Phosphine-catalysed [3 + 2] cycloadditions of buta-2,3-dienoates with [60]fullerene

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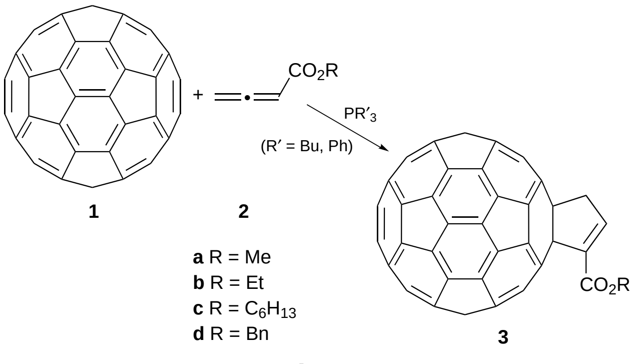
[60]Fullerene reacts with buta-2,3-dienoates in the presence of phosphine to form alkyl 3′*H*-1,2-([1′,2′]cyclopenta)-[60]fullerene-5′-carboxylates.

Cycloaddition reactions provide the most successful methodologies for the functionalization of fullerene.[1] A number of 1,3-dipoles, such as diazomethanes,[2] azides[3] and azomethine ylides[4] are known to react with [60]fullerene. Here we describe the phosphine-catalysed [3 + 2] cycloadditions of buta-2,3-dienoates with [60]fullerene. The [3 + 2] cycloadditions of buta-2,3-dienoates with electron-deficient alkenes have been reported by Zhang *et al.* recently.[5] This reaction provides a very efficient route to the synthesis of cyclopentene. Here [60]fullerene was used as the dipolarophile and the expected products were obtained with good yields (Scheme 1).

The reaction of [60]fullerene with **2a** and tributylphosphine was carried out at room temperature under nitrogen. Isolation on silica gel using toluene as eluent afforded **3a**† and unreacted [60]fullerene. The yield of **3a** was 42% (95% based on consumed [60]fullerene). For **2b**, **2c** and **2d**, the reactions were carried out at 80 °C and triphenylphosphine was used as catalyst. The yields (corrected for the recovered fullerene, shown in parentheses) for **3b**, **3c** and **3d** were 78 (81.6), 52 (89) and 88.5% (92%), respectively.

The FD-MS spectrum of **3a** gives the molecular ion peak at *m*/*z* 818 ($C_{65}H_6O_2$, 100%). In the FT-IR spectrum, the absorption bands for the alkenic and the carbonyl groups are located at 1638 and 1722 cm^{-1}, respectively. The ^1H NMR spectrum [600 MHz; CS_2–$(CD_3)_2CO$, 10 : 1] of **3a** shows three signals at δ 3.87 (3H, s, OMe), 4.61 (2H, d, J 2.64 Hz, CH_2) and 7.77 (1H, t, J 2.64 Hz, =CH). The ^{13}C NMR spectrum [150.9 MHz; CS_2–$(CD_3)_2CO$, 10 : 1] shows 35 signals in total, of which two signals are found to be overlapped. Peaks at δ 48.28, 52.09, 69.91, 72.08 and 163.13 are obviously due to the methylene group, the methoxy group, the two sp^3 carbons of the cage and the carbonyl group, respectively. The ^{13}C NMR spectrum is also consistent with the proposed structure, as C_s symmetry requires 32 signals for the fullerene skeleton. Compound **3b** is almost insoluble in solvent, and only FT-IR and ^1H NMR spectra were obtained. For **3c** and **3d**,‡ all the spectra agree the proposed structure.

