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Thermal and catalytic reactions of ethyl diazopyruvate with [60]fullerene

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ABSTRACT

New stable [6,6]-methano cycloadducts and fulleropyrazolines containing electron-withdrawing groups have been obtained by the reaction of ethyl diazopyruvate with [60]fullerene. The results obtained by a systematic study conducted both in thermal and catalytic conditions have provided crucial indications concerning the mechanism of this important cluster opening process in fullerene chemistry.

1. Introduction

Since the discovery of [60]fullerene (**1**) in 1985,[1] the research of suitable procedures for its functionalization has become one of the main challenges in organic chemistry.[2] Synthetic [60]fullerene derivatives have indeed found numerous potential applications ranging from chemical to biological and technological field. Being an electron deficient polyolefin, [60]fullerene (**1**) chemistry is largely governed by its peculiar reactivity in radical and nucleophilic additions. However, although several synthetic methodologies have been devised, the [*n*+2]-cycloadditions surely represent the most employed and powerful tool for the functionalization of **1**.[3]

Diazo compounds, in particular, have been shown to react with **1** to give a variety of synthetically versatile [60]fullerene derivatives.[4–6] Thus, diazomethane and monoalkyl diazomethanes react with **1** to give the corresponding pyrazoline derivatives **2** as the result of a [3+2]-cycloaddition of the diazo compound to the [6,6]-double bond of **1** (Scheme 1).[4] The isolated pyrazoline **2** was reported to decompose in thermal conditions to afford almost exclusively the [5,6]-open rearranged fulleroids, while the photolytic extrusion of a nitrogen molecule furnished a mixture of [5,6]-open and [6,6]-closed derivatives (Scheme 1). Also the thermal addition of diazoesters to **1** leads to unstable fulleropyrazolines, which after nitrogen elimination afford as kinetic products the corresponding [5,6]-bridged methanofullerenes with an intact 60 π-electron system and an open transannular bond along with minor amounts of the corresponding [6,6]-bridged structures with 58 π-electrons and a closed transannular bond (Scheme 1).[5a] In a previous paper, we have described the dirhodium(II)tetraacetate-mediated decomposition of ethyl diazoacetate and ethyl diazomalonate in the presence of **1**.[5b] In this case, the dirhodium(II)tetraacetate-catalyzed reaction of diazoesters with **1** behaved similarly to the reaction with Fischer-type carbene complexes or phosphonium ylides,[7] or with carbenes generated from diazirines[8] or oxadiazolines[9] leading to the selective formation of the corresponding [6,6]-closed methanofullerenes **3** (Scheme 1). More recently, we have reported on the thermal reaction of dimethyl diazomethylphosphonate with **1** describing the unusual, preferential formation of **3** along with a minor amount (3:1) of only one [5,6]-open fulleroid.[5c] Thermal addition of diazoketones to **1** has been found to give different results.[6] In fact, the selective formation of [6,6]-closed compounds **3** along with the presence of dihydrofuran-fused derivatives **6** has been described. Upon heating for 24 h in 1-methylnaphthalene the pure methano-bridged derivatives rearranged leading to the formation of **6** (Scheme 1), as previously reported for fullerene-aziridines.[10]

The inherent nucleophilicity of the various classes of diazo compounds strongly affects their reaction mechanism with **1**, playing a crucial role in the formation of the above-described products. Following our continuing interest in diazo chemistry,[11]

