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Solvent-free Mechanochemical and Liquid-phase Reaction of [60]Fullerene with Ethyl 2-Diazopropionate

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Abstract: The solvent-free mechanochemical reaction and the liquid-phase reaction of C_{60} with ethyl 2-diazopropionate prepared *in situ* or preformed from alanine ethyl ester hydrochloride and sodium nitrite have been investigated. Methanofullerene **1** and fulleroids **2** and **3** from these reactions were obtained, meanwhile the pyrazoline intermediate was not observed. Fulleroids **2** and **3** can be converted to methanofullerene **1** in refluxing toluene.

Keywords: [60]Fullerene, ethyl 2-diazopropionate, methanofullerene, fulleroid.

The addition of diazo compounds to [60]fullerene (C_{60}) is one of the first investigated reactions in fullerene chemistry[1]. The reactions of C_{60} with mono- and diphenyldiazomethane[1,2], diazomethane and dimethyldiazomethane[3], diazoacetates[4], diazomalonates[5] and diazoamides[6] in solution have been reported. Solvent-free mechanochemical reactions of fullerenes were developed due to the low solubility of fullerenes in common organic solvents and some unusual fullerene reactions that could only occur in the solid-state reaction[7]. Since the first solid-state reaction of C_{60} with ethyl bromoacetate and zinc under high-speed vibration milling (abbreviated as HSVM) was studied in 1996[8], there have been reports on reactions of C_{60} catalyzed by various potassium salts, alkali metals, or solid amines to prepare fullerene dimers and trimers[9], [4+2] reaction of C_{60} with condensed aromatic compounds[10], with phthalazine[11] and with di(2-pyridyl)-1,2,4,5-tetrazine[12], reaction of C_{60} with dichlorodiphenylsilane and lithium[13], reactions of C_{60} with organic bromides and alkali metals[14], reaction of C_{60} and *N*-alkylglycines with and without aldehydes[15], and reaction of C_{60} with active methylene compounds[16] 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. When we conducted the reaction of C_{60} with ethyl diazoacetate or octyl diazoacetate, we found that the pyrazoline formed could be isolated and was stable in refluxing toluene[17], and thus questioned the mechanism of the formation of methanofullerene and fulleroid from the reaction of C_{60} with alkyl diazoacetates in

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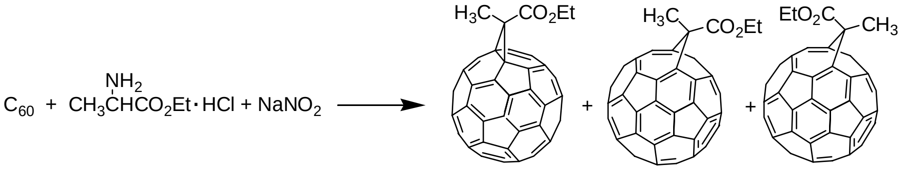
refluxing toluene *via* 1,3-dipolar cycloaddition pathway[1b,4a]. It seemed interesting to see what would happen if substituted diazoacetate was employed in this reaction. In this paper, we report the study on the solvent-free mechanochemical reaction as well as liquid-phase reaction of C_{60} with ethyl 2-diazopropionate prepared *in situ* or preformed from alanine ethyl ester hydrochloride and sodium nitrite.

The reaction of C_{60} with alanine ethyl ester hydrochloride and sodium nitrite was utilized to prepare ethyl 2-diazopropionate *in situ* under the HSVM conditions. A mixture of C_{60} (14.4 mg, 0.02 mmol), alanine ethyl ester hydrochloride (3.1 mg, 0.02 mmol) and sodium nitrite (7.0 mg, 0.10 mmol) was vigorously milled at a frequency of 3500 cycles per minute for 30 min under the HSVM conditions. The combined reaction mixture from two runs was separated on a silica gel column with CS_2/toluene as an eluent to give unreacted C_{60} (12.8 mg, 44%) and a mixture of methanofullerene **1** and fulleroids **2** and **3** (14.5 mg, 44%) (**Scheme 1**).

The ratio of compounds **1**, **2**, **3** was 1.2:1:4.6, which was determined by the integration of methylene group in the ^{1}H NMR spectrum. The ^{1}H NMR chemical shifts of compounds **1**-**3** were assigned based on Diederich's work on the reaction of C_{60} with ethyl diazoacetate in refluxing toluene[4a]. Methanofullerene **1** had a quartet peak at 4.49 ppm and a triplet peak at 1.48 ppm due to the OCH_2CH_3 group, and a singlet at 2.50 ppm for the bridgehead methyl group. For the isomers of **2** and **3**, the corresponding chemical shifts are 4.58, 1.44 and 1.46 ppm, and 4.21, 1.30 and 3.18 ppm, respectively. Unlike the fulleroids generated from the reaction of C_{60} with diazoacetate[4], fulleroid **3** with methyl group located above the 5-membered ring dominates over fulleroid **2** with the bulkier ethoxycarbonyl group located above the 5-membered ring. The structure assignment of methanofullerene **1** was further ascertained by spectral characterization of pure **1**[18], which was obtained by refluxing a mixture of compounds **1**-**3** in toluene. The complete conversion of fulleroids **2** and **3** to methanofullerene **1** could be achieved by refluxing 24.6 mg of compounds **1**-**3** in 25 mL of toluene for 15 h. Furthermore, the structure of fulleroid **3**[19] was confirmed by the ^{13}C NMR spectrum of a sample mainly containing fulleroid **3**.

