Phosphine-catalysed cycloaddition of buta-2,3-dienoates and but-2-ynoates to [60]fullerene

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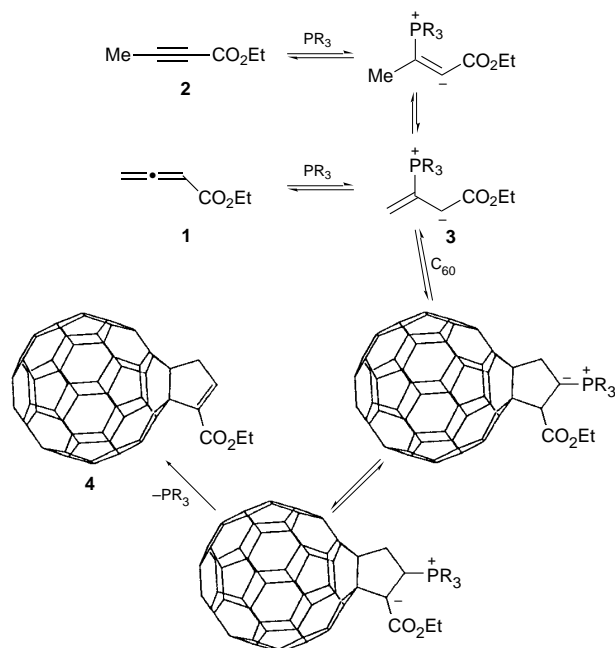
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In the presence of phosphine catalysts, ethyl buta-2,3-dienoate and ethyl but-2-ynoate undergo [3 + 2] as opposed to [2 + 2] dipolar cycloaddition to [60]fullerene.

Cycloadditions have proved to be the most generally useful method yet devised for attaching organofunctional groups to fullerenes.[1] In these processes the cage often behaves as the electron deficient component, so that alkenes bearing electron-withdrawing groups serve as useful models for reactions. Recently Zhang and Lu[2] described a novel [3 + 2] annulation technique for preparing cyclopentenes, based on the phosphine-catalysed cycloadditions of buta-2,3-dienoates and but-2-ynoates to electron-deficient alkenes. We have successfully applied their methodology to [60]fullerene.

In a typical reaction, ethyl buta-2,3-dienoate **1** (21.26 mg, 0.19 mmol, 1.7 equiv.) and 5 mol% of tributylphosphine (1.92 mg, 9.5 μmol) were added successively to a solution of [60]fullerene (80.4 mg, 0.11 mmol) in toluene (200 cm^3), and the mixture was stirred at ambient temperature under nitrogen for 17 h. Thin layer chromatography (TLC) (silica) of a sample of the resulting red–brown solution revealed the presence of unreacted [60]fullerene and one major product **4**. Removal of the solvent *in vacuo* and flash chromatography (toluene–hexane, 7:3; silica gel) of the residue gave [60]fullerene, followed by **4** (43%, pure by TLC). Use of **1** in excess of 1.7 equiv. resulted in a lower yield of **4** due to a marked increase in the proportion of products arising from multiple cycloadditions to the cage.

When ethyl but-2-ynoate **2** was used instead of **1**, forcing conditions (refluxing benzene, 20 h) were required to produce **4**, albeit in lower yield (23%). At ambient temperature, all of the [60]fullerene was recovered together with unwanted byproducts due to slow decomposition of **2**.

