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Grinding-induced synthesis of heterocyclic fullerene derivatives under solvent-free conditions

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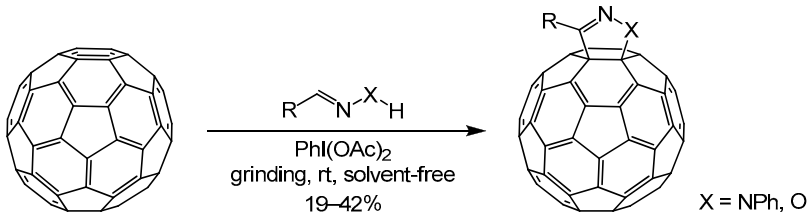


In this research, a green, easy, and effective solvent-free procedure for the synthesis of heterocyclic fullerene derivatives has been achieved *via* 1,3-dipolar cycloaddition reaction of C_{60}, substituted arylhydrazones/oximes, and $PhI(OAc)_2$ under grinding as a simple physical-mechanical method. This approach does not involve any hazardous organic solvent and has various advantages including design of safe reaction conditions moderate to good yields and short reaction times.

Keywords: fullerene, fulleroisoxazoline, fulleropyrazoline, cycloaddition reaction, grinding, solvent-free synthesis.

Since the discovery of fullerenes[1] and their isolation in bulk,[2] the research of suitable procedures for their functionalization has become an important challenge in organic chemistry.[3] In particular, the most numerous member of the fullerene family, C_{60}, has obtained the highest interest as C_{60}-based molecules. Fullerene-based nanomaterials exhibit a broad range of interesting features in material science and biological application.[4–10] The double bonds between two hexagons in the structure of C_{60} are dienophilic, which enables the molecule to undergo a variety of addition reactions including cycloaddition,[11,12] cyclopropanation,[13] addition of organometallic reagents[14] and photoinduced electron transfer reaction.[15] Among the different types of cycloaddition reactions[16–19] available for the preparation of heterocyclic fullerene derivatives, 1,3-dipolar cycloaddition demonstrates a powerful tool due to the fact that C_{60} behaves as an electron-deficient olefin. Synthesis of five-membered cycles *via* the addition of 1,3-dipoles to alkenes is a typical organic reaction. In fact, 1,3-dipolar cycloaddition reactions are beneficial for the construction of carbon–carbon bonds and for the preparation of heterocyclic compounds.[20] Thus, different 1,3-dipoles, including azomethine ylides, diazo compounds, azides, nitrile oxides, nitrile ylides, nitrile imines, pyrazolinium ylides, and carbonyl ylides, have been reported to react with fullerenes.[21–30] Fullerene-based heterocyclic rings such as fulleroisoxazolines and fulleropyrazolines with attractive chemical, electrochemical, and photophysical properties[31] can be readily synthesized through various procedures such as addition of nitrile imine and nitrile oxide to C_{60}.[32–37] These reactive intermediates can be easily produced from arylhydrazones/oximes as suitable and accessible substrates. However, the organic addends are good donors to fullerene when they join to C_{60}. Electrochemical studies demonstrate that the cycloadducts show better electron acceptor properties than the parent C_{60}. Hence they can be used as a donor-accepting dyads in photovoltaic devices and improve their performance.[38]

Green chemistry concentrates on research that can help to reduce or eliminate the negative environmental effects and the amount of undesired hazardous chemicals (including solvents) and increases the selectivity of the product formation.[39] Solvent-free syntheses have recently obtained much consideration. These procedures have many advantages including high efficiency and selectivity, easy separation, purification, and mild reaction conditions. Moreover, they are not only environmentally safe but also economically beneficial because toxic wastes can be minimized or eliminated, so the costs of waste treatment are also reduced.[40] Various types of mechanochemical devices have been used to provide mechanical activation energy. They differ in their capacity and efficiency and can be mostly

categorized into two classes such as grinding devices and milling devices. Grinding is an effective instrument that allows a highly efficient mixing of substrates under solvent-free conditions. This method is applied as the most suitable and simple tool for a mechanochemical reaction using a mortar and a pestle, which promotes the reactions through grinding mixing and triturating. Grinding procedure has been widely used by Toda et al. to study several solvent-free organic reactions.[41,42] In organic chemistry various applications of grinding procedure including C–C bond formation,[43,44] synthesis of nanocrystallines[45] and nanoparticles,[46] synthesis of heterocycles,[47] and fullerene modifications[48] have been reported.

