ORGANIC
LETTERS

2008
Vol. 10, No. 5
873−876

Decatungstate-Mediated Radical Reactions of C_{60} with Substituted Toluenes and Anisoles: A New Photochemical Functionalization Strategy for Fullerenes

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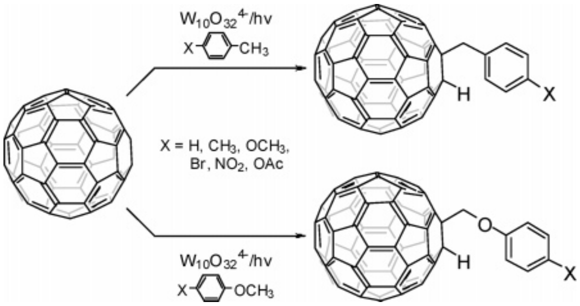
Received December 14, 2007

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$_4$N)$_4$W$_{10}$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.[1] 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.[2] Free-radical reactions were one of the first investigated reactions of fullerene C_{60}.[3] 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_{60} as a radical sponge.[4] For example, up to 11 phenyl groups, 15 benzyl groups, and 34 methyl groups have been reported to add to C_{60}.[4] 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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[1] Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.

[2] (a) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807−815. (b) Wudl, F. *J. Mater. Chem.* **2002**, *12*, 1959−1963.

[3] (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.

[4] (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.

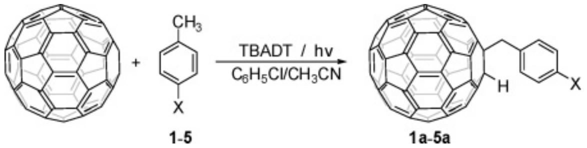
10.1021/ol7030125 CCC: $40.75

transformations[5] and to a lesser extent under unaerobic conditions in synthetically useful chemical processes.[6] 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_{60}.

Herein, we describe a convenient, highly efficient, TBADT-mediated 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 corresponding functionalized fullerenes **1a**−**5a** in moderate to good yields.[7] This reaction was carried out simply by irradiating a solution of C_{60} with 1000 equiv of substrate **1**−**5** and 0.8 equiv of TBADT, in a mixture of chlorobenzene/acetonitrile (85:15)[8] using a 300 W xenon lamp.[9] This is the first report concerning the isolation and characterization of C_{60} monoadducts via a single benzyl radical addition.

Table 1. TBADT-Mediated Reaction of Para-Substituted Toluenes **1**−**5** with C_{60}[a]

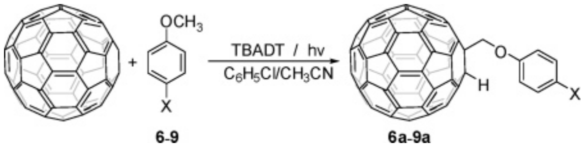


substrate	X	irradiation time, min	product yield,[b] %
1	H	180	35
2	CH_3	40	45
3	Br	180	50
4	OAc	300	15
5	NO_2	180	8

[a] For general considerations, see the Suppporting Information. [b] Isolated yield.

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).[10]

Table 2. TBADT-Mediated Reaction of Para-Substituted Anisoles **6**−**9** with C_{60}[a]

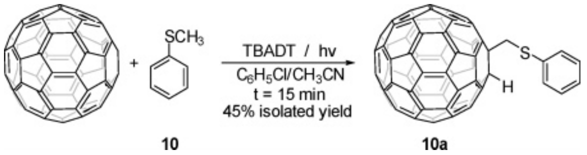


substrate	X	irradiation time, min	product yield,[b] %
6	H	30	35
7	OCH_3	90	35
8	Br	30	50
9	NO_2	180	10

[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.

Scheme 1. TBADT-Mediated Reaction of Thioanisole **10** with C_{60}



The structures of the novel compounds **2a**−**10a** were unambiguously established by UV-vis, FTIR, ^1H and ^{13}C NMR spectroscopic techniques, as well as by mass spectrometry. As diagnostic signals in the ^1H NMR spectra ($CDCl_3/CS_2$), the $-CH_2-$ benzyl protons of 1,2-dihydro-[60]fullerenes **1a**−**5a** resonate at δ 4.71−4.90 ppm, whereas the protons attached on the fullerene core have a character-

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[5] 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.

[6] 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.

[7] 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.

[8] 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_{60}.

[9] 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.

[10] 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.

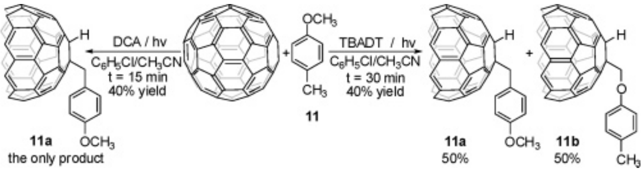
istic absorption at 6.58−6.65 ppm due to the deshielding effect of C_{60}. In the ^{13}C NMR spectra, the benzylic carbon atom appears at δ 52.55−53.19 ppm, while the C_{60}-H sp^3 carbon resonates at 59.03−59.59 ppm. The corresponding ^1H and ^{13}C NMR signals of the compounds **6a**−**10a** were also identified either upfield or downfield shifted compared to the corresponding NMR signals of **1a**−**5a** (see the Supporting Information). More importantly, the ^{13}C NMR spectra of compounds **1a**−**10a** exhibit all of the patterns that correspond to a C_{60} derivative with C_s symmetry induced by the addition of two different addends (achiral) to the 6,6-junction bond of C_{60}. Thus, there are 30 ^{13}C NMR signals (one or two of which may be overlapped) for the sp^2 carbons of the C_{60} core and two signals for the sp^3-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).[3a] The high energy absorptions at ca. 330 and 258 nm are attributed to the fullerene moiety.[11]

