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Photooxidation of aryl alkanes by a decatungstate/triethylsilane system in the presence of molecular oxygen

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Abstract—Decatungstate photocatalyzes the oxidation of aryl alkanes to the corresponding tertiary hydroperoxides and alcohols, in the presence of molecular oxygen. The addition of triethylsilane to the reaction mixture substantially increases the proportion of hydroperoxide formed.
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The oxidation of an inactivated C–H bond in a saturated hydrocarbon represents one of the most important and synthetically useful transformations possible.[1,2] This transformation is not generally very selective and previously had only been observed when severe conditions were employed, such as high temperatures and pressures, or high-energy radiation. Over the last few years, important advances have been achieved using polyoxometalates, such as decatungstate $W_{10}O_{32}^{4-}$, in the catalytic transformation of such organic materials.[3–14] It is generally accepted that illumination of $W_{10}O_{32}^{4-}$ generates a charge-transfer excited state, $W_{10}O_{32}^{4-*}$, which decays in about 30 ps to the longer-lived reactive intermediate designated as wO.[8–11] This reactive intermediate interacts with organic substrates (XH) to produce radicals, which in the presence of molecular oxygen may be trapped to give peroxy compounds.[9]

$$W_{10}O_{32}^{4-} \xrightarrow{hv} W_{10}O_{32}^{4-*} \rightarrow wO \xrightarrow{XH} H^+W_{10}O_{32}^{5-} + X\bullet$$
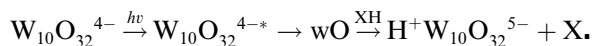
It has been shown that alkanes are oxidized in decatungstate photosensitized reactions to produce alcohols and carbonyl compounds (Scheme 1). However, most of
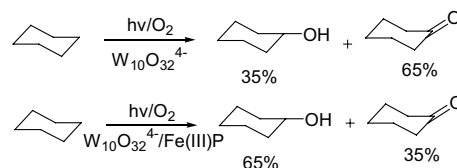
Scheme 1. Decatungstate catalyzed oxidation of cyclohexane.[6c]

the work thus far has been focused on mechanistic aspects of this reaction[4–7] with little or no attention devoted to the synthetic possibilities.

Our recent study on the mechanism of the decatungstate sensitized oxidation of aryl alkanols to the corresponding aryl ketones,[14] prompted us to investigate the oxidation of aryl alkanes using the same oxidative system. In general, the oxidation of aryl alkanes, such as cumene (isopropyl benzene) and ethylbenzene, using polyoxometalates $Mn_2ZnW(ZnW_9O_{34})_2^{12-}$ and $PRuMo_{11}O_{39}^{4-}$ as photocatalysts, has been shown to lead mainly to the C–C bond cleavage products, as shown in Scheme 2.[15]
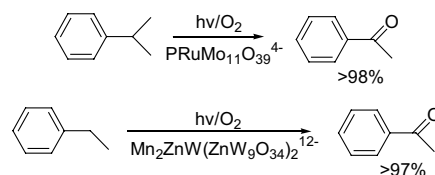
Scheme 2. Heteropolyoxometals catalyze the photooxidation of cumene and ethylbenzene.[15]

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Table 1. Decatungstate sensitized photooxidation of *para*-substituted cumenes **1**–**4** in the presence of O_2 and Et_3SiH
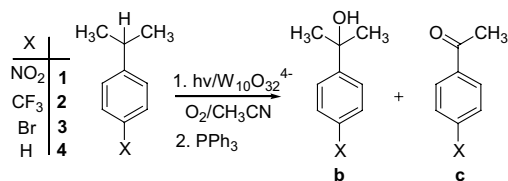
Entry	Substrate[a]	Et_3SiH	Time (h)	% Conversion[b]	**b** (%)[b]	**c** (%)[b]
1	**1**	—	5	85	80	20
2	**1**	1 equiv	5	69	>99	<1
3	**1**	3 equiv	5	26	100	—
4	**2**	—	4	95	77	23
5	**2**	1 equiv	4	89	86	14
6	**2**	3 equiv	4	69	86	14
7	**3**	—	2.5	99	75	25
8	**3**	1 equiv	2.5	89	95	5
9	**3**	3 equiv	2.5	84	98	2
10	**4**	—	2.5	90	61	39
11	**4**	1 equiv	2.5	68	94	6
12	**4**	3 equiv	2.5	38	97	3

[a] The cumene (0.03 M) was irradiated (Xenon lamp, 300 W, $\lambda > 300$ nm) in the presence of $[Bu_4N]_4W_{10}O_{32}$ (5.5×10^{-4} M), in acetonitrile, at 5–10 °C.
[b] Determined by gas chromatography after reduction with PPh_3 and ^1H NMR spectroscopy. The error was ±1% and ±4%, respectively.

