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) resins[1] may be reduced by decreasing the formaldehyde content[2] 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,[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,[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

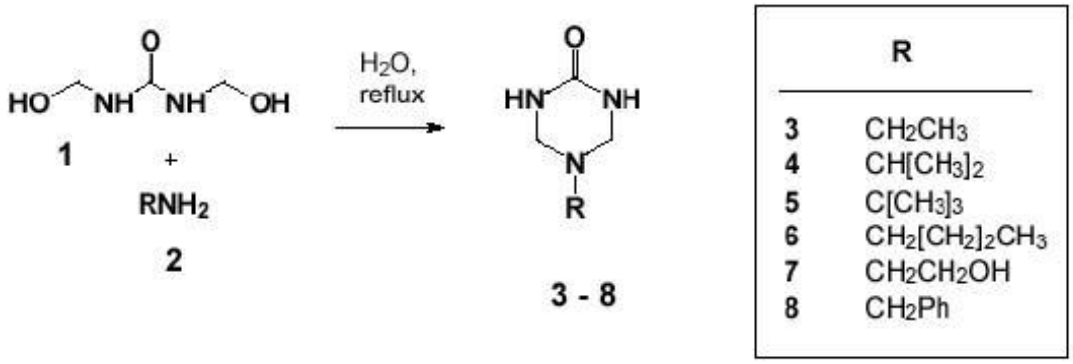
The triazinones **3-8** were prepared, following Burke's method,[6] from dimethylolurea **1** and the corresponding primary amines **2** (Scheme 1). A combination of high-resolution, comparative low-resolution and metastable peak data was used to explore the fragmentation of these compounds. Selected 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)

Compd	R^1	R^2	R^3	A	B	**C**	**D**	**E**	**F**	**G**	**H**	**I**
3	Me	H	H	129[a] (23.1)	128[a] (100.0)	114[a] (5.2)	100[b] (2.4)	-[c]	83[b] (5.5)	99[a] (15.8)	85[a] (21.9)	56[a] (7.6)
4	Me	H	Me	143[a] (13.0)d	142[b] (28.7)	128[a] (100)d	100[b] (2.6)	85[b] (9.9)	83[b] (3.6)	113[b] (10.6)	99[a] (24.2)d	56[b] (62.8)
5	Me	Me	Me	157[a] (8.7)	156[a] (5.5)	142[a] (88.2)	100[a] (13.0)	85[a] (3.3)	83[b] (2.5)	127[b] (0.5)	113[b] (17.3)	56[a] (6.7)
6	Pr	H	H	157[a] (39.8)	156[a] (60.7)	114[a] (100)	100[a] (4.5)	85[a] (63.9)	83[b] (2.8)	127[a] (17.1)	113[a] (19.0)	56[a] (15.2)
7	CH_2OH	H	H	145[a] (3.6)d	144[a] (23.1)d	114[a] (100)d	100[b] (2.4)	85[a] (86.6)d	83[b] (5.4)	115[b] (64.0)	101[b] (13.0)	56[b] (64.8)
8	Ph	H	H	191[a] (2.4)	190[a] (12.5)	190[a] (0.9)	100[a] (45.4)	85[a] (1.3)	83[b] (5.8)	161[a] (1.5)	147[a] (4.4)	56[a] (2.6)

[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.