To explore the mechanism of this reaction, a series of experiments were performed. Initially, the source of the hydrogen atom in $RC_{60}H$ was investigated. The photocatalyzed reaction of **1** and **6** with C_{60} was performed in separate experiments, first in a mixture of dry C_6H_5Cl/CD_3CN (85:15) and then in a mixture of C_6H_5Cl/CH_3CN 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^3 carbon), as determined by ^1H 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_{60}. Furthermore, compounds **1a** and **6a** do not exchange their proton in a measurable amount (^1H NMR) since no deuterium incorporation could be detected after a sample of **1a** or **6a** in a 85:15 mixture of C_6H_5Cl/CH_3CN had been agitated with D_2O for several hours or even upon irradiation. Finally, no H−D exchange observed (^1H NMR) when a deaerated solution of **1a** (3 mg, 3.7 μmol) was irradiated in the presence of TBADT and 0.5% D_2O, 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.[5b,12] Both mechanisms give rise to the same substrate-derived organic radical $R^{\bullet}$, 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_{60}. DCA is a well-established ET photosensitizer in a polar solvent such as acetonitrile.[13] 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,[13] it is plausible that in this case the DCA photocatalyzed functionalization of C_{60} 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.[14]

Scheme 2. Product Distribution in the TBADT- and DCA-Mediated Reactions of 4-Methylanisole **11** with C_{60}



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.[15] 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.[16]

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 α,α,α-trideutero-*p*-xylene **2**-d_3. The reaction of **2**-d_3 was performed similarly with those described previously in this work (Scheme 3), using a 400-fold excess of the **2**-d_3 substrate with respect to C_{60}. The ratio of these products **2a**-d_3 and **2b**-d_3, which is the result of an intramolecular isotopic competition between the $-CH_3$ and $-CD_3$ substituents of **2**-d_3, is proportional to the primary isotope

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(11) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett.* **1991**, *177*, 394−398.

(12) (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.

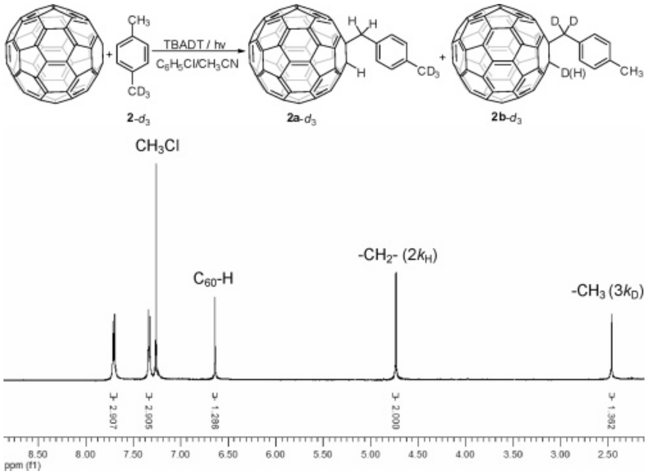
(13) (a) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083−6088. (b) Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659−2662.

(14) 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.

(15) (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.

(16) Easily oxidizable substrates exhibit larger quenching rate constants of the reactive state of TBADT. At very low oxidation potentials back-electron 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.

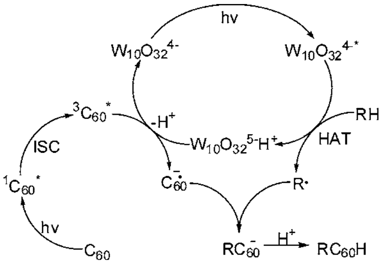
Scheme 3. Determination of the Intramolecular PIE in the Reaction of **2**-d_3 with C_{60} by ^1H NMR Spectroscopy



effect of k_H/k_D. ^1H NMR integration of the methylene $-CH_2-$ signals of **2a**-d_3 as well as the methyl hydrogens of **2b**-d_3 determined the primary isotope effect $k_H/k_D = 2.20 \pm 0.09$ (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_3 is partially deuterated (37% D incorporation on the fullerene cage). This result indicates that the intermediate C_{60} anion can also be trapped by a proton originated from the reaction moisture. Indeed, this is consistent with the deuteration observed on the C_{60} core when in the reaction mixture of **1** or **6** with C_{60} was added 0.5% D_2O.

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

Scheme 4. Proposed Mechanism for the TBADT-Catalyzed Reaction of Aromatic Compounds **1**−**11** with Fullerene C_{60}



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.

Acknowledgment. The Greek National Scholarships Foundation (IKY) is acknowledged for providing a three year fellowship to M.D.T. The financial support of the Greek Secretariat of Research and Technology (PYTHAGORAS II 2005) is also acknowledged. We are grateful to Prof. T. Drewello at Warwick University for performing the MALDI MS analyses. M.D.T thanks Professor J. S. Siegel for his gracious hospitality during his stay at the University of Zurich.

Supporting Information Available: Detailed experimental procedures, spectral data, ^1H and ^{13}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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(17) (a) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277−2279. (b) Arbogast, J.; Darmanyan, A.; Foote, C. S.; Rubin, Y.; Diederich, F.; Alvarez, M.; Anz, S.; Whetten, R. *J. Phys. Chem.* **1991**, *95*, 11−12.

(18) 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.

(19) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, *120*, 8060−8068.