

## THERMOLYSIS OF 1,2,3-TRIAZINES

Takashi Itoh, Mamiko Okada, Kazuhiro Nagata, and Akio Ohsawa\*

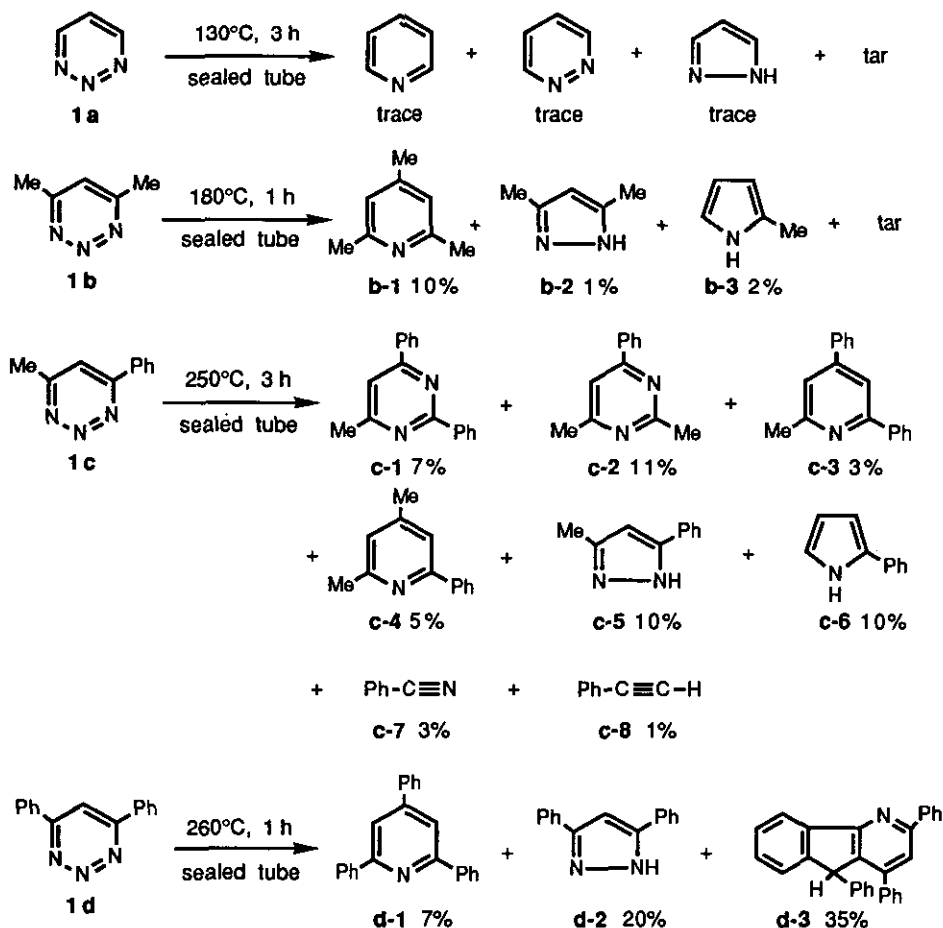
*School of Pharmaceutical Sciences, Showa University, 1-5-8 Hatanodai  
Shinagawa-ku, Tokyo 142, Japan*

**Abstract** - Thermal reactions of 1,2,3-triazines were investigated using neat thermolysis and flash vacuum thermolysis (FVT). Neat thermolysis afforded the products which were derived from intermolecular reaction, whereas unimolecular degradation occurred by FVT to give alkyne, nitrile and nitrogen. The selectivity of the reaction was considered using molecular orbital calculations.

In recent years we have been investigating the synthesis<sup>1</sup> and reaction<sup>2</sup> of monocyclic 1,2,3-triazines (1). Although their aromaticity was confirmed by <sup>1</sup>H-nmr<sup>3</sup> and X-ray crystallographic analysis,<sup>4</sup> the ring system is moderately unstable and readily underwent the Diels-Alder reaction as a diene.<sup>5</sup> Thus we needed to study the thermal reactivity of 1,2,3-triazine ring. In this paper we describe the result of thermal degradation of monocyclic 1,2,3-triazines.

