J. Chem. Research (S), 1998, 504–505
J. Chem. Research (M), 1998, 2033–2055

N-Dealkylation of Aliphatic Tertiary Amines and Diamines with Cyanuric Chloride: Crystal Structure of 2,4-Dichloro-6-(*N*-ethyl-*N*-isopropylamino)-*s*-triazine

N. Dastagiri Reddy,[a] Anil J. Elias*[a] and Ashwani Vij[b]

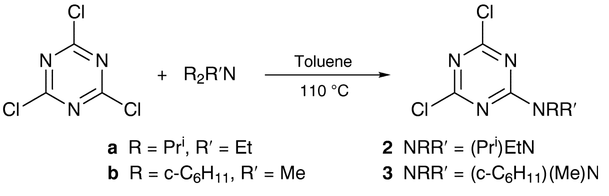
[a] *Department of Chemistry, Indian Institute of Technology, Kanpur, 208 016, UP, India*
[b] *Single Crystal Diffraction Laboratory, University of Idaho, Moscow, Idaho, 83843, USA*

Aliphatic tertiary amines and diamines undergo *N*-dealkylation on reacting with cyanuric chloride and form dialkylamino-*s*-triazines (**2**–**11**); the structure of **2** has been confirmed by X-ray structural analysis.

Chlorocarbaphosphazenes of the type $(ClCN)_n(PNCl_2)_{3-n}$ ($n = 1,2$) when reacted with polyfluorinated diols have been reported to dealkylate tertiary amines which were used as HCl scavengers.[7] Interestingly it was only the C–Cl bonds of the carbaphosphazenes which were involved in the dealkylations and therefore it was of interest to examine the mode and extent to which $(ClCN)_3$ will react with tertiary amines especially sterically hindered and unsymmetrical amines and diamines. In addition, the products of the dealkylation reactions were dialkylamino substituted *s*-triazines which Katritzky *et al.* from recent stereodynamic investigations have shown to demonstrate unusual structural and spectral behaviour.[9] Herein we report the reactions of cyanuric chloride with $NEt(Pr^i)_2$, $NMe(c\text{-}C_6H_{11})_2$, $(Me_2N)CH_2(NMe_2)$, $(Me_2N)(CH_2)_2(NMe_2)$, $(OC_4H_8N)CH_2(NC_4H_8O)$ and $1,4\text{-}Me_2(NC_4H_8N)$ where interesting selectivity is observed with regard to the cleavage of the alkyl groups. Reactions of NEt_3 and NPr_3 with cyanuric chloride have also been reinvestigated. We also report the crystal structure of 2,4-dichloro-6-(*N*-ethyl-*N*-isopropylamino)-*s*-triazine, **2** showing a short exocyclic C–N bond with partial double bond character.

Reactions of tertiary amines with cyanuric chloride proceed in toluene quite readily with the selective cleavage of an alkyl group from the amine and formation of dialkylamino substituted *s*-triazines in moderate to good yields. In the reactions of hindered tertiary amines *N*,*N*-diisopropylethylamine and *N*,*N*-dicyclohexylmethylamine with cyanuric chloride, preferential cleavages of isopropyl and cyclohexyl groups were found to be favoured respectively as shown in Scheme 1. Unlike other less hindered tertiary amines, both these amines were found to substitute only one of the ring chlorine atoms of cyanuric chloride under the reaction conditions adopted. On reinvestigating the reactions of NEt_3 and NPr_3 with cyanuric chloride, we observed that the reaction can also lead to the tris(dialkylamino) substituted products **4** and **6** in addition to the previously described 2-chloro-4,6-bis(dialkylamino) derivatives **5** and **7**.

