Acyl Radicals from Acylsilanes: Photoredox Catalyzed Synthesis of Unsymmetrical Ketones

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ABSTRACT: Acyl radicals were smoothly generated from acylsilanes under photoredox catalyzed conditions. These radicals were formed upon UVB, solar, or visible light irradiation by using decatungstate and acridinium salts as photocatalysts. Acylation of Michael acceptors resulted in a smooth preparation of unsymmetrical ketones in up to 89% yield.

Acyl radicals are valuable intermediates for the preparation of ubiquitous functional groups in nature, such as unsymmetrical ketones and amides.[1] One of the most common way to generate these intermediates is starting from acyl selenides in the presence of an organotin reagent and a radical initiator.[1] A greener approach consists in the use of aldehydes as starting materials and light to promote the $C(sp^2)$-H homolytic cleavage of the formyl hydrogen,[2] facilitated by the low bond dissociation energy of this C-H bond (88.7 kcal mol^{-1} for propanal).[3] Our group (and others) demonstrated that tetrabutylammonium decatungstate ($(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$, TBADT)[4,5] can be used in the role of photocatalyst for the generation of acyl radicals via a Hydrogen Atom Transfer (HAT) process.[6] This smooth process, however, may fail if the H-atom donor contains other labile C-H bonds, as it was observed in the case of piperonal, where the activation of the methylene hydrogens in the benzodioxole ring was exclusive.[7]

This calls for alternative strategies for acyl radicals generation and a reasonable choice is photoredox catalysis.[8] Unfortunately, this approach appears unsuccessful, due to the electrochemical inertia of aldehydes ($E^{ox}_{1/2} > +2$ V vs SCE,[9a] estimated *ca.* +3.5 V vs SCE;[9b,c] $E^{red}_{1/2} \sim$ -1.65 V vs. SCE for benzaldehyde).[9d] Nevertheless, the incorporation of a redox active moiety (an electroauxiliary group)[10] in the acyl radical precursor may drive the oxidation/reduction under very mild and controlled conditions. In fact, some groups recently studied the formation of acyl radicals from RC(=O)X derivatives under photoredox catalyzed conditions (Scheme 1). α-Keto acids were used as a source of acyl radicals (Scheme 1, case a).[11] These compounds are quite easily oxidized when in the anionic form ($E^{ox}_{1/2} \sim$ +1.0 V vs SCE)[11a] and Ru(II) complexes,[11a] Eosin,[11b] Ir(III) complexes,[11c-g] and acridinium salts[11h] promoted the acyl radical formation via oxidation and ensuing elimination of carbon dioxide from the resulting carboxylyl radical. Acyl radicals were also formed through the photocatalyzed reduction of in situ prepared (mixed) anhydrides (case b[12a] and c[12b]) or acyl chlorides (Scheme 1, case d[12c]). In these approaches, however, expensive Ir(III) complexes were in most cases mandatory to photocatalyze the reac-

tion. Moreover, the procedures summarized in Scheme 1 were mainly used to generate aroyl radicals (Ar-C(=O)•) and, only to a lesser extent, aliphatic acyl radicals (Alk-C(=O)•).

Scheme 1. Photoredox Catalyzed Generation of Acyl Radicals.

HLB: household light bulb, DMA: *N,N*-dimethylacetamide
DMDC: dimethyl dicarbonate
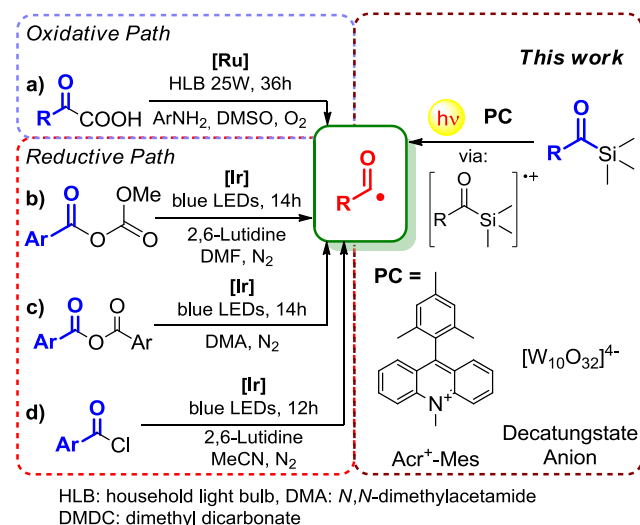
Accordingly, we started thinking that a cheaper and more direct method to generate acyl radicals was needed: an interesting and unexplored class of compounds worth to be tested is that of acylsilanes. These compounds are emerging as interesting building blocks in organic synthesis due to their diverse reactivity modes,[13,14] including photochemical conversion into reactive siloxycarbenes.[15] Even more interestingly, acylsilanes are prone to undergo electrochemical oxidation ($E^{ox}_{1/2}$ of decanoyltrimethylsilane = + 1.33 V vs SCE)[9a] and the resulting radical cations easily lose a silyl cation and an acyl cation chemistry resulted by oxidation of the corresponding acyl radicals.[9a,16]