Tricyclohexylphosphine (PCy$_3$) and PBu$_3$ showed comparable catalytic activity in the cycloaddition of **1** to [60]fullerene, whereas reaction was much slower with triphenylphosphine (PPh$_3$). The difference is greater with **2**; in this case PPh$_3$ appears not to catalyse the reaction. These observations are in line with the greater nucleophilicity of PBu$_3$ and PCy$_3$ relative to PPh$_3$ and are compatible with Scheme 1.
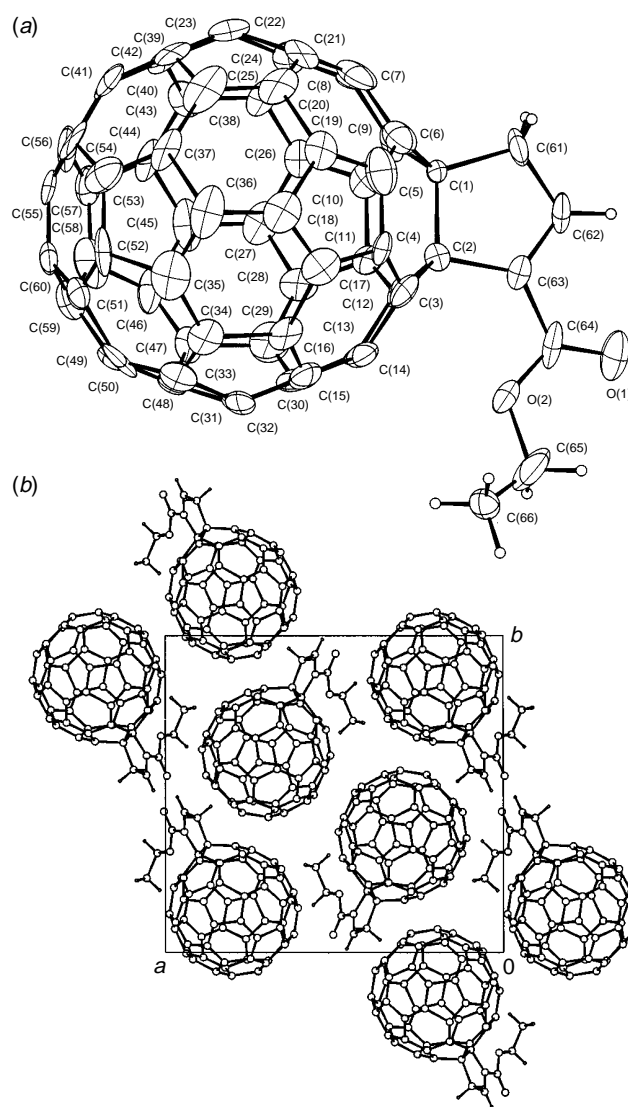

Fig. 1 (*a*) X-Ray crystal structure of **4** and (*b*) representation of the crystal packing in the unit cell

Scheme 1

The EI-MS of **4** displays the anticipated molecular ion peak at m/z 832, together with peaks at m/z 804 and 759 corresponding to loss of ethene and the ethyl carboxylate moiety, respectively.
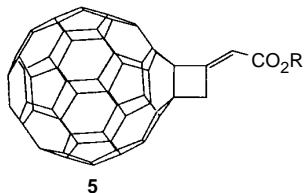
The FT-IR spectrum of **4** reveals a strong absorption at 1715 cm^{-1} due to the ester carbonyl group. The 577 cm^{-1} band, characteristic of the parent fullerene, is split into several weaker signals which, in conjuction with the strong 527 cm^{-1} band, is commensurate with addition across the [6,6] double bond in [60]fullerene.

The ^{1}H NMR spectrum of **4** (300 MHz; CS$_2$–CDCl$_3$, 1:1) exhibits a triplet at δ 7.98 (J 2.6 Hz) due to the β vinyl proton, which is coupled to the adjacent methylene protons giving rise to a doublet at δ 4.77 (J 2.6 Hz).The ethyl group resonances are as expected: δ 4.53 (J 7.1 Hz, q) and δ 1.59 (7.1 Hz, t).

