Cycloaddition of phosphorylnitrile oxide to C_{60}

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The reaction of (diisopropoxyphosphoryl)nitrile oxide with C_{60} leads to mono- and diadducts, which are characterized by ^{1}H, ^{13}C, ^{31}P NMR, IR and UV-VIS spectroscopy as isoxazoline derivatives of fullerene; the addition takes place across a 6,6 ring junction.

Fullerenes are known[1] to undergo cycloaddition with a variety of dipolar reagents. However, data concerning the use of organophosphorus reagents in these reactions are, to our knowledge, absent and therefore the influence of any phosphorus-containing fragment in any dipolarophile on these reactions is unknown. We propose here for the first time the use of a phosphorus-containing dipolarophile — phosphorylnitrile oxides — for the functionalisation of fullerene. It was interesting to study the influence of the phosphoryl fragment in the dipolarophile on the regiochemistry of cycloaddition to fullerene.

Phosphorylnitrile oxides are synthesized by the treatment of oximes of (dialkoxyphosphoryl)carbonylhalides with triethylamine in organic solvent at low temperature.[2] They may be used in reactions with compounds possessing unsaturated bonds, either after removal of triethylamine hydrochloride or *in situ*. To study the functionalisation of fullerene we used both methods, which led to the same reaction products.

In the first case the interaction of fullerene (1 equiv.) with (diisopropoxyphosphoryl)nitrile oxide (2 equiv.) was carried out in toluene at –20 °C with constant stirring. In the second case triethylamine was added to the mixture of fullerene with oxime of (diisopropoxyphosphoryl)carbonyl chloride at –200 °C. After 5 h the reaction flasks were gradually heated up to room temperature. HPLC analysis of the crude reaction mixtures indicated that in both cases three products were formed. The relative ratio of these products in the reaction mixture changed depending on the reaction time (Figure 1). The products and unreacted fullerene were separated by column chromatography on silica gel. The reaction mixture before chromatography was washed with water to remove triethylamine hydrohloride, when the reaction was carried out *in situ*. All three products were isolated, compound **1** (10% yield) as a dark-brown powder and compounds **2** and **3** (25% and 21%, respectively) both as orange–brown powders. The structure of these products was studied by ^{1}H, ^{13}C, ^{31}P NMR, IR and UV-VIS spectroscopy and their composition was determined by elemental analysis.

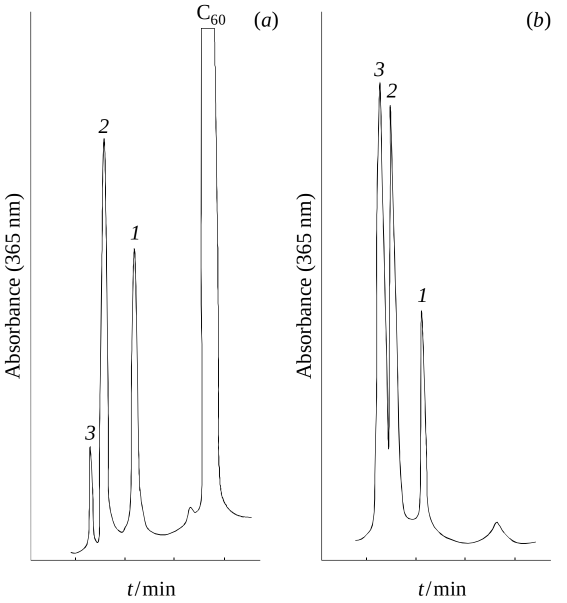
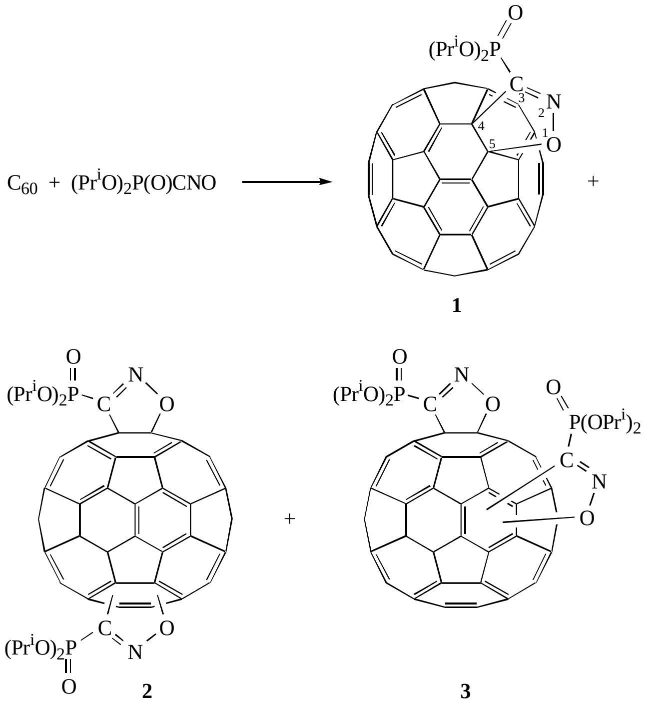