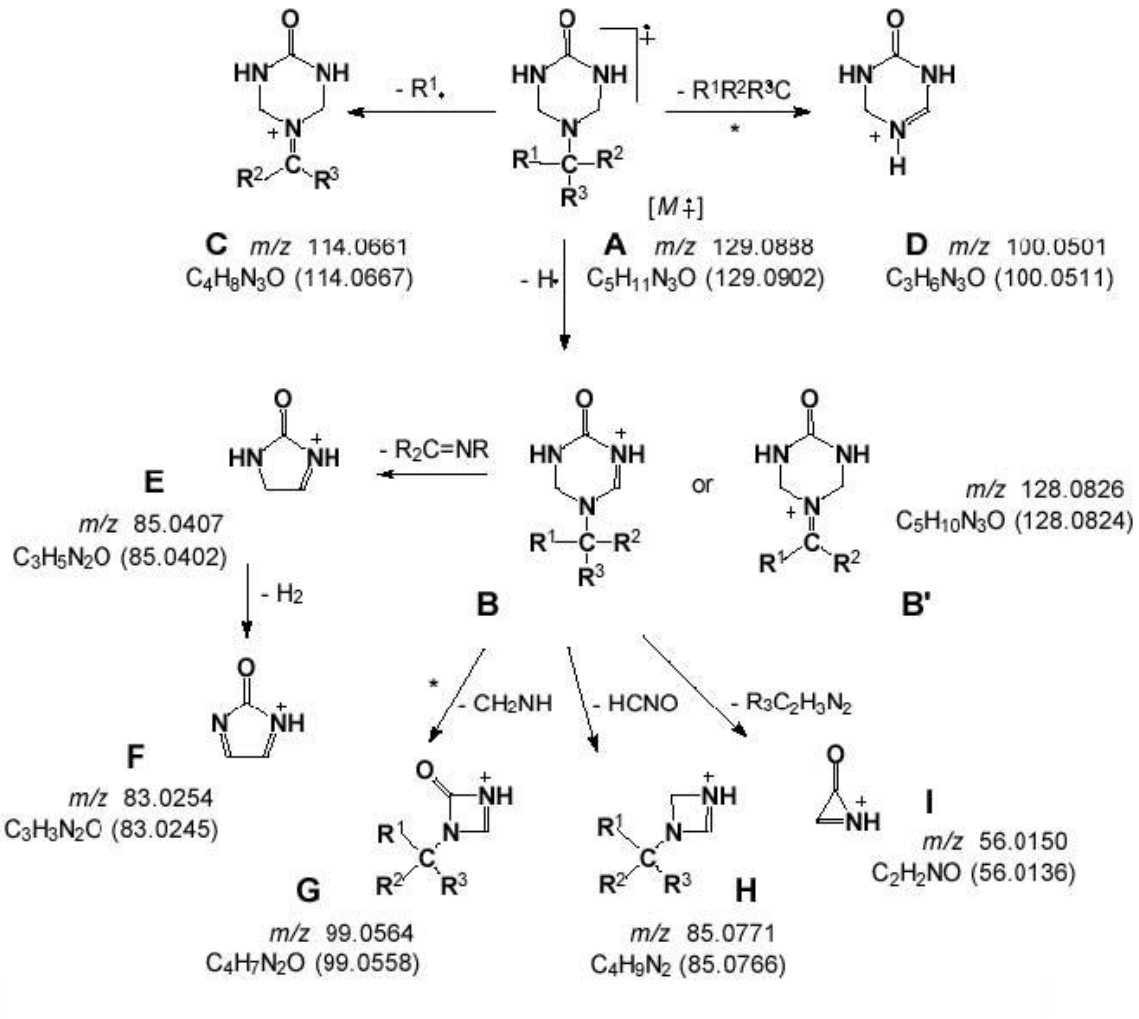
In all cases, loss of a hydrogen atom or an alkyl radical (R^1\$) from the *5-substituent* of the molecular ion **A** would account for the corresponding even-electron species **B'** and **C** (Scheme 2).



Scheme 1

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 (R_2C=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, CH_2=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 $CH_3NH$$ 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 aziriniminium species **I**.