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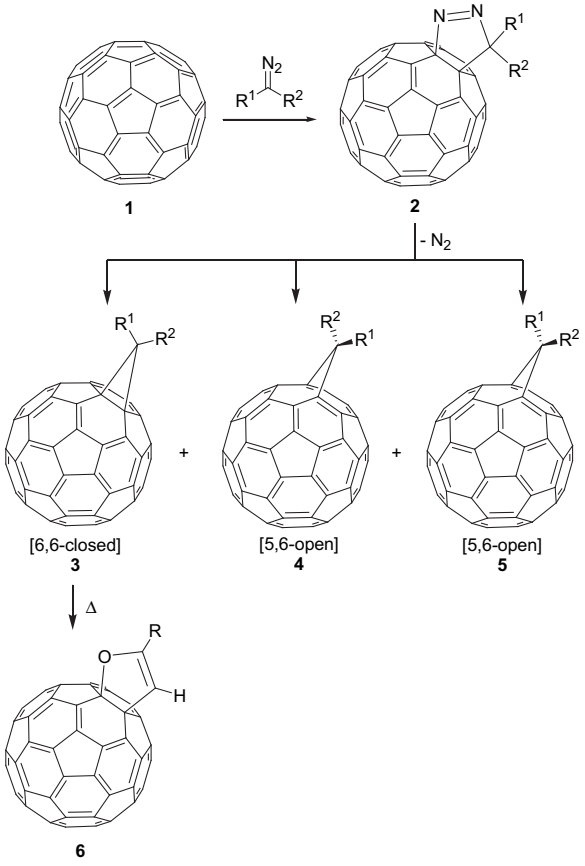
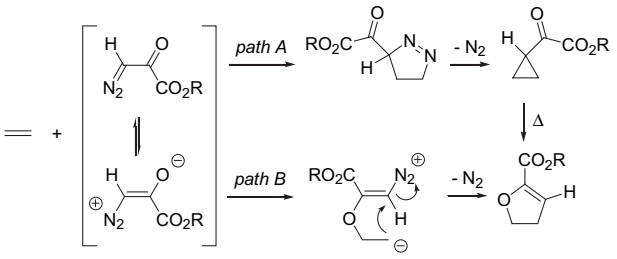


Scheme 1. Reaction of [60]fullerene (**1**) with diazo compounds.

and with the aim of further exploring the reactivity of diazo compounds toward the [60]fullerene olefinic system, we now have succeeded in reacting ethyl diazopyruvate (EDP, **7**) with **1** (Table 1). The presence of an electron-withdrawing group directly bonded to the carbonyl function would affect the α-diazocarbonyl reactivity thus producing marked differences in the addition reaction.

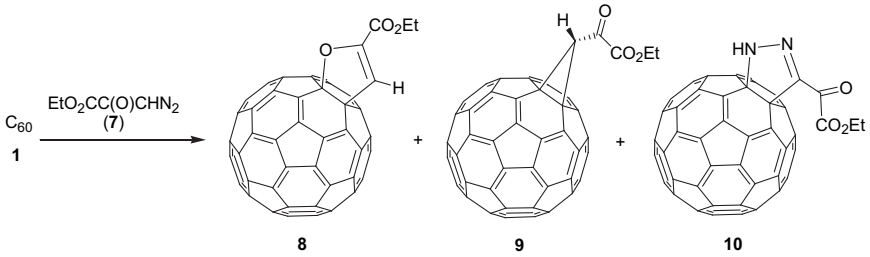
2. Results and discussion

Table 1 illustrates the results obtained when a solution of EDP (**7**) is added to a solution of [60]fullerene (**1**) with distinct reaction conditions both in thermal and catalytic processes. Thus, when **7** was thermally reacted with **1** in 1-methylnaphthalene at 30 and 45 °C (Table 1, entry 1 and 2) a mixture constituted by **8**, **9**, and **10** was obtained in 20% overall yield. When the reaction was carried out in toluene at 50 °C, **10** was obtained as the sole reaction product with 13% isolated yield (Table 1, entry 5). An increase in the reaction temperature was accomplished with a different composition in the reaction mixture. Accordingly, when EDP (**7**) was reacted with **1** in 1-methylnaphthalene at 60 °C (Table 1, entry 3) and 110 °C (Table 1, entry 4) a progressive increase in the formation of **8** and **9** was observed with a concomitant decrease of the fulleropyrazoline **10**, which completely disappeared at 110 °C. The formation of **10** as a stable product is noteworthy, being one of the few examples of an isolated and fully characterized fulleropyrazoline substituted with an electron-withdrawing group.[5e] When **10** was heated in toluene at 80 °C for 24 h the dihydrofuran derivative **8** and the [6,6]-closed methano adduct **9** were obtained in 1:1 ratio, as shown by HPLC and ^{1}H NMR analysis.[5a] The formation of a dihydrofuran derivative in addition to the cyclopropane adducts by reaction of an olefin with methyl diazopyruvate has been already reported:[12] the product has been hypothesized to take place either directly in the reaction mixture or as a rearrangement of the *syn*-isomeric cyclopropane adduct (Scheme 2). Dihydrofuran derivatives have also been described by reaction of alkylvinyl ethers with diazo compounds again



