EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201402990

Reactivity of [60]Fullerene with Primary Nitro Compounds: Addition or Catalysed Condensation to Isoxazolo[60]fullerenes

Giacomo Biagiotti,[a,b] Stefano Cicchi,[b] Francesco De Sarlo,[b] and Fabrizio Machetti*[a]

In memory of Giulio Del Giusto on the 100th anniversary of his birth

Keywords: Cycloaddition / Condensation reactions / Fullerenes / Copper / Nitro compounds

The catalysed condensation of [60]fullerene with ethyl nitroacetate (**1b**) or analogous activated nitro derivatives to afford isoxazolino[60]fullerenes has been achieved in both homogeneous and heterogeneous conditions. This direct synthetic approach is more convenient than previous methods. Model reactions with electron-poor dipolarophiles led to either condensation to isoxazolines or to conjugate addition products, depending on the nitro compound and catalyst. The former product was favoured by the use of Cu^{II} in the catalytic system. Conversely, [60]fullerene underwent catalytic condensation, even in the absence of copper(II) salts, only with activated nitro compounds and addition only with nitroalkanes in excess base. Note, the formal conjugated fullerene addition product was obtained in isomeric form, as previously reported. A possible explanation is presented for this contrasting behaviour.

Introduction

[60]Fullerene is one of the most popular "artificial molecules"[1–4] due to its unique eye-catching geometry as well as its peculiar chemical and physical properties. This has stimulated intense and thorough studies of its reactivity[5,6] and the applications of its functionalised derivatives in different fields.[7,8] In addition, [60]fullerene is a useful model for the development of new processes for the functionalisation of carbon nanomaterials.[9] Hence, the development of methods for the functionalisation of fullerenes is of great significance and tremendous efforts have been dedicated to this goal over the past few decades, as documented in the large number of papers and reviews that have been published.[7a,10] Among these reactions, cycloadditions have a privileged position,[11] particularly those of dienes or 1,3-dipoles[12] with high-energy HOMOs because the peculiar double bond encountered in fullerenes is electrophilic so that even Grignard reagents are able to add to it.[13] Thus, fulleroisoxazolines have been obtained as a result of the 1,3-dipolar cycloadditions to [60]fullerene of either nitrile oxides[14,15] or silylnitronates followed by elimination.[16] These reactions are usually carried out in toluene owing to the slight solubility of [60]fullerene[17] but recently solvents in which this compound is more soluble have been employed.[18]

The intermediate nitrile oxides were produced either from hydroxamoyl chlorides[15] or by dehydration of primary nitro compounds.[19] However, the latter procedure is now superseded by the catalytic condensation of the same starting materials. This protocol, performed in a single pot, avoiding the use of dehydrating reagents and the formation of byproducts derived from them, might be included in the so-called click-chemistry processes.[20] These condensation reactions have been successfully carried out with other dipolarophiles either in chloroform, ethanol[21–23] or water,[24,25] and the solvent employed has been shown to affect both the mechanism and the results of the reaction. In view of the possible application of this protocol[26,27] to [60]fullerene, with its poor solubility in most common solvents, we decided to investigate the course of some model reactions under various conditions before attempting condensation reactions with [60]fullerene. Subsequently, the known addition of nitroalkanes and other unactivated primary nitro compounds in basic conditions will be reconsidered.[28]

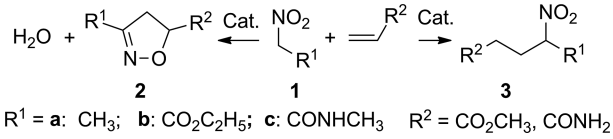
[a] Istituto di Chimica dei Composti Organometallici del Consiglio Nazionale delle Ricerche, c/o Dipartimento di Chimica Ugo Schiff,
Via della Lastruccia 13, 50019 Sesto Fiorentino (Firenze), Italy
E-mail: fabrizio.machetti@unifi.it
fabrizio.machetti@cnr.it
http://www.iccom.cnr.it/
http://www2.chim.unifi.it/
[b] Dipartimento di Chimica Ugo Schiff, Università degli Studi di Firenze,
Via della Lastruccia 13, 50019 Sesto Fiorentino (Firenze), Italy
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402990.

Results and Discussion

Model Reactions

We performed model experiments with different solvents and catalyst at various concentrations. Chloroform, toluene, chlorobenzene and 1-chloronaphthalene were chosen as solvents in which [60]fullerene has increasing solubility (0.16, 2.8, 7.0 and 51 mg/mL or 0.00022, 0.0039, 0.0097 and 0.071 M, respectively).[17]

We have previously shown that compounds containing electron-deficient double bonds, on treatment with "active" primary nitro compounds (i.e., bearing an EWG geminal to the nitro group) in chloroform, undergo either cycloaddition/condensation to give isoxazole derivatives **2** or conjugate addition to yield **3**, depending on the catalyst employed and the Michael acceptor (Scheme 1).[29]



Scheme 1. Model reactions: competition between conjugate addition and cycloaddition/condensation between nitro compounds and electron-poor alkenes.

Thus, ethyl nitroacetate (**1b**) on catalysis by only DABCO (1,4-diazabicyclo[2.2.2]octane) as base selectively underwent conjugate addition to give **3b** (R^2 = $CONH_2$ or CO_2CH_3) not only in chloroform but in other solvents as well (Scheme 1 and Table 1).

Table 1. Model reactions of **1b** and electron-poor dipolarophiles with only base (DABCO) as catalyst (Scheme 1).[a,b]

Entry	Solvent	R^2	Yield [%][c]	
			2	**3**
1	chloroform	$CONH_2$	traces	53
2	toluene	$CONH_2$	0	99
3	1-chloronaphthalene	$CONH_2$	0	87
4	chloroform	CO_2CH_3	2	68
5	toluene	CO_2CH_3	2	83
6	1-chloronaphthalene	CO_2CH_3	0	80

[a] DABCO: 1,4-diazabicyclo[2.2.2]octane. [b] Reagents and conditions: **1b** (2.5 equiv.), DABCO (0.1 equiv.), 60 °C, 24 h; see the Exp. Sect. for details. [c] The spectroscopic yields were determined by ^{1}H NMR spectroscopy with the use of an internal standard.

Nitroalkanes did not react under these conditions. However, we have previously shown that on addition of a Cu^{II} salt to the base, the cycloaddition/condensation predominated in chloroform and not only active nitro compounds but also nitroalkanes underwent condensation selectively.[29,30] Their reactions in various solvents with catalytic Cu^{II} are reported in Table 2. The condensation of nitroethane with acrylamide was successful in chloroform, but not in toluene or 1-chloronaphthalene (entries 1–3). With methyl acrylate, the condensation of nitroethane occurred slowly to give moderate yields after 24 h, and more base (*N*-methylpiperidine, 0.5 equiv.) was usually used in these reactions (entries 4–6).

Table 2. Model reactions under Cu^{II}/NMP catalysis in various solvents.[a,b]

Entry	R^1	R^2	Solvent[c]	Base [M]	Yield [%][d]	
					2	**3**
1	CH_3	$CONH_2$	A	0.15	77	0
2	CH_3	$CONH_2$	B	0.15	0	0
3	CH_3	$CONH_2$	C	0.15	0	0
4	CH_3	CO_2CH_3	A	0.15	50[e]	0
5	CH_3	CO_2CH_3	B	0.15	11	0
6	CH_3	CO_2CH_3	C	0.15	26	0
7[f]	$CO_2C_2H_5$	$CONH_2$	A	0.030	99	0
8	$CO_2C_2H_5$	$CONH_2$	B	0.030	98	0
9	$CO_2C_2H_5$	$CONH_2$	D	0.030	98	0
10	$CO_2C_2H_5$	$CONH_2$	C	0.030	45	8
11	$CO_2C_2H_5$	CO_2CH_3	A	0.030	94	4
12[g]	$CO_2C_2H_5$	CO_2CH_3	B	0.030	55	11
13	$CO_2C_2H_5$	CO_2CH_3	C	0.030	69	22
14	$CONHCH_3$	CO_2CH_3	C	0.030	53	0
15	$CONHCH_3$	$CONH_2$	C	0.030	98	0

[a] NMP: *N*-methylpiperidine. [b] Reagents and conditions: 0.75 M **1**, 0.30 M dipolarophile, 0.015 M Cu^{II}, 24 h; see Exp. Sect. for more details. [c] A: chloroform, B: toluene, C: 1-chloronaphthalene, D: chlorobenzene. [d] The spectroscopic yields were determined by ^{1}H NMR spectroscopy with the use of an internal standard. [e] Value at 40 h. No product at 24 h. [f] The same experiment repeated in a six-fold diluted reaction mixture gave a 42% spectroscopic yield. After 120 h the spectroscopic yield was 78%. [g] The same experiment repeated in a 75-fold diluted reaction mixture (0.0125 M **1b** + 0.004 M methyl acrylate) failed, no conversion being observed after 24 h.

The failure of the condensation reactions in toluene and 1-chloronaphthalene might be related to the poor solubility of acrylamide and the Cu^{II} salt in these cases, whereas a higher solubility is expected for reactions of activated nitro derivatives, for which Cu^{II} complexes are known.[31] In fact, the reaction of ethyl nitroacetate (**1b**) with acrylamide (Scheme 1, R^2 = $CONH_2$) under the usual conditions (0.757 M **1b** + 0.303 M acrylamide) gave the product **2b** (R^2 = $CONH_2$) after 24 h at 60 °C in all the solvents considered (entries 7–10) with a minor amount of the addition product **3b** (R^2 = $CONH_2$) obtained in 1-chloronaphthalene (entry 10). With methyl acrylate, both products **2b** (R^2 = CO_2CH_3) and **3b** (R^2 = CO_2CH_3) were obtained from **1b**, the isoxazoline **2b** (R^2 = CO_2CH_3) being predominant (entries 11–13).

