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Decatungstate As Photoredox Catalyst: Benzylation of Electron-Poor Olefins

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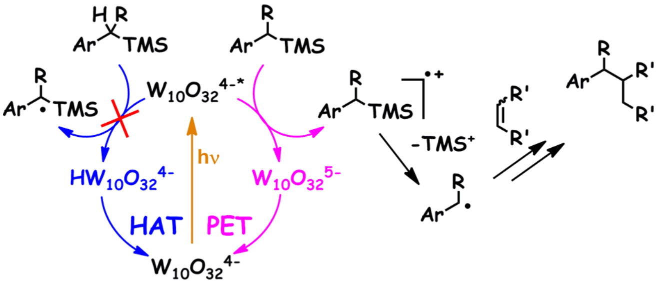
ABSTRACT



Excited tetrabutylammonium decatungstate (TBADT), known to activate a variety of compounds via hydrogen atom transfer (HAT), has now been applied as a photoredox catalyst for the effective oxidative cleavage of benzyl silanes and radical benzylation of reducible olefins occurring in isolated yields from poor to excellent.

Polyoxometalates (POMs) are metal−oxygen clusters showing an amazing variety of properties.[1a−e] Some POMs show interesting photochemical activity, as demonstrated by the pioneering work by Hill.[1f] The most widely studied among them is the decatungstate anion ($[W_{10}O_{32}]^{4-}$),[2a] usually employed as a tetrabutylammonium salt (TBADT). This salt found some applications as a photocatalyst both under aerated conditions, as in the photooxidation of alkanes, alkenes, and alcohols,[2] and under anaerobic conditions for the photoactivation of C−H bonds in alkanes,[3a,b] amides,[3c] aldehydes,[3d] ethers,[3e] and aromatic alcohols,[3f] and as an innovative photocatalyst for the degradation of organic pollutants in water.[2a] Two photochemical processes compete upon TBADT excitation, viz. hydrogen atom transfer (HAT)[4] and electron transfer (ET).[5] The former mainly operates in the presence of substrates containing weak C−H bonds (as in the case of alcohols),[3f,6] while the latter takes place when the reaction involves easily oxidizable substrates, such as aromatic amines or aromatic hydrocarbons.[7a,b] Of the two paths, only HAT has been exploited for *synthetic* applications.[2a] Thus, to make the ET path viable, the redox potential of reagent R ($E(R^{\bullet+}/R)$) must be lower than the redox potential of the decatungstate excited state ($E([W_{10}O_{32}]^{4-}*/[W_{10}O_{32}]^{5-})$). Assessing this point is complicated by the fact that the reactive state is a *relaxed* excited state (the **wO** species), whose identity is still

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[1] (a) Long, D.-L.; Tsunashima, R.; Cronin, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 1736. (b) Yu, R.; Kuang, X.-F.; Wu, X.-Y.; Lu, C.-Z.; Donahue, J. P. *Coord. Chem. Rev.* **2009**, *253*, 2872. (c) Nomiya, K.; Sakai, Y.; Matsunaga, S. *Eur. J. Inorg. Chem.* **2011**, 179. (d) Dupré, N.; Rémy, P.; Micoine, K.; Boglio, C.; Thorimbert, S.; Lacôte, E.; Hasenknopf, B.; Malacria, M. *Chem.—Eur. J.* **2010**, *16*, 7256. (e) Yunxiang, Q.; Zhenshan, H. *Curr. Org. Chem.* **2009**, *13*, 1347. (f) Hill, C. L. *Synlett* **1995**, 127.

[2] (a) Tzirakis, M. D.; Lykakis, I. N.; Orfanopoulos, M. *Chem. Soc. Rev.* **2009**, *38*, 2609. (b) Molinari, A.; Bratovcic, A.; Magnacca, G.; Maldotti, A. *Dalton Trans.* **2010**, *39*, 7826.

