Fragmentation patterns in the electron impact mass spectra of 1,3,5-triazin-2-one derivatives

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Abstract
Fragmentation patterns in the electron impact (EI) mass spectra of a series of 5-substituted 1,3,5-triazin-2-ones, prepared from the reaction of dimethylolurea with selected primary amines, have been elucidated using a combination of high-resolution, comparative low-resolution and metastable peak analysis. In addition to characteristic fragmentations, in which the triazine nucleus remains intact, the 5-substituted 1,3,5-triazin-2-ones appear to exhibit a series of extrusion/ring-contraction processes, resulting in the formation of 3- and 4-membered ring fragments. Resonance-stabilised even-electron ions, arising, in each case, from loss of a hydrogen atom from the molecular ion, are considered pivotal in the formation of these heterocyclic fragments.

Keywords: Triazinone, mass spectrometry, fragmentation patterns

Introduction

The emission of formaldehyde from urea-formaldehyde (UF) resins1 may be reduced by decreasing the formaldehyde content2 and adding cross-linking agents such as ammonia or melamine during the resinification process. The inclusion of ammonia has been found to result in the formation of triazine-urea-formaldehyde resins, the presence of three reactive sites in the triazine nucleus permitting cross-linking.3 While the mass spectra of 1,3,5-triazines have been
investigated,\textsuperscript{4} to our knowledge, no such studies of 1,3,5-triazin-2-ones have been reported. As part of a study of UF resins,\textsuperscript{5} we have prepared a series of 5-substituted 1,3,5-triazin-2-ones and, here, we discuss the electron impact (EI) mass spectra of the latter systems.

**Results and Discussion**

The triazinones 3-8 were prepared, following Burke’s method,\textsuperscript{6} from dimethylolurea 1 and the corresponding primary amines 2 (Scheme 1). A combination of high-resolution, comparative low-resolution and metastable peak data was used to explore the fragmentation of these compounds. Selected MS data are summarised in Table 1 and the proposed fragmentation pathways are outlined in Schemes 2 and 3.

**Table 1.** Selected peaks (m/z; followed, in parentheses, by % relative abundance) from EI mass spectra of 1,3,5-triazin-2-ones 3-8, classified according to ion types A-I (Scheme 2)

<table>
<thead>
<tr>
<th>Compd</th>
<th>R$^1$</th>
<th>R$^2$</th>
<th>R$^3$</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
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<tr>
<td>3</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>129$^a$</td>
<td>128$^a$</td>
<td>114$^a$</td>
<td>100$^b$</td>
<td>-c</td>
<td>83$^b$</td>
<td>99$^a$</td>
<td>85$^a$</td>
<td>56$^a$</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(23.1)</td>
<td>(100.0)</td>
<td>(5.2)</td>
<td>(2.4)</td>
<td>(5.5)</td>
<td>(15.8)</td>
<td>(21.9)</td>
<td>(7.6)</td>
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<tr>
<td>4</td>
<td>Me</td>
<td>H</td>
<td>Me</td>
<td>143$^a$</td>
<td>142$^b$</td>
<td>128$^a$</td>
<td>100$^b$</td>
<td>85$^b$</td>
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<td>99$^a$</td>
<td>56$^b$</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(13.0)$^d$</td>
<td>(28.7)</td>
<td>(100)$^d$</td>
<td>(2.6)</td>
<td>(9.9)</td>
<td>(3.6)</td>
<td>(10.6)</td>
<td>(24.2)$^d$</td>
<td>(62.8)</td>
</tr>
<tr>
<td>5</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>157$^a$</td>
<td>156$^a$</td>
<td>142$^a$</td>
<td>100$^b$</td>
<td>85$^a$</td>
<td>83$^b$</td>
<td>127$^b$</td>
<td>113$^b$</td>
<td>56$^a$</td>
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<td>(5.5)</td>
<td>(88.2)</td>
<td>(13.0)</td>
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<td>(2.5)</td>
<td>(0.5)</td>
<td>(17.3)</td>
<td>(6.7)</td>
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<td>83$^b$</td>
<td>127$^a$</td>
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<td>(39.8)</td>
<td>(60.7)</td>
<td>(100)</td>
<td>(4.5)</td>
<td>(63.9)</td>
<td>(2.8)</td>
<td>(17.1)</td>
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<td>7</td>
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<td>H</td>
<td>145$^a$</td>
<td>144$^a$</td>
<td>114$^a$</td>
<td>100$^b$</td>
<td>85$^a$</td>
<td>83$^b$</td>
<td>115$^b$</td>
<td>101$^b$</td>
<td>56$^b$</td>
</tr>
<tr>
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<td>(23.1)$^d$</td>
<td>(100)$^d$</td>
<td>(2.4)</td>
<td>(86.6)$^d$</td>
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<td>(64.0)</td>
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<td>(64.8)</td>
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<tr>
<td>8</td>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>191$^a$</td>
<td>190$^a$</td>
<td>190$^a$</td>
<td>100$^a$</td>
<td>85$^a$</td>
<td>83$^b$</td>
<td>161$^a$</td>
<td>147$^a$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2.4)</td>
<td>(12.5)</td>
<td>(0.9)</td>
<td>(45.4)</td>
<td>(1.3)</td>
<td>(5.8)</td>
<td>(1.5)</td>
<td>(4.4)</td>
<td>(2.6)</td>
</tr>
</tbody>
</table>