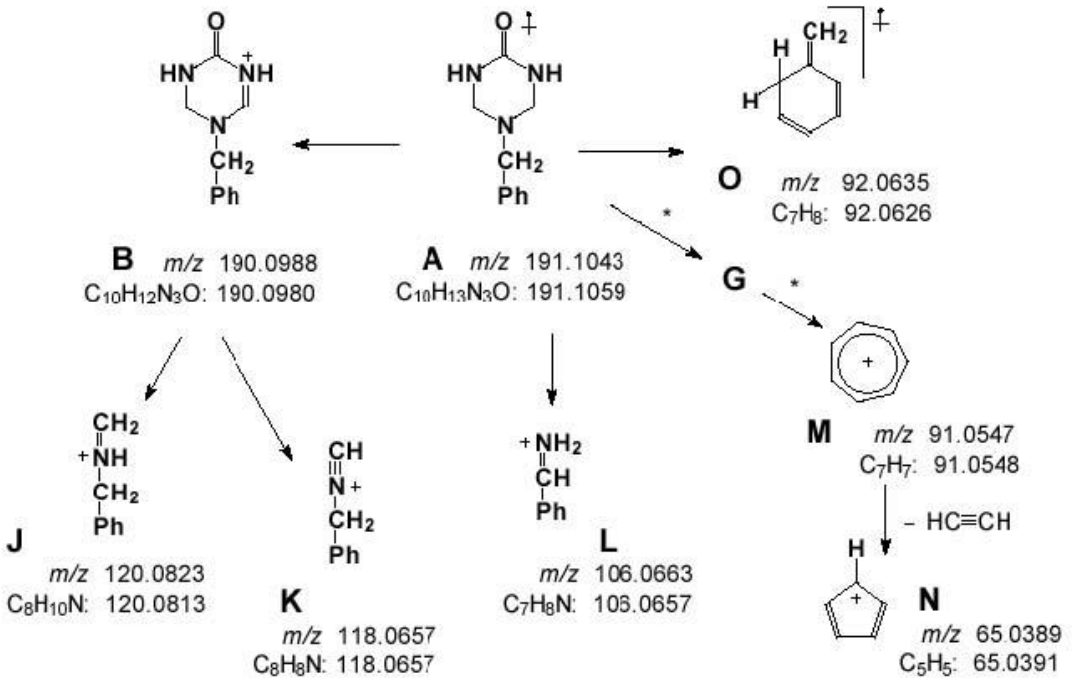


Scheme 2

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** (R^1 = Me, R^2 = R^3 = 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**.

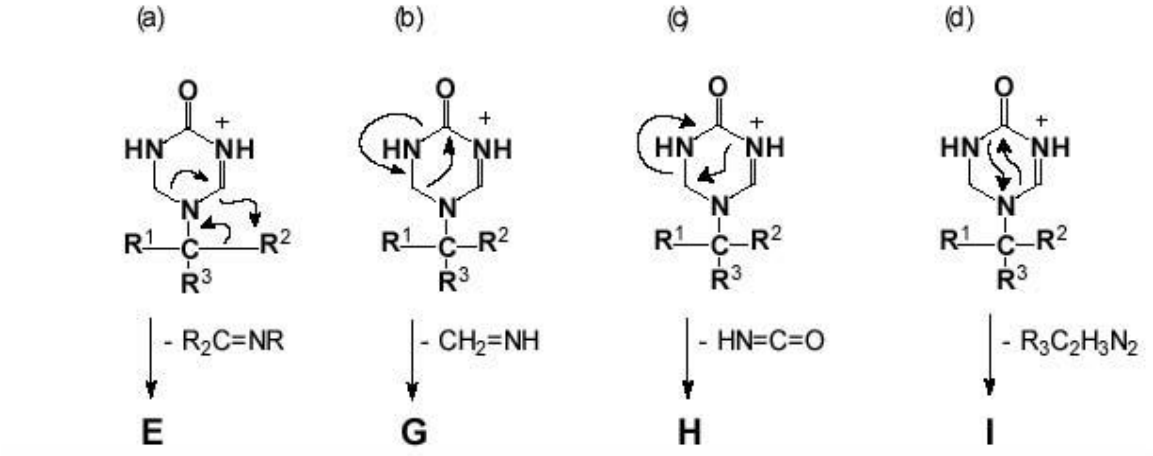


Figure1. Proposed fragmentations of the cations of type **B** to account for the formation of the heterocyclic fragments, **E**, **G**, **H** and **I**.

