Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 62 (2006) 5527–5535
Tetrahedron

# Photomediated synthesis of β-alkylketones from cycloalkanes

Daniele Dondi,[a,b] Anna Maria Cardarelli,[a] Maurizio Fagnoni[a,*] and Angelo Albini[a,*]

[a]*Department of Organic Chemistry, University of Pavia, Via Taramelli 10, 27100 Pavia, Italy*
[b]*Research Unit of the INCA Consortium, University of Pavia, I-27100 Pavia, Italy*

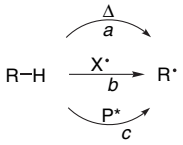
Received 16 November 2005; revised 21 February 2006; accepted 9 March 2006
Available online 12 April 2006

**Abstract**—β-Cycloalkylketones are prepared through a photomediated radical addition reaction onto enones starting from the corresponding alkanes (i.e., cyclopentane, -hexane, -heptane, -dodecane and adamantane). The alkyl radicals are generated via hydrogen abstraction by either an organic (benzophenone) or an inorganic (tetrabutylammonium decatungstate, TBADT) photomediator. Isolated yields vary in the range 30–80%. Benzophenone has to be considered as a reagent, since it is used in an equimolar amount with respect to enone and is completely consumed in the reaction. On the contrary, TBADT is shown to behave as a photocatalyst, which is active for at least 50 cycles. The potential of photomediated reactions for the generation of radicals from unusual precursors and the synthetic significance of this method are discussed.


## 1. Introduction

β-Alkylketones are prepared by conjugate addition starting from alkyl halides and α,β-unsaturated ketones under either anionic[1a] (by using organometallic species) or radical conditions.[1] An obvious improvement in terms of atom economy would be the substitution of alkanes for alkyl halides or other derivatives. Unfortunately, the direct activation of C–H bonds in alkanes still remains one of the 'Holy Grail in chemistry'.[2] Many efforts have been devoted to the activation of aromatic and olefinic hydrogens[3] by using metal (especially ruthenium[3d]) based complexes. Surprisingly, the activation of aliphatic C–H bonds has received much less attention despite the fact that saturated hydrocarbons constitute the main fraction of the available feedstock. This can be ascribed to the poor tendency of alkanes to become coordinated on metal centers. Furthermore, even when such activation has been achieved, the synthetic use has been mostly addressed to forming a C-heteroatom bond (e.g., in oxygenation reactions) rather than a C–C bond.[3,4]

The noncatalytic activation of alkanes generally requires rather harsh conditions and this leads to a poor selectivity. Thermolysis at a sufficient high temperature is a possibility (Scheme 1, path *a*) but the control of the reaction is difficult. Thus, the thermal synthesis of 4-cyclohexylbutanone (12% yield) from cyclohexane and 3-buten-2-one at a high temperature (ca. 400 °C) and pressure[5] is to our knowledge the only case where a β-cycloalkylketone has been prepared starting directly from the alkane and the enone. A method for the functionalization of alkanes under milder conditions than those of the above reaction is desirable as a green alternative.[6a] Electrophilic radicals such as hydroxy or acyloxy radicals ($X^{\bullet}$, path *b*) can be generated at a lower temperature and abstract a hydrogen, but again the reaction is difficult to control;[6b] the same radicals can be produced photochemically at room temperature, but the precursors, e.g., benzoylperoxide, absorb at too short a wavelength to make a photoreaction practical.




**Scheme 1.** Activation of C–H bonds in alkanes.

A range of compounds are known that absorb strongly in the near UV and in the excited state react with alkanes at a high rate either via hydrogen abstraction or via electron transfer and deprotonation[6c] (P*, path *c*). These can be used as photomediators for the activation of aliphatic C–H bonds (path *c*).[6c,d]

Indeed, we have demonstrated that radicals obtained through hydrogen abstraction from the corresponding cycloalkanes by benzophenone add to electrophilic olefins, viz, unsaturated nitriles,[7a] fumaramides[7b] (also bearing chiral auxiliaries), and ketene-*S*,*S*-dioxides[7c] and form new C–C bonds. A potentially useful variation is employing a heterogeneous sensitizer, easily recovered at the end of the reaction.

*Keywords*: Alkanes; Alkylation; C–H activation; Enones; Photochemistry; Radicals and radical reactions.
* Corresponding authors. Fax: +39 0382 987323; e-mail: fagnoni@unipv.it

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.03.028

A polymer-bound benzophenone has been reported to be effective for the functionalization of alkynes bearing electron-withdrawing groups.[8] There are a few further examples of this type in the literature.[9]

Furthermore, inorganic materials such as semiconductor oxides or sulfides ($TiO_2$, ZnS) or their soluble analogues, polyoxometallates are known to abstract hydrogen when excited from organic molecules, but they are generally used for the oxidative decomposition of organic contaminants and water depollution rather than for synthesis. There are a few preparative applications known,[10] although these mainly do not concern alkanes. There is, however, a recent report that tetrabutylammonium decatungstate (TBADT) can act as a photocatalyst in the synthesis of β-cycloalkylnitriles from cycloalkanes with essentially the same yield as benzophenone.[11]

Since the activation of aliphatic C–H bonds is a major target, further studies appeared worthwhile. Indeed, while the initial step, H abstraction by an excited state, has been thoroughly studied in the photochemical literature by using both organic compounds such as ketones and inorganic derivatives such as polyoxometallates, little is known on the subsequent reactions of the radicals and in particular on their trapping by electrophilic olefins and on the scope of the resulting photomediated reactions for the formation of C–C bonds.

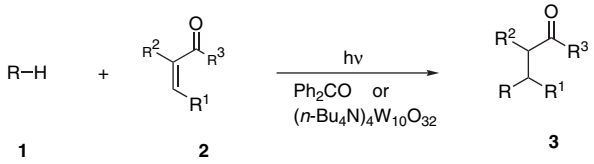
We presently report the synthesis of β-cycloalkylketones from cycloalkanes and α,β-unsaturated ketones. This was thought to represent a significant test because the enones may interfere with the aromatic ketones used as photomediators thus highlighting a possible difference with the use of polyoxometallates for that function. Furthermore α,β-unsaturated ketones have been less commonly used than other electrophilic alkenes in radical alkylation reactions, therefore this study may give some information about the synthetic scope of the method.

## 2. Results

Four cyclic alkanes (**1a–d**) and one bicyclic alkane (adamantane, **1e**) were explored in this work as precursors of the alkyl radicals. The unsaturated ketones used as radical traps included an open-chain enone (3-buten-2-one, **2j**), two cyclic enones (cyclopentenone **2k**, cyclohexenone **2l**), and one bicyclic enone (methylenenorbornanone **2m**). The synthesis of β-cycloalkylketones was carried out under two different conditions according to the photomediator used (either an aromatic ketones or TBADT).

### 2.1. Photochemical alkylation in the presence of an aromatic ketone (Method A)

The alkylation was carried out by using a solution of an enone **2** (0.05–0.1 M) in the presence of an equimolar amount of benzophenone (or xanthone) as the photomediator and an excess of an alkane **1** (see Table 1 and Scheme 2, Method A). Benzene was routinely used as the solvent due to its low hydrogen donating ability.[4] Less toxic solvents such as *t*-BuOH or dimethylcarbonate (DMC) were also used.




