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Are the pyrazolines formed from the reaction of [60]fullerene with alkyl diazoacetates unstable?

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Abstract—[60]Fullerene-fused pyrazolines **1** were prepared by the reaction of C_{60} with alky diazoacetates under the solid-state high-speed vibration milling conditions as well as in toluene solution. Pyrazolines **1** were stable in refluxing toluene and its thermolysis process in 1,2-dichlorobenzene was investigated, the decomposition rates and activation energies of pyrazolines **1** were obtained. The current work demonstrated that the liquid-phase reaction of C_{60} with alkyl diazoacetates undergoes via 1,3-dipolar cycloaddition pathway at room temperature, or proceeds via carbene mechanism at a temperature of refluxing toluene, thus clarifies the previous ambiguity of its reaction mechanism.

1. Introduction

Nucleophilic additions, free radical additions, carbene additions, 1,3-dipolar cycloadditions are widely known to occur with fullerenes.[1] The addition of diazo compounds to [60]fullerene (C_{60}) is one of the first investigated reactions in fullerene chemistry.[2] The reaction of C_{60} with mono- and diphenyldiazomethane,[2,3] diazomethane and dimethyldiazomethane,[4] diazoacetates,[5] diazomalonates[6] and diazoamides[7] has been reported. Preliminary result of the reaction of C_{60} with ethyl diazoacetate was first described by Wudl in a review,[2b] and detailed investigation of the reaction of C_{60} with alkyl diazoacetates in refluxing toluene was later on reported by Diederich's group.[5a] In these reactions, they could not obtain the evidence of the formation of the pyrazoline intermediates.[5a] The isolated pyrazoline compounds from the reaction of C_{60} with diazomethane[4a] and monoalkyl diazomethanes[8] were reported to decompose in refluxing toluene and at 70 °C or below, respectively. All these studies seem to support the claim that pyrazolines formed from the reaction of C_{60} with diazo compounds are unstable at a temperature of refluxing toluene or below.

Solvent-free mechanochemical reactions of fullerenes were developed because fullerenes have low solubility in common organic solvents and some unusual fullerene reactions could only occur in the solid-state reaction.[9] Since the first solid-state reaction of C_{60} with ethyl bromoacetate and zinc under high-speed vibration milling (abbreviated as HSVM) conditions was studied in 1996,[10] there have been reports on reactions of C_{60} catalyzed by various potassium salts, alkaline metals, or solid amines to prepare fullerene dimers and trimers,[11] [4+2] reaction of C_{60} with condensed aromatic compounds,[12] with phthalazine[13] and with di(2-pyridyl)-1,2,4,5-tetrazine,[14] reaction of C_{60} with dichlorodiphenylsilane and lithium,[15] reaction of C_{60} with organic bromides and alkali metals,[16] reaction of C_{60} and *N*-alkylglycines with and without aldehydes,[17] reaction of C_{60} with active methylene compounds[18] under the HSVM conditions. As a continuation of the mechanochemical reactions of fullerenes under the HSVM conditions, we have investigated the mechanochemical reaction of C_{60} with diazo compounds. Preliminary work on the HSVM reaction of C_{60} with 9-diazofluorene has been described.[9b] In that case, the pyrazoline intermediate generating the final methanofullerene product could not be isolated. However, when we conducted the reaction of C_{60} with alkyl diazoacetates, we found that the formed pyrazoline could be isolated and turned out stable in refluxing toluene, and thus questioned the mechanism of the formation of methanofullerene and fulleroid from the reaction of C_{60} with alkyl diazoacetates in refluxing toluene via 1,3-dipolar cycloaddition pathway.[2b,5a] In this paper, we report the preparation of fullerene-fused pyrazolines under the solid-state HSVM conditions as well as in the liquid-phase solution and their thermolysis behavior.

Keywords: C_{60}; Diazo compounds; Pyrazoline; Glycine ester; Sodium nitrite; Thermolysis; Solvent-free; High-speed vibration milling.
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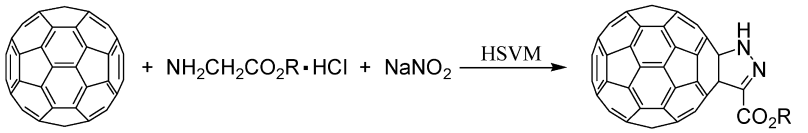


1a R=Et
1b R=$(CH_2)_7CH_3$

Scheme 1.

