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An efficient one-step synthesis of fulleroisoxazolines and fulleropyrazolines mediated by (diacetoxyiodo)benzene

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ABSTRACT

An efficient one-step strategy for the synthesis of fulleroisoxazolines/fulleropyrazolines from fullerene and aldoximes/hydrazones mediated by $PhI(OAc)_2$ has been described.

Chemical modification is one of the most important research fields in the fullerene chemistry. 1,3-Dipolar cycloaddition plays an important role in the preparation of modified fullerenes for application in medicinal chemistry and materials science. Up to now various 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.[1] Although fulleropyrrolidines have been by far the most studied and versatile derivatives obtained from 1,3-dipolar cycloadditions, other fullerene-fused pentagonal heterocyclic rings, such as fulleroisoxazolines or fulleropyrazolines, are also known to show appealing chemical, electrochemical, and photophysical properties. For example, fulleroisoxazolines undergo an efficient retro-cycloaddition reaction in the presence of an excess of a dienophile and Cu(II) catalysis, which can be selectively used in the presence of malonate or pyrrolidine cycloadducts.[2] The electrochemical properties of the fulleroisoxazoline and fulleropyrazoline compounds in which a heteroatom is directly linked to the C_{60} cage were investigated to show the same or better acceptor character than C_{60}. It is different from fulleropyrrolidines which usually exhibit a decrease in electron affinity with respect to the parent C_{60}.[3] Fulleroisoxazolines or fulleropyrazolines have been readily obtained by addition of nitrile oxides or nitrilimine to [60]fullerene in moderate yields through different methods. Meier firstly reported the addition reaction of C_{60} with nitrile oxides which was generated through dehydration of nitroalkanes with phenylisocyanate and Et_3N.[4] The most commonly used method for the preparation of fulleroisoxazolines or fulleropyrazolines includes two steps: first synthesis of hydroximinoyl halides or hydrazonoyl halides from aldoxime or hydrazone using NCS or NBS and then reacting with fullerene through dehydrohalogenation in the presence of organic base.[5] An alternative procedure involved the generation of corresponding dipole from hydrazones under microwave irradiation.[6] It should be noted that this microwave process does not occur upon conventional heating. Isoxazoline-fused fullerenes can also be prepared from the reactions of [60]fullerene with *N*-silyloxynitrones, formed from nitoalkene and Me_3SiCl/Et_3N, after acid treatment.[7] Irngartinger also reported that the nitrile oxides generated from ester of glycine hydrochloride using $NaNO_2$.[8] Despite so many ways for preparation of fulleroisoxazolines or fulleropyrazolines, the scope of these protocols is limited by two-step processes, basic and anhydrous condition. Herein, we developed a convenient method to achieve fulleroisoxazolines or fulleropyrazolines by a one-step reaction of [60]Fullerene with aldoximes or hydrazones mediated by (diacetoxyiodo)benzene.

Hydrazone has a vinyl C–H and an N–H bond and aldoxime has a vinyl C–H and an O–H bond. Their structures are similar to enamine and enol, respectively (Fig. 1). It was reported that the $Mn(OAc)_3{\cdot}2H_2O$ can mediate the oxidative radical cycloaddition of β-keto esters, beta-diketones, and β-enamino compounds to C_{60}.[9] Considering the structure similarities, we presumed that this reaction may also be applicable to hydrazone or aldoxime substrates. The first substrate examined was benzaldoxime **1a**. When a mixture of C_{60} (36.0 mg), benzaldoxime **1a** (1 equiv), and $Mn(OAc)_3{\cdot}2H_2O$ (1 equiv) was stirred in 20 mL toluene for 24 h at room temperature, no reaction occurred. While the reaction temperature was raised to 100 °C, the desired product **2a** was isolated in 13% yield along with several by-products after 4 h of stirring.

The result was not so satisfying. Then we considered using $PhI(OAc)_2$ as an oxidant, which has been used as a common and unique oxidant in many reactions,[10] to substitute for $Mn(OAc)_3{\cdot}2H_2O$. In earlier documents $PhI(OAc)_2$ has also been used in the

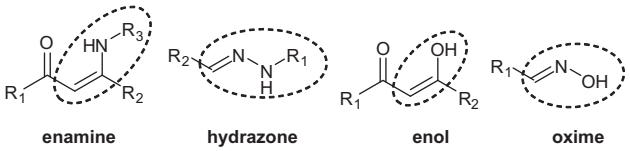

Figure 1.