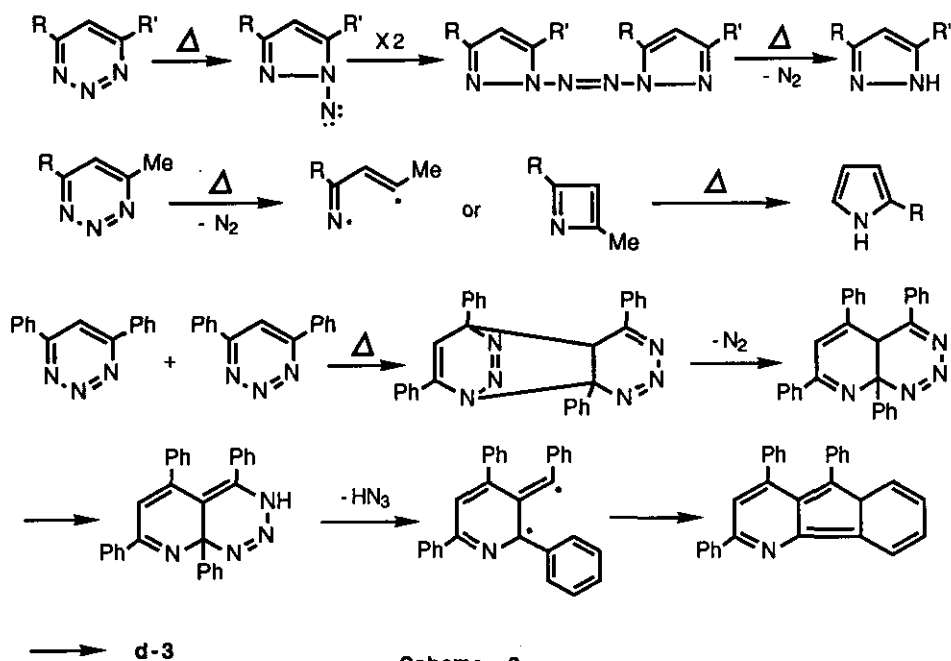
### Neat thermolysis of 1,2,3-triazines

It was reported that heating the 4,5,6-triaryl-1,2,3-triazines without a solvent at 250°C afforded mainly the indenone imines.<sup>6</sup> Unsubstituted 1,2,3-triazine (1a) has melting point at 71°C, but on heating up to 130°C 1a was decomposed to tar accompanied by the evolution of gas. Only trace amount of pyridine, pyridazine, and pyrazole were detected. Introduction of substituents raised the decomposition temperature, thus 4,6-dimethyl-(1b) and 4-methyl-6-phenyltriazine (1c) being degraded at 180°C and 250°C, respectively (Scheme 1). The decomposition of 1b afforded collidine (b-1), dimethylpyrazole (b-2), and 2-methylpyrrole (b-3) other than tar. 4-Methyl-6-phenyltriazine (1c) gave pyrimidines (c-1, c-2), pyridines (c-3, c-4), a pyrazole (c-5), 2-phenylpyrrole (c-6), benzonitrile (c-7), and phenylacetylene (c-8). 4,6-Diphenyltriazine (1d) resisted the thermolysis most, and heating at 260°C afforded 1,3,9-triphenylindeno[3,2-b]pyridine (d-3)<sup>7</sup> other than pyridine (d-1) and pyrazole (d-2) derivatives. The formations of pyridine, pyridazine, and pyrimidine derivatives were supposed to be derived from Diels-Alder reactions between two moles of 1,2,3-triazines. That is, 1,2,3-triazines were shown to act as both dienes and dienophiles at high temperature.<sup>8</sup>



