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Reactions of [60]fullerene with alkynes promoted by OH^-†

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In the current work, the reactions of [60]fullerene with alkynes promoted by OH^- (base) are addressed. The treatment of C_{60} with alkynes in the presence of TBAOH produces alkynylation products (R-C_{60}–H) with high selectivity in *o*-DCB at 100 °C. Plausible reaction mechanisms were proposed. This work provides a convenient and environmental friendly method for the functionalization of fullerenes.

Fullerenes functionalized with alkynyl groups are particularly valuable in materials science and organic chemistry due to their excellent electrochemical properties, among others. The combination of fullerene and acetylene units is not only a potential precursor for developing novel fullerene-based dimers or polymers,[1,2] but also can promote the conjunction pathway with a supramolecular framework providing new properties. For example, it has been reported that fullerene covalently linked to acetylenic polythiophene produces unique photoelectronic properties.[3,4] On the other hand, alkynes are considered as one of the most outstanding building blocks for unsaturated molecular scaffolds in organic synthesis, owing to their transformation potential into various functional groups.[5–8]

Up to now, the easiest method to achieve acetylene derivatives of C_{60} is based on reactions of fullerene with alkynyllithium. Komatsu *et al.* reported the synthesis, characterization and properties of the first acetylene derivative of C_{60} containing a trimethylsilyl ethynyl group or a phenylethynyl group.[9,10] Diedrish *et al.* prepared a series of alkynylfullerenes using the same method.[1,11] However, the use of organolithium reagents led to complex experimental conditions, due to them being extremely sensitive to air and moisture.[12] Hence, new methods for the preparation of alkynylfullerene compounds are necessary, reducing the steps involved in the synthesis, and responding to new regulations associated with sustainability. In this sense, these new procedures would not only be efficient, selective, high-yielding, but also easy to operate and environmentally friendly.

In this work, our group deeply worked on the new functionalized chemistry of fullerenes with alkynes and found that the nucleophilic carbon functionalization of C_{60} with alkynes could be mediated by OH^-. In this sense, TBAOH (tetra-*n*-butylammoniumhydroxide) was used as a source of OH^-, because it is cheap, environment friendly, and allows getting a high efficiency in the transformations. This new process allows getting highly functionalized alkynylfullerene derivatives through a one-step reaction. Furthermore, the protocol is simple, and works with a wide range of alkynes. Interestingly, different types of alkynes undergo diverse reaction pathways.

A series of phenylacetylene compounds were chosen as model substrates to optimize the reaction. The experimental procedure for the new nucleophilic reaction is very simple: a mixture composed by C_{60} (36 mg) and a series of alkynes (20 equiv.) was stirred in *o*-DCB (*o*-dichlorobenzene) with a solution 1.0 mol L^{-1} of TBAOH/CH_3OH (150 µL, 3 equiv.), as the OH^- source, under argon gas for 1 h at 100 °C. The colour of the reaction gradually changed from purple to dark green after the addition of TBAOH/CH_3OH. It was observed that the use of an excess TBAOH or longer reaction time did not improve the yield because of the formation of polar side products, like multiple addition compounds.[13] Subsequently, a trifluoroacetic acid treatment, produced the different alkynylfullerenes **2a–2d** with 1,2-addition and the yield is 35.2%, 29%, 21.1%, 31.5%, respectively (listed in Table 1) after separation by Buckyprep column. The trifluoroacetic acid is working as the donor of protons. The 1,4-substituted phenylacetylene with both electron-donating and electron-withdrawing groups on the phenyl could be used in the reaction as it can be observed in Table 1.

The structures of 1,2-addition C_{60} compounds **2a–2d** were fully characterized and elucidated by their HRMS, ^{1}H NMR, ^{13}C

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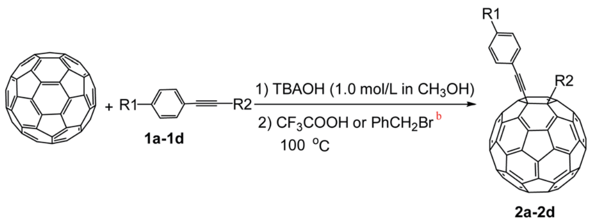
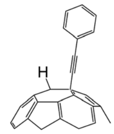
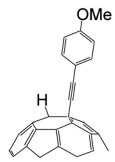
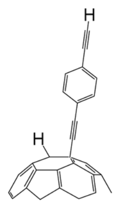
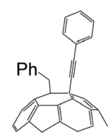
Table 1 Alkynylation of C_{60}[a]



