UNEXPECTED CYCLOTRIMERIZATION OF PHENYL CYANATE; DOES CHAPMAN REARRANGEMENT OCCURRED IN THE MASS SPECTROMETRIC IONIZATION OF 2,4,6-TRIPHENOXY-1,3,5-*S*-TRIAZINE?

Nader Noroozi-Pesyan*
Department of Chemistry, Faculty of Science, Urmia University, 57159, Urmia, Iran
noroozi@alumni.iut.ac.ir or pesyan@gmail.com

Abstract: Unexpected novel cyclotrimerization of phenyl cyanate gave 2,4,6-triphenoxy-1,3,5-*s*-triazine **3** with excellent yield. No special catalyst is used in this reaction!. The mass spectra of **3** is investigated and it shows some fragments generated by McLafferty and Chapman rearrangements.

Introduction

Among a wide variety of heterocycles that have been explored for developing pharmaceutically important molecules, such as organic compounds containing triazine ring (1-13). Triazines are applicable compounds in synthetic organic chemistry, such as; 2,4,6-tris(ethoxycarbonyl)-1,3,5-*s*-triazine a useful diene used by Boger *et al* for the synthesis of pyrimidine derivatives (14-17).

Monofunctional cyanates could be rapidly and quantitatively trimerized to cyclic cyanurates by catalytic quantities of $AlCl_3$ (18). Trimerization of isocyanates is common, by organozinc amines and alkoxides an example of homogeneous coordination catalysis involving a template effect (19). A series of substituted aliphatic nitriles have been trimerized to their corresponding pyrimidine structures under solvent-free conditions in the presence of catalytic quantities of potassium *tert*-butoxide using a focused microwave reactor (20). The reaction of phenylacetonitrile with $InMe_3$ in boiling toluene in a molar ratio of 3:1 leads to a trimerization of the nitrile with evolution of methane (21). There are several reaction pathways for trimerization reactions for the synthesis of aromatic ring *via* many different catalysts, such as; Acetylene trimerization on Ag, Rh, and Pd atoms supported on the MgO (22), half-sandwich titanium complexes with a pendant ethereal group, $CH_3OCH_2CH_2CpTiCl_3$, $CH_3OCH(CH_3)CH_2CpTiCl_3$, and tetrahydrofurfurylcyclopentadienyltitanium trichloride activated by MAO have been found to trimerize ethylene with high selectivity and moderate activity (23), catalytic trimerization of 2- and 4-cyanopyridine isomers to the triazine derivatives in presence of magnesium phthalocyanine is carried out (24). The unusual transformation of β-aryl-β-haloacroleins into valuable triaroylbenzenes the presence of amine is required for the trimerization procedure since it is involved in the formation of iminium-enamine intermediate (25). The reactivity of uncatalysed and catalysed cyanate ester resin in solvent was investigated under room temperature conditions by Owusu *et al.* At room temperature, the uncatalysed resin was non-reactive in the solvents while a triazine reaction leading to the polymerization of cyanate monomer occurred in the catalysed systems (26). The *s*-triazine nucleus can be most readily synthesized by the cyclic trimerization of nitriles, generally under conditions of acid catalysis (27). 2,4,6-Triaryloxy- and triphenoxy-1,3,5-*s*-triazines were synthesized by reactions of 2,4,6-trichloro-1,3,5-*s*-triazine with alkylated phenol and phenol, respectively, in the presence of metallic sodium or sodium hydroxide whereas 2,4,6-Tris(4-hydroxyphenyl)-1,3,5-*s*-triazine was prepared by trimerization of *p*-cyanophenol (28).

The intramolecular rearrangements in 2,4,6-substituted-*s*-triazines, the mass spectrometric isomerization and fragmentation of some *N*-cycloalkylamino derivatives with three-, five-, six-, seven-, eight- and ten-membered rings are investigated. In the mass spectra of the some of these compound derivatives, two consecutive processes, consisting of "McLafferty+1" rearrangement decomposition as the primary, and McLafferty rearrangement as the secondary, appeared to be the dominant reactions (29).