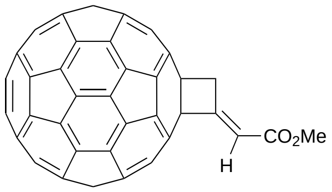


Scheme 1

Recently, the phosphine-mediated reaction of but-2-ynoates with [60]fullerene was reported by Liou *et. al*.[6] The authors declared that [2 + 2] cycloaddition product **4** was formed from the reaction of [60]fullerene with methyl but-2-ynoate. The phosphine-catalysed [3 + 2] cycloadditions of but-2-ynoates and electron-deficient alkenes have been reported in literature.[5] Both the products and intermediates of this reaction have been proved to be the same as those of the reactions of buta-2,3-dienoates. This suggested to us that compound **4** was probably the same as **3a**. In fact, the FD-MS, FTIR, ^1H NMR and ^{13}C NMR spectra of **3a** are almost identical to those of **4**.

In order to prove our assumption, compound **4** was prepared from the reaction of methyl but-2-ynoates with [60]fullerene by the procedure described by Liou. It is reasonable to conclude that compound **4** is indeed identical to **3a**, for a mixture of **3a** and **4** showed only one peak by HPLC.§ This result encouraged us to check the structure of **3a** more carefully.

The cyclopentene structure of **3a** is further substantiated by the HMQC and HMBC NMR spectra. Assignable NMR spectral data are shown in Fig. 1. In the HMQC spectrum, the alkenic proton at δ 7.77 is found to be connected to the carbon atom at δ 144.05. In the HMBC spectrum, the alkenic proton (δ 7.77) shows correlations with both of the sp^3 carbons of the fullerene cage, which indicates that there are two or three bonds between this proton and the two carbon atoms. The structure with a four-membered ring **4** is ruled out, for the alkenic proton is either three or four bonds away from the addition site; this means that the HMBC spectrum for **4** would give only one correlation peak between the alkenic proton and the addition site carbons. The reasoning which led to the four-membered



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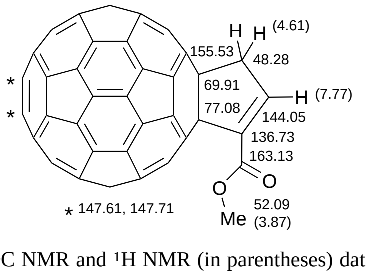
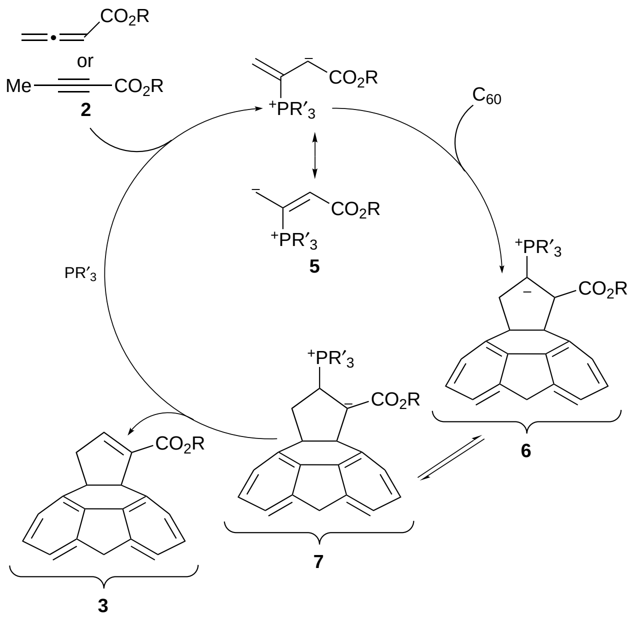


Fig. 1 ^{13}C NMR and ^1H NMR (in parentheses) data for **3a**



Scheme 2

ring structure was that Liou assigned the small coupling constant observed to an allylic coupling. In fact, in the spectra of smaller rings, the coupling constant between aliphatic and alkenic protons (CH_2–CH=C) is quite small.[7] For example, the $J_{1,5}$ of cyclopentene is 2.1 Hz.[8]

A possible mechanism for the reaction is outlined in Scheme 2. As reported by Zhang *et. al.*,[5] phosphine first reacts with buta-2,3-dienoate or but-2-ynoate to form **5**, and then a [3 + 2] cycloaddition occurs. Product **3** is given with the regeneration of phosphine.