**1a** R = Cyclopentyl
**b** R = Cyclohexyl
**c** R = Cycloheptyl
**d** R = Cyclododecyl
**e** R = Adamantyl

**2j** $R^1 = R^2 = H$, $R^3 = CH_3$
**k** $R^2 = H$, $R^1$-$R^3$ = -$(CH_2)_2$-
**l** $R^2 = H$, $R^1$-$R^3$ = -$(CH_2)_3$-
**m** $R^1 = H$, $R^2$-$R^3$ = 1,3-cyclopentadiyl

**Scheme 2.** Photomediated synthesis of β-cycloalkylketones.

**Table 1**. Photomediated synthesis of β-cycloalkylketones **3** starting from cycloalkanes **1**

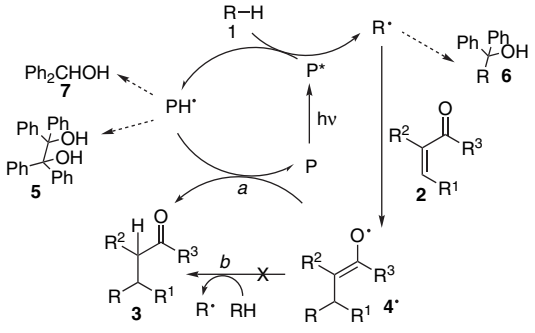
| Enone | Product | Method A[a] | | | Method B[a] | | |
|---|---|---|---|---|---|---|---|
| | | Alkane (M) | % Yield[b] | Irradiation time (h) | Alkane (M) | % Yield[b] | Irradiation time (h) |
| **2j** | **3aj** | **1a** (3) | [c] | 24 | **1a** (0.5) | 36 | 16 |
| **2j** | **3bj** | **1b** (3) | [c] | 24 | **1b** (0.5) | 55 | 16 |
| **2j** | **3cj** | **1c** (3) | [c] | 24 | **1c** (0.5) | 56 | 16 |
| **2k** | **3ak** | **1a** (2) | 46[d] | 20 | **1a** (0.5) | 38 | 16 |
| **2k** | **3bk** | **1b** (neat) | 50 | 20 | **1b** (0.5) | 35, 43[e] | 16 |
| **2k** | **3ck** | **1c** (3) | 66[d] | 18 | **1c** (0.5) | 41 | 16 |
| **2k** | **3dk** | **1d** (1) | 48 | 15 | **1d** (0.5) | 20[f] | 18 |
| **2k** | **3ek** | **1e** (0.2) | 65 | 20 | **1e** (0.1) | 15[f] | 18 |
| **2l** | **3al** | **1a** (3) | 55 | 20 | **1a** (0.5) | 33 | 16 |
| **2l** | **3bl** | **1b** (neat) | 55 | 20 | **1b** (0.5) | 31 | 16 |
| **2l** | **3cl** | **1c** (3) | 52 | 26 | **1c** (0.5) | 43 | 16 |
| **2l** | **3dl** | **1d** (1) | 36 | 26 | **1d** (0.2) | 15[f] | 18 |
| **2l** | **3el** | **1e** (0.2) | 40 | 26 | **1e** (0.1) | 21 | 18 |
| **2m** | **3am** | **1a** (3) | [c] | 20 | **1a** (0.5) | 45 | 16 |
| **2m** | **3bm** | **1b** (3) | 80[g] | 20 | **1b** (0.5) | 49 | 16 |
| **2m** | **3cm** | **1c** (4.1) | 80[g] | 20 | **1c** (0.5) | 45 | 16 |

[a] Method A: benzophenone (0.05–0.1 M) and enone (0.05–0.1 M) irradiated in a cycloalkane/benzene mixture as the solvent (unless otherwise stated). Method B: TBADT ($2\times10^{-3}$ M) and enone (0.1 M) irradiated in a cycloalkane/acetonitrile mixture as the solvent (unless otherwise stated).
[b] Isolated yields.
[c] No alkylation products were detected via GC analysis.
[d] *t*-BuOH as the solvent.
[e] Reaction carried out in an immersion-well apparatus.
[f] Benzene/acetonitrile 1:1 as the solvent.
[g] Dimethylcarbonate (DMC) as the solvent; xanthone as the photomediator ($\lambda$=366 nm).

In Table 1 the results with $\lambda_{exc}$=310 nm are reported. Blank tests were carried out, since at this wavelength part of the light used was absorbed by the enones. Thus, compounds **2j–m** were irradiated in the absence of benzophenone in order to assess the role of competing photoreactions resulting for their direct excitation. Actually, irradiation of both **2k** and **2l** in neat benzene led to the formation of a mixture of dimers as previously reported.[12] On the other hand, the same enones **2k** and **2l** have been reported to abstract hydrogen from alkanes and to form α- and β-alkylketones in variable amounts.[13] In our hands, however, irradiation at 310 nm of these enones in a cyclohexane/benzene 1:2 mixture for 24 h did not give the expected alkylated ketones (as determined by GC analysis), while, as indicated in Table 1, these were formed in moderate to good yield in the presence of an equimolar amount of benzophenone. Furthermore, the same products were formed in the presence of $Ph_2CO$ upon irradiation at 360 nm, where **2k** and **2l** did not absorb.

The use of a lower molar amount of benzophenone (e.g., 50%) led to a less efficient alkylation. As an example, the yield of alkylated ketone **3bl** dropped from 55 to 33% under these conditions. On the other hand, increasing the benzophenone concentration above equimolecular did not improve the alkylation yield. Using neat alkane as the solvent mostly gave complex mixtures, including the desired alkylated ketones, although this choice gave good results in a couple of instances (see below).

In all of the reactions studied small variable amounts of cycloalkylbenzenes and of byproducts arising from benzophenone (e.g., alkyl diphenylmethanols) were detected by GC. As an example, in the synthesis of cycloalkyl derivatives **3bk–m**, benzopinacol (**5**, ca. 40%), benzhydrol (**7**, 10%), and cyclohexyldiphenylmethanol (**6**, 10%, R=cyclohexyl in Scheme 3) were determined by HPLC analysis.




**Scheme 3.** Photomediated generation and reactivity of alkyl radicals from alkane.

Other aromatic ketones could be used. Actually, with methylenenorbornanone **2m**, xanthone was preferred to benzophenone (λ=360 nm, DMC as the solvent), because byproducts from the former photomediator were better separated from the alkylated ketones by chromatography. However, this held for the cyclohexyl and cycloheptyl derivatives (**3bm** and **3cm**), which were isolated in ca. 80% yield while the cyclopentyl homologue **3am** was not obtained.

Furthermore, not all of the enones tested reacted as desired. In particular, the open-chain derivative **2j** was not alkylated under these conditions, either in benzene or in DMC or *t*-BuOH, as well as by using either benzophenone or xanthone ($\lambda_{exc}$=310 or 366 nm), while cyclic and bicyclic analogues reacted in moderate to good yields.

Alkanes were used at 2–4 M concentration, except for high-boiling compounds such as **1d–e**. These were used at a lower concentration due to both the limited solubility and the difficulty in the removal of excess from the raw photolyzate. With adamantane (**1e**, 0.2 M) the alkylation yields were satisfactory and only 1-adamantyl derivatives were obtained. Cyclododecane (**1d**) could be used in 1 M concentration, though the separation of the alkylated ketones required a careful separation by column chromatography.