The high field ^{13}C NMR (125.76 MHz; CS$_2$–CDCl$_3$, 4:1) of **4** shows signals corresponding to the ethyl group (δ 14.49, 47.75), the methylene carbon (δ 61.29), and the fullerene cage sp^3 carbons (δ 69.54, 76.55). The sp^2 region exhibits 32 signals, one of which, the carbonyl carbon (δ 163.03), was assigned on the basis of its chemical shift. A further two signals (δ 128.34, 136.60) were assigned on the basis of ^{13}C{^{1}H } decoupling to the unsaturated carbons of the cyclopentene ring. The remaining 28 signals† correspond to the carbons of the fullerene core; two of single intensity, 24 of double intensity and two of quadruple intensity. Assuming that the latter are due to the incidental overlap of two sets of double intensity signals, and that the single intensity peaks correspond to the carbons which lie on the mirror plane, the number of resonances is consistent with the expected C_s symmetry of the molecule.

Slow evaporation of a toluene–CS$_2$ solution of **4** yielded black needle-like crystals, suitable for X-ray analysis, on the basis of which the structure of **4** was conclusively assigned‡ (Fig. 1).

Recently Liou and Cheng[3] described the PCy$_3$-mediated reaction of alkyl 2-ynoates to [60]fullerene, and formulated the products as arising from a formal [2 + 2] cycloaddition generating **5**, as opposed to **4**. The authors based their structural conclusions exclusively on NMR evidence. We repeated this procedure with ethyl but-2-ynoate (reaction at ambient rather than the reflux temperature; 10-fold excess of ynoate) and found the NMR spectra of the product to be identical in all respects to **4**. We thus conclude that Liou and Cheng assigned the incorrect structure to the cycloadduct. It is noteworthy that Zhang and Lu[2] obtained only products arising from [3 + 2] as opposed to [2 + 2] cycloadditions of ynoates and butadienoates with electron-deficient alkenes

A viable mechanism for the reaction as originally proposed[2] is presented in Scheme 1. Nucleophilic attack of the tertiary phosphine on the β allenic or acetylenic carbon atom, followed by a prototropic shift (or series of shifts in the case of the ynoate substrate) generates the dipolar intermediate **3**, which undergoes a [3 + 2] cycloaddition to [60]fullerene. A further prototropic shift in the initial cycloadduct and subsequent β-elimination of the phosphine generates **4**.

Footnotes

† *Selected spectroscopic data* for **4**; ^{13}C NMR: δ 156.00, 149.74, 148.33, 147.25, 147.15, 146.23, 146.20, 146.08, 145.95, 145.90, 145.46, 145.26, 145.17, 145.08, 144.95, 143.76, 144.37, 142.65, 142.61, 142.36, 142.11, 142.02, 141.94, 141.49, 140.21, 139.18, 135.52, 134.53.

‡ *Crystal structure data* for **4**: C$_{66}$H$_8$O$_2$, M = 832.7, orthorombic, space group $P_{na}2_1$ (no. 33), a = 18.531(3), b = 17.253(3), c = 10.022(5) Å, U = 3204(2) Å^3, Z = 4, D_c = 1.73 g cm^{-3}, $F(000)$ = 1680. Crystal size 0.2 × 0.2 × 0.02 mm, Mo-Kα radiation, λ = 0.71073 Å, μ = 0.1 mm^{-1}. Data collected on an Enraf-Nonius CAD4 diffractometer at 293 K. There were 2984 unique reflections measured for 2 < θ < 25°, with 1672 having $I > 2\sigma(I)$. Non-H atoms were located by direct methods (SHELXS-86) and refined on F^2 with all reflections (SHELXL-93). H-atoms were included in riding mode. The structure is disordered in the ratio 76:24, with the minor sites related to the major sites by reflection through a plane perpendicular to the c axis and passing through the centroid of the C$_{60}$ sphere. The coordinates for the minor occupancy molecule were generated from those of the major sites and then refined as a rigid body with isotropic thermal parameters. Final residuals were $R1$ = 0.062 [for I > 2σ(I)] and $wR2$ = 0.186 (for all data).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/304.

References

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