Figure 1 HPLC chromatograms (C_{18} reversed-phase column, 60% toluene/40%-Pr^{i}OH as mobile phase, 0.3 ml min^{-1}, detection at 365 nm by UV absorbance) of the crude reaction mixture: (*a*) 3 h, –20 °C; (*b*) 40 h, room temperature.



1

2
mixture of isomers
trans-1, *trans*-2, *trans*-3, *trans*-4

3
mixture of isomers
e, *cis*-2, *cis*-3

The elemental analysis data for compound **1** shows that it is a monoadduct of C_{60} and nitrile oxide.[†] This product has one ^{31}P NMR signal (162 MHz, $CDCl_3$) at δ –0.98. Its ^{1}H NMR spectrum (250 MHz, $CDCl_3$) includes two doublets at δ 1.46 (6H, 2CH$_3$, Pr^i, $^3J_{HH} = 5$ Hz) and at δ 1.43 (6H, 2CH$_3$, Pr^i, $^3J_{HH} = 5$ Hz) and a multiplet at δ 5.09–4.96 (2H, 2OCH, Pr^i), which suggests that the isopropoxy groups at the phosphorus atom are not equivalent.

The IR (KBr) spectrum of compound **1** shows $\nu_{C_{60}}$ 526 cm^{-1}, $\nu_{P=O}$ 1262, ν_{P-O} 998 and $\nu_{C=N}$ 1572 cm^{-1}. It should be noted that the ^{1}H, ^{31}P NMR and IR spectral data are in agreement with the spectra of other compounds containing diisopropoxyphosphoryl-substituted isoxazoline fragments.[2] The UV-VIS spectrum of a yellow solution of compound **1** in hexane exhibits λ_{max} at 215 nm (lg ε = 4.77 dm^3 mol^{-1} cm^{-1}), 253 (4.73) and 312 (4.22) due to fullerene, which is shifted to the low wavelength region relative to the spectrum of pure C_{60}, together with a weak but sharp peak at 424 nm and a weak, broad band at 458 nm. The peak at 424 nm is reported to be highly diagnostic of closed 6,6-bridged fullerene derivatives.[3] The proposed structure of **1** as a monoadduct corresponds to the C_s

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[†] Compound **1**. Found (%): C, 87.38; H, 2.92; N, 1.46; P, 3.12. Calc. for $C_{67}H_{14}NO_4P\cdot(C_6H_5CH_3)\cdot(C_6H_{14})_{0.5}$ (%): C, 87.01; H, 2.73; N, 1.32; P 2.92.