Unlike these results, we report herein that decatungstate photosensitizes the oxidation of a series of aryl alkanes to afford mainly the corresponding tertiary hydroperoxides. Furthermore, in the presence of 1 equiv of triethylsilane,[16] this oxo-functionalization reaction can be fine-tuned becoming synthetically viable. Application of this new oxidative system to a series of *para*-substituted cumenes is summarized in Table 1.
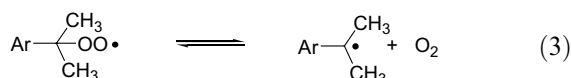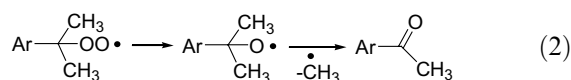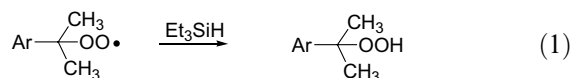
The decatungstate (5.5×10^{-4} M) photosensitized oxidation of *para*-substituted cumenes **1**–**4** (0.03 M) was carried out in acetonitrile or acetone, as the solvent, in the presence of O_2 with a 300 W Xenon lamp ($\lambda > 300$ nm) as the light source. The extent of reaction and the product distribution were monitored by gas chromatography following the reduction of the initially obtained tertiary hydroperoxides to their corresponding alcohols using triphenylposphine.

Irradiation of 2-(4-nitrophenyl)propane (**1**), 2-[4-(trifluoromethyl)phenyl]propane (**2**), 2-(4-bromophenyl)-propane (**3**) and 2-phenylpropane (**4**) at 5–10 °C initially afforded the corresponding tertiary hydroperoxides **1a**–**4a**, and following reduction, the alcohols **1b**–**4b**, as the major products, accompanied by only minor amounts of the corresponding carbonyl compounds **1c**–**4c**. Hydroperoxides **1a**–**4a** were directly reduced by PPh_3 to the corresponding alcohols **1b**–**4b**, therefore the former compounds have not been included in Table 1. The initial ratio of hydroperoxide (**a**) to alcohol (**b**) prior the reduction depended on the irradiation time and was found to be around 4:1. The ratio **a**/**b** was measured by comparison of the integrals for the ^1H NMR signals of the two methyl groups of the tertiary hydroperoxide and alcohol, which have a 0.012 ppm difference in chemical shift when the spectra are taken using a 500 MHz spectrometer. After recording the ^1H NMR measurements of the initial mixtures, the hydroperox-

ides were reduced using triphenylphosphine to afford the corresponding alcohols. It is interesting to note that even in substrates **1** and **2** where the *para*-substituent is an electron-withdrawing group (NO_2 and CF_3), the tertiary alcohols **1b** and **2b** were formed in good yields (Table 1).

The same substrates were then used in photooxidations carried out in the presence of 1 or 3 equiv of Et_3SiH. As shown in Table 1, a substantial increase in the proportion of alcohol present in the final reaction mixture was observed accompanied by a small to moderate reduction in the conversion. For example, addition of 1 equiv of Et_3SiH to the reaction mixture of substrate **1** (Table 1, entry 2) followed by irradiation for the standard period, gives a substantial increase in the relative yield of the alcohol when compared to the analogous case where Et_3SiH is absent (Table 1, entry 1). This trend was also demonstrated by substrates **2**–**4**, entries 5, 8 and 11 (Table 1). It is interesting to note that the addition of Et_3SiH suppresses the formation of products arising from C–C bond cleavage, thereby giving this hydroxyl functionalization of cumenes considerable synthetic value. This point is clearly demonstrated by substrate **1** (Table 1, entries 1 and 2) where in the presence of 1 equiv of Et_3SiH the decatungstate photosensitized oxo-functionalization of **1** affords the tertiary aryl alcohol with at best no trace of other products. Similarly, substrates **2**, **3** and **4** also impressively illustrate this point. In the absence of Et_3SiH (Table 1, entries 4, 7 and 10), substantial amounts of the aryl ketones are formed, whereas in the presence of 1 equiv of Et_3SiH the amount of the C–C bond cleavage product decreases by a factor between 2 and 6. An increase of triethylsilane to a threefold excess leaves the relative yield of the alcohol practically unchanged, however, it decreases substantially the extent of conversion (Table 1, entries 2, 3, 11 and 12).