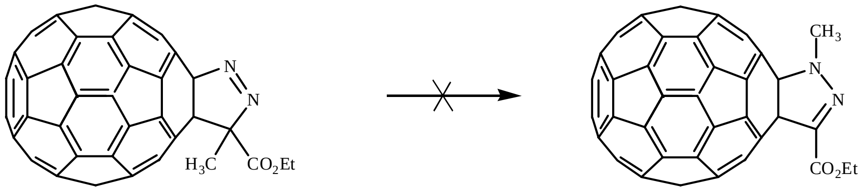
The HSVM reaction of C_{60} with equimolar amount of preformed ethyl 2-diazopropionate for 5 min gave 79% of recovered C_{60} and 14% of the mixture of compounds **1**, **2** and **3** in a ratio of 1.1:1:2.5. When the reaction time was extended to 15 min, 60% of unreacted C_{60} and 27% of compounds **1**-**3** in a ratio of 3.6:1:3.6 were obtained. The relative amount of methanofullerene **1** among the three isomers increased with the

Scheme 1



1 **2** **3**

Scheme 2



4 **5**

milling time, indicating that fulleroids **2** and **3** was converted to methanofullerene **1** during the milling process. This is verified by the percentage increase of methanofullerene **1** after HSVM treatment of a mixture of compounds **1**-**3**.

The liquid-phase reaction of C_{60} (18 mg, 0.025 mmol) with alanine ethyl ester hydrochloride (12 mg, 0.075 mmol) and sodium nitrite (200 mg, 2.9 mmol) in toluene was also conducted and allowed to proceed at room temperature for 16 h. Usual work-up afforded 46% of compounds **1**, **2** and **3** in a ratio of 4:1:10 along with 40% of unreacted C_{60}. The large excess amounts of insoluble alanine ethyl ester hydrochloride and sodium nitrite required and much longer reaction time in this liquid-phase reaction reflect the advantage of HSVM technique.

As in the HSVM reaction of C_{60} with 9-diazofluorene[7b], the pyrazoline intermediate could not be detected either in solvent-free HSVM reaction or liquid-phase reaction of C_{60} with ethyl 2-diazopropionate. This may be explained by the instability of 1-pyrazoline **4**, if formed during the reaction process, due to its failure of isomerization to 2-pyrazoline **5** (**Scheme 2**), in contrast to the observation that the 1-pyrazoline generated from the reaction of C_{60} with diazoacetate rearranges to the more stable 2-pyrazoline[17].

Compounds **1**-**3** could be generated by either 1,3-dipolar cycloaddition followed by rapid loss of dinitrogen or thermal decomposition of diazo compound followed by addition of the formed carbene. Even though the carbene mechanism is preferred and no evidence of the formation of pyrazoline intermediate could be obtained, the 1,3-dipolar cycloaddition mechanism can not be excluded for the formation of compounds **1**-**3** from the reaction of C_{60} with ethyl 2-diazopropionate.

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18. **Spectral data of 1:** ^{1}H NMR (300 MHz, CS$_2$/CDCl$_3$ = 1:1): δ 4.49 (q, 2H, *J* = 7.1 Hz), 2.50 (s, 3H), 1.48 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, CS$_2$/CDCl$_3$ = 1:1): δ 167.49 (*C*OO), 147.28 (2C), 146.00 (2C), 145.26 (2C), 144.93 (4C), 144.90 (2C), 144.88 (4C), 144.56 (1C), 144.50 (2C), 144.40 (1C), 144.38 (2C), 144.30 (2C), 144.26 (2C), 143.96 (2C), 143.60 (2C), 143.38 (2C), 142.98 (2C), 142.86 (1C), 142.79 (3C), 142.72 (2C), 142.65 (2C), 141.97 (2C), 141.91 (2C), 141.83 (2C), 141.75 (2C), 140.81 (2C), 140.59 (2C), 138.00 (2C), 137.85 (2C), 76.55 (sp^3-*C* of C$_{60}$), 62.35 (O*C*H$_2$CH$_3$), 44.25 (*C*COO), 15.54 (CH$_3$), 14.39 (OCH$_2$*C*H$_3$); FT-IR (KBr): ν/cm^{-1} 1737, 1456, 1427, 1182, 1132, 526; UV-Vis (CHCl$_3$): λ_{max}/nm 690, 493, 427, 326, 281.
19. **Selected spectral data of 3:** ^{1}H NMR (300 MHz, CS$_2$/CDCl$_3$ = 1:1) δ 4.18 (q, 2H, *J* = 7.1 Hz), 3.16 (s, 3H), 1.30 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, CS$_2$/CDCl$_3$ = 1:1) δ 169.13 (*C*OO), 147.34 (2C), 144.81 (2C), 144.58 (2C), 144.26 (1C), 143.90 (2C), 143.73 (4C), 143.56 (2C), 143.41 (1C), 143.36 (2C), 143.23 (2C), 143.15 (2C), 142.96 (2C), 142.92 (2C), 142.67 (2C), 142.64 (2C), 142.28 (2C), 142.23 (2C), 141.98 (1C), 141.84 (2C), 141.65 (2C), 141.49 (2C), 141.37 (2C), 139.98 (2C), 138.79 (2C), 138.74 (2C), 138.39 (2C), 137.72 (2C), 136.68 (1C), 135.49 (2C), 134.72 (2C), 134.15 (2C), 61.62 (O*C*H$_2$CH$_3$), 53.54 (*C*COO), 25.63 (CH$_3$), 14.13 (OCH$_2$*C*H$_3$).

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