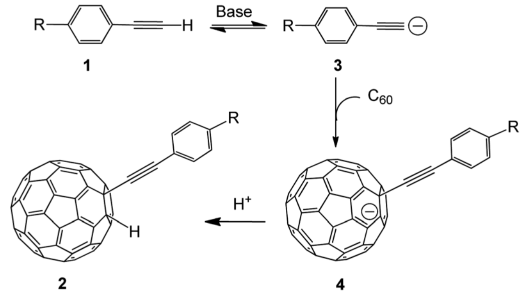
Entry	1	R1	R2	2a–2d[b]	Yield (%)[c]
1	**1a**	H	H		35.2
2	**1b**	OMe	H		29.0
3	**1c**	CCH	H		21.1
4	**1d**	H	CO_2Et		31.5

[a] All reactions were performed in *o*-DCB using an oil bath at 100 °C. Molar ratio of compound **1** : C_{60} = 20 : 1. [b] CF_3COOH was used in the reaction of C_{60} with **1a–1c**. While $PhCH_2Br$ was used in the case of C_{60} with **1d**. [c] Isolated yield.

NMR, and UV-vis spectra. The products **2a–2c** exhibited proper molecular weights in their mass spectra. The ^{13}C NMR spectra for **2a–2c** clearly exhibited no more than 29 peaks in the range of 134–152 ppm, associated with the sp^2-carbons of the fullerene cage, which is consistent with the *Cs* symmetry of their molecule structure, and the peak placed at 54–55 ppm for the sp^3-carbon of fullerene and alkyne. The UV-vis spectra for all products showed a peak at 434 nm, which is the characteristic peak of the 1,2-adducts of C_{60}.

The previous analysis allows proposing a reaction mechanism for the formation of **2a–2d** as is shown in Scheme l. First, the reaction of terminal alkynes **1** with TBAOH/CH_3OH generates an intermediate compound **3**, which suffers a nucleophilic addition to produce **4** (RC_{60}^-). The protonation of the intermediate species **4** leads to the formation of the product **2**.

The reactivity of other types of alkynes in the same conditions was also studied. The derivatives **2a** (in general conditions), and **2d** (when CF_3COOH changed to $PhCH_2Br$) were



Scheme 1 Proposed mechanism for the formation of **2a–2c**.

curiously obtained when the terminal alkynes were transformed into ethylphenylpropiolate. The structures composed by two different C_{60}-with alkynes were studied and determined through their HRMS, ^{1}H NMR, ^{13}C NMR, and UV-vis spectra. The results indicated that the cleavage of ethylphenylpropiolate occurred at the C–C bond, specifically, between phenylpropynyl and ethoxycarbonyl. This fact is confirmed by the crystal structure of **2d** (Fig. 1).

A plausible mechanism for the formation of **2a** and **2d** compounds is deduced in the Scheme 2. The substrate **5** undergoes hydrolysis (under base conditions) to produce a carboxylic anion, which decomposes to CO_2. Because the conjugated phenylethynyl group can disperse the negative charge, it makes it possible to form the intermediate **6.** The α,β-unsaturated carboxylic acid **6** undergo decarboxylation[14] and generates a carbanion **3** in base condition to attack C_{60}. The protonation or nucleophilic addition of benzyl bromide produces **2a** and **2d**, respectively.

The reactivity of the ester group was deeply studied using ethyl propiolate as substrate, which has a weak acid proton and an electron-withdrawing ester group in its structure. It is interesting to observe that the reactions of C_{60} with **7** using TBAOH/CH_3OH (1.0 mol L^{-1}) and TBAOH/isopropanol (1.0 mol L^{-1}) led to different products as the unprecedented

