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Reaction of [70]Fullerene with Tetraethyl Methylenediphosphonate or Diethyl (Cyanomethyl)phosphonate Revisited

Guan-Wu Wang,*[a,b] Hai-Tao Yang,[a] Ping Wu,[a] and Cong-Zhou Wang[a]

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The reaction of C_{70} with $CH_2(PO_3Et_2)_2$ or $CH_2(PO_3Et_2)CN$ in the presence of NaH has been reinvestigated. The reaction of C_{70} with the former phosphonate affords five products. Products **1**–**3** have molecular structures C_{70}>$CH(PO_3Et_2)$, whereas products **4** and **5** have molecular structures C_{70}>$C(PO_3Et_2)_2$. In contrast, only one product **6**, with a molecular structure C_{70}>$C(PO_3Et_2)CN$, could be isolated from the reaction of C_{70} with $CH_2(PO_3Et_2)CN$ and NaH. Ultrasonication was used to shorten the reaction times and increase the product yields. No product resulting from addition to the C7–C21 bond of C_{70} was observed in either cycloaddition reaction. Accordingly, the previously reported major products **3** and **6**, which were assigned as the C7–C21 isomers, should be reassigned as the C1–C2 isomers. This correction is very important for understanding the reactivity of C_{70}. Our reassignments are further supported by theoretical calculations. The newly isolated minor products **1**, **2**, and **4** were identified as the C5–C6 isomers. The present work proves that the reactivity order of the bonds in C_{70} for these two reactions is C1–C2 > C5–C6. These results resolve the confusion caused by previous incorrect product assignments.

Introduction

A number of fullerene derivatives have been synthesized by using, for example, nucleophilic, cycloaddition, and radical reactions. However, most of the investigations have focused on the reactions of [60]fullerene (C_{60}),[1] and far fewer reports have concerned the reactions of [70]fullerene (C_{70}) and other higher fullerenes.[1d,2] It is generally accepted that the order of reactivity for the double bonds of C_{70} (Figure 1) is C1–C2 > C5–C6 > C7–C21 for a cycloaddition reaction.[1d,2–7] Most of the reported cycloaddition reactions of C_{70} afforded two[4] or three[5] monoadduct isomers, or gave only one monadduct isomer with regioselective addition at the C1–C2 bond.[6] Four monoadduct isomers from the reaction of C_{70} with benzyne have been isolated, and it was found that the C7–C21 bond was the least reactive, being even less reactive than the C7–C8 bond.[7] However, a recent paper on the reaction of C_{70} with tetraethyl methylenediphosphonate [$CH_2(PO_3Et_2)_2$] and diethyl (cyanomethyl)phosphonate [$CH_2(PO_3Et_2)CN$], in the presence of sodium hydride (NaH), claimed that the obtained C_{70}>$CH(PO_3Et_2)$ and C_{70}>$C(PO_3Et_2)CN$ were the C7–C21 isomers, rather than the more common C1–C2 isomers.[8] The product assignments implied that the C7–C21 bond was more reactive than the C1–C2 bond, which contradicted the general reactivity trend of C_{70}.[1d,2] We suspected that the products were incorrectly assigned. These misassignments, if proven true, could cause confusion and lead to wrong conclusions about the reactivity order for the double bonds of C_{70}. In a continuation of our interest in fullerene chemistry,[7,9] and surprised by the above-mentioned product assignments, we decided to reinvestigate these two reported reactions[8] to clarify these issues. Our reinvestigation proves that the previously reported C7–C21 isomers for C_{70}>$CH(PO_3Et_2)$ and C_{70}>$C(PO_3Et_2)CN$[8] were indeed incorrectly assigned, and should be corrected as the C1–C2 isomers. Furthermore, careful separation has allowed the isolation of another three minor isomeric products, i.e., both of the two possible C5–C6 isomers of C_{70}>$CH(PO_3Et_2)$ and the single C5–C6 isomer of C_{70}>$C(PO_3Et_2)_2$, which were not reported in the previous

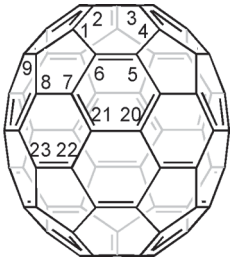

Figure 1. The structure and partial numbering[3] of C_{70}.

[a] Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry,
University of Science and Technology of China, Hefei, Anhui, 230026 P. R. China
Fax: +86-551-360-7864
E-mail: gwang@ustc.edu.cn
[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University,
Lanzhou, Gansu 730000, P. R. China

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work,[8] from the reaction of C_{70} with $CH_2(PO_3Et_2)_2$ and NaH. In this paper, we present these results and support our reassignments with theoretical calculations.

Results and Discussion

The reaction of C_{70} with an equimolar amount of $CH_2(PO_3Et_2)_2$ and excess NaH in chlorobenzene was first conducted under the reported reaction conditions.[8] Separation of the reaction mixture on a silica gel column, eluting with chlorobenzene/acetone or toluene/ethyl acetate, afforded unreacted C_{70} as the first fraction followed by two additional fractions. Analysis of the second and third fractions by high-performance liquid chromatography (HPLC) on a Zorbax Sil column showed that they contained, respectively, a mixture of three products (in a ratio of 8:6:86) and two products (in a ratio of 16:84) (Figure 2).

