

## Photochemistry of S-Phenacyl Xanthates

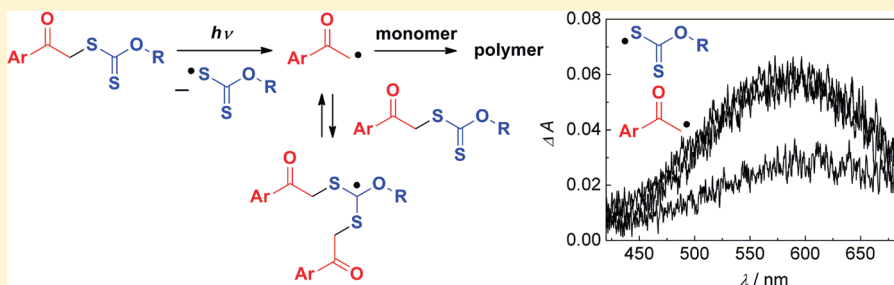
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**S** Supporting Information

### ABSTRACT:



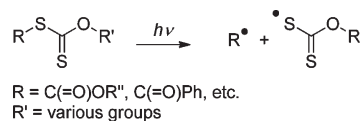
Various synthetically readily accessible S-phenacyl xanthates are shown to undergo photoinitiated homolytic scission of the C–S bond in the primary step. The resultant fragments, phenacyl and xanthic acid radicals, recombine to form symmetrical 1,4-diketones and xanthogen disulfides, respectively, in high to moderate chemical yields in chemically inert solvents. They can also be efficiently trapped by a hydrogen-atom-donating solvent to give acetophenone and xanthic acid derivatives. The latter compound is in situ thermally converted to the corresponding alcohol in high chemical yields. S-Phenacyl xanthates could thus be utilized as synthetic precursors to the above-mentioned compounds or as photoremovable protecting groups for alcohols in which the xanthate moiety represents a photolabile linker. The photochemically released phenacyl radical fragments efficiently but reversibly add to the thiocarbonyl group of the parent xanthate molecule. The kinetics of this degenerative reversible addition–fragmentation transfer (RAFT)/macromolecular design via the interchange of xanthates (MADIX) mechanism was studied using laser flash photolysis (LFP) and density functional theory (DFT) calculations. The rate constants of the RAFT addition step,  $k_{\text{add}} \sim 7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , and phenacyl radical addition to a double bond of 1,1-diphenylethylene,  $k_{\text{add}} \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , in acetonitrile were experimentally determined by LFP. In addition, photoinitiation of the methyl methacrylate polymerization by S-phenacyl xanthate is demonstrated. The polydispersity index of the resulting poly(methyl methacrylate) was found to be  $\sim 1.4$ . We conclude that S-phenacyl xanthates can serve simultaneously as photoinitiators as well as RAFT/MADIX agents in polymerization reactions.

### INTRODUCTION

During the past century, reactions of xanthates (or dithiocarbonates), such as Chugaev elimination<sup>1</sup> or Barton–McCombie radical deoxygenation,<sup>2</sup> have received considerable attention from both synthetic and mechanistic points of view. Because of the lower dissociation energy of the C–S bond, xanthates can be readily used as (photo)initiators of radical reactions (Scheme 1).<sup>3–5</sup> S-Acyl xanthates, producing acyl radicals, are particularly useful because they absorb in the visible region.<sup>5–8</sup>

Alkyl and acyl xanthates have been reported as RAFT (reversible addition–fragmentation transfer)/MADIX (macromolecular design via the interchange of xanthates) agents in polymerizations reactions.<sup>3,9–15</sup> These mechanistically identical methodologies revolutionized the field of free-radical polymerization because they enable control of the molecular weight and architecture of the resulting polymer. The key process is characterized by addition ( $k_{\text{add}}$ ) of a radical ( $\text{R}^\bullet$ ) to the thiocarbonyl

### Scheme 1. Photolysis of Xanthates

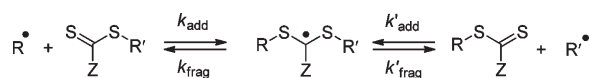


group to form a relatively stable radical intermediate (Scheme 2). This addition is reversible; the intermediate can fragment to the radicals  $\text{R}^\bullet$  ( $k_{\text{frag}}$ ) and  $\text{R}'^\bullet$  ( $k'_{\text{frag}}$ ) formed from the corresponding substituent. In polymerization reactions, the radical species are the growing polymer chain radicals. The equilibrium shown in Scheme 2 then ensures equal probability for all chains to grow.

