Phosphine-mediated [2 + 2] Cycloaddition of Internal Alk-2-ynoate and Alk-2-ynone to [60]Fullerene

Kou-Fu Liou and Chien-Hong Cheng*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

Treatment of $RCH_2C{\equiv}CCOX$ with [60]fullerene in the presence of tricyclohexylphosphine (PCy_3) afforded a [2 + 2] cycloaddition product (**1**: R = H, X = OMe; **2**: R = Bu, X = OMe; **3**: R = X = Me which resulted from addition of the β,γ-carbons of $RCH_2C{\equiv}CCOX$ to the carbon–carbon double bond across a 6/6 ring junction of [60]fullerene.

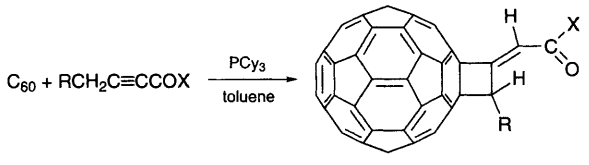
Cycloadditions to fullerenes provide important routes for the preparation of fullerene derivatives.[1–7] Several examples of [2 + 2][1] cycloadditions to fullerenes are known. In most cases, photochemical methods were employed for these [2 + 2] cycloadditions. Here, we report a new method of constructing alkylidene cyclobutane rings *via* a new [2 + 2] cycloaddition of alk-2-ynoate or alk-2-ynone to [60]fullerene mediated by tricyclohexylphosphine (PCy_3) (Scheme 1). Surprisingly, this cycloaddition occurs across the β,γ-carbons instead of α,β-carbons of the alk-2-yne.

Treatment of methyl but-2-ynoate ($MeC{\equiv}CCO_2Me$) with [60]fullerene in the presence of PCy_3 at ambient temperature, followed by separation of the mixture on a silica gel column with toluene as eluent, afforded the [2 + 2] cycloaddition product **1**† in 22.8% yield. (75.9% [60]fullerene was recovered). No product was formed in the absence of PCy_3, indicating that this phosphine acts as a catalyst in the reaction. The mass spectral data of this product showing a molecular ion at *m/z* 818 is consistent with a monoadduct of methylbut-2-ynoate to [60]fullerene. The ^1H NMR spectrum exhibits a singlet, a doublet and a triplet at δ 3.93, 4.63 and 7.82 assigned to the protons of the methyl, methylene and alkene groups, respectively, on the alkylidene cyclobutane ring. Evidence for [2 + 2] cycloaddition across the β,γ-carbons of but-2-ynoate and across a 6/6 ring junction on [60]fullerene is provided by the observed magnetic equivalency of the two methylene protons, which exhibit a weak allylic coupling (*J* 2.7 Hz) with the alkenic proton. The observed number of ^{13}C NMR signals, which indicate the presence of C_s symmetry, is in agreement with the proposed structure **1**. Further proof of a cyclobutane moiety in **1** comes from the results of a ^{13}C DEPT experiment that led us to assign the resonances for the methylene carbon, the two fused quaternary sp^3 carbons on the [60]fullerene fragment and the exocyclic tertiary alkenic carbon at δ 47.58, 69.30, 77.50 and 143.59, respectively. The observed highly deshielded NMR signal of the alkenic proton at δ 7.82, which is shifted *ca.* 2 ppm downfield relative to a normal α-proton of a α,β-unsaturated ester, suggests that this proton is orientated towards a five-membered ring (structure **A**).The strong paramagnetic current associted with the five-membered rings of fullerenes has been shown to cause downfield shifts of the NMR signals of protons oriented toward them.[8] Based on the observed chemical shift of the alkenic proton, the ester group is assigned *cis* to the methylene group on the 4-membered ring.