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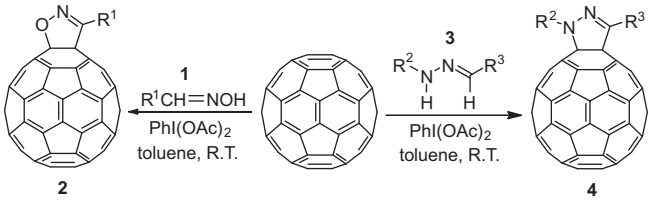
cycloaddition reaction of nitrile oxide or nitrilimine with electron deficient olefins such as ethyl acrylate or acrylonitrile.[11] Das has reported the hypervalent iodine-mediated interaction of aldoxime with activated alkene including Baylis–Hillman adducts and intramolecular [3+2] reaction for reparation of benzopyrano and furopyrano-2-isoxazoline derivatives.[12] Gan has reported the $PhI(OAc)_2$-mediated reaction of amino acid ester with C_{60}, from which pyrrolidino[60]fullerene and aziridino[60]fullerene could be formed selectively controlled by iodine.[13] Most recently, Ciufoline reported the $PhI(OAc)_2$-mediated tandem oxidative dearomatization of phenols/intramolecular nitrile oxide cycloaddition sequences leading to useful synthetic intermediates.[14]

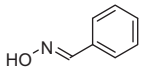
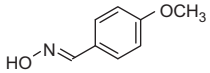
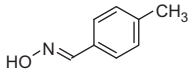
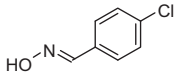
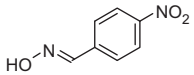
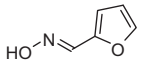
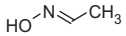
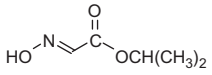
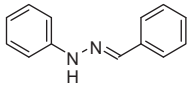
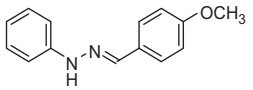
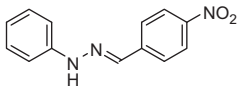
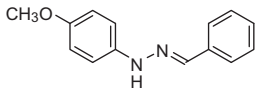
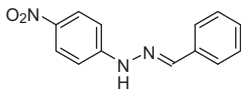
To our satisfaction, when a mixture of C_{60} (36.0 mg), benzaldoxime **1a** (1 equiv), and $PhI(OAc)_2$ (1 equiv) was stirred in 20 mL toluene for 100 min at room temperature (Table 1), the desired fulleroisoxazolines **2a** was obtained in good yield (51%). The process was greatly accelerated by using $PhI(OAc)_2$ compared to using $Mn(OAc)_3{\cdot}2H_2O$. This is a simple method of constructing isoxazoline cycle on fullerene through 1,3-dipolar reaction. The condition was so mild and convenient that we hope to discover the scope of this methodology.

In order to extend the utility of this reaction, we carried out the reaction using different kinds of aldoximes (**1b**–**h**) under the same condition (Scheme 1). The results, summarized in Table 1, showed that all the reactions proceeded smoothly whether the R^1 was aryl, furyl, alkyl, or ester group, and gave moderate to good yields in short time at room temperature.[15] The yield of the reaction is higher when R^1 is a phenyl than when R^1 is an aliphatic, furyl, or ester

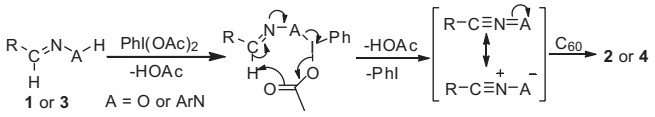


Scheme 1.

Table 1
Results of the reaction of C_{60} with aldoximes or hydrazones promoted by (diacetoxyiodo)benzene at room temperature[a,15]

	Substrate	Product	Time (min)	Yield [b] (%)	Recovered C_{60} (%)
1a		**2a**[5a]	100	51	42
1b		**2b**[5a]	90	46	43
1c		**2c**	90	44	39
1d		**2d**	90	42	54
1e		**2e**	90	37	55
1f		**2f**[5d]	90	15	70
1g		**2g**[4]	170	28	59
1h		**2h**	90	17	74
3a		**4a**[16]	60	34	55
3b		**4b**	45	20	72
3c		**4c**[17]	35	36	55
3d		**4d**[17]	35	19	70
3e		**4e**[5m]	60	27	65

[a] All reactions were performed in toluene at room temperature; molar ratio of C_{60}:**1** or **3**:$PhI(OAc)_2$ = 1:1:1.
[b] Isolated yield.



Scheme 2.

group. The electronic property of the substituent group on the phenyl ring had little influence on the reaction. It is an easy and efficient method to prepare fulleroisoxazolines directly from aldoximes.