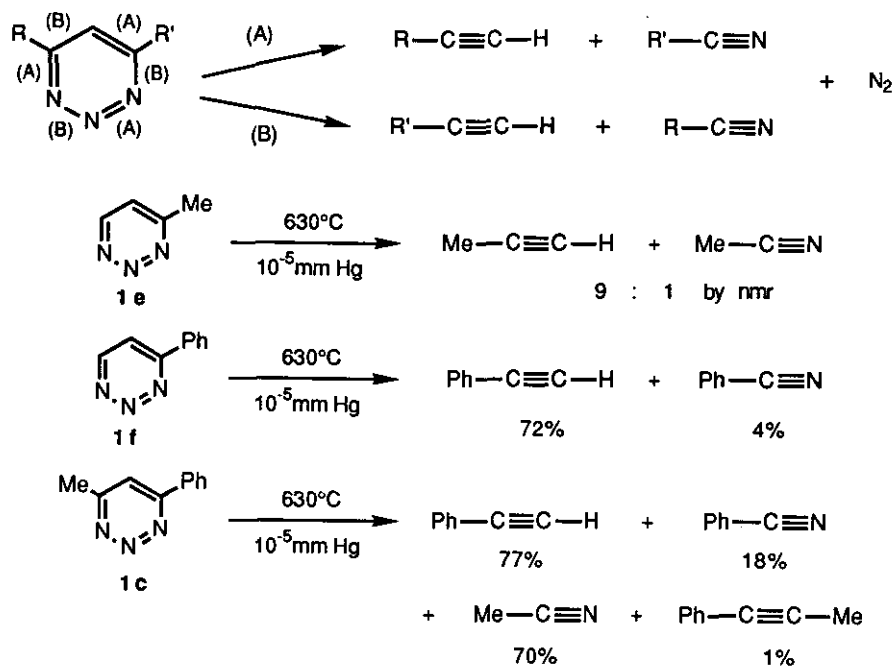
Scheme 1

The reaction mechanisms to pyrazoles, pyrroles, and an indenopyridine were supposed as shown in Scheme 2. Pyrazoles were thought to be formed by thermal isomerization of triazine to an *N*-nitrene, which dimerized to an azo compound, and the succeeding denitrogenation and hydrogen abstraction might afford pyrazoles. Pyrroles were obtained from denitrogenation of methyl-substituted triazine. The biradical or the azacyclobutadiene intermediate<sup>8</sup> thus obtained was isomerized to a pyrrole. The formation of **d-3** was through rather complicated path, one of which we considered is shown in Scheme 2. First, two triazines were dimerized *via* Diels-Alder reaction followed by denitrogenation to afford a dihydrotriazinopyridine intermediate. The intermediate was isomerized and succeeding azido elimination gave a biradical, which was cyclized to indenopyridine (**d-3**).



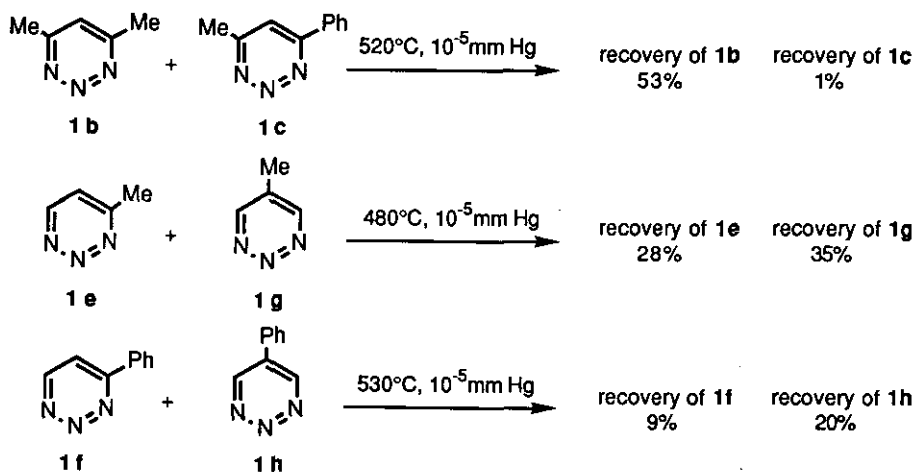
### Flash Vacuum Thermolysis of 1,2,3-Triazines

Ei-ms of 1,2,3-triazines showed very weak  $M^+$  ion peak, and fragment ions corresponding to acetylenes and nitriles were dominant.<sup>1a</sup> Therefore it was suggested that triazine was fragmented to an acetylene, a nitrile, and nitrogen in vapor phase. Flash vacuum thermolysis (FVT)<sup>9</sup> is an available method for many organic syntheses, and we have been investigating the application of FVT to heterocycles.<sup>10</sup> As was expected, a 1,2,3-triazine was thermolyzed to an acetylene and a nitrile according to Scheme 3. In the case of unsymmetrically substituted triazines, two kinds of acetylenes and nitriles were obtained according to the fragment pattern (A) or (B). However, it was revealed that the fragmentation proceeded almost selectively (Scheme 3). 4-Methyltriazine (1e) was decomposed to propyne and acetonitrile in the ratio of 9 to 1, which was confirmed by nmr. 4-Phenyltriazine (1f) afforded phenylacetylene and benzonitrile in 72% and 4% yields, respectively. These facts suggested that the presence of a substituent group made the adjacent C-N bond break more readily than the opposite C-N bond. In the case of 4-methyl-6-phenyltriazine, formation of phenylacetylene was in preference to that of benzonitrile. Thus, phenyl group is more effective on the C-N bond scission than methyl group. In this reaction, small amount of 1-phenylpropyne was obtained. The compound cannot be obtained from the concerted ring opening reaction, and the plausible formation mechanism is discussed below.