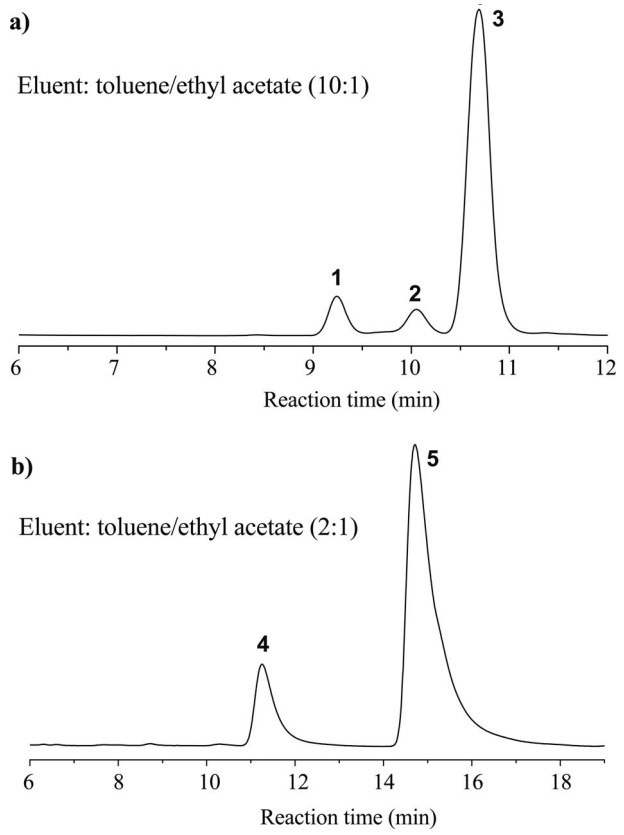
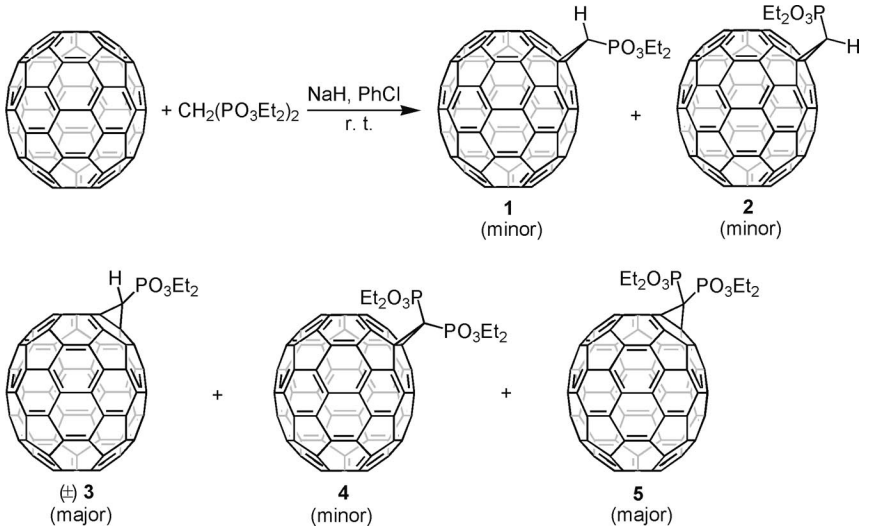


Figure 2. HPLC chromatograms of the second fraction (a) and the third fraction (b). Conditions: 4.6× 250 mm Zorbax Sil column, toluene/ethyl acetate mobile phase (1 mL/min), UV/Vis detection at 370 nm.

The ^1H NMR spectrum (see the Supporting Information) of the second fraction closely matches that reported by Yin et al.[8] in Figure S10, and corresponds to that of the first brown fraction reported in the literature. Taking the ^1H NMR spectrum and HPLC trace of the second fraction into account, the sample of the previously reported C_{70}>$CH(PO_3Et_2)$ may have been impure and probably contained another two minor products. Very low yields (less than 10% total yield) were obtained in our hands by stirring the reaction mixture at room temperature,[8] thus ultrasonication was employed to shorten reaction time and increase the product yields. Sonication of the reaction mixture of C_{70} with four equivalents of $CH_2(PO_3Et_2)_2$ and excess NaH in chlorobenzene resulted in much higher yields (25% total yield). When the aforementioned second fraction containing products **1**–**3** was separated on a longer silica gel column with less polar eluent, the first band and the last 1/3 portion of the second band gave pure product **1** and product **3**, respectively. The first 1/3 portion of the second band, which was enriched with compound **2**, was further separated by HPLC on a Zorbax Sil column to afford pure product **2**. The third fraction containing products **4** and **5** was further separated on a silica gel column to give pure minor product **4**, and then the pure major product **5**. Therefore, we obtained a total of five products, rather than two products as described in the previous report,[8] from the reaction of C_{70} with $CH_2(PO_3Et_2)_2$ and NaH (Scheme 1).