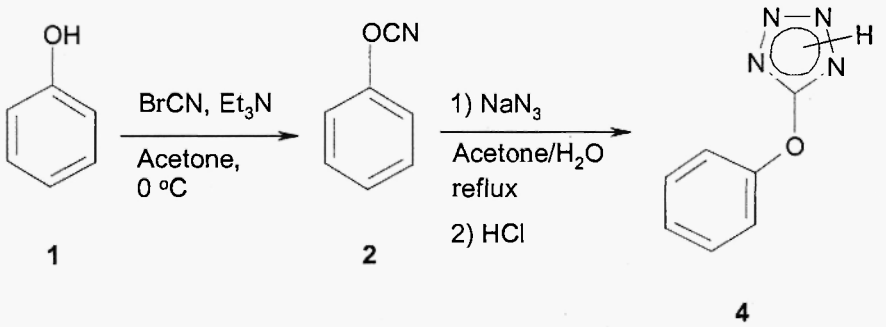
Experimental

The ^{1}H-NMR spectra were recorded on JEOL JNMα-500 (500 MHz) and ^{13}C-NMR spectra were measured on JEOL JNMα-500 (125 MHz) instrument in $CDCl_3$ relative to TMS and the FT-IR spectra were obtained on Perkin-Elmer 1760X. MS data were measured on a GC-MS FISSION TRIO 1000 instrument (70 eV). Melting point (uncorrected) were taken on a Gallenkamp apparatus.

2,4,6-triphenoxy-1,3,5-*s*-triazine (3). In a three necked round bottom flask equipped with mechanical stirrer, ice-bath, dissolved phenol (0.3 mol) and cyanogen bromide (0.311 mol) in 150 ml acetone. Added drop wise 43.5 ml triethylamine (0.314 mol) dissolved in 100 ml acetone in separatory funnel at 0 °C during 60 minutes. The white color triethylammonium hydrogen bromide salt precipitated. After completion reaction during 3 hours, the white color salt is filtered and yellow color liquid obtained. Amount of solvent removed under reduced pressure and equipped at the refrigerator for two over nights. The yellow oily liquid to be solidified, filtered, washed with few ml acetone, the fibrous white solid (**3**) obtained, m.p. 230-231 °C [Lit. 232-235 °C] (Found: C, 70.7; H, 4.3; N, 11.0. $C_{21}H_{15}O_3N_3$ requires: C, 70.6; H, 4.2; N, 11.7 %). FT-IR (cm^{-1}) 3059 (C-H Ar), 1620 (C=N), 1556 (C=N), 1487 (C=C); ^{1}H NMR δ 7.13 (m, 2H), 7.21 (m, 1H), 7.34 (m, 2H). ^{13}C NMR δ 121.38, 126.04, 129.45, 151.56, 173.66; MS: m/z: 357(M^+), 265, 264(100%), 238, 196, 189, 168, 145, 121, 77.