In *t*-BuOH the reaction was less satisfactory, although yields comparable to those in benzene were obtained in some cases (see the synthesis of ketones **3ak** and **3ck**, in Table 1). In DMC the yields were in average 20–30% lower, except for the case of **3bm** or **3cm**, obtained in the same yield as in benzene. In the synthesis of **3bk** and **3bl**, the alkylation was most effective in neat alkane (yields ca. 50%) with no extensive formation of byproducts.

### 2.2. Photochemical alkylation in the presence of TBADT (Method B)

Differently from Method A, the photomediator was used in a much lower concentration ($2\times10^{-3}$ M) than to the unsaturated ketone (0.1 M) with acetonitrile as the solvent (in the reactions involving cyclododecane, a benzene/acetonitrile mixture was conveniently used). The salt is soluble in MeCN, not in less polar solvents, and photoinduced hydrogen abstraction from alkanes has been previously demonstrated to occur under these conditions.[11] During irradiation the intense blue color of reduced tungstate was apparent.

Both increasing and decreasing the concentration of TBADT lowered to some extent the alkylation yields. The photoinduced reaction was carried out, as in Method A, by external irradiation at 310 nm. Somewhat better yields were obtained by performing the reaction on a larger scale by internal irradiation (mercury arc) in an immersion-well apparatus (see the case of product **3bk** in Table 1). The relatively low solubility of the alkanes in MeCN (0.1–0.5 M) prevented their use in excess as large as in Method A. In general, isolated yields were modest, but the scope was wider (e.g., alkylation of enone **2j** was successful in this case) and workup was expeditious, viz, limited to evaporation of the solvent and separation of the alkylated products from the solid catalyst by bulb-to-bulb distillation.

### 2.3. Comparison of the methods

As it appears in Table 1, higher yields of cycloalkylketones could be obtained when using benzophenone rather than TBADT. However, in the former case the irradiation was carried out in benzene or in a moderately polar solvent such as DMC, which allowed a larger starting concentration of the alkanes (up to 3–4 M rather than 0.5 M). In order to compare the efficiency of aromatic ketones and tungstate as photomediators a further set of experiments was carried out under the same conditions (acetonitrile as the solvent,

**Table 2**. Comparison between aromatic ketones and TBADT as photomediators in the synthesis of β-cycloalkylketones[a]

| Product | % Yield[b] (Method A)[c] | % Yield[b] (Method B)[d] |
|---|---|---|
| **3ak** | 22 | 38 |
| **3bk** | 34 | 35 |
| **3ck** | 44 | 41 |
| **3al** | 7 | 33 |
| **3bl** | 9 | 31 |
| **3cl** | 16 | 43 |
| **3am** | <2 | 45 |
| **3bm** | 10 | 49 |
| **3cm** | 15 | 45 |

[a] Reactions in acetonitrile, 0.5 M alkane irradiated at 310 nm for 16 h.
[b] GC determined yields.
[c] Benzophenone (0.1 M) as the photomediator.
[d] TBADT ($2\times10^{-3}$ M) as the photomediator.

0.5 M alkane, 16 h of irradiation). The results are gathered in Table 2.

This shows that the yields of β-cycloalkylketones are consistently about 40% when Method B was used, while with Method A, the yields largely depended on the structure of both the alkane and the enone and were generally lower than in the former case, except for the alkylation of cyclopentenone.

## 3. Discussion

As reported above, β-cycloalkylketones can be prepared under mild conditions by radical alkylation of enones, exploiting the photomediated generation of the key alkyl radicals by hydrogen abstraction directly from alkanes. Aromatic ketones and TBADT do not act as photosensitizer, i.e., the activation is not based on energy or electron transfer, but on a chemical reaction, H abstraction.[14] We prefer using the general term photomediator for such photoactivating species. When this is regenerated in a following thermal step (see below) the specific term photocatalyst will be used. The dependence of the reaction efficiency on experimental parameters and the possibility that the method has preparative significance are briefly discussed below.

The reaction can in principle be carried out in neat alkane when this is a low-boiling liquid and an organic photomediator is used. However, solubility is a limit with some photomediators (e.g., xanthone, $\leq 9\times10^{-3}$ M in cyclohexane) and side products are generally more abundant under these conditions, thus making this choice unpractical except than in a few cases (**3bk**, **3bl**). Accordingly, a cosolvent must be used that is transparent to the light used and is a poor hydrogen donor. With Method A, benzene gives good results, as previously observed in the alkylation of unsaturated nitriles,[7a] despite the fact that the benzophenone triplet lifetime is somewhat shorter in this solvent[15] and variable amounts of cycloalkylbenzenes byproducts are formed.[7a] More environmentally benign DMC and *t*-BuOH can be used, though the yields are as high as those obtained in benzene only in some cases (see Table 1). Acetonitrile is also a possibility and actually the only practical choice for an inorganic photomediator such as TBADT (Method B), although alkanes are poorly dissolved in this solvent.

Three specific limitations can be considered for the photomediated alkylation of enones differently from the case of other electrophilic olefins. First, the UV absorption of these compounds is more red-shifted than that of unsaturated nitriles or esters, and thus these absorb part of the light when a 310 nm lamp is used. However, blank tests showed that competitive absorption slows down the reaction, but leads to no significant alkylation on the time scale where the photosensitized reaction occurs.

Second, enones may quench the triplet of the photomediator and thus hinder hydrogen abstraction. Benzophenone and xanthone have a triplet energy of 287[7a] and 309 kJ mol$^{-1}$,[7a] respectively. As for enones, cyclopentenone **2k** has a higher triplet (305 kJ mol$^{-1}$)[16] with respect to homologue **2l** (263 kJ mol$^{-1}$).[17,18] Indeed, Table 2 shows that cyclopentenone **2k**, for which quenching of triplet benzophenone is endothermic, is more efficiently alkylated than **2l**. As shown in Table 1, however, when the irradiation time is increased, alkylated products are obtained also in the other cases. When occurring, triplet quenching is not involved in the alkylation. The short lifetime of enone triplets (from 8 to 30 ns)[19] limits their reactivity (see Scheme 3) and indeed no reaction occurs by direct irradiation of the enones as shown by blank tests (see the invariance of the product distribution when changing the exciting wavelength).

Finally, coplanar enones are effective electrophiles under these conditions, but alkylation of conformationally free 3-buten-2-one **2j** (see Table 1) appears to be too slow to occur with the low steady state radical concentration generated under benzophenone photomediation.[20] When the rate of formation is further limited by using a lower concentration of alkane (Table 2), the dependence on the enone coplanarity is apparent in the alkylation yield (cyclopentenone > cyclohexenone ≈ methylenenorbornanone).

The use of TBADT has a larger scope. The high molar extinction coefficient of this photomediator in acetonitrile ($\varepsilon_{323}=1.35\times10^4$ M$^{-1}$ cm$^{-1}$) allows total absorption of the irradiation even when the decatungstate anion is for the most part present in the reduced form (see below). Apparently no physical quenching of the hydrogen-abstracting excited state by the enone occurs.[22a] The generation of the radicals proceeds at such a pace (see below) that the alkylation is efficient independently on the structure of the enone used.