All of the five products were fully characterized by MS, by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, and by FTIR and UV/Vis analysis. The two major isolated products corresponded to the two adducts reported previously.[8] Product **5** was identified as the C1–C2 isomer of C_{70}>$C(PO_3Et_2)_2$ by comparison of its spectroscopic data with those reported in the literature;[6k,8] it had the same structure as that assigned by Yin et al.,[8] and correlates to the second brown fraction in the reference. The ^1H NMR spectrum of product **3**, which was the second major product, resembled that of C_{70}>$CH(PO_3Et_2)$ previously reported,[8] except for the presence of a clear multiplet (δ = 4.1 ppm) and a doublet (δ = 2.6 ppm) (due to isomers **1** and **2**, see below) and other impurities that were present in Figure S10 of the previous study.[8] The signal/noise (S/N) ratio of the ^{13}C NMR spectrum of product **3** was superior to that reported by Yin et al.[8] in Figure S11 and allowed unambiguous assignments of its ^{13}C NMR peaks. Importantly, no peak at δ = 29.68 ppm, which was assigned as the bridgehead methine carbon, was present.[8] Instead, a doublet peak at δ = 17.68 ppm with $^1J_{CP}$ = 185.8 Hz appeared in the ^{13}C NMR spectrum of product **3** and should be assigned as the methine carbon. The observed upfield shift (14.55–15.65 ppm) for the bridgehead carbon of product **3** relative to that of the corresponding C_{60} analogue (δ = 32.23[8] and 33.33[10] ppm) is reasonable because the bridgehead carbon of compound **5** (δ = 25.11 ppm[6k]) has approximately the same upfield shift compared to that of its C_{60} counterpart (δ = 39.38[6k] and 39.84[10] ppm). It can be clearly seen that four sp^2-carbon atoms of the C_{70} cage at δ = 146.61 ($^3J_{CP}$ = 4.3 Hz), 143.00 ($^3J_{CP}$ = 5.6 Hz), 139.96 ($^3J_{CP}$ = 4.6 Hz), and 137.23 ($^3J_{CP}$ = 5.2 Hz) ppm are split by the phosphorus atom. The couplings of the four sp^2-carbon atoms with the phosphorus atom were not mentioned in the early work.[8] The observation of an additional 59 peaks including five overlapping peaks in the 156–130 ppm region for the remaining 64 sp^2-carbon atoms of the C_{70} skeleton, and two nonequivalent sp^3-carbon atoms of the C_{70} moiety at δ = 63.03 ($^2J_{CP}$ = 4.9 Hz) and 61.99 ($^2J_{CP}$ = 4.6 Hz) ppm indi-



Scheme 1. Reaction of C_{70} with $CH_2(PO_3Et_2)_2$ and NaH.

cates that product **3** is a molecule with C_1 symmetry. Nevertheless, the ^{13}C NMR spectrum of C_{70}>$CH(PO_3Et_2)$ cannot unambiguously differentiate the C7–C21 isomer from the C1–C2 isomer because both have a molecular structure with C_1 symmetry.

Conclusive evidence for the structural assignment of product **3** came from its UV/Vis spectrum. UV/Vis spectral patterns are extremely useful for fullerene structural assignments. It is known that different types of C_{70} products have quite different UV/Vis spectral patterns, whereas the same type of C_{70} products display similar and characteristic absorption patterns.[4–7] In 1994, Meier et al. noted the similarity of the UV/Vis spectra of the C1–C2 and C5–C6 isomers of their synthesized C_{70} isoxazoline derivatives[5a] to those of $C_{70}H_2$.[11] Their further investigations indicated that C1–C2 isomers bearing different addends gave rise to similar UV/Vis spectral profiles.[12] The same phenomenon was observed for the corresponding C5–C6 isomers. In 1995, Wilson and Lu demonstrated the UV/Vis spectral similarity of the C1–C2 and C5–C6 isomers of the C_{70}-fused pyrrolidine derivative to those of $C_{70}H_2$, and stated that UV/Vis spectra were also characteristic of the addition pattern and would be useful in future structure assignments.[5d] We notice that product **3** has nearly the same UV/Vis spectral pattern to that of compound **5** (Figure 3), and also to other ring-fused C1–C2 isomers of C_{70} monoadducts, especially those of C_{70} monoadducts fused with a three-membered ring,[4c,4f,5c,5g,5h,6e,6k] indicating that product **3** is, in fact, the C1–C2 isomer, rather than the previously assigned C7–C21 isomer.[8]

A combination of ^1H and ^{13}C NMR analyses, together with UV/Vis spectroscopy, was used to assign the structure of the fullerene compounds.[12c] The minor products **1** and **2** were characterized as the C5–C6 isomers, which are regioisomers of the C1–C2 adduct **3**, as deduced from their spectroscopic data. Products **1** and **2** show the same molecular ion peak at m/z = 990. The UV/Vis spectra of products **1** and **2** are almost identical (Figure 3), and are nearly the

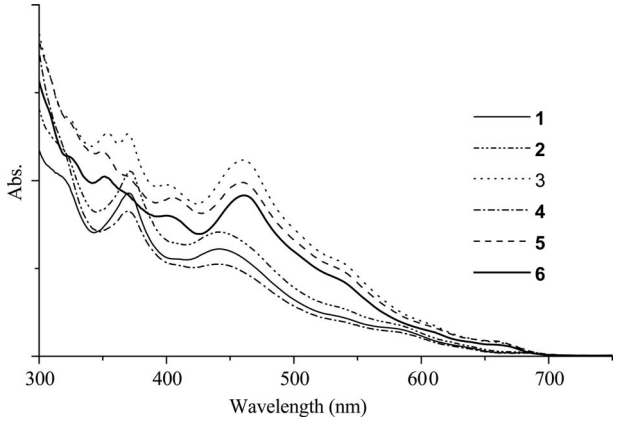


Figure 3. Comparison of the UV/Vis spectra of compounds **1**–**6**.

same as those of other C5–C6 adducts of C_{70},[4f,5c,5g,5h] again demonstrating that they are C5–C6 isomers. Generally, the groups stretching over the pole of C_{70} exhibit higher chemical shifts than others over the less pyramidalized carbon atoms.[5a,12c,12d] The δ_H shift of the methine hydrogen atom of compound **1** (δ = 2.91 ppm) is more downfield than that of compound **2** (δ = 2.65 ppm), whereas the δ_H trends for the ethoxy group of compounds **1** (δ = 4.21–4.11 and 1.33 ppm) and **2** (δ = 4.47–4.41 and 1.53 ppm) are exactly the opposite. This fact indicates that the methine hydrogen atom at the bridgehead should protrude towards the pole and the middle belt for compounds **1** and **2**, respectively. Products **1** and **2** exhibit similar ^{13}C NMR spectra; there were no more than 36 lines, including four half-intensity peaks and two doublet peaks, as a result of splitting by the phosphorus atom, for the 68 sp^2-carbon atoms of the C_{70} skeleton in the 153–125 ppm region, and a doublet at approximately 57 ppm ($^2J_{CP} \approx$ 4–5 Hz) for the two sp^3-carbon atoms of the C_{70} moiety, which is consistent with their C_s molecular symmetry. The methine carbon appears as a doublet peak at δ = 18.59 and 19.70 ppm for