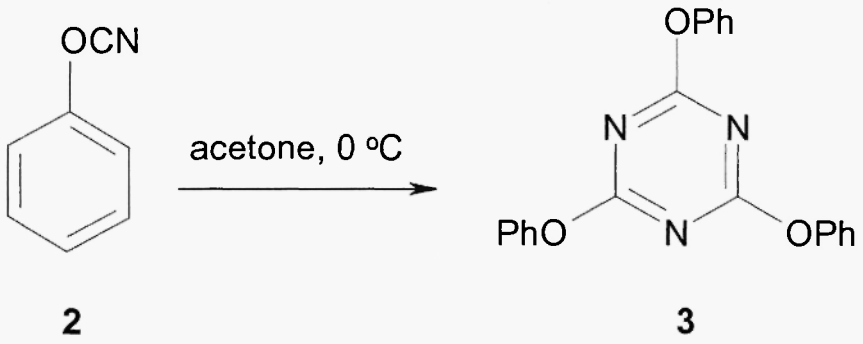
Results and Discussions

In this work, one convenient and novel route for the cyclotrimerization of phenyl cyanate is reported. Our first aim was attempt to synthesis of 5-phenoxy tetrazole **4** from phenyl cyanate **2** *via* 1,3-dipolar cycloaddition reaction of phenyl cyanate and sodium azide (**Scheme-1**). Previously, the reaction of **2** as starting material with sodium azide obtained **4** in good yield (30-33). We also synthesized **2** from reaction of phenol **1** with cyanogen bromide, BrCN in the presence of triethylamine, Et_3N according to reported references (**Scheme-1**) (30-33). Surprisingly, in this research, the phenyl cyanate cyclotrimerized unexpectedly in acetone at the refrigerator for minimum two days before next stepe reaction with sodium azide (**Scheme-2**). The structure of **3** is elucidated by various spectroscopic methods completely. In the ^{13}C NMR spectra, the peak of 173.66 ppm is related to carbon atoms of *s*-triazine aromatic ring. Other peaks; 121.38, 126.04, 129.45, 151.56 ppm has been derived and related to *ortho*, *para*, *meta* and *ipso* carbon atoms of phenyl ring respectively. ^{1}H NMR spectra shows three-difference multiple peaks; 7.13, 7.21 and 7.34 ppm are related to *o*-H, *p*-H and *m*-H on phenyl rings respectively. On the other hand, the melting point and FT-IR spectra of 1,3,5-triphenyl isocyanurate **6** no conformed with the experimental data (the melting point of **6** is 283-284 °C, $\nu_{C=O}$1710 cm^{-1} (34)). No amidic carbonyl bond absorption observed in FT-IR spectra of **3**. These are sufficient for demonstration of the formation of **3**. Neither **2** isomerized to phenyl isocyanate **5** nor **3** isomerized to **6** at low temperature (**Scheme-3**).



