Mass Spectra of 2,4,6-Tris(dimethoxycarbonylmethylene)hexahydro-*s*-triazine and 2,4,6-Tris(diethoxycarbonylmethylene)hexahydro-*s*-triazine. Evidence for Fragmentation by Successive Intramolecular Rearrangements.

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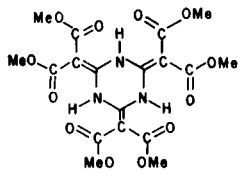
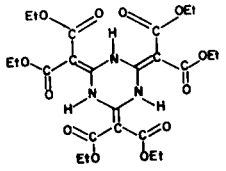
Previous studies of malonic ester derivatives of triazine (2,3) have indicated the intramolecular proton chelation present in 2,4,6-tris(dimethoxycarbonylmethylene)hexahydro-*s*-triazine (I) and 2,4,6-tris(diethoxycarbonylmethylene)hexahydro-*s*-triazine (II). These structures should lend themselves to facile intramolecular rearrangements



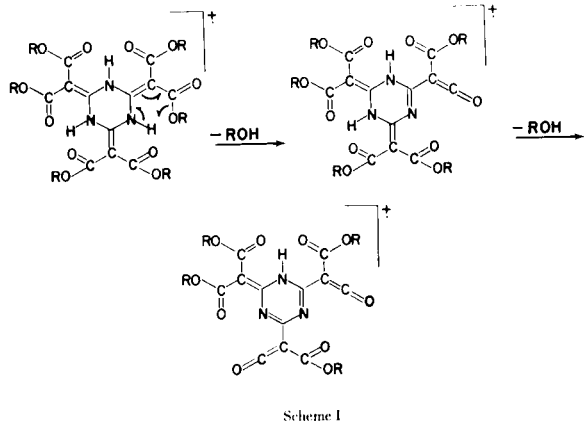
I



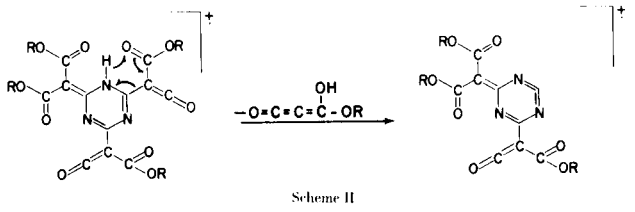
II

of the molecular ions characterized by transfer of protons to neighboring oxygen atoms. The results of this study confirm that the major fragments in the electron-impact mass spectra of both compounds I and II can be interpreted as due to successive intramolecular rearrangements. The region of the mass spectrum above m/e 200 containing most of the major fragments for both compounds is shown in Figure I. The base peak for the methyl derivative (I) arises by loss of two molecules of methanol, and the base peak for the ethyl derivative (II) arises by loss of two molecules of ethanol consistent with Scheme I, to give fragments at m/e 439 and 407, and at m/e 509 and 463, respectively.

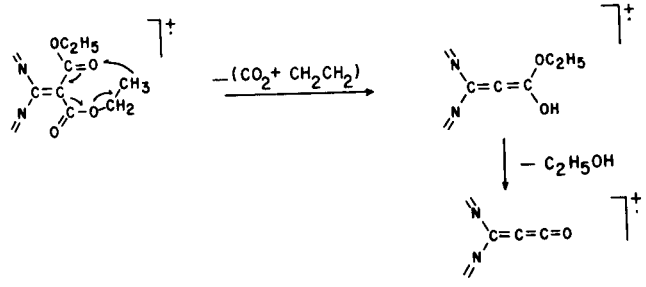
Another intramolecular rearrangement of the McLafferty type (4) can occur as in Scheme II. This rearrangement explains the loss of mass 100 for the methyl derivative (I) yielding the large peak at m/e 307