Encouraged by these results, we further extended the $PhI(OAc)_2$-mediated 1,3-dipolar reaction to hydrazones **3a**–**e** and C_{60} (Scheme 1). When a mixture of C_{60} (36.0 mg), hydrazones **3a**–**e** (1 equiv), and $PhI(OAc)_2$ (1 equiv) was stirred in 20 mL toluene for a designated time at room temperature, fulleropyrazolines **4a**–**e** could also be obtained (Table 1). Yields were fair to good. The substituent group R^2 or R^3 on the phenyl ring had little influence on the yield. This makes it clear that $PhI(OAc)_2$ is a very good oxidant to mediate the 1,3-dipolar reaction of C_{60} with hydrazones or aldoximes. A plausible mechanism for the generation of nitrile oxides and nitrile imines is illustrated in Scheme 2.

All of the known products were confirmed by comparison of their spectral data with those reported in the literature. The identification of new compounds **2c**–**e**, **2h**, and **4b** was fully confirmed by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV–vis spectra. Take **2c** as an example. The MALDI-TOF mass spectrum of **2c** showed the molecular ion peak at *m*/*z* 853. The ^{1}H NMR spectrum of **2c** displayed two doublets at 7.31 and 8.03 ppm for the phenyl ring and a singlet at 2.44 ppm for the CH_3 group. In the ^{13}C NMR spectrum of **2c** there were 34 peaks in the range of 126–148 ppm due to the sp^2 carbons of the C_{60} skeleton and phenyl ring and two peaks at about 72 and 102 ppm for the two sp^3 carbons of the C_{60} along with a peak at 153.18 ppm for the *C*═N, fully consistent with the C_s symmetry of its molecular structure. The UV–vis spectrum of **2b** exhibited a peak at 427 nm, which is a diagnostic absorption for the mono-adduct of C_{60} at the 6:6-junction. The other new compounds (**2c**–**e**, **2h**, and **4b**) were characterized in a similar way.

In summary, we have explored a useful procedure for the synthesis of fulleroisoxazolines/fulleropyrazolines from fullerene and aldoximes/hydrazones mediated by $PhI(OAc)_2$, which represents a significant improvement over existing methods. It is practical with many advantages such as one-step reaction, no demanding anhydrous operation, short reaction time, and wide utility.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.038.

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15. Typical procedure for the synthesis of fulleroisoxazolines **2** and fulleropyrazolines **4**: a mixture of C_{60} (36.0 mg, 0.05 mmol), aldoximes **1** or hydrazones **3** (0.05 mmol), and $PhI(OAc)_2$ (0.05 mmol) was dissolved in 20 mL of toluene and stirred at room temperature for a desired time. The solvent was then evaporated in vacuo, and the residue was separated on a silica gel column using CS_2 or CS_2–toluene as the eluent to afford unreacted C_{60} and adduct **2** or **4**. *Compound* **2a**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.15–8.13 (m, 2H), 7.52–7.50 (m, 3H); **2b**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.12 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); **2c**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$, all 2C unless indicated) δ 153.18 (1C, *C*═N), 147.72 (1C), 147.22 (1C), 146.36, 146.23, 146.21, 145.96, 145.90, 145.89, 145.58, 145.39, 145.19, 145.11, 144.88, 144.78, 144.62, 144.39, 144.07, 142.97, 142.82 (4C), 142.45 (4C), 142.32, 142,27, 142.09, 141.68, 140.78 (1C, aryl *C*), 140.29, 140.27, 136.98, 136.64, 129.76 (aryl *C*), 128.83 (aryl *C*), 126.23 (1C, aryl *C*), 104.01 (1C, sp^3-*C* of C_{60}), 79.29 (1C, sp^3-*C* of C_{60}), 21.63 (1C, *C*H_3); UV–vis ($CHCl_3$) λ_{max} nm 256, 316, 427, 679; FT-IR ν/cm^{-1} (KBr) 2919, 2852, 1509, 1300, 1183, 979, 864, 813, 619, 569, 526; MS (MALDI-TOF) *m*/*z* 853; **2d**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$, all 2C unless indicated) δ 153.28 (1C, *C*═N), 147.74 (1C), 147.24 (1C), 146.38, 146.25, 146.23, 145.97, 145.92, 145.83, 145.61, 145.39, 145.21, 145.13, 144.76, 144.72, 144.47, 144.39, 144.07, 142.98, 142.84 (4C), 142.46 (4C), 142.32, 142,27, 142.09, 141.70, 140.33, 140.30, 137.02, 136.65, 130.61(1C, aryl *C*), 129.09 (1C, aryl *C*), 129.03 (aryl *C*), 128.87 (aryl *C*), 104.16 (1C, sp^3-*C* of C_{60}), 79.21 (1C, sp^3-*C* of C_{60}); UV–vis ($CHCl_3$) λ_{max} nm 256, 317, 427, 678; FT-IR ν/cm^{-1} (KBr) 2921, 2852, 1506, 1303, 1180, 1094, 979, 862, 823, 570, 526; MS (MALDI-TOF) *m*/*z* 873; **2e**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.44 (d, J = 9.0 Hz, 2H), 8.37 (d, J = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$, all 2C unless indicated) δ 151.86 (1C, *C*═N), 148.90 (1C, aryl *C*), 147.77 (1C), 147.31 (1C), 146.44, 146.30 (4C), 146.04, 145.98, 145.73, 145.28 (6C), 145.16, 144.55, 144.41, 144.00, 143.78, 143.69, 143.04, 142.93, 142.91, 142.49 (4C), 142.24 (4C), 141.98, 141.73, 140.45, 140.41, 137.31, 136.58, 135.17 (1C, aryl *C*), 129.59 (aryl *C*), 124.09 (aryl *C*), 105.14, (1C, sp^3-*C* of C_{60}), 78.19 (1C, sp^3-*C* of C_{60}); UV–vis ($CHCl_3$) λ_{max} nm 256, 317, 426, 678; FT-IR ν/cm^{-1} (KBr) 2920, 2852, 1511, 1338, 1304, 1181, 1105, 982, 846, 770, 747, 688, 606, 526; MS (MALDI-TOF) *m*/*z* 884; **2f**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 7.65 (d, J = 1.8 Hz, 1H), 7.38 (d, J = 3.5 Hz, 1H), 6.63 (dd, J = 3.5, 1.8 Hz, 1H); **2g**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 2.74 (s, 3H); **2h**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 5.38 (sept, J = 6.2 Hz, 1H), 1.49 (d, J = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$, all 2C unless indicated) δ 159.10 (1C, *C*OO),