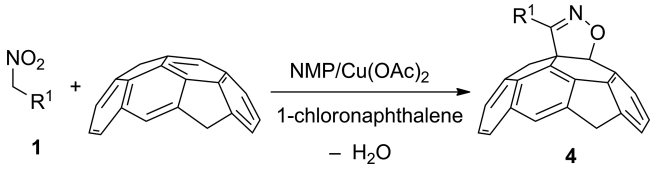
The model reaction in chloroform, at the concentration corresponding to fullerene solubility in 1-chloronaphthalene, was successful (Table 2, entry 7, footnote [f]). However, the reaction between **1b** and methyl acrylate in more dilute toluene solution (Table 2, entry 12, footnote [g]) failed.

N-Methylnitroacetamide (**1c**) in 1-chloronaphthalene selectively gave the isoxazolines **2c** (R^2 = CO_2CH_3 or $CONH_2$) provided the reactions with acrylamide and methyl acrylate were carried out at 80 °C whilst stirring (entries 14 and 15). The amide **1c** (m.p. 75–76 °C)[25] is insoluble in 1-chloronaphthalene, but reactions are known to take place even in spite of heterogeneous conditions, especially emulsions.[24,25]

Synthesis of [60]Fulleroisoxazolines

The model reactions considered above (Table 2) showed that condensations of nitro compounds can be successfully carried out in 1-chloronaphthalene, even at a dipolarophile concentration corresponding to [60]fullerene solubility (Table 2, entry 7, footnote [f]). Thus, [60]fullerene was treated in 1-chloronaphthalene solution with ethyl nitroacetate (**1b**) in the presence of the Cu^{II}/NMP catalytic system. After 5 d at 60 °C and removal of solvent by column chromatography, analysis of the products showed a considerable yield of the condensation product **4b** (Table 3), but, unlike the model reactions, no conjugate adduct was observed, even in the absence of a copper salt. Some condensation products in a 2:1 ratio were detected in the reaction catalysed by only the base. Preliminary removal of the solvent by distillation in vacuo was ruled out to avoid excessive heating, thus, 1-chloronaphthalene was separated from the products by column chromatography.

Table 3. [60]Fulleroisoxazolines **4** obtained by copper/base-catalysed condensation of nitro compounds **1** with [60]fullerene.[a]



1 4

Entry	1	R^1	4	Yield [%] 4[b]	Yield [%] C_{60}[c]
1	**1a**	CH_3	**4a**	traces[d]	–
2	**1b**	$C(=O)OCH_2CH_3$	**4b**	31 (52)	40
3[e]	**1c**	$C(=O)NHCH_3$	**4c**	42 (66)	36
4	**1d**	$C(=O)NHCH_2CH_2NHC(=O)OC(CH_3)_3$	**4d**	28 (50)	44
5	**1e**	$C(=O)C_6H_5$	**4e**	38 (46)	39
6	**1f**	$P(=O)(OCH_2CH_3)_2$	**4f**	22 (53)	58

[a] All the reactions were carried out with 50 mg (0.069 mmol) of [60]fullerene, nitro compound **1** (0.173 mmol), copper acetate (0.00345 mmol) and NMP (0.0069 mmol) in 1-chloronaphthalene (1.0–1.4 mL) at 60 °C unless otherwise stated; see Exp. Sect. for details. [b] Yield of isolated product based on [60]fullerene; the values in parentheses are based on consumed [60]fullerene. [c] Recovered by chromatography. [d] The main product was the oxime **5a** (see below), along with the corresponding bis- and tris-adducts; see Exp. Sect. for details. [e] Reaction carried out at 80 °C.

By using a gradient of suitable eluent, unreacted fullerene, 1-chloronaphthalene and the products were collected in sequence: yield of monoadduct 31%, or 52% based on consumed fullerene and 60% conversion (Table 3, entry 2).

The same reaction carried out in toluene under the same conditions disregarding solubility was successful, in spite of the heterogeneous conditions, with a yield of 18%; considering 48% conversion, the yield based on converted fullerene was 38%. Homogeneous conditions for the same reaction in toluene would require extreme dilution of the reagent and catalyst with loss of reactivity, as we evidenced in our model reactions (Table 2, entry 7, footnote [g]).

The procedure in 1-chloronaphthalene established above, applied to other activated nitro compounds, allowed various functional groups to be anchored to fullerene (Table 3). 3-Carbamoyl[60]fulleroisoxazolines (**4c**, **4d**) have never been reported before. This interesting functionalisation can be efficiently achieved by condensation of nitroacetamides **1c** and **1d** with [60]fullerene under the usual conditions. *N*-Methylnitroacetamide (**1c**) was obtained by aminolysis of ethyl nitroacetate with aqueous methylamine in large excess, as reported previously.[32] The amide **1d** was prepared in low yield by heating methyl nitroacetate with a slight excess of *tert*-butyl (2-aminoethyl)carbamate in water/pyridine. Better results were obtained by performing the reaction with a four-fold excess of the amine in methanol at room temperature for 3 days. Crude **1d** can be purified by flash chromatography (m.p. 120–121 °C, yield 32%), but washing with hexane gave a product (m.p. 113–114 °C, yield 78%) pure enough for further reaction. In both cases, the excess amine was recovered in part.

Benzoylnitromethane (**1e**) reacted under the same conditions in the presence of copper acetate to give the corresponding 1:1 condensation product **4e** in addition to minor amounts of polyadducts (Table 3, entry 5).

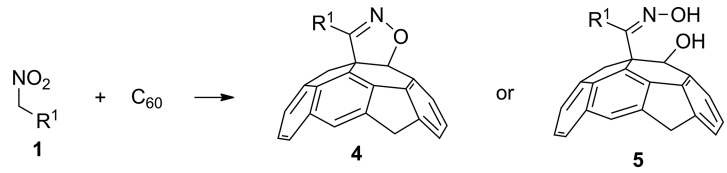
The [60]fulleroisoxazolines **4** are generally poorly soluble in common deuteriated solvents used for NMR spectroscopy such as chloroform and acetone. In particular, the severe insolubility of the amide **4c** even with CS_2 as a co-solvent made it necessary to add 1-chloronapthalene as a co-solvent for the acquisition of ^{13}C NMR spectra.

Phosphonate [60]fulleroisoxazolines have been reported only by Sinyashin and co-workers,[33] who synthesised them by the cycloaddition of (diisopropoxyphosphoryl)nitrile oxide and [60]fullerene. Unlike other nitrile oxides, this reaction gave two bis-adducts as the main products in addition to the mono-adduct. The catalytic procedure described herein with diethyl (nitromethyl)phosphonate (**1f**) led to only the monoadduct **4f** (Table 3, entry 6). Diethyl (nitromethyl)phosphonate (**1f**) was prepared by slight modifications of previously reported procedures.[34,35]

Reactions in Excess Base

The reactions of [60]fullerene with various nitro compounds in large excess of reagents and base (triethylamine) have previously been reported to afford hydroxy oximes **5**, which corresponds to the addition of a nitro compound to [60]fullerene (Table 4).[28,36] The reaction was successful with nitroethane (**1a**)[37] in excess of base (35%, entry 1), whereas with a catalytic amount of base (triethylamine or DABCO), the oxime was isolated in low yield (8 and 21%, respectively) only after prolonged heating (Table 4 entries 2 and 3). On the other hand, activated nitro compounds **1b** and **1c** in excess TEA led only to the decomposition of the nitro compounds, whereas with a catalytic amount of base (DABCO) the dehydrated cycloadducts **4b** and **4c** were the main products with minor amounts of poly-cycloadducts. When a catalytic amount of Cu^{II} was added to the base, the formation of poly-cycloadducts decreased (Table 3 and 4).

Table 4. Reactions of nitro compounds **1** with [60]fullerene in the presence of base under a variety of conditions.



a: $R^1 = CH_3$; **b**: $C(=O)OC_2H_5$; **c**: $C(=O)NHCH_3$

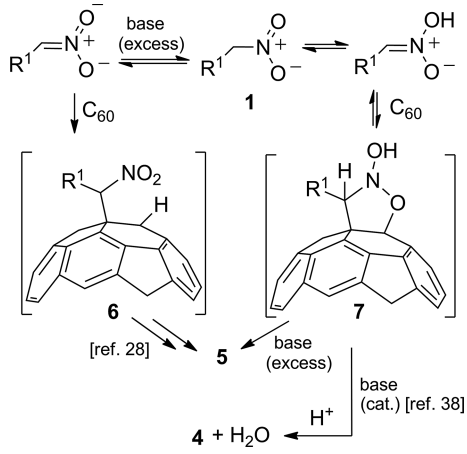
Entry	**1** (equiv.)[a]	Solvent[b]	Conditions	Base (equiv.)[a]	Products [%]		
					4	**5**	C_{60}[c]
1[d]	**a** (20)	D	2 h, room temp.	TEA[e] (20)	–	35	12
2	**a** (2.5)	C	5 d, 60 °C	TEA (0.1)	–	8	4[f]
3	**a** (2.5)	C	5 d, 60 °C	DABCO (0.1)	–	21	34
4	**b** (2.5)	C	5 d, 60 °C	TEA (0.1)	16	–	68
5	**b** (20)	D	2 h, room temp.	TEA (20)	–	–	92
6	**c** (20)	D	2 h, room temp.	TEA (20)	–	–	90
7	**b** (2.5)	C	5 d, 60 °C	DABCO (0.1)	29	–	7
8	**b** (2.5)	C	5 d, 60 °C	DABCO (1)	15	–	8

[a] Equivalents with respect to [60]fullerene. [b] C: 1-chloronaphthalene, D: chlorobenzene. [c] Recovered by chromatography. [d] The experiment described previously by Ohno et al.[28] was repeated in our laboratory and gave similar results. [e] TEA: triethylamine. [f] More 60[fullerene] was recovered in mixture with 1-chloronaphthalene.