Herein, we wish to report an efficient, eco-friendly, and facile physical grinding approach for the synthesis of fullerene derivatives *via* 1,3-dipolar cycloaddition of fullerene with arylhydrazones/oximes under solvent-free conditions.

In this research, cycloaddition reactions of C_{60} and substituted arylhydrazones **1a**–**i** and oximes **3a**–**g** mediated by (diacetoxyiodo)benzene under conventional and grinding conditions is studied to prepare the corresponding fulleropyrazolines **2a**–**i** and fulleroisoxazolines **4a**–**g**. Under grinding conditions, synthesis of fulleropyrazoline and fulleroisoxazoline derivatives is discussed as an eco-friendly and efficient procedure to promote 1,3-dipolar cycloaddition reactions (Scheme 1).

As an example, a mixture of equimolar amounts of C_{60}, benzaldehyde phenylhydrazone (**1a**), and $PhI(OAc)_2$ was ground by mortar and pestle at room temperature (Table 1, entry 1). The desired fulleropyrazoline **2a** was obtained in 34% yield. In order to extend the range of various cycloadducts, we carried out the reaction using different kinds of arylhydrazones and oximes under this green approach. The heterocyclic fullerene derivatives **2b**–**i**, **4b**–**g** were prepared in the same manner by reaction of the arylhydrazones **1b**–**i** and oximes **3b**–**g** with C_{60} in the presence of $PhI(OAc)_2$ at room temperature.

According to Table 1, grinding approach is more convenient in the yields and the reaction time than conventional conditions.[49] Under grinding, the transformations with moderate to good yields were carried out without any significant amounts of unsuitable side product.

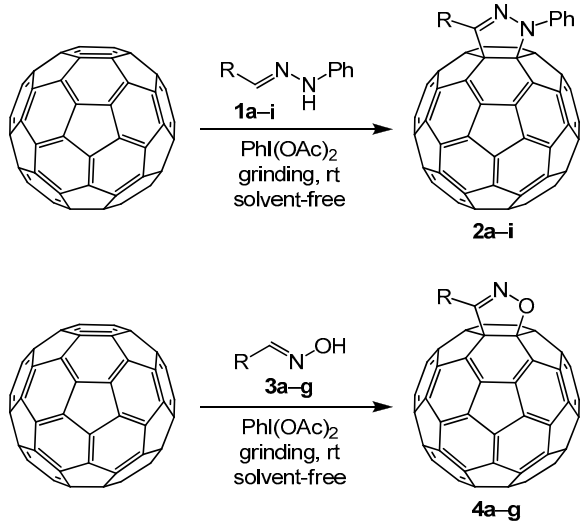
Since fullerene C_{60} is a polyalkene with less reactivity than other alkenes, about half of the unreacted fullerene can be recovered using extraction with toluene after completion of the reaction.

Mildness, short reaction times, work-up easiness, high efficient, and convenient conditions are the superiorities of this green protocol for the synthesis of fulleropyrazolines and fulleroisoxazolines compared to the previously described methods.[20,38,49] Also one of the most prominent advantages of grinding method is the absence of toxic solvent.

The plausible mechanism for the efficient synthesis of heterocyclic fullerene derivatives under grinding conditions was suggested (Scheme 2).