A set of catalysts was thus tested to check the feasibility of the photocatalytic oxidation of acylsilanes (Table 1). We

started to explore the reactivity of tetrabutylammonium decatungstate (TBADT, $(nBu_4N)_4[W_{10}O_{32}]$), a polyoxometalate well known to promote (besides HAT reactions)[5,6] Single Electron Transfer (SET) processes, even under sunlight irradiation.[17] In fact, the reactive species of this photocatalyst is the dark state dubbed **wO**,[17d] having an estimated oxidation potential (E^*_{red} [**wO**/$[W_{10}O_{32}]^{5-}$]) around +2.44 V vs SCE.[18] Among visible light photocatalysts, we chose to screen 9-mesityl-10-methylacridinium tetrafluoroborate (Acr$^+$-Mes; E^*_{red} [*Acr$^+$-Mes/Acr$^\bullet$-Mes] = +2.06 V vs SCE),[19a] 2,4,6-triphenylpyrillium tetrafluoroborate (TPT, E^*_{red} [*pyr$^+$/pyr$^\bullet$] > +1.9 V vs SCE)[19b] and Ru(bpz)$_3$[PF$_6$]$_2$ (E^*_{red} [*Ru^{II}/Ru^I]= +1.3 V vs SCE; bpz = 2,2'-bipyrazine).[19c] As a model reaction, we then planned to acylate Michael acceptors for the synthesis of substituted ketones in what can be considered a sila-Stetter like reaction, usually requiring high amounts (30 mol%) of thiazolium salts and the presence of a strong base.[20] The crucial point here was the choice of the light source (see Supporting Information) since the direct absorption of the acylsilanes led to a competitive carbene chemistry.[15]

We started our optimization studies from the photocatalyzed addition of acetyltrimethylsilane **1a** onto dimethyl maleate **2a** (Table 1) and TBADT was the first photocatalyst tested. As apparent from Table 1 (entries 1-6), the best yield of dimethyl 2-acetylsuccinate **3** (72%, entry 3) was found with a 2 mol% loading of the photocatalyst, a slight excess of **1a** (1.2 equiv.) in MeCN-H$_2$O 5/1 mixture under irradiation for 8 h adopting phosphor-coated lamps with an emission centered at 310 nm. Irradiation at 366 nm or under solar simulated conditions (entries 5, 6) led to lower yields. Blank experiments demonstrated that light and the catalyst were necessary for the desired acylation to occur (see Table S1).

With the aim to shift the irradiation range to visible light,[8] we focused on colored photoorganocatalysts. Accordingly, the same model reaction was investigated by using Acr$^+$-Mes (5 mol%)[19a] upon 410 nm LED irradiation. At the beginning, chloroform was used as the solvent, but the product was formed only in traces (entry 7). However, the yield markedly increased when a protic solvent was added (e.g. MeOH, entry 8), reaching 65% yield in neat MeOH (entry 9). A good yield of **3** (81% yield, entry 11) was obtained by increasing the concentration of the photocatalyst (up to 10 mol%) and by adopting a 0.15 M amount of **1a** under air equilibrated conditions. Gratifyingly, the acylation occurred with no need of additives (e.g. PhSH) usually required to regenerate the photocatalyst (see Table S1).[21] Finally, both a pyrylium salt (entries 12, 13) and Ru(bpz)$_3{}^{2+}$ (entry 14) were tested, but the desired product **3** was not detected. With the optimal conditions in hand for both TBADT and Acr$^+$-Mes (entries 3 and 11, respectively), we turned our attention to the olefin scope in the reaction with acetylsilane **1a** (Tables 2 and 3). First, olefins having different EWG groups were subjected to TBADT-photocatalyzed acetylation (Table 2).

