Base-catalysed oxidative [3+2]cycloaddition reaction of [60]fullerene with β-dicarbonyl compounds

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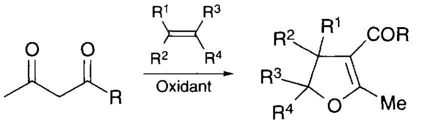
The ambiphilic nature of β-keto esters and β-diketones allows cycloaddition to C_{60} in the presence of piperidine to give dihydrofuran-fused C_{60} derivatives *via* oxidative cyclization complimentary to the concerted process.

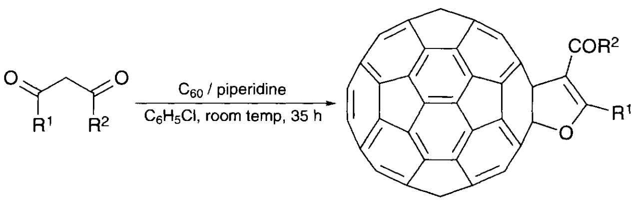
Cycloaddition is one of the most reliable methodologies for functionalization of fullerenes as they possess a low LUMO level and addition occurs selectively across 6,6-ring junctions.[1] Heterocyclic five-membered ring fusions to C_{60} have been achieved mainly by concerted 1,3-dipolar cycloaddition including diazoalkane,[2] nitrile oxide,[3] nitrile imine,[4] azomethine ylide[5] and cyclic dipole,[6] and by Pd-catalysed [3+2]cycloaddition,[7] while carbocyclic fusion has been performed using a trimethylenemethane-like intermediate.[8]

In addition to these cyclization methods, we have now found novel formal [3+2]cycloaddition of β-dicarbonyl compounds; their ambiphilic nature allowed the reaction with C_{60} in the presence of a base at both ends of the methylene carbon and carbonyl oxygen to give a dihydrofuran-fused C_{60} derivative after spontaneous oxidation. This type of cycloaddition has been known to occur with normal olefins if a metallic oxidant promotes the reaction (Scheme 1).[9]

The reaction with C_{60}, in contrast, involves facile and concomitant oxidation without the aid of an oxidizing reagent and therefore constitutes a method peculiar to cycloaddition to C_{60} and complementary to the concerted process. In fullerene chemistry, several examples of the smooth oxidative addition have been reported in the reaction with diamines.[10] Grignard reagents[11] and diborane[12] (followed by H_2O_2 oxidation).



Scheme 1



1 2

	R¹	R²	Yield (%)[a] (% recovered C_{60})
a	Me	OCMe₃	59 (40)
b	Me	OEt	60 (45)
c	-C₆H₄O- (*ortho*)		39 (64)
d	CH₂CO₂Me	OMe	27 (54)
e	Me	Me	48 (37)
f	-(CH₂)₃-		49 (54)

[a] Based on consumed C_{60}

Scheme 2

The reaction with *tert*-butyl acetoacetate **1a** is a typical case for the formal [3+2]cycloaddition reaction of β-dicarbonyl compounds (Scheme 2). It was carried out simply by treating C_{60} with 1.5 equiv. of **1a** and 3 equiv. of piperidine in chlorobenzene at ambient temperature under a nitrogen atmosphere. During stirring (*ca.* 1.5 d), the solution changed gradually from purple to dark brown. After evaporation of the solvent and reagent under reduced pressure, the residue was subjected to silica gel chromatography to give a cycloadduct **2a** (59% yield based on consumed C_{60}) together with unreacted C_{60} (40% recovery). The product was first deduced as a 1 : 1 cycloadduct by FAB-MS measurement which indicated the molecular ion peak at *m*/*z* 876. From a mechanistic point of view, the binucleophile **1a** might give rise to cyclopropane-fused C_{60} as a result of double addition at the active methylene carbon.[13] However a methanofullerene structure was incompatible with the following IR and ^{13}C NMR data. The IR spectrum showed absorption at 1699 and 1640 cm^{-1} due to an unsaturated ester moiety. The ^{13}C NMR signals (125 MHz, CS_2–$CDCl_3$ 1 : 1) included two lines at δ 72.45 and 102.58 due to sp³-junction carbons and 30 lines at δ 135.36–148.66 due to sp²-C_{60} ring carbons,† which proved the C_s-symmetry of this molecule. The chemical shifts of the dihydrofuran ring carbons (δ 105.88 and 163.66) were consistent with those reported for 2-methyl-4,5-dihydrofuran-3-carboxylate (δ 102.9 and 166.5).[14] The ¹H NMR spectrum (500 MHz) had signals due to substituents at δ 1.53 for Buᵗ and 2.83 for Me, and the UV–VIS spectrum showed absorption at 433 nm, diagnostic of the 1 : 1 cycloadduct of C_{60} at the 6,6-junction.

Several experimental conditions were examined for the above reaction. As a base, piperidine was superior to triethylamine which did not give the expected product, and use of the base in a catalytic amount greatly decreased the yield. Ambient temperature was better than higher ones (*ca.* 60 °C) at which C_{60} was not effectively consumed. A β-diester (*e.g.* dimethyl malonate) did not react under the conditions employed for **1a**. In addition to other β-keto esters such as ethyl acetoacetate **1b**, 4-hydroxycoumarin **1c** and dimethyl acetonedicarboxylate **1d**, β-diketones such as acetylacetone **1e** and cyclohexane-1,3-dione **1f** were reactive enough to give cycloadducts **2b–f** respectively, in comparable yields (Scheme 2).

Although the mechanism is unclear at present (for example, details of the addition and oxidation steps, and the preference for the formation of five- rather than a three-membered ring), the observed formal [3+2]cycloaddition reaction provides a method of novel type of fusion to C_{60}, being useful for heterocyclization.

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Footnote

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† ^{13}C NMR data at this region: δ 135.36, 137.49, 139.35, 139.93, 141.52, 141.60, 142.34, 142.35, 142.48, 142.63, 142.74, 142.81, 142.86, 144.30,

144.57, 144.64, 144.84, 145.05, 145.22, 145.42, 145.75, 145.99, 146.05, 146.20, 146.24, 146.49, 147.36, 147.57, 148.07 and 148.66 (signals due to substituents on the dihydrofuran ring: 15.77, 28.57, 81.58 and 168.57).

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