[3] (a) Dondi, D.; Cardarelli, A. M.; Fagnoni, M; Albini, A. *Tetrahedron* **2006**, *62*, 5527. (b) Ryu, I.; Tani, A.; Fukuyama, T.; Ravelli, D.; Fagnoni, M.; Albini, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1869. (c) Angioni, S.; Ravelli, D.; Emma, D.; Dondi, D.; Fagnoni, M.; Albini, A. *Adv. Synth. Catal.* **2008**, *350*, 2209. (d) Esposti, S.; Dondi, D.; Fagnoni, M.; Albini, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 2531. (e) Tzirakis, M. D.; Orfanopoulos, M. *Org. Lett.* **2008**, *10*, 873. (f) Lykakis, I. N.; Tanielian, C.; Seghrouchni, R.; Orfanopoulos, M. *J. Mol. Catal. A: Chem.* **2007**, *262*, 176.

[4] (a) Tanielian, C.; Schweitzer, C.; Seghrouchni, R.; Esch, M.; Mechin, R. *Photochem. Photobiol. Sci.* **2003**, *2*, 297. (b) Kothe, T.; Martschke, R.; Fischer, H. *J. Chem. Soc., Perkin Trans. 2* **1998**, 503.

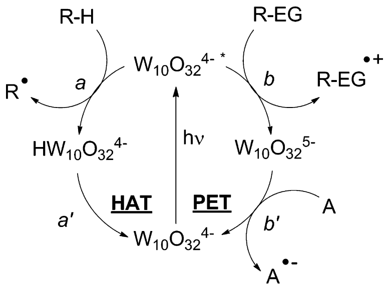
[5] (a) Tanielian, C.; Seghrouchni, R.; Schweitzer, C. *J. Phys. Chem. A* **2003**, *107*, 1102. (b) Nosaka, Y.; Takei, T.; Fujii, N. *J. Photochem. Photobiol. A: Chem.* **1995**, *92*, 173.

[6] Lykakis, I. N.; Vougioukalakis, G. C.; Orfanopoulos, M. *Org. Lett.* **2003**, *5*, 2875.

[7] (a) Texier, I.; Delaire, J. A.; Giannotti, C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1205. (b) Duncan, D. C.; Fox, M. A. *J. Phys. Chem. A* **1998**, *102*, 4559. (c) Duncan, D. C.; Netzel, T. L.; Hill, C. L. *Inorg. Chem.* **1995**, *34*, 4640.

10.1021/ol301900p

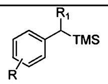
Scheme 1. Possible Pathways in Tetrabutylammonium Decatungstate (TBADT) Photocatalyzed Reactions



not fully known.[7c] Previous studies estimated that the **wO** potential ranges from 2.26 to 2.61 V (vs SCE),[7a] thus taking the lower limit $E(R^{\bullet+}/R) < 2.26$. An approach for facilitating the ET path is to incorporate an electroauxiliary group (EG) in the reagent. This would lower $E(R^{\bullet+}/R)$ and open a reactive path for the radical cation.[8] The trimethylsilyl group (TMS) has been largely used in this role in electrochemical or photoinduced electron transfer (PET) reactions[8,9] and is split off from the radical cation generating a radical.[8] However, introducing a TMS group is no guarantee that the reaction follows an ET path. Indeed, HAT can remain the major path, as shown in the case of *N*-methyl-*N*-(trimethylsilylmethyl)acetamide,[3c] where only silicon-containing products were formed despite the fact that the oxidation potential of this amide was estimated to be $E_{1/2} < 2.29$ V vs SCE and thus suitable for undergoing a monoelectronic oxidation by **wO**. In addition, if the process has to be photocatalytic, TBADT (used in a few percent proportion) must be regenerated; otherwise the conversion will stop when this is consumed. In the HAT mechanism, $[HW_{10}O_{32}]^{4-}$ typically undergoes a back hydrogen transfer reaction (Scheme 1, path *a'*) and this regenerates the photocatalyst.