The reaction of methyl oct-2-ynoate with [60]fullerene in the presence of PCy_3 at 70 °C also gave a [2 + 2] cycloaddition product **2**‡ in 13.4% yield. The ^1H NMR signal at δ 7.67 for the alkene proton exhibits an allylic coupling of *J* 2.4 Hz with that of the methine proton at δ 4.53 on the 4-membered ring. This observation indicates that products **1** and **2** have a similar structures. However, unlike **1**, product **2** possesses an asymmetric centre at the methine carbon leading to the diastereotopic nature of the protons in each methylene group of the butyl chain in the ^1H NMR spectrum. Furthermore, the asymmetric centre reduces the symmetry of **2** to C_1, yielding separate signals for each carbon in the ^{13}C NMR spectrum. To date, only a few [60]fullerene adducts that display C_1 symmetry have been reported.[4,9]

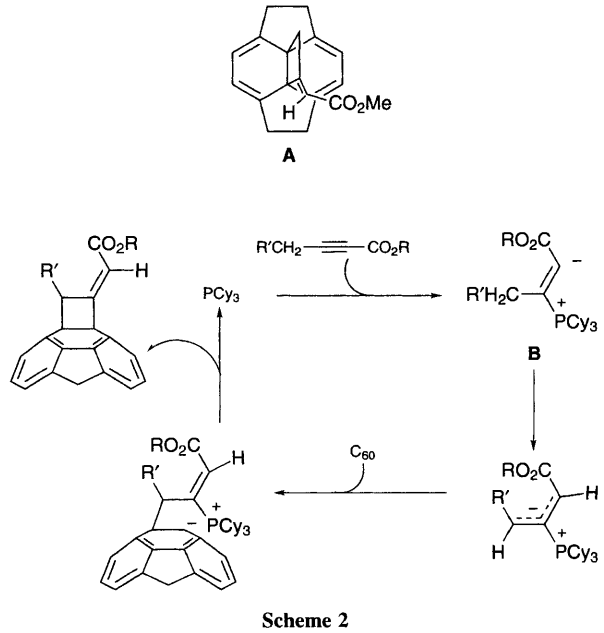
Similarly, hex-3-yn-2-one reacts with [60]fullerene in the presence of PCy_3 at 70 °C to give **3**§ in 17.3% yield. The ^1H NMR and mass spectral data are consistent with a [2 + 2] β,γ-cycloaddition adduct of hex-3-yn-2-one to [60]fullerene. As product **3** is much less soluble than **1** or **2** in common NMR solvents, its ^{13}C NMR spectrum was not recorded.

The observed [2 + 2] cycloadditions are closely related to phosphine-catalysed isomerization of alk-2-ynoates,[10] addition of carbon nucleophiles to the γ-position of alk-2-ynoates[11] and cyclotrimerization of alkyne with [60]fullerene.[7] Nucleophilic attack of phosphines at the β-positions of 2-ynoates initiates these cycloadditions. The dipolar intermediate (**B**, Scheme 2) then undergoes a 1,3-proton shift from the γ- to α-carbon, creating a γ-carbanion. Nucleophilic addition of this anion to a [60]fullerene molecule, followed by back attack at the β-position of the 2-ynoate to which the PCy_3 is attached, affords the [2 + 2] product with correct geometry. Scheme 2 outlines a possible mechanism for these cycloadditions. The dipolar intermediate **B** is expected to favour a *cis* geometry for the phosphonium cation and the electron pair on the α-carbanion due to the strong Coulomb attraction, consistent with the observed geometry of the ene group in the final [2 + 2] product. Alternatively, PCy_3 may act as a base, removing one proton



1 R = H, X = OMe
2 R = $MeCH_2CH_2CH_2$, X = OMe
3 R = X = Me

Scheme 1



Scheme 2

from the γ-carbon and generating a γ-carbanion. Nucleophilic addition of this anion to a [60]fullerene molecule, counterattack at the β-position of the 2-ynoate, followed by protonation, gives the desired [2 + 2] product.

The present [2 + 2] cycloadditions provide a new method of constructing a fused four-membered ring containing a reactive ene ester or enone group on fullerenes. Moreover, the employment of an asymmetric phosphine may allow the synthesis of asymmetric [60]fullerene derivatives. It is still unusual in organic synthesis to use a phosphine in [2 + 2] cycloadditions, although scattered reports on the use of phosphines as nucleophilic catalysts have appeared.[11,12]

We thank Professor G. R. Her and his group for mass spectral data analysis and the National Science Council of the Republic of China (NSC 84-2113-M-007-035 CC) for support of this research.