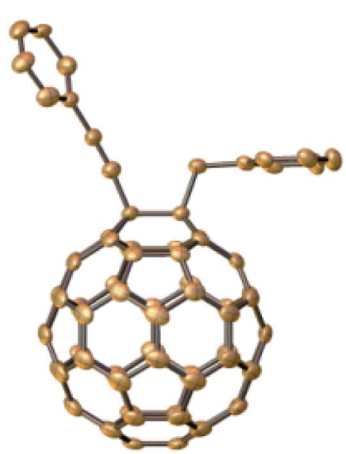
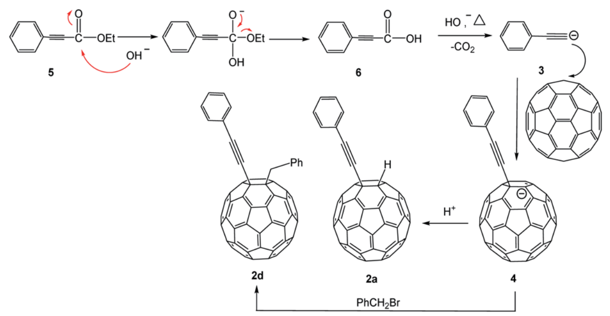


Fig. 1 Single crystal structure of **2d** with 30% ellipsoid probability (hydrogens are omitted). The CCDC number of the crystal structure is: 2082000.



Scheme 2 Proposed mechanism for the formation of **2d**.

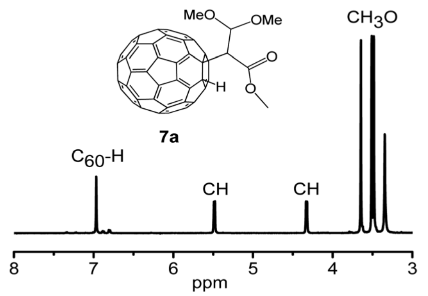


Fig. 3 Expanded ^{1}H NMR spectrum of **7a** recorded using CS_2/(DMSO-d_6 as the external lock) measured in a 600 MHz instrument.

product **7a** and **7b** with an isolated yield of 35.2% and 11.8% respectively. In addition, three CH_3O^- groups were incorporated in the adduct **7a**, apparently, methanol participates in the reaction and two bonds of alkyne are broken. Nevertheless, the alkynylfullerene derivative **7c** with an isolated yield of 27.5% was obtained at room temperature (Fig. 2). The reaction between C_{60} with 7 and TBAOH/CH_3OH (1.0 mol L^{-1}), suggests that methanol participates in the reaction. Obviously, the reactions follow different routes in the presence of methanol and isopropanol.

The structure of derivatives **7a–7c** were estimated through HRMS, ^{1}H NMR, ^{13}C NMR, HMBC, HSQC and UV-vis spectra. HRMS (+ESI) of **7a** and HRMS (-ESI) of **7c** show the protonated molecular ions ($[M + H]^+$) and ($[M-H]^-$), which are placed at 869.6473 and 817.0260, respectively (Fig. S23 and S29 in ESI†). These are in good agreement with the assigned structures (**7a:** $C_{66}H_{13}O_4^{\ +}$, calcd. 869.0814; **7c:** $C_{65}H_5O_2^{\ -}$, calcd. 817.0290). The 1,2-addition pattern of **7a** and **7c** was further confirmed through UV-vis spectra which shown a characteristic sharp peak placed at 435 nm. Fig. 3 displays the ^{1}H NMR spectrum of **7a**, where the methoxy protons are characterized by the three singlets situated at 3.48, 3.51, and 3.65 ppm, respectively.[13,15] The C_{60}–H proton was observed at 6.97 ppm. The ratio defined by peak area of the methoxy protons and the C_{60}–H proton is 3 : 1, consist with the addends added to C_{60} is methoxy groups, and indicated that the methanol from TBAOH solution took part in the reaction. Two methoxy protons (3.51 and 3.65 ppm) show $^{3}J_{CH}$ correlations with the carbon of the methenyl group respectively (Fig. S26 in ESI†), which indicates that these two methoxyl groups were linked to the same carbon of methenyl. HSQC NMR (Fig. S27 in ESI†) confirmed the structure of **7a**. It should be noted that there is another peak with a retention time at 6.8 min associated with a HPLC trace of the reaction of C_{60} with TBAOH/CH_3OH (1.0 mol L^{-1}) (Fig. S5 in ESI†). Data extracted from HRMS, ^{1}H NMR, ^{13}C NMR, HMBC, HSQC and UV-vis spectra, lead us to inferred that the peak placed before **7a** belongs to product **7b** (Fig. S29–S33 in ESI†).

