Polyoxotungstate Photoinduced Alkylation of Electrophilic Alkenes by Cycloalkanes

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Abstract: Alkyl radical obtained by irradiation of tetrabutylammonium decatungstate in acetonitrile in the presence of cycloalkanes (C_5H_{10}, C_6H_{12}, C_7H_{14}) are efficiently trapped by electrophilic alkenes (acrylonitrile, isopropylydenmalonitrile, isopropylydencyanoacetate) to give the corresponding alkylated aliphatic nitriles. The reaction can be carried out up to complete conversion of the alkene with reasonable (in most cases 60–65%) yields. Addition of the radicals to the alkene is followed by electron transfer from reduced decatungstate regenerating the sensitizer (turn over number up to 60). Steady-state measurements, EPR evidence, deuteration experiments and attempted intramolecular trapping of the adduct radical support the mechanistic proposal.

Keywords: alkylation • C–H activation • photocatalysis • photochemistry • radicals

Introduction

Photoexcited polyoxometalate anions, such as the decatungstate $W_{10}O_{32}{}^{4-}$,[1] react with organic molecules in solution. Much work has been devoted to the mechanistic aspects of these photochemical processes[2] or to applications such as photomicrolithography[3] and the photocatalytic decontamination of toxic materials.[4] However, these reactions are not destitute of synthetic interest, in particular when applied to the generation of alkyl radicals from alkanes [Eq. (1)],[5] thus contributing a mild activation path for the activation of aliphatic C–H bonds.[6]

$$W_{10}O_{32}^{4-}{}^{*} + RH \rightarrow H^{+}\,W_{10}O_{32}^{5-} + R^{\cdot} \qquad (1)$$

The reaction as represented in Equation (1) actually is a gross oversimplification, and much work has been devoted to clarify mechanistic questions, such as which of the excited states of the decatungstate participates into the chemical step, which is the protonation state of the reduced species, most often designed as $H^{+}W_{10}O_{32}{}^{5-}$, and whether the alkyl radical (and possibly other radical intermediates formed in the course of the reaction) remains bonded to the polyoxotungstate.[2,7] As for the reactions of the alkane, it has been demonstrated that alkyl radicals add to ethylene, 1-hexene, acetylene,[8] carbon monoxide,[9] nitriles[10] and cyanoformate[11] forming a C–C bond, besides adding to oxygen to give hydroperoxides and alcohols and ketones from them.[7,12] Somewhat surprising, the most typical reaction of alkyl radicals, addition to *electrophilic* alkenes[13] has not been explored. Since the most useful synthetic paths for organic compounds via alkyl radicals are based on the last reaction, due to the well known nucleophilic character of such species, we deemed it worthwhile to explore the potential of decatungstate photocatalysis in this direction.

Results

The experiments were carried out by irradiating 0.002 M tetrabutylammonium decatungstate (TBADT) in acetonitrile. The solutions were degassed by freeze-degas-thaw cycles. When a 0.5 M cyclohexane solution was used, 0.025 M each of both bicyclohexyl and cyclohexyl methyl ketone were formed by a 3 h irradiation. An analogous experiment in the presence of 0.1 M 1-hexene gave some hexylcyclohexane (**1**, 4% with respect to the starting alkene) and a reduced yield of the above products (Scheme 1, Table 1). Both experiments duplicated the results previously obtained by Hill under essentially identical conditions and, again as in his case, prolonged irradiation only marginally increased the yield of the products.[8]

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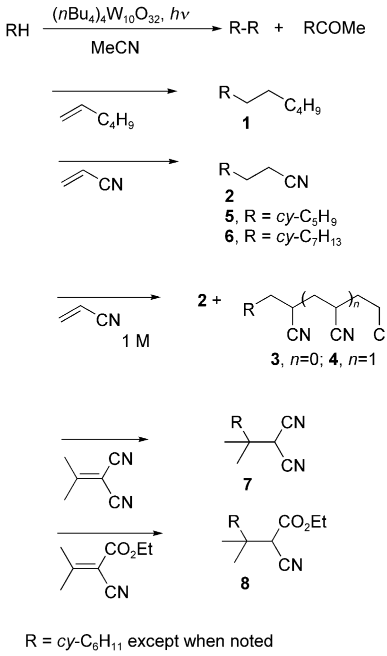


Scheme 1.