products **1** and **2**, respectively, with $^1J_{CP}$ = 187 Hz. In addition, the δ_P shift of compound **1** (δ = 17.04 ppm) is more upfield than that of compound **2** (δ = 17.23 ppm) due to the different orientation of the phosphonate group, which correlates well with the δ_H shift of their counterparts from the ethoxy group in these two compounds.

Product **4** proved to be an isomer of product **5** because their mass spectra gave the same molecular weight (*m*/*z* = 1126). Again, the assignment of product **4** as the C5–C6 isomer was confirmed by its UV/Vis spectrum, as shown in Figure 3. The UV/Vis spectral patterns of products **1**, **2**, and **4** were nearly identical. In the ^{1}H NMR spectrum of product **4**, two sets of signals for the ethoxy groups were observed, and their chemical shifts were more upfield relative to product **5**, which is consistent with the assigned C5–C6 isomer. The ^{13}C NMR spectrum of product **4** was also consistent with the expected C_s molecular symmetry. Although only one singlet at δ = 15.01 ppm in the ^{31}P NMR spectrum of product **5** was observed, two doublets at δ_P = 15.36 and 14.63 ppm with $^3J_{PP}$ = 8.6 Hz were observed for isomeric product **4** due to the splitting of the two magnetically nonequivalent phosphorus atoms.

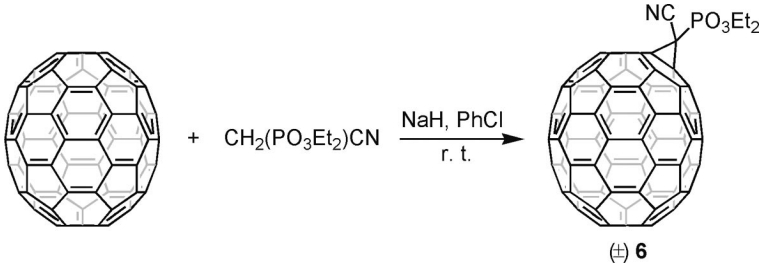
Intriguingly, the ratio of the combined yields of 5,6-isomers **1** and **2** to the yield of the C1–C2 isomer **3** (14:86) for C_{70}>CH(PO_3Et_2) is close to that of the ratio of C5–C6 isomer **4** to 1,2-isomer **5** (16:84) for C_{70}>C(PO_3Et_2)$_2$. These product distributions (**1/2/3** = 8:6:86, **4/5** = 16:84) accord very well with the general observation that, in the cycloaddition of C_{70}, the C1–C2 bond is the most reactive site and that the C5–C6 bond is the second most reactive site.[4–7]

Only one monoadduct isomer **6** could be isolated from the reaction of C_{70} with $CH_2(PO_3Et_2)CN$ and NaH (Scheme 2), as reported by Yin et al.[8] None, or only trace amounts, of other products were formed for other regioisomers of adduct **6** and arising from loss of the phosphate ester group or the cyano group. This phenomenon differs from that for the reaction of C_{70} with $CH_2(PO_3Et_2)_2$ and NaH.

The ^{1}H NMR spectrum of adduct **6** was the same as that reported by Yin et al.,[8] whereas the ^{13}C NMR spectrum of adduct **6** had a much better S/N ratio and did not suffer from interference from solvent peaks, thus making the peak assignments more reliable. Similar to product **3**, four sp^2-carbon atoms of the C_{70} skeleton at δ = 142.86 ($^3J_{CP}$ = 2.3 Hz), 139.73 ($^3J_{CP}$ = 3.8 Hz), 136.38 ($^3J_{CP}$ = 2.5 Hz), and 134.76 ($^3J_{CP}$ = 3.9 Hz) ppm were split by the phosphorus atom. An additional 58 peaks, including six overlapped signals are observed that correspond to the remaining 64 sp^2-carbon atoms of C_{70} in the range of 130–152 ppm. A doublet peak for the methine carbon at δ = 13.24 ppm with $^1J_{CP}$ = 180.6 Hz, which was not observed in the previous work,[8] can be clearly seen in this spectrum. The methine carbon of product **6** is also dramatically shifted upfield relative to that of the corresponding C_{60} analogue (δ = 30.9 ppm[13]). It should be noted that the two-bond splitting of the cyano carbon by the phosphorus atom is not observed. A similar lack of splitting for the methyl carbon by the phosphorus atom in C_{60}>C(PO_3Et_2)CH_3 was attributed to a small spin–spin coupling constant between the carbon atom of the methyl group and the phosphorus atom.[14] The two peaks at δ = 64.32 and 64.35 ppm are assigned to the two sp^3-carbon atoms of C_{70} as either different chemical shifts with no splitting by the phosphorus atom, or as coincidently identical chemical shifts with a coupling constant $^2J_{CP}$ = 2.9 Hz. Similar to product **3**, the recorded ^{13}C NMR spectrum of adduct **6** cannot distinguish between the C1–C2 isomer and the C7–C21 isomer. Once again, the UV/Vis spectrum of adduct **6** (Figure 3), which is similar to those obtained from products **3** and **5** as well as other C1–C2 adducts of C_{70},[4c,4f,5c,5g,5h,6e,6k] provides convincing evidence for its assignment as the C1–C2 isomer. By comparing the UV/Vis spectra in Figure 3, it is clear that the two different types of products, that is, the C1–C2 isomers **3**, **5**, and **6** and the C5–C6 isomers **1**, **2**, and **4** exhibit different and characteristic absorption patterns for each type of addition product.