$^a$ Atomic composition of fragment confirmed by high resolution analysis; % relative abundance from high-resolution spectrum.  
$^b$ Low-resolution MS data.  
$^c$ In this case, ion E has same nominal mass (m/z 85) as fragment H.  
$^d$ % Relative abundance from low-resolution spectrum.

In all cases, loss of a hydrogen atom or an alkyl radical (R$^1$$^1$) from the 5-substituent of the molecular ion A would account for the corresponding even-electron species B$^+$ and C (Scheme 2).
However, loss of a ring hydrogen would afford fragments of type B, in which delocalisation may be extended by involvement of the N(5) lone pair; consequently, ions of structural type B are considered more likely than the isomeric systems B’. Loss of the 5-substituent itself leads to the formation of cation D (m/z 100), which is common to all of the compounds examined; there is, in fact, metastable peak evidence for the direct formation of cation D from both the molecular ion A and the M-1 fragment B.

In addition to the foregoing fragmentations, in which the triazine nucleus remains intact, the 5-substituted 1,3,5-triazin-2-ones 3-8 appear to exhibit a series of extrusion/ring-contraction processes, resulting in the formation of 3- and 4-membered ring fragments. The resonance-stabilised cations B are considered pivotal in the formation of these heterocyclic fragments (E-I). Thus, elimination of a neutral imine (R₂C=NR) from the cation B would afford, in each case, the common, diazolium ion E (m/z 85) (see Figure 1a), dehydrogenation of which gives cation F (m/z 83). On the other hand, extrusion of the neutral molecules, CH₂=NH or HN=C=O, from cations of type B would afford fragments which retain the 5-alkyl substituent and which have been tentatively formulated as the diazetinones G and their deoxo analogues H, respectively. Access to these latter ions (G and H) is attributed to the similar, but fragment-specific eliminations depicted in Figures 1b and 1c; while there is metastable peak support for the fragmentation, BG, there is similar evidence, in some cases, for the loss of CH₃NHS from the molecular ion, i.e. AG. Elimination of a moiety containing the 5-substituent (Figure 1d) would account for the common cation at m/z 56, tentatively formulated as the azirinimium species I.

Scheme 1
Scheme 2

Mass-spectral fragmentation pathways for the 1,3,5-triazin-2-ones 3 - 8. Accurate masses (m/z) are followed, in parentheses, by calculated formula masses for compound 3 (R¹ = Me, R² = R³ = H); an asterisk indicates a pathway supported by metastable peak data.