2. Results and discussion

The reaction of glycine ethyl ester hydrochloride with sodium nitrite was utilized to prepare ethyl diazoacetate in situ under the HSVM conditions. A mixture of C_{60}, glycine ethyl ester hydrochloride and sodium nitrite in a molar ratio of 1:1:2 was vigorously milled for 30 min under the HSVM conditions to give pyrazoline **1a** in 48% yield (87% based on consumed C_{60}) (Scheme 1).

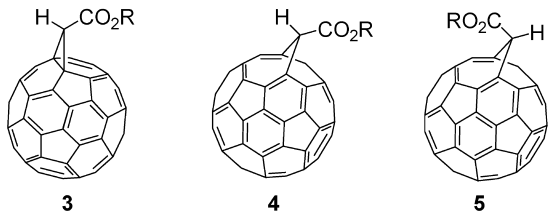
The structure of the [60]fullerene-fused pyrazoline derivative **1a** was determined by MS, IR, UV–vis, and ^{1}H NMR spectral data. The APCI MS of **1a** gave M^- at 834 as the base peak. The IR spectrum of **1a** showed absorptions at 3250, 1706, and 1546 cm^{-1} for the N–H, carbonyl and C=N groups, respectively, besides those peaks at 1425, 1172, 573 and 528 cm^{-1} for the C_{60} skeleton. The sharp absorption at 425 nm in the UV–vis spectrum is characteristic for the closed [6,6]-adducts.[1] The ^{1}H NMR spectrum of **1a** exhibited a quartet at 4.44 ppm and a triplet at 1.47 ppm of the OCH_2CH_3 group and a singlet at 7.91 ppm of the acidic N–H. Due to the very low solubility of **1a**, its ^{13}C NMR spectrum could not be obtained.

In order to ascertain the pyrazoline structure for the product obtained, we employed the glycine ester with long alkyl chain to increase the solubility of the product and thus measured its ^{13}C NMR spectrum. [60]Fullerene-fused pyrazoline **1b** was prepared in the same way as **1a** by using glycine octyl ester hydrochloride in place of glycine ethyl ester hydrochloride. Pyrazoline **1b** was fully characterized by the above spectral means. As expected, satisfactory ^{13}C NMR spectrum of **1b** was obtained. Twenty nine lines including one overlapping line between 135–148 ppm of the sp^2 carbons and two peaks at 88.45 and 77.38 ppm of the sp^3 carbons for the [60]fullerene skeleton of **1b** were observed, indicating its C_s symmetry.

2-Pyrazolines **1** were obtained via isomerizations of 1-pyrazolines **2** which were formed directly by the 1,3-dipolar cycloadditions of alkyl diazoacetates generated in situ from glycine ester hydrochlorides and sodium nitrite with C_{60} (Scheme 2). The observation of acidic proton at about 8 ppm for N–H in the ^{1}H NMR spectrum, which disappeared upon the addition of D_2O, the lack of the absorption at 1560 cm^{-1} for N=N vibration in the IR spectrum,[4a,8] and the C_s symmetry rather than C_1 symmetry inferred from the ^{13}C NMR spectrum all support the conclusion that the isolated product is 2-pyrazoline **1** rather than 1-pyrazoline **2**.

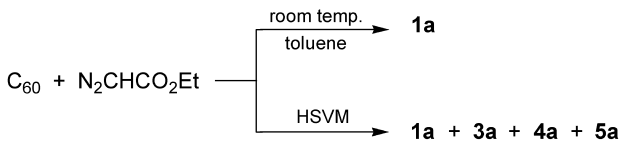
Pyrazolines **1a** and **1b** could be prepared in 51% yield by liquid-phase reaction of C_{60} with glycine ester hydrochloride and sodium nitrite at a molar ratio of 1:5:200 in toluene at room temperature. But this liquid-phase reaction required large excess of insoluble reagents and much longer reaction time to reach comparable yield as under the solvent-free HSVM conditions. This clearly shows the advantage of the solid-state HSVM reaction over the liquid-phase reaction.

