Cyclotrimerization of Alkynes with [60]Fullerene in the Presence of Tricyclohexylphosphine

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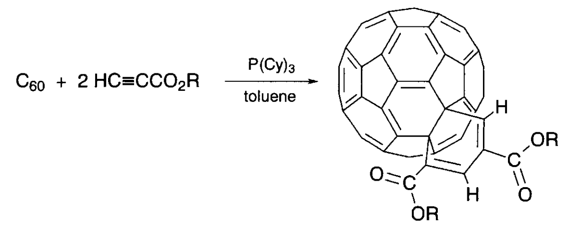
Treatment of [60]fullerene with $HC\equiv CCO_2R$ in the presence of P(Cy)$_3$ at ambient temperature affords a cyclotrimerization product (R = Et, **1**; Me, **2**) which results from a head-to-tail addition of two $HC\equiv CCO_2R$ units to a 6–6 ring junction of [60]fullerene based on the observed spectral data.

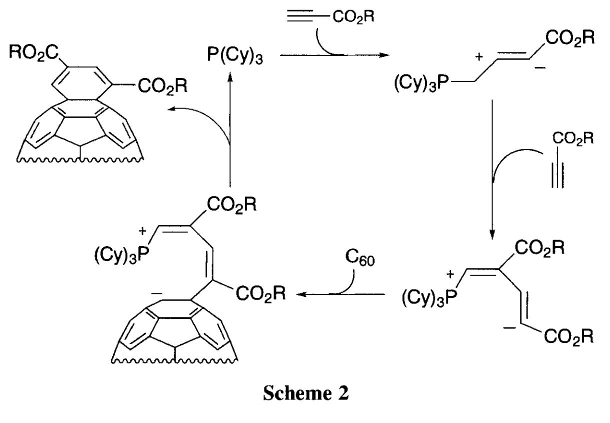
Functionalization of fullerenes by cycloaddition reactions provides important routes for the preparation of [60]fullerene derivatives.[1–6] Various types of [1 + 2],[1] [2 + 2],[2] [3 + 2],[3] [4 + 2][4,5] and [8 + 2][6] cycloaddition to fullerenes have been developed. Owing to their pronounced electron-acceptor properties,[7] fullerenes are suited for reactions with dipolar reagents to give cyclization products.[8] We report here a new and powerful method for the construction of a cyclohexadiene ring on [60]fullerene *via* dipolar cotrimerization with 2-ynoates. These reactions involve unusual phosphine-induced nucleophilic addition and cyclization.

Slow addition of ethyl propiolate ($HC\equiv CCO_2Et$) to a toluene solution containing [60]fullerene and tricyclohexylphosphine [P(Cy)$_3$] at ambient temperature afforded (Scheme 1) a formal [2 + 2 + 2] cycloaddition product **1** in 23.3% yield (75.0% [60]fullerene was recovered). In the absence of P(Cy)$_3$, no product was formed. Other phosphines such as PPh_3, $P(OPh)_3$ and NEt_3 did not catalyse this cycloaddition. The structure of **1** was determined based on its mass, NMR and IR spectra.† Analysis of **1** by FAB-MS shows the molecular ion at *m/z* 916 confirming its formulation as an adduct of two ethyl propiolate units to [60]fullerene. The presence of ester groups is supported by the strong IR carbonyl (C=O) absorption at 1711 cm^{-1} and carbon–oxygen (C–O) absorptions at 1211 and 1222 cm^{-1}. The ^{1}H NMR spectrum exhibits two alkenic proton resonances at δ 9.12 (d, J = 0.77 Hz) and 6.98 (d, J = 0.77 Hz) as well as two quartets and two triplets for the methylene and methyl protons, respectively. These observed spectral data strongly support a head-to-tail addition of the two propiolate units to [60]fullerene as indicated in **1**. The ^{13}C NMR spectrum of **1** supports the presence of C_s symmetry resulting from cycloaddition across a 6–6 ring junction of [60]fullerene. Thirty-four signals in the sp^2 region were observed with the resonances for the carbonyl carbons and the tertiary alkene carbons on the six-membered ring appearing at σ 165.55, 163.58, 139.61 and 120.55, respectively. The remaining 30 (maximum 32 signals are expected) peaks are attributed to the quaternary sp^2 carbons in the six-membered ring and [60]fullerene fragment. Two resonances at δ 146.05 and 145.55 are significantly stronger than the others, presumably owing to overlapping signals. In addition, there are six resonances in the sp^3 region atrributed to the carbons (δ 74.34 and 76.00) on the 6–6 ring junction of [60]fullerene and to the two ethyl groups on the six-membered ring. A drastic difference in the chemical shifts of the two alkenic protons (Δδ = 2.14 ppm) and the alkenic carbons (Δδ = 19.06 ppm) to which the protons are connected was observed.



1 R = CH$_2$Me
2 R = Me

Scheme 1



Scheme 2

Under similar conditions for the formation of **1**, [60]fullerene reacts with methyl propiolate to afford product **2**‡ in 16.6% yield and recovered [60]fullerene in 74.0%. The mass spectrum shows the molecular ion at *m/z* 888, which supports the formulation of two methyl propiolate and one [60]fullerene units. Analysis of the ^{1}H and ^{13}C NMR spectra of this product confirms **2** as a head-to-tail cyclotrimerization adduct of methyl propiolate with [60]fullerene, analogous to **1** in structure.