The increase in hydroperoxide formation may be rationalized on the basis of trapping of the cumylperoxyl radical by Et_3SiH, as shown in Eq. 1.[16] Thus, decomposition to the corresponding aryl ketone (Eq. 2),[17,18] or rearrangement of the peroxyl radical to give the corresponding cumyl radical (Eq. 3),[19–21] are suppressed significantly. This possibility requires that the rate of reduction of the radical intermediates, Eqs. 1 and 2, by Et_3SiH, must be faster or at least competitive to the corresponding decomposition pathways leading to the cleavage product, i.e. the aryl ketone (Eq. 2).

$$Ar\!-\!\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\!-\!OO\bullet \quad \xrightarrow{Et_3SiH} \quad Ar\!-\!\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\!-\!OOH \qquad (1)$$

$$Ar\!-\!\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\!-\!OO\bullet \;\longrightarrow\; Ar\!-\!\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\!-\!O\bullet \;\xrightarrow[-CH_3]{\bullet}\; Ar\!-\!\overset{O}{\overset{\|}{C}}\!-\!CH_3 \qquad (2)$$

$$Ar\!-\!\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\!-\!OO\bullet \;\rightleftharpoons\; Ar\!-\!\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\!\bullet + O_2 \qquad (3)$$

To examine further this oxidative system we next sought to study the photooxidation of ethylbenzene **5** in the presence or absence of Et_3SiH. The oxidation of secondary aryl alkanes to the corresponding alcohols is a difficult transformation because oxidation of the initially formed alcohol to the corresponding carbonyl compound is faster in this case.[14] To this end, only a few reports deal with the catalytic aerobic oxidation of secondary aryl alkanes using polyoxometalates as catalysts.[15] In these reports carbonyl compounds were detected as the sole or major products. In contrast, as can be seen from Table 2, the oxidation of ethylbenzene **5** with decatungstate in the presence of triethylsilane and molecular oxygen, shows a slight preference for formation of the secondary hydroperoxide (which after PPh_3 reduction affords the corresponding alcohol) instead of the fully oxidized product, acetophenone **4c**. As the irradiation time increases, the ratio of **5b/4c** decreases due to the further oxidation of the hydroperoxide **5a** and alcohol **5b** to acetophenone.

To obtain more information regarding the stereoelectronic factors that control the oxidation of aryl alkanes,[19a–c] we chose to study the decatungstate photooxidation of fluorine derivatives such as fluorene (**6**), 9-methyl-9*H*-fluorene (**7**) and 9-phenyl-9*H*-fluorene (**8**) (Table 3). In these substrates the enforced planarity of the two phenyl rings[19c] leads to the formation of a highly stabilized carbon-centred radical, one that is also less sterically hindered compared to 1,1-diphenylmethylene systems. Recently, it has been proposed that such structural parameters can attenuate the reactivity of carbon-centred radicals with molecular oxygen.[19a–c]

As seen from Table 3, photooxidation of fluorene **6** produces fluorenol **6b** and fluorenone **6c** in a ratio of 40:60. However, when R is methyl or phenyl (substrates **7** and

Table 2. Decatungstate sensitized photooxidation of ethylbenzene **5** in the presence of O_2 and Et_3SiH
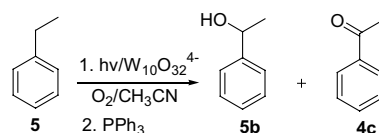
Time (h)	Et_3SiH^a	% Conversion^{a,b}	**5b** (%)^b	**4c** (%)^b
0.5	—	24	58	42
0.5	1 equiv	24	74	26
1	—	47	51	49
1	1 equiv	48	60	40
1.5	—	69	38	62
1.5	1 equiv	65	50	50
2	—	83	29	71
2	1 equiv	75	42	58
2.5	—	89	22	78
2.5	1 equiv	83	35	65
4	—	100	—	100
4	1 equiv	93	16	84

^{a} Ethylbenzene (0.03 M) was irradiated (Xenon lamp, 300 W) in the presence of $[Bu_4N]_4W_{10}O_{32}$ (5.5×10^{-4} M), in acetonitrile, at 5–10 °C.
^{b} Determined by gas chromatography after reduction with PPh_3 and ^1H NMR spectroscopy with errors of ±1% and ±4%, respectively.