At the beginning step, the reactive intermediates **A**, nitrile imines or nitrile oxides, were formed *in situ* by the interaction of arylhydrazones or oximes and (diacetoxyiodo)benzene. Then the desired cycloadducts were synthesized *via* 1,3-dipolar cycloaddition between dipoles **A** and fullerene. Under grinding approach, the great improvement in the reaction conditions is due to the introducing effective mechanochemical energy resulted in the suitable contacts of substrates. Under these conditions, nitrile imines or nitrile oxides **A** as very reactive chemical intermediates are formed very fast, so speeding 1,3-dipolar cycloadditions.

Scheme 1



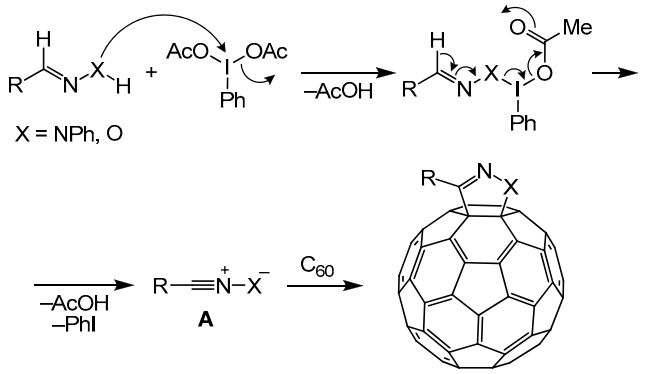
1, **2 a** R = Ph, **b** R = 4-$O_2NC_6H_4$, **c** R = 4-$MeOC_6H_4$, **d** R = 4-MeC_6H_4, **e** R = 4-$Me_2NC_6H_4$, **f** R = 4-ClC_6H_4, **g** R = 2-Py, **h** R = 2-thienyl, **i** R = 2-Fur;
3, **4 a** R = 4-$O_2NC_6H_4$, **b** R = 4-ClC_6H_4, **c** R = 4-$Me_2NC_6H_4$, **d** R = 4-$MeOC_6H_4$, **e** R = 2-Py, **f** R = 2-thienyl, **g** R = 2-Fur

Table 1. Synthesis of heterocyclic fullerene derivatives under conventional and grinding conditions*

Starting compound	Product	Conventional method**		Grinding method	
		Time, h	Yield, %	Time, h	Yield, %
1a	**2a**[38]	60	30	10	34
1b	**2b**[38]	30	31	5	35
1c	**2c**[38]	45	25	8	30
1d	**2d**[49]	100	31	15	34
1e	**2e**[49]	40	22	5	30
1f	**2f**	100	25	15	32
1g	**2g**	180	20	20	27
1h	**2h**	60	30	10	35
1i	**2i**	40	15	5	25
3a	**4a**[38]	90	36	15	37
3b	**4b**[38]	90	41	15	42
3c	**4c**[34]	60	32	10	34
3d	**4d**[38]	90	34	15	35
3e	**4e**	40	18	10	19
3f	**4f**[34]	50	22	10	23
3g	**4g**[34]	90	18	15	20

* Isolated yields are given. All the obtained products have high melting points (>300°C). In literature[50] the melting point is reported only for compound **2a**, being also >300°C.
** PhMe, rt.

Scheme 2



The structures of new products were studied using ^{1}H, ^{13}C NMR, IR, and mass-spectroscopy data as well as by elemental analysis. The mass spectra of the heterocyclic cycloadducts **2a**–**i**, **4a**–**g** show the $[M]^+$ peak. The signals corresponding to the organic addend of these compounds appear in the ^{1}H NMR spectra. The chemical shifts of these signals are observed at lower field compared with the corresponding starting arylhydrazone or oxime. The ^{1}H NMR spectra of cycloadducts **2a**–**i** are characterized by absence of the imine proton signal, which is present in the ^{1}H NMR spectra of starting arylhydrazones **1a**–**i** (for example, in the spectra of compound **1h** it appears at ~9.50 ppm, see Fig. 1). This change also confirms the proposed structure of the reaction products.