147.80 (1C, *C*═N), 147.20 (1C), 147.17 (1C), 146.99, 146.38, 146.36, 146.34, 145.99 (4C), 145.71, 145.32, 145.20, 145.19, 144.59, 144.21, 144.20, 143.76, 143.09, 142.89 (4C), 142.84, 142.70, 142.49, 142.48, 142.41, 142.19, 141.86, 141.78, 140.28, 140.16, 136.97, 136.49, 106.04 (1C, sp^3-*C* of C_{60}), 79.49 (1C, sp^3-*C* of C_{60}), 71.19 (1C, OCH), 21.86 (*CH*$_3$); UV–vis ($CHCl_3$) λ_{max} nm 256, 316, 431, 677; FT-IR v/cm^{-1} (KBr) 2922, 2852, 1739, 1713, 1584, 1508, 1370, 1172, 1151, 1094, 1003, 829, 767, 606, 571, 526; MS (MALDI-TOF) *m*/*z* 849; **4a**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.21 (d, *J* = 7.2 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H); **4b**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$, all 2C unless indicated) δ 160.40 (1C, Aryl *C*), 147.50 (1C), 147.10 (1C), 146.49, 146.29, 146.16, 145.99, 145.90, 145. 83, 145.77, 145.75, 145.62, 145.31, 145.16 (4C), 145.09, 145.07, 144.24, 144.22, 143.09, 142.83, 142.78, 142.38, 142.35, 142.28, 142.22, 142.12, 141.80, 140.20, 139.62, 136.32, 136.23, 130.32 (aryl *C*), 129.19 (aryl *C*), 124.89 (1C, aryl *C*), 123.68 (aryl *C*), 114.24 (aryl *C*), 91.82 (1C, sp^3-*C* of C_{60}), 81.86 (1C, sp^3-*C* of C_{60}), 55.08 (1C, OCH_3); UV–vis ($CHCl_3$) λ_{max} nm 257, 316, 426, 679; FT-IR v/cm^{-1} (KBr) 2924, 2853 1606, 1594, 1579, 1510, 1489, 1325, 1255, 1176, 1100, 1022, 837, 829, 763, 752, 692, 587, 546, 526; MS (MALDI-TOF) *m*/*z* 944; **4c**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.54 (d, *J* = 9.0 Hz, 2H), 8.28 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H); **4d**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.21 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.44 (t, *J* = 7.1 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H); **4e**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 8.28 (d, *J* = 9.4 Hz, 2H), 8.24 (d, *J* = 9.4 Hz, 2H), 8.19–8.17 (m, 2H), 7.52–7.50 (m, 3H).

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