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RESEARCH ARTICLE

Wittig approach to the synthesis of cyclopentene-fullerene C_{60} derivative

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Abstract

The one-pot reaction of dibenzoylacetylene and fullerene in the presence of triphenylphosphine lead to the synthesis of 1-benzoyl-3-phenyl cyclopentene-[60] fullerene through Wittig mechanism. The structure of the main product is determined through its MS, ^{1}H and ^{13}C NMR, IR and UV spectral data.

Introduction

Since fullerene family was discovered at the end of last century, many important aspects on these molecules have been accumulated to form a new scientific field. The hydrophobicity, three-dimensionality, nano size and electronic configuration make them an appealing subject in different areas(Liu et al. 2013; Perezet al. 2013; Thilgen et al. 2006)especially in biology and medicine(Baati et al. 2012; Ma et al. 2010; Theriot et al. 2010;Bobylev et al. 2011;Meng et al. 2010; Xu et al. 2011;Tsumoto et al. 2010). However, the difficult processibility of fullerenes has led to the developments of methods for the functionalization of them. One of the synthetic methods for the functionalization of fullerene has focused on utilizing electron-deficient acetylenes and phosphorus compounds (Chen et al. 2009; Chuang et al. 2003).

It was found that the most reactions of fullerene with acetylenic compounds and phosphines gave fullerene derivatives consisting of a phosphorus ylide group and a cyclopropane ring on the fullerene moiety(Chuang etal. 1999; Yamaguchi et al. 1997). Also, the five-membered ring attachments to the C_{60} can be achieved from a vinylcyclopropane-type ring expansion(Chuang et al. 2003)or cycloaddition reaction(Shu et al. 1997). In this work, we have reported the reaction of dibenzoylacetylene with C_{60} in the presence of PPh_3 leading to the synthesis of cyclopenten adduct through Wittig route.

Experimental

Triphenylphosphine and C_{60} were obtained from fluka and were used without further purification. Dibenzoylacetylene was prepared by a known method(Bowden et al. 1946).

Melting point was measured on an Electrothermal 9100 apparatus. The NMR spectra were recorded at 500 (^{1}H) and 125 (^{13}C) MHz on a Brucker 500-AVANCE FT-NMR instrument with $CDCl_3$ as solvent. Chemical shifts (δ) are reported relative to TMS as the internal standard. IR spectra were recorded on a Bomem MB-100 IR spectrometer. High-resolution mass spectra (HRMS) were taken on a JEOL JMS- 700Ms spectrometer by electron impact (EI), chemical ionization (CI) and fast atom bombardment (FAB) methods. UV-vis spectra were recorded on a Jasco UV-V 530 spectrometer. Column chromatography was performed using 230-400 mesh merck silica gel and mixtures of hexane, dichloromethane and EtOAc were used as eluents.

Preparation of cyclopentene-[60] fullerene derivative 1

To the mixture of C_{60} (0.0357 g, 0.050 mmol), PPh_3 (0.0259 g, 0.099 mmol), and toluene (25 mL) was injected via a syringe pump a solution consisting of dibenzoylacetylene (0.0175 g, 0.075 mmol) and CH_2Cl_2 (10 mL) with an injection rate of 3.4 mL/h. After addition, the system was refluxed for 72 h. The solution was concentrated in a vacuum system to ca. 2 mL. The mixture was separated first on a silica gel column eluted first with toluene to recover unreacted C_{60} and then with a mixture of hexane, ethyl acetate, and dichloromethane (2:1:1). The fraction consisting of compound **1** (R_f = 0.51) was collected. After solvent removal, the product was washed with hexane to afford the desired pure yellow solid (0.0401 g) in 86% yield. Spectral data for compound **1** follow. m.p. >250 °C;^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 - 8.10 (m, 10 H. Ph), 7.69 (d, $^3J_{HH}$= 6 Hz,1H), 4.02 (d, $^3J_{HH}$= 6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.52, 135.14, 135.02, 134.97, 134.84, 134.79, 134.72, 134.66, 134.58, 134.44, 134.27, 134.19, 133.98, 133.78, 133.61, 133.49, 133.35, 133.18, 130.92, 130.69, 130.57, 130.33, 128.93, 128.84, 128.72, 128.69, 31.95, 29.73, 29.39 ppm; FTIR: ν_{max} / cm^{-1}= 3018, 2924, 1680, 1528, 1219, 771; UV-vis: λ_{max}/nm= 336; FAB-MS m/z: 941 (M^+ +1, 60), 720 (80), HRMS (FAB): calcd for $C_{76}H_{12}O$ $[M+ H]^+$ 941.1061; found 941.1045.