Accurate masses (m/z) are followed, in parentheses, by calculated formula masses; an asterisk indicates a pathway supported by metastable peak data.

The 5-benzyl derivative 8, not surprisingly, exhibits a number of additional, characteristic fragmentations, all of which are supported by high-resolution data (Scheme 3). The base peak, in this case, corresponds to the tropylium cation M (m/z 91), metastable peak data supporting its formation via the sequence, AGM.
Scheme 3

Additional mass-spectral fragmentation pathways for 5-benzyl-1,3,5-triazin-2-one 8.

Figure 1. Proposed fragmentations of the cations of type B to account for the formation of the heterocyclic fragments, E, G, H and I.
Experimental Section

General Procedures. NMR spectra were recorded in CDCl₃ on a Bruker AMX 400 NMR spectrometer and referenced using the solvent signals (δ_H 7.25 and δ_C 77.0 ppm). Low-resolution mass spectra were obtained on Hewlett-Packard 5988A and Finnigan Mat GCQ mass spectrometers. High-resolution EI data were collected on a VG-70SEQ mass spectrometer equipped with an MSS MASPEC II/32 data station (Cape Technikon Mass Spectrometry Unit), using high-resolution magnetic scans and B/E metastable scanning. Dimethylourea 1 [m.p. 129-130 °C (lit. 7 126-129 °C)] was prepared following a reported method.7 The synthesis of the 1,3,5-triazone derivatives, of which compounds 3 and 7 [158-159 °C (lit. 6 158 °C)] are known, is illustrated by the following example.

5-(2-hydroxyethyl)hexahydro-1,3,5-triazin-2-one (7). 2-Aminoethanol (2.5 ml, 0.042 mol) was added, with cooling, to dimethylolurea 1 (5.0 g, 0.042 mol) in water (7 ml). The resulting solution was heated at 90-100 °C for two hours and then kept at room temperature overnight. The reaction mixture was concentrated under reduced pressure, and the solid residue recrystallised twice from ethanol to afford 5-(2-hydroxyethyl)hexahydro-1,3,5-triazin-2-one 7 (2.9 g, 47 %), (Found: M⁺ 145.0853. Calc. for C₅H₁₁N₃O₂: M⁺, 145.0851); υ_max(KBr/cm⁻¹) 3320 (OH), 3220 (NH) and 1660 (CO); δ_H (400 MHz; DMSO-d₆) 2.65 (2H, t, 1'-CH₂), 3.50 (2H, m, 2'-CH₂), 3.99 (4H, s, 2xCH₂), 4.51 (lH, br s, OH) and 6.27 (2H, br s, NH); δ_C (100 MHz; DMSO-d₆) 52.1 (1'-CH₂), 59.7 (2'-CH₂), 61.6 (2xCH₂) and 154.7 (CO); m/z 145 (M⁺, 3.6 %) and 114 (100).

Analytical data for the new 1,3,5-traizinone derivatives prepared in this study are as follows.

5-Ethylhexahydro-1,3,5-triazin-2-one (3). 8 (2.0 g, 19 %), m.p. 156-158 °C. (Found: M⁺ 129.0910. C₅H₁₃N₃O requires: M⁺, 129.0902); υ_max (KBr/cm⁻¹) 3220 (NH) and 1660 (CO); δ_H (400 MHz; DMSO-d₆) 1.03 (3H, t, CH₃), 2.61 (2H, q, 1'-CH₂), 3.99 (4H, d, 2xCH₂) and 6.15 (2H, br s, NH); δ_C (100 MHz; DMSO-d₆) 13.0 (CH₃), 43.1 (1'-CH₂), 60.4 (2xCH₂) and 154.7 (CO); m/z 145 (M⁺, 3.6 %) and 114 (100).

