1011. 1,3,5-*Triazines. Part V.*[1] *The Reactions of Cyanuric Chloride with NN-Dialkyl-anilines, -toluidines, and -xylidines*

By R. A. Shaw and P. Ward

The reactions of cyanuric chloride, $N_3C_3Cl_3$, with a series of *NN*-dialkylanilines, $PhNR_2$ [$NR_2 = NMe_2$, pyrrolidinyl, NEtMe, NEt_2, NPr^n_2, NPr^i_2, NBu^n_2 and $N(CH_2Ph)_2$], have been investigated. Under comparable conditions the first three amines give a mixture of aminodichloro-, $N_3C_3Cl_2{\cdot}NRPh$, and diaminochloro-1,3,5-triazines, $N_3C_3Cl(NRPh)_2$. The remaining *NN*-dialkylanilines yield mixtures of aminodichloro-1,3,5-triazines and (*p*-dialkylaminophenyl)dichloro-1,3,5-triazines, $N_3C_3Cl_2{\cdot}C_6H_4{\cdot}NR_2$-*p*. *NN*-Diethyltoluidines and *NN*-diethylxylidines having *ortho*- or *para*-methyl substituents give only aminodichloro-derivatives, whilst those having only *meta*-methyl groups give mixtures similar to that from *NN*-diethylaniline, but with a higher proportion of carbon-substituted products. The reactions of these amines, which behave as ambident, neutral nucleophiles, are discussed in terms of their structures.

WHILST the action of ammonia, and of primary and secondary amines, on cyanuric chloride (I) has been widely studied,[2] the corresponding reactions with tertiary amines have, until lately, received scant or no attention. Recently, however, Kober and Rätz[3] have dealt with a series of tertiary aliphatic, and mixed aliphatic–aromatic amines leading to, depending on the reaction conditions and structure of the amine, mono-, di-, and triamino-1,3,5-triazines; and Golesworthy, Shaw, and Smith[4] have reported the reaction of *NN*-diethylaniline with cyanuric chloride, from which two products were isolated, one a monoamino-derivative, $N_3C_3Cl_2{\cdot}NEtPh$, obtained by attack at the nitrogen atom followed by dealkylation, the other a nuclear substitution product (*p*-diethylaminophenyl)dichloro-1,3,5-triazine, $N_3C_3Cl_2{\cdot}C_6H_4{\cdot}NEt_2$-*p*. In this latter study[4] diethylaniline obviously behaves as an ambident nucleophile, a subject which has received considerable attention in recent years, and has been reviewed by Gompper.[5]

We now report the effects upon the course of the reaction with cyanuric chloride of varying the *N*-alkyl groups in a series of *NN*-dialkylanilines, as well as of introducing one

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[1] Part IV, W. Hewertson, R. A. Shaw, and B. C. Smith, *J.*, 1964, 1020.

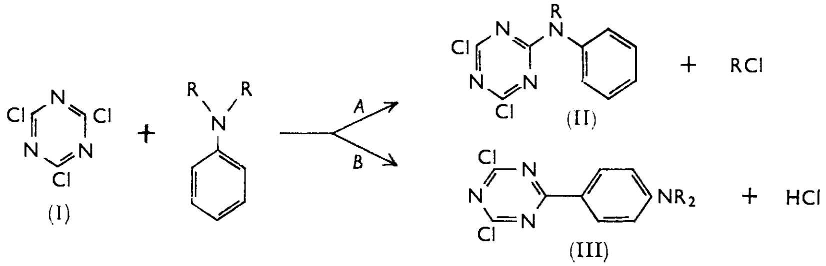
[2] E. M. Smolin and L. Rapoport, " The Chemistry of Heterocyclic Compounds. *s*-Triazines and Derivatives," Interscience, New York, 1959, p. 55.

[3] E. Kober and R. Rätz, *J. Org. Chem.*, 1962, **27**, 2509.

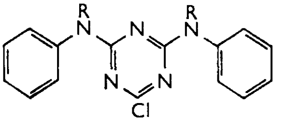
[4] R. C. Golesworthy, R. A. Shaw, and B. C. Smith, *J.*, 1962, 1507.