Suggested Mechanism

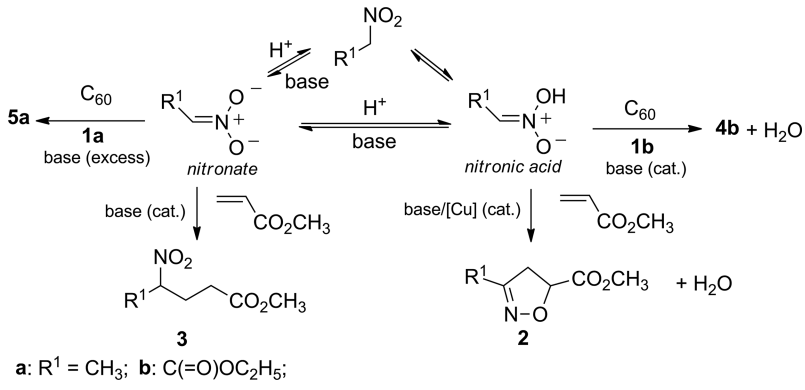
The overall reactivity of [60]fullerene with primary nitro compounds in 1-chloronaphthalene is illustrated in Scheme 2, in addition to the model reaction of methyl acrylate in the same solvent (these are consistent with the known behaviour in chloroform).[21,23,29]

The results of these reactions are strongly dependent upon the nature of the nitro compound and the amount of base employed (whether excess or catalytic). Ethyl nitroacetate (**1b**) underwent condensation with [60]fullerene under base catalysis in the same manner as with methyl acrylate, although in the latter case addition of Cu^{II} salt was required to favour condensation over addition (see Table 2, entry 13). No addition product analogous to **3** has been evidenced with [60]fullerene under base catalysis (with or without Cu^{II}) nor in excess base. On the other hand, addition products of this kind (**6**, Scheme 3) have been claimed as intermediates in the reaction of nitroethane (and other nitroalkanes, but not ethyl nitroacetate) with [60]fullerene in excess base,[28] leading to the oxime **5**.



Scheme 3. Plausible reaction mechanism.

The conversion of the adduct **6** into oxime **5** is explained through the formation of several intermediates, for which evidence is lacking. In our opinion, the cycloaddition of



a: $R^1 = CH_3$; **b**: $C(=O)OC_2H_5$;

Scheme 2. Reactivity of electron-poor alkenes and [60]fullerene with primary nitro compounds.

nitronic acid to [60]fullerene to give the unstable intermediate adduct **7** (Scheme 3) accounts for both results: dehydration to **4** in acid medium[38] and isomerisation of **7** to the oxime **5** in excess base. Activated nitro compounds such as ethyl nitroacetate are unable to produce the intermediate cycloadduct **7** in excess base because they mainly exist as the conjugated base (nitronate), the amount of the nitronic acid being too low for appreciable cycloaddition.

Conclusions

Model reactions of ethyl nitroacetate (**1b**) with electron-poor dipolarophiles are scarcely affected by the solvent employed (Tables 1 and 2). Thus, reactions of [60]fullerene with several "activated" primary nitro compounds were carried out in 1-chloronaphthalene, in which [60]fullerene has the highest solubility (0.071 M). Base-catalysed condensation to [60]fulleroisoxazolines (**4**) was the predominant reaction (Table 3), giving moderate yields of the products even with only base as catalyst.

However, nitroethane did not undergo a similar condensation, but was converted into oxime **5a**, particularly in excess base, as has previously been reported[28] (Table 4). The synthesis of [60]fulleroisoxazolines **4** offers a valid alternative to the use of unfriendly chloroximes as nitrile oxide precursors.

Experimental Section

General Methods and Materials: Melting points were determined in capillary tubes with a Büchi 510 apparatus. Chromatographic separations were performed on silica gel 60 (40–6.3 μm) with analytical-grade solvents, driven by a positive pressure of air; R_f values refer to TLC (visualised with UV light and/or by dipping the plates into a solution of permanganate or anisaldehyde followed by heating with a heat gun) carried out on alumina-backed plates coated with 25-mm silica gel (Merck F254). Solvents were removed by evaporation on a rotavap at room temperature, except for 1-chloronaphthalene, which was removed by chromatography. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Mercuryplus 400 spectrometer (operating at 400 MHz for ^{1}H and 100.58 MHz for ^{13}C) unless otherwise stated. ^{31}P NMR spectra were recorded with a Bruker spectrometer (operating at 162 MHz). The ^{1}H NMR spectroscopic data are reported as [multiplicity, coupling constant(s) in Hz, integration]; the multiplicity is denoted by s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br. = broad signal. The multiplicities of the ^{13}C NMR signals (s, d, t, q; for compounds **1f** and **4f**, the multiplicity for C–H are reported along with C–P coupling constants) and the assignments were determined by means of gHSQC and gHMBC experiments. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: 7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). ^{31}P NMR chemical shifts are given relative to H_3PO_4 (δ = 0 ppm) as external reference. ESI (electronspray ionisation) mass spectra were recorded (infusing the sample solution directly into the ESI chamber by syringe pump) with a ThermoFisher LCQ-Fleet ion-trap instrument and spectra were recorded by using either ESI^+ or ESI^- techniques. Ion mass/charge (m/z) ratios are reported as values in atomic mass units followed by the intensities relative to the base peak in parentheses. HRMS was performed with an LTQ-Orbitrap high-resolution mass spectrometer (Thermo, San Jose, CA, USA) equipped with a conventional ESI source (negative polarity). IR spectra were recorded with a Perkin–Elmer 881 spectrophotometer. Elemental analyses were carried out with a Perkin–Elmer 240C Elemental Analyser apparatus. All compounds were named by using Autonom® (Beilstein Information Systems) and modified as appropriate. Commercially available (Lancaster and Aldrich) nitroethane (**1a**), methyl nitroacetate, ethyl nitroacetate (**1b**), benzoylnitromethane (**1e**), organic bases, 99% HNO_3 (density 1.52), 1-chloronaphthalene (technical grade, 1.192 g/mL at 20 °C), acrylamide (solubility: in chloroform 2.66 g/100 mL,[39] slightly soluble in toluene and 1-chloronaphthalene), methyl acrylate and fullerene were used as supplied. $CHCl_3$ (ethanol-free) was filtered through a short pad of potassium carbonate just before use. Chloroacetone was distilled before use. Toluene was distilled from CaH_2 before use. Copper(II) acetate and copper powder were used as supplied. *N*-Methylnitroacetamide (**1c**) was prepared following a previously reported procedure from ethyl nitroacetate (**1b**).[32] *tert*-Butyl (2-aminoethyl)carbamate was prepared in 70% yield following a previously reported procedure[40] starting from ethylenediamine; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.41 [s, 9 H, C(CH_3)$_3$], 2.76 (t, J = 6.2 Hz, 2 H, CH_2NH_2), 3.26 (q, J = 6.0 Hz, 2 H, CH_2NH), 4.94 (br. s, 1 H, CON*H*) ppm; CH_2NH_2 protons were not detected. Diethyl (2-oxopropyl)phosphonate was prepared in 36% yield as a pale-yellow liquid following a previously reported procedure[41] starting from chloroacetone and triethyl phosphite (Michaelis–Arbuzov reaction);[42,43] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (t, J = 14.4 Hz, 6 H, 2 CH_3CH_2O), 2.28 (s, 3 H, CH_3CO), 3.04 [d, J(H,P) = 23.2 Hz, 2 H, CH_2P], 4.04–4.22 (m, 4 H, 2 CH_3CH_2O) ppm. Acetyl nitrate ($AcONO_2$) was prepared by mixing 99% HNO_3 (d = 1.52; 0.713 g, 11.33 mmol) and acetic anhydride (1.157 g, 11.33 mmol) at –10 to –5 °C and keeping, whilst stirring, the mixture at –7 °C for 4 h.[44]

Model Reactions with DABCO as Catalyst: (Table 1) The spectroscopic yields reported in Table 1 refer to reactions performed in a homemade apparatus in which several reactions were carried out simultaneously under controlled stirring and temperature. A mixture of ethyl nitroacetate (**1b**, 1.06 mmol), DABCO (4.8 mg, 0.0424 mmol), methyl acrylate or acrylamide (0.424 mmol) and dimethyl sulfone (5–10 mg) in the indicated solvent (1.4 mL) was kept at 60 °C. After 24 h the reaction mixture was concentrated under reduced pressure and the ^{1}H NMR spectrum ($CDCl_3$) recorded (except with 1-chloronaphthalene, for which a portion was withdrawn from the reaction mixture and diluted with 0.6 mL of $CDCl_3$). Integration of the CH_3 proton signals of the internal standard (s, 2.93 ppm) and the more reliable signals of **2** and **3** gave the spectroscopic yield. Table 1, entries 1–3: integration of methylenic protons for **3b** (R^2 = $CONH_2$; m, 2.50–2.38 ppm) and 4-H protons for **2b** (R^2 = $CONH_2$; dd, 3.33 ppm); entries 4–6: integration of methyl protons for **3b** (R^2 = CO_2CH_3; s, 3.65 ppm) and **2b** (R^2 = CO_2CH_3; s, 3.78 ppm). In the case of an unclear result, a duplicate experiment was performed.