Reactions of tertiary diamines with cyanuric chloride were found to proceed in two different modes depending entirely on the nature of the diamine and the stability of the carbonium ion formed after dealkylation. Reactions of tetramethylmethylenediamine and *N*,*N*′-methylenebismorpholine with cyanuric chloride resulted in the formation of $[NC(NMe_2)]_3$ **8** and $[NC(NC_4H_8O)]_3$ **12** respectively, indicating that the formation of the stable amino carbonium ions $R_2NCH_2^+$ is the determining factor for dealkylation. However under identical reaction conditions we observed that tetramethylethylenediamine and 1,4-dimethylpiperazine behave differently. Here dealkylation of the methyl groups of the tertiary amine is favoured and we have isolated and characterized the triazine bridged compounds $[N(C_2H_4)_2N][N_3C_3(NEt_2)_2]_2$ **9** and $[(Et_2N)_2C_3N_3]_2[N(Me)(CH_2)_2N(Me)]$ **10**.



Scheme 1

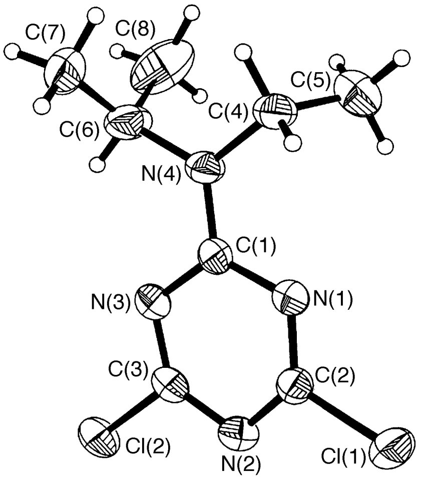


Fig. 1 Molecular structure of $Et(Pr^i)NC_3N_3Cl_2$ **2** showing the atom numbering scheme

Interestingly the structure of **2** (Fig. 1) shows that the exocyclic C(1)–N(4) bond is unusually short (1.329 Å) in comparison to the other C–N bonds originating from N(4) and the sum of the angle around N(4) is 360° indicating an sp^2 hybridized nitrogen. This increased double bond character of the exocyclic C–N bonds resulting from the conjugation of the lone pair of the amino nitrogen with the electron deficient triazine ring seems to be an additional factor favouring the dealkylation of the tertiary amine. The mode of dealkylation seems to be dependent primarily on the stability of the carbocation of the cleaved group while the extent to which it occurs appears to depend more on steric considerations and reaction conditions.

Crystal Data for **2**.—$C_8H_{12}Cl_2N_4$; $M_r = 235.12$, $F(000) = 976$, orthorhombic, $a = 12.0367(2)$, $b = 13.5206(3)$, $c = 13.6167(2)$ Å, $V = 2216.03(7)$ Å^3, space group *Pbcn*, $T = 193$ K, $Z = 8$, $D_c = 1.409$ Mg m^3, graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.554$ mm^{-1}, Siemens SMART diffractometer with a CCD detector at −54 °C, ($R_{int} = 00508$). The structure was solved by direct

---

*To receive any correspondence.

methods.[24] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference electron density maps. The final R indices are $[I > 2\sigma(I)]$; $R(F) = 0.054$ and $wR(F^2) = 0.101$. The range of estimated standard deviations for the bond lengths and angles are 0.003–0.006 Å and 0.2–0.4° respectively.

We thank the Royal Society of Chemistry, Cambridge, England and the Department of Science and Technology, India for financial assistance in the form of research grants. N.D.R thanks the University Grants Commission (UGC), India for a research fellowship.

Techniques used: X-Ray crystallography, ^{1}H NMR, IR, MS

References: 25

Schemes: 3

Figure: 1

Table 1: Comparison of α hydrogen chemical shifts of dialkylamino triazine derivatives with their parent tertiary amines

Table 2: Selected bond lengths and angles of compound **2**

Table 3: Atomic coordinates and equivalent isotropic displacement parameters for **2**

Appendix: Tables of structure refinement, fractional atomic coordinates for non-H and H atoms, anisotropic thermal parameters and bond lengths and angles for **2**

Received, 25th February 1998; Accepted, 6th May 1998
Paper E/8/01596A

References cited in this synopsis

7 A. Vij, A. J. Elias, R. L. Kirchmeier and J. M. Shreeve, *Inorg. Chem.*, 1997, **36**, 2730.
9 A. R. Katritzky, I. Ghiviriga, P. J. Steel and D. C. Oniciu, *J. Chem. Soc., Perkin Trans. 2*, 1996, 443 and references therein.
24 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.