[5] R. Gompper, *Angew. Chem. Internat. Edn.*, 1964, **3**, 525.

or two nuclear methyl groups into *NN*-diethylaniline. The reactions follow, under suitable circumstances, two simultaneous routes (*A*) and (*B*):



The hydrogen chloride from reaction (*B*) reacts with further dialkylaniline and thus removes a proportion of the reagent from the reaction mixture. This does not always occur, since the effectiveness of amines as hydrogen halide scavengers will depend upon their basicities and upon the reaction temperature. Whilst most of the amines described in this Paper lead, under our experimental conditions, only to monosubstituted products, a few of them react further to give diamino-derivatives (IV). The derivatives (II) and (IV) obtained by replacement at the nitrogen atom of the dialkylanilines are colourless, whilst those with the triazine linked to the aromatic ring possess an intense yellow colour. The monosubstituted dichlorotriazines (II) and (III) are crystalline solids, but the disubstituted derivatives are either liquids or low-melting solids.


(IV)

The review by Gompper [5] shows that most attention has so far been devoted to studies of ambident anionic nucleophiles; reactions of neutral ambident nucleophiles are not very well represented. Among the latter, only two have some bearing on our work; (i), the reaction of phenol with homoallylic chloride,[6] leading to oxygen as well as to *ortho*- and *para*-carbon substitution; and (ii), the reaction of *N*-methylaniline with chlorotricyanoethylene and tetracyanoethylene,[7] giving with the former exclusively nitrogen substitution and with the latter exclusively *para*-carbon substitution. When *NN*-dimethylaniline was employed, both reagents gave the *para*-substituted compounds, the former in a few minutes, the latter needing several hours. In these examples, however, the leaving groups, chloride and cyanide ions, respectively, are different.

Numerous authors [8] in the field of ambident anionic nucleophiles have drawn attention to the importance of reaction variables such as the nature of the solvent, and the influence of homogeneity or heterogeneity, on the nature and the ratio of the products; hence, we have endeavoured to keep the reaction conditions constant and have carried out the present study in the absence of solvent, using a cyanuric chloride (I) to dialkylaniline ratio of 1 : 2. The reactions were carried out at 90° for 8 hr. The extent of the reaction, together with the composition of the products, is summarised in Table 1. The percentage of the individual products isolated is reproducible to $\pm 2\%$. Total triazine recovery (starting material and products) amounted to $\geqslant 90\%$, no cyanuric chloride being recovered in reactions 1—4. Only very small amounts of tar were observed and no other compounds could be detected by thin-layer chromatography. Most of the unaccounted

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[6] J. L. Corbin, H. Hart, and C. R. Wagner, *J. Amer. Chem. Soc.*, 1962, **84**, 1740.

[7] C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1960, **82**, 6132.

[8] *E.g.*, N. Kornblum and A. P. Laurie, *J. Amer. Chem. Soc.*, 1959, **8**, 2705; N. Kornblum, P. J. Berrigan, and W. J. le Noble, *ibid.*, 1960, **82**, 1257; N. Kornblum, P. Pink, and K. V. Yorka, *ibid.*, 1961, **83**, 2779; N. Kornblum and R. Seltzer, *ibid.*, p. 3668; N. Kornblum, P. J. Berrigan, and W. J. le Noble, *ibid.*, 1963, **85**, 1141; N. Kornblum, R. Seltzer, and P. Haberfield, *ibid.*, p. 1148; N. Kornblum and P. Pink, *Tetrahedron*, 1963, **19**, Supp. 1, 17; D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Amer. Chem. Soc.*, 1958, **80**, 1391; D. Y. Curtin and D. H. Dybvig, *ibid.*, 1962, **84**, 225; J. P. Ferris, C. E. Sullivan, and B. G. Wright, *J. Org. Chem.*, 1964, **29**, 87.

triazine was probably lost by volatilisation of cyanuric chloride during the reaction and isolation procedures.

TABLE 1

The reaction of cyanuric chloride with dialkylarylamines at 90° for 8 hr., molar ratio 1 : 2

No.	Amine	Extent of reaction (%)	Composition of products (%)		
			(III)	(II)	(IV)
1	*N*-Phenylpyrrolidine	94·0	—	25	75
2	*NN*-Dimethylaniline	92·0	—	55	45
3	*N*-Ethyl-*N*-methylaniline	90·9	0·2	60	40
4	*NN*-Diethylaniline	95·5	30	70	—
5	*NN*-Di-n-propylaniline	74·5	40	60	—
6	*NN*-Di-isopropylaniline	40·5	19	81	—
7	*NN*-Di-n-butylaniline	62·9	43	57	—
8	*NN*-Dibenzylaniline	29·2	41	59	—
9	*NN*-Diethyl-2-toluidine	38·6	—	100	—
10	*NN*-Diethyl-3-toluidine	75·0	55	45	—
11	*NN*-Diethyl-4-toluidine	77·5	—	100	—
12	*NN*-Diethyl-2,3-xylidine	45·9	—	100	—
13	*NN*-Diethyl-2,5-xylidine	54·9	—	100	—
14	*NN*-Diethyl-2,6-xylidine	33·8	—	100	—
15	*NN*-Diethyl-3,5-xylidine	61·0	58	42	—

