulting aryl cyanates [169,199].

The formation of 2,4,6-triphenoxy-1,3,5-triazine from cyanogen chloride and sodium phenoxide [148,150,202] probably occurs by a similar mechanism to scheme (4).

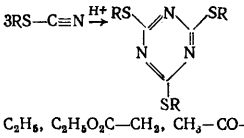
IX. 1,3,5-TRIAZINES FROM THIOCYANIC ACID AND ITS DERIVATIVES

Thiocyanic acid exists in tautomeric equilibrium with isothiocyanic acid. In aqueous solution the equilibrium is strongly displaced towards thiocyanic acid [203], which can be trimerised to 1,3,5-triazine-2,4,6-trithiol (XLI). Only one case has yet been found [204] in which the thiocyanic acid formed in a reaction has been 23% converted into (XLI) and 77% into a linear polymer (XLII).



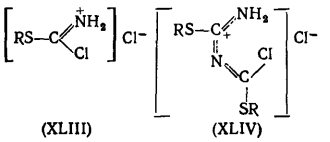
(XLI) (XLII)

In contrast to alkyl cyanates, alkyl thiocyanates trimerise in the presence of acid catalysts to 2,4,6-trialkylthio-1,3,5-triazines (Ref. 1, p. 111), without formation of thio-compounds analogous to isocyanurates (Section VII) [205-207]:



R = CH_3, C_2H_5, $C_2H_5O_2C-CH_2$, $CH_3-CO-CH_2$.

When heated in the absence of a catalyst, pure methyl thiocyanate does not trimerise, but isomerises into methyl isothiocyanate [205].



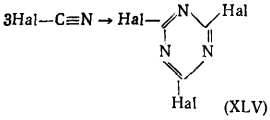
(XLIII) (XLIV)

Alkyl thiocyanates form adducts from hydrogen halides [39,194]. Those with two molecules of the latter (XLIII) resemble the corresponding adducts of acetonitrile [193] in being unstable at room temperature [194]. Adducts of structure (XLIV) have since been obtained [39] on the introduction of hydrogen chloride into alkyl thiocyanates (RSCN, where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_8H_{17}, $C_6H_5CH_2$); when heated, they were converted into the corresponding 1,3,5-triazines.

Trimerisation of aryl thiocyanates has not been reported: they have been used solely as "dienophiles" in mixed trimerisation (Section XI).

X. 2,4,6-TRIHALOGENO-1,3,5-TRIAZINES (CYANURIC HALIDES) FROM CYANOGEN HALIDES

Many studies have been made of the trimerisation of cyanogen halides to 2,4,6-trihalogeno-1,3,5-triazines (XLV):

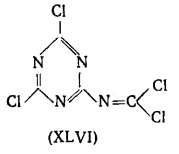


(XLV)

a) Hal = F; b) Hal = Cl; c) Hal = Br .

The more reactive the cyanogen halide, the more readily does it trimerise and polymerise: whereas liquid cyanogen fluoride is rapidly converted into (XLVa) and a polymer even at room temperature [208], trimerisation of the chloride [209-231] and the bromide [232-234] requires the presence of catalysts (acids, metal oxides or sulphides, activated carbon, zeolites, etc.). Trimerisation of cyanogen iodide has not been reported.

Together with the trimer (XLVb) have been isolated tetramers



(XLVI)

and polymers [209-212]. In some cases [209,211] the compound (XLVI) is the main product. It can be converted into (XLV) by being heated with activated carbon to 400 to 450°C. [213]

Most of the investigations on the trimerisation of cyanogen halides have been made on the chloride. Little research has been done on the mechanism of the reaction

catalysed by hydrogen chloride and by Lewis acids [aluminium chloride, boron, tin(IV), and phosphorus(V) fluorides] [209-211,214-219,231,234]. Catalysis with hydrogen chloride involves initial formation of an adduct with cyanogen chloride¶, which is then converted into a dimer. The latter reacts further either with another molecule of cyanogen chloride to give the trimer (XLVb) or with another dimer molecule to form the tetramer (XLVI).[209,210]

Good yields of (XLVb) have been obtained by using as catalysts metal sulphides and oxides,[212,220-222] activated carbon,[220-228] and also zeolites.[229,230] The catalyst poisoning that occurs with activated carbons can be diminished by introducing into them china, graphite, or quartz.[224]

Malinin et al.[216,218,223] have investigated the kinetics of the trimerisation of cyanogen chloride in the gas phase† on activated carbon at 280–540°C, and have found that the reverse reaction takes place above 430°C. They have suggested[218,223] a kinetic model for the range 440–540°C that takes into account the reverse reaction, the decrease in catalytic activity with time, and also the observed reaction velocities:

$$A + [K] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [AK] \qquad (5.1)$$

$$[AK] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [AK^*] \qquad (5.2)$$

$$2[AK^*] \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [2AK^*] + [K] \qquad (5.3)$$

$$[2AK^*] + [AK^*] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} [3AK^*] + [K] \qquad (5.4)$$

$$[3AK^*] \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} B + [K] \qquad (5.5)$$

$$[AK] \xrightarrow{k_6} [AK^{**}]$$

$$A = ClCN;\quad B = Cl\text{–}(C_3N_3)\text{–}Cl;\quad [K] = \text{Catalyst.} \qquad (5.6)$$