The signals of aromatic protons, which appear at 6.7–7.3 ppm in the ^{1}H NMR spectra of arylhydrazones **1a**–**i**, are shifted down field in fulleropyrazolines **2a**–**i** and appear at 7.1–8.0 ppm (Fig. 1). This shift has been attributed in other fullerene derivatives to the existence of a charge transfer complex between the organic addend and the C_{60} cage.[50]

In conclusion, the effective method for the grinding-mediated solvent-free synthesis of fulleropyrazolines and fulleroisoxazolines is described. The application of this technique does not involve any hazardous organic solvent and has various advantages including design of safe reaction conditions, moderate to good yields, shorter reaction times, and environmentally friendly procedure.

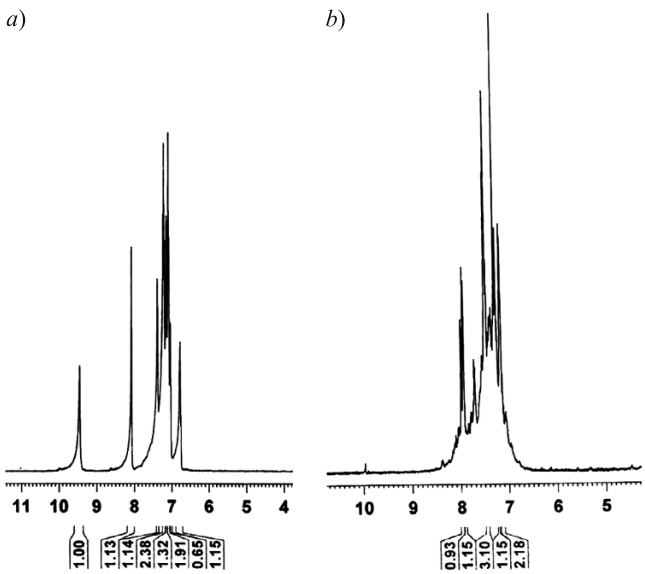


Figure 1. ^{1}H NMR spectrum of *a*) 2-thiophencarboxaldehyde phenylhydrazone (**1h**); *b*) 1'-phenyl-3'-(2-thienyl)pyrazolino[4',5':1,2]-[60]fullerene (**2h**)

Experimental

FT-IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer (400 and 100 MHz, respectively) in $CDCl_3$–CS_2, 1:1, TMS as internal standard. Mass spectra were recorded by Finnigan-MAT-8430 mass spectrometer (EI, 70 eV). Elemental analysis was performed on a Carlo Erba EA 1108 analyzer. Melting points were determined on an Electro thermal 9200 apparatus. TLC analysis was performed on TLC plastic plates (Sigma-Aldrich), eluent PhMe. Silica gel 60 (high-purity grade, pore size 60 Å, 70–230 mesh, 63–200 μm, Merck) was used for column chromatography, eluent was PhMe. Crystalline C_{60} powder (99.9%) was purchased from Sigma-Aldrich company. All solvents and reagents were purchased from Sigma-Aldrich and Fluka and used without further purification. (Diacetoxyiodo)benzene was synthesized according to the literature method.[51] Substituted arylhydrazones **1a**–**i** and oximes **3a**–**g** were synthesized according to the literature methods.[52]

Grinding experiments were performed on a typical mortar and pestle.

Synthesis of heterocyclic fullerene derivatives 2a–i and 4a–g by conventional method (General Method).[49] Fullerene C_{60} (36 mg, 0.05 mmol), arylhydrazone **1a**–**i** or oxime **3a**–**g** (0.05 mmol), and $PhI(OAc)_2$ (16 mg, 0.05 mmol) were dissolved in PhMe (20 ml). The mixture was stirred under nitrogen atmosphere at room temperature for proper time. After completion of the reaction as monitored by TLC, the mixture was purified by column chromatography to afford the cycloadducts **3a**–**i**, **4a**–**g**.