The proposed overall mechanism is depicted in Scheme 3. This allows pointing out similarities and differences between using ketones and using the polyoxotungstate as photomediator (P).

Hydrogen abstraction is much faster with TBADT ($k_H=3.7\times10^7$ M$^{-1}$ s$^{-1}$ from cyclohexane in MeCN)[22b] than with $Ph_2CO$ ($k_H=7.5\times10^5$ M$^{-1}$ s$^{-1}$ for the same case).[23] The relatively low rate of this step in the latter case explains the limited and conditions dependent efficiency of aromatic ketones as discussed above. H abstraction leads in any case to a persistent (P$^{\bullet}$, viz, TBADTH$^{\bullet}$[24] or $Ph_2C^{\bullet}OH$) and a reactive (R$^{\bullet}$) radical, the former one rapidly accumulating in solution. Indeed, the blue color of reduced decatungstate develops and spectrophotometric determination shows that ca. 90% of the initial amount is present in the reduced

form after 1–2 h.[25] A small portion of the salt remains in the oxidized form and carries on the reaction by absorbing at 310 nm. The ketyl radicals also accumulate, though not to such a high concentration, the limit being given by the dimerization rate constant ($k=7\times10^8\ M^{-1}\ s^{-1}$)[26] to form benzopinacol, indeed a major product.

The cosolvents used are known to be poorer hydrogen donors than the alkanes.[27] The alkyl radicals are trapped by enones **2** forming adduct (enol) radicals **4**$^{\bullet}$. The rate of this process can be estimated as about $k=10^6\ M^{-1}\ s^{-1}$.[28] The rate of addition of 1-adamantyl radical onto electron-poor olefin has been reported to be two orders of magnitude faster than that of cyclohexyl radical ($k\approx10^8\ M^{-1}\ s^{-1}$).[29,30] This explains that the adamantyl derivatives **3ek** and **3el** are obtained in a satisfactory yield despite the fact that this alkane can be used only at low concentration (0.1–0.2 M) and the selective formation of the 1-adamantyl derivatives, as already observed in other related photocatalyzed reactions.[7]

Another main difference between the two photochemical methods involves the fate of the radical adduct **4**$^{\bullet}$. Reduced TBADTH$^{\bullet}$ is subject to disproportionation but has no irreversible decay available. Importantly, it is oxidized back to TBADT by electron transfer to the radical adducts as previously demonstrated for the case of the addition to α,β-unsaturated nitriles.[11] In the present case:

$$\text{TBADTH}^{\bullet} + \mathbf{4}^{\bullet} \rightarrow \text{TBADT} + \mathbf{4}^{-} + \text{H}^{+} \rightarrow \text{TBADT} + \mathbf{3}$$

In other term, path *a* is 100% effective, i.e., the mediator is regenerated and functions as a nonconsumed catalyst (Scheme 3). This is different for the case of ketyl radicals $Ph_2C^{\bullet}OH$. These dimerize to **5** (and couple with R$^{\bullet}$, a less important process in view of the largely different steady state concentration of the two radicals). Thus benzophenone is not regenerated and indeed must be used in an equimolar amount. However, H transfer to **4**$^{\bullet}$ is negligible, in keeping with the high stabilization of the ketyl radical, known from various examples (e.g., $Ph_2C^{\bullet}OH$ does not transfer a hydrogen to PhCO$^{\bullet}$, while $Me_2C^{\bullet}OH$ transfers a hydrogen to $Ph_2CO$ in a markedly exothermic process).[31] Furthermore, hydrogen abstraction from the alkanes by radical **4**$^{\bullet}$ (path *b* in Scheme 3) does not take place significantly.

The same characteristic had been previously noticed in the alkylation of unsaturated nitriles by alkanes. On the contrary when the radical precursor is a better hydrogen donor, e.g., a dioxolane, path *b* becomes accessible. In that case, formation of the end product regenerates an alkyl radical.[21] Thus a short chain may operate and indeed with dioxolane a lower amount (e.g., 20–40%) of the photomediator can be used.[32]

To summarize, in the alkylation by alkanes benzophenone acts as a reagent, while TBADT behaves as a catalyst and operates with a turnover number >50.[33]

## 4. Conclusion

The synthesis of β-cycloalkylketones was accomplished by photomediated reaction between cycloalkanes and enones, which is advantageous in term of atom economy. Both aromatic ketones and decatungstate salts can be used for the photochemical C–H activation of alkanes, although only the latter one is an actual photocatalyst. Yields of alkylated ketones are in most cases moderate, but the potential interest of the method is the use of an abundant and unexpensive starting material such as an alkane rather than an alkyl bromide or iodide. Furthermore, the use of the highly toxic stannanes typical of conventional radical alkylation is avoided. It is likely that a further improvement may be obtained by supporting the photocatalyst on a solid support, thus carrying out a more expeditious heterogeneous reaction. Work in this direction is in progress.

## 5. Experimental

All of the starting materials were of commercial origin. The starting enones were purified by distillation immediately before use. The photochemical reaction was carried out in quartz tubes by using a nitrogen-purged solution and irradiating in a multilamp reactor by using 6×15 W phosphor-coated lamps with emission maximum at 310 nm (in the presence of TBADT) or 366 nm (in the case of **2m** in the presence of xanthone). A larger scale synthesis of compound **3bk** was accomplished by irradiation in an immersion-well apparatus by using a 125 W high-pressure mercury arc through Pyrex while maintaining a nitrogen flux (see below).

The workup procedure consisted in concentration in vacuo of the photolyzed solution, followed by column chromatography (silica gel with various cyclohexane/ethyl acetate mixtures as the eluant) or, in the case of reactions with tungstates, by bulb-to-bulb distillation at reduced pressure.

The amount of compounds **5**–**7** formed was determined by HPLC (AQUASIL C18 (250×4.6 mm) column, MeCN/water from 70:30 to 90:10, flux 1 mL min$^{-1}$) with UV detection at $\lambda$=250 nm.

### 5.1. Preparation of tetrabutylammonium decatungstate (TBADT)

The preparation of TBADT described previously by Yamase[34] was modified as follows: tetrabutylammonium bromide (2.4 g) and sodium tungstate dihydrate (5 g, Aldrich) were dissolved each in 1 L of deionized water and kept at 90 °C. Concentrated hydrochloric acid was added dropwise to both solutions in order to adjust the pH at 2. The pH of the tungstate solution was carefully checked and maintained at pH 2 with additional hydrochloric acid, until the pH did not change appreciably. At this point, the two solutions were mixed and maintained at 90 °C for 30 min under stirring. A white suspension of TBADT was formed and filtered on a short silica gel column. The solid phase was washed initially with water and then with acetonitrile in order to dissolve all of the TBADT. After elimination of the solvent in vacuo, the raw decatungstate was purified by crystallization (from a water/acetonitrile mixture, 80% yield based on the content of tungsten). The end product showed a >90% of purity as evaluated by UV analysis ($\varepsilon_{323}=1.35\times10^4\ dm^3\ mol^{-1}\ cm^{-1}$ in acetonitrile[34]).