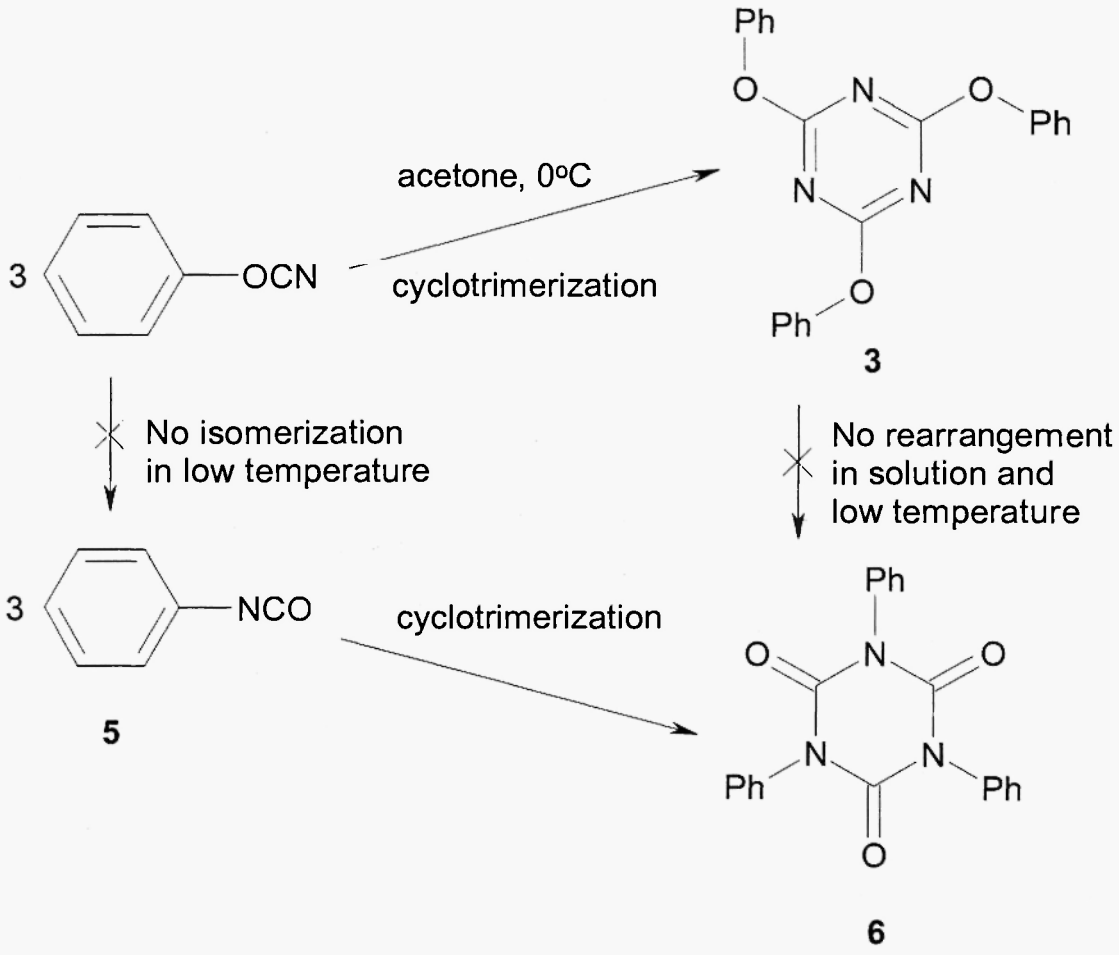
Scheme-1

Interestingly, in this cyclotrimerization reaction no used any special catalyst that rarely occurred. Therefore, the obtained compound **3** from this route is important and noticeable. The **3** is obtained under neutral mild condition in excellent yield. The triethylamine is converted to triethylammonium hydrogen bromide salt that uesed in the reaction between phenol and cyanogen bromide at **Scheme-1** that removed from reaction mixture by the filtration. Therefore, it is concluded that triethylamine and/or triethylammonium hydrogen bromide salt are not interfered for the formation of **3**.