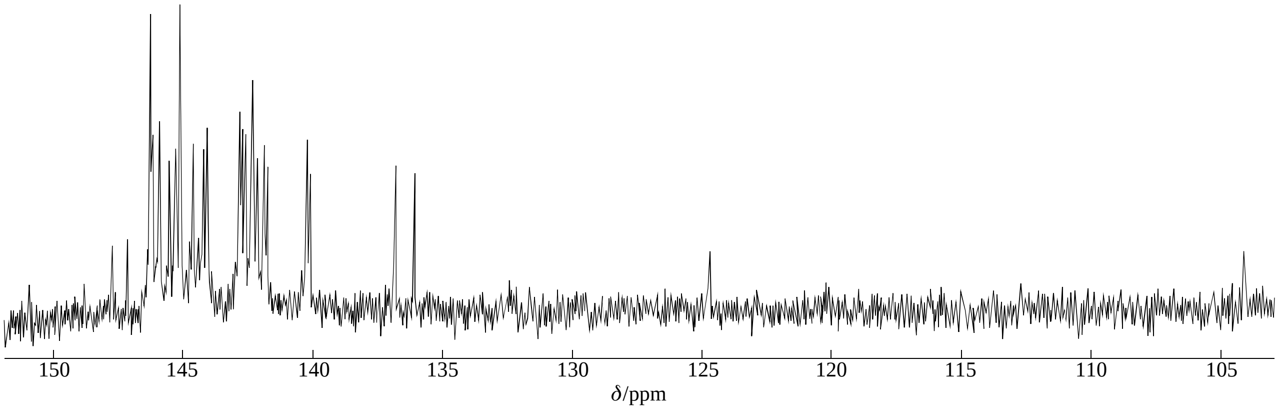

Figure 2 ^{13}C NMR spectrum of **1** ($CDCl_3$) between δ 105 and 150.

symmetry of the molecule. In the fullerene region (δ 75 and 150) the ^{13}C NMR spectrum of **1** should contain 30 sp^2 carbon signals and two sp^3 carbon signals, but only 28 sp^2 carbon signals are observed (Figure 2) due to the accidental overlap of signals, and two signals at δ 124.7 and 104.1, corresponding to C-4 and C-5.[‡] The sp^3 carbon signals in the ^{13}C NMR spectra of monoadducts of organonitrile oxides with C_{60} were observed at δ 75 and 110.[4–6] The downfield shift of these signals in the spectrum of compound **1** is probably associated with the electron-withdrawing influence of the phosphoryl fragment. The same position of the sp^3 signals of the fullerene fragment (δ 120.62 and 94.19) was observed in the spectrum of the product of reaction between C_{60} and diazomethane.[7] It should be noted that coupling constants between the carbon of the fullerene fragment and the phosphorus atom have not been detected. Probably these have small values. The ^{13}C NMR spectrum of compound **1** shows a doublet at δ 149.8 with $^1J_{PC}$ of 216.1 Hz corresponding to the carbon of the C=N bond in the isoxazoline ring.[2] The ^{13}C NMR spectral data are in agreement with the proposed structure **1** as a monoadduct of fullerene and phosphorylnitrile oxide. The structure of **1** is analogous to the structure of the organic isoxazoline monoadduct of C_{60}.[4–6]

It should be noted that all published papers concerning the reactions of organonitrile oxides with fullerene suggest the formation of only monoadducts,[4,5] and although in the reaction of C_{60} with 2-RSO_2-benzonitrile oxides diadducts,[6] were isolated, they were not characterized. Moreover, the yields of these monoadducts were low and the type of other products was not clear.

Elemental analysis of products **2** and **3** show that they are diadducts of phosphorylnitrile oxide and fullerene.[§] Their IR spectra contain the same absorption bands as the spectrum of compound **1**, but the relative intensities of these bands are different. These bands, which are typical of the fullerene fragment, have much lower intensities in the spectra of **2** and **3**, relative to the spectrum of **1**. The ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of adduct **2** contains four signals, at δ –0.52, –0.84, –1.25 and –1.94 (intensity ratio 22:20:3:2, respectively) and the spectrum of **3** contains three signals, at δ –0.51, –1.58 and –2.03 (10:1:1).