Results and discussions

Treatment of dibenzoylacetylene with C_{60} in the presence of PPh_3 in toluene at reflux temperature gave a cyclopentene-fulleren adduct (compound **1**) in 86% yield. (scheme1)

Scheme 1. The reaction of the synthesis of compound **1**

The structure of the product **1** is determined through its MS, ^{1}H and ^{13}C NMR, IR and UV spectral data on the basis of the well-established chemistry of trivalent phosphorus nucleophiles(Corbridge 1995). It is reasonable to assume that phosphorus ylide(**a**) results from initial addition of PPh_3 to the dibenzoylacetylene. Further attack of the latter at a C_{60} molecule followed by ring clousure through back attack at the carbon β of C_{60} to the adjacent carbonyl of the ylide moiety. For the formation of the compound **e**, triphenylphosphine oxide eliminated from the resulting phosphorous betaine **c** or oxaphosphetane intermediated **d**.

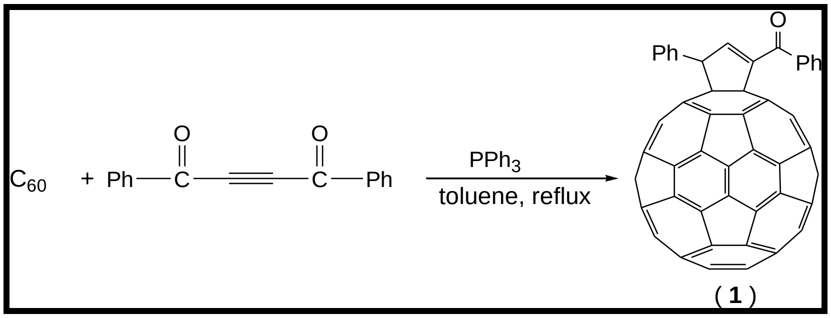
The main product **1** can be obtained from displacement of double bond to the more stable position and subsequent protonation of it by the moisture content in the reaction medium (scheme 2).

Scheme 2. Mechanism of the synthesis of compound **1**

The ^{1}H NMR spectrum of **1** exhibited a doublet for H_a (δ= 4.02 ppm), a doublet for H_b with the same coupling constant (δ= 7.69 ppm) and the phenyl residues gave rise to characteristic signals in the aromatic region (δ= 7.15 – 8.10 ppm) (Figure 1).

Fig. 1.^{1}H NMR spectra of the compound **1** at 298° K

The proton decoupled ^{13}C NMR spectrum of **1** showed three distinct resonances in the aliphatic region (δ= 29.39 – 31.95 ppm) for the two sp^3 carbons on the fullerene moiety and the quaternary sp^3 carbon resonances on the cyclopentene moiety and also displayed a signal for carbonyl group at δ= 203.52 ppm. The residue sp^2 carbons have appeared at about δ= 128.69 – 135.14 ppm. Partial assignment of these resonances is given in the experimental section. Also, ^{31}P NMR spectra of **1** indicate the absence of phosphorus element in this product. The structural identification of compound **1** made on the basis of NMR spectrums was supported by its IR analysis which in the carbonyl region (1680 cm^{-1}) displayed one distinct absorption band for the C=O group.



