## Decatungstate-Mediated Radical Reactions of C<sub>60</sub> with Substituted Toluenes and Anisoles: A New Photochemical Functionalization Strategy for Fullerenes

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## ABSTRACT



A convenient, highly efficient, decatungstate-mediated chemical methodology to functionalize fullerenes is demonstrated. A variety of radicals have been generated by the photochemical interaction of tetrabutylammonium decatungstate [ $(n-Bu_4N)_4W_{10}O_{32}$ ] and para-substituted toluenes, anisoles, and thioanisole and effectively trapped by the [60]fullerene affording the corresponding 1,2-dihydro[60]fullerene monoadducts in moderate to good yields.

[60]Fullerene, the most abundant representative of the fullerene family, was produced for the first time in macroscopic quantities in 1990.<sup>1</sup> Since then, various types of reactions of fullerenes have been developed to synthesize a great diversity of fullerene compounds, some of which have seen potential applications in material sciences and medicinal chemistry.<sup>2</sup> Free-radical reactions were one of the first investigated reactions of fullerene C<sub>60</sub>.<sup>3</sup> Since this molecule has 30 carbon—carbon double bonds, multiple additions of a variety of radicals can take place very readily, warranting characterization of C<sub>60</sub> as a radical sponge.<sup>4</sup> For example, up to 11 phenyl groups, 15 benzyl groups, and 34 methyl groups have been reported to add to  $C_{60}$ .<sup>4</sup> Subsequently, the resulting reaction mixture consists of many and hard to separate products.

On the other hand, over the past decades, tetrabutylammonium decatungstate (TBADT) mediated radical reactions have been explored extensively and have found widespread applications in organic synthesis. In particular, decatungstate has been successfully used in many oxidative chemical

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<sup>(1)</sup> Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354–358.

<sup>(2) (</sup>a) Nakamura, E.; Isobe, H. Acc. Chem. Res. 2003, 36, 807–815.
(b) Wudl, F. J. Mater. Chem. 2002, 12, 1959–1963.

<sup>(3) (</sup>a) Hirsch, A.; Brettreich, M. *Fullerenes, Chemistry and Reactions*; Wiley-VCH: Weinheim, Germany, 2005. For recent examples of radical reactions of  $C_{60}$ , see: (b) Gan, L. C. R. Chimie **2006**, 9, 1001–1004. (c) Wang, G. W.; Li, F. B. J. Nanosci. Nanotechnol. **2007**, 7, 1162–1175.

<sup>(4) (</sup>a) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274–6275. (b) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183–1185.

transformations<sup>5</sup> and to a lesser extent under unaerobic conditions in synthetically useful chemical processes.<sup>6</sup> However, no studies have been reported to date concerning the formation of phenoxymethyl and phenylthiomethyl radicals derived from substituted anisoles and thioanisole, respectively, by the photoexcited TBADT ( $W_{10}O_{32}^{4-}$ ). More interestingly, there is no published work to date concerning the employment of TBADT as a catalyst for the functionalization of the fullerene C<sub>60</sub>.

Herein, we describe a convenient, highly efficient, TBADTmediated chemical methodology to functionalize fullerenes. The mechanism of this reaction seems to be complicated as two well-established photosensitizers are involved, namely TBADT and  $C_{60}$ . However, apart from the synthetic value of this reaction, a major mechanistic insight has been achieved.

The reaction of  $C_{60}$  with a variety of benzyl radicals derived from para-substituted toluenes 1-5 in the presence of TBADT was first investigated (Table 1), affording the





 $^a$  For general considerations, see the Supporting Information.  $^b$  Isolated yield.

corresponding functionalized fullerenes **1a**–**5a** in moderate to good yields.<sup>7</sup> This reaction was carried out simply by irradiating a solution of C<sub>60</sub> with 1000 equiv of substrate **1**–**5** and 0.8 equiv of TBADT, in a mixture of chlorobenzene/acetonitrile (85:15)<sup>8</sup> using a 300 W xenon lamp.<sup>9</sup> This is the first report concerning the isolation and characterization of C<sub>60</sub> monoadducts via a single benzyl radical addition.