Scheme I



Scheme II



Scheme III

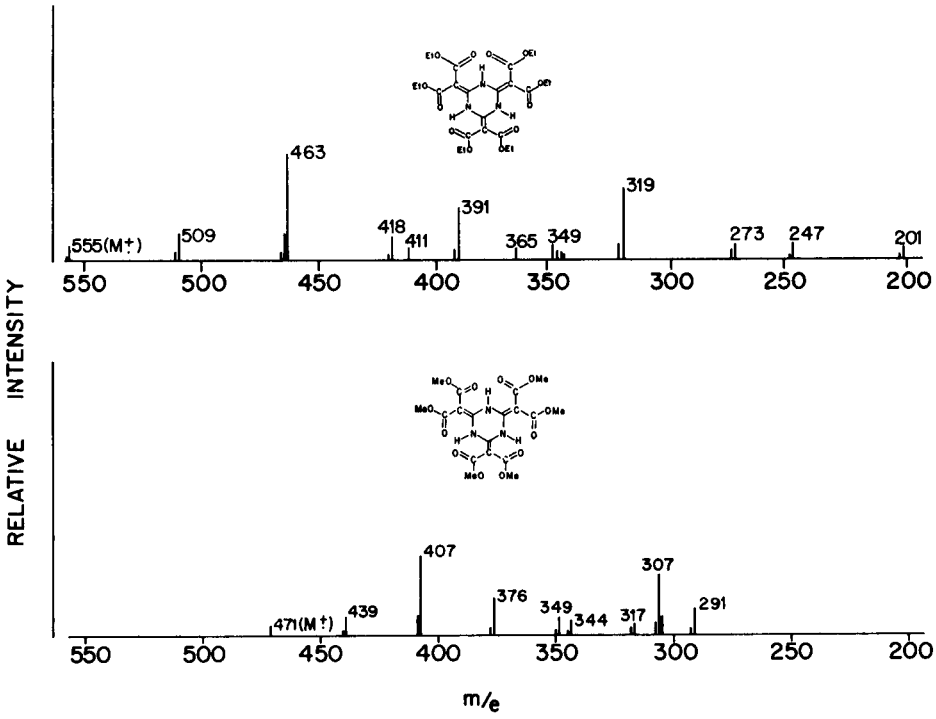


Table I

Mass Spectral Data for 2,4,6-Tris(diethoxycarbonylmethylene)hexahydro-*s*-triazine (a)

Measured Mass	Calcd.	Err. (ppm)	Intensity	Formula	Assignment (b)
555.2134	555.2063	12.5	24	$C_{24}H_{33}N_3O_{12}$	M^+
509.1659	509.1644	2.7	31	$C_{22}H_{27}N_3O_{11}$	M^+ - 46
464.1305	464.1259	10.2	27	$C_{19/1}H_{21}N_3O_{10}$	(C13 peak)
463.1289	463.1226	13.2	100	$C_{20}H_{21}N_3O_{10}$	M^+ - 2(46)
437.1429	437.1433	-0.9	6	$C_{19}H_{23}N_3O_9$	M^+ - (46 + 72)
418.0946	419.0885	14.5	25	$C_{18}H_{16}N_3O_9$	M^+ - 3(46) + H
411.1697	411.1641	13.8	9	$C_{18}H_{25}N_3O_8$	M^+ - 2(72)
392.1022	392.1048	-6.9	13	$C_{18/1}H_{17}N_3O_8$	(C13 peak)
391.1031	391.1015	4.3	38	$C_{17}H_{17}N_3O_8$	463 - 72
365.1237	365.1222	4.2	9	$C_{16}H_{19}N_3O_7$	509 - 2(72)
349.0920	349.0909	3.2	12	$C_{15}H_{15}N_3O_7$	463 - 114
346.0631	346.0674	-12.7	9	$C_{15}H_{12}N_3O_7$	418 - 72
345.0603	345.0596	1.9	5	$C_{15}H_{11}N_3O_7$	463 - (72 + 46)
320.0823	320.0837	-4.6	12	$C_{13/1}H_{13}N_3O_6$	(C13 peak)
319.0791	319.0803	-3.9	65	$C_{14}H_{13}N_3O_6$	M^+ - 2(72 + 46)
295.0835	295.0803	10.5	5	$C_{12}H_{13}N_3O_6$	
293.1025	293.1011	4.7	7	$C_{13}H_{15}N_3O_5$	M^+ - 3(72) - 46
274.0428	274.0463	-13.0	9	$C_{12}H_8N_3O_5$	273 + H
273.0360	273.0385	-9.3	10	$C_{12}H_7N_3O_5$	509 - 2(72 + 46)
248.0687	248.0671	6.6	6	$C_{11}H_{10}N_3O_4$	247 + H
247.0623	247.0592	12.2	10	$C_{11}H_9N_3O_4$	319 - 72
228.0051	228.0045	2.7	9	$C_{10}H_2N_3O_4$	274 - 46
202.0243	202.0252	-4.5	8	$C_9H_4N_3O_3$	201 + H
201.0188	201.0174	7.2	17	$C_9H_3N_3O_3$	M^+ - 3(72 + 46)
93.0087	93.0089	-1.5	16	$C_4H_{1}N_2O$	
68.0124	68.0136	-17.7	27	C_3H_2NO	