Scheme 3

Next, relative stabilities of triazines were estimated using 1:1 mixture of various triazines as starting materials<sup>11</sup> (Scheme 4). The recovery of the compound was considered as the relative stability to heat. The data suggested that the substituent at 4-position make triazine ring be more labile than the one at C-5, and that phenyl group labilized the ring more than methyl group did.



Scheme 4

### Molecular Orbital Calculations

In order to understand phenomena observed under FVT conditions, *ab initio* molecular orbital calculations were carried out using Gaussian 80H programs at the Computer Center of the University of Tokyo. For simplicity, 4-methyl-1,2,3-triazine (**1e**) was adopted as a model compound. It was assumed that 1,2,3-triazines decomposed in a concerted manner because of exclusive formation of acetylenes and nitriles.<sup>12,13</sup>

At first, full geometry optimization of **1e** was carried out at the HF/4-31G level. Figure 1 shows the bond lengths and the overlap populations of **1e**. The sums of the bond lengths belonging to group A and B are 4.083Å and 4.107Å, respectively, which indicate that preferentially cleaving bonds lengthen at the ground state. This suggests that the ground state geometry prefigures the reaction path.<sup>14</sup> The sums of the overlap populations are 1.8802 (group A) and 1.7854 (group B). Since overlap population corresponds to the amount of electron which belongs to the chemical bond, the value is supposed to exhibit the relative bond strength.<sup>15</sup> Therefore, the calculated overlap populations also support the experimental result.

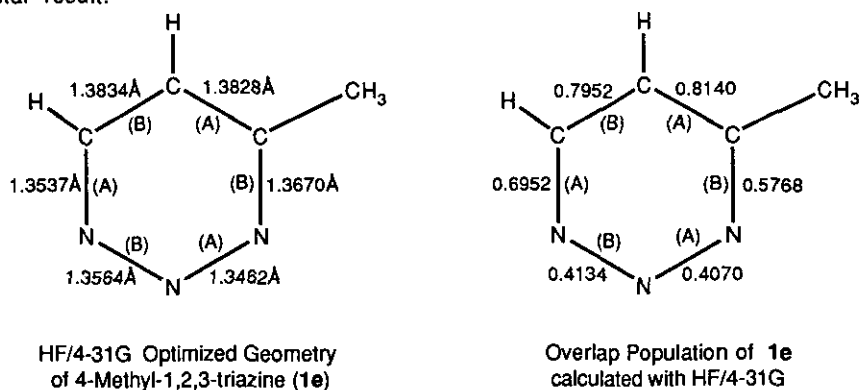


Figure 1

Next, total energies of the decomposition products were calculated (Table 1). Using the data, heats of reaction of both fragmentation (A) and (B) were calculated (Figure 2). The results show that the path B, which occurred experimentally, is less exothermic than the path A.

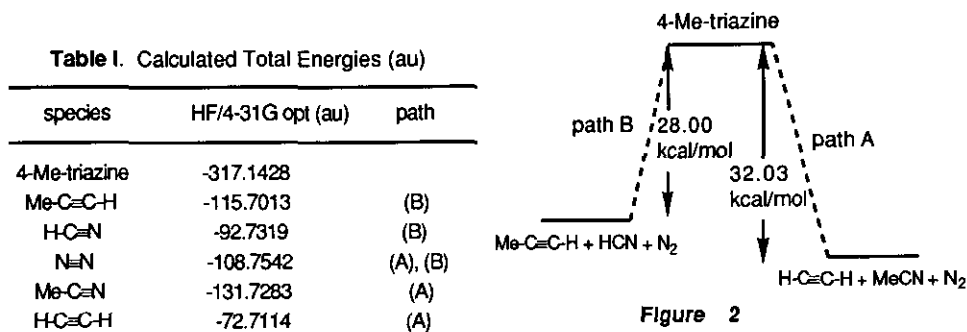
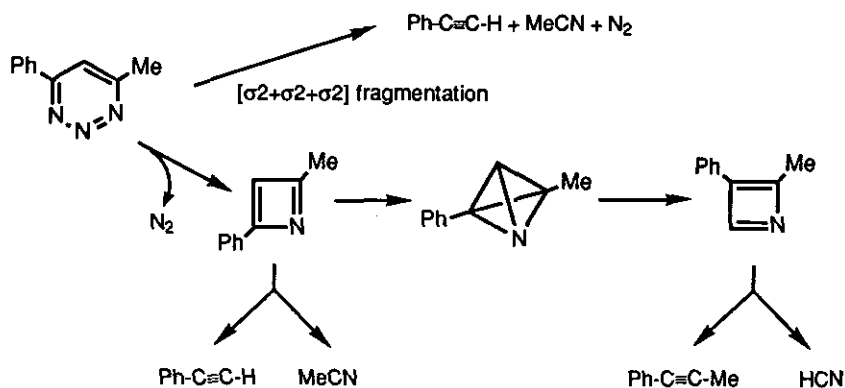