### 5.2. Photocatalyzed synthesis of β-cycloalkylketones. General procedures

Method A: Alkane **1** (from 0.1 M to neat), unsaturated ketone **2** (from 0.05 to 0.1 M), and benzophenone (xanthone in the case of **2m**, 0.1 M) were dissolved in the solvent chosen (benzene, *t*-BuOH or DMC), and the resulting solution was deareated and then irradiated until **2** was consumed. The workup procedure consisted in concentration in vacuo of the photolyzed solution followed by column chromatography (silica gel with cyclohexane/ethyl acetate mixtures as eluant).

Method B: A solution of alkane **1** (0.2–0.5 M in acetonitrile), unsaturated ketone **2** (0.1 M), and TBADT ($2\times10^{-3}$ M) was deareated and then irradiated until **2** was consumed. The workup procedure consisted in concentration in vacuo of the photolized solution followed by bulb-to-bulb distillation at reduced pressure. Chromatographic separation (see above) was used in the reactions in the presence of **1d** and **1e**.

**5.2.1. 4-Cyclopentylbutan-2-one (3aj).**[35] Method B: A solution of 850 μL (9 mmol, 0.5 M) of **1a**, 150 μL (1.8 mmol) of **2j**, and 120 mg of TBADT (36 μmol, $2\times10^{-3}$ M) in 18 mL of acetonitrile was irradiated for 16 h and **3aj** (90 mg, 36%) was isolated as a colorless oil. $^1$H NMR and infrared spectra were in accordance with literature data.[35] $^{13}$C NMR ($CDCl_3$) $\delta$ 25.0 ($CH_2$), 29.7 ($CH_3$), 29.9 ($CH_2$), 32.5 ($CH_2$), 39.5 (CH), 43.0 ($CH_2$), 210 (CO). Anal. Calcd for $C_9H_{16}O$: C, 77.09, H, 11.50. Found: C, 76.8, H, 11.4.

**5.2.2. 4-Cyclohexylbutan-2-one (3bj).**[36] Method B: 1 mL (9 mmol, 0.5 M) of **1b**, 150 μL (1.8 mmol) of **2j**, and 120 mg of TBADT were dissolved in 18 mL of acetonitrile. The solution was then irradiated for 16 h and 150 mg of **3bj** (55%, colorless oil) were isolated. The spectroscopic data were in accordance with literature data.[36] Anal. Calcd for $C_{10}H_{18}O$: C, 77.87, H, 11.76. Found: C, 77.7, H, 11.6.

**5.2.3. 4-Cycloheptylbutan-2-one (3cj).**[37] Method B: 1.1 mL (9 mmol, 0.5 M) of **1c**, 150 μL (1.8 mmol) of **2j**, and 120 mg of TBADT were dissolved in 18 mL of acetonitrile. After 16 h of irradiation 165 mg (56%) of **3cj** were isolated as a colorless oil.

Compound **3cj**: $^1$H NMR ($CDCl_3$) $\delta$ 1.05–1.2 (2H, m), 1.3–1.7 (13H, m), 2.1 (3H, s), 2.35–2.45 (2H, t, $J$=7 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$ 26.2 ($CH_2$), 28.3 ($CH_2$), 29.7 ($CH_3$), 31.7 ($CH_2$), 34.2 ($CH_2$), 38.7 (CH), 41.8 ($CH_2$), 209 (CO). IR (neat) $\nu$/cm$^{-1}$ 2920, 2853, 1720, 1500, 1360, 1170. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51, H, 11.98. Found: C, 78.4, H, 12.1.

**5.2.4. 3-Cyclopentylcyclopentanone (3ak).**[38] Method A: 3.7 mL of **1a** (40 mmol, 2 M), 165 μL of **2k** (2 mmol, 0.1 M), and 365 mg of benzophenone (2 mmol, 0.1 M) were dissolved in 16 mL of *t*-BuOH and the solution was irradiated for 20 h. After chromatographic purification product **3ak** was obtained as a colorless oil (140 mg, 46%).

Method B: A solution of 1.1 mL (12 mmol, 0.5 M) of **1a**, 200 μL (2.4 mmol) of **2k**, and 160 mg of TBADT (48 μmol, $2\times10^{-3}$ M) in 23 mL of acetonitrile was irradiated for 16 h and 140 mg (38%) of **3ak** were obtained.

The spectroscopic data of compound **3ak** were in accordance with literature data.[38] Anal. Calcd for $C_{10}H_{16}O$: C, 78.90, H, 10.59, O, 10.51. Found: C, 79.4, H, 10.1.

**5.2.5. 3-Cyclohexylcyclopentanone (3bk).**[36] Method A: To 20 mL of **1b** were added 165 μL of **2k** (2 mmol, 0.1 M) and 365 mg of benzophenone (2 mmol, 0.1 M). The resulting solution was irradiated for 20 h yielding 170 mg of **3bk** (50%) as a colorless oil.

Method B: 1.2 mL (11 mmol, 0.5 M) of **1b**, 200 μL (2.4 mmol) of **2k**, and 160 mg of TBADT were dissolved in 22 mL of acetonitrile. Irradiation of the resulting mixture (16 h) yielded 140 mg (35%) of **3bk**.

Compound **3bk** was obtained in a somewhat larger scale (650 mg, 43% yield) and in a shorter time (9 h) starting from 4.5 mL (4.5 mmol) of cyclohexane, 750 μL (9 mmol) of **2k**, and 590 mg (0.18 mmol) of TBADT in 90 mL of MeCN after irradiation in an immersion-well apparatus.

The spectroscopic data of compound **3bk** were in accordance with literature data.[36] Anal. Calcd for $C_{11}H_{18}O$: C, 79.46, H, 10.91, O, 9.62. Found: C, 79.0, H, 10.1.

**5.2.6. 3-Cycloheptylcyclopentanone (3ck).** Method A: 18.0 mL of **1c** (150 mmol, 3 M), 420 μL of **2k** (5.0 mmol, 0.1 M), and 910 mg of $Ph_2CO$ (5.0 mmol, 0.1 M) were dissolved in 32 mL of *t*-BuOH and irradiated for 18 h. Compound **3ck** (66%, 595 mg) were obtained as a colorless oil.

Method B: 1.4 mL (12 mmol, 0.5 M) of **1c**, 200 μL (2.4 mmol) of **2k**, and 160 mg of TBADT were dissolved in 22 mL of acetonitrile. The solution was then irradiated for 16 h finally giving 176 mg (41%) of **3ck**.

**3ck**: $^1$H NMR ($CDCl_3$) $\delta$ 1.1–2.1 (m, 16H), 2.1–2.35 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ 26.2 ($CH_2$), 26.7 ($CH_2$), 27.6 ($CH_2$), 28.3 ($CH_2$), 31.6 ($CH_2$), 32.6 ($CH_2$), 38.9 ($CH_2$), 43.4 (CH), 43.6 ($CH_2$), 44.5 (CH), 219.6 (CO). IR (neat) $\nu$/cm$^{-1}$ 2920, 2853, 1741, 1460, 1403. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06, H, 12.16. Found: C, 79.0, H, 12.0.

**5.2.7. 3-Cyclododecylcyclopentanone (3dk).** Method A: 10 g of **1d** (60 mmol, 1 M), 0.5 mL of **2k** (6.0 mmol, 0.1 M), and 1.09 g of benzophenone (6.0 mmol, 0.1 M) were dissolved in 60 mL of benzene. The solution was irradiated for 15 h and 709 mg of **3dk** (48%) were obtained as a glassy solid.