Received, 5th June 1995; Com. 5/03581C

Footnotes

† Compound **1** was prepared according to the following procedure. To a 250 cm^3 side-arm flask containing [60]fullerene (0.108 g, 0.15 mmol) and tricyclohexylphosphine (0.140 g, 0.50 mmol) under nitrogen was added toluene (75 cm^3). The system was then stirred at ambient temperature until the [60]fullerene had dissolved. Addition of methyl but-2-ynoate (0.176 g, 1.80 mmol) *via* syringe was followed by stirring at ambient temperature for 4 h. The solution was then filtered through a short silica gel column to remove the coloured material. Concentration followed by separation on a silica gel column using toluene as eluent recovered [60]fullerene (0.082 g, 0.011 mmol) in 75.9% yield and afforded **1** (0.0280 g, 0.034 mmol) in 22.8% yield. *Spectral data* for **1**: ν_{max}(KBr)/cm^{-1} 1722, 1638, 1427, 1324, 1239, 1186, 1115, 1089, 1001, 875, 765, 726. 574 and 527; λ_{max}($CHCl_3$)/nm (log ε) 258 (5.07), 328 (4.55), 428 (3.47) and 697 (2.27); δ_H (300 MHz, $CDCl_3$: CS_2 = 1 : 1) 3.93 (3 H, s, OCH_3), 4.63 (2 H, d, *J* 2.7 Hz, CH_2) and 7.82 (1 H, t, *J* 2.7 Hz, C*H*); δ_C (150 MHz, $CDCl_3$: CS_2 = 1 : 2) 47.58 (CH_2), 51.68 (CH_3), 69.30, 73.53, 134.40, 135.37, 136.27, 139.13, 140.08, 141.37, 141.80, 141.88, 141.97, 142.23, 142.48, 142.52, 142.90, 143.59 (=*C*H), 144.23, 144.79, 144.96, 145.04, 145.12, 145.33, 145.76, 145.95, 146.07, 147.01, 147.12, 148.10, 149.52, 155.76 and 163.20; FAB MS *m/z* 820 (M + 2^+, 13%) 819 (M + 1^+, 21) 818 (M^+, 23), 722 (35), 721 (77) and 720 (100).

‡ Compound **2** was prepared according to a procedure similar to that for **1** except that oct-2-ynoate was used and the solution was heated at 70 °C for 12 h. [60]Fullerene was recovered in 74.1% yield and **2** was isolated in 13.4% yield from the reaction. *Spectral data* for **2**: ν_{max}(KBr)/cm^{-1} 2926, 2854, 1722, 1641, 1434, 1307, 1243, 1187, 1117, 1091, 879, 731 and 527; λ_{max} ($CHCl_3$)/nm (log ε) 257 (4.74), 326 (4.38), 428 (3.55) and 698 (2.25); δ_H (300 MHz, C_6D_6 : CS_2 = 1 : 1) 0.99 (3 H, t, *J* 7.3 Hz, CH_3), 1.45 (2 H, m, CH_2), 1.63 (1 H, m, CH_2), 1.74 (1 H, m, CH_2), 2.09 (1 H, m, CH_2), 2.41 (1 H, m, CH_2), 3.69 (3 H, s, OCH_3), 4.53 (1 H, m, CH_3) and 7.67 (1 H, d, *J* 2.4 Hz, =C*H*); δ_C (150 MHz, $CDCl_3$: CS_2 = 1 : 2) 14.13 (CH_3), 22.96 (CH_2), 30.66 (CH_2), 35.39 (CH_2), 52.16 (*C*H), 57.84 (OCH_3), 74.45, 133.96, 135.40, 135.68, 135.71, 135.96, 139.21, 139.35, 139.68, 140.21, 141.63, 141.88, 141.93, 141.99, 142.15, 142.41, 142.61, 142.66,142.72, 143.07, 143.09, 144.47, 144.51, 144.86, 145.32, 145.35, 145.37, 145.47, 145.94, 145.97, 146.00, 146.10, 146.20, 146.28, 146.37, 147.25, 147.35, 148.13, 148.25(=CH), 150.82, 151.12, 153.02, 157.19 and 164.27; FAB MS *m/z* 876 (M + 2^+, 18%) 875 (M + 1^+, 29) 874 (M^+, 29), 722 (37), 721 (80) and 720 (100).