Table 1. Alkylation of unsaturated nitriles by cycloalkanes upon decatungstate photocatalysis.

Alkane, 0.5 M	Trap, 0.1 M	Products (% Yield)[a]		
		R–R	RCOMe	Adducts
cyclohexane	none	5	5	
	1-hexene	1	1.5	**1** (4)
	AN			**2** (63)
	AN (1 M)			**2** (21), **3** (31), **4** (11)
	IPMN			**7**, 66
	IPCA			**8**, 58
	CMHN			**9**, 45
cyclopentane	AN			**5**, 30
cycloheptane	AN			**6**, 51

[a] After 3 h irradiation with 0.002 M TBADT, see Experimental Section.

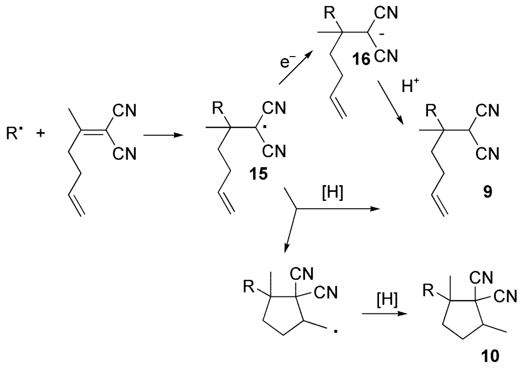
However, the use of an electrophilic alkene such as acrylonitrile (AN, 0.1 M) led to a much more efficient reaction, yielding 63% of cyclohexylpropionitrile (**2**, Scheme 1) in 3 h. Furthermore, very little (<1%) of bicyclohexyl and the ketone were formed under this condition and no other product was detected. Preparative experiments for products separation and identification were similarly carried out in argon flushed solutions (see Experimental Section). Competition experiments with 1-hexene and AN both present (both 0.1 M) gave >100 AN trapping versus cyclohexene trapping.

When a 1 M rather than 0.1 M AN concentration was used, a more complex product distribution resulted, and products containing two and three AN units (compounds **3** and **4**) were among the major products, with **3** actually the most abundant one.

The reaction could be easily extended to other cycloalkanes, as shown in Scheme 1 and Table 1, at least for those sufficiently soluble in acetonitrile, such as cyclopentane and cycloheptane (0.1 M), which yielded nitriles **5** and **6**.

We then used further electrophilic alkenes. With isopropylydenmalononitrile (IPMN) alkylation was successful giving malononitrile **7** and similarly adduct **8** was obtained from isopropylydencyanacetate (IPCA). On the other hand, using tetracyanoethylene (TCNE, 0.001 M) caused the rapid development of yellow color and no alkylated product was formed.

The course of the alkylation was further probed by using a ω-alkenyl derivative of IPMN, 2-cyano-3-methylhept-6-dienecarbonitrile, CMHN. A single product was obtained in this case and recognized as the 3-(ω-alkenyl)-3-cyclohexylhept-6-enecarbonitrile (**9**). On the contrary, cyclized dinitrile **10** that we had previously obtained through radical addition onto CMHN under different conditions (see Scheme 2)[14] was not formed in the present case.



Scheme 2.

The origin of the α-hydrogen atom in the alkylated nitriles obtained was tested. Thus, using perdeuterocyclohexane in the reaction with AN led to no detectable deuteration, while adding 0.5% D_2O led to substantial deuterium incorporation (50%, see Table 2). Duplication of the experiment with IPMN was precluded by the fast proton exchange of the resulting dinitrile.[15a]

Table 2. Deuteration in the alkylated nitriles.