Model Reactions with Cu^{II}/NMP as Catalyst in Various Solvents: (Table 2) The spectroscopic yields reported in Table 2 refer to reactions performed as above. A mixture of nitro compound (**1a**, **1b** or **1c**, 1.06 mmol), NMP (entries 1–6: 21.0 mg, 0.212 mmol; entries 7–15: 4.2 mg, 0.0424 mmol), $Cu(OAc)_2$ (3.85 mg, 0.021 mmol), methyl acrylate or acrylamide (0.424 mmol) and dimethyl sulfone (5–10 mg) in the indicated solvent (1.4 mL) was kept at 60 °C (80 °C for entries 14 and 15). After 24 h the reaction mixture was concentrated under reduced pressure (except for 1-chloronaphthalene, see above) and the ^{1}H NMR spectrum ($CDCl_3$, D_2O for entry 14) recorded. For entry 14, the reaction mixture was extracted

with D_2O (3 × 1 mL) and the ^1H NMR spectrum (D_2O) recorded. Integration of the CH_3 proton signals of the internal standard (s, 2.93 ppm) and the more reliable signals of **2** and **3** gave the spectroscopic yield. Table 2, entries 1–6: integration of 5-H proton of **2a** (R^2 = CO_2Me; dd, 4.98 ppm; R^2 = $CONH_2$; dd, 4.96 ppm); no signals of the adducts[45] or bis-adducts[46] were observed. Entries 7–10: integration of methylenic protons for **3b** (R^2 = $CONH_2$; m, 2.50–2.38 ppm) and 4-H protons for **2b** (R^2 = $CONH_2$; dd, 3.33 ppm). Entries 11–13: integration of methyl protons for **3b** (R^2 = CO_2CH_3; s, 3.65 ppm) and **2b** (R^2 = CO_2CH_3; s, 3.78 ppm). Entry 14: integration of 4-H for **2c** (R^2 = CO_2CH_3; dd, 3.52 ppm). Entry 15: integration of the 4-H proton for **2c** (R^2 = $CONH_2$; dd, 3.46 ppm).

***tert*-Butyl [2-(2-Nitroacetamido)ethyl]carbamate (1d):** At 80 °C in a slight excess of amine: *tert*-Butyl (2-aminoethyl)carbamate (1.61 g, 10.08 mmol) was added to a mixture of methyl nitroacetate (8.4 mmol, 0.625 mL), pyridine (1.05 mL) and water (1.05 mL) and the reaction mixture stirred at 80 °C in a sealed tube. After 3 h the reaction mixture was cooled and concentrated under reduced pressure. The residue was dissolved in water, cooled and the solution acidified to pH 4 with 3 N HCl. The solution (about 20 mL) was then extracted with $CHCl_3$ (5 × 18 mL). The combined organic phases were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was subjected to flash column chromatography on silica gel (petroleum ether/AcOEt = 1:2, R_f = 0.31) to yield pure **1d** (315 mg, 14%) as a yellowish powder, m.p. 115–116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.46 [s, 9 H, C(CH_3)$_3$], 3.34 (m, 2 H, CH_2NH), 3.44 (m, 2 H, CH_2NH), 5.1 (s, 2 H, CH_2NO_2) ppm. ^{13}C NMR (100.58 MHz, CD_3OD): δ = 28.3 [q, 3 C, C(CH_3)$_3$], 41.4 (t, CH_2NH), 41.7 (t, CH_2NH), 79.6 (residual $CDHNO_2$), 81.1 [s, $C(CH_3)_3$], 159.4 [s, NH$COC(CH_3)_3$], 160.7 (s, CONH) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$, sparingly soluble): δ = 29.6 [q, 3 C, $C(CH_3)_3$], 39.6 (t, CH_2NH), 41.8, (t, CH_2NH), 77.9, (t, CH_2NO_2), 80.3, [s, $C(CH_3)_3$], 160.7 (s, CO) ppm; NH$COOC(CH_3)_3$ carbon not detected. IR (KBr): $\tilde{\nu}$ = 3354 (w) [N–H], 3457 (w) [N–H], 2977 (w) [C–H], 1672 (s) [C=O], 1566 (s), 1546 (s) [NO_2], 1508 (s), 1448 (w), 1384 (w), 1367 (w), 1340 (w), 1282 (m), 1255 (m), 1166 (m) cm^{-1}. MS (ESI^-): *m*/*z* = 246 [M – 1]$^-$. $C_9H_{17}N_3O_5$ (247.25): calcd. C 43.72, H 6.93, N 17.00; found C 43.36, H 7.36, N 17.07.

At room temperature with an excess of amine: Methyl nitroacetate (0.905 g, 7.60 mmol) was added to an ice-cold solution of *tert*-butyl (2-aminoethyl)carbamate (4.870 g, 30.4 mmol) in MeOH (9 mL). The clear reaction mixture was stirred at room temperature for 3 d and then concentrated under reduced pressure. The residue was dissolved in water (8 mL) and the resulting solution (ice-cooled) was acidified to pH 4 with 3 N HCl. The solution (about 50 mL) was then extracted with $CHCl_3$ (5 × 50 mL). The combined organic phases were dried with Na_2SO_4, filtered and concentrated under reduced pressure to give crude **1d** (1.545 g) containing residual methyl nitroacetate. The crude product was further purified by washing with hexane to yield pure **1d** (1.459 g, 78%) as a white powder, m.p. 114–115 °C. $C_9H_{17}N_3O_5$ (247.25): calcd. C 43.72, H 6.93, N 17.00; found C 43.36, H 7.30, N 17.22. *tert*-Butyl (2-aminoethyl)carbamate was recovered (1.09 g, 30% of the excess used) by extraction of the aqueous solution at pH 11 (ice-cooled solution added with 3 N NaOH) with CH_2Cl_2 (5 × 50 mL).

The crude product obtained by the same procedure from the ester (0.50 g, 4.2 mmol) and the amine (2.69 g, 16.8 mmol), purified by flash chromatography on silica gel (petroleum ether/AcOEt = 1:2, R_f = 0.31), yielded pure **1d** (336 mg, 32%) as a white powder, m.p. 120–121 °C. $C_9H_{17}N_3O_5$ (247.25): calcd. C 43.72, H 6.93, N 17.00; found C 43.70, H 6.71, N 16.25. *tert*-Butyl-(2-aminoethyl)carbamate was recovered (1.015 g, 50% of the excess used) as reported above. The spectroscopic data are identical for the three samples.

Diethyl (Nitromethyl)phosphonate (1f): Diethyl (nitromethyl)phosphonate (**1f**) was prepared by slight modifications of reported procedures.[34,35] A 25 mL two-necked round-bottomed flask equipped with a thermometer was charged with diethyl (2-oxopropyl)phosphonate (2.0 g, 10.3 mmol) and acetic anhydride (1.073 g). At an internal temperature of 32 °C, freshly prepared (stored in an ice-bath) acetyl nitrate ($AcONO_2$) was added dropwise carefully keeping the temperature below 35 °C. After 1 h at room temperature, water was added (6 mL) and after a further 1 h the reaction mixture was extracted with diethyl ether (5 × 8 mL). The combined organic phases were dried with Na_2SO_4, filtered, concentrated under reduced pressure and the residue purified by flash chromatography (silica gel, petroleum ether to petroleum ether/EtOAc = 1:2) to afford **1f** (R_f = 0.45, 841 mg, 42%) as a pale-yellow liquid (turned brown after standing for a few days). Eventually, traces of an unknown compound were removed by dissolving the crude material in 0.1 M NaOH (30 mL) and washing with chloroform (2 × 20 mL). Subsequent acidification of the aqueous solution with 10% HCl (to pH 3) and extraction with chloroform (3 × 20 mL) gave, after drying with Na_2SO_4 and concentration at reduced pressure, pure **1f**. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.36 (t, *J* = 7.0 Hz, 6 H, CH_3CH_2), 4.19–4.27 (m, 4 H, CH_3CH_2), 4.90 [d, ^2J(H,P) = 15.4 Hz, 2 H, CH_2P] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 16.2 [q, ^3J(C,P) = 5.4 Hz, CH_3], 64.3 (t, $^2J_{C\text{-}P}$ = 6.9 Hz, CH_2O), 72.1 [t, ^1J(C,P) = 141.9 Hz, CH_2NO_2] ppm. ^{31}P NMR ($CDCl_3$, 80.95 MHz): δ = 9.24 ppm.[47] IR ($CDCl_3$): $\tilde{\nu}$ = 2985 (w), 1557 (s) [NO_2], 1370 (w) [NO_2], 1274 (m) [P=O], 1167 (w), 1062 (m), 1025 (s) cm^{-1}. MS (ESI^-): *m*/*z* = 196 [M – 1]$^-$. $C_5H_{12}NO_5P$ (197.13): calcd. C 30.46, H 6.14, N 7.11; found C 30.41, H 5.96, N 6.72.