Table 3. Decatungstate sensitized photooxidation of 9-substituted fluorenes **6–8** in the presence of O_2 and Et_3SiH
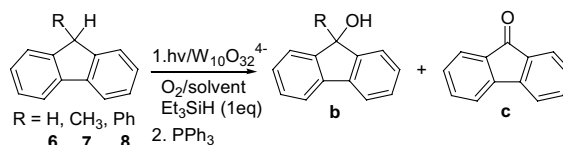

Substrate^a	Time (h)	% Conversion^b	**b** (%)^b	**c** (%)^b
6	1	25	40	60
6	2	40	25	75
6	4	60	20	80
7	1	30	>98	<2
7	2	50	95	5
7	3	64	94	6
8	1	10	100	–
8	2	20	>99	<1
8	4	41	>98	<2

^{a} Substituted fluorenes (0.03 M) were irradiated (Xenon lamp, 300 W) in the presence of $[Bu_4N]_4W_{10}O_{32}$ (5.5×10^{-4} M), in acetonitrile and acetone, at 5–10 °C.
^{b} Determined by GC after reduction with PPh_3 and ^1H NMR spectroscopy with errors of ±1% and ±4%, respectively.

8) the corresponding tertiary hydroperoxides **7a** and **8a** (which are reduced by PPh_3 to **7b** and **8b**), were formed as the major or sole products. In the case of substrate **8**, although high selectivity favouring formation of the alcohol is observed, the reaction conversion compared to substrate **7** is substantially lower. This result indicates that because of steric reasons, the phenyl substituent adopts an orthogonal conformation (with respect to the plane of the fluorene) and the tertiary radical formed from **8** is sterically less accessible to molecular oxygen compared to the corresponding radical intermediate
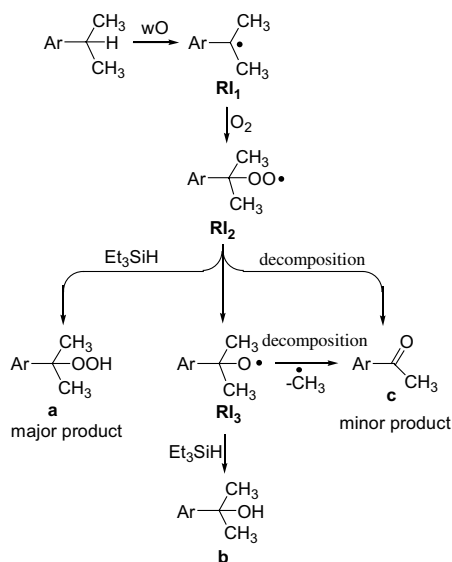
Scheme 3. Proposed mechanism of the decatungstate/Et$_3$SiH system oxidation of aryl alkanes.

derived from substrate **7** where the R substituent is a small and freely rotating methyl group.[19c]

It is interesting to note that lower conversions were also observed in the oxidations of 4-nitro and 4-trifluoromethylphenyl propanes (Table 1, substrates **1** and **2**). These results support the proposal that the electron delocalization of the cumyl radical intermediate **RI**$_1$ (Scheme 3) by the electron-withdrawing group of the *para*-phenyl substituent reduces the radical's reactivity towards molecular oxygen.[19b]

A plausible mechanism that may rationalize these results is shown in Scheme 3. In the first step, under the influence of irradiation, the decatungstate anion converts to the relatively long-lived intermediate wO,[8,9] which is the species responsible for the C–H bond cleavage, which forms the corresponding tertiary radical intermediate **RI**$_1$. It is established that hydrogen abstraction transfer (HAT) of this type takes place in the rate-determining step of such reactions.[8,11,14] The single-electron-reduced species of decatungstate H$^+$W$_{10}$O$_{32}^{5-}$ is re-oxidized in the presence of molecular oxygen to give again W$_{10}$O$_{32}^{4-}$ and a molecule of hydrogen peroxide.[8,9a] In the case of an electron transfer (ET) mechanism, a high yield of the C–C bond cleavage products would be expected.[22] The peroxyl and/or alkoxy intermediates (**RI**$_2$ and **RI**$_3$) can be trapped by Et$_3$SiH to form the tertiary hydroperoxides and alcohols, respectively, as the major products. However in a recent study,[16e] the rate constant of the reduction of cumylperoxyl radical with silanes was found to be in the range of 0.10–0.90 M^{-1} s^{-1}. This low rate value is not consistent with a fast trapping of the peroxyl or alkoxyl radicals by Et$_3$SiH. Further study is required in order to rationalize the exact role of Et$_3$SiH in the title reaction.

In conclusion, the decatungstate photosensitized oxidation of aryl alkanes in the presence of triethylsilane

and molecular oxygen is a convenient and mild transformation forming mainly the corresponding tertiary hydroperoxides and alcohols. The reasonable to high chemical yields, the small amount of the C–C bond cleavage products present, and the easy reduction of the hydroperoxides to the corresponding alcohols, render the title reaction synthetically useful.

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