Table 1. Optimization of the Reaction Conditions.^{a}

Entry	Photocatalyst	**1a** (M)	Solvent	Time (h)	Light Source	**2a** Consumption (%)	Yield (%)^b
1	TBADT (2 mol %)	0.1	MeCN	8	310 nm	30	62^c
2	TBADT (2 mol %)	0.1	MeCN-H$_2$O 5/1	8	310 nm	72	71
3	**TBADT (2 mol %)**	**0.12**	**MeCN-H$_2$O 5/1**	**8**	**310 nm**	**100**	**72**
4	TBADT (2 mol %)	0.12	MeCOMe-H$_2$O 5/1	8	310 nm	100	52
5	TBADT (2 mol %)	0.12	MeCN-H$_2$O 5/1	8	366 nm	65	52
6	TBADT (2 mol %)	0.12	MeCN-H$_2$O 5/1	8	SolarBox^d	100	63
7	Acr$^+$-Mes (5 mol%)	0.12	CHCl$_3$	48	410 nm ^{e}	< 5	Traces
8	Acr$^+$-Mes (5 mol%)	0.12	CH$_2$Cl$_2$-MeOH 1/1	48	410 nm ^{e}	23	20
9	Acr$^+$-Mes (5 mol%)	0.15	MeOH	48	410 nm ^{e}	68	65
10	Acr$^+$-Mes (10 mol%)	0.15	MeOH	48	410 nm ^{e}	85	75
11	**Acr$^+$-Mes (10 mol%)**	**0.15**	**MeOH**	**48**	**410 nm ^{e,f}**	**100**	**81**
12	Pyrylium salt (2 mol%)	0.12	MeCN	24	410 nm ^{e}	< 5	n.d.
13	Pyrylium salt (2 mol%)	0.12	MeCN-H$_2$O 5/1	24	410 nm ^{e}	< 5	Dirty reaction
14	Ru(bpz)$_3{}^{2+}$ (5 mol%)	0.12	MeCN-H$_2$O 5/1	24	450 nm ^{e}	< 5	n.d.

^{a} Reaction conditions: **1a** (0.1-0.15 M), **2a** (0.1 M), photocatalyst (n mol%) in 1 mL of the chosen solvent under deaerated conditions (see SI). ^{b} Gas Chromatography (GC) yields referred to the consumption of the limiting reagent (**2a**), using n-dodecane as internal standard. ^{c} A complex mixture containing **3** was formed. ^{d} Irradiation carried out with a solar simulator equipped with a 1.5 kW Xe lamp, 500W·m^{-2}. ^{e} Irradiation carried out with one LED (1W). ^{f} Under air equilibrated conditions.

Table 2. Olefin Scope for the Acetylation of Electron-Poor Olefins.[a]

Reaction scheme: 1a (0.12 M) + 2 (0.1 M) → 3-13; TBADT (2 mol%), hν (310 nm), 8 h, MeCN-H₂O 5/1

Entry	Olefin 2	Product, yield[b]
1	2a (dimethyl maleate, COOMe/COOMe)	3, 69; 72[c]; 73[d]
2	2b (COOMe)	4, 60
3	2c (CN)	5, 47[e]
4	2d (CN)	6, 56
5	2e (vinyl ketone)	7, 55
6	2f (SO₂Ph)	8, 61
7	2g (maleic anhydride)	9, 63[f]
8	2h (N-methylmaleimide)	10, 79
9	2i (COOEt, CN)	11, 63
10	2j (COOEt, CN)	12, 64
11	2k (CN, CN)	13, 89
12	2l (CN, CN, phenyl)	14, traces

[a] Reaction conditions (see entry 3, Table 1). [b] Isolated yield after silica gel chromatography. [c] See text for apparatus description, Flow Rate: 0.05 mL min⁻¹. [d] 16 h Sunlight irradiation (see SI) [e] 0.15 M 1a. [f] Obtained by spontaneous decarboxylation of the resulting acetylsuccinic acid.