General Procedure for the Reactions of Nitro Compounds 1a–f with [60]Fullerene: (Table 3) 1-Chloronaphthalene (1 mL, but 1.4 mL for **1c**) was added to fullerene (50 mg, 0.069 mmol, 1 equiv.), nitro compound **1a–f** (0.173 mmol, 2.5 equiv.), copper acetate (0.6 mg, 0.00345 mmol, 0.05 equiv.) and *N*-methylpiperidine (0.7 mg, 0.9 μL, 0.0069 mmol, 0.1 equiv.). Then the mixture was maintained at 60 °C (but 80 °C for **1c** and **1d**) for 5 d whilst stirring in a sealed tube.

Reaction of Nitroethane (1a) with [60]Fullerene to Give Isoxazolino-[60]fullerene 4a and Oxime 5a: TLC analysis of the brown mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92, UV-detected), and spots at R_f = 0.66 and R_f = 0. The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient petroleum ether to toluene then toluene/AcOEt) conducted under a slight pressure of air provided fulleroisoxazoline **4a** (less than 1 mg, R_f = 0.66 toluene as eluent) and fractions containing the adduct **5a** (2.9 mg, see below for spectroscopic data) and analogous polyadducts {bis-adducts: 6.2 mg; MS (ESI^-): *m*/*z* = 869 [M – 1]$^-$; tris-adducts: 16.2 mg; MS (ESI^-): *m*/*z* = 944 [M – 1]$^-$}. Due to the meagre amount obtained, compound **4a** was only partially characterised. **4a**: ^1H NMR (400 MHz, $CDCl_3$): δ = 2.73 (s, CH_3) ppm.[14a] MS (ESI^-): *m*/*z* (%) = 777 (100) [M]$^-$. Attempted reactions with more copper acetate or copper powder instead of copper acetate, less base (0.1 equiv.) or in chloroform did not afford a higher yield of fulleroisoxazoline **4a**.

Reaction of Ethyl Nitroacetate (1b) with [60]Fullerene to Give Isoxazolino[60]fullerene 4b: TLC analysis of the brown reaction mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92, UV-detected) and [60]-

fullero-3-ethoxycarbonylisoxazoline (**4b**) (R_f = 0.78). The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient petroleum ether to toluene) conducted under a slight pressure of air provided recovered 1-chloronaphthalene (880 mg, 74%), [60]fullerene (19.9 mg, 40% recovered) and **4b** (after washing with pentane, 18.1 mg, dark-brown powder, 31%). The yield based on consumed [60]fullerene was 52%. The same reaction repeated with more NMP (3.8 mg, 0.5 equiv.) gave a lower yield of isoxazoline **4b** (14.5 mg, 25%) and 30.6 mg of recovered C_{60}. **4b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (t, J = 7.4 Hz, 3 H, CH_3CH_2), 4.57 (q, J = 7.4 Hz, 2 H, CH_3CH_2) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$ + 0.02 M [Cr(acac)$_3$]): δ = 14.2 (CH_3CH_2), 63.0 (CH_3CH_2), 76.6 (isoxazoline-C-4), 106.2 (isoxazoline-C-5), 136.5, 137.0, 140.2, 141.7, 141.8, 142.1, 142.3, 142.4, 142.8, 142.9, 143.0, 143.5, 144.1, 144.2, 144.5, 145.1, 145.2, 145.3, 145.7, 146.0, 146.2, 146.3, 146.4, 146.8, 147.2, 147.3, 147.8, 159.8 ppm. IR (KBr): $\tilde{\nu}$ = 2973 (w), 2951 (w), 2920 (w), 1720 (s) [C=O], 1584 (w) [C=N], 1329 (m), 1174 (s) [C_{60}], 1138 (s), 526 (s) [C_{60}] cm^{-1}. MS (ESI$^-$): m/z = 835 [M]$^-$. HMRS (ESI$^-$): calcd. for $C_{64}H_5NO_3$ [M]$^-$ 835.0269; found 835.0268 (±0.0001). $C_{64}H_5NO_3$ (835.73): calcd. C 91.98, H 0.46, N 1.68; found C 91.60, H 0.49, N 1.60.

Reaction to Give 4b in the Presence of NMP/[Cu] as Catalyst in Toluene: Toluene (1.4 mL) was added to [60]fullerene (50 mg, 0.069 mmol, 1 equiv.), ethyl nitroacetate (23 mg, 19 μL, 0.173 mmol, 2.5 equiv.), copper acetate (0.6 mg, 0.00345 mmol, 0.05 equiv.) and *N*-methylpiperidine (0.7 mg, 0.9 μL, 0.0069 mmol, 0.1 equiv.), and then the mixture was maintained at 60 °C for 5 d whilst stirring in a sealed tube. TLC analysis of the brown mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98) and isoxazoline **4b** (R_f = 0.78). The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient petroleum ether/toluene = 2:1 to toluene) conducted under a slight pressure of air provided [60]fullerene (26 mg, 52% recovered) and fulleroisoxazoline **4b** (after washing with pentane, 11 mg, dark-brown powder, 19%). The yield based on consumed [60]fullerene was 39%. The spectroscopic and analytical data of **4b** are identical to those reported above.

Reaction of *N*-Methylnitroacetamide (1c) with [60]Fullerene to Yield Isoxazolino[60]fullerene 4c: TLC analysis of the brown reaction mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92, UV-detected), **4c** (R_f = 0.22) and an additional spot at R_f = 0. The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient petroleum ether to toluene then toluene/AcOEt = 10:1 for the tail) conducted under a slight pressure of air provided recovered 1-chloronaphthalene (1.34 g, 80%), C_{60} (18.2 mg, 36%) and fulleroisoxazoline **4c** (23.8 mg, 42%; the yield based on consumed [60]fullerene was 66%) along with traces of the 2:1 cycloadduct (R_f = 0.2, eluent toluene/AcOEt = 10:1). The latter compound was obtained only in traces and hence was not fully characterised: MS (ESI$^-$): m/z (%) = 919 [M]$^-$. **4c**: ^{1}H NMR ($CDCl_3$): δ = 3.11 (d, J = 4.8 MHz, 3 H, CH_3NH) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$ with 0.02 M [Cr(acac)$_3$]): δ = 29.7 (CH_3NH), 136.0, 136.8, 139.8, 140.0, 141.4, 141.5, 141.8, 141.9, 142.1, 142.2, 142.3, 142.4, 142.5, 143.7, 143.8, 143.9, 144.2, 144.8, 145.0, 145.3, 145.5, 145.6, 145.9, 146.0, 146.9, 147.4, 148.3 ppm. IR (KBr): $\tilde{\nu}$ = 3371 (s) (N–H), 1726 (s) [C=O], 1597 (w) [C=N], 1183 (m) [C_{60}], 1121 (s), 579 (m) [C_{60}], 526 (s) [C_{60}] cm^{-1}. MS (ESI$^-$): m/z (%) = 820 (100) [M]$^-$. HMRS (ESI$^-$): calcd. for $C_{63}H_3N_2O_2$ 819.0194 [M – H]$^-$; found 819.0204 (± 0.0001).

Reaction of *N*-(tert-Butoxycarbonylaminoethyl)nitroacetamide (1d) with [60]Fullerene to Yield Isoxazolino[60]fullerene 4d: TLC analysis of the brown reaction mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98) and 1-chloronaphthalene (R_f = 0.92, UV-detected) along with a spot at R_f = 0. Subsequent TLC analysis (eluent toluene/AcOEt = 3:1) showed the presence of [60]fulleroisoxazoline **4d** (R_f = 0.60). The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient petroleum ether to toluene then toluene to AcOEt) conducted under a slight pressure of air provided recovered 1-chloronaphthalene (890 mg, 74%), C_{60} (22 mg) and pure **4d** (after washing with hexane, as a dark brown-powder, 20.8 mg, 28%; the yield based on unrecovered fullerene C_{60} was 50%). **4d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 [s, 9 H, $(CH_3)_3C$], 3.42–3.50 (m, 2 H, CH_2NH), 3.60–3.66 (m, 2 H. CH_2NH), 4.90 (br. s, 1 H, N*H*), 7.73 (br. s, 1 H, N*H*) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$ with 0.02 M [Cr(acac)$_3$], 102400 transients): δ = 28.22 (q, 3 C, 3 CH_3), 39.81 (br. t, CH_2NH), 40.95 (t, CH_2NH), 75.8 (isoxazoline-C-4), 80.1 [$C(CH_3)_3$], 105.5 (isoxazoline-C-5), 136.2, 137.0, 140.1, 140.3, 141.7, 141.8, 142.1, 142.3, 142.4, 142.5, 142.6, 142.7, 142.8, 144.0, 144.1, 144.2, 144.5, 145.1, 145.3, 145.6, 145.9, 146.0, 146.2, 146.3, 147.1, 147.8, 148.3, 159.4 ppm. IR (KBr): $\tilde{\nu}$ = 3383 (m) [N–H], 3326 (m) [N–H], 2923 (m) [C–H], 1688 (s) [C=O], 1594 (w) [C=N], 1533 (m), 1443 (w), 1363 (w), 1272 (m), 1167 (m) 526 (m) cm^{-1}. MS (ESI$^-$): m/z (%) = 949 (100) [M]$^-$. HMRS (ESI$^-$): calcd. for $C_{69}H_{15}N_3O_2$ 949.1063 [M]$^-$; found 949.1054 (±0.0001).