Method B: 1.7 g of **1d** (10 mmol, 0.5 M), 170 μL of **2k** (2 mmol), and 135 mg of TBADT (41 μmol, $2\times10^{-3}$ M) were dissolved in 20 mL of benzene/acetonitrile 1:1. The solution was then irradiated for 18 h and after column chromatography on silica gel 100 mg of **3dk** (20%) were obtained.

**3dk**: $^1$H NMR ($CDCl_3$) $\delta$ 1.1–1.6 (m, 24H), 1.7–1.9 (m, 1H), 2.0–2.5 (m, 5H). $^{13}$C NMR ($CDCl_3$) $\delta$ 21.0 ($CH_2$), 21.1 ($CH_2$), 22.6 ($CH_2$), 22.71 ($CH_2$), 22.75 ($CH_2$), 22.8 ($CH_2$), 24.9 ($CH_2$), 25.51 ($CH_2$), 25.54 ($CH_2$), 26.1 ($CH_2$), 27.2 ($CH_2$), 28.0 ($CH_2$), 38.9 ($CH_2$), 40.6 (CH), 41.1 (CH), 43.9 ($CH_2$), 219.9 (CO). IR (neat) $\nu$/cm$^{-1}$ 2929, 2868, 1743,

1470, 1445. Anal. Calcd for $C_{17}H_{30}O$: C, 81.54, H, 12.07. Found: C, 81.4, H, 11.9.

**5.2.8. 3-(1-Adamantyl)-cyclopentanone (3ek).** Method A: A solution of 1.36 g of **1e** (10 mmol, 0.2 M), 420 μL of **2k** (5.0 mmol, 0.1 M), and 910 mg of benzophenone (5.0 mmol, 0.1 M) in 50 mL of benzene was irradiated for 20 h. After chromatographic separation (silica gel, using first neat cyclohexane and then cyclohexane/ethyl acetate 97:3 as eluant) 680 mg of **3ek** (65%) were obtained as a glassy solid.

Method B: 272 mg of **1e** (2 mmol, 0.1 M), 170 μL of **2k** (2 mmol), and 135 mg of TBADT were dissolved in 20 mL of benzene/acetonitrile 1:1. The solution was then irradiated for 18 h and 65 mg of **3ek** (15%) were isolated after column chromatography on silica gel.

Compound **3ek**: $^1$H NMR ($CDCl_3$) $\delta$ 1.1–2.1 (m, 18H), 2.1–2.4 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ 22.4 ($CH_2$), 28.4 (CH), 29.0, 31.7 ($CH_2$), 36.2 ($CH_2$), 37.1 ($CH_2$), 38.7 ($CH_2$), 39.0 ($CH_2$), 39.9 ($CH_2$), 42.5 ($CH_2$), 46.0 ($CH_2$), 48.6 (CH), 48.7 (CH), 219.9 (CO). IR (neat) $\nu$/cm$^{-1}$ 2981, 2845, 1739, 1492, 1446. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52, H, 10.16. Found: C, 82.6, H, 10.0.

**5.2.9. 3-Cyclopentylcyclohexanone (3al).**[39] Method A: 5.5 mL of **1a** (60 mmol, 3 M), 190 μL of **2l** (2 mmol, 0.1 M), and 365 mg of benzophenone (2 mmol, 0.1 M) were dissolved in 14 mL of benzene and the solution was irradiated for 20 h yielding **3al** as a colorless oil (178 mg, 54%).

Method B: A solution of 1.1 mL (12 mmol, 0.5 M) of **1a**, 232 μL (2.4 mmol) of **2l**, and 160 mg of TBADT in 22 mL of acetonitrile was irradiated for 16 h affording 130 mg (33%) of **3al**.

The spectroscopic data of compound **3al** were in accordance with literature data.[39]

**5.2.10. 3-Cyclohexylcyclohexanone (3bl).**[40] Method A: To 24 mL of **1b** were added 230 μL of **2l** (2.4 mmol, 0.1 M) and 437 mg of benzophenone (2.4 mmol, 0.1 M). The resulting solution was irradiated for 20 h. Compound **3bl** (55%, 238 mg) were isolated as a colorless oil.

Method B: A solution of 1.2 mL (12 mmol, 0.5 M) of **1b**, 230 μL (2.4 mmol) of **2l**, and 160 mg of TBADT in 22 mL of acetonitrile was irradiated for 16 h yielding 130 mg (33%) of **3bl**.

The spectroscopic data of compound **3bl** were in accordance with literature data.[40] Anal. Calcd for $C_{12}H_{20}O$: C, 79.94, H, 11.18. Found: C, 79.7, H, 10.8.

**5.2.11. 3-Cycloheptylcyclohexanone (3cl).** Method A: 18 mL of **1c** (150 mmol, 3 M), 480 μL of **2l** (5.0 mmol, 0.1 M), and 910 mg of benzophenone (5 mmol, 0.1 M) were dissolved in 32 mL benzene. Irradiation for 26 h of the solution formed afforded 505 mg of **3cl** (52%) as a colorless oil.

Method B: a solution of 1.5 mL (12 mmol, 0.5 M) of **1c**, 232 μL (2.4 mmol) of **2l**, and 160 mg of TBADT in 24 mL of acetonitrile was irradiated for 16 h giving 200 mg (43%) of **3cl**.

Compound **3cl**: $^1$H NMR ($CDCl_3$) $\delta$ 1.1–1.8 (m, 16H), 1.8–2.4 (m, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ 25.6 ($CH_2$), 26.9 ($CH_2$), 27.0 ($CH_2$), 28.1 ($CH_2$), 30.9 ($CH_2$), 41.5 ($CH_2$), 43.6 (CH), 45.2 ($CH_2$), 45.6 (CH), 212.6 (CO). IR (neat) $\nu$/cm$^{-1}$ 2929, 2868, 1743, 1470, 1445. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35, H, 11.41. Found: C, 80.3, H, 11.3.

**5.2.12. 3-Cyclododecylcyclohexanone (3dl).** Method A: 8.40 g of **1d** (50.0 mmol, 1 M), 480 μL of **2l** (5.0 mmol, 0.1 M), and 910 mg of benzophenone (5.00 mmol, 0.1 M) were dissolved in 50 mL of benzene. After irradiation for 26 h of the solution formed, 474 mg of **3dl** (36%) were obtained as a colorless solid (mp 166–168 °C).

Method B: A solution of 0.67 g of **1d** (4 mmol, 0.2 M), 190 μL of **2l** (2 mmol), and 135 mg of TBADT in 20 mL of benzene/acetonitrile 1:1 was irradiated for 18 h yielding 80 mg of **3dl** (15%).