Reagents	Solvent	α-Deuteration
C_6D_{12}, AN	CH_3CN	α[D]**2**, <5%
C_6H_{12}, AN	CH_3CN, 0.5% D_2O	α[D]**2**, 50%

In the above experiments with TBADT and cyclohexane the solution turned to the blue color characteristic of the $H^+W_{10}O_{32}^{5-}/H_2W_{10}O_{32}^{4-}$ mixture, as previously described.[10a,15b] The color developed also in the presence of the electrophilic alkenes and the course of the reaction was followed by determining the amount of reduced polyanion and alkylated product on the same sample under degassed conditions at various irradiation times. The results are reported in Figure 1. In order to have a mechanistic significance, the data are presented in the form of number of electrons accepted by the polyoxotungstate to yield the blue reduced form (left-hand ordinate) and moles of alkylated nitrile formed (right-hand ordinate). As it appears from the figure, reduced polyoxotungstate developed in minutes when irradi-

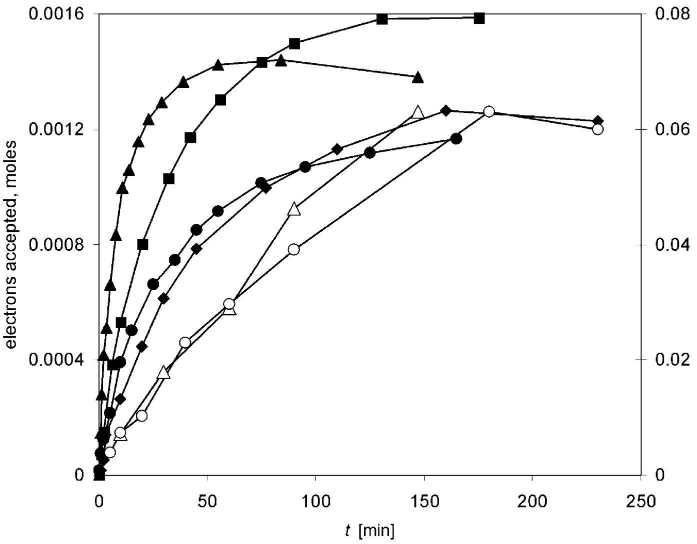


Figure 1. Results from the irradiation of 0.002 M tetrabutylammonium decatungstate (TBADT) in acetonitrile in the presence of 0.5 M cyclohexane. Filled symbols (left-hand scale): moles of electrons accepted by the decatungstate as measured by the formation of the two reduced forms. Empty symbols (right-hand scale): moles of alkylated products formed. (●) No additive; (■) 0.1 M 1-hexene; (▲,△) 0.1 M AN; (◆,◇) 0.1 M IPMN.

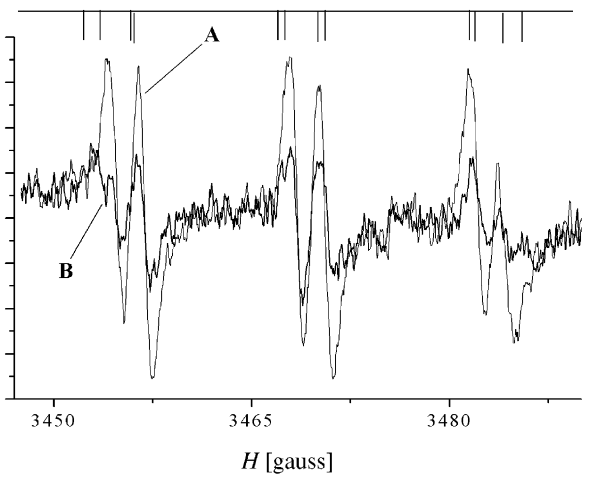


Figure 2. EPR spin trapping spectra obtained irradiating ($\lambda >$ 300 nm) TBADT (0.002 M) in a nitrogen-flushed solution containing cyclohexane (0.3 M), AN (0.1 M) and PBN (0.05 M). A) After a few seconds irradiation ($a_N = 13.9$ G, $a_H = 2.2$ G, light line); B) after 20 min irradiation ($a_N = 14.3$ G, $a_H = 3.4$ G, heavy line).

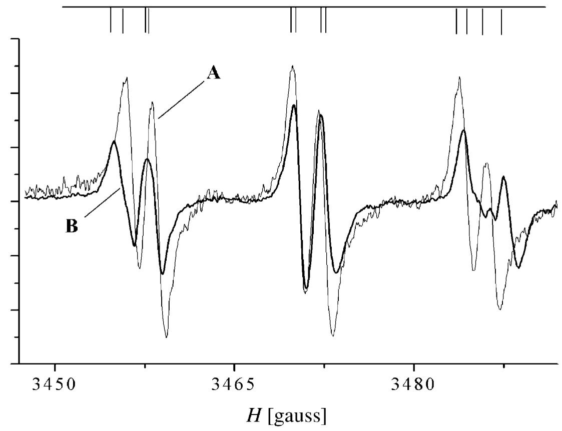


Figure 3. EPR spin trapping spectra obtained irradiating ($\lambda > 300$ nm) TBADT (0.002 M) in a nitrogen-flushed solution containing cyclohexane (0.3 M), IPMN (0.1 M) and PBN (0.05 M). A) After a few seconds irradiation ($a_N = 13.9$ G, $a_H = 2.2$ G, light line); B) after 5 min irradiation ($a_N = 15.0$ G, $a_H = 2.9$ G, heavy line).

