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Synthesis of Hydrophosphorylated Fullerene under Neutral Conditions

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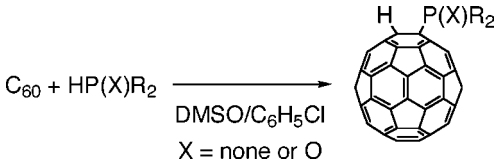
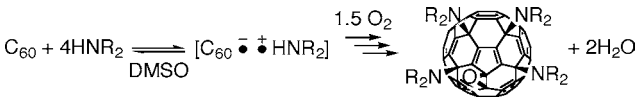
ABSTRACT



A variety of phosphorous compounds such as secondary phosphines, phosphine oxides, phosphinates, and phosphonates undergo addition to [60]fullerene in DMSO/C_6H_5Cl without extraneous reagents to produce hydrophosphorylated fullerene derivatives in moderate to high yield.

The recently reported oxoamination reaction of [60]fullerene (C_{60}) (Scheme 1) is rather striking as a method for chemical

Scheme 1



modification of carbon clusters in that the procedure is extremely simple (just stir two reactants together under atmospheric pressure of molecular oxygen), scalable, and high-yielding and produces water as the only side product.[1,2] The key driving force is the formation of a radical ion pair in the presence of dimethyl sulfoxide (DMSO). Following this lead, we examined the reaction of an isoelectronic secondary phosphine to gain simple access to phosphorous fullerene derivatives. Here we report the synthesis of hydrophosphorylated C_{60} achieved just by mixing C_{60} and $R_2P(O)H$ or R_2PH in DMSO/C_6H_5Cl without extraneous reagents (Table 1). The addition of the P−H bond to C_{60} takes place exclusively in a 1,2-manner in yields moderate but comparable (31−60%; 53−89% based on conversion of C_{60}) to that achieved previously by more complex and wasteful methods.[3,4]

The experimental procedure of the new hydrophosphorylation reaction is very simple and can be carried out on a gram scale: an equimolar mixture of C_{60} (1.00 g) and $HP(O)Ph_2$ was stirred in 20% DMSO/C_6H_5Cl under air for 48 h. After aqueous workup, silica gel chromatography (C_6H_5Cl then 10% ethyl acetate/toluene) gave 738 mg of the 1,2-addition compound **3**, $Ph_2P(O)C_{60}H$ (54%; 75% based on recovery of C_{60}, which was 28%, Table 1, entry 1). The use of excess phosphorous reagent or longer reaction time did not improve the yield because of the formation of polar side

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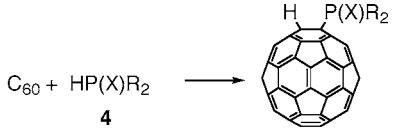
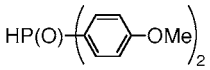
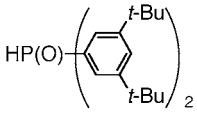
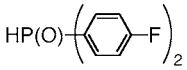
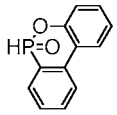
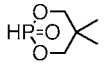
Table 1. Hydrophosphorylation of C_{60}



entry	4	eq	solvent[a,b]	temp/time	yield[c]
1	$HP(O)Ph_2$	1.0	A	rt/48 h	54% (75%)
2	$HP(O)Ph_2$	1.0	B	rt/6 h	60% (86%)
3	$HP(O)Ph_2$	1.0	C	rt/96 h	47% (71%)
4	$HPPh_2$	6.0	A	rt/12 h	57%[d] (57%)
5		1.0	A	rt/48 h	50% (81%)
6		1.0	A	rt/18 h	55% (89%)
7		1.0	A	rt/60 h	37% (84%)
8	HP(O)MePh	1.0	A	rt/31 h	31% (74%)
9	HP(O)PhOEt	12	A	80 °C/24 h	46% (55%)
10		12	A	45 °C/18 h	50% (54%)
11	$HP(O)(OMe)_2$	20	B	120 °C/8 h	40% (53%)
12		20	A	120 °C/30 h	43% (56%)

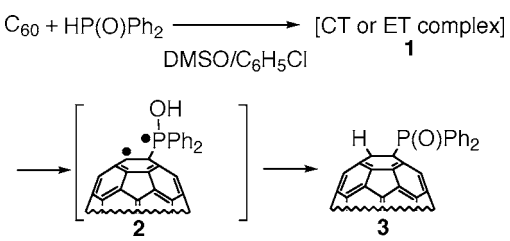
[a] Solvents: (A) 20% DMSO/C_6H_5Cl, (B) 20% HMPA/C_6H_5Cl, (C) 20% DMF/C_6H_5Cl. [b] All the reactions were carried out in the dark. [c] Isolated yield. Yield in parentheses shows yield based on conversion of C_{60}. See Supporting Information for details. [d] Product was obtained as phosphine oxide **3** after air-oxidation.