A reaction mechanism is proposed and shown in the Scheme 3. The key is that the alcoholic solution (in the TBAOH) could affect the structure of the final products. Ethyl propiolate **7** is an α,β-unsaturated carbonyl compound in the reaction. Methanol attacks to β-carbon (basic conditions), and produces the intermediate **8**. To verify the alcohol exchange reaction, a control experiment between **7** and TBAOH/CH_3OH (1.0 mol L^{-1}, 150 μL, 3 equiv.) in *o*-DCB was carried out for 1 h at 100 °C. As expected, ^{1}H NMR spectra of the reaction shows peaks at 4.26 ppm (q, 2H) and 1.32 ppm (t, 3H), which are associated with methylene and methyl protons of compound **7**, respectively. In addition, the peak around 3.80 ppm is associated with methyl proton of methyl propiolate (Fig. S42 in ESI†), and it reveals that the crude contains both ethyl propiolate **7** and methyl propiolate, confirming the alcohol exchange reaction. Therefore, **7a** and **7b** products are both detected. However, similar reactions do not take place in the case of phenylacetylene and ethylphenylpropiolate are used as substrates, probably due to the steric hindrance of the phenyl ring in the molecule. The produced intermediate **8** generates **9** *via* Michael addition.[15,16] A

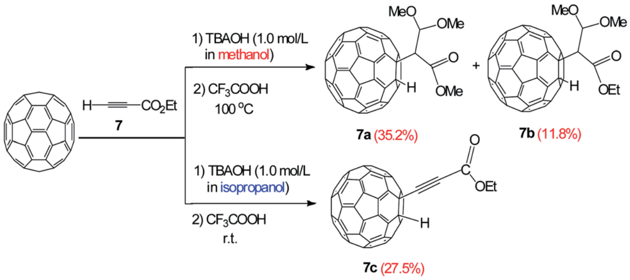
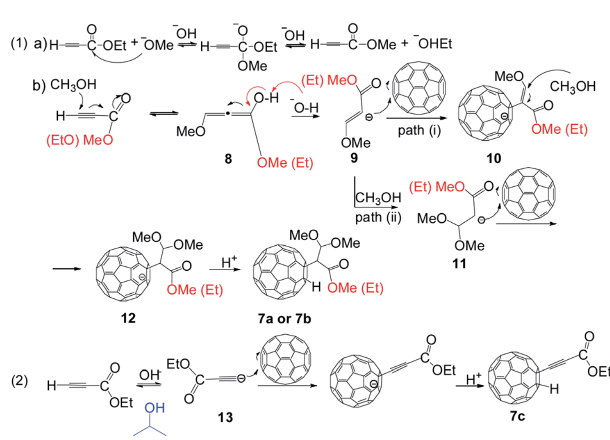


Fig. 2 Reaction of C_{60} and **7** in the presence of OH^-.



Scheme 3 Proposed mechanism for the formation of **7a–7c**.

part of **9** produces **11** through alcohol exchange reaction. The Michael addition, and subsequent protonation, would afford the generation of **7a** and **7b**. However, the Michael addition reaction was restricted when methanol was changed to isopropanol. This fact was ascribed to two reasons: (1) the steric effect of isopropanol; (2) the lower reactivity of isopropanol.[17–19] Thus, a deprotonation reaction of **7** happens when isopropanol is present. The generated intermediate **13** undergoes through nucleophilic addition and protonation to produce **7c**.

Conclusions

In summary, we have found that the addition of alkynes to C_{60} can now be achieved without the use of heavy metals and alkynyllithium, under simple reactiond which were mediated by OH^-. In the reaction of C_{60} with ethyl propiolate, the use of alcoholic solution in the TBAOH was found to be crucial. The reaction performed under methanol afforded a Michael-addition product, but Michael-addition was restrained while the reaction under isopropanol. Through the nucleophilic addition, we have introduced alkynes, a versatile functional group to C_{60} under mild conditions, and the monoadducts may also prove to be useful for other applications.

Conflicts of interest

There are no conflicts of interest.

Acknowledgements

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