ated in the presence of cyclohexane in MeCN. The color developed faster when acrylonitrile was added, while it grew at a somewhat slower rate in the presence of IPMN, at least in the first part of the conversion. In all cases, a plateau was reached and this was not much different in the three experiments, corresponding to 60–70 % conversion of the polyoxotungstate into the reduced form (using the published ε values for the two reduced forms, see below).[15b] The alkylated adducts with both AN and IPMN developed at roughly the same rate and in a molar amount much larger than that of reduced TBADT accumulating.

It is apparent from Table 1 that TBADT is acting as a photocatalyst, since about 0.06 moles products are formed when 0.002 moles of it are used. For mechanistic indication, we considered as turn-over number the ratio between the alkylated products formed and the electrons accepted by the photocatalyst, calculated from Figure 1. In the alkylation of AN, the ratio was 6 at the beginning of the reaction (4 % AN converted) and grew to 46 in the advanced phase (60 % AN converted) and it similarly grew from 12 to 60 with IPMN.

EPR experiments were also carried out. Irradiation of TBADT in an oxygen-equilibrated 0.3 M cyclohexane solution in MeCN in the presence of 0.05 M α-phenyl *N-tert*-butylnitrone (PBN) gave rise to a triplet of doublets attributable to the trapping of the cyclohexyl radical, in agreement with previous work.[16] When a similar experiment was carried out in a nitrogen-flushed solution to which 0.1 M AN had been added, the same signal was initially observed but after 20 min was superseded by a new triplet of doublets, corresponding to the trapping of a different C-centered radical (Figure 2). Using 0.1 M IPMN gave a similar result, with the second radical being revealed earlier (5 min, Figure 3). Indeed, this signal appeared also with a 1×10^{-3} M concentration of IPMN, though the reaction was slower and the second radical developed at a longer time (ca. 20 min). The spectra of the second radical had a different structure with the two alkenes, as showed by the different coupling constants. No significant signals were detected when omitting TBADT or cyclohexane or when leaving the solution in the dark. With 1×10^{-3} M TCNE the nine-lines signals corresponding to the TCNE radical anion was present from the beginning along with the triplet of doublets resulting from the trapping of the cyclohexyl radical.

The role of oxygen was also investigated. Repeating the small-scale experiments with cyclohexane and AN omitting degassing showed that, while the deep blue color of reduced polyoxotungstate did not develop, alkylation to yield product **2** proceeded steadily, though at rate about one forth than in oxygen-free solution. In preparative experiments, irradiation of TBADT in non de-aerated solutions containing cyclohexane led to small amounts of cyclohexanone and cyclohexanol, but in the presence of AN or IPMN, alkylated nitriles **2** and **5** were formed in good yield also when omitting degassing.

Discussion

The basic photochemical reactions of polyoxotungtate complexes have been fully clarified by extensive mechanistic investigations.[2,7] In essence, electron and hydrogen transfer generate alkyl radicals according to Equation (1). Reverse hydrogen atom transfer [Eq. (2)] then competes with coupling [Eq. (3)] or trapping [by a suitable reagent X, Eq. (4)] of the radicals. Hydrogen transfer to the adduct radicals formed in the latter case may occur according to Equation (5). Furthermore, the reduced polyoxotungstate disproportionates on a relatively long (up to seconds) time scale yielding the diprotonated two-electron reduced anion [Eq. (6)].

$$H^{+}W_{10}O_{32}^{5-} + R^{\cdot} \rightarrow W_{10}O_{32}^{4-} + RH \tag{2}$$

$$2\,R^{\cdot} \rightarrow \text{products } (R_2,\ \text{alkenes etc.}) \tag{3}$$

$$R^{\cdot} + X \rightarrow R\text{-}X^{\cdot} \tag{4}$$

$$H^{+}W_{10}O_{32}^{5-} + R\text{-}X^{\cdot} \rightarrow W_{10}O_{32}^{4-} + R\text{-}XH \tag{5}$$