§ Compound **3** was prepared according to a procedure similar to that for **1** except that hex-3-yn-2-one and tricyclohexylphosphine (0.25 mmol) were used and the solution was heated at 70 °C for 1 h. [60]Fullerene was recovered in 62.0% yield and **3** was isolated in 17.3% yield from the reaction. *Spectral data* at **3**: ν_{max}(KBr)/cm^{-1} 3045, 2956, 2922, 2854, 1723, 1665(s), 1628, 1508, 1433, 1358, 1248, 1184, 864, 619, 561 and 525(s); λ_{max}($CHCl_3$)/nm (log ε) 255 (4.97), 325 (4.45), 431 (3.43) and 696 (2.28); δ_H (300 MHz, $CDCl_3$: CS_2 = 1 : 1) 7.60 (1 H, d, *J* 2.6 Hz, =C*H*), 4.73 (1 H, dq, *J* 2.6, 7.5 Hz, C*H*), 2.74 (3 H, s, CH_3) and 2.05 (3 H, d, *J* 7.5 Hz, CH_3); FABMS *m/z* 819 (M + 3^+, 15%) 818 (M + 2^+, 34) 817 (M + 1^+, 54) 816 (M^+, 45), 723 (12), 722 (34), 721 (76) and 720 (100).

References

1 S. R. Wilson, Y. Wu, N. A. Kaprinidis and D. I. Schuster, *J. Org. Chem.*, 1993, **58**, 6548; X. Zhang, A. Romero and C. S. Foote, *J. Am. Chem. Soc.*, 1993, **115**, 11024; M. Prato, M. Maggini, G. Scorrano and V. Lucchini, *J. Org. Chem.*, 1993, **58**, 3613; S. Yamago, A. Takeichi and E. Nakamura, *J. Am. Chem. Soc.*, 1994, **116**, 1123.

2 M. Prato, T. Suzuki, H. Foroudian, Q. Li, K. Khemani, F. Wudl, J. Leonetti, R. D. Little, T. White, B. Rickborn, S. Yamago and E. Nakamura, *J. Am. Chem. Soc.*, 1993, **115**, 1594; M. S. Meier and M. Poplawska, *J. Org. Chem.*, 1993, **58**, 4524; L. L. Shiu, T. I. Lin, S. M. Peng, G. R. Her, D. D. Ju, S. K. Lin, J. H. Hwang, C. Y. Mou and T. Y. Luh, *J. Chem. Soc., Chem. Commun.*, 1994, 647.

3 T. Tago, T Minowa, Y. Okada and J. Nishimura, *Tetrahedron Lett.*, 1993, **34**, 8461.

4 E. Beer, M. Feuerer, A. Knorr, A. Mirlach and J. Daub, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1087.

5 A. Hirsch, I. Lamparth and T. Grösser, *J. Am. Chem. Soc.*, 1994, **116**, 9385 and references therein.

6 Y. Rubin, S. Khan, D. I. Freedberg and C. Yeretzian, *J. Am. Chem. Soc.*, 1993, **115**, 344; M. Tsuda, T. Ishida, T. Nogami, S. Kurono and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1993, 1296; V. M. Rotello, J. B. Howard, T. Yadav, M. M. Conn, E. Viani, L. M. Giovane and A. L. Lafleur, *Tetrahedron Lett.*, 1993, **34**, 1561; P. Belik, A. Gügel, J. Spickermann and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 78; J. A. Schlueter, J. M. Seaman, S. Taha, H. Cohen, K. R. Lykke, H. H. Wang and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 972.

7 K. F. Liou and C. H. Cheng, submitted for publication in *J. Chem. Soc., Chem. Commun.*

8 M. Prato, T. Suzuki, F. Wudl, V. Lucchini and M. Maggini, *J. Am. Chem. Soc.*, 1993, **115**, 7876.

9 J. Averdung, E. Albrecht, J. Lauterwein, H. Luftmann, J. Mattay, H. Mohn, W. H. Müller and H.-U. ter Meer, *Chem. Ber.*, 1994, **127**, 787.

10 B. M. Trost and U. Kazmaier, *J. Am. Chem. Soc.*, 1992, **114**, 7933.

11 B. M. Trost and C. J. Li, *J. Am. Chem. Soc.*, 1994, **116**, 3167; 10 819.

12 E. Vedejs and S. T. Diver, *J. Am. Chem. Soc.*, 1993, **115**, 3358; T. Hanemoto, Y. Baba and J. Inanaga, *J. Org. Chem.*, 1993, **58**, 299.