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Preparation and Structure of a Novel Methano[60]fullerene Containing a Stable P-Ylid

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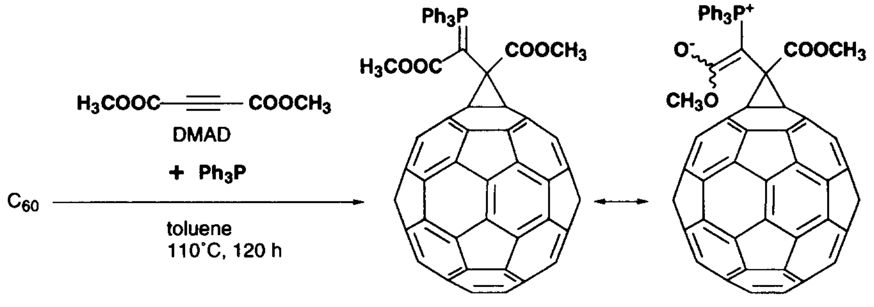
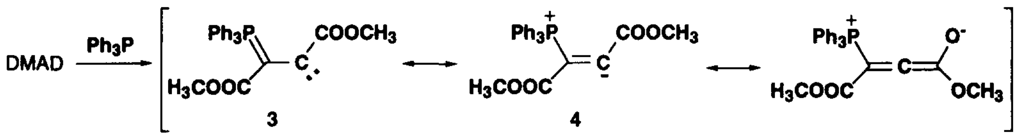
Abstract: A novel methanofullerene containing a stable phosphorous ylid is obtained from a reaction of fullerene (C_{60}) with a 1:1 mixture of triphenylphosphine and dimethyl acetylenedicarboxylate. © 1997 Elsevier Science Ltd.

Cyclopropanation of fullerenes by a carbene or carbanion intermediate is a important methodology to prepare new fullerene-based materials.[1,2] The method is very useful to introduce various functional groups on the cyclopropane for modifying various physical and chemical properties of fullerene derivatives. However, because of limitation of carbene and carbanion precursors, which are α-halo-β-diesters, diazo compounds and so on, the available functional groups on the cyclopropane are limited. Described herein are the preparation and structure of a new methano[60]fullerene containing a stable P-ylid structure.

Fullerene (C_{60}) reacted with an equimolar mixture of dimethyl acetylenedicarboxylate (DMAD) and triphenylphosphine (2 equiv. to C_{60}) in toluene at 110 °C for 120 h to give the methanofullerene (**1**)[3] in 61% isolated yield, 97% yield based on the conversion, as a dark-brown solid mass. Compound **1** is stable enough to be purified by column chromatography on silica gel. When triisopropylphosphine which is known as the catalyst for [3+2] cycloaddition of allene and acetylene derivatives toward C_{60}[4,5,6] was employed instead of Ph_3P in the reaction, C_{60} was not consumed even under forced conditions. It is known that the reaction of DMAD and Ph_3P produces the carbene-ylid intermediate (**3**) which is sufficiently stabilized by resonance.[7,8] Thus, **1** apparently is obtained by [2+1] cycloaddition of **3** or the zwitterion (**4**) to a 6–6 bond of C_{60}.



1 (61% isolated) **2**



The MS spectrum and elemental analyses of **1** support the formula ($C_{84}H_{21}O_4P$) of 1:1:1 adduct of C_{60}, DMAD, and Ph_3P. ^{31}P NMR (2 signals) and ^1H NMR (4 CH_3O signals) suggest that **1** existed as a ca. 3:2 mixture of two rotational isomers caused by resonance between P and the neighboring C=O group (illustrated as **2**).[9] In the ^{31}P NMR spectrum at 90 °C, significant peak broadening was observed in the 2 signals which, however, did not collapse into one signal even at 110 °C. There exist 84 signals in the ^{13}C NMR spectrum of **1**, and the C_s structure of **1** requires 42 signals for each rotermer. In the ^{13}C NMR spectrum, there were detected 3 pairs of sp^3 carbons at δ 77.23 and 76.54, 75.47 and 75.20, and 40.07 and 38.77 which could be assigned evidently as the cyclopropane ring carbons of the methanofullerene structure. The UV absorption at 430 nm is typical of methanofullerene.[2] Reaction of **1** with *p*-nitrophenylbenzaldehyde at 110 °C in toluene did not give the desired product of the Wittig reaction but yielded a single product whose structure was not clear.[10] Further investigation on the chemical and physical properties of **1** is in progress.

References and Notes

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3. Compound **1**: mp. 215 - 220 °C (dec); TLC (SiO_2) R_f = 0.79 (toluene/ethyl acetate = 1:1); HPLC (Develosil® SIL 4.6 x 250; toluene/ethyl acetate = 19:1) v_R 17.8 ml; ^{31}P NMR ($CDCl_3$): δ 23.14, 21.75; ^1H NMR: δ 8.20-7.35 (m, Ph), 3.90 (s, OCH_3), 3.83 (s, OCH_3), 3.78 (s, OCH_3), 3.24 (s, OCH_3); ^{13}C NMR: δ 171.93 (CO), 171.75 (CO), 169.83 (CO), 169.63 (CO), 151.92, 151.18, 149.66, 148.05, 147.86, 147.70, 146.54, 146.15, 145.94, 145.75, 145.54, 145.28, 145.11, 145.03, 144.87, 144.78, 144.67, 144.59, 144.55, 144.26, 144.08, 144.02, 143.74, 143.65, 142.92, 142.88, 142.83, 142.72, 142.43, 142.27, 142.23, 142.08, 142.04, 141.85, 141.67, 141.19, 140.87, 140.65, 140.55, 139.76, 139.30, 139.20, 138.67, 138.41, 138.18, 137.83, 136.59, 135.81, 135.45, 134.71, 134.60, 134.43 (Ph), 134.33 (Ph), 133.12, 133.09, 132.24 (Ph), 132.11 (Ph), 132.02, 131.92, 131.88, 130.86, 130.72, 129.24 (Ph), 129.12 (Ph), 128.97 (Ph), 128.86 (Ph), 128.53, 128.41, 77.23 (bridge head), 76.54 (bridge head),75.47 (bridge head), 75.20 (bridge head), 52.76 (OCH_3), 52.55 (OCH_3), 50.81 (OCH_3), 49.28 (OCH_3), 40.07 (bridge), 38.77 (bridge), 29.58 (J_{C-P} = 21 Hz), 29.50 (J_{C-P} = 31 Hz); IR (KBr) v 3057, 2924, 2854, 1726 (C=O), 1618, 1435, 1383, 1296, 1250, 1233, 1186, 1161, 747, 714, 693, 525 cm^{-1}; UV (cyclohexane) λ nm (ε) 493 (3300), 430 (4600), 325 (71500); FAB MS *m/z* 1125 [M + H], 1110[-CH_3], 1094 [-OCH_3], 1066 [-2CH_3], 1065 [-$COOCH_3$], 720 [C_{60}]. Anal. Calcd for $C_{84}H_{21}O_4P$ (1125.06): C, 89.68; H, 1.88. Found: C, 89.70; H,1.81.
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10. Since this product showed no triphenylphosphine and 2 carbomethoxy signals on the ^1H NMR spectra, and its FAB MS spectrum has no characteristic signals except *m/z* 720, we are now trying crystallization.

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