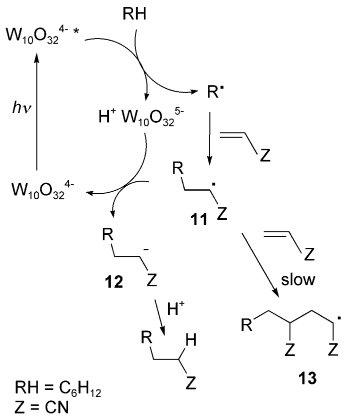
$$H^{+}W_{10}O_{32}^{5-} \rightarrow W_{10}O_{32}^{4-} + H_2W_{10}O_{32}^{4-} \tag{6}$$

Formation of alkyl radicals according to Equation (1) has been well documented, for example by spin trapping,[16] as has their trapping by aliphatic alkenes and alkynes.[8] Such addition processes are interesting as a way for the direct functionalization of inactivated C–H bonds, but occur slowly (Φ <0.05) and only up to a low extent. As an example, Hill reported that ethylcyclohexane is formed from cyclohexane and ethene with 83% selectivity and 8–9% conversion after 78 h, and conversion could not be brought over 10%.[8] This is probably due to the "persistent radical effect",[7b,17] namely to the fact that, while highly reactive alkyl radicals are consumed through various paths (dimerization, disproportionation to alkenes and other unidentified), a more persistent species such as $H^{+}W_{10}O_{32}^{5-}$ builds up and this in turn increases the role of reverse reactions such as that in eq. 2, thus inhibiting the progress of the addition. Therefore, the process has limited synthetic interest, except when a good trap for the nucleophilic radical is available, as in the case for CO or cyanoformates. In particular, the reaction in the presence of oxygen has been studied in detail. This leads rather efficiently to alcohols or ketones (Φ 0.35). Dioxygen traps the alkyl radicals and the resulting peroxyl radicals are reduced to hydroperoxides by $H^{+}W_{10}O_{32}^{5-}$.[7a,12a]

Table 1 shows that in the absence of any trap cyclohexyl radicals couple to bicyclohexyl, disproportionate or add to acetonitrile. The last process gives cyclohexyl methyl ketone and has been suggested to involve previous reduction of the radical to the carbanion.[10] All of the products were obtained in a low yield, in keeping with the literature.[8] When present, 1-hexene is alkylated, again in a low yield. This is due to the fact that reaction of the cyclohexyl radical with a nucleophilic alkene is not favored and thus the persistent radical effect limits the conversion, just as in the absence of traps.

The present experiments show that with an electrophilic alkene the TBADT photoinduced reaction of cyclohexane is rather efficient (Φ 0.25) and can be carried out up to elevate conversion with no declining of the yield (Figure 1). As one may expect from the well known behavior of alkyl radicals in solution,[13] addition to AN is more than 100 times as effective as addition to 1-hexene. The rate constant for the addition of cyclohexyl radical to methyl acrylate has been recently measured as $3.3\times10^{6}\,\text{M}^{-1}\,\text{s}^{-1}$ at 25 °C.[18]

The detailed mechanism of the formation of radicals has been previously explored and both a hydrogen abstraction and an electron transfer-radical cation deprotonation mechanism have been considered, the former one appearing more likely.[2a,7a] The present trapping corresponds to the first step of the classical conjugate radical addition,[13] but since there is no hydrogen donor in solution, the stabilized (and much less electrophilic) adduct radical **11** is reduced by the persistent $H^{+}W_{10}O_{32}^{5-}$ species to anion **12** (see Scheme 3). Reduction of the α-cyano radical **11**, characterized by a high electron affinity,[19] is efficient, while this is not the case for the starting alkyl radical (compare E_{red} for TBADT, −1.2 V,[2a] and for *sec*-butyl radical, ca. −1.35 V vs SCE,[20] and take into account that other reactions including alternative paths, such as Equations (3), (4), limit its steady state concentration). As mentioned above,[10] reduction of $R^{\cdot}$ to R^{-} has a role in the absence of traps and probably explains the formation of small amounts of methyl ketone via attack of the carbanion to the solvent acetonitrile and hydrolysis of the resulting imine.