In order to further exploit this powerful functionalization strategy for  $C_{60}$ , we studied the potential reactivity of anisoles

**6–9** toward TBADT. To our delight, the reactivity of the intermediate para-substituted phenoxymethyl radicals (derived from anisoles **6–9**) toward  $C_{60}$  was even higher, under the same experimental conditions reported above (Table 2).<sup>10</sup>





 $^a$  For general considerations, see the Supporting Information.  $^b$  Isolated yield.

Since the reaction of anisoles 6-9 with  $C_{60}$  leads directly to ethers 6a-9a in good yields, it was of interest to investigate the reaction of thioanisole 10 with  $C_{60}$  (Scheme 1). Indeed, following the previous photocatalytic procedure,



the phenylthiomethyl radical was efficiently trapped by  $C_{60}$  to yield for the first time a thioether fullerene derivative (**10a**) in high yield.

The structures of the novel compounds 2a-10a were unambiguously established by UV-vis, FTIR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic techniques, as well as by mass spectrometry. As diagnostic signals in the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>/CS<sub>2</sub>), the -CH<sub>2</sub>- benzyl protons of 1,2-dihydro-[60]fullerenes **1a-5a** resonate at  $\delta$  4.71-4.90 ppm, whereas the protons attached on the fullerene core have a character-

<sup>(5)</sup> For selected examples, see: (a) Tanielian, C. *Coord. Chem. Rev.* **1998**, *178–180*, 1165–1181. (b) Tanielian, C.; Seghrouchni, R.; Schweiter, C. J. Phys. Chem. A **2003**, *107*, 1102–1111. (c) Lykakis, I. N.; Tanielian, C.; Orfanopoulos, M. Org. Lett. **2003**, *5*, 2875–2878. (d) Tzirakis, M. D.; Lykakis, I. N.; Panagiotou, G. D.; Bourikas, K.; Lycourghiotis, A.; Kordulis, C.; Orfanopoulos, M. J. Catal. **2007**, *252*, 178–189 and references cited therein.

<sup>(6)</sup> For selected examples, see: (a) Jaynes, B. S.; Hill, C. L. J. Am. Chem. Soc. **1995**, 117, 4704–4705. (b) Dondi, D.; Fagnoni, M.; Molinari, A.; Maldotti, A.; Albini, A. Chem. Eur. J. **2004**, 10, 142–148. (c) Esposti, S.; Dondi, D.; Fagnoni, M.; Albini, A. Angew. Chem., Int. Ed. **2007**, 46, 2531– 2534.

<sup>(7)</sup> Compound **1a** has been previously synthesized by reaction of  $C_{60}$  dianion with benzyl bromide, see: Chen, J.; Cai, R-F.; Huang, Z-E.; Wu, H-M.; Jiang S-K.; Shao, Q-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1553–1554.

<sup>(8)</sup> It is known that most of the reactions employing TBADT are carried out in acetonitrile (or rarely in another polar solvent). On the other hand, it is well known that only traces of fullerene are able to be diluted in acetonitrile, if any. However, a 85:15 ratio of chlorobenzene/acetonitrile mixture was found to be the most efficient solvent for suppressing the dilution problems for both TBADT and C<sub>60</sub>.

<sup>(9)</sup> The reaction of toluenes 1-5 with  $C_{60}$  is also effective using a lower amount of TBADT and/or substrate 1-5, but the yields and/or the reaction times required were too low for a synthetic application.

