## Studies of Reactions of 1,3,5-Trimethylbiuret and 1,3-Dimethylurea with Chloroform

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1,3,5-Trimethylbiuret and 1,3-dimethylurea react with chloroform at temperatures above 200 °C to produce 1,3,5-trimethyl-1,3,5-triazinane-2,4,6-trione (**5**), and 1,3,5-trimethyl-1,3,5-triazinane-2,4,6-trione [methyl isocyanate (MIC) trimer] (**3**), besides minor quantities of other by-products, *via* trimerization reactions involving MIC, isocyanic acid, and *N*-methylenemethylamine.

In the course of investigating the chemical aspects of the methyl isocyanate (MIC) incident which occurred in Bhopal,<sup>1</sup> previously unreported reactions involving 1,3,5-trimethylbiuret (1) and/or 1,3-dimethylurea (2) with chloroform were

$$\begin{array}{cc} MeNHCONMeCONHMe \longrightarrow MeNHCONHMe + MeNCO \\ (1) & (2) & (1) \end{array}$$

discovered. When (1) is heated above 200 °C with chloroform in a stainless steel reactor, there is produced, in addition to MIC trimer (1,3,5-trimethyl-1,3,5-triazinane-2,4,6-trione) (3), two additional cyclic materials, 1,3,5-trimethyl-1,3,5triazinane-2,4-dione  $(4)^2$  and 1,3-dimethyl-1,3,5-triazinane-2,4,6-trione (5).<sup>3</sup> Dichloromethane and the hydrochlorides of various methylated amines were also found in the reaction mixture. The composition of selected products when a mixture of (1) and chloroform is heated at 225 °C for various periods of time up to 1 h is profiled in Figure 1. Within 20 min of heating all of (1) and (2) had disappeared with concomitant appearance of (3), (4), and (5). Under these conditions there is gradual decomposition of (4) on continued heating. Products qualitatively similar in composition were also obtained by heating, under similar conditions, appropriate mixtures of (2) with chloroform, (1) or (2) with dichloromethane, or MIC and water with chloroform or dichloromethane.

The proposed mechanistic pathways leading to (4) and (5) are depicted in Schemes 1 and 2, respectively. The postulated intermediacies of *N*-methylenemethylamine (equation 4) and isocyanic acid (equation 8) received strong support by the fact that when a mixture of (1), methylurea, and 1,3,5-trimethyl-1,3,5-triazinane (trimer of *N*-methylenemethylamine)<sup>4</sup> was heated without solvent at 225 °C for 15 min in the presence of

(2) 
$$\frac{\text{Heat}}{\text{HCl}}$$
 MeNCO + MeNH<sub>2</sub> · HCl (2)

$$CHCl_3 \xrightarrow{Fe} CH_2Cl_2 + HCl$$
(3)

$$CH_2Cl_2 + MeNH_2 \longrightarrow CH_2 = NMe + 2HCl$$
 (4)

$$2MeNCO + CH_2 = NMe \longrightarrow (4)$$
 (5)

## Scheme 1

$$MeNH_2 \cdot HCl \Longrightarrow NH_3 \cdot HCl + Me_2NH \cdot HCl + Me_3N \cdot HCl$$
(6)

$$MeNCO + NH_3 \Longrightarrow MeNHCONH_2$$
 (7)

$$MeNHCONH_2 \xrightarrow{Heat} HNCO + MeNH_2 \cdot HCl \qquad (8)$$

$$2MeNCO + HNCO \longrightarrow (5) \tag{9}$$

ca. 0.5-1.0% of gaseous hydrogen chloride, the same mixture of products was obtained as that produced by heating (1) with chloroform. However, on heating the same mixture without methylurea, <1.0% of (5) was formed, but in the absence of hydrogen chloride, (2) and unchanged methylurea are the predominant products.

Hydrogen chloride, which is generated from chloroform, apparently facilitates<sup>5</sup> the decomposition of (1) and (2) to produce MIC and methylamine hydrochloride. At these operating temperatures, the latter is known to disproportionate<sup>6</sup> to an equilibrium mixture of products as shown in



Figure 1. Kinetic profile of selected products when (1) (37.6 wt %) and chloroform (62.4 wt %) are heated at 225 °C in stainless steel (316) reactors.



**Figure 2.** The <sup>13</sup>C n.m.r. spectra of the dione (4) in CDCl<sub>3</sub> normalized with respect to peak 2, were determined on a JEOL FX90 Q FT spectrometer operating at 22.5 MHz. Spectrum (A), sample containing 11.5 mg of dione from unenriched CHCl<sub>3</sub> and spectrum (B), containing 3.3 mg of dione derived from 10% enriched <sup>13</sup>CHCl<sub>3</sub>, were run for 13 150 scans with a radiofrequency pulse width of 5.7  $\mu$ s. Peaks are numbered as on the structural diagram.

equation (6). Ammonium chloride is subsequently converted into isocyanic acid (equations 7 and 8), a precursor to (5). Implicit in the reaction of (1) and chloroform, but not depicted in Schemes 1 and 2, is the cyclotrimerization of MIC to give (3).

Incorporation of chloroform into the dione (4) via its reduction<sup>7</sup> to dichloromethane (equation 3) has also been verified using <sup>13</sup>CHCl<sub>3</sub>. The enhanced peak due to the C-3 methylene group in the <sup>13</sup>C n.m.r. spectrum of the dione (4) (Figure 2) as well as the complete incorporation of <sup>13</sup>C (by g.c.-mass spectrometry) in the dichloromethane, which is produced in the reaction, support the proposed mechanism. A species of iron chloride or its complex is strongly suggested as being involved in catalysing the reduction of chloroform to dichloromethane.

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