Scheme 2. Mechanism for dihydrofuran derivative formation with diazopyruvates.

Table 1
Thermal and catalytic decomposition of [60]fullerene (**1**) in the presence of EDP (**7**)

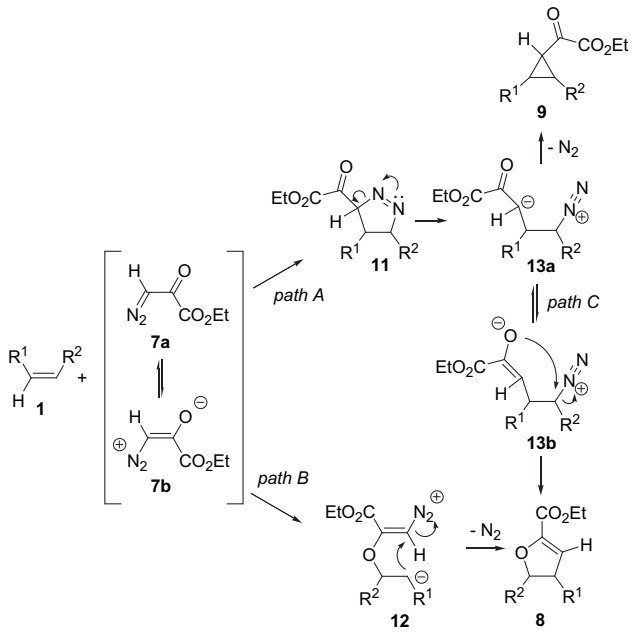


Entry	Condition	Solvent	*T* (°C)	*t* (h)	Yield[a] (%)	Product ratio[a] (%)		
						8	**9**	**10**
1	Thermal	1-Me-naphthalene	30	120	20	27	6	67
2	Thermal	1-Me-naphthalene	45	40	20	22	7	71
3	Thermal	1-Me-naphthalene	60	16	15	33	11	56
4	Thermal	1-Me-naphthalene	110	16	19	50	50	—
5	Thermal	Toluene	50	72	13	—	—	100
6	Rh (cat.)	1-Me-naphthalene	80	26	9	18	82	—
7	Rh (cat.)	1-Me-naphthalene	110	26	14	18	82	—
8	$Cu(Acac)_2$	1-Me-naphthalene	80	26	8	20	80	—
9	Rh (cat.)	Toluene	80	26	—	—	—	—
10	Rh (cat.)	Toluene	refl.	26	—	—	—	—

[a] Determined after purification by silica gel chromatography.

through a formal 1,3-dipolar addition (path A).[13] Moreover, the formation of a dihydrofuran derivative has been hypothesized to occur as the result of a thermal rearrangement of the corresponding [6,6]-closed methano adduct (path B, Scheme 2).[6] Nevertheless, in our case this transformation did not occur.

On the basis of the observed behavior of the pyrazoline **10**, the thermal rearrangements that lead to the dihydrofuran derivative **8** and the cyclopropane derivative **9** can be explained with the mechanism depicted in Scheme 3 (path A,C). In fact, the pyrazoline **11**, formed by the [3+2] cycloaddition of the diazo-form **7a** to the [60]fullerene olefinic double bond, can undergo an electronic rearrangement that consequently produces the carbanion intermediate **13a**. Nitrogen can then be eliminated either with a direct ring closure to form the cyclopropane ring (**9**) or, after enolization (**13b**), a ring closure to get the dihydrofuran derivative **8** (Scheme 3).