Diederich and co-workers reported that the reaction of C_{60} with alkyl diazoacetates in refluxing toluene afforded a mixture of methanofullerene and fulleroids, but the pyrazoline intermediates were not obtained.[5a] Our anticipated products from the reaction of C_{60} with glycine ester hydrochloride and sodium nitrite under the HSVM conditions are the mixture of compounds **3**, **4** and **5**. Therefore the isolation of pyrazoline **1** was surprising. We then carried out the reaction of C_{60} with ethyl diazoacetate at room temperature in order to see if we could obtain pyrazoline **1a**. To our delight, the reaction of C_{60} with 10 equiv. of ethyl diazoacetate in toluene for 10 h at room temperature gave

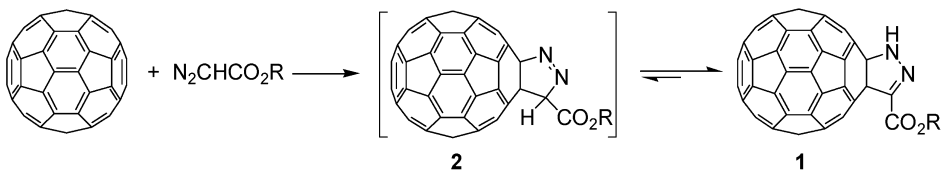


3 **4** **5**

3a, **4a**, **5a**: R = CH_2CH_3; **3b**, **4b**, **5b**: R = $(CH_2)_7CH_3$



Scheme 3.



2 **1**

Scheme 2.

pyrazoline **1a** (Scheme 3) in 47% yield (96% based on consumed C_{60}) with no evidence of the formation of compounds **3a**, **4a** and **5a**. When the reaction was conducted in refluxing toluene, only bridged fullerenes **3a**, **4a** and **5a** were obtained, as reported by Diederich's group. Meanwhile, the HSVM reaction of C_{60} with pre-formed ethyl diazoacetate in a molar ratio of 1:1 for only 6 min afforded pyrazoline **1a** as the major product in 45% yield along with a mixture of compounds **3a**, **4a** and **5a** in 19% yield (Scheme 3).

Methanofullerene **3** and fulleroids **4** and **5** might be formed through the loss of N_2 from 1-pyrazoline **2**.[2b,5a] With isolated pure 2-pyrazoline **1** in hand, **1** we investigated its thermal stability and the possible transformation into compounds **3**, **4** and **5** through the loss of N_2. 2-Pyrazoline **1a** was stable in refluxing toluene. However, when pyrazoline **1a** was heated in 1,2-dicholorobenzene (ODCB) at 180 °C for 10 h, most of **1a** decomposed to a mixture of compounds **3a**, **4a** and **5a**, as confirmed by HPLC analysis and ^{1}H NMR measurement. The thermal decomposition process of pyrazolines **1a** and **1b** at different temperatures in ODCB was followed by HPLC analysis on an analytical Buckyprep column with 326 nm as the detection wavelength. The concentration of remained pyrazoline **1** after heating for a certain time was determined by the initial concentration of **1** and the relative peak areas of **1** and products **3**, **4** and **5**. As shown in Figures 1 and 2, ln *C* vs reaction time displayed good linear relationship at different temperatures. The decomposition of pyrazoline **1** was therefore a first-order reaction. The derived decomposition rates at different temperatures and activation energies of pyrazolines **1a** and **1b** are listed in Table 1.

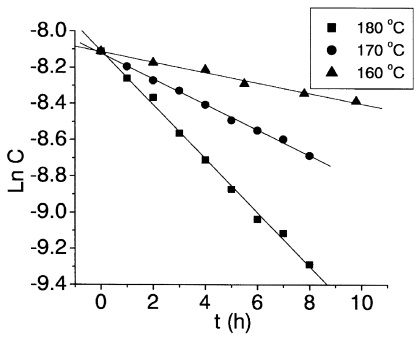


Figure 1. The linear plot of ln *C* vs reaction time of **1a** at temperatures of 160, 170 and 180 °C with initial concentration of 3.0×10^{-4} M.