Reaction of Benzoylnitromethane (1e) with [60]Fullerene to Yield Isoxazolino[60]fullerene 4e: TLC analysis of the brown reaction mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92, UV-detected), [60]-fullero-3-benzoylisoxazoline (**4e**) at R_f = 0.84 and byproducts at R_f = 0.54 and 0.28. The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient petroleum ether to toluene) conducted under a slight pressure of air provided[48] recovered 1-chloronaphthalene (940 mg, 78%), recovered C_{60} (19.7 mg) and fulleroisoxazoline **4e** (black-brown powder, 22.6 mg, 38%; the yield based on consumed fullerene C_{60} was 46%). **4e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.66 (m, 2 H, Ph-H_{meta}), 7.70–7.79 (m, 1 H, Ph-H_{para}), 8.46–8.52 (d, 2 H, Ph-H_{ortho}) ppm. ^{13}C NMR {100.58 MHz, $CDCl_3$ with 0.02 M [Cr(acac)$_3$]}: δ = 81.82 (isoxazoline-C-4), 105.4 (isoxazoline-C-5), 128.6 (Ph-*C*), 130.6 (Ph-*C*), 134.4 (Ph-*C*), 136.0 (Ph-*C*), 136.1, 137.1, 140.2, 141.7, 142.1, 142.3, 142.4, 142.5, 142.6, 142.7, 142.8, 143.0, 144.1, 144.2, 144.6, 145.1, 145.3, 145.6, 145.9, 146.1, 146.2, 146.3, 146.9, 147.1, 147.7, 151.5 (isoxazoline-C-3), 185.6 (*C*OPh) ppm. IR (KBr): $\tilde{\nu}$ = 3040 (w), 2921 (m), 2851 (m), 1647 (s) [C=O], 1574 (m), 1446 (m), 1324 (m), 1261 (m), 1166 (m), 1090 (w), 1064 (w), 1010 (m), 981 (w), 920 (m), 842 (s), 800 (w), 753 (m), 668 (m), 562 (m) [C_{60}], 523 (s) [C_{60}] cm^{-1}. MS (ESI$^-$): m/z (%) = 867 (100) [M]$^-$. HMRS (ESI$^-$): calcd. for $C_{68}H_5NO_2$ 867.0320 [M]$^-$; found 867.0316 (± 0.0001).

Reaction of Diethyl (Nitromethyl)phosphonate (1f) with [60]Fullerene to Yield Isoxazolino[60]fullerene 4f: TLC analysis of the brown reaction mixture (toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92, UV-detected), and a spot at R_f = 0. Subsequent TLC analysis (eluent toluene/AcOEt = 4:1) showed the presence of fulleroisoxazoline **4f** (R_f = 0.57). The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient hexane to toluene then toluene to AcOEt) conducted under a slight pressure of air provided recovered 1-chloronaphthalene (900 mg, 76%), C_{60} (29.4 mg, 58%) and **4f** (dark powder, 13.7 mg, 22%; the yield based on consumed fullerene C_{60} was 53%). **4f**: ^{1}H NMR (400 MHz, $CDCl_3$, * minor isomer): δ = 1.43 [td, ^3J(H,H) = 7.2, ^4J(H,P) = 0.8 Hz, 6 H, 2 CH_3CH_2O], 1.48* [td, ^3J(H,H) = 7.2, ^4J(H,P) =

0.8 Hz, 6 H, 2 CH_3CH_2O], 4.43 (m, 4 H, 2 CH_3CH_2O) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$ with 0.02 M [Cr(acac)$_3$], * minor isomer): δ = 16.22 [d, ^3J(C,P) = 7.0 Hz, CH_3CH_2O], 16.29* [d, ^3J(C,P) = 7.0 Hz, CH_3CH_2O], 64.44 [d, ^2J(C,P) = 6.0 Hz, CH_3CH_2O], 64.72* [d, ^2J(C,P) = 6.0 Hz, CH_3CH_2O], 78.90 [d, ^2J(C,P) = 19.0 Hz, isoxazoline-C-4], 104.2 [d, ^3J(C,P) = 6.0 Hz, isoxazoline-C-5], 136.1, 136.8, 140.1, 140.3, 141.7, 141.8, 142.1, 142.2, 142.3, 142.5, 142.7, 142.8, 142.9, 143.9, 144.0, 144.1, 144.6, 145.1, 145.2, 145.6, 145.8, 145.9, 146.0, 146.2, 146.3, 147.1, 147.7, 149.3 [d, ^1J(C,P) = 213.0 Hz, isoxazoline-C-3] ppm. ^{31}P NMR (121.4 MHz, $CDCl_3$, * minor isomer): δ = 2.14, 1.32* ppm. IR (KBr): $\tilde{\nu}$ = 2907 (w), 1619 (w) [C=N], 1429 (w), 1270 (m) [P=O], 1020 (s), 611 (w), 526 (m) [C_{60}] cm^{-1}. MS (ESI$^-$): *m*/*z* (%) = 899 [M]$^-$ (100). HMRS (ESI$^-$): calcd. for $C_{65}H_{10}NO_4P$ 899.0348 [M]$^-$; found 899.0349 (± 0.0001).

General Procedure for the Reactions of Nitro Compounds 1 with [60]Fullerene and Base Under Various Conditions: (Table 4) The solvent was added to [60]fullerene (50 mg, 0.069 mmol in 1 mL 1-chloronaphthalene or 10 mg, 0.014 mmol in 2 mL chlorobenzene or 10 mL of chlorobenzene for entry 1), nitro compound and base (as indicated in Table 4) and maintained under the conditions indicated whilst stirring in a sealed tube.

Reactions of Nitroethane (1a): In chlorobenzene with excess triethylamine at room temp. (entry 1): The product **5a** was evidenced in the brown reaction mixture by TLC (eluent toluene/AcOEt = 1:1, R_f = 0.90). Solvent removal and chromatography conducted under a slight pressure of air (eluent toluene then toluene to AcOEt) gave recovered C_{60} (5.6 mg, 12%), monoadduct oxime **5a** (19 mg, 35%) and polyadducts including a bis-adduct: 15.4 mg; MS (ESI$^-$): *m*/*z* = 869 [M – 1]$^-$. **5a**: ^1H NMR (CS_2/[D_6]acetone = 3:2, 100.6 MHz): δ = 2.83 (s, 3 H, CH_3), 6.48 (s, 1 H, O*H*), 7.32 (s, 1 H, O*H*) ppm; on treatment with D_2O, the singlets at 6.48 and 7.32 ppm disappeared. MS (ESI$^-$): *m*/*z* = 794 [M – 1]$^-$. IR (KBr): $\tilde{\nu}$ = 3389 (br., m), 2907 (s), 2840 (m), 1625 (w) [C=N], 1546 (w), 1423 (m), 1374 (m, w), 1264 (s), 1104 (w), 1040 (m), 1028 (m), 887 (m), 727 (m), 528 (s) [C_{60}] cm^{-1}. The above reaction has been previously reported (with partial experimental details) to give 46% yield of the oxime **5a**.[28]

In 1-chloronaphthalene with triethylamine (0.1 equiv) at 60 °C (entry 2): TLC analysis of the brown mixture (eluent toluene/AcOEt = 5:1) showed the presence of unreacted fullerene (R_f = 1) and 1-chloronaphthalene (R_f = 0.95, UV-detected) along with a spot at R_f = 0.66 (corresponding to oxime **5a**) and a spot at R_f = 0 (corresponding to polyadducts analogous to **5**). The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (hexane to toluene then toluene to AcOEt as eluent) conducted under a slight pressure of air provided recovered pure C_{60} (2 mg, 4%), a mixture of 1-chloronaphthalene and C_{60}, monoadduct **5a** (4.4 mg, 8%, spectroscopic data as above) and polyadducts (24 mg). TLC analysis of the latter (AcOEt/MeOH = 5:1) showed the presence of three close spots (UV-detected). MS (ESI) analysis of this fraction showed the presence of bis-, tris- and tetrakis-adducts.

In 1-chloronaphthalene with DABCO (0.1 equiv) at 60 °C (entry 3): Work up as for entry 2 gave C_{60} (17.2 mg, 34%), 1-chloronaphthalene (1.10 g, 92%), monoadduct **5a** (11.1 mg, 21%, spectroscopic data as above) and a mixture of polyadducts (11.3 mg). TLC analysis of the latter (AcOEt/MeOH = 5:1) showed the presence of three different spots (UV-detected). MS (ESI$^-$) analysis of this fraction showed the presence of bis- (*m*/*z* = 869 [M – 1]$^-$), tris- (*m*/*z* = 944 [M – 1]$^-$), and tetrakis-adducts (*m*/*z* = 1019 [M – 1]$^-$).

Reactions of Ethyl Nitroacetate (1b): In 1-chloronaphthalene with triethylamine (0.1 equiv) at 60 °C (entry 4): TLC analysis of the brown mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92) and **4b** (R_f = 0.78). The crude reaction mixture was loaded directly onto the top of a column of silica gel (3 × 10 cm). Chromatography (gradient hexane to toluene then toluene to AcOEt) conducted under a slight pressure of air provided 1-chloronaphthalene (1.12 mg, 94% recovered), C_{60} (34 mg, 68% recovered), isoxazoline **4b** after washing with pentane and a dark-brown powder (9.4 mg, 16%). The yield based on consumed [60]fullerene was 48%. The spectroscopic and analytical data of **4b** are as reported above.