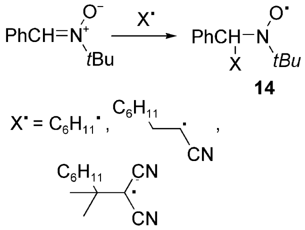


Scheme 3.

Deuteration experiments (Table 2) support the role of anion **12** by the positive result with D_2O. On the other hand, the negative result with C_6D_{12} indicate that neither hydrogen back donation from reduced polyoxotungstate, nor hydrogen abstraction from the alkane by the adduct radical (at any rate thermodynamically unfeasible) have any role. In neat MeCN, the α proton reasonably arises from traces of water present.

In keeping with this hypothesis, incorporation of further AN units becomes significant (accounting for $^2/_3$ of the isolated products) at 1 M AN, when concentration is high enough to make relatively slow addition by nucleophilic radical **11** to AN (rate constant ca. $1\times10^4\,\text{M}^{-1}\text{s}^{-1}$) competitive with reduction. Addition yields radical **13** (Scheme 3). Incorporation of two or three alkene units has been previously detected in some conjugate alkylation reactions of radicals to acrylonitrile, though the products have not been isolated.[21]

The intermediacy of both cyclohexyl radical and of adduct radicals **11** with both AN and IPMN is also evidenced by trapping by phenyl-*tert*-butylnitrone to give the corresponding nitroxyl radicals **14** (Figures 2 and 3). EPR experiments also show that the highly stabilized α,α-dicyano radical adduct from IPMN builds up to a larger concentration than in the case of the monocyano radical from AN.



Further support to the mechanism comes from the fact that when using CMHN as the trap, no cyclization takes place, while this is the main process (cyclized **10** vs open chain **9** 3 to 1)[14] when the cyclohexyl radical is generated by an alternative method, for example hydrogen abstraction from cyclohexane by triplet benzophenone. Under the present conditions, on the contrary, the 5-hexenyl radical **15** is reduced by $\text{H}^+\text{W}_{10}\text{O}_{32}{}^{5-}$ accumulated to a significant concentration to give anion **16**, so that cyclization is completely inhibited (Scheme 2).

Electron transfer to the radical adduct regenerates the starting polyoxometalate that is used in catalytic amounts and operates with an initial turn-over number of 6 with AN and 12 with IPMN. The latter trap scavenges alkyl radicals more efficiently and also yields a more easily reduced adduct radical. Regeneration of TBADT is not complete and part of $\text{H}^+\text{W}_{10}\text{O}_{32}{}^{5-}$ undergoes disproportionation (known rate constant $1\times10^7\,\text{M}^{-1}\text{s}^{-1}$)[7f] to give the two-electrons reduced form $\text{H}_2\text{W}_{10}\text{O}_{32}{}^{4-}$ (see Figure 1). As mentioned above, the efficiency of this step is lower in the reaction with IPMN due to the faster reoxidation. During irradiation, an increasing fraction of the polyoxoanion is accumulated in the reduced form, arriving at about $^2/_3$ with the electrophilic alkenes (up to $^4/_5$ in their absence, see Figure 1), but a sufficient amount of it remains to make the photocatalytic action continue, also thanks to the choice of the irradiation wavelength at 310 nm, where TBADT absorbs strongly. Thus, the turn over number at high conversion is about 60, that is 60 moles of the alkene are alkylated for every electron accepted by TBADT to give $\text{H}^+\text{W}_{10}\text{O}_{32}{}^{4-}$. The preparative significance of the method is indicated by alkylation yields attaining 66 % with the photocatalyst used in a 1 to 50 proportion with respect to the alkene.