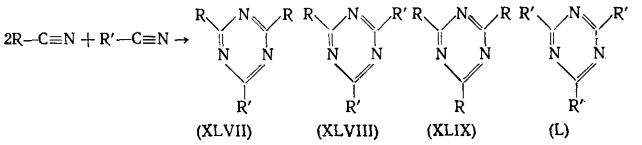
In the first stage (5.1) a molecule of cyanogen chloride is sorbed on the activated carbon, the product is activated [AK*] (5.2), and then other molecules of cyanogen chloride are added (5.3 and 5.4). After this the trimer is desorbed, and the active catalyst [K] returns to the reaction (5.5). Equation (5.6) represents the case in which cyanogen chloride does not trimerise but forms polymers $(ClCN)_n$, where $n > 3$. The trimerisation of cyanogen chloride on highly active carbons is apparently due to the presence of a graphite phase, on which cyanogen chloride molecules can be spatially oriented[229].

Wolf and Renger[229,230] have examined the influence of additions of crystalline molecular sieves on the trimerisation of cyanogen chloride. Coordination of the chloride molecules on the oxygen atoms of the catalyst facilitates their subsequent interaction to form the 1,3,5-triazine ring. The trimerisation of cyanogen chloride is a first-order reaction[229] with an activation energy of 15.2 kcal mole^{-1}.

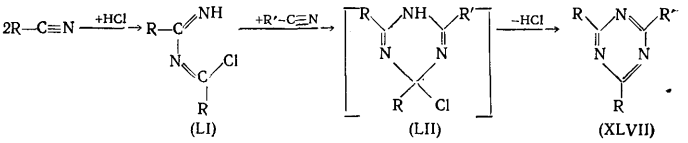
Cyanuric halides (XLV) can be obtained not only from cyanogen halides but also directly from the halogens and hydrogen cyanide without intermediate isolation of the cyanogen halides[214,215,217,232,234].

XI. MIXED CYCLOTRIMERISATION

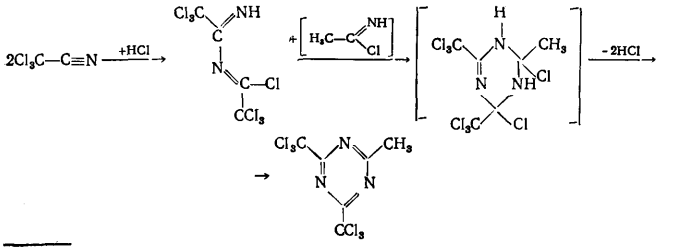
The mixed trimerisation of two or three compounds containing a cyano-group can yield theoretically four or ten different 1,3,5-triazines. Only the former case



has been investigated experimentally (Table 6). The catalytic activity of Brønsted and Lewis acids towards this reaction increases in the sequence from gaseous hydrogen chloride[40,50,237-243] through hydrogen chloride plus a Lewis acid to hydrogen chloride plus aluminium bromide[50,244]. In general aluminium bromide is a relatively inactive catalyst[50]. Grundmann[40] showed that catalysis by hydrogen chloride is accompanied by selective mixed trimerisation by dienophilic addition of the cyanide RCN to the adduct (LI) to form the trimer (XLVII):



The intermediate complex (LII) evolves hydrogen chloride spontaneously with the formation of (XLVII). Successful selective mixed trimerisation to (XLVII) depends on the ability of the cyanides to form "dienes" (LI) and on the relative "dienophilic" activities of RCN and R′CN. When RCN forms a "diene", the products (XLVII) and (XLIX) may be expected. If the rate of addition of R′CN to the "diene" far exceeds that of RCN, the product (XLVII) is formed selectively. This occurs in the reactions of trichloroacetonitrile, catalysed by hydrogen chloride, with acetonitrile,[40,50] aryl cyanides,[40,242] and thiocyanates [50]‡ (Table 6, No. 2, 4, and 5). In the catalysed reaction between trichloroacetonitrile and acetonitrile (2 : 1) more rapid conversion is obtained[50] by using an equimolecular mixture of the ready prepared "diene" (LI) (R = CCl_3) and the equimolecular adduct of acetonitrile with hydrogen chloride instead of "free" acetonitrile:



¶ Hydrogen fluoride acts on cyanogen halides in the absence of moisture at 200–450°C to form bistrifluoromethylamine $(CF_3)_2NH$.[235]

†Humphries and Nicholson[236] calculated the heat of formation of (XLVb) as 72.9 kcal mole^{-1} from the reaction 3 ClCN (gas) → $(ClCN)_3$ (liq.).