Scheme 3. Mechanistic hypothesis for dihydrofuranofullerenes formation with ethyl diazopyruvate (**7**).

In order to further explore the synthetic possibilities of this reaction, we submitted **1** to the catalytic decomposition of EDP (**7**) by utilizing rhodium(II)acetate dimer or copper acetylacetonate (Table 1). When the rhodium-catalyzed decomposition of **7** has been performed in toluene (entries 9 and 10) no reaction products were obtained. Instead, when catalytic or stoichiometric amounts of catalyst were employed in 1-methylnaphthalene as solvent at 80–110 °C (entries 6–8) the dihydrofuranofullerene **8** and the methanofullerene **9** were obtained in 8–14% yield with an approximate ratio of 1:4, respectively, as shown by HPLC analysis. In these conditions, the fulleropyrazoline derivative **10** was not detected.

The compounds were identified by ^{1}H and ^{13}C NMR analysis and their structures were confirmed by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). In particular, the ^{1}H NMR spectrum of the cyclopropane derivative **9** showed the presence of a methine signal at 5.8 ppm while the spectrum of dihydrofuran derivative **8** exhibited an olefinic singlet at 7.0 ppm.

Differently the ^{1}H NMR spectrum of the pyrazoline derivative **10** showed a singlet at 8.7 ppm of the acidic N–H, which disappeared upon the addition of D_2O. The N–H function was confirmed by the FTIR spectrum that indicated a peak at 3267 cm^{-1}. Regarding the ^{13}C NMR analysis, characteristic for dihydrofuran derivative **8** with respect to the cyclopropane derivative **9** is the absence of the carbonyl-C-atom resonance at δ=183 ppm and the absence of the signal of the CH-bridge in the typical range of about 40 ppm. Due to the very low solubility of **10**, its ^{13}C NMR could not be obtained. All the derivatives were also examined by UV/vis spectroscopic analysis. The electronic absorption spectra of compounds **8**–**10** are similar but completely different from [60]fullerene (**1**). As an example, **8** showed a sharp band with λ_{max} near 430 nm, which seems to be highly characteristic for 'closed' 6–6 ring-bridged fullerene derivatives (Fig. 1).[5a] Compared with the spectrum of **1**, the long-wavelength absorption band between 450 and 700 nm is much less structured and its maximum is hypsochromically shifted to near 500 nm in all the derivatives (data not shown). For a further

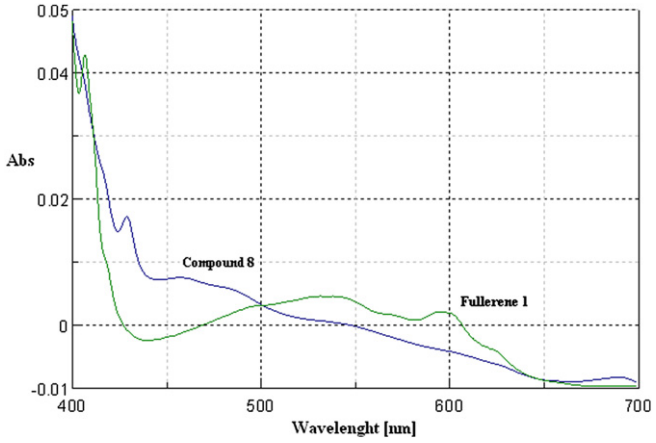


Figure 1. Electronic absorption spectra of dihydrofuran derivative **8** and [60]fullerene (**1**).