Figure 2

The same example was obtained from the calculation for the degradation pathway of 1,2,3,4-tetrazine.<sup>16</sup> Finally, formation mechanism of 1-phenyl-1-propyne from **1c** was considered. In this case, the degradation was not concerted  $[\sigma 2+\sigma 2+\sigma 2]$  reaction, but it was supposed that denitrogenation proceeded to form azacyclobutadiene, which was isomerized *via* azatetrahedron and fragmented to 1-phenyl-1-propyne (Scheme 5).



Scheme 5

Since azacyclobutadiene<sup>17</sup> is one of the noteworthy cyclic compounds,<sup>18</sup> possibility of the existence as an intermediate was considered using MO calculations. Unsymmetrical triazine (**1e**) can afford two isomeric azacyclobutadienes (**2a** and **2b**) in Figure 3. Figure 4 shows the energy differences of **1e** between **2a** and **2b** respectively, which indicated that **2b** was generated more readily from **1e**. Since this suggests that the compound **1e** would be decomposed to acetylene and acetonitrile, the experimental data might be contradictory to the assumption of azacyclobutadiene intermediate. Therefore, further investigation of MO calculations, especially those of transition states seems to be necessary.

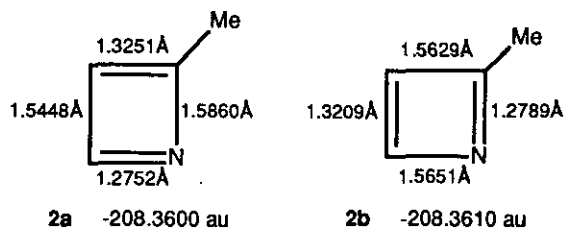
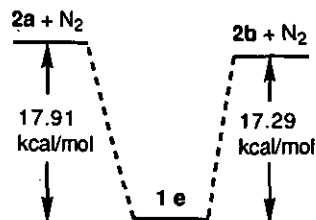
Figure 3 HF/4-31G Optimized Geometry of **2a** and **2b**

Figure 4

#### ACKNOWLEDGEMENT

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## EXPERIMENTAL

All melting points were taken on a Yanaco micro melting point apparatus and are uncorrected. The ir spectra were recorded on a JASCO A-102 spectrophotometer. The ms and gcms were measured with a JEOL JMS-D300 instrument. The  $^1\text{H}$ -nmr and  $^{13}\text{C}$ -nmr spectra were taken on JEOL JNM-FX100 and GX400 spectrometers using tetramethylsilane as an internal standard. The gas chromatography was performed with Shimadzu GC-9A using 2% SE-30 on Chromosorb as a column packing material.

### Neat Thermolysis of 1,2,3-Triazine

1,2,3-Triazine (10 mmol) was placed in a sealed tube, which was purged with argon. The tube was heated in an oil bath (130°C-260°C) for 1-3 h. The reaction mixture was chromatographed on alumina ( $\text{CH}_2\text{Cl}_2$ ) to afford the products. Commercially available authentic samples were used for the identification and quantification of the products. Compounds (**c-1**,<sup>19</sup> **c-2**,<sup>19</sup> **c-3**,<sup>20</sup> and **c-4**<sup>21</sup>) were identified by the comparison of spectral and physical data with those of reported samples. Structure of **d-3** was confirmed by the X-ray crystallographic analysis.<sup>7</sup>

### Flash Vacuum Thermolysis of 1,2,3-Triazine

Thermolysis of 1,2,3-triazines was conducted without a carrier at 480-630°C/10<sup>-5</sup>mm Hg. Triazines were distilled into a quartz tube (15 cm X 1 cm) from a flask heated by surrounding it with a Nichrome wire. The quartz tube was heated with a furnace. Products were collected in a cold trap (liquid N<sub>2</sub>). The reaction mixture was analyzed by glc or nmr using standard samples.

### Molecular Orbital Calculations

The *ab initio* calculations were carried out with GAUSSIAN80H program as installed on a HITAC M-200H/280H at the Computer Center of the University of Tokyo. Geometries were fully optimized with Cs symmetry constraints using the gradient techniques in the program.

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