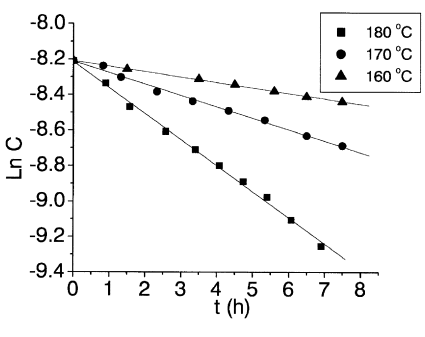
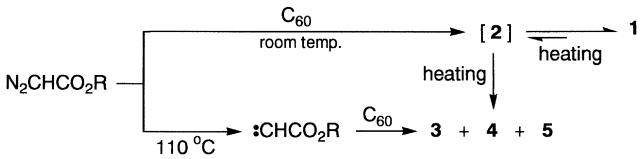


Figure 2. The linear plot of ln *C* vs reaction time of **1b** at temperatures of 160, 170 and 180 °C with initial concentration of 2.7×10^{-4} M.

Table 1. Decomposition rates at different temperatures and activation energies of pyrazolines **1a** and **1b**

Compound	**1a**			**1b**		
Temperature (°C)	160	170	180	160	170	180
$k\times10^2$ (h^{-1})	2.87	7.03	14.87	3.05	6.42	14.65
Ea (kJ mol^{-1})	134			128		

Diederich and co-workers conducted the reaction of C_{60} with ethyl diazoacetate in refluxing toluene for 7 h and only obtained methanofullerene **3a** and fulleroids **4a** and **5a** in a ratio of 1:1:3.[5a] They stated that both 1,3-dipolar cycloaddition followed by rapid loss of N_2 as well as thermal decomposition of diazo compound followed by addition of the formed carbene could explain the formation of the methanofullerene **3** and fulleroid compounds **4** and **5**. Even though they did not obtain any evidence of the formation of pyrazoline intermediates, they could not exclude the 1,3-dipolar cycloaddition mechanism. They proposed that both mechanisms could actually occur concurrently in the refluxing toluene.[5a] We found that when 2-pyrazoline **1a** was heated in refluxing toluene for the same reaction time (7 h) as for the reaction of C_{60} with ethyl diazoacetate, only about 5% of a mixture of **3a**, **4a**, and **5a** was obtained. This fact along with the thermolysis behavior of pyrazolines **1** indicates that once pyrazolines **1** are formed through the 1,3-diploar cycloaddition under the HSVM conditions or at room temperature in toluene, it is hard to lose N_2 to form bridged fullerene derivatives **3**, **4** and **5** at the temperature of refluxing toluene. Therefore compounds **3**, **4** and **5** resulting from the reaction of C_{60} with alkyl diazoacetates in refluxing toluene should be formed via carbene mechanism. Our observed transformation of 2-pyrazoline **1** into methanofullerene **3** and fulleroids **4** and **5** should proceed through the loss of N_2 from 1-pyrazoline **2**, which is generated by unfavorable rearrangement of the conjugated 2-pyrazoline **1** and thus requires high temperature (Scheme 4).



Scheme 4.

Since the known 1-pyrazoline-fused fullerenes are reported to decompose easily in refluxing toluene,[4a] 70 °C or even slightly elevated temperature (>20 °C),[8] the high activation energy required for the formation of methanofullerene **3** and fulleroids **4** and **5** from 2-pyrazoline **1** probably reflects that the rearrangement of the conjugated 2-pyrazoline **1** to non-conjugated 1-pyrazoline **2** is highly energy-consuming and is the rate-determining step.

The temperature of the contents inside the capsule of the high-speed vibration mill does not reach up to 100 °C,[11b] which is lower than the decomposition temperature of pyrazoline **1**. The HSVM reaction of C_{60} with ethyl diazoacetate giving a mixture of **1a**, **3a**, **4a**, and **5a** indicated that both 1,3-dipolar cycoaddition and carbene mechanisms were working. Ethyl diazoacetate may not be stable under

our HSVM conditions and part of ethyl diazoacetate may lose N_2 to generate carbene species, which reacts with C_{60} to form **3a**, **4a** and **5a** in a ratio (1:1.3:2.7) close to that in the liquid-phase reaction of C_{60} with ethyl diazoacetate in refluxing toluene.