In chlorobenzene with excess of triethylamine at room temp. (entry 5): TLC analysis of the brown mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92) and the **1b**·N(Et_3) salt (R_f = 0). Solvent removal and chromatography conducted under a slight pressure of air (gradient petroleum ether to toluene) gave recovered C_{60} (9.2 mg, 92%). MS (ESI$^-$) analysis of the crude reaction mixture showed the presence of **1b** (*m*/*z* = 132 [M – 1]$^-$).

In 1-chloronaphthalene with DABCO (0.1 equiv) at 60 °C (entry 7): The same work-up reported above for the preparation of **4b** (Table 3) provided 1-chloronaphthalene (904 mg, 76% recovered), C_{60} (3.6 mg, 7% recovered) and isoxazoline **4b** (after washing with pentane, 16.8 mg, 29% as a dark-brown powder; the yield based on consumed [60]fullerene was 31%). The spectroscopic and analytical data of **4b** are identical to those reported above.

In 1-chloronaphthalene with stoichiometric DABCO at 60 °C (entry 8): The same work-up reported above for the preparation of **4b** (Table 3) provided 1-chloronaphthalene (890 mg, 75% recovered), C_{60} (3.8 mg, 8% recovered), isoxazoline **4b** (after washing with pentane, 8.7 mg, 15% as a dark-brown powder; the yield based on consumed [60]fullerene was 26%). The spectroscopic and analytical data of **4b** are identical to those reported above.

Reaction of *N*-Methylnitroacetamide (1c): In chlorobenzene with excess of triethylamine at room temp. (entry 6): TLC analysis of the brown mixture (eluent toluene) showed the presence of unreacted fullerene (R_f = 0.98), 1-chloronaphthalene (R_f = 0.92) and the **1c**·N(Et_3) salt (R_f = 0). Solvent removal and chromatography conducted under a slight pressure of air (gradient petroleum ether to toluene) gave recovered C_{60} (9.0 mg, 90%). MS (ESI) analysis of the crude reaction mixture showed the presence of **1c** (*m*/*z* = 117 [M – 1]$^-$).

Supporting Information (see footnote on the first page of this article): 1H and 13C NMR spectra of compounds **1d**, **1f** and **4b**–**4f**, and ^{31}P NMR spectrum of **1f**.

Acknowledgments

Dr. Elena Trogu is acknowledged for carrying out preliminary experiments. The authors thank the Italian Ministero dell'Università e della Ricerca (MIUR) (project: FIRB 2011 prot., grant number RBAP11ETKA) and the Ente Cassa di Risparmio di Firenze for financial support. Maurizio Passaponti (Università di Firenze) is acknowledged for technical support.

[1] For its serendipitous discovery, see: H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–164.

[2] For its first-time production in isolable quantities (milligrams), see:W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354–358.

[3] For its preparation in macroscopic amounts (grams), see: a) J. B. Howard, J. T. McKinnon, Y. Makarovsky, A. L. Lafleur, M. E. Johnson, *Nature* **1991**, *352*, 139–141; b) J. B. Howard, J. T. McKinnon, M. E. Johnson, Y. Makarovsky, A. L. Lafleur, *J. Phys. Chem.* **1992**, *96*, 6657–6662; c) K.-H. Homann, *Angew. Chem. Int. Ed.* **1998**, *37*, 2434–2451; *Angew. Chem.* **1998**, *110*, 2572.

[4] For the large-scale production of highly pure [60]fullerene (kilograms), see: a) J.-F. Tremblay, *Chem. Eng. News* **2003**, *81*, 13–14; b) K. Nagata, E. Dejima, Y. Kikuchi, M. Hashiguchi, *Org. Process Res. Dev.* **2005**, *9*, 660–662; c) M. Hashiguchi, K. Nagata, K. Tanaka, Y. Matsuo, *Org. Process Res. Dev.* **2012**, *16*, 643–646.

[5] For some pioneering works, see: a) T. Suzuki, Q. Li, K. C. Khemani, F. Wudl, Ö. Almarsson, *Science* **1991**, *254*, 1186–1188; b) C. Bingel, *Chem. Ber.* **1993**, *126*, 1957–1959; c) M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.

[6] For reactions that occur on the fullerene surface but are not observed with standard alkenes, see, as examples: a) N. Martín, M. Altable, S. Filippone, A. Martín-Domenech, R. Martínez-Álvarez, M. Suarez, M. E. Plonska-Brzezinska, O. Lukoyanova, L. Echegoyen, *J. Org. Chem.* **2007**, *72*, 3840–3846; b) W. Zhang, T. M. Swager, *J. Am. Chem. Soc.* **2007**, *129*, 7714–7715; c) G.-W. Wang, X.-P. Chen, X. Cheng, *Chem. Eur. J.* **2006**, *12*, 7246–7253; d) T. Oshima, H. Kitamura, T. Higashi, K. Kokubo, N. Seike, *J. Org. Chem.* **2006**, *71*, 2995–3000.

[7] a) A. Hirsch, M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, Germany, **2005**; b) D. M. Guldi, N. Martín (Eds.), *Fullerenes: From Synthesis to Optoelectronic Properties*, Kluwer Academic Publishers, Dordrecht, The Netherlands, **2002**; c) R. Taylor, *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*, Imperial College Press, London, **1999**.

[8] a) D. M. Guldi, F. Zerbetto, V. Georgakilas, M. Prato, *Acc. Chem. Res.* **2005**, *38*, 38–43; b) D. Bonifazi, O. Enger, F. Diederich, *Chem. Soc. Rev.* **2007**, *36*, 390–414; c) J. L. Delgado, M. A. Herranz, N. Martín, *J. Mater. Chem.* **2008**, *18*, 1417–1426; d) B. C. Thompson, J. M. Fréchet, *Angew. Chem. Int. Ed.* **2008**, *47*, 58–77; *Angew. Chem.* **2008**, *120*, 62; e) D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski, N. Martín, *Chem. Soc. Rev.* **2009**, *38*, 1587–1597; f) A. M. López, A. Mateo-Alonso, M. Prato, *J. Mater. Chem.* **2011**, *21*, 1305–1318.

[9] See, for examples: a) ref.[6b]; b) I. Guryanov, F. M. Toma, A. Montellano López, M. Carraro, T. Da Ros, G. Angelini, E. D'Aurizio, A. Fontana, M. Maggini, M. Prato, M. Bonchio, *Chem. Eur. J.* **2009**, *15*, 12837–12845.

[10] a) R. Taylor, D. R. M. Walton, *Nature* **1993**, *363*, 685–693; b) E. N. Karaulova, E. I. Bagrii, *Russ. Chem. Rev.* **1999**, *68*, 889–908; *Usp. Khim.* **1999**, *68*, 979–998; c) N. Martín, M. Altable, S. Filippone, A. Martín-Domenech, *Synlett* **2007**, 3077–3095; d) P. A. Troshin, R. N. Lyubovskaya, *Russ. Chem. Rev.* **2008**, *77*, 305–349; *Usp. Khim.* **2008**, *77*, 323–369.

[11] M. A. Yurovskaya, I. V. Trushkov, *Russ. Chem. Bull.* **2002**, *51*, 367–443; *Izv. Akad. Nauk Ser. Khim.* **2002**, 343–413.

[12] For 1,3-dipolar cycloadditions, see: M. A. Yurovskaya, A. A. Ovcharenko, *Chem. Heterocycl. Compd.* **1998**, *34*, 261–266; *Teor. Eksp. Khim. Khim. Geterotsikl. Soedin.* **1998**, 291–297.

[13] A. Hirsch, *Synthesis* **1995**, 895–913.

[14] For first examples, see: a) M. S. Meier, M. Poplawska, *J. Org. Chem.* **1993**, *58*, 4524–4525; b) H. Irngartinger, C. M. Köhler, U. Huber-Patz, W. Krätschmer, *Chem. Ber.* **1994**, *127*, 581–584; for stable nitrile oxides, see: c) V. N. Drozd, V. I. Sokolov, F. M. Stoyanovich, *Dokl. Akad. Nauk* **1994**, *339*, 52–54; d) M. S. Meier, D. J. Rice, C. Thomas, V. Majidi, R. Pogue, M. Povlawska, *Mater. Res. Soc. Simp. Proc.* **1995**, *359*, 369–372.

[15] For selected examples, see: a) H. Irngartinger, A. Weber, T. Escher, *Liebigs Ann.* **1996**, 1845–1850; b) H. Irngartinger, P. W. Fettel, *Tetrahedron* **1999**, *55*, 10753–10760; c) B. Illescas, J. Rifé, R. M. Ortuño, N. Martín, *J. Org. Chem.* **2000**, *65*, 6246–6248; d) H. Irngartinger, A. Weber, T. Escher, *Eur. J. Org. Chem.* **2000**, 1647–1651; e) T. Da Ros, M. Prato, *J. Org. Chem.* **2000**, *65*, 4289–4297.

[16] M. Ohno, A. Yashiro, S. Eguchi, *Synlett* **1996**, 815–816.