5-Isopropylhexahydro-1,3,5-triazin-2-one (4). (1.9 g, 51 %), m.p.179-180 °C. (Found: M⁺ 143.1064 C₆H₁₃N₃O requires: M⁺, 143.1058); υ_max (hexachlorobutadiene mull / cm⁻¹) 3226 (NH) and 1673 (CO); δ_H (400 MHz; DMSO-d₆) 1.05 (6H, d, 2xCH₂), 2.93 (1H, septet, CH), 4.06 (4H, d, 2xCH₂) and 6.18 (2H, br s, NH); δ_C (100 MHz; DMSO-d₆) 21.0 (2xCH₃), 45.9 (CH), 58.5 (2xCH₂) and 155.0 (CO); m/z 143 (M⁺, 13.0%) and 128 (100).

5-t-Butylhexahydro-1,3,5-triazin-2-one (5). (2.7 g, 41 %), m.p. 181-182 °C. (Found: M⁺
157.1209. C\(_7\)H\(_{15}\)N\(_3\)O requires: \(M^+, 157.1215\); \(\nu_{\text{max}}\) (KBr/cm\(^{-1}\)) 3220 (NH) and 1690 (CO); \(\delta_H\) (400 MHz; DMSO-\(d_6\)) 28.2 (3xCH\(_3\)), 52.9 [(CH\(_3\))\(_3\)C], 56.7 (2xCH\(_2\)) and 155.4 (CO); \(m/z\) 157 (M\(^+\), 11.6 %) and 58 (100)

**5-Butyhexahydro-1,3,5-triazin-2-one (6)**. (1.5 g, 23 %), m.p.128-130 °C (Found: M\(^+\) 157.1218. C\(_7\)H\(_{15}\)N\(_3\)O requires: \(M^+, 157.1215\)); \(\nu_{\text{max}}\) (hexachlorobutadiene mull/cm\(^{-1}\)) 3223 (NH) and 1666 (CO); \(\delta_H\) (400 MHz; DMSO-\(d_6\)) 0.88 (3H, t, CH\(_3\)), 1.32 (2H, m, CH\(_3\)CH\(_2\)), 1.40 (2H, m, NCH\(_2\)CH\(_2\)), 2.55 (2H, t, NCH\(_2\)CH\(_2\)), 3.97 (4H, d, 2xCH\(_2\)) and 6.25 (2H, br s, NH); \(\delta_C\) (100 MHz; DMSO-\(d_6\)) 13.7 (CH\(_3\)), 19.8, 29.5 and 48.8 ([CH\(_2\)]\(_3\)), 60.8 (2xCH\(_2\)) and 154.7 (CO); \(m/z\) 157 (M\(^+\), 27.5 %) and 42 (100).

**5-Benzylhexahydro-1,3,5-triazin-2-one (8)**. (0.4 g, 5 %), m.p.190-192 °C. (Found: M\(^+\) 191.1050. C\(_{10}\)H\(_{13}\)N\(_3\)O requires: \(M^+, 191.1058\)); \(\nu_{\text{max}}\) (hexachlorobutadiene mull/cm\(^{-1}\)) 3062 (NH) and 1681 (CO); \(\delta_H\) (400 MHz; DMSO-\(d_6\)) 3.78 (2H, s, CH\(_2\)Ph), 3.99 (4H, d, 2xCH\(_2\)), 6.35 (2H, br s, NH), 7.25 - 7.34 (5H, ArH); \(\delta_C\) (100 MHz; DMSO-\(d_6\)) 53.3 (CH\(_2\)Ph), 60.5 (2xCH\(_2\)), 127.1, 128.2, 128.7 and 138.2 (ArC) and 154.6 (CO); \(m/z\) 191 (M\(^+\), 0.9%) and 91 (100).

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**References**

8. This compound has been reported as a component in a resin mixture, but does not appear to have been isolated or characterized previously.