The observed cycloaddition is closely related to the phosphine-catalysed isomerization of 2-ynoates.[9] P(Cy)$_3$ acts as a nucleophile and a leaving group in these reactions. Nucleophilic attack of P(Cy)$_3$ at the β-position of a 2-ynoate is probably the first step for these reactions. Subsequent nucleophilic attack of the resulting dipolar species at another 2-ynoate and then at a [60]fullerene molecule, followed by counterattack at the β-position of the first 2-ynoate and then at a [60]fullerene molecule, followed by counterattack at the β-position of the first 2-ynoate unit where the P(Cy)$_3$ is attached, affords the cycloaddition product. Scheme 2 outlines this proposed mechanism. *Syn* addition, which is required for the cyclotrimerization, is much more favoured than *anti* addition due to the stronger Coulombic attraction of the phosphonium cation and the α-carbanion with a *cis* arrangement, relative to a *trans* structure.

We have demonstrated a new method for cycloaddition to [60]fullerene which enables us to introduce reactive enester groups, onto fullerenes, that are ready for further functionalizations. Examples of phosphines which act as nucleophilic catalysts have been reported,[10] but it is virtually unknown in organic synthesis to use phosphine in cycloadditions. Studies on these aspects are in progress.

We thank the National Science Council of the Republic of China (NSC 84-2113-M-007-035 CC) for support of this research.

Received, 21st April 1995; Com. 5/02543E

Footnotes

† Compound **1** was synthesized according to the following procedure. To a 250 ml side-arm flask containing [60]fullerene (0.108 g, 0.15 mmol) and tricyclohexylphosphine (0.070 g, 0.25 mmol) under 1 atm of N$_2$ was added toluene (60 ml). The system was then stirred at ambient temp. until

[60]fullerene was dissolved. To the system ethyl propiolate was added with stirring (0.176 g, 1.8 mmol) in toluene (15 ml) *via* a syringe pump over 2 h. The solution was stirred at the same temp. for 3 h and was then filtered through a short silcia gel column to remove the coloured material. Concentration, followed by separation on a silica gel column using toluene as eluent recovered [60]fullerene (0.081 g, 0.112 mmol) in 75.0% yield and afforded compound **1** (0.0320 g, 0.0349 mmol) in 23.3% yield. *Selected data*: ^{1}H NMR (300 MHz, C_6D_6–CS_2 1 : 2) δ 1.22 (t, J = 7.1 Hz, 3 H, $\mathrm{C}H_3$), 1.25 (t, J = 7.1 Hz, 3 H, $\mathrm{C}H_3$), 4.17 (q, J = 7.1 Hz, 2 H, $\mathrm{C}H_2$), 4.22 (q, J = 7.1 Hz, 2 H, $\mathrm{C}H_2$), 6.98 (d, J = 0.77 Hz, 1 H, =$\mathrm{C}H$), 9.12 (d, J = 0.77 Hz, 1 H, =$\mathrm{C}H$); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 14.26 ($C\mathrm{H}_3$), 14.31 ($C\mathrm{H}_3$), 61.06 ($C\mathrm{H}_2$), 61.96 ($C\mathrm{H}_2$), 74.34, 76.00, 120.55 (=$C\mathrm{H}$), 135.17, 136.08, 139.53, 139.61 (=$C\mathrm{H}$), 140.46, 141.65, 141.82, 141.85, 142.07, 142.31, 142.61, 142.80, 142.83, 143.10, 144.42, 144.49, 145.17, 145.34, 145.47, 145.55, 146.05, 146.20, 146.38, 146.42, 147.06, 147.36, 147.43, 148.11, 148.73, 154.87, 160.72, 163.58, 165.55; IR(KBr) ν/cm^{-1} 1711 (s), 1621, 1371, 1308, 1222 (s), 1211 (s), 1139, 1080, 1027, 864, 798, 625, 526 cm^{-1}; UV–VIS (chloroform) λ_{max}/nm(log ε) 256 (5.01), 324 (4.50), 430 (3.44), 437 (3.41) 694 (2.26); FAB-MS *m/z* (rel. intens.) 918 ([M + 2]$^+$, 20) 917 ([M + 1]$^+$, 32) 916 (M$^+$, 31), 722 (30), 721 (73), 720 (100).

‡ Compound **2** was prepared by following a procedure similar to that described for **1**. [60]Fullerene in 74.0% yield was recovered from the reaction. *Selected spectral data*: ^{1}H NMR (300 MHz, C_6D_6–CS_2 1 : 1) δ 3.65 (s, 3 H, $\mathrm{OC}H_3$), 3.68 (s, 3 H, $\mathrm{OC}H_3$), 6.99 (d, J = 0.98 Hz, 1 H, =$\mathrm{C}H$), 9.11 (d, J = 0.98 Hz, 1 H, =$\mathrm{C}H$); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 52.10 ($\mathrm{O}C\mathrm{H}_3$), 52.69 ($\mathrm{O}C\mathrm{H}_3$), 61.38, 74.29, 120.33 (=$C\mathrm{H}$), 135.22, 136.14, 139.66, 139.81 (=$C\mathrm{H}$), 140.52, 141.71, 141.86, 141.89, 142.13, 142.37, 142.66, 142.86, 142.90, 143.16, 144.47, 144.55, 145.23, 145.40, 145.54, 145.61, 146.09, 146.26, 146.44, 146.47, 146.89, 147.49, 148.04, 148.66, 154.81, 160.90, 164.06, 165.97; IR(KBr) ν/cm^{-1} 1716 (s), 1624, 1431, 1372, 1311, 1225 (s), 1213 (s), 1141, 1111, 730, 526; UV–VIS (chloroform) λ_{max}/nm (log ε) 255 (5.07), 308 (4.62) 325 (4.52), 428 (3.47) 695 (2.35); FAB-MS *m/z* (rel. intens.) 890 ([M + 2]$^+$, 15) 889 ([M + 1]$^+$, 24) 888 (M$^+$, 25), 722 (29), 721 (72), 720 (100).

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