[17] For complete fullerene solubility in common and unusual solvents, see: a) R. F. Ruoff, D. S. Tse, P. Malhotra, D. C. Lorents, *J. Phys. Chem.* **1993**, *97*, 3379–3383; b) R. G. Makitra, R. E. Pristanskii, R. I. Flyunt, *J. Gen. Chem.* **2003**, *73*, 1227–1232; *Zh. Obshch. Khim.* **2003**, *73*, 1299–1304.

[18] J. K. Sørensen, J. Fock, A. H. Pedersen, A. B. Petersen, K. Jennum, K. Bechgaard, K. Kilsa, V. Geskin, J. Cornil, T. Bjørnholm, M. Brøndsted Nielsen, *J. Org. Chem.* **2011**, *76*, 245–263.

[19] The generation of nitrile oxide from nitro compounds has rarely been reported, see, for example, ref.[14a].

[20] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; *Angew. Chem.* **2001**, *113*, 2056.

[21] a) L. Cecchi, F. De Sarlo, F. Machetti, *Tetrahedron Lett.* **2005**, *46*, 7877–7879; b) F. Machetti, L. Cecchi, E. Trogu, F. De Sarlo, *Eur. J. Org. Chem.* **2007**, 4352–4359.

[22] L. Cecchi, F. De Sarlo, F. Machetti, *Synlett* **2007**, 2451–2453.

[23] L. Cecchi, F. De Sarlo, F. Machetti, *Chem. Eur. J.* **2008**, *14*, 7903–7912.

[24] E. Trogu, C. Vinattieri, F. De Sarlo, F. Machetti, *Chem. Eur. J.* **2012**, *18*, 2081–2093.

[25] L. Guideri, F. De Sarlo, F. Machetti, *Chem. Eur. J.* **2013**, *19*, 665–677.

[26] F. De Sarlo, F. Machetti, *Condensation of Primary Nitro Compounds to Isoxazole Derivatives: Stoichiometric to Catalytic*, in: *Methods and Applications of Cycloaddition Reactions in Organic Syntheses* (Ed.: N. Nishiwaki), Wiley, New York, **2014**, p. 205–222.

[27] For recent applications, see: a) J. Chau, S. Xu, M. A. Ciufolini, *J. Org. Chem.* **2013**, *78*, 11901–11910; b) S. F. Nielsen, D. R. Greve, G. Grue-Sùerensen, C. Ryttersgaard, S. C. Shou, A. G. Sams, WO2012 003829; *Chem. Abstr.* **2012**, *156*, 148477; c) D. J. Parks, W. H. Parsons, R. W. Colburn, S. K. Meegalla, S. K. Ballentine, C. R. Illig, N. L. Y. Qin, T. L. Hutchinson, M. L. Lubin, D. Stone, J. F. Baker, C. R. Schneider, J. Ma, B. P. Damiano, C. M. Flores, M. R. Player, *J. Med. Chem.* **2011**, *54*, 233–247; d) M. Brasholz, S. Saubern, G. P. Savage, *Aust. J. Chem.* **2011**, *64*, 1397–1401; e) M. R. Player, D. J. Parks, W. Parsons, S. K. Meegalla, C. R. Illig, S. K. Ballentine, WO2010 045166; *Chem. Abstr.* **2010**, 152, 470455; f) G. Griffioen, T. Van Dooren, V. Rojas de La Palma, K. Shelley, A. Marchand, S. Allasia, A. Kilonda, P. Chaltin, WO2010 142801; *Chem. Abstr.* **2011**, 154, 64628; g) P. Quadrelli, B. Bovio, A. Piccinini, P. Caramella, F. De Sarlo, F. Machetti, *Tetrahedron* **2009**, *65*, 10679–10684; h) G. Cremonesi, C. La Rosa, P. Dalla Croce, F. Fontana, C. Fiorelli, *Tetrahedron: Asymmetry* **2008**, *19*, 2850–2855.

[28] M. Ohno, A. Yashiro, Y. Tsunenishi, S. Eguchi, *Chem. Commun.* **1999**, 827–828.

[29] E. Trogu, F. De Sarlo, F. Machetti, *Chem. Eur. J.* **2009**, *15*, 7940–7948.

[30] For examples of nitroethane-conjugated addition to electron-poor olefins, see: a) O. von Schickh, *Angew. Chem.* **1950**, *62*, 547–556; b) S. Kambe, H. Yasuda, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2549–2551; c) D. W. Chasar, *Synthesis* **1982**, *10*, 841–842; d) S. G. Zlotin, A. V. Bogolyubov, G. V. Kryshtal, G. M. Zhdankina, M. I. Struchkova, V. A. Tartakovsky, *Synthesis* **2006**, *22*, 3849–3854; e) J. M. Patterson, M. W. Barnes, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2715–2716.

[31] A. Corsico Coda, G. Desimoni, A. Gamba, G. Invernizzi, P. P. Righetti, P. F. Seneci, G. Tacconi, *Gazz. Chim. Ital.* **1985**, *115*, 111–118.

[32] L. Cecchi, F. De Sarlo, F. Machetti, *Eur. J. Org. Chem.* **2006**, 4852–4860.

[33] a) O. G. Sinyashin, I. P. Romanova, F. R. Sagitova, V. A. Pavlov, V. I. Kovalenko, Y. V. Badeev, N. M. Azancheev, A. V. Ilya-

sov, A. V. Chernova, I. I. Vandyukova, *Mendeleev Commun.* **1998**, *8*, 79–81; b) L. V. Ermolaeva, V. E. Kataev, S. I. Strobykin, A. P. Timosheva, V. I. Kovalenko, I. P. Romanova, O. G. Sinyashin, *Izv. Akad. Nauk Ser. Khim.* **2002**, *51*, 593–601.

[34] a) K. A. Petrov, V. A. Chauzov, N. N. Bogdanov, I. V. Pastukhov, *J. Gen. Chem. USSR* **1974**, 1617; *Zh. Obshch. Khim.* **1974**, *44*, 1649; b) A. A. Neimysheva, S. S. Muratov, E. V. Smirnov, L. M. Solntseva, *J. Gen. Chem. USSR* **1976**, 942; *Zh. Obshch. Khim.* **1976**, *46*, 940.

[35] A. V. Chemagin, N. V. Yashin, Y. K. Grishin, T. S. Kuznetsova, N. S. Zefirov, *Synthesis* **2010**, 259–266.

[36] For another example of base-catalysed oxidative cycloadditons to [60]fullerene, see: M. Ohno, A. Yashiro, S. Eguchi, *Chem. Commun.* **1996**, 291–292.

[37] The reaction was successful with other non-activated nitro compounds such as benzylnitromethane and 4-nitrobutanoates but failed with nitromethane.

[38] The excess of the activated nitro compound with a pK_a similar to that of AcOH provides acidity when the base is catalytic.

[39] E. L. Carpenter, H. S. Davis, *J. Appl. Chem.* **1957**, *7*, 671–676.

[40] A. P. Krapcho, C. S. Kuell, *Synth. Commun.* **1990**, *20*, 2559–2564.

[41] R. G. Harvey, T. C. Myers, H. I. Jacobson, E. V. Jensen, *J. Am. Chem. Soc.* **1957**, *79*, 2608–2612.

[42] a) A. Michaelis, R. Kaehne, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1048–1055; b) A. E. Arbuzov, *Ph. D. Dissertation*, St. Petersburg, **1905**; c) A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.* **1906**, *38*, 687 (*Chem. Zentrabl.* **1906**, *2*, 1639).

[43] B. A. Arbuzov, *Pure Appl. Chem.* **1964**, *9*, 307–336.

[44] S. S. Novikov, L. I. Khmel'nitskii, T. S. Novikova, *Russ. Chem. Bull. Int. Ed.* **1965**, *14*, 90–95; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 103–110.

[45] R. Ballini, G. Bosica, *Eur. J. Org. Chem.* **1998**, 355–357.

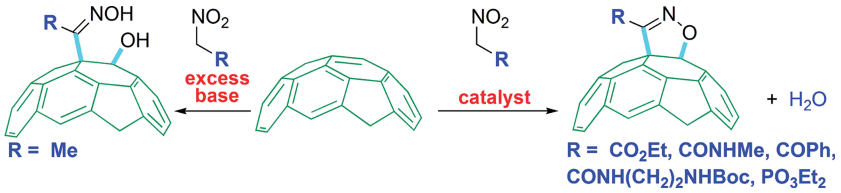
[46] S. G. Zlotin, A. V. Bogolyubov, G. V. Kryshtal, G. M. Zhdankina, M. I. Struchkova, V. A. Tartakovsky, *Synthesis* **2006**, *22*, 3849–3854.

[47] For an interesting and detailed description of the NMR spectra of **1f**, see: L. T. Byrne, V. Ferro, S. Stevenson, R. V. Stick, *Magn. Reson. Chem.* **1994**, *32*, 749–752.

[48] No furazan side-product was observed, see: L. Cecchi, F. De Sarlo, C. Faggi, F. Machetti, *Eur. J. Org. Chem.* **2006**, 3016–3020.

Received: July 25, 2014
Published Online: ■

EurJOC European Journal of Organic Chemistry



Isoxazolino[60]fullerenes have been synthesised directly from activated nitro compounds by a catalytic process (DABCO or NMP/[Cu]). The protocol is simple, versatile and tolerant towards diverse functional groups. A mechanism is proposed to explain both this condensation and the known addition with nitroethane in excess base.

Keywords: Cycloaddition / Condensation reactions / Fullerenes / Copper / Nitro compounds