‡Although in acid medium thiocyanates isomerise readily into isothiocyanates[245], formation of the latter has not been observed in mixed cyclotrimerisation[243,244].

Table 6. Mixed cyclotrimerisation of cyano-compounds RCN and R'CN.

No.	R	R'	1,3,5-Triazines*				Reactivity of cyano-compound		Ref.
			(XLVII)	(XLVIII)	(XLIX)	(L)	diene formation	dienophilicity	
1	Cl	H	+		(+)		RCN ≫ R'CN	R'CN > RCN	237
2	Cl_3C	CH_3; C_2H_5	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	40, 50, 238–240
3	Cl_3C	Alk	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	50**, 240
4	Cl_3C	RS	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	243***, 244
5	Cl_3C	Ar	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	40, 50, 241***, 242
6	Cl_3C	$C_2H_5O_2C$	+	+	+	+	RCN ~ R'CN	RCN ~ R'CN	40
7	Cl_2HC	CH_3	+	–	+	–	RCN ≫ R'CN	R'CN > RCN	243
8	$C_2H_5O_2C$; Cl	CH_3	+	–	+	–	RCN ≫ R'CN	R'CN > RCN	40
9	C_6H_5O	HO	+	(+)	–	–	RCN > R'CN	R'CN > RCN	246***
10	HS	Ar	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	246****

*Symbols: + = trimer isolated; (+) = traces of trimer found; – = compound not formed.

**Mixed trimerisation proceeded better if the reaction mixture was heated to 150–200°C after the introduction of hydrogen chloride. In all other cases the reactions were conducted in the range from –40 to 25°C.

***Reaction conducted under pressure.

****Cyclotrimerisation took place in the absence of a catalyst.

Compound (XLVII) is formed only[67,238,239] when the molecular ratio RCN : R'CN ≤ 2.

The main product (XLVII) of the reaction between cyanogen chloride and hydrogen cyanide (2 : 1) is accompanied by traces of 2,4,6-trichloro-1,3,5-triazine (XLIX),[237] which indicates competitive addition of cyanogen chloride (RCN) to (LI). In the reaction between ethyl cyanoformate or cyanogen chloride and acetonitrile (2 : 1),[40] however, this last compound (R'CN) adds preferentially to (LI) (Table 6, No. 8).

If both cyano-compounds are able to form "dienes", three types of reaction are hypothetically possible. When the rates of formation of the "diene" (LI) and of subsequent addition of "its own" nitrile with separation of (XLIX) exceed the corresponding rates for the other nitrile, the homotrimerisation products (XLIX) and (L) should be formed exclusively. In the second alternative both "dienes" prefer to react solely with the "foreign" nitrile, and only the mixed trimerisation products (XLVII) and (XLVIII) should be formed. Neither type of reaction has yet been met in practice.

The third case—formation of all four structures (XLVII)–(L)—is realised with trichloroacetonitrile and ethyl cyanoformate (2 : 1) (Table 6, No. 6). The proportions on the products (R = CCl_3, R' = C_2H_5COO) can easily be controlled by varying the reaction conditions[40]. Thus initial treatment of trichloroacetonitrile with hydrogen chloride to form the "diene" followed by introduction of the ester yields (XLVII) as the main product. When hydrogen chloride is introduced into a mixture of the two nitriles, however, the main product will be (XLVIII): i.e. the rate of "diene" formation is greater from the ester than from the nitrile.[40]

Only qualitative information is available on uncatalysed mixed cyclotrimerisation[246]. The proportions of the products suggest[246] that RCN ≪ R'CN in "dienophilicity", while RCN ≫ R'CN in tendency to diene formation (Table 6, No. 9 and 10). A few cases of mixed cyclotrimerisation have been reported also in which nitriles are apparently formed as intermediate products during the reaction[67,240,241,247].

o0o

In conclusion we must note the great theoretical and practical value of research on the cyclotrimerisation of compounds containing cyano-groups. As a consequence of the large number of investigations in this field, especially during recent years, the influence of the chemical structure of the initial cyano-compounds, the catalysts, and also several other factors has been elucidated. This in turn has permitted the directed synthesis of 1,3,5-triazines having valuable combinations of properties. For example, 1,3,5-triazines containing perfluorinated substituents are stable up to ~500°C and can be used as thermostable heat-transfer agents and lubricants.

Further fundamental research is required on the reaction mechanism. Mixed cyclotrimerisation of various cyano-containing compounds has great prospects, enabling the synthetic possibilities to be greatly extended.

At the present time several cyano-compounds—hydrocyanic acid, cyanogen chloride, cyanamide, acrylonitrile, etc.—are large-tonnage industrial products. Several 1,3,5-triazines (cyanuric chloride, melamine, cyanuric acid, and their derivatives) are produced on a large scale.

In view of the simplicity and technical importance of the cyclotrimerisation of compounds containing cyano-groups, industry may be expected in the near future to make use of many valuable new monomeric and polymeric products containing 1,3,5-triazine rings.

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