Experimental Section

General Procedures. NMR spectra were recorded in $CDCl_3$ 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 ºC (lit.[7] 126-129 ºC)] was prepared following a reported method.[7] The synthesis of the 1,3,5-triazone derivatives, of which compounds **3** [8] and **7** [158-159 ºC (lit.[6] 158 ºC)] 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 ºC 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: $\mathbf{M}^+$ 145.0853. Calc. for $C_5H_{11}N_3O_2$: *M*, 145.0851); υ_{max} (KBr/cm^{-1}) 3320 (OH), 3220 (NH) and 1660 (CO); δ_H (400 MHz; DMSO-d_6) 2.65 (2H, t, 1'-CH_2), 3.50 (2H, m,2'-CH_2), 3.99 (4H, s, 2xCH_2), 4.51 (lH, br s, OH) and 6.27 (2H, br s, NH); δ_C (100 MHz; DMSO-d_6) 52.1 (1'-CH_2), 59.7 (2'-CH_2), 61.6 (2 x CH_2) 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 ºC. (Found: $\mathbf{M}^+$ 129.0910. $C_5H_{11}N_3O$ requires: *M*, 129.0902); υ_{max} (KBr/cm^{-1}) 3220 (NH) and1650 (CO); δ_H (400 MHz; DMSO-d_6) 1.03 (3H, t, CH_3), 2.61 (2H, q, 1'-CH_2), 3.99 (4H, d, 2xCH_2) and 6.15 (2H, br s, NH); δ_C (100 MHz; DMSO-d_6) 13.0 (CH_3), 43.1 (1'-CH_2), 60.4 (2xCH_2) and 154.8 (CO); *m/z* 129 (M^+, 30.2 %) and 128 (100).

5-Isopropylhexahydro-1,3,5-triazin-2-one (4). (1.9 g, 51 %), m.p.179-180 ºC. (Found: $\mathbf{M}^+$ 143.1064 $C_6H_{13}N_3O$ requires: *M*, 143.1058); υ_{max} (hexachlorobutadiene mull / cm^{-1}) 3226 (NH) and 1673 (CO); δ_H (400 MHz; DMSO-d_6) 1.05 (6H, d, 2xCH_3), 2.93 (1H, septet, CH), 4.06 (4H, d, 2xCH_2) and 6.18 (2H, br s, NH); δ_C (100 MHz; DMSO-d_6) 21.0 (2xCH_3), 45.9 (CH), 58.5 (2xCH_2) 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 ºC. (Found: $\mathbf{M}^+$

157.1209. $C_7H_{15}N_3O$ requires: *M*, 157.1215); υ_{max} (KBr/cm^{-1}) 3220 (NH) and1690 (CO) ; δ_H (400 MHz; DMSO-d_6) 28.2 (3xCH_3), 52.9 [$(CH_3)_3C$)], 56.7 (2xCH_2) and 155.4 (CO); *m/z* 157 (M^+, 11.6 %) and 58 (100)

5-Butylhexahydro-1,3,5-triazin-2-one (6). (1.5 g, 23 %), m.p.128-130 ºC (Found: **M**$^+$ 157.1218. $C_7H_{15}N_3O$ requires: *M*, 157.1215); υ_{max} (hexachlorobutadiene mull /cm^{-1}) 3223 (NH) and 1666 (CO); δ_H (400 MHz; DMSO-d_6) 0.88 (3H, t, CH_3), 1.32 (2H, m, CH_3CH_2), 1.40 (2H, m, NCH_2CH_2), 2.55 (2H, t, NCH_2CH_2), 3.97 (4H, d, 2xCH_2) and 6.25 (2H, br s, NH); δ_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 ºC. (Found: **M**$^+$ 191.1050. $C_{10}H_{13}N_3O$ requires: *M*, 191.1058); υ_{max} (hexachlorobutadiene mull /cm^{-1}) 3062 (NH) and 1681 (CO); δ_H (400 MHz; DMSO-d_6) 3.78 (2H, s, CH_2Ph), 3.99 (4H, d, 2xCH_2), 6.35 (2H, br s, NH), 7.25 - 7.34 (5H, ArH); δ_C (100 MHz; DMSO-d_6) 53.3 (CH_2Ph), 60.5 (2xCH_2), 127.1, 128.2, 128.7 and138.2 (ArC) and 154.6 (CO); *m/z* 191 (M^+, 0.9%) and 91 (100).

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