Compound **3dl**: $^1$H NMR ($CDCl_3$) $\delta$ 1.1–2.0 (m, 26H), 2.0–2.5 (m, 6H). $^{13}$C NMR ($CDCl_3$) $\delta$ 22.2 ($CH_2$), 22.3 ($CH_2$), 23.2 ($CH_2$), 23.3 ($CH_2$), 23.5 ($CH_2$), 23.6 ($CH_2$), 24.3 ($CH_2$), 25.2 ($CH_2$), 25.6 ($CH_2$), 25.7 ($CH_2$), 26.0 ($CH_2$), 26.1 ($CH_2$), 28.6 ($CH_2$), 38.0 (CH), 41.4 ($CH_2$), 41.5 (CH), 45.6 ($CH_2$), 212.6 (CO). IR (neat) $\nu$/cm$^{-1}$ 2931, 2868, 1711, 1468, 1445. Anal. Calcd for $C_{18}H_{32}O$: C, 81.75, H, 12.20. Found: C, 81.8, H, 12.1.

**5.2.13. 3-(1-Adamantyl)-cyclohexanone (3el).**[41] Method A: 436 mg of **1e** (3.2 mmol, 0.2 M), 150 μL of **2l** (1.6 mmol, 0.1 M), and 284 mg of benzophenone (1.6 mmol, 0.1 M) were dissolved in 16 mL of benzene, the solution was irradiated for 26 h. After column chromatography on silica gel, 65 mg of **3el** (40%) were obtained as a white solid (mp 58–60 °C, lit.[41] 60.2–61.6 °C).

Method B: 272 mg of **1e** (2 mmol, 0.1 M), 190 μL of **2l** (2 mmol), and 135 mg of TBADT in 20 mL acetonitrile were irradiated at 310 nm for 18 h. The solution was evaporated at reduced pressure and distilled in vacuo to give 97 mg of **3el** (0.42 mmol, 21%).

Compound **3el**: $^1$H NMR ($CDCl_3$) $\delta$ 1.1–1.95 (m, 19H), 1.95–2.4 (m, 5H). $^{13}$C NMR ($CDCl_3$) $\delta$ 24.4 ($CH_2$), 25.5 ($CH_2$), 28.5 (CH), 34.2 ($CH_2$), 37.0 ($CH_2$), 39.2 ($CH_2$), 41.4 ($CH_2$), 41.9 ($CH_2$), 49.5 (CH), 213.2 (CO). IR (neat) $\nu$/cm$^{-1}$ 2920, 2848, 1711, 1492, 1446. Anal. Calcd for $C_{16}H_{24}O$: C, 82.70, H, 10.41. Found: C, 82.4, H, 10.1.

**5.2.14. 3-Cyclopentylmethyl-bicyclo[2.2.1]heptan-2-one (3am).** Method B: A solution of 1.1 mL (12 mmol, 0.5 M) of **1a**, 280 μL (2.4 mmol) of **2m**, and 160 mg of TBADT in 22 mL of acetonitrile was irradiated for 16 h affording 200 mg (45%) of **3am** as a colorless oil.

Compound **3am**: $^1$H NMR ($CDCl_3$) $\delta$ 0.8–1.8 (m, 20H), 2 (m, 1H), 2.5 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ 21.2 ($CH_2$), 24.9 ($CH_2$), 25.0 ($CH_2$), 25.2 ($CH_2$), 31.8 ($CH_2$), 32.2 ($CH_2$), 33.1 ($CH_2$), 37.0 ($CH_2$), 38.3 (CH), 38.4 (CH), 50.4 (CH), 53.0 (CH). IR (neat) $\nu$/cm$^{-1}$ 2950, 2873, 1740.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20, H, 10.48. Found: C, 81.0, H, 11.2.

**5.2.15. 3-Cyclohexylmethyl-bicyclo[2.2.1]heptan-2-one (3bm).**[42] Method A: 10 mL (90 mmol, 3 M) of **1b**, 280 μL (2.3 mmol, 0.08 M) of **2m**, and 440 mg of xanthone (2.3 mmol, 0.08 M) were dissolved in 20 mL of DMC. The solution was irradiated for 20 h and 380 mg of **3bm** (80%) were formed as a colorless syrup.

Method B: A solution of 1.2 mL (12 mmol, 0.5 M) of **1b**, 280 μL (2.4 mmol) of **2m**, and 160 mg of TBADT in 22 mL of acetonitrile was irradiated for 16 h giving 240 mg (49%) of **3bm**.

The spectroscopic data of compound **3bm** were in accordance with literature data.[42] MS (*m*/*z*) 206 ($M^+$, 15), 110 (32), 82 (100), 67 (46), 55 (28), 41 (27). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50, H, 10.75. Found: C, 81.7, H, 10.5.

**5.2.16. 3-Cycloheptylmethyl-bicyclo[2.2.1]heptan-2-one (3cm).** Method A: 15 mL (0.12 mol, 4.1 M) of **1c**, 280 μL (2.3 mmol, 0.08 M) of **2m**, and 440 mg of xanthone (2.3 mmol, 0.08 M) were dissolved in 15 mL of DMC. The solution was irradiated for 20 h and 401 mg of **3cm** (80%) were isolated as a colorless syrup.

Method B: A solution of 1.4 mL (12 mmol, 0.5 M) of **1c**, 280 μL (2.4 mmol) of **2m**, and 160 mg of TBADT in 22 mL of acetonitrile was irradiated for 16 h giving 260 mg (45%) of **3cm**.

Compound **3cm**: $^1$H NMR ($CDCl_3$) $\delta$ 0.7–1.95 (m, 24H), 2.1 (m, 1H), 2.6 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ 21.1 ($CH_2$), 25.1 ($CH_2$), 26.0 ($CH_2$), 26.1 ($CH_2$), 28.2 ($CH_2$), 28.4 ($CH_2$), 32.8 ($CH_2$), 34.0 ($CH_2$), 35.4 ($CH_2$), 36.9 ($CH_2$), 37.1 (CH), 38.3 (CH), 50.4 (CH), 51.5 (CH). IR (neat) $\nu$/cm$^{-1}$ 2940, 2870, 1750, 1100. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76, H, 10.98. Found: C, 81.6, H, 10.8.

## Acknowledgements

Partial support of this work by Murst, Rome is gratefully acknowledged. D.D. thanks INCA for a fellowship.