It is noteworthy that two 5,6-isomers for C_{70}>CH(PO_3Et_2) exist, i.e., products **1** and **2**, in which the methine hydrogen atom protrudes towards the pole and towards the middle belt of C_{70}, respectively. However, for the 1,2-isomer of C_{70}>CH(PO_3Et_2) only one product (**3**) could be isolated. Product **3** is actually a racemic mixture with the methine hydrogen atom stretching towards the left and towards the right of C_{70}, respectively. Nevertheless, the racemic mixture containing both enantiomers has the same polarity on a silica gel column and gives rise to the same NMR spectroscopic data. The same is true for the 1,2-isomer of C_{70}>C(PO_3Et_2)CN, and only one product (compound **6**), could be separated.

To further confirm our reassignments, the relative energies of products **1**–**3**, **6**, and other regioisomers **7**–**16** (Figure 4) were calculated at the B3LYP/6-31G**//AM1



Scheme 2. Reaction of C_{70} with $CH_2(PO_3Et_2)CN$ and NaH.

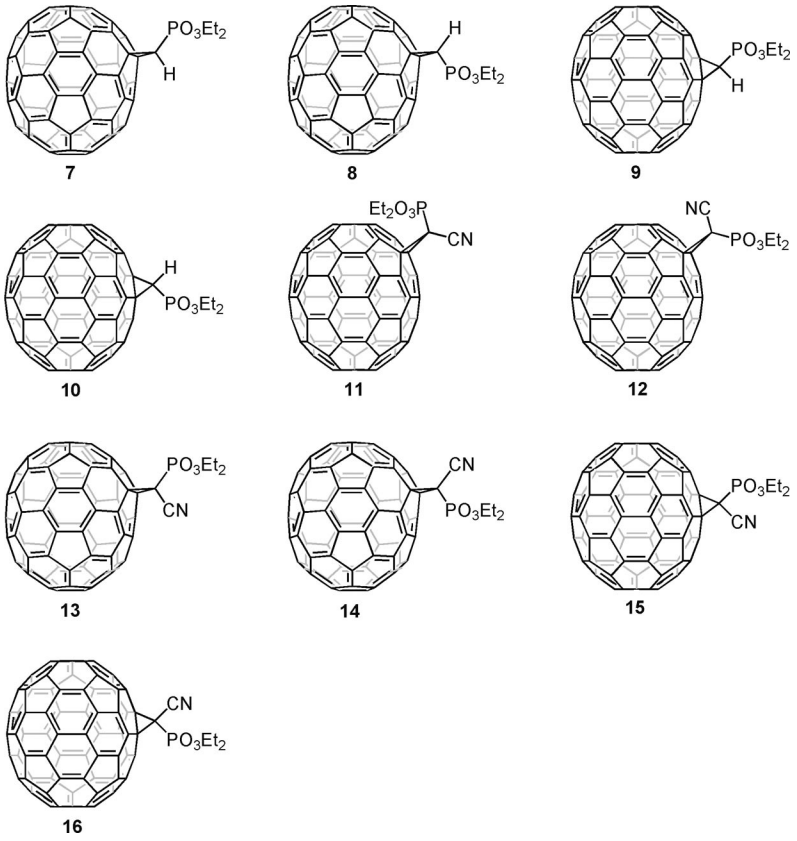


Figure 4. Structures of compounds **7**–**16**.

level,[15] and are listed in Table 1. Details of the AM1 optimized geometries and B3LYP/6-31G**//AM1 single-point energies for the isomers of C_{70}>CH(PO_3Et_2) and C_{70}>CCN(PO_3Et_2) are shown in the Supporting Information.

Table 1. Relative energies of compounds **1**–**3** and **6**–**16**.[a]

	C1–C2 isomer	C5–C6 isomer		C7–C8 isomer		C7–C21 isomer	
C_{70}>CH(PO_3Et_2)	0.0 (**3**)	2.7 (**1**)	2.0 (**2**)	9.4 (**7**)	12.2 (**8**)	17.0 (**9**)	17.2 (**10**)
C_{70}>C(PO_3Et_2)CN	0.0 (**6**)	1.5 (**11**)	2.2 (**12**)	11.2 (**13**)	13.9 (**14**)	15.7 (**15**)	17.1 (**16**)

[a] In kcal/mol and relative to the C1–C2 isomer. Compound numbers are given in parentheses.

As seen from Table 1, for both C_{70}>CH(PO_3Et_2) and C_{70}>C(PO_3Et_2)CN, the C1–C2 isomers are most stable, and the C7–C21 isomers are much less stable than the C1–C2 isomers by over 15 kcal/mol, thus explaining the preferred formation of the C1–C2 isomers.

Conclusions

The reaction of C_{70} with $CH_2(PO_3Et_2)_2$ and NaH was reinvestigated and found to afford products C_{70}>CH(PO_3Et_2) **1**–**3** and C_{70}>C(PO_3Et_2)$_2$ **4** and **5** as a regioisomeric mixture in each case. Compared with the previously reported work,[8] three additional minor isomeric products (compounds **1**, **2**, and **4**) have been isolated and fully characterized. The major products **3** and **5** and minor products **1**, **2**, and **4** were identified as the C1–C2 and C5–C6 isomers, respectively. In contrast, the reaction of C_{70} with $CH_2(PO_3Et_2)CN$ and NaH gave only one product C_{70}>C(PO_3Et_2)CN as the C1–C2 isomer. Ultrasonication was successfully employed to shorten the reaction times and increase the product yields. The previously reported C7–C21 isomers[8] for C_{70}>CH(PO_3Et_2) (**3**) and C_{70}>C(PO_3Et_2)CN (**6**) should be corrected as the C1–C2 isomers. These reassignments are further validated by theoretical calculations. The present reinvestigation confirms that the reactivity of the C1–C2 bond in C_{70} is higher than that of the C5–C6 bond for these two reactions, and eliminates the confusion caused by previous product misassignments.