Correspondingly, in the ET mechanism, efficient reoxidation of the reduced cluster (or of the two-electron reduced species formed by dismutation)[10] is required, also because back electron transfer to the donor radical cation would otherwise compete and quench any chemical reactions. Thus, a successful ET catalyzed alkylation requires reoxidation of $[W_{10}O_{32}]^{5-}$ by a sacrificial acceptor (A, path *b'*). Oxygen could be used in this role, but would also trap alkyl radicals, thus restricting the palette of viable processes to oxygenation reactions. To avoid this limitation, a *reducible* trap can be used, such as an electrophilic olefin in the twofold role of trap for the radicals and electron acceptor. In view of the above, a favored case for testing TBADT as a photoredox catalyst for synthetic applications would be using benzyltrimethylsilanes as radical precursors[9,11] and maleic anhydride and related alkenes as electrophilic traps/oxidizing agents.[12] The results are presented below (Tables 1, 2). Preparative experiments involved the TBADT-photocatalyzed reactions of a number of benzylsilanes (**1**–**8**) with electrophilic alkenes (**9**–**13**) upon irradiation for 24 h by means of phosphor-coated lamps (λ_{irr} centered at 310 nm). Blank experiments showed that parent benzyltrimethylsilane (**1**) was not appreciably consumed when irradiated in neat acetonitrile for 24 h under these conditions, either alone or with maleic anhydride (**9**). The results are gathered in Table 2, where both the silane conversion (initial concentration 0.1 M) and the yield of the benzylated alkene are reported. An excess of the electrophilic olefin (0.2 M) was routinely used to ensure the full consumption of the starting silane. The excess olefin could be limited, however, at least in some cases. As an example, the starting concentration of olefin **9** could be decreased to 0.15 M in the benzylation with **1** (0.1 M) that gave open chain 2-benzylsuccinic acid (**14**) in *ca.* 90% yield. The reactivity of benzyltrimethylsilane in the presence of a catalytic amount (2 mol %) of TBADT was examined in neat acetonitrile (condition A), in neat MeCN/H_2O 5:1 (condition B) and in MeCN/H_2O 5:1 solution containing 0.5 M $LiClO_4$ (condition C). The irradiation of parent **1** in the presence of conjugated alkenes **9** to **13** under condition A gave variable results, from 27% conversion and no benzylated product with maleimide **11c** (see Table S1; in this case a precipitate was formed on the reaction vessel walls) to 100% conversion and 90% benzylation with maleic anhydride **9**.

Table 1. Formal Redox Potential ($E^{\circ\prime}$) of the Compounds Used in This Work

benzylsilane		$E^{0'}(R^{\bullet+}/R)$[V *vs* SCE]
1	R = H; R' = H	1.55
2	R = 4-OMe; R' = H	1.28
3	R = 4-Me; R' = H	1.46
4	R = 4-*t*-Bu; R' = H	1.55
5	R = 4-Cl; R' = H	1.61
6	R = 3-OMe; R' = H	1.66
7	R = 4-CN; R' = H	1.81
8	R = H; R' = Me	1.49
olefin		$E^{0'}(R/R^{\bullet-})$[V *vs* SCE]
9	Maleic Anhydride	-0.88
10	Fumaronitrile	-1.31
11a	*N*-Phenyl maleimide	-1.09
11b	*N*-Methyl maleimide	-1.21
11c	Maleimide	-1.25
12	Dimethyl Fumarate	-1.47
13	Dimethyl Maleate	-1.65

Under condition B both parameters increased, in some cases remarkably, except in the reaction with **9**, where the

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(8) Yoshida, J.-i.; Kataoka, K.; Horcajada, R.; Nagaki, A. *Chem. Rev.* **2008**, *108*, 2265.

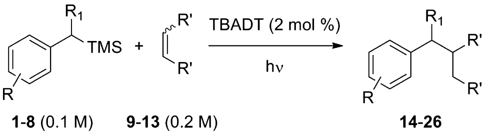
(9) Albini, A.; Fagnoni, M. In *Molecular and Supramolecular Photochemistry*; Griesbeck, A. G., Mattay, J., Eds.; Synthetic Organic Photochemistry; Dekker: New York, 2005; Vol. 12, p 453.