Grinding-based synthesis of heterocyclic fullerene derivatives 2a–i and 4a–g (General Method). A mixture of fullerene C_{60} (36 mg, 0.05 mmol), arylhydrazone **1a**–**i** or oxime **3a**–**g** (0.05 mmol), and $PhI(OAc)_2$ (16 mg, 0.05 mmol) was ground using mortar and pestle at room temperature for proper time. After completion of the reaction as monitored by TLC, the mixture was purified by column chromatography to afford the cycloadducts **3a**–**i**, **4a**–**g**. ^{1}H, ^{13}C NMR and IR spectral data of the known compounds **2a**–**e**, **4a**–**d**,**f**,**g** match the reported in the literature.[34,38,49]

3'-(4-Chlorophenyl)-1'-phenylpyrazolino[4',5':1,2]-[60]fullerene (2f). Brown powder. IR spectrum, ν, cm^{-1}: 3100 (=C–H s), 1626 (C=N s), 1600, 1453 (C=C s), 1094 (C–Cl s), 872 (=C–H oop. bend, Ar), 753, 692 (=C–H oop. bend, Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.91–7.27 (2H, m, H Ph); 7.32 (2H, d, *J* = 8.0, H Ar); 7.36–7.40 (1H, m, H Ph); 7.48 (2H, d, *J* = 8.0, H Ar); 7.69–8.25 (2H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 86.1; 90.5; 110.3; 112.6; 113.0; 115.9; 116.5 (2C); 117.2; 118.8; 119.6; 122.7; 124.5; 125.1 (2C); 127.9 (2C); 128.1 (2C); 131.4; 133.2 (2C); 134.8; 136.1; 137.5 (2C); 137.9; 138.6; 141.2 (2C); 142.6; 145.7; 146.5 (2C); 152.8; 155.2 (2C); 163.1;

165.4; 169.1 (2C). Mass spectrum, *m*/*z* (I_{rel}, %): 949 $[M]^+$ (5), 91 (100). Found, %: C 92.45; H 1.06; N 3.12. $C_{73}H_9ClN_2$. Calculated, %: C 92.36; H 0.96; N 2.95.

1'-Phenyl-3'-(2-pyridyl)pyrazolino[4',5':1,2][60]-fullerene (2g). Brown powder. IR spectrum, ν, cm^{-1}: 3150 (=C–H s), 1629 (C=N s), 1600, 1462 (C=C s), 1566, 1491 (C=C s, Py), 881 (=C–H oop. bend, Py), 753, 689 (=C–H oop. bend, Ph) ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.17 (1H, t, *J* = 7.5, H Ar); 7.27 (2H, d, *J* = 8.0, H Ar); 7.36 (1H, t, *J* = 7.5, H Ar); 7.47 (1H, t, *J* = 7.5, H Ar); 7.76–7.90 (2H, m, H Ar); 8.38–8.60 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 75.1; 85.9; 111.4; 112.3; 113.4; 114.9 (2C); 116.5; 117.1; 119.2; 121.7; 123.6; 125.2 (2C); 127.1 (2C); 129.0 (2C); 130.2; 133.5; 135.4 (2C); 136.2; 137.1; 138.7 (2C); 140.2 (2C); 141.7; 143.1; 145.0; 146.5; 150.9 (2C); 152.2; 153.7 (2C); 155.1; 157.5; 160.0; 162.2; 164.0; 166.9; 168.0 (2C). Mass spectrum, *m*/*z* (I_{rel}, %): 915 $[M]^+$ (5), 91 (100). Found, %: C 94.54; H 0.91; N 4.66. $C_{72}H_9N_3$. Calculated, %: C 94.42; H 0.99; N 4.59.