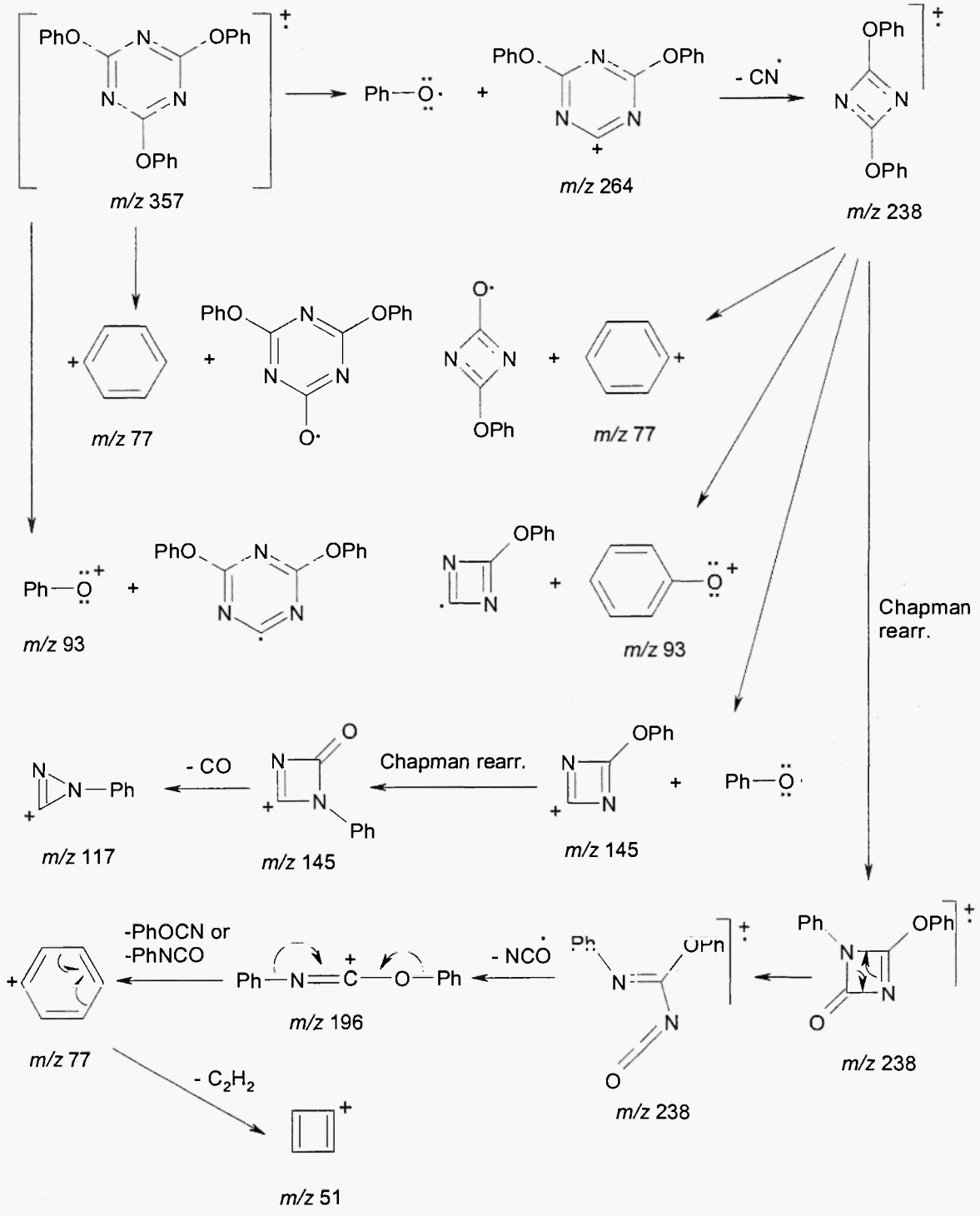
2 **3**

Scheme-2

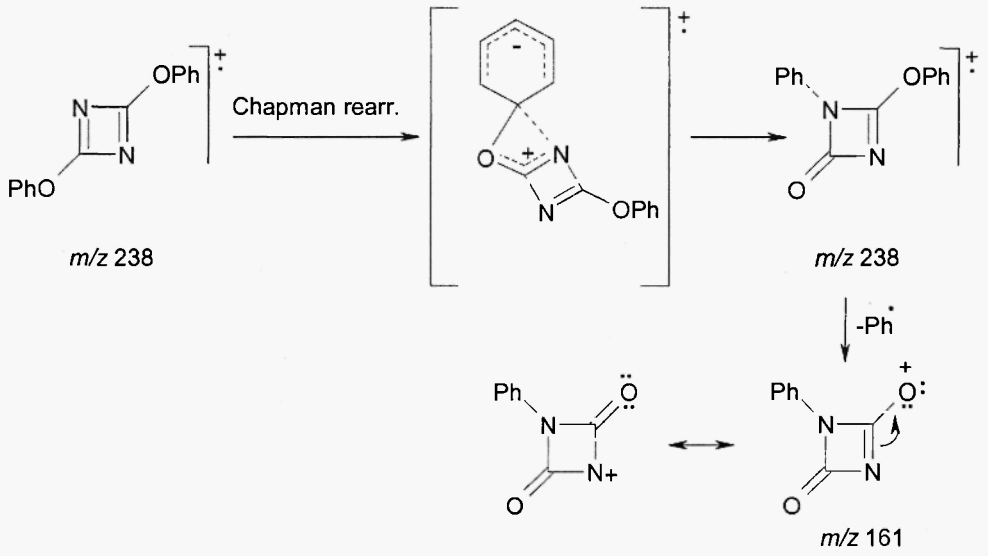


Scheme-3

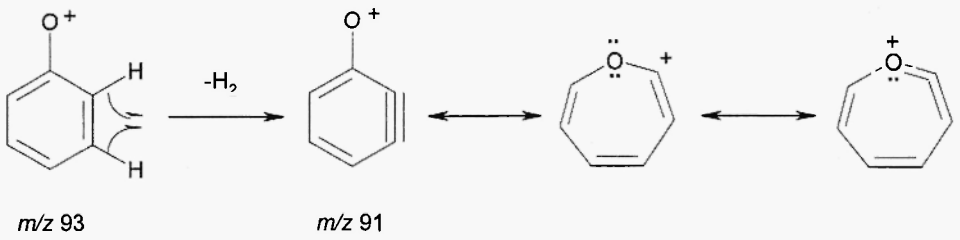
We interested for investigation of the mass spectra of **3** since this spectra shows some significant fragments. The Electron-Impact induced rearrangement reactions of organic molecules interpreted by Djerassi *et al.* More recently, it has been found that groups other than hydrogen, such as alkyl, aryl, hydroxyl, etc., also can migrate after electron bombardment (35) and also mass spectra of some of *s*-triazines have been interpreted (36,37) but it not pointed to unexpected rearrangement(s). In this work, the $M^{+\cdot}$, *m/z* 357 (≈2% abundance) molecular ion mass derived from **3**. The most abundant fragment ions produced by EI decomposition are; *m/z* 264 (100% abundance), *m/z* 238 (≈45%), *m/z* 196 (≈20%), *m/z* 145 (≈20%), *m/z* 121 (≈48%), *m/z* 77 (≈82%). The base peak is of the 2,4-diphenoxy-*s*-triazine ion and is the loss of phenoxy radical from **3**. This fragment gives *m/z* 238 is the ion radical fragment of 2,4-diphenoxy-1,3-diazete by loss of cyanide radical. It is rearranged to 1-*N*-phenyl-1,3-diazetidin-4-one ion radical by Chapman rearrangement (38-42) in electron impact mass spectrometer apparently. The fragment of *m/z* 196 generated by the only path way of through Chapman rearrangement of the 2,4-diphenoxy-1,3-diazete moiety at the **Scheme-4**. The Chapman rearrangement has been shown to be an intramolecular reaction in which a 1,3-shift of an aryl and/or phenyl group from oxygen to nitrogen takes place. That is, the reaction requires the formation of a four-membered ring in the transition state (**Scheme-5**), and maybe considered as a nucleophilic attack by nitrogen on the migrating aryl and/or phenyl group (38). The imidoyl isocyanate derivative with *m/z* 238 is generated by the