In summary, [60]fullerene-fused pyrazolines **1** prepared by the reaction of C_{60} with alky diazoacetates under the solid-state HSVM conditions and in toluene solution turned out stable at a temperature of refluxing toluene. The thermolysis process at higher temperatures in 1,2-dichlorobenzene was investigated, the decomposition rates and activation energies of [60]fullerene-fused pyrazolines **1** were obtained. The present work establishes that the liquid-phase reaction of C_{60} with alkyl diazoacetates undergoes via 1,3-dipolar cycloaddition pathway at room temperature and proceeds via carbene mechanism at the temperature of refluxing toluene, thus clarifies the previous ambiguity of its reaction mechanism.[5a]

3. Experimental

3.1. General procedures

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CS_2/CDCl_3$. IR spectra were recorded on a Shimadzu 8600 FT IR spectrometer. UV–vis spectra were obtained on a Shimadzu UV-2501 PC spectrometer. APCI and MALDI-TOF mass spectra in negative mode were taken on a Finnigan TSQ7000 and a Bruker BIFLEXIII spectrometer with 4-hydroxy-α-cyanocinnamic acid as the matrix, respectively. High-performance liquid chromatography analysis was conducted on an Agilent 1100 liquid chromatograph with a diode-array detector using a Cosmosil Buckyprep column (4.6 mm×250 mm) with toluene as the eluent. For the HPLC measurements, the reaction mixture was monitored at 326 nm, and the relative ratios of C_{60} and its derivatives' peak areas were taken as the relative amounts of C_{60} and its derivatives. Their actual amounts should be slightly different due to the slightly different molar extinction coefficients for C_{60} and its derivatives at 326 nm, but will not affect our treatment.

All solvent-free reactions were performed using a vibration mill that consists of a capsule and a milling ball made of stainless steel. The capsule containing the milling ball was fixed in a home-built vibration arm, which was vibrated vigorously at a rate of 3500 cycles per minute.[11b]

C_{60} (>99.9%) was purchased from 3D Carbon Cluster Material Co. of Wuhan University in China. Glycine ester hydrochloride derivatives were prepared by the reaction of glycine with corresponding alcohol through the bubbling of dry hydrogen chloride, and ethyl diazoacetate was prepared by the reaction of the obtained glycine ethyl ester hydrochloride with sodium nitrite according to the reported procedures.[19,20]

3.1.1. Reaction of C_{60} with glycine ethyl ester hydrochloride and sodium nitrite under the HSVM conditions. A mixture of C_{60} (14.4 mg, 0.02 mmol), glycine ethyl ester hydrochloride (2.8 mg, 0.02 mmol) and sodium nitrite (2.8 mg, 0.04 mmol) was vigorously vibrated for 30 min. The combined reaction mixture from two runs was separated on a silica gel column with toluene as the eluent to give unreacted C_{60} (13.0 mg, 45%) and pyrazoline **1a** (16.0 mg, 48%). **1a**: ^1H NMR (300 MHz, $CS_2/CDCl_3$) δ (ppm) 7.91 (s, 1H), 4.44 (q, J=7.2 Hz, 2H), 1.47 (t, J=7.2 Hz, 3H); FT-IR (KBr) ν (cm^{-1}) 3300, 2977, 2952, 2867, 1706, 1546, 1425, 1373, 1329, 1172, 1133, 1098, 1016, 796, 772, 573, 528; UV–vis ($CHCl_3$) λ_{max} (nm) 246, 275, 313, 425, 684; APCI MS m/z 834 (M^-).