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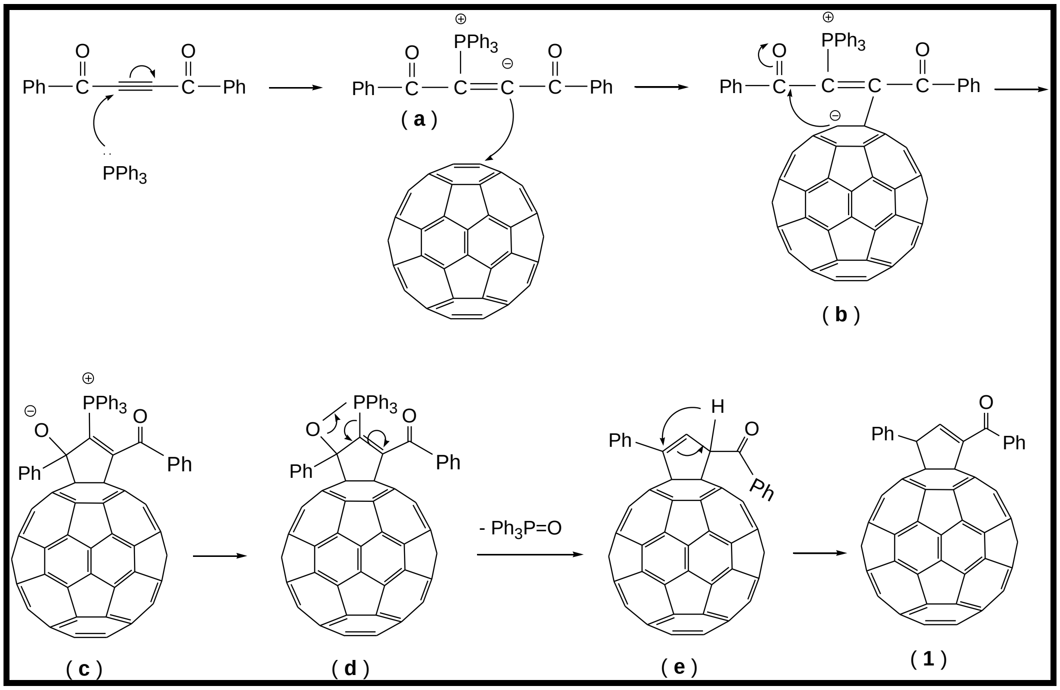

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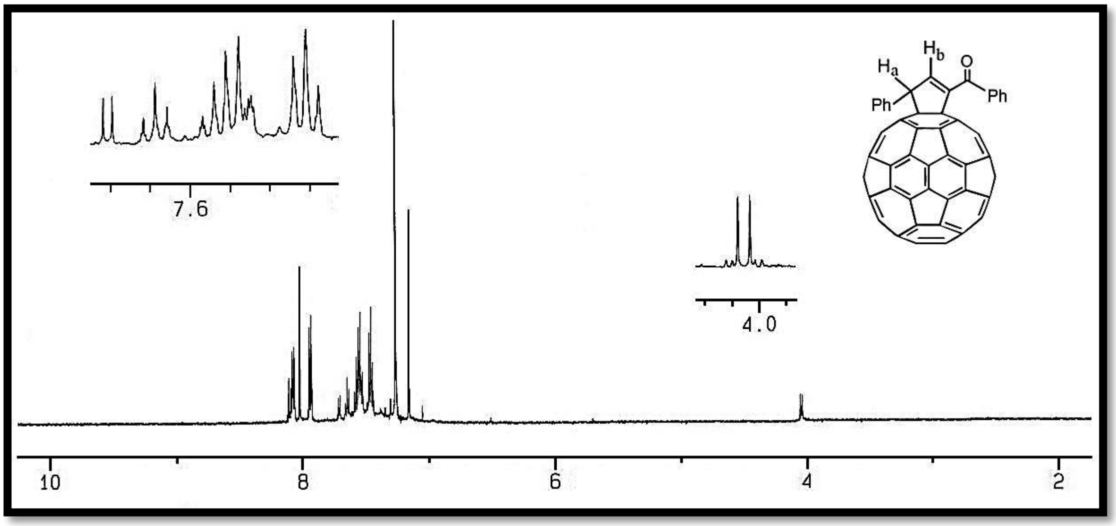

Fig. 1.^{1}H NMR spectra of the compound **1** at 298° K

Conclusion

We have demonstrated Wittig mechanism to produce cyclopentene-[60] fullerene derivative based on the one-pot reaction of triphenylphosphine with dibenzoylacetylene and C_{60} which has not been reported as yet. We think the electron-deficient acetylenes with ketone functional group can react with fullerene through this mechanism. But, further efforts are currently under way in our group to prepare related derivatives with new reagents.

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