<sup>(10)</sup> For comparison reasons, the conditions for the preparation of 1a-5a adducts were also applied in this case. The reaction of anisoles 6-9 with  $C_{60}$  is also effective using a lower amount of the substrate. For instance, the reaction of  $C_{60}$  with a 100-fold excess of 6 resulted 6a in a 30% yield within 8 h.

istic absorption at 6.58–6.65 ppm due to the deshielding effect of C<sub>60</sub>. In the <sup>13</sup>C NMR spectra, the benzylic carbon atom appears at  $\delta$  52.55–53.19 ppm, while the C<sub>60</sub>-H sp<sup>3</sup> carbon resonates at 59.03–59.59 ppm. The corresponding <sup>1</sup>H and <sup>13</sup>C NMR signals of the compounds **6a–10a** were also identified either upfield or downfield shifted compared to the corresponding NMR signals of **1a–5a** (see the Supporting Information). More importantly, the <sup>13</sup>C NMR spectra of compounds **1a–10a** exhibit all of the patterns that correspond to a C<sub>60</sub> derivative with *C<sub>s</sub>* symmetry induced by the addition of two different addends (achiral) to the 6,6junction bond of C<sub>60</sub>. Thus, there are 30 <sup>13</sup>C NMR signals (one or two of which may be overlapped) for the sp<sup>2</sup> carbons of the C<sub>60</sub> core and two signals for the sp<sup>3</sup>-hybridized fullerenyl carbons.

In the UV-vis absorption spectra, all of the compounds 1a-10a showed a weak absorption around 432 nm, which is diagnostic for 1,2-adducts of fullerene (while 1,4-adducts exhibit a broad absorption band at ca. 445 nm).<sup>3a</sup> The high energy absorptions at ca. 330 and 258 nm are attributed to the fullerene moiety.<sup>11</sup>

To explore the mechanism of this reaction, a series of experiments were performed. Initially, the source of the hydrogen atom in RC60H was investigated. The photocatalyzed reaction of 1 and 6 with C<sub>60</sub> was performed in separate experiments, first in a mixture of dry C<sub>6</sub>H<sub>5</sub>Cl/CD<sub>3</sub>CN (85: 15) and then in a mixture of C6H5Cl/CH3CN containing 0.5%  $D_2O$ . No measurable deuteration resulted in the first case, while in the second set of experiments, the products 1a and 6a were highly deuterated (deuterium incorporation more than 80% at the  $C_{60}$  sp<sup>3</sup> carbon), as determined by <sup>1</sup>H NMR integration (see the Supporting Information). This result indicates the formation of the fullerene anion as a reactive intermediate in the TBADT-mediated reactions of C<sub>60</sub>. Furthermore, compounds 1a and 6a do not exchange their proton in a measurable amount (<sup>1</sup>H NMR) since no deuterium incorporation could be detected after a sample of 1a or 6a in a 85:15 mixture of C<sub>6</sub>H<sub>5</sub>Cl/CH<sub>3</sub>CN had been agitated with  $D_2O$  for several hours or even upon irradiation. Finally, no H-D exchange observed (<sup>1</sup>H NMR) when a deaerated solution of 1a (3 mg,  $3.7 \,\mu$ mol) was irradiated in the presence of TBADT and 0.5% D<sub>2</sub>O, under the experimental conditions mentioned above.

It should be also mentioned that TBADT is known to react with organic substrates either through an electron transfer (ET) or a hydrogen atom transfer (HAT) mechanism.<sup>5b,12</sup> Both mechanisms give rise to the same substrate-derived organic radical R<sup>•</sup>, and hence, the distinction between these two mechanistic paths is not straightforward. In order to clarify this issue, we used 9,10-dicyanoanthracene (DCA) as the photosensitizer in the reaction of 4-methylanisole **11** with C<sub>60</sub>. DCA is a well-established ET photosensitizer in a polar solvent such as acetonitrile.<sup>13</sup> The only product obtained from this reaction was **11a**, while the corresponding TBADT- catalyzed reaction of 11 gave the two adducts 11a and 11b in equimolar amounts (Scheme 2). Consequently, it is



reasonable to assume that two different mechanisms operate in the DCA- and TBADT-mediated reactions. As we already mentioned, since previous results support an ET mechanism on the DCA photocatalyzed reactions with aromatic substrates,<sup>13</sup> it is plausible that in this case the DCA photocatalyzed functionalization of C<sub>60</sub> proceeds also through the same mechanism. It is likely therefore that a HAT mechanism from both  $-CH_3$  and  $-OCH_3$  groups of **11** predominates in the corresponding TBADT-catalyzed reactions.<sup>14</sup>