3.1.2. Reaction of C_{60} with glycine octyl ester hydrochloride and sodium nitrite under the HSVM conditions. A mixture of C_{60} (14.4 mg, 0.02 mmol), glycine octyl ester hydrochloride (6.8 mg, 0.03 mmol) and sodium nitrite (4.2 mg, 0.06 mmol) was vigorously vibrated for 30 min. The combined reaction mixture from two runs was separated on a silica gel column eluted with toluene to give unreacted C_{60} (13.0 mg, 45%) and pyrazoline **1b** (17.9 mg, 49%). **1b**: ^1H NMR (300 MHz, $CS_2/CDCl_3$) δ (ppm) 8.01 (s, 1H), 4.39 (t, J=6.7 Hz, 2H), 1.85–1.75 (m, 2H), 1.43–1.28 (m, 10H), 0.89 (t, J=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$) δ (ppm) 161.78 (COO), 147.63 (1C), 147.42 (2C), 147.15 (1C), 146.30 (2C), 146.25 (2C), 146.01 (2C), 145.95 (2C), 145.90 (2C), 145.69 (2C), 145.50 (2C), 145.21 (2C), 145.18 (2C), 144.36 (2C), 144.32 (2C), 144.20 (2C), 144.09 (2C), 143.93 (2C), 143.05 (2C), 142.88 (2C), 142.79 (2C), 142.56 (2C), 142.34 (2C), 142.29 (2C), 142.18 (4C), 141.83 (2C), 140.35 (2C), 140.47 (2C), 136.30 (2C), 135.86 (2C), 134.72 (C=N), 88.45 (sp^3-C of C_{60} cage), 77.38 (sp^3-C of C_{60} cage), 66.17 (OCH_2), 32.04 (CH_2), 29.52 (CH_2), 29.47 (CH_2), 28.94 (CH_2), 26.30 (CH_2), 22.98 (CH_2), 14.36 (CH_3); FT-IR (KBr) ν (cm^{-1}) 3285, 2920, 2850, 1701, 1542, 1462, 1427, 1330, 1169, 1133, 1098, 1020, 974, 772, 574, 527; UV–vis λ_{max} (nm) 246, 275, 313, 425, 685; MALDI-TOF MS m/z 918 (M^-).

3.1.3. Reaction of C_{60} with glycine ethyl ester hydrochloride and sodium nitrite in toluene solution. A mixture of C_{60} (30.8 mg, 0.043 mmol), 5 equiv. of glycine ethyl hydrochloride (29.7 mg, 0.215 mmol) and 200 equiv. of sodium nitrite (593 mg, 8.60 mmol) in 30 mL of toluene was stirred in the dark for two days. The resulting brown solution was filtrated to remove the excess ester hydrochloride and sodium nitrite and evaporated in vacuo. The residue was separated on a silica gel column with toluene as the eluent to afford unreacted C_{60} (12.5 mg, 41%) and pyrazoline **1a** (18.1 mg, 51%).

3.1.4. Reaction of C_{60} with glycine octyl ester hydrochloride and sodium nitrite in toluene solution. A mixture of C_{60} (36.0 mg, 0.05 mmol), 5 equiv. of glycine ethyl hydrochloride (55.8 mg, 0.25 mmol) and 200 equiv. of sodium nitrite (690 mg, 10.0 mmol) in 30 mL of toluene was stirred in the dark for 12 h. The resulting brown solution was filtrated to remove the excess ester hydrochloride and sodium nitrite and evaporated in vacuo. The residue was separated on a silica gel column with toluene as the eluent to afford unreacted C_{60} (15.7 mg, 44%) and pyrazoline **1b** (23.4 mg, 51%).

3.1.5. Reaction of C_{60} with ethyl diazoacetate in toluene solution. A mixture of C_{60} (30.8 mg, 0.043 mmol) and ethyl

diazoacetate (47.3 μL, 0.43 mmol) in 30 mL of toluene was stirred for 10 h at room temperature. The brown solution was evaporated in vacuo, and the residue was separated on a silica gel column with toluene as the eluent to give the unreacted C_{60} (16.0 mg, 51%) and pyrazoline **1a** (16.4 mg, 47%).

3.1.6. Reaction of C_{60} with ethyl diazoacetate under the HSVM conditions. A mixture of C_{60} (14.4 mg, 0.02 mmol) and ethyl diazoacetate (2.2 μL, 0.02 mmol) was vigorously vibrated for 6 min. The combined reaction mixture from two runs was separated on a silica gel column with CS_2 as the eluent to afford unreacted C_{60} (4.9 mg, 17%), mixture of methanofullerene **3a** and fulleroids **4a** and **5a** (6.2 mg, 19%), and then with toluene as the eluent to give pyrazoline **1a** (15.0 mg, 45%). The ratio of **3a**, **4a** and **5a** was 1:1.3:2.7 as determined by ^{1}H NMR spectrum.

3.1.7. Thermolysis of pyrazoline 1. Two miligrams of pyrazoline **1** was dissolved in 8 mL of ODCB, and heated in an oil bath at the desired temperature. The thermolysis process was followed by the HPLC analysis on a Buckyprep column with toluene as the eluent. The concentration of remained pyrazoline **1** after heating was determined by the initial concentration of **1** and the relative peak areas of **1** and products **3**, **4** and **5** monitored at 326 nm.

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