Table 1 shows that, under the stated conditions, cyanuric chloride reacts to completion with the first four amines. Of these, *NN*-dimethylaniline and *N*-phenylpyrrolidine give exclusively mono- (II) and di-aminotriazines (IV), whilst *NN*-diethylaniline yields a 1 : 2 mixture of the *para*-carbon substituted (III) and nitrogen-substituted (II) mono-derivatives. *N*-Ethyl-*N*-methylaniline is a borderline case, giving predominantly mono- (II) and di-amino-derivatives (IV), with only a trace of the *para*-carbon substituted compound (III). To differentiate further between these four amines, the conditions necessary to obtain complete reaction were investigated. At 90°, *NN*-dimethylaniline and *N*-phenylpyrrolidine required only ½ hr., *N*-ethyl-*N*-methylaniline 1½ hr., and *NN*-diethylaniline 8 hr. for all the cyanuric chloride to be consumed. With *NN*-dimethyl- and *N*-ethyl-*N*-methyl-aniline, methyl chloride was evolved, as the exclusive product in the first case, and with ethyl chloride (3%) in the second. No gas evolution occurred with *N*-phenylpyrrolidine, the alkyl group being here part of a ring which on cleavage afforded *N*-(δ-chloro-n-butyl)-*N*-phenylaminodichloro-1,3,5-triazine. There is a progressive decrease in the speed of the reaction, accompanied by an increase in the ratio of carbon to nitrogen substituted products, with increasing length of the unbranched *N*-alkyl groups, both effects tending to a limiting value.

It is obvious that the reaction routes leading to carbon and to nitrogen derivatives are different, the latter possibly passing through a quaternary halide intermediate,[3] or a charge-transfer complex.[9,10] Increasing the length of the n-alkyl chains probably causes some steric hindrance to the quaternisation reaction (without substantially decreasing the mesomeric effect) [11] and hence decreases its speed relative to that of *para*-carbon substitution. Furthermore, the increasing inductive effects of the alkyl chains will increase the susceptibility of the *para*-position towards electrophilic attack.

The reactions described in this Paper thus form a link between quaternisation reactions of aniline derivatives with, say, alkyl halides on the one hand, and nuclear substitution reactions such as bromination and nitrosation on the other. We have noted that the decreased reaction rates with cyanuric chloride (I), of the series *NN*-dimethyl-, *N*-ethyl-*N*-methyl-, and *NN*-diethyl-aniline are paralleled by their reactivities in quaternisation

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[9] O. Hassel and C. Rømming, *Quart. Rev.*, 1962, **16**, 1.

[10] S. K. Das, R. A. Shaw, and B. C. Smith, *Chem. Comm.*, 1965, 176.

[11] J. A. C. Th. Brouwers, S. C. Bijlsma, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1958, **77**, 1080.

reactions with alkyl halides. However, our observation that with *N*-ethyl-*N*-methylaniline the reaction favours overwhelmingly elimination of the methyl rather than that of the ethyl group is in complete contrast to the observations by Reade and co-workers,[12] who report that in the reaction of *p*-nitro-*N*-ethyl-*N*-methylaniline with nitrous acid the product consists of 17·4% of the *N*-ethyl- and 82·6% of the *N*-methyl-nitrosamine, suggesting that the ethyl group is displaced in preference to the methyl.

As anticipated, the overall speed of reaction of *NN*-dibenzylaniline, compared to that of dialkylanilines, is reduced by the presence of the electron withdrawing phenyl groups, but the ratio of carbon to nitrogen products is of the same order as for the higher *NN*-di-n-alkylanilines, both centres being deactivated to the same extent.

On examining the effect of branching at the α-carbon of the aliphatic group, we found that with *NN*-di-isopropylaniline the overall extent of the reaction is considerably reduced compared with that of the unbranched dialkylanilines, and that the ratio of carbon to nitrogen products has been somewhat reduced. Presumably the two bulky isopropyl groups present a considerable degree of steric hindrance at the nitrogen atom, and also hinder the nitrogen from attaining maximum conjugation with the aromatic ring, thus decreasing the activation of the *para*-position.