The reaction was satisfactory with unsaturated esters **2a** and **2b** (up to 69% yield) and afforded the corresponding keto esters **3** and **4**. The synthesis of **3** was repeated also under flow conditions, exploiting a photochemical apparatus made by a PTFE tubing coiled around the cooling system (made of quartz) of a 125 W medium pressure Hg lamp.[22] To our delight, this apparatus allowed to obtain in 4 h a yield (72%) comparable to that observed under batch conditions (reactor volume: 12 mL, flow rate: 0.05 mL min⁻¹). Noteworthy, compound **3** (73% yield) was likewise prepared upon exposure to direct solar light for two days (8 h per day, see SI).

The presence of a methyl group in the β-position of crotonitrile **2d** allowed to isolate product **6** in a higher yield with respect to **5**, despite acrylonitrile (**2c**) was used in a higher amount (0.15 M). 1,4-Diketone **7** and β-keto sulfone **8** were isolated in a good yield (> 50%) starting from vinyl ketone **2e** and vinyl sulfone **2f**, respectively. Anhydride **2g** afforded the Stetter adduct that, upon spontaneous ring opening and CO₂ loss, afforded levulinic acid **9** in 63% yield. Reaction with maleimide **2h** to give product **10** worked better (79% yield). 1,1-Disubstituted alkenes **2i-2l** were interesting substrates since in the first two cases the acylation led to trifunctionalized derivatives **11** and **12**, again in more than 60% yield. The acylation of **2k** gave the best yield in the series (89%) but acylation of dinitrile **2l**, led to a complex mixture, where **14** was obtained only in traces. Next, we tested selected reactions reported in Table 2 under visible-light by using Acr⁺-Mes (Table 3). We obtained good results for some electron-poor olefins, *i.e.* **2a**, **2e**, **2f** and **2l**. Interestingly, this visible-light methodology allowed us to isolate product **14** in a good yield (55%) through irradiation with LEDs centered at 410 nm. Nevertheless, we found that when using some Michael acceptors (*e.g.* **2b-d** and **2g**), a dirty reaction was observed and the expected ketones were formed in a lower amount (traces in some cases) with respect to the same reaction photocatalyzed by TBADT.

Table 3. Selected Examples of Acr⁺-Mes Visible-Light Photocatalyzed Acetylation of Electron-Poor Olefins.[a]

Reaction scheme: 1a (0.15 M) + 2 (0.1 M) → 3, 7, 8, 14; Acr⁺-Mes (10 mol%), hν (410 nm), 48 h, MeOH

Entry	Olefin 2	Product, yield[b]
1	2a (COOMe/COOMe)	3, 81; 71[c]
2	2e (vinyl ketone)	7, 71
3	2f (SO₂Ph)	8, 75
4	2l (CN, CN, phenyl)	14, 55

[a] Reaction conditions (see entry 11, Table 1). [b] Isolated yield after silica gel chromatography. [c] Reaction carried out under direct sunlight irradiation (40 h); 69% consumption of **2a**.

We then extended the scope of the reaction to other alkyl or aryl acylsilanes by using TBADT (method A, Table 4) and Acr⁺-Mes (method B) as the photocatalysts. Heptanoylsilane **1b** was used to prepare substituted ketones **15-17** in satisfying yields. As for acylsilane **1c**, the synthesis of ketones **18-20** was satisfying in the presence of Acr⁺-Mes, while TBADT gave lower yields due to the formation of a significant amount of 3-penylpropanal (50-70%, Table 4). Finally, we tested benzoylsilane **1d** but no ketone **21** was formed under the two conditions tested (even at 450 nm for Acr⁺-Mes) and benzaldehyde quickly accumulated during the irradiation. This was probably due to the strong competitive absorption of this aromatic acylsilane (see Figures S1, S2) causing a direct photochemistry of **1d**.[15]

**Table 4. Scope of the Acylation Reaction.**[a]

substrate	method	product	yield (%)[b]
1b (C_6H_{13}COTMS)	A / B	**15**	73% / 31%
1b	A / B	**16**	58% / 43%
1b	A / B	**17**	61% / 78%
1c	A / B	**18**	16%[c] / 23%
1c	A / B	**19**	10%[c] / 30%
1c	A / B	**20**	10%[c] / 44%
1d	A / B	**21**	n.d. / n.d.