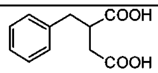
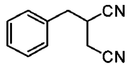
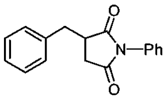
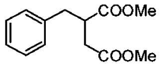
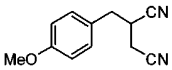
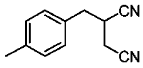
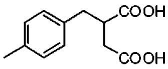
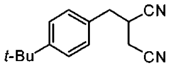
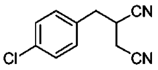
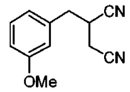
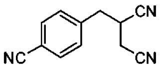
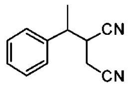
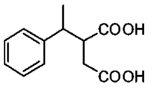
(10) Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, 793.

(11) (a) Zhuikov, V. V. *Russ. J. Gen. Chem.* **1997**, *67*, 887. (b) Taylor, K.; Miura, K.; Akinfaderin, F.; Fry, A. J. *J. Electrochem. Soc.* **2003**, *150*, D85.

(12) Some of these systems have been previously investigated under TiO_2 photocatalysis. See: (a) Cermenati, L.; Richter, C.; Albini, A. *Chem. Commun.* **1998**, 805.

Table 2. TBADT Photocatalyzed Benzylation of Electron-Poor Olefins



reagents	product	conditions,[a] yield % (silane conversion %) A	B	C
1, **9**	 **14**	90 (100) 95 (92)[b]	96 (72)	-
1, **10**	 **15**	78 (59)	91 (78)	89 (100) 95 (86)[c]
1, **11a**	 **16a**	54 (52)	67 (90)	68 (100) 65 (89)[c]
1, **12**	 **17**	91 (32)	96 (57)	97 (67)
1, **13**	**17**	60 (10)	73 (45)	63 (48)
2, **10**	 **18**	58 (31)	59 (49)	90 (100) 74 (100)[c]
3, **10**	 **19**	34 (71)	57 (74)	54 (78) 47 (72)[c]
3, **9**	 **20**	84 (80)	89 (75)	-
4, **10**	 **21**	48 (65)	74 (85)	80 (100) 96 (83)[c]
5, **10**	 **22**	64 (59)	94 (100)	93 (100) 93 (100)[c]
6, **10**	 **23**	46 (50)	27 (75)	85 (100) 80 (100)[c]
7, **10**	 **24**	27 (33)	54 (63)	54 (80) 67 (100)[d]
8, **10**	 **25**[e]	78 (76)	91 (90)	93 (100) 98 (95)[c]
8, **9**	 **26**[e]	97 (90)[f]	99 (83)[f]	-

[a] Reaction mixture irradiated for 24 h with ten 15 W phosphor-coated lamps (λ_{irr} = 310 nm); Condition A: MeCN as the solvent; B: MeCN/H_2O 5:1 as the reaction medium; C: 0.5 M $LiClO_4$ in MeCN/H_2O 5:1 solution as the reaction medium. Conversions and yields are based on silane consumption. [b] 0.15 M olefin. [c] 0.1 M olefin. [d] 40 h irradiation time. [e] Equimolar mixture of diastereoisomers. [f] 2,3-Diphenylbutane **26′** (as a mixture of diastereoisomers) was obtained in 3% yield (see Supporting Information for details).

change was limited. Under condition C the conversion was further increased and was consistently in the range 85–100%, except for the reactions with dimetyl fumarate (67%) and dimethyl maleate (48%), while the benzylation yield generally did not change with respect to condition B (in the range 52 to 97%). Ring-substituted benzylsilanes **2** to **7** were examined in the presence of fumaronitrile **10** and in representative cases of maleic anhydride **9**. Again, the conversion was variable under condition A (31 to 80%), with a benzylation yield ranging from 27 (for the 4-cyano derivative **7**) to 84% (for the 4-methyl derivative **3**). Likewise, improved results were obtained under condition B, while the conversion reached 100% under condition C for the 4- and 3-methoxy (**2** and **6**), the 4-*t*-butyl (**4**), and 4-chloro (**5**) derivatives, with a benzylation yield of 80–93%. Less successful were the reactions of the 4-methyl (**3**) (78% conversion, 54% benzylation) and 4-cyano (**7**) derivatives (respectively 80 and 54%). In the case of **7**, however, increasing the irradiation time to 40 h allowed improvement of both parameters. The effect of chain substitution was also tested by using the α-methylbenzylsilane **8** which gave satisfactory results already under condition A and excellent results under B and C. On the other hand, acrylonitrile, cyclohexenone and methyl acrylate were poorly alkylated by **1** under the present conditions and the silane remained essentially unaffected (not reported in Table 2).