The mechanism requires that the electrophilic alkene added functions as a trap, not interfering with the sensitization cycle (Scheme 3). Indeed, this holds true for AN ($E_\text{red} = -2.6$ V vs SCE)[22] and IPMN (−1.75),[22] but the limits of the method are clearly shown by the fact that TCNE (+0.23)[23] is reduced to the radical anion [Eq. (7), as indicated by the EPR and by the yellowing of the solution], making alkylation impossible.

$$\text{H}^+\,\text{W}_{10}\text{O}_{32}^{5-} + \text{TCNE} \rightarrow \text{W}_{10}\text{O}_{32}^{4-} + \text{TCNE}^{\cdot-} + \text{H}^+ \qquad (7)$$

Importantly, this is a stoichiometric process in terms of light absorbed, not a photoinitiated chain process, that would be impossible due to the stability of the radical adduct. This makes the process less oxygen-sensitive. In fact, oxygen slows down the alkylation but does not inhibit it, which is not quite surprising when one takes into account that this is *no* chain process. Thus, the oxygen effect is limited to the competition with the alkene (the latter being a hundred times more concentrated) for the radical, but the multiplicative effect of chain reactions is lacking. Actually, we found that the preparative alkylation could be carried out to a satisfactory conversion also when omitting de-aeration. Apparently, the slowing down of the alkylation due to radical trapping by oxygen is in part compensated for by the much lower conversion of the polyoxometallate into the reduced form, which is re-oxidized by oxygen (the solution remains of a pale blue), and thus by the greater light fraction absorbed by the active species.

Conclusion

Photocatalysis by polyoxoanions, and in particular by TBADT, can be considered a mild and efficient method for the generation of alkyl radicals from alkanes. The mechanism of the primary steps in the TBADT–alkane–MeCN system has been studied in detail elsewhere. For the present purpose, the significant point is that radicals are trapped by electrophilic alkenes in a reaction (Scheme 3) that follows a path quite similar to that proved for the trapping by oxygen to give hydroperoxides. In this way, conjugate alkylations have been obtained that extend the classical radical alkylation reactions since the radical precursor is an alkane, rather than a bromide or iodide, and represent a mild method for the activation of aliphatic C–H bond with C–C bond formation. This significantly adds to the synthetic appeal of polyoxoanions photoinduced reactions.

Experimental Section

Materials: Tetrabutylammonium decatungstate (TBADT) was prepared according to a published procedure.[24] The electrophilic alkenes IPMN, IPCA[25] and CMHN[14] were prepared as previously reported. The other materials and the solvents were of commercial origin.

Preparative irradiations: These were carried out in 1 cm diameter quartz tubes containing a solution (6 mL) of TBADT (40 mg, 0.002 M), the alkane (0.5 M) and the electrophilic alkene (0.1 M). These were purged with purified Argon for 10 min, serum capped and irradiated for 15–20 h in a multilamp apparatus fitted with six 15 W phosphor-coated lamps (center of emission 310 nm). The irradiated solution was flushed with oxygen until colorless, passed through a 4 cm layer of neutral alumina and evaporated. The residue was first examined by GC/MS and then chromatographed on silica gel by using cyclohexane and cyclohexane/ethyl acetate 98:2. With IPMN essentially the same results were obtained also when omitting degassing.

Compounds **2**, **5**, **6** and **9** were identical to samples prepared through alternative procedures.[14] Hexylcyclohexane was recognized by comparison of the GC/MS spectrum with literature data,[26] bicyclohexyl and cyclohexylmethylketone by comparison of the GC/MS spectrum with that of authentic samples.

2-Cyclohexylmethylpentanedicarbonitrile (3): colorless syrup; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.8$–1.8 (m, 13H), 1.95 (m, 2H; 3-H$_2$), 2.6 (m, 2H; 4-H$_2$), 2.85 (m, 1H; 2-H); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ = 15.8 (CH$_2$; 4-C), 26.2 (CH$_2$), 26.3 (CH$_2$), 26.6 (CH$_2$; cyclohexyl ring), 28.7 (CH), 29.0 (CH$_2$), 32.7 (CH$_2$), 33.8 (CH$_2$), 35.8 (CH), 39.8 (CH$_2$), 118.0 (CN), 120.4 (CN); GC/MS: *m/z* (%): 190 (68), 150 (25), 135 (62), 122 (18), 108 (43), 95 (37), 82 (48), 65 (100).