(a) Peaks having intensities 5% of base peak above mass 60 are listed. (b) Loss of 46 represents ethanol, loss of 72 represents ethylene and carbon dioxide, and loss of 114 is shown by Scheme II. Note that a peak at m/e 483 for M^+ - 72 is observable with intensity 3.3% of base peak.

from the base peak at m/e 407. For the ethyl derivative (II), this rearrangement results in a mass loss of 114 which is consistent with a fragment at m/e 349 being formed from the fragment at m/e 463.

One additional rearrangement shown in Scheme III can account for most of the remaining rearrangement fragments in the mass spectra of both compounds I and II. This rearrangement leads to loss of mass 72 for the ethyl derivative (II) by elimination of the highly stable molecules ethylene and carbon dioxide. This scheme also predicts a mass loss of 58 for the methyl derivative (I), thus accounting for the fragments at m/e 349, 407 - 58; m/e 317, 407 - (58 + 32); and m/e 291, M^{+} - 2(58 + 32).

In support of these successive intramolecular rearrangements, the high resolution mass spectral results for the ethyl derivative (II) are given in Table I, with the assignments as indicated. The formulas of the fragments obtained are consistent with fragmentation of the substituents by stepwise rearrangements until the stable fragment at m/e 201 is formed corresponding to three rearrangements shown in Scheme III. The only significant fragments due to ring cleavage are at m/e 68 and 93 containing one and two nitrogen atoms, respectively. This is in agreement with a mass spectral study of other substituted *s*-triazines (5) which found that major fragmentation involved the substituents rather than the triazine ring. In addition to the fragments given in Table I, diffuse metastable peaks occur throughout the spectrum, among these being metastable peaks attributable to mass loss 46 (509 → 463 and 349 → 303) and to mass loss 72 (463 → 391 and 391 → 319).

EXPERIMENTAL

High-resolution, electron-impact mass spectra were obtained with an AEI MS-902 mass spectrometer operated at an ionizing voltage of 70 eV and an effective resolving power of approximately 12,000. The samples were introduced into the ion source by means of a direct-insertion probe. The ion source temperature was maintained at 180°, which is well below the temperature of thermal decomposition for both ester derivatives. Calibration of m/e values was accomplished by simultaneously bleeding in the reference, perfluorokerosene. The signal output from the mass spectrometer was digitized and processed by an on-line PDP-8 computer. The tris(dimethyl malonate) and tris(diethyl malonate) derivatives of *s*-triazine used in this study were analytical samples of material prepared as previously described (2,3).

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REFERENCES

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