ring opening of 1-*N*-phenyl-1,3-diazetidin-4-one ion radical. The ion fragment *m/z* 196 obtained by loss of isocyanate radical. This fragmentation is the powerful evidence for involving Chapman rearrangement. The phenyl cyanate and/or phenyl isocyanate can released by heterolytic bond cleavage of between carbon atom in phenyl ring and nitrogen and/or oxygen atom of *m/z* 196 ion fragment for obtaining *m/z* 77 fragment respectively. Moreover, 2,4-diphenoxy-1,3-diazete give *m/z* 145 fragment by loss of phenoxy radical that rearranged to 1-*N*-phenyl-1,3-diazetidin-4-one ion by Chapman rearrangement. This cation generate ion fragment with *m/z* 117 (≈3% abundance) by loss of carbon monoxide (CO). The phenoxy ion (PhO^+, *m/z* 93, with ≈10% abundance) can also generated from $M^{+\cdot}$ of **3** by cleavage of the bond between oxygen and carbon atoms of *s*-triazine ring. The fragment of *m/z* 77 is of the formation of phenyl ion (Ph^+) and it's evolution of natural acetylene released 1,3-cyclobutadiene ion, *m/z* 51 fragment (37%) (**Scheme-4**). The fragment of *m/z* 91 generated by loss of H_2 from *m/z* 93 (**Scheme-6**). The phenyl cyanate ion radical can obtain by Retro Diels-Alder reaction and then it's twice protonated obtained fragment of *m/z* 121. Intramolecular McLafferty rearrangement of phenyl cyanate obtained cyanic acid ion radical, *m/z* 43 by loss of benzyne (**Scheme-7**). It seems the McLafferty rearrangement can occurred with one phenyl ring in 2,4,6-triphenoxy-1,3,5-*s*-triazine **3** moiety for generation *m/z* 281 fragment. This fragment can tautomerized to 2-hydroxy-4,6-diphenoxy-1,3,5-*s*-triazine and then converted to *m/z* 264 by loss of hydroxyl radical. The fragment of *m/z* 238 can also prepared from *m/z* 281 by loss of natural cyanic acid by ring contracting of (1H,2H)-4,6-diphenoxy-*s*-triazine-2-one ion radical (**Scheme-8**).