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Footnotes

† *Spectral data* for **3a**: FTIR ν(KBr)/cm^{-1} 1722, 1638, 1428, 1328, 1240, 1188, 1116, 1090, 1000, 878, 766, 728, 575, 528; FD-MS *m*/*z* 818 ($C_{65}H_6O_2$, 100%), 720 (C_{60}, 5); ^{13}C NMR [150.9 MHz; CS_2–$(CD_3)_2CO$, 10 : 1] δ_C (number of carbon atoms) 48.28 (CH_2), 52.09 (OCH_3), 69.91 and 77.08 (sp^3-C for C_{60}), 135.05 (2), 135.96 (2), 136.73 (quaternary alkenic C), 139.61 (2), 140.69 (2), 141.98 (2), 142.43 (4, overlapped), 142.54 (2), 142.59 (2), 142.86 (2), 143.10 (2), 143.13 (2), 143.52 (2), 144.05 (=CH), 144.85 (4, overlapped), 145.51 (2), 145.60 (2), 145.64 (2), 145.72 (2), 145.94 (2), 146.37 (2), 146.43 (2), 146.55 (2), 146.68 (2), 146.72 (2), 147.61 (1), 147.71 (1), 149.01 (2), 150.34 (2), 156.53 (2), 163.13 (C=O).

‡ *Selected data* for **3c**: FD-MS *m*/*z* 889 (M$^+$ + 1 for $C_{70}H_{16}O_2$, 100%); ^{1}H NMR [600 MHz; CS_2–$(CD_3)_2CO$, 10 : 1] δ_H 0.91 (3H, t, Me), 1.33 (4H, m, CH_2CH_2), 1.40 (2H, m, CH_2), 2.00 (2H, m, CH_2), 4.24 (2H, t, OCH_2), 4.60 (2H, d, *J* 2.64 Hz, allyl–CH_2), 7.76 (1H, t, *J* 2.64 Hz); ^{13}C NMR [150.9 MHz; CS_2–$(CD_3)_2CO$, 10 : 1] δ_C 15.00, 23.73, 26.76, 29.63, 32.43, 48.19, 65.64, 70.04, 77.05, 135.05, 135.97, 136.73 (quaternary alkenic C), 139.55, 140.74, 141.94, 142.43, 142.46, 142.54, 142.60, 142.86, 143.10, 143.13, 143.52, 143.84 (=CH), 144.86, 145.52, 145.59, 145.64, 145.72, 145.91, 146.37, 146.44, 146.55, 146.68, 146.72, 147.61, 147.70, 149.06, 150.45, 156.61, 162.78. For **3d**: FD-MS *m*/*z* 894 ($C_{71}H_{10}O_2$, 100%); ^{1}H NMR [600 MHz; CS_2–$(CD_3)_2CO$, 10 : 1] δ_H 4.60 (2H, d, *J* 2.64 Hz, CH_2), 5.27 (2H, s, OCH_2), 7.23–7.28 (3H, m, arom.), 7.35 (2H, d, arom.), 7.81 (1H, t, *J* 2.64 Hz, =CH); ^{13}C NMR [150.9 MHz; CS_2–$(CD_3)_2CO$, 10 : 1] δ_C 48.26, 67.28, 69.99, 77.06, 128.94, 129.13, 135.07, 135.99, 136.05, 136.64 (quaternary alkenic C), 139.57, 140.67, 141.95, 142.42, 142.52, 142.59, 142.85, 143.08, 143.12, 143.51, 144.58 (=CH), 144.85, 145.52, 145.59, 145.62, 145.71, 145.92, 146.36, 146.43, 146.54, 146.68, 146.71, 147.60, 147.70, 149.05, 150.28, 156.54, 162.60.

§ Experimental conditions: silica gel Si60 (5 μm), 240 × 5 mm; mixture of hexane and toluene (1 : 1, *v*/*v*) used as eluent; flow rate, 1.0 ml min^{-1}; detection, UV at 310 nm.

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