Assuming that a HAT mechanism is operating in these reactions, then the observed reactivity of compounds 1-11 should be mirrored in the C–H bond dissociation energies (BDEs). For instance, it has been postulated that electron-withdrawing substituents strengthen the benzylic C–H bond and electron-donating substituents weaken it.<sup>15</sup> It is thus not unreasonable to expect that, when the para substituent is the nitro group, the BDE of the benzyl C–H bond in *p*-nitrotoluene **5** would be greater than that in toluene **1**. On this basis, **5** should be less reactive than toluene in hydrogen abstractions, as found. Moreover, the longer reaction time required in the reaction of *p*-dimethoxybenzene **7** compared to **6** and **8** should be rationalized on the basis of the low oxidation potential of **7**, which probably causes a large quenching of the reactive state of TBADT.<sup>16</sup>

To probe this mechanism further and obtain information on the extent of bond breaking, we measured the intramolecular primary isotope effect (PIE) of this reaction. To this end, we prepared the  $\alpha, \alpha, \alpha$ -trideutero-*p*-xylene **2**-*d*<sub>3</sub>. The reaction of **2**-*d*<sub>3</sub> was performed similarly with those described previously in this work (Scheme 3), using a 400-fold excess of the **2**-*d*<sub>3</sub> substrate with respect to C<sub>60</sub>. The ratio of these products **2a**-*d*<sub>3</sub> and **2b**-*d*<sub>3</sub>, which is the result of an intramolecular isotopic competition between the  $-CH_3$  and  $-CD_3$ substituents of **2**-*d*<sub>3</sub>, is proportional to the primary isotope

<sup>(11)</sup> Hare, J. P.; Kroto, H. W.; Taylor, R. Chem. Phys. Lett. 1991, 177, 394-398.

<sup>(12) (</sup>a) Duncan, D. C.; Fox, M. A. J. Phys. Chem. A 1998, 102, 4559–4567.
(b) Texier, I.; Delaire, J. A.; Giannotti, C. Phys. Chem. Chem. Phys. 2000, 2, 1205–1212.

<sup>(13) (</sup>a) Eriksen, J.; Foote, C. S. J. Am. Chem. Soc. 1980, 102, 6083–6088. (b) Eriksen, J.; Foote, C. S. J. Phys. Chem. 1978, 82, 2659–2662.

<sup>(14)</sup> The DCA catalyst is herein utilized for qualitative and not quantitive purposes (e.g., for clarification of the mechanism of the corresponding TBADT-mediated reactions). In this work, DCA was found to be unreactive or much less reactive than TBADT, toward substrates 1-10. Therefore, DCA should not be considered as an alternative catalyst to TBADT.

<sup>(15) (</sup>a) Zavitsas, A. A.; Pinto, J. A. J. Am. Chem. Soc. 1972, 94, 7390–7396.
(b) Zavitsas, A. A.; Rogers, D. W.; Matsunaga, N. J. Org. Chem. 2007, 72, 7091–7101.

<sup>(16)</sup> Easily oxidizable substrates exhibit larger quenching rate constants of the reactive state of TBADT. At very low oxidation potentials backelectron transfer to  $W_{10}O_{32}^{4-}$  becomes favorable and no  $W_{10}O_{32}^{5-}$  is observed; for example, in the case of N,N-dimethylaniline, no reduced TBADT is observed; see: Tanielian, C.; Schweitzer, C.; Seghrouchni, R.; Esch, M.; Mechin, R. *Photochem. Photobiol. Sci.* **2003**, *2*, 297–305. See also reference 12a.



effect of  $k_{\rm H}/k_{\rm D}$ . <sup>1</sup>H NMR integration of the methylene -CH<sub>2</sub>- signals of **2a**-*d*<sub>3</sub> as well as the methyl hydrogens of **2b**-*d*<sub>3</sub> determined the primary isotope effect  $k_{\rm H}/k_{\rm D} = 2.20 \pm 0.09$  (Scheme 3). This substantial PIE indicates an extensive C-H(D) bond breaking in the transition state of the first slow radical forming step. Another important finding from this experiment concerns the source of the fullerenyl hydrogen. The adduct **2b**-*d*<sub>3</sub> is partially deuterated (37% D incorporation on the fullerene cage). This result indicates that the intermediate C<sub>60</sub> anion can also be trapped by a proton originated from the reaction moisture. Indeed, this is consistent with the deuteration observed on the C<sub>60</sub> core when in the reaction mixture of **1** or **6** with C<sub>60</sub> was added 0.5% D<sub>2</sub>O.