m/z 357
m/z 264
m/z 238
m/z 77
m/z 77
m/z 93
m/z 93
Chapman rearr.
m/z 117
m/z 145
m/z 145
Chapman rearr.
m/z 77
m/z 196
m/z 238
m/z 238
m/z 51

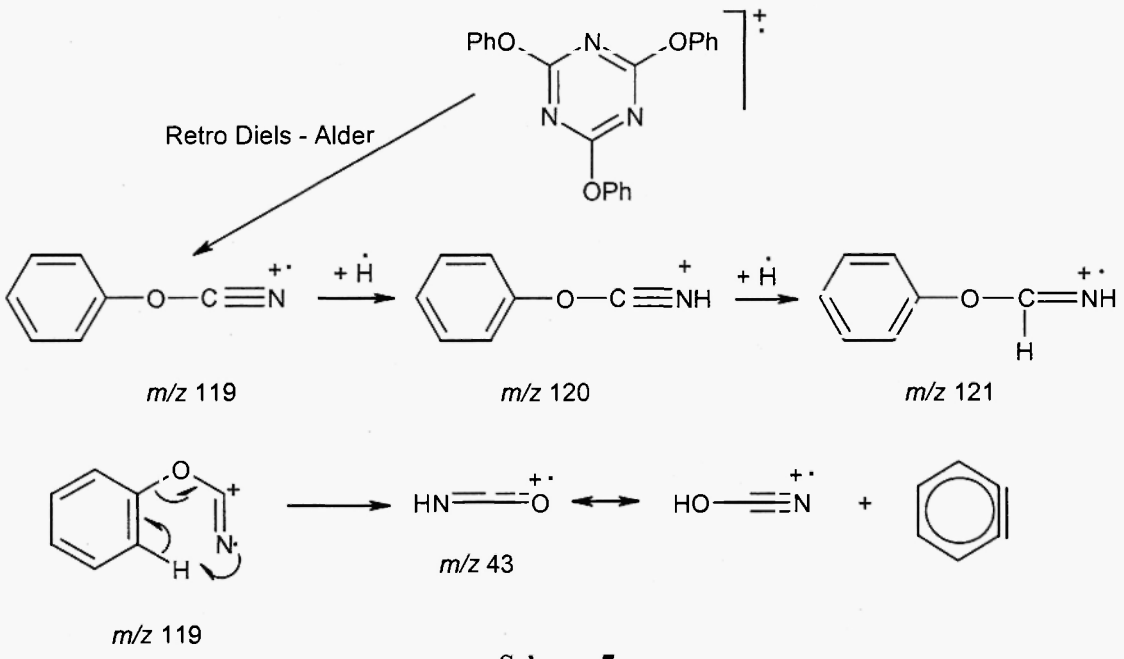
Scheme-4



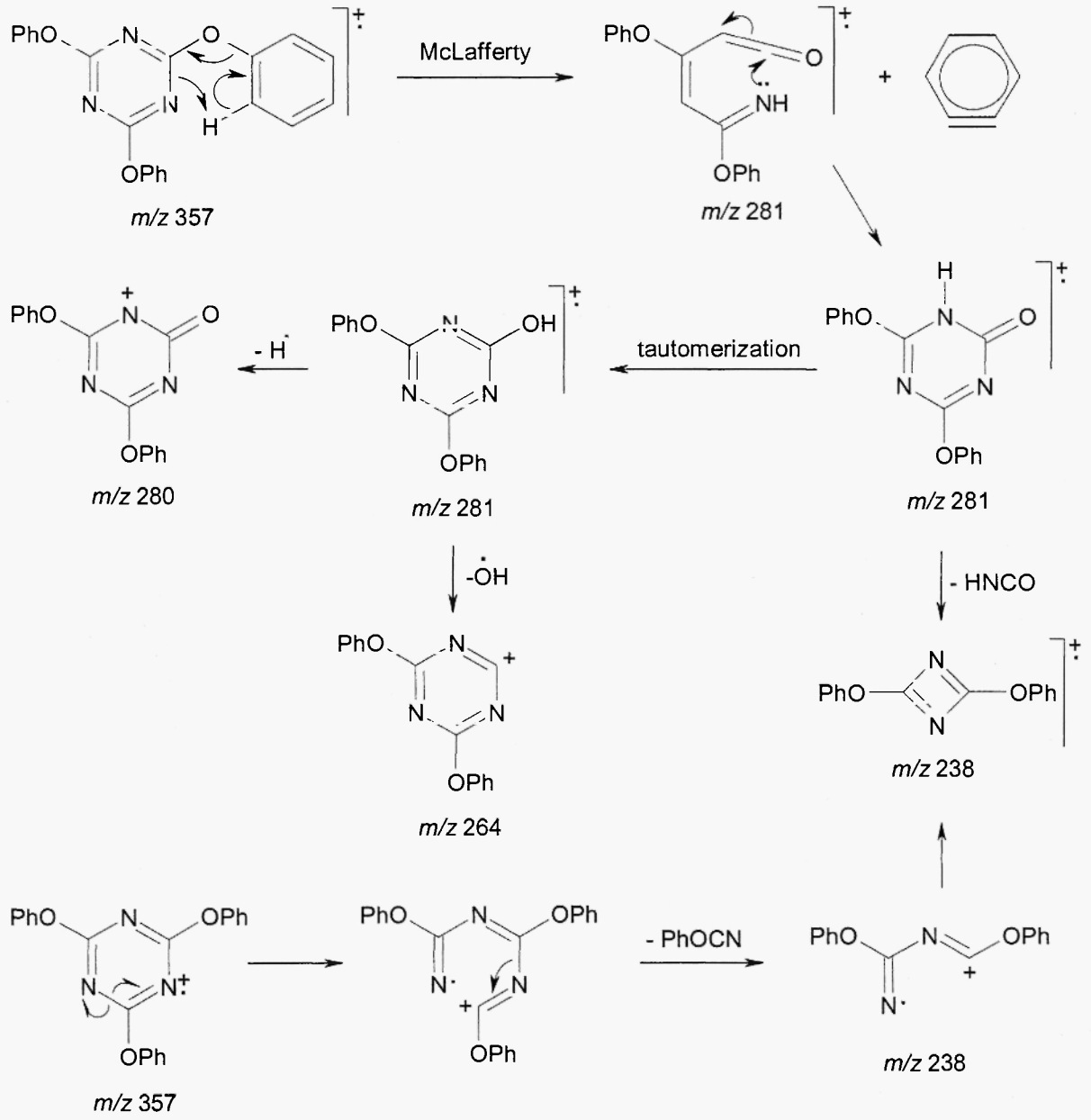
Scheme-5



Scheme-6



Scheme-7



Scheme-8

Conclusions

In conclusion, many trimerization reactions usually carried out in the presence of acid, base or organometallic compounds as a catalyst. In this new unexpected cyclic trimerization reaction no used any special catalyst and is carried out unexpectedly at the neutral mild condition based on experimental observation. Some of main fragments such as; *m/z* 196 ion fragment generated due to Chapman rearrangement apparently. We are developing more studies about this reaction mechanism.

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