It is known[1] that nine positions are available for a second addition to a monoadduct of C_{60}. The second addition to these positions leads, in accordance with Hirsch's nomenclature,[1] to four *trans*-, two equatorial- and three *cis*-isomers. When seven isomers of the diadducts of $C_{62}(COOEt)_4$[8] and five isomers of $C_{60}[OsO_4(t\text{-bupy})_2]_2$[9] were separated by preparative HPLC, firstly *trans*-, then equatorial- and then finally *cis*-isomers eluted from the column. These diadducts were identified as products of addition exclusively to the 6,6-ring double bonds of C_{60}. According to these data, together with the number and relative intensities of the signals in the ^{31}P NMR spectra of products **2** and **3**, it may be assumed that product **2** is a mixture of *trans*-isomers, and product **3** is a mixture of equatorial- and *cis*-isomers of C_{60} and nitrile oxide diadduct. The ^{1}H and ^{13}C NMR spectra of these products indicate that they are a mixture of isomers. The ^{1}H NMR spectra of products **2** and **3** show broad signals at δ 1.40 and 5.00, corresponding to the protons of the methyl and methine groups of the diisopropoxyphosphoryl fragments. The ^{13}C NMR spectra show three groups of lines in the region corresponding to a phosphoryl substituent [at δ 23.0–24.5 (CH_3), 73.5–74.5 (CH)], the isoxazoline ring and fullerene fragments (at δ 105–150). The UV-VIS spectrum of product **2** shows λ_{max} at 222 (4.99), 246 (4.96) and a shoulder at 310 nm (4.51). In the spectrum of product **2** the first and second bands are very broad and blue shifted in comparison with the spectra of C_{60} and monoadduct **1**. In the spectrum of product **3** the first and second bands overlap and give one broad band at 226 nm (4.83) with a shoulder at 312 nm (4.32). The spectra of products **2** and **3** between 500 and 700 nm are identical to that of C_{60} and monoadduct **1**, but are much less structured. The increase in the band widths and their shifts relative to that in the spectrum of C_{60} and monoadducts are typical for diadducts.[10]

In conclusion, these data show that reaction of (diisopropoxyphosphoryl)nitrile oxide with C_{60} leads to mono- and diadducts. It is interesting to note that diadducts are the main products in our reaction, contrary to the published data, in which the main products are monoadducts.[4–6] This seems to be an important feature of the influence of the phosphoryl fragment. Since these are the first C_{60} phosphorus-containing isoxazoline derivatives, mono- and diadducts may serve as the starting point from which to obtain new derivatives of fullerene, and may also be useful for biological investigations.

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[‡] Compound **1**. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) δ: 104.12 (C_{60}, 1C), 124.71 (C_{60}, 1C), 136.02 (C_{60}, 2C), 136.77 (C_{60}, 2C), 140.00 (C_{60}, 2C), 140.19 (C_{60}, 2C), 141.72 (C_{60}, 2C), 141.85 (C_{60}, 2C), 142.12 (C_{60}, 2C), 142.25 (C_{60}, 2C), 142.29 (C_{60}, 2C), 142.34 (C_{60}, 2C), 142.59 (C_{60}, 2C), 142.69 (C_{60}, 2C), 142.77 (C_{60}, 2C), 142.80 (C_{60}, 2C), 144.05 (C_{60}, 2C), 144.08 (C_{60}, 2C), 144.20 (C_{60}, 2C), 144.61 (C_{60}, 2C), 145.09 (C_{60}, 4C), 145.25 (C_{60}, 2C), 145.53 (C_{60}, 2C), 145.87 (C_{60}, 2C), 145.90 (C_{60}, 2C), 146.14 (C_{60}, 2C), 146.19 (C_{60}, 2C), 146.23 (C_{60}, 4C), 147.14 (C_{60}, 1C), 147.72 (C_{60}, 1C), 149.80 (d, 1C, C=N, $^1J_{PC}$ = 216.1 Hz).

[§] Compound **2**. Found (%): P, 5.06. Calc. for $C_{74}H_{28}N_2O_8P_2\cdot(C_6H_5CH_3)$ (%): P, 5.03.

Compound **3**. Found (%): P, 5.76. Calc. for $C_{74}H_{28}N_2O_8P_2$ (%): P, 5.46.

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