Attention was now turned to the effect of nuclear methyl substituents. For both toluidines and xylidines we confined our attention to the *NN*-diethyl derivatives. Of the *NN*-diethyltoluidines the 2-methyl isomer reacted slowest, whilst the 3- and 4-methyl isomers reacted at comparable rates, all three toluidines giving lower total yields than the corresponding aniline. Both the 2- and the 4-methyl isomers yielded only *N*-substituted derivatives. The reasons for this are, however, different. With *NN*-diethyl-*p*-toluidine the *para*-position is blocked, and the reaction occurs exclusively at the nitrogen atom. In this reaction, as in all others we have investigated so far, no trace of *ortho*-substituted derivatives could be observed. With the 2-methyl isomer we have an example of the *ortho*-effect. The 2-methyl group prevents the *NN*-diethylamino-group from attaining a sufficient degree of conjugation with the aromatic nucleus, and hence for steric reasons decreases activation at a ring position. Furthermore, because of decreased mesomerism the nitrogen atom acquires properties more akin to that of a tertiary aliphatic amine. The combined effect of the *ortho*-methyl together with the two *N*-ethyl groups will hinder also the approach of the reagent in the quaternisation. Early results, suggesting a small amount of *para*-substitution, were later shown to be due to contamination of the commercially obtained amine with the *meta*-isomer.

With the 3-methyl derivative *para*-carbon substitution was favoured at the expense of nitrogen substitution, compared with the products from *NN*-diethylaniline. An increase of electron density at the *para*-position would be expected from the inductive effect of the 3-methyl group, and it appears that steric hindrance to the incoming electrophile plays little part, or at least is overshadowed by the activating influence. With the toluidines and xylidines, as with the anilines, some points of comparison with nitrosation and bromination emerge. Reade and his co-workers,[12,13] and Emerson,[14] have shown that if the active nuclear positions of an aniline derivative are blocked by methyl groups, displacement of an *N*-alkyl group occurs, giving a nitrosamine. In the very accurate work of Bell and Ramsden,[15] and Dubois and his co-workers [16] on the bromination of anilines, toluidines, and xylidines we find a close parallel to our work. In general, bromination of the *para*-position is preferred, and only when this is blocked by a methyl group does bromination of the *ortho*-position occur in substantial amounts. Nitrosation, which,

[12] G. P. Crowley, G. J. G. Milton, T. H. Reade, and W. M. Todd, *J.*, 1940, 1286.

[13] M. F. Aitkin and T. H. Reade, *J.*, 1926, 1896; G. J. G. Milton and T. H. Reade, *J.*, 1936, 1749.

[14] W. S. Emerson, *J. Amer. Chem. Soc.*, 1941, **63**, 2023.

[15] R. P. Bell and E. N. Ramsden, *J.*, 1958, 161.

[16] J. E. Dubois, P. Alcais, and G. Barbier, *Compt. rend.*, 1962, **254**, 3000; J. E. Dubois, *Tetrahedron Letters*, 1964, **35**, 2397.

even more than bromination, is akin to our work, as nuclear as well as *N*-nitroso-derivatives occur, is unfortunately less well documented.

The effects observed with the toluidines are even more emphasised with the xylidines. Overall reactivity is greatest with the 3,5-derivative, and least with the 2,6-analogue. We further note that one *ortho*-methyl group is sufficient entirely to suppress nuclear substitution by cyanuric chloride, and even the activating influence of a *meta*-methyl group as in 2,3- and 2,5-xylidines is not sufficient to overcome this. The 3,5-derivative gives the most favourable ratio of carbon to nitrogen substituted products of all the amines examined. It is noteworthy that even two methyl groups in the *ortho*-positions to the incoming cyanuric chloride molecule as in *NN*-diethyl-3,5-xylidine do not offer a great deal of steric hindrance. This is probably due to the lack of *ortho*-substituents on the 1,3,5-triazine derivative.

In the alkylation of phenoxides it was observed that the presence of quaternary ammonium halide favours oxygen substitution.[8] Neither on adding additional amine hydrochloride to our reaction mixture, nor on carrying out the reaction in a solvent (anhydrous benzene or light petroleum) in which the amine hydrochloride formed is insoluble, did we observe a noticeable difference in the ratio of carbon to nitrogen substituted products.

The structures of the compounds described in this Paper were confirmed for the *NN*-diethylaniline derivatives by unambiguous independent syntheses,[4] and for the remainder were based on their infrared and ^{1}H n.m.r. spectra, which will be published later.