[a] Method A: **1** (0.12 M), **2** (0.1 M), TBADT (2 mol%) in 15 ml of MeCN-H_2O 5/1 irradiated at 310 nm. Method B: **1** (0.15 M), **2** (0.1 M), Acr⁺-Mes (10 mol%) in 10 ml of MeOH (see SI) irradiated at 410 nm. [b] Isolated yield. [c] A 50-70% amount of 3-phenylpropanal detected.

As for the mechanistic aspects of this reaction, we measured the redox potentials of acylsilanes **1a-d**. $E^{ox}_{1/2}$ are in the +1.26 – +1.51 V vs SCE range, being **1b** and **1d** the most and least oxidizable of the series (see Table S2). We deem that a similar mechanism operates for both TBADT and Acr⁺-Mes (Scheme 2). We propose that their excited states (**PC***) are capable of oxidizing the acylsilanes tested (**1**) to the corresponding radical cations **1**•⁺. Loss of the Me_3Si^+ cation gave the nucleophilic acyl radical, in turn prone to add onto electron-poor olefins (**2**). The resulting radical adducts **I**• were then reduced by the reduced form of the photocatalyst (to **II**⁻) and protonation finally afforded the desired products (**3-21**).

Scheme 2. Proposed Mechanism for the Photoredox Catalyzed Synthesis of Unsymmetrical Ketones.
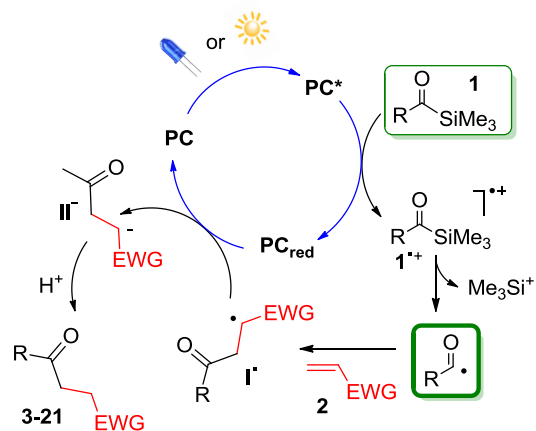
This general scheme is largely documented for the TBADT photocatalyzed functionalization of olefins.[4,5] However, we assume that the mechanism reported in Scheme 2 likewise operates in the case of Acr⁺-Mes, since neither sulfur containing additives (e.g. PhSH) nor oxygen were mandatory for the regeneration of the photocatalyst.[21] On the other hand, the capability of diacyanoalkyl radicals to serve as oxidants for Acr-Mes• is documented[23a,b] and the feasibility of this electron transfer process was apparent by the value of the reduction potential of Acr⁺-Mes ($E^{red}_{1/2}$ ca. -0.57 V vs SCE),[23c] that is quite similar to the reduction potentials of the cyanomethyl radical ($E^{red}_{1/2}$ ca. -0.72 V vs SCE)[23d] or •CH_2COOEt ($E^{red}_{1/2}$ ca. -0.63 V vs SCE).[23d]

In conclusion, the first use of acylsilanes in phototoredox catalysis has been reported. The use of decatungstate and acridinium salts as photocatalysts allowed for the use of solar/visible light to promote the reaction. Aliphatic acyl radicals were smoothly obtained and used for the acylation of Michael acceptors for the efficient synthesis of unsymmetrical ketones. The approach is mild and green since the 1,4-difunctionalized derivatives formed may be prepared by simply exposing the reaction vessel to sunlight, thus performing the so called window-ledge chemistry.[4a]

ASSOCIATED CONTENT

Supporting Information. Experimental details about the used materials, sample preparation, experiments and analytical data (NMR). This material is available free of charge via the Internet at http://pubs.acs.org.

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