analytical characterization, a selective HPLC separation of compounds **8**–**10** and [60]fullerene (**1**) has been accomplished by using a Pirkle type (*R*)-phenylglycine and 3,5-dinitrobenzoic acid amide linkage stationary phase. Due to the high hydrophobicity of [60] fullerene derivatives, HPLC separation was optimized under direct mode. The use of the Pirkle type chiral stationary phase guaranteed a high level of selectivity ($\alpha \geq 1.4$), probably due to selective hydrogen bonding and π–π donor–acceptor interactions. Under the reported chromatographic conditions, [60]fullerene (**1**) (t_R=5 min) was the first eluted compound, while **8** (t_R=9 min) and **9** (t_R=12 min) were more strongly retained. Compound **10** showed a higher hydrophilicity and, since it strongly interacts with the stationary phase, it needed a more polar mobile phase to be eluted. High resolution with a t_R of 8 min was obtained by using a solution of toluene/hexane (90:10, v/v).

3. Conclusions

In summary, we describe here the first study of a transition metal induced carbenoid addition of EDP (**7**) to [60]fullerene (**1**). This method provides access to stable electron-withdrawing substituted cyclopropane and pyrazoline fullerene adducts, useful building blocks for the synthesis of new fullerene-based products possessing unique physico-chemical and biological properties.

4. Experimental section

4.1. General methods

All reagents were commercially available unless otherwise noted. All reactions were carried out in dried glassware under a dry nitrogen atmosphere. The final products were purified by chromatography on silica gel (70–230 mesh). TLC was performed on

aluminum backed silica plates (silica gel 60 F_{254}). All the reactions were performed using distilled solvent. ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 75 MHz using the solvents indicated below. Chemical shifts are reported in parts per million. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad signal. FT-IR spectra were obtained on a Nicolet Avatar 320 E.S.P. instrument; ν_{max} is expressed in cm^{-1}. HPLC separation and relative chromatograms were obtained by using a Jasco PU-980 solvent delivery system, connected to a Jasco MD 910 multiwavelength detector with a Reodyne model 7725 injector with a 20 μl loop. The chromatographic separations were carried out on a Chirex phase amide type 3001 Phenomenex 5 μm (I.D. 250×4.6 mm) column. Electronic absorption spectra were registered on a Jasco V-530 double beam spectrophotometer, using 1 cm quartz cell. Suitable settings were: width 2 nm, scan speed 400 nm min^{-1}, UV range 300–800 nm. MALDI mass measurements were performed using a REFLEX time-of-flight instrument (Bruker-Franzen Analytik, Bremen, Germany), equipped with a SCOUT ion source, operating in positive linear mode. Ions, formed by a pulsed UV laser beam (nitrogen laser, λ=337 nm) were accelerated to 25 kV. Pulsed ion extraction (PIE) was performed applying a voltage of 22.3 kV for 150 ns to the second grid. 2,5-Dihydroxybenzoic acid was used as matrix. Three independent mass measurements were made for each sample, to evaluate the reproducibility of the mass measurement, which was always in the range 0.1–0.05%.

4.2. Synthesis of ethyl diazopyruvate (7)[14]

To an ethereal solution of diazomethane (400 mL) was added dropwise a solution of ethyl oxalyl chloride (6 mL, 53 mmol) in dry ether (70 mL) under nitrogen atmosphere and magnetic stirring at 0 °C. The mixture was reacted for 1 h at 0 °C, and then concentrated under vacuum till a volume of about 20 mL. Filtration by reduced pressure gave the desired product as yellow crystal (79%). Mp: 74 °C. ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, J=6.8 Hz, 3H), 4.25 (q, J=6.8 Hz, J=14 Hz, 2H), 6.18 (s, 1H). IR (Nujol): 2100, 2120, 1730, 1740 cm^{-1}.

4.2.1. General method for the thermal-catalyzed decomposition of diazopyruvate ***7***. A solution of ethyl diazopyruvate (**7**) (580 mg, 4.1 mmol) in anhydrous toluene (30 mL) was added at room temperature to a magnetically stirred solution of [60]fullerene (**1**) (300 mg, 0.41 mmol) and in anhydrous toluene (20 mL) under nitrogen atmosphere. The resulting mixture was reacted for 72 h at the same temperature. The solvent was evaporated under vacuum and the resulting residue was washed with ether and purified by silica gel chromatography. Elution with toluene afforded unreacted **1**, then the dihydrofuran derivative **8** followed by cyclopropane derivative **9**. Elution with toluene containing 10% ethyl acetate afforded the more polar fullerene-pyrazoline derivative **10**.