Experimental Section

Reaction of C_{70} with $CH_2(PO_3Et_2)_2$ and NaH: The reaction was first conducted under the reported reaction conditions.[8] To a solution of C_{70} (20.0 mg, 0.024 mmol) and $CH_2(PO_3Et_2)_2$ (6.0 μL, 0.024 mmol) in anhydrous chlorobenzene (10 mL) at r.t., was added NaH (0.25 g). After 2 h (reaction monitored by TLC), the reaction mixture was filtered through a silica gel plug to remove excess NaH and other insoluble materials. The combined filtrate obtained from four runs was poured onto a silica gel column (2 × 8 cm). Elution with toluene and ethyl acetate (10:1) afforded 55.2 mg (69.0%) of recovered C_{70}, and then 4.5 mg (4.8%) of a mixture of products **1**, **2**, and **3**, which corresponded to the first brown fraction reported

by Yin et al.[8] The product ratio of **1/2/3** (8:6:86) is based on the peak areas of the HPLC trace on a Zorbax Sil column [4.6 × 250 mm; detection at 370 nm; toluene/ethyl acetate (10:1) as eluent]. Further elution of the reaction mixture with toluene and ethyl acetate (5:2) gave 2.8 mg (2.6%) of a mixture of products **4** and **5**. The **4/5** ratio (16:84) is based on the peak areas of the HPLC trace on a Zorbax Sil column [4.6 × 250 mm; detection at 370 nm; toluene/ethyl acetate (2:1) as eluent].

The low product yields obtained prompted us to employ ultrasonication to accelerate the reaction. To a mixture of C_{70} (42.0 mg, 0.05 mmol) and $CH_2(PO_3Et_2)_2$ (50.0 μL, 0.20 mmol) in anhydrous chlorobenzene (15 mL) was added NaH (0.40 g) and the mixture was sonicated at r.t. with a Branson ultrasonic cleaner for 8 min. The combined reaction mixture from two runs after filtration through a silica gel plug was separated on a silica gel column (2 × 8 cm). Elution with toluene and ethyl acetate (10:1) afforded 22.1 mg (26.3%) of recovered C_{70}, and then 15.1 mg (15.3%) of a mixture of products **1**–**3** (in a ratio of 8:6:86). Further elution of the reaction mixture with toluene and ethyl acetate (5:2) gave 10.9 mg (9.7%) of a mixture of products **4** and **5** (in a ratio of 16:84). The fraction containing products **1**–**3** was further separated on a long silica gel column (2 × 60 cm) with toluene and ethyl acetate (40:1) as the eluent to afford pure product **1** (ca. 1 mg) as a distinct band, followed by a mixture of products **2** and **3** as a second band. Pure product **3** was obtained by collecting the last 1/3 portion of the second band. The first 1/3 portion of the second band, in which product **2** was enriched, was separated by HPLC on a Zorbax Sil column [4.6 × 250 mm; petroleum ether/ethyl acetate (20:1) as eluent at 1 mL/min] to give pure product **2**. The fraction containing products **4** and **5** was further separated on a silica gel column [2 × 10 cm; toluene/ethyl acetate (3:1) as eluent] to give pure product **4**, followed by pure major product **5**.[8] The purities of products **1**–**5** were checked by HPLC with a Zorbax Sil column (4.6 × 250 mm), and were found to be over 98%.

Compound 1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.21–4.11 (m, 4 H, OCH_2), 2.91 (d, $^2J_{H,P}$ = 4.1 Hz, 1 H, CH), 1.33 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 17.04 (s, 1 P) ppm. ^{13}C NMR [75.5 MHz, CS_2/$CDCl_3$, with Cr(acac)$_3$ as relaxation reagent, all 2C unless indicated]: δ = 152.85 (1 C), 151.21, 149.75, 149.56, 149.37 (1 C), 149.31 (1 C), 149.30, 148.77, 148.51 (4 C), 148.13, 148.00, 147.31, 147.19 (1 C), 147.12, 146.92, 146.86, 146.74, 145.91, 145.85, 145.40 (4 C), 144.82, 144.44, 144.22, 143.87 (d, $^3J_{C,P}$ = 4.1 Hz), 143.05, 143.01, 142.07, 141.56, 138.21 (d, $^3J_{C,P}$ = 5.4 Hz), 132.31, 131.94, 131.82, 131.19, 129.42, 63.07 (d, $^2J_{C,P}$ = 6.2 Hz, O*C*H$_2$CH$_3$), 56.97 (d, $^2J_{C,P}$ = 4.7 Hz, sp^3-*C* of C_{70}), 18.59 (d, $^1J_{C,P}$ = 187.2 Hz, 1 C, *C*PO$_3$Et$_2$), 16.54 (d, $^3J_{C,P}$ = 5.7 Hz, OCH$_2$*C*H$_3$) ppm. UV/Vis ($CHCl_3$): λ_{max} = 318, 371, 441, 536, 582, 635, 682 nm. FTIR (KBr): $\tilde{\nu}$ = 2958, 2922, 2852, 1430, 1388, 1256, 1134, 1046, 1019, 975, 852, 793, 702, 672, 642, 575, 542, 503, 456 cm^{-1}. HRMS (ESI$^-$): calcd. for $C_{75}H_{11}O_3P$ [M]$^-$ 990.0446; found 990.0435.