As far as the overall mechanism of this reaction is concerned, the above experimental studies combined with literature data indicate that a sequence of definite steps are involved in the conversion of  $C_{60}$  into the adducts**1a**-**11a** and **11b**. A mechanistic approach of this functionalization is presented in Scheme 4. The initial steps of the reaction involve the photoexcitation of both the catalyst TBADT and





the reagent  $C_{60}$ . The singlet excited state ( ${}^{1}C_{60}^{*}$ ) of the fullerene C<sub>60</sub> almost quantitively decays via intersystem crossing (ISC) to the energetically lower-lying triplet excitedstate of  $C_{60}$  ( ${}^{3}C_{60}^{*}$ ).<sup>17</sup> On the other hand, the simultaneous illumination of the TBADT anion (W10O324-) generates a charge-transfer excited state, W10O324-\*, which reacts exclusively with organic substrates (RH), to give radicals (R•) and a persistent tungstate species  $(W_{10}O_{32}^{5-})$ .<sup>18</sup> This reduced form of decatungstate is reoxidized by the triplet excitedstate of  $C_{60}$  ( ${}^{3}C_{60}$ \*) leading to the radical anion of fullerene  $(C_{60}^{\bullet-})$ . Since the redox potential of the couple  $W_{10}O_{32}^{4-}$  $W_{10}O_{32}^{5-}$  ( $E_{red} = -0.97$  V/NHE or -0.74 vs SCE)<sup>12b</sup> is more negative than the first reduction potential of  ${}^{3}C_{60}^{*}$  ( $E_{red} =$ 1.14 V vs SCE),  $^{17a}$  the electron transfer from  $W_{10}O_{32}{}^{5-}$  to  ${}^{3}C_{60}*$  is expected to occur readily. Because of the proper redox potentials, the possibility of an electron transfer from  $W_{10}O_{32}^{5-}$  to the ground state of  $C_{60}$  ( $E_{red} = -0.42$  V vs SCE)<sup>17a</sup> cannot be excluded.<sup>19</sup> Control experiments showed that in the absence of TBADT and/or hv no reaction occurred for several hours. The final step involves, the coupling of  $C_{60}$  radical anion with the organic radical (R<sup>•</sup>) followed by protonation of the resulting anion  $(RC_{60}^{-})$  to yield the 1-substituted 1,2-dihydro[60]fullerenes (RC<sub>60</sub>H).

These successful derivatizations of fullerene  $C_{60}$  should open the way to a new functionalization strategy and to a variety of compounds which may have further applications. Experiments concerning the present methodology for the functionalization of  $C_{60}$  are in progress.

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**Supporting Information Available:** Detailed experimental procedures, spectral data, <sup>1</sup>H and <sup>13</sup>C NMR, FTIR, and UV-vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(18)</sup> The mechanism of photoexcitation of the TBADT catalyst and its interaction with organic substrates is well established by other research groups. For selected examples, see: (a) Duncan, D. C.; Netzel, T. L.; Hill, C. L. *Inorg. Chem.* **1995**, *34*, 4640–4646. (b) Texier, I.; Delouis, J. F.; Delaire, J. A.; Giannotti, C.; Plaza, P.; Martin, M. M. *Chem. Phys. Lett.* **1999**, *311*, 139–145. (c) Ermolenko, L. P.; Giannotti, C.; Delaire, J. A. J. *Chem. Soc., Perkin Trans. 2* **1997**, *25*–30. (d) Tanielian, C.; Duffy, K.; Jones, A. J. Phys. Chem. B **1997**, *101*, 4276–4282. See also references 5a,b, 6b, and 12.