To gain indications of the mechanism involved, flash photolysis experiments were carried out. In accordance with the literature, the reactive excited state of decatungstate (**wO**) was revealed at $\lambda = 780$ nm, with a lifetime $\tau = 54$ ns in neat acetonitrile.[7a] In the presence of *p*-methoxybenzylsilane (**2**), this transient was quenched with a linear Stern–Volmer plot (see Figure S3), from which a rate constant of $7.1(5) \times 10^8$ M^{-1} s^{-1} was determined. No persistent absorption was observed, contrary to the case of H-donating quenchers, for which a long-lived signal has been observed and attributed to $[HW_{10}O_{32}]^{4-}$ that absorbs in the same region.[7a]

The above results demonstrate that benzylation reactions have been obtained under decatungstate photocatalysis. Such reactions play an important role in fine chemistry and in the synthesis of pharmaceuticals and agrochemicals.[13a,b] These involve cationic alkylations of aromatics and heteroaromatics[13c] and the more recently developed transition-metal catalyzed benzylations.[13a,b,d,e]

Benzyl radicals are usually generated upon single electron transfer oxidation of benzyl silanes or phenylacetates (see below). However, these are rather persistent intermediates and are inefficiently trapped, as witnessed by the high proportion of competitive homocouplings to give bibenzyls that are generally observed in such reactions.[13f] This contrasts with the more favorable course of various

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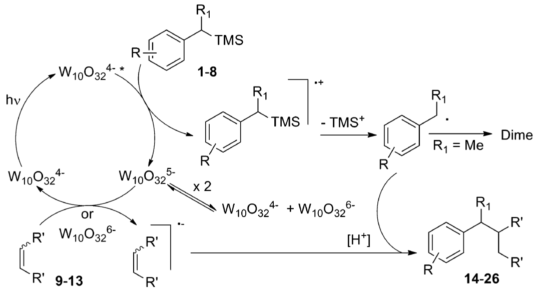
(13) (a) Weaver, J. D.; Recio, A., III; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846. (b) Liégault, B.; Renaud, J.-L.; Bruneau, C. *Chem. Soc. Rev.* **2008**, *37*, 290. (c) Noji, M.; Konno, Y.; Ishii, K. *J. Org. Chem.* **2007**, *72*, 5161. (d) Ackermann, L.; Barfüsser, S.; Kornhaass, C.; Kapdi, A. R. *Org. Lett.* **2011**, *13*, 3082. (e) Mertins, K.; Iovel, I.; Kischel, J.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 238. (f) Baciocchi, E.; Rol, C.; Rosato, G. C.; Sebastiani, G. V. *J. Chem. Soc., Chem. Commun.* **1992**, 59.

(14) For example, see: Freccero, M.; Fasani, E.; Albini, A. *J. Org. Chem.* **1998**, *58*, 1740. Hatoum, F.; Gallagher, S.; Baragwanath, L.; Lex, J.; Oelgemöller, M. *Tetrahedron Lett.* **2009**, *50*, 6335. Cermenati, L.; Freccero, M.; Venturello, P.; Albini, A. *J. Am. Chem. Soc.* **1995**, *117*, 7869. Brivio, L.; Caronna, T.; Fontana, F.; Gambarotti, C.; Mele, A.; Natali Sora, I.; Punta, C.; Recupero, F. *J. Photochem. Photobiol. A: Chem.* **2010**, *214*, 112.