Compound 2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47–4.41 (m, 4 H, OCH_2), 2.65 (d, $^2J_{H,P}$ = 3.9 Hz, 1 H, CH), 1.53 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 17.23 (s, 1 P) ppm. ^{13}C NMR [75.5 MHz, $CDCl_3$, with Cr(acac)$_3$ as relaxation reagent, all 2C unless indicated]: δ = 152.78 (1 C), 151.42, 149.82, 149.78, 149.46 (1 C), 149.40, 149.26 (1 C), 149.06, 148.72, 148.43, 148.20, 148.13, 147.28 (3 C), 147.15, 147.05, 146.97, 146.86, 145.97, 145.94 (4 C), 145.33, 145.02, 144.73, 144.47, 144.20, 143.74, 143.37, 141.97, 141.95 (d, $^3J_{C,P}$ = 3.6 Hz), 139.72 (d, $^3J_{C,P}$ = 5.2 Hz), 132.26, 131.97, 131.75, 131.28, 125.94, 63.51 (d, $^2J_{C,P}$ = 6.1 Hz, O*C*H$_2$CH$_3$), 56.80 (d, $^2J_{C,P}$ = 4.2 Hz, sp^3-*C* of C_{70}), 19.70 (d, $^1J_{C,P}$ = 187.1 Hz, 1 C, *C*PO$_3$Et$_2$), 16.74 (d, $^3J_{C,P}$ = 5.9 Hz, OCH$_2$*C*H$_3$) ppm. UV/Vis ($CHCl_3$): λ_{max} = 318, 371, 441, 536, 582, 635, 683 nm. FTIR (KBr): $\tilde{\nu}$ = 2968, 2924, 2854, 1430, 1261, 1160, 1128, 1045, 1021, 973, 843, 794, 684, 674, 649, 572, 527, 456 cm^{-1}. HRMS (ESI$^-$): calcd. for $C_{75}H_{11}O_3P$ [M]$^-$ 990.0446; found 990.0457.

Compound 3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.59–4.39 (m, 4 H, OCH_2), 2.93 (d, $^2J_{H,P}$ = 5.0 Hz, 1 H, CH), 1.62 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.52 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 17.19 (s, 1 P) ppm. ^{13}C NMR [75.5 MHz, $CDCl_3$, with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated]: δ = 155.91, 155.23, 151.99, 151.57, 151.43, 151.17, 151.14, 150.98, 150.64, 150.58, 150.56, 149.38, 149.31, 149.29, 149.27, 149.23, 149.00, 148.67, 148.59, 148.53, 148.43, 148.39, 148.37, 148.36 (2 C), 148.31, 147.66, 147.61, 147.53, 147.36, 147.29, 146.92, 146.86, 146.61 (d, $^3J_{C,P}$ = 4.3 Hz), 146.36, 145.96 (2 C), 145.88 (2 C), 145.28, 144.20, 143.98, 143.83, 143.82, 143.59, 143.38, 143.27, 143.21, 143.00 (d, $^3J_{C,P}$ = 5.6 Hz), 142.67, 142.60, 142.01, 141.92, 141.84, 140.19, 139.96 (d, $^3J_{C,P}$ = 4.6 Hz), 138.77, 137.23 (d, $^3J_{C,P}$ = 5.2 Hz), 133.85, 133.70, 132.73, 132.69, 130.86, 130.81 (2 C), 130.76 (2 C), 130.72, 63.64 (d, $^2J_{C,P}$ = 6.2 Hz, O*C*H$_2$CH$_3$), 63.56 (d, $^2J_{C,P}$ = 6.1 Hz, O*C*H$_2$CH$_3$), 63.03 (d, $^2J_{C,P}$ = 4.9 Hz, sp^3-*C* of C_{70}), 61.99 (d, $^2J_{C,P}$ = 4.6 Hz, sp^3-*C* of C_{70}), 17.68 (d, $^1J_{C,P}$ = 185.8 Hz, *C*H), 16.85 (d, $^3J_{C,P}$ = 5.7 Hz, OCH$_2$*C*H$_3$), 16.74 (d, $^3J_{C,P}$ = 5.8 Hz, O*C*H$_2$CH$_3$) ppm. UV/Vis ($CHCl_3$): λ_{max} = 325, 354, 370, 400, 459, 538, 609, 661 nm. FTIR (KBr): $\tilde{\nu}$ = 2975, 2922, 2852, 1510, 1428, 1255, 1161, 1136, 1045, 1021, 972, 795, 672, 576, 531, 454 cm^{-1}. HRMS (ESI$^-$): calcd. for $C_{75}H_{11}O_3P$ [M]$^-$ 990.0446; found 990.0461.