1'-Phenyl-3'-(2-thienyl)pyrazolino[4',5':1,2][60]-fullerene (2h). Brown powder. IR spectrum, ν, cm^{-1}: 3150 (=C–H s), 1631 (C=N s), 1600, 1489 (C=C s), 1595, 1428 (C=C s, thiophene), 871 (=C–H oop. bend, thiophene), 751, 695 (=C–H oop. bend, Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.13–7.20 (2H, m, H Ar); 7.24 (1H, t, *J* = 5.0, H Ar); 7.46–7.52 (3H, m, H Ar); 7.94 (1H, d, *J* = 8.0, H Ar); 7.98 (1H, d, *J* = 8.0, H Ar). ^{13}C NMR spectrum, δ, ppm: 52.2; 78.2; 123.9 (2C); 124.1; 124.5; 125.4 (2C); 125.9; 126.0; 126.2; 126.8; 127.6; 128.3 (2C); 128.7; 129.1 (2C); 129.3 (2C); 130.0; 130.5; 131.2; 132.5; 133.4; 135.6; 136.8; 137.0; 138.2; 139.7; 140.2; 141.5; 142.0; 143.1 (2C); 144.0; 145.2. Mass spectrum, *m*/*z* (I_{rel}, %): 920 $[M]^+$ (4), 91 (100). Found, %: C 92.50; H 0.92; N 3.10; S 3.82. $C_{71}H_8N_2S$. Calculated, %: C 92.60; H 0.88; N 3.04; S 3.48.

3'-(2-Furyl)-1'-phenylpyrazolino[4',5':1,2][60]-fullerene (2i). Brown powder. IR spectrum, ν, cm^{-1}: 3100 (=C–H s), 1628 (C=N s), 1600, 1420 (C=C s), 1454, 1400 (C=C s, Fur), 850 (=C–H oop. bend, Fur), 751, 693 (=C–H oop. bend, Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.30–7.70 (6H, m, H Ar); 8.90 (2H, d, *J* = 8.0, H Ar). ^{13}C NMR spectrum, δ, ppm: 76.1; 84.5; 109.6; 111.5; 112.9; 113.1 (2C); 115.6; 116.5; 120.1; 121.3; 123.4; 124.2 (2C); 125.1 (2C); 127.6 (2C); 131.9; 133.2; 134.5 (2C); 135.2; 137.1; 139.6 (2C); 140.1 (2C); 141.0; 143.5; 144.0; 146.1; 151.2 (2C); 152.9; 153.3 (2C); 156.2; 157.5; 159.1; 161.4; 163.6; 165.0; 167.1. Mass spectrum, *m*/*z* (I_{rel}, %): 904 $[M]^+$ (10), 91 (100). Found, %: C 94.32; H 0.97; N 3.19. $C_{71}H_8N_2O$. Calculated, %: C 94.24; H 0.89; N 3.10.

3'-(2-Pyridyl)isoxazolo[4',5':1,2][60]fullerene (4e). Brown powder. IR spectrum, ν, cm^{-1}: 3001 (=C–H s), 1630 (C=N s), 1600, 1461 (C=C s, Py), 799 (=C–H oop. bend, Py). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.40 (1H, t, *J* = 8.0, H Py); 7.93 (1H, t, *J* = 8.0, H Py); 8.47 (1H, d, *J* = 7.5, H Py); 8.62 (1H, d, *J* = 7.5, H Py). ^{13}C NMR spectrum, δ, ppm: 77.5; 86.1; 110.2; 111.5; 113.4; 115.9 (2C); 116.7; 117.2; 119.8; 122.0; 124.3; 125.1 (2C); 128.9 (2C); 129.5; 130.1; 132.7; 135.6; 136.3; 137.8; 138.4; 139.2 (2C); 141.9; 142.3; 144.5; 146.7; 150.2; 151.8; 152.2 (2C); 155.0; 157.1; 160.8; 163.0; 165.2. Mass spectrum, *m*/*z* (I_{rel}, %): 840 $[M]^+$ (2), 91 (100). Found, %: C 94.12; H 0.53; N 3.42. $C_{66}H_4N_2O$. Calculated, %: C 94.29; H 0.48; N 3.33.

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