4.2.2. General method for the $Rh_2(OAc)_4$-catalyzed decomposition of diazopyruvate ***7***. A solution of ethyl diazopyruvate (**7**) (580 mg, 4.1 mmol) in anhydrous 1-methylnaphthalene (50 mL) was added within 6 h at 110 °C via syringe pump to a magnetically stirred solution of [60]fullerene (**1**) (300 mg, 0.41 mmol) and $Rh_2(OAc)_4$ (18.1 mg, 0.041 mmol) in anhydrous 1-methylnaphthalene (20 mL) under nitrogen atmosphere. The resulting mixture was reacted for 26 h at the same temperature. The solvent was evaporated under vacuum and the resulting residue was washed with ether and purified as previously described.

*4.2.3. 1,2-Dihydro-(4-carboxyethyl-4,5-dihydrofuran)-[60]fullerene (**8**).* ^{1}H NMR (CS_2/$CDCl_3$, 2:1) δ: 1.54 (3H, t, J=7.2 Hz), 4.55 (2H, q, J=6.8, 14 Hz), 7.04 (s, 1H). ^{13}C NMR (CS_2/$CDCl_3$, 2:1) δ: 14.76, 63.30, 103.62, 136.49, 137.36, 140.07, 140.85, 141.90, 141.98, 142.34, 142.44, 142.57, 142.85, 142.92, 143.09, 143.26, 143.61, 144.51, 144.86, 145.12, 145.18, 145.23, 145.36, 145.40, 145.48, 145.61, 145.76, 146.17, 146.27, 146.40, 146.46, 146.52, 147.60, 148.07, 148.28, 149.34, 159.62. MALDI-MS: m/z 836 [M+H]$^+$, m/z 858 [M+Na]$^+$. HPLC t_R=9 min (toluene/hexane, 40/60, v/v). UV/vis (toluene): λ_{max}/nm ~430.

*4.2.4. Ethyl 1,2-methano[60]fullerene-61-α-ketocarboxylate (**9**).* ^{1}H NMR (CS_2/$CDCl_3$, 2:1) δ: 1.54 (3H, t, J=7.2 Hz), 4.55 (2H, q, J=6.8, 14 Hz), 5.80 (s, 1H). ^{13}C NMR (CS_2/$CDCl_3$, 2:1) δ: 14.10, 40.84, 63.16, 71.76, 136.50, 140.67, 140.80, 141.03, 141.59, 141.88, 142.03, 142.19, 142.58, 142.86, 143.10, 143.49, 143.74, 144.30, 144.43, 144.71, 144.82, 144.98, 144.99, 145.04, 145.08, 147.48, 159.85, 183.35. MALDI-MS: m/z 835 [M+H]$^+$, m/z 856 [M+Na]$^+$. HPLC t_R=12 min (toluene/hexane, 40/60, v/v). UV/vis (toluene): λ_{max}/nm ~430.

*4.2.5. 1,2-Dihydro-(3-carboxyethyl-4,5-pyrazolino)-[60]fullerene (**10**).* ^{1}H NMR (CS_2/$CDCl_3$, 2:1) δ: 1.50 (3H, t, J=6.8 Hz), 4.52 (2H, q, J=6.8, 14 Hz), 8.73 (br s, 1H). FTIR (KBr) ν(cm^{-1}): 3267, 2973, 1740, 1656, 1513. MALDI-MS: m/z 864 [M+H]$^+$, m/z 885 [M+Na]$^+$, m/z 900 [M+K]$^+$. HPLC t_R=8 min (toluene/hexane, 90/10, v/v). UV/vis (toluene): λ_{max}/nm ~430.

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.06.067.

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