## References and notes

1. (a) Liu, J.-Y.; Jang, Y.-J.; Lin, W.-W.; Liu, J.-T.; Yao, C.-F. *J. Org. Chem.* **2003**, *68*, 4030–4038 and reference cited therein; (b) Jang, D. O.; Cho, D. H. *Synlett* **2002**, 631–634.
2. Arndsten, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154–162.
3. (a) Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *36*, 223–233; (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633–639; (c) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932; (d) Komiya, S.; Hirano, M. *Ruthenium in Organic Synthesis*; Murahashi, S.-I., Ed.; Wiley-VCH: Weinheim, 2004; pp 345–355; (e) Larsch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471–2526.
4. Tabushi, I.; Fukunishi, K. *J. Org. Chem.* **1974**, *39*, 3748–3750.
5. Metzger, J.; Hartmanns, J.; Koll, P. *Tetrahedron Lett.* **1981**, *22*, 1891–1894.
6. (a) Fokin, A. A.; Schreiner, P. R. *Adv. Synth. Catal.* **2003**, *345*, 1035–1052; (b) Interesting results have been obtained by using phase-transfer chemistry; See: Schreiner, P. R.; Lauenstein, O.; Butova, E. D.; Gunchenko, P. A.; Kolomitsin, I. V.; Wittkopp, A.; Feder, G.; Fokin, A. A. *Chem. Eur. J.* **2001**, *7*, 4996–5003; (c) Fokin, A. A.; Schreiner, P. R. *Chem. Rev.* **2002**, *102*, 1551–1594; (d) Albini, A.; Fagnoni, M. *Chim. Oggi.* **2005**, *22*, 36–38.
7. (a) Cardarelli, A. M.; Fagnoni, M.; Mella, M.; Albini, A. *J. Org. Chem.* **2001**, *66*, 7320–7327; (b) Campari, G.; Mella, M.; Fagnoni, M.; Albini, A. *Tetrahedron: Asymmetry* **2000**, *11*, 1891–1906; (c) Gonzalez-Cameno, A. M.; Mella, M.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2000**, *65*, 297–303.
8. Doohan, R. A.; Geraghty, N. W. A. *Green Chem.* **2005**, *7*, 91–96.
9. Manfrotto, C.; Mella, M.; Freccero, M.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **1999**, *64*, 5024–5028; Fraser-Reid, B.; Anderson, R. C.; Hisks, D. R.; Walker, D. L. *Can. J. Chem.* **1977**, *55*, 3986–3995.
10. Kisch, H. *Adv. Photochem.* **2001**, *26*, 93–143.
11. Dondi, D.; Fagnoni, M.; Molinari, A.; Maldotti, A.; Albini, A. *Chem. Eur. J.* **2004**, *10*, 142–148.
12. (a) Ruhlen, J. L.; Leermakers, P. A. *J. Am. Chem. Soc.* **1967**, *89*, 4944–4948; (b) Lam, E. Y. Y.; Valentine, D.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 3482–3487.
13. Wolff, S.; Schreiber, W. L.; Smith, A. B.; Agosta, W. *J. Am. Chem. Soc.* **1972**, *94*, 7797–7806.
14. The term 'chemical sensitization' has also been used for this process, the most common case being 'Type I' photooxygenation.
15. (a) Bell, J. A.; Linschitz, H. *J. Am. Chem. Soc.* **1963**, *85*, 528–533; (b) Schuster, D. I.; Brizzolara, D. F. *J. Am. Chem. Soc.* **1970**, *92*, 4357–4365.
16. Arnaut, L. G.; Caldwell, R. A.; Elbert, J. E.; Melton, L. A. *Rev. Sci. Instrum.* **1992**, *63*, 5381–5389.
17. Schuster, D. J.; Heibel, G. E.; Caldwell, R. A.; Tang, W. *Photochem. Photobiol.* **1990**, *52*, 645–648.
18. The triplet energy of 3-buten-2-one **2j** has shown to be difficult to determine but probably ranges from 250 to 294 kJ/mol; see Garcia-Exposito, E.; Bearpark, M. J.; Ortuno, R. M.; Branchadell, V.; Robb, M. A.; Wilsey, S. *J. Org. Chem.* **2001**, *66*, 8811–8814.
19. Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816–3822.
20. The same difference had been previously observed in the photomediated radical addition of 1,3-dioxolan-2-yl radicals onto enones. See Ref. 21.
21. Mosca, R.; Fagnoni, M.; Mella, M.; Albini, A. *Tetrahedron* **2001**, *57*, 10319–10328.
22. (a) See also Dondi, D.; Fagnoni, M; Albini, A. *Chem.—Eur. J.*, doi:10.1002/chem.200501216; (b) Tanielian, C.; Seghrouchni, R.; Schweitzer, C. *J. Phys. Chem. A* **2003**, *107*, 1102–1111.
23. (a) Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953–958; (b) Johnston, L. J.; Lougnot, D. J.; Wintgens, V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 518–524.
24. The reduced form of TBADT is indicated here shortly as TBADTH$^{\bullet}$. Actually the structure is $W_{10}O_{32}^{5-}H^+$. This disproportionates to the starting anion and to doubly reduced $W_{10}O_{32}^{6-}$. See: Tanielian, C. *Coord. Chem. Rev.* **1998**, *178–180*, 1165–1181.
25. Actually, as it has been shown in the literature, a mixture of 1- and 2-electron reduced decatungstate is formed. See Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton*

*Trans.* **1984**, 793–799; Tanielian, C.; Seghrouchni, R.; Schweitzer, C. *J. Phys. Chem. A* **2003**, *107*, 1102–1111.
26. Shield, S. R.; Harris, J. M. *Anal. Chem.* **1998**, *70*, 2576–2583.
27. As an example, triplet benzophenone abstract a hydrogen from MeCN with a rate constant of ca. $1.3\times10^2\ M^{-1}\ s^{-1}$; see: Naguib, Y. M. A.; Steel, C.; Cohen, S. G. *J. Phys. Chem.* **1987**, *91*, 3033–3036; the rate constant for the same process with TBADT is ca. $1.2\times10^5\ M^{-1}\ s^{-1}$ Tanielian, C.; Duffy, K.; Jones, A. *J. Phys. Chem. B* **1997**, *101*, 4276–4282.
28. This is the middle value between the rate constant for the addition of the methyl and the *t*-Bu radicals onto acrolein; see: Fischer, H.; Radom, L. *Angew. Chem.* **2001**, *113*, 1380–1414; *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1340–1371.
29. Beckwith, A. L. J.; Poole, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 9489–9497.
30. Recupero, F.; Bravo, A.; Bjørsvik, H.-R.; Fontana, F.; Minisci, F.; Piredda, M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2399–2406.
31. Demeter, A.; Bérces, T. *J. Phys. Chem.* **1991**, *95*, 1228–1232.
32. Dondi, D.; Caprioli, I.; Fagnoni, M.; Mella, M.; Albini, A. *Tetrahedron* **2003**, *59*, 947–957.
33. The polytungstate was effective for 50 cycles under the present conditions. Doubling the amount of polytungstate in the synthesis of **3bk** led to only a small increase of the yield (44% with respect to 35%) whereas the yields dropped to 20.5% when using 0.2 M (in the place of 0.1 M) olefin.
34. Yamase, T.; Usami, T. *J. Chem. Soc., Dalton Trans.* **1988**, 183–190.
35. Ono, N.; Kamimura, A.; Miyake, H.; Hamamoto, I.; Kaji, A. *J. Org. Chem.* **1985**, *50*, 3692–3698.
36. Jones, P.; Reddy, C. K.; Knochel, P. *Tetrahedron* **1998**, *54*, 1471–1490.
37. Collins, P. W.; Gasiecki, A. F.; Perkins, W. E.; Gullikson, G. W.; Jones, P. H.; Bauer, R. F. *J. Med. Chem.* **1989**, *32*, 1001–1006.
38. Wipf, P.; Xu, W.; Smitrovich, J. *Tetrahedron* **1994**, *50*, 1935–1954.
39. Baguley, P. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2073–2082.
40. Liu, J.; Jang, Y.; Lin, W.; Liu, J.; Yao, C. *J. Org. Chem.* **2003**, *68*, 4030–4038.
41. Ohno, M.; Ishizaki, K.; Eguchi, S. *J. Org. Chem.* **1988**, *53*, 1285–1288.
42. Petrier, C.; De Souza Barbosa, J.; Dupuy, C.; Luche, J. L. *J. Org. Chem.* **1985**, *50*, 5761–5765.