EXPERIMENTAL

Cyanuric chloride was purified by recrystallisation from carbon tetrachloride. The primary aromatic amines, or where possible the tertiary amines, were obtained commercially from B.D.H. Ltd., or Eastman Kodak Ltd., and the former were alkylated by the method of Thomas *et al.*[17] *NN*-Di-isopropylaniline was prepared by the method of Hinman and Hollmann.[18] The tertiary amines were purified by distillation from potassium hydroxide pellets or sodium, or by formation of their hydrochlorides, recrystallisation of these from ethanol, followed by treatment with sodium hydroxide solution, separation, drying, and distillation. All b. p.s corresponded with literature values. Solvents used were dried by conventional methods. Light petroleum of b. p. 60—80° was used.

Melting points were observed on a Reichert–Kofler micro-heating stage fitted with a polarising microscope.

General Description of Procedure.—Cyanuric chloride (1/40 mole) was added to the tertiary amine (1/20 mole) in a 25-ml. 2-necked pear-shaped flask fitted with gas inlet and outlet, in an oil-bath maintained at 90°. Dry nitrogen was bubbled through the mixture to flush out the alkyl halide formed, which was condensed in two traps in series, maintained at acetone–solid carbon dioxide, and liquid air temperatures, respectively. After the appropriate time, the reaction mixture was removed from the oil-bath, cooled, the mixture extracted with anhydrous benzene, and the extract filtered to remove any amine hydrochloride present. This benzene extract was treated in one of two ways.

(i) Dry gaseous hydrogen chloride was passed into the benzene solution, when the hydrochlorides of starting amine and the carbon-substituted product were precipitated. This solid was filtered off, dissolved in water, and the solutions made alkaline with 1N-sodium hydroxide and extracted with ether. The ether layer was separated, washed with water, and dried (Na_2SO_4). After removal of solvent, the residue was distilled at 0·01 mm., when the starting amine distilled out, usually below 65°. The solid residue was then recrystallised from light petroleum. The filtrate from the gaseous hydrogen chloride treatment was washed with water and the solvent removed under reduced pressure. The solid residue consisted of nitrogen-substituted products and cyanuric chloride. The latter was readily removed by sublimation, and the residue recrystallised from light petroleum.

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[17] D. G. Thomas, J. H. Bellman, and C. E. Davis, *J. Amer. Chem. Soc.*, 1946, **68**, 895.

[18] W. N. Hinman and W. G. Hollmann, U.S.P. 2,150,832 (*Chem. Abs.*, 1939, **33**, 4599).

(ii) The extract was transferred to a column of silica gel M.F.C. grade (Hopkins and Williams Ltd.) and eluted with solvent mixtures varying between 100% light petroleum and 100% benzene. The compounds were eluted in the order, starting amine, cyanuric chloride (I), carbon substituted (III), nitrogen substituted (II), and di-nitrogen substituted compounds (IV). M. p.s and analyses of the products are given in Table 2.