Compound 4: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.51–4.41 (m, 4 H, OCH_2), 4.16–4.03 (m, 4 H, OCH_2), 1.54 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 1.25 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 15.36 (d, $^3J_{P,P}$ = 8.6 Hz, 1 P), 14.63 (d, $^3J_{P,P}$ = 8.6 Hz, 1 P) ppm. ^{13}C NMR [75.5 MHz, $CDCl_3$, with Cr(acac)$_3$ as relaxation reagent, all 2C unless indicated]: δ = 153.41 (1 C), 151.43, 149.92, 149.65 (1 C), 149.56, 149.41 (1 C), 149.08, 148.83, 148.79, 148.59, 148.29, 148.24, 147.81, 147.76, 147.46 (1 C), 147.28, 147.08, 146.90, 146.07, 145.84, 145.74, 145.27, 145.05, 144.86, 144.36, 144.33, 144.14, 142.97, 139.89 (dd, $^3J_{C,P}$ = 5.9, 4.0 Hz), 139.75, 139.07 (dd, $^3J_{C,P}$ = 5.7, 4.5 Hz), 132.16, 131.85, 131.41, 131.36, 130.29, 64.08 (d, $^2J_{C,P}$ = 6.4 Hz, O*C*H$_2$CH$_3$), 63.67 (d, $^2J_{C,P}$ = 6.4 Hz, O*C*H$_2$CH$_3$), 59.45 (t, $^2J_{C,P}$ = 3.8 Hz, sp^3-*C* of C_{70}), 16.73 (d, $^3J_{C,P}$ = 6.1 Hz, OCH$_2$*C*H$_3$), 16.38 (t, $^3J_{C,P}$ = 6.0 Hz, OCH$_2$*C*H$_3$) ppm. UV/Vis ($CHCl_3$): λ_{max} = 370, 441, 536, 582, 635, 684 nm. FTIR (KBr): $\tilde{\nu}$ = 2976, 2924, 2852, 1428, 1258, 1161, 1094, 1055, 1019, 977, 834, 796, 730, 666, 645, 597, 579, 530, 458 cm^{-1}. HRMS (ESI$^-$): calcd. for $C_{79}H_{20}O_6P_2$ [M]$^-$ 1126.0735; found 1126.0722.

Reaction of C_{70} with $CH_2(PO_3Et_2)CN$ and NaH: The previously described reaction conditions were adopted to obtain adduct **6**.[8] To a solution of C_{70} (20.0 mg, 0.024 mmol) and $CH_2(PO_3Et_2)CN$ (4.3 mg, 0.024 mmol) in anhydrous chlorobenzene (10 mL) at r.t. was added NaH (0.25 g), the reaction mixture was stirred for 4 h, and filtered through a silica gel plug to remove excessive NaH and other insoluble materials. The combined reaction mixture was poured onto a silica gel column (2 × 8 cm) and eluted with toluene and ethyl acetate (10:1) to give 62.1 mg (77.6%) of recovered C_{70}, and then 2.5 mg (2.6%) of product **6**.

Ultrasonication was also employed to improve the product yield. To a solution of C_{70} (42.0 mg, 0.05 mmol) and $CH_2(PO_3Et_2)CN$ (32 μL, 0.20 mmol) in anhydrous chlorobenzene (15 mL) at r.t., was added NaH (0.25 g) and the mixture was sonicated at r.t. with a Branson ultrasonic cleaner for 8 min. The same work-up procedure

from two runs afforded 36.1 mg (43.0%) of recovered C_{70}, and 4.0 mg (3.9%) of product **6**. The purity of adduct **6** was checked by HPLC and found to be over 95%. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 4.70–4.55 (m, 2 H, OCH_2), 4.51–4.41 (m, 2 H, OCH_2), 1.72 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.54 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.05 (s, 2 P) ppm. ^{13}C NMR [75.5 MHz, CS_2/$CDCl_3$, with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated]: δ = 155.12, 154.41, 151.20, 151.18, 151.03 (2 C), 150.99, 150.73, 150.44, 150.41, 150.40, 149.30, 149.27 (2 C), 149.25 (2 C), 149.11, 149.05, 148.77, 148.70, 148.65, 148.39, 148.37, 148.36, 148.35, 147.98, 147.39, 147.35, 147.21, 147.13, 147.08, 146.84 (2 C), 146.44, 146.10 (2 C), 145.78, 145.76, 145.41, 144.67, 144.57, 143.92, 143.84, 143.81, 143.71, 143.66, 143.58, 143.27, 142.99, 142.90, 142.86 (d, $^3J_{C,P}$ = 2.3 Hz), 142.54, 141.62, 141.59, 141.00, 139.73 (d, $^3J_{C,P}$ = 3.8 Hz), 136.38 (d, $^3J_{C,P}$ = 2.5 Hz), 134.76 (d, $^3J_{C,P}$ = 3.9 Hz), 133.53, 133.49, 132.64, 132.54, 131.19, 131.14, 130.97, 130.93, 130.77 (2 C), 113.03 (CN), 65.45 (d, $^2J_{C,P}$ = 6.5 Hz, O*C*H_2CH$_3$), 65.29 (d, $^2J_{C,P}$ = 6.5 Hz, O*C*H_2CH$_3$), 64.35 (sp^3-*C* of C_{70}), 64.32 (sp^3-*C* of C_{70}), 16.78 (d, $^3J_{C,P}$ = 5.6 Hz, OCH$_2$*C*H$_3$), 16.59 (d, $^3J_{C,P}$ = 5.6 Hz, O*C*H$_2$CH$_3$), 13.24 (d, $^1J_{C,P}$ = 180.6 Hz, *C*CN) ppm. UV/Vis ($CHCl_3$): λ_{max} = 325, 352, 369, 399, 461, 538, 609, 661 nm. FTIR (KBr): $\tilde{\nu}$ = 2974, 2924, 2852, 2239, 1429, 1276, 1161, 1132, 1092, 1040, 1016, 796, 728, 669, 581, 535, 459 cm^{-1}. HRMS (ESI$^-$): calcd. for $C_{76}H_{10}NO_3P$ [M]$^-$ 1015.0398; found 1015.0416.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compounds **1**–**4** and **6**, AM1-optimized geometries and B3LYP/6-31G**//AM1 single-point energies for the isomers of C_{70}>CH(PO_3Et_2) and C_{70}>CCN(PO_3Et_2).

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