benzylations via *photoinduced electron transfer*. In the latter case, however, benzyl radicals coupled with another *odd-electron* species, viz. the radical anion of the acceptor, likewise formed in the ET step.[9,14] In one case the benzyl radical was generated from a benzyl silane by a thermal SET reaction and trapped by an *N*-acyliminium ion.[15] The benzylation of *olefins* considered here has only a few precedents, including the radical addition onto an enamine generated in situ by organocatalysis[16a] or onto the photogenerated radical anion of highly reducible olefins (such as 1,1-dicyanoethenes).[16b] Very recently, Naito et al. reported the functionalization of electron-poor olefins based on the C−H activation in (substituted) toluenes by using the Et_3B/O_2 system as a radical initiator, albeit the use of a high temperature (180 °C) and of the H-donor as neat reaction medium undermined the synthetic potential of the process.[16c] A milder functionalization was again obtained photochemically by using TiO_2 as the photocatalyst.[12a] The reactions carried out in the present work can be safely recognized as involving ET from the benzylic derivatives to excited decatungstate (see Scheme 2), as supported by various evidence. Thus, quenching of the reactive decatugstate **wO** does not form persistent $[HW_{10}O_{32}]^{4-}$ and occurs at a high rate (7×10^8 M^{-1} s^{-1}), quite similar to those reported for *bona fide* single electron donors, such as naphthalene or phenanthrene.[7a] The benzylic derivatives considered here are oxidized at 1.28 to 1.81 V vs SCE (Table 1), and thus ET is exothermic by 10−30 kcal mol^{-1}, taking into account the uncertainty of the **wO** potential. Fragmentation of the silane radical cation is then thermodynamically allowed (log k_{cl} *ca.* 6.36 for compound **2**).[17a] Indeed, only Si-free products were obtained; e.g., with methyl-substituted silane **3** no competitive deprotonation occurs as judged from the product structure, in accordance with the indication that desilylation is *ca.* 100 times faster with respect to deprotonation.[17a] The cleavage is known to be nucleophile-assisted,[17b] and this is well in accordance with the increased yields in water admixed solvent (condition B) and when the ionic strength is increased (condition C).[17c] Finally, the high yield of benzylation requires some comment. Persistent species such as benzyl radicals react sluggishly with modest electrophiles such as those tested in this work. The typical result is a significant or predominant proportion of bibenzyl derivatives. In the present case, however, no such products were formed, except for a small amount in the case of the hindered α-radical from **8**. A viable rationalization is that the olefin serves the function of sacrificial acceptor. The redox potentials of the alkenes used here ($E(A/A^{•-})$) are in the range −0.88 to −1.65 V vs SCE and should be compared with that of the ground state of the photoactive species $E([W_{10}O_{32}]^{4-}/[W_{10}O_{32}]^{5-})$ that was measured to be around −0.9 V vs SCE.[18] The comparison is only qualitative, since the actual value of this potential depends on the water content of the medium[10] and on the disproportionation of $[W_{10}O_{32}]^{5-}$ that generates the more reducing anion $[W_{10}O_{32}]^{6-}$ (*ca.* −1.4 V vs SCE).[10,18] ET to the alkene at the second branch of the photocatalytic process causes two positive effects on the efficiency of the reaction. First, back electron transfer to $R^{•+}$ is limited; second, the radical anion of the alkene is formed. This is a much better trap for benzyl radicals than the neutral form and explains the success of the benzylation. Under these conditions the olefin is used in (almost) an equimolar amount, making the reaction convenient for application. *A contrario* evidence includes attempts to extend the reaction to less reducible olefins such as acrylonitrile ($E_{1/2}$ = −2.17 V vs SCE),[19a] cyclohexenone ($E_{1/2}$ = −2.20 V vs SCE),[19b] and methyl acrylate ($E_{1/2}$ = *ca.* −2.90 V vs SCE)[19c] that led to only small amounts of benzylated derivatives, while most of the starting silane remained unreacted.

Scheme 2. Proposed Reaction Mechanism



To our knowledge, the reactions above are the first preparative application of a TBADT-photocatalyzed synthesis involving the ET rather than the more common HAT mechanism. Perhaps more importantly, this smooth procedure, which is formally analogous to a reductive Heck,[20] adds to the small group of known benzylations of alkenes via benzyl radicals. Prediction of the success of the reaction can be reached by taking into account the redox potential of both the benzylsilane and the unsaturated trap, with reference to Scheme 2.

Supporting Information Available. ^1H NMR, ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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