TABLE 2

Analyses of 1,3,5-triazine derivatives

Amine no.	Compound	M. p.	Found (%)				Formula	Required (%)			
			C	H	Cl	N		C	H	Cl	N
1	$N_3C_3Cl_2[N(CH_2)_4Cl\cdot Ph]$	108°	47·1	3·8	31·8	—	$C_{13}H_{13}Cl_3N_4$	47·1	3·95	32·1	—
	$N_3C_3Cl[N(CH_2)_4Cl\cdot Ph]_2$	(B. p. 130/1 mm.)	57·8	5·6	—	—	$C_{23}H_{26}Cl_3N_5$	57·7	5·4	—	—
2	$N_3C_3Cl_2(NMePh)$	131—133	47·4	3·7	—	21·8	$C_{10}H_8Cl_2N_4$	47·1	3·2	—	22·0
	$N_3C_3Cl(NMePh)_2$	85—87	62·5	4·8	11·05	21·85	$C_{17}H_{16}ClN_5$	62·7	4·95	10·9	21·5
3	$N_3C_3Cl_2(NEtPh)$	116·5—117	49·4	4·0	26·0	20·9	$C_{11}H_{10}Cl_2N_4$	49·1	3·8	26·4	20·8
	$N_3C_3Cl(NEtPh)_2$	80—81	63·9	5·7	10·3	19·65	$C_{19}H_{20}ClN_5$	64·5	5·7	10·0	19·8
4	$N_3C_3Cl_2(NEtPh)$	116·5—117	49·4	4·0	26·0	20·9	$C_{11}H_{10}Cl_2N_4$	49·1	3·8	26·4	20·8
	$N_3C_3Cl_2(C_6H_4\cdot NEt_2)$	157—157·5	52·3	5·1	23·7	18·4	$C_{13}H_{14}Cl_2N_4$	52·5	4·8	23·9	18·9
5	$N_3C_3Cl_2(NPr^nPh)$	100—101	50·9	4·3	25·2	20·0	$C_{12}H_{12}Cl_2N_4$	50·9	4·3	25·0	19·8
	$N_3C_3Cl_2(C_6H_4\cdot NPr^n{}_2)$	108—109	55·2	5·6	22·25	17·5	$C_{15}H_{18}Cl_2N_4$	55·4	5·6	21·8	17·2
6	$N_3C_3Cl_2(NPr^iPh)$	157·5—158	51·3	4·3	24·7	19·7	$C_{12}H_{12}Cl_2N_4$	50·9	4·3	25·0	19·8
	$N_3C_3Cl_2(C_6H_4\cdot NPr^i{}_2)$	139—141	55·1	5·8	—	17·1	$C_{15}H_{18}Cl_2N_4$	55·4	5·6	21·8	17·2
7	$N_3C_3Cl_2(NBu^nPh)$	98·5—99	52·6	4·7	23·65	18·9	$C_{13}H_{14}Cl_2N_4$	52·5	4·7	23·9	18·9
	$N_3C_3Cl_2(C_6H_4\cdot NBu^n{}_2)$	65—67	57·6	6·1	19·9	15·6	$C_{17}H_{22}Cl_2N_4$	57·75	6·2	20·0	15·9
8	$N_3C_3Cl_2[N(CH_2Ph)Ph]$	69—70	56·5	4·1	—	—	$C_{15}H_{12}Cl_2N_4$	56·4	3·8	—	—
	$N_3C_3Cl_2[C_6H_4\cdot N(CH_2Ph)_2]$	120—122	65·8	4·8	16·0	13·2	$C_{23}H_{18}Cl_2N_4$	65·6	4·3	16·8	13·3
9	$N_3C_3Cl_2[NEt(C_6H_4Me)]$	133·5—134	51·0	4·3	24·9	19·85	$C_{12}H_{12}Cl_2N_4$	50·9	4·3	25·0	19·8
10	$N_3C_3Cl_2[NEt(C_6H_4Me)]$	76·5—78	51·1	4·2	24·95	19·8	$C_{12}H_{12}Cl_2N_4$	50·9	4·3	25·0	19·8
	$N_3C_3Cl_2[C_6H_3(Me)\cdot NEt_2]$	131·5—132	54·4	4·9	22·9	17·7	$C_{14}H_{16}Cl_2N_4$	54·0	5·2	22·8	18·0
11	$N_3Cl_3Cl_2[NEt(C_6H_4Me)]$	133—134	50·9	4·3	25·2	20·0	$C_{12}H_{12}Cl_2N_4$	50·9	4·3	25·0	19·8
12	$N_3C_3Cl_2[NEt(C_6H_3Me_2)]$	116—116·5	52·7	4·9	23·5	18·8	$C_{13}H_{14}Cl_2N_4$	52·5	4·75	23·9	18·85
13	$N_3C_3Cl_2[NEt(C_6H_3Me_2)]$	141—142	52·6	4·8	23·8	19·0	$C_{13}H_{14}Cl_2N_4$	52·5	4·75	23·9	18·85
14	$N_3C_3Cl_2[NEt(C_6H_3Me_2)]$	87—88	52·3	4·8	23·7	19·0	$C_{13}H_{14}Cl_2N_4$	52·5	4·75	23·9	18·85
15	$N_3C_3Cl_2[NEt(C_6H_3Me_2)]$	144—145	52·6	4·8	23·65	18·8	$C_{13}H_{14}Cl_2N_4$	52·5	4·75	23·9	18·85
	$N_3C_3Cl_2[C_6H_2(Me)_2\cdot NEt_2]$	135—136	55·1	5·6	21·5	17·0	$C_{15}H_{18}Cl_2N_4$	55·4	5·6	21·8	17·2

Methyl and ethyl chloride were separated and estimated using a Perkin-Elmer Fractometer gas–liquid chromatographic apparatus with a 1-m. silicone column operating at 40°. The carrier gas was hydrogen. The machine was calibrated with gaseous methyl and ethyl chloride obtained from the Shell Chemical Company. The gases evolved were further identified by comparison of their infrared spectra with authentic samples.

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