products, likely, multiple addition products. The use of DMSO was mandatory as in the case of the oxoamination reaction, whereas the role of chlorobenzene is just to dissolve C_{60}. Hexamethylphosphoramide (HMPA) and dimethylformamide (DMF) also accelerate the reaction; the reaction rate and the product yield increased in an order of DMF < DMSO < HMPA (Table 1, entries 1−3). This order follows that of the donor number of the solvent,[5] similarly to the oxoamination and reduction of C_{60}.[1,6] Carcinogenic HMPA is not an ideal solvent, and DMF does not offer any practical merit over DMSO. The 1,2-monoaddition reaction can be performed equally successfully in air and did not give any of the tetraaddition product that one may expect to form in a manner shown in Scheme 1 for the amine reaction.

Ph_2PH also undergoes addition in a 1,2-addition manner to give $Ph_2PC_{60}H$. This product, however, is exceedingly sensitive to oxidation in air owing to the photoactivity of the fullerene moiety[3] and was isolated as the corresponding phosphine oxide in 57% yield (Table 1, entry 4).

The mechanism of the reaction is uncertain at this time, since we could not detect any intermediate such as the radical ion pair that was spectroscopically observed in the amine reaction (Scheme 1). This may be due to either low concentration, very short lifetime, or the absence of such a species. Nonetheless, the key role of DMSO makes us believe that the reaction takes place through a charge transfer (CT) or an electron transfer (ET) complex by interaction between phosphine oxide and C_{60} (Scheme 2). One may also consider

Scheme 2



that the reaction takes place via a tautomeric form (R_2POH) rather than the phosphine oxide form ($R_2P(O)H$). The complex then undergoes C−P bond formation to generate a diradical that may have a structure **2**,[7] which finally produces the product **3**. We defer further mechanistic discussion until we obtain more experimental data pertaining to the reaction pathway.

The contrast in the reactivity between nitrogen and phosphorous compounds merits some comments: a secondary amine reacts with C_{60} to generate the radical ion pair and does not lead to C−N bond formation (Scheme 1). The C−N bond formation takes place only in the presence of molecular oxygen, which oxidizes the fullerene radical anion and produces the oxoamination product. We surmise that the exclusive monophosphorylation in Scheme 2 is the result of rapid isomerization of the second intermediate **2** to the final product **3** that does not take place in the case of a secondary amine.

The scope of reaction is summarized in Table 1. The hydrophosphorylated fullerene was obtained in 50%, 55%, and 37% yield, respectively, with the diarylphosphine oxide bearing alkoxy-, bulky alkyl-, and fluoro-substituents (Table 1, entries 5−7). We also obtained the corresponding adduct

(5) Donor number of each solvent is as follows: HMPA = 38.8 kcal/mol, DMSO = 29.8 kcal/mol, and DMF = 26.6 kcal/mol. See: Reichardt, C. *Solvents and Solvents Effects in Organic Chemistry*, 3rd ed; Wiley: Weinheim, 2003.

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from the reaction of methylphenylphosphine oxide (entry 8). Phosphinate and phosphonate were less reactive and did not undergo the hydrophosphorylation reaction under the same temperature condition as the one used for phosphine oxide. However, both phosphinate and phosphonate reacted with C_{60} at elevated temperature.[8] Phosphinate gave the corresponding hydrophosphorylated fullerene, when excess phosphinate and C_{60} were heated in DMSO/C_6H_5Cl (Table 1, entries 9 and 10). The reaction of phosphonate was slower and, at 120 °C, gave the corresponding adduct in moderate yield (Table 1, entries 11 and 12). The reaction of the phosphonate in HMPA also took place faster than in DMSO.

Phosphorous compounds bearing fullerene moiety have attracted considerable recent interest for their chemistry,[3,4] bioactivity,[9] and optical properties.[10] To meet such needs, a variety of synthetic methods have been reported. Among these, the method described in this Letter is unique for its simplicity and scalability and will find use, for instance, in the studies of amphiphilic fullerene[11] and carbon nanotubes.[12]

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Supporting Information Available: Experimental procedures and NMR and MS spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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