4-Cyano-2-cyclohexylmethylheptanedicarbonitrile (4): (diastereoisomers mixture; the sample obtained by chromatography was somewhat contaminated by dinitrile **3**), colorless syrup; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\delta = 0.8$–1.9 (m, 13H), 2.05 (m, 2H; 6-H), 2.6 (m, 2H; 3-H), 2.9–3.1 (two m, 2H; 2-H, 4-H ; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 15.6$ (CH$_2$), 26.3 (CH$_2$), 26.6 (CH$_2$), 27.0 (CH), 28.0 (CH$_2$), 29.0 (CH), 30.3 (CH), 32.7 (CH$_2$), 33.9 (CH$_2$), 40.2 (CH$_2$), 118.5 (CN), 120.2 (CN), 120.3 (CN); GC/MS (two peaks with almost identic pattern): *m/z* (%): 243 (8), 203 (12), 188 (15), 150 (18), 137 (20), 122 (12), 108 (24), 82 (23), 55 (100).

2-(1-Cyclohexyl-1-methylethyl)propanedicarbonitrile (7): colorless solid; m.p. 48–50 °C; elemental analysis calcd (%) for C 75.7, H 9.7, N 14.5; found: C 75.74, H 9.54, N 14.72; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\delta =$ 1.2 (s, 6H; Me$_2$), 1.0–1.95 (several m, 11H; cyclohexyl), 3.7 (s, 1H; 2-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.7 (CH$_3$), 25.9 (CH$_2$), 26.3 (CH$_2$), 27.1 (CH$_2$), 33.5 (CH), 41.0, 44.1 (CH), 112.1 (CN); IR (melt): $\tilde{\nu}$ = 2253 cm^{-1}; GC/MS: *m/z* (%): 190 (1) [M^+], 175 (1), 125 (4), 107 (3), 83 (100).

Ethyl 2-cyano-3-cyclohexyl-3-methylbutanoate (8): colorless syrup; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 1.1 (s, 3H; Me), 1.3 (s, 3H, Me), 1.0–1.9 (several m, 11H; cyclohexyl), 1.35 (t, 3H; Me), 3.6 (s, 1H; 2-H), 4.25 (q, 2H; CH$_2$); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 13.4 (CH$_3$), 20.9 (CH$_3$), 21.7 (CH$_3$), 25.6 (CH$_2$), 25.9 (CH$_2$), 26.1 (CH$_2$), 26.4 (CH$_2$), 26.6 (CH$_2$), 40.3, 44.9 (CH), 46.5 (CH), 61.6 (CH$_2$), 116.3 (CN), 165.6 (CO); IR (neat): $\tilde{\nu}$ = 2246, 1742 cm^{-1}; GC/MS: *m/z* (%): 237 (10) [M^+], 164 (18), 140 (21), 124 (65), 114 (42), 82 (100).

Steady state measurements: Solutions (2 mL) of 0.002 M TBADT in MeCN containing the appropriate additives in 1 cm optical path spectrophotometric couvettes were degassed by five freeze-degas-thaw cycles (to 10^{-6} Torr). The samples were irradiated by means of a focalised Osram 150 W high-pressure mercury arc fitted by an interference filter at 313 nm or a band-pass filter (the first one for quantum yield measurements, the latter for comparing reactivities, see the results after 3 h irradiation in Table 1). Light absorbed was determined by using a photometer and the light flux was measured through ferrioxalate actinometry. Formation of the alkylated products was determined by GC on the basis of calibration curves by using an internal standard (biphenyl). Formation of the two reduced forms of TBADT was monitored by spectroscopy in the visible on the basis of the known molecular extinction coefficient of such molecules.[15b]

EPR Measurements: EPR spectra were recorded with a X-band Bruker 220 SE spectrometer that was calibrated by using α,α'-diphenylpicrylhydrazyl. EPR spin trapping experiments were performed using α-phenyl, *N-tert* butyl nitrone (PBN) as a spin trap. In a typical experiment CH$_3$CN solution containing TBADT (0.002 M), C_6H_{12} (0.3 M), PBN (0.05 M) and an alkene (AN or IPMN, 0.1 M, or TCNE 0.001 M) were deoxygenated by nitrogen flushing and put in the EPR cell under inert atmosphere. An analogous experiment has been carried out with an oxygen equilibrated solution in the absence of the alkene. Then, photochemical excitation was carried out with light of wavelength higher than 300 nm directly inside the instrument cavity, using a flat quartz cell as the reaction vessel. Analogous experiments were performed irradiating in the absence of TBADT, or in the absence of C_6H_{12}, or in the dark.

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