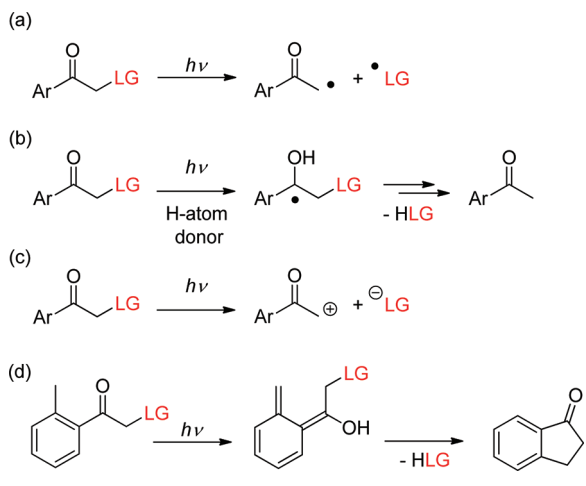
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Scheme 2. RAFT/MADIX Process



Scheme 3. Photoreactivity of Phenacyl Compounds

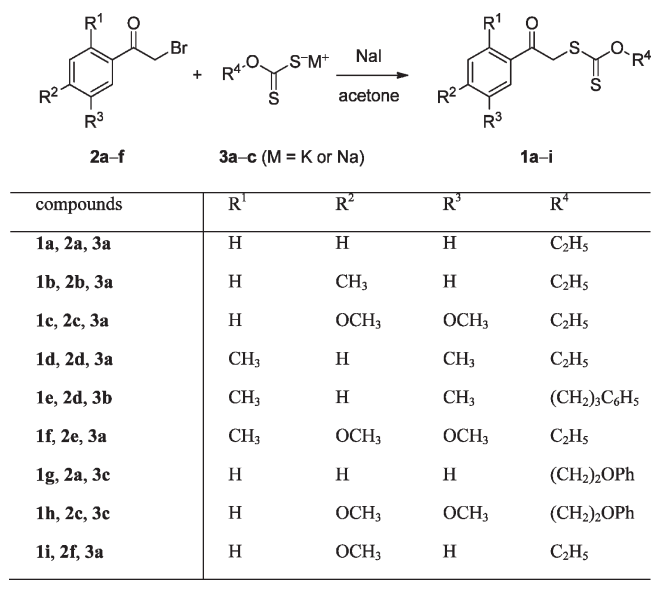


The nature of the Z group (often the alkoxy group) affects the stability of the radical intermediate.<sup>15</sup>

Photochemical reactions of phenacyl compounds have been the subject of interest for several decades. In 1973, Sheehan and Umezawa reported that direct UV irradiation of 4-methoxyphenacyl esters in dioxane solutions gives acetophenone and a carboxylic acid in good yields.<sup>16</sup> Homolytic scission of the ester C–O bond, which would result in formation of the phenacyl and acyloxy radicals (Scheme 3a; leaving group, LG = O(C=O)R), has not been confirmed because the reaction did not yield any detectable amount of dibenzyl as an anticipated product of phenylacetoxyl radical decarboxylation. Later, Banerjee and Falvey studied photochemical cleavage of phenacyl esters in the presence of hydrogen atom donors by laser flash photolysis.<sup>17</sup> They proposed a mechanism that involves hydrogen abstraction from a hydrogen-atom donor by the excited carbonyl group (photoreduction<sup>18</sup>) of phenacyl ester via a ketyl ester intermediate (Scheme 3b). When a relatively stable radical can be released from the  $\alpha$ -carbon, phenacyl radicals are indeed produced in the primary homolytic step (Scheme 3a). This has been demonstrated in the reactions of phenacyl halogenides,<sup>19–22</sup> sulfides,<sup>23</sup> azides,<sup>24</sup> mercury halides,<sup>25</sup> or sulfonium<sup>26</sup> salts. An alternative mechanism, formation of the phenacylium cation (Scheme 3c) from phenacyl ammonium salts upon irradiation via a heterolytic cleavage of the C–N bond, has also been proposed.<sup>27</sup> Phenacyl ammonium salts can then be used as photoinitiators for cationic polymerization reactions.<sup>27,28</sup> 2-Alkyl-substituted acetophenones were utilized as a new photoremovable protecting group<sup>18,29–31</sup> for various functional groups, such as carboxylic acids, phosphates, sulfonates, alcohols, amines, and amino acids.<sup>32–35</sup> This reaction is based on the intramolecular hydrogen-atom abstraction, photoenol formation, and release of a leaving group as an anion (photoenolization; Scheme 3d).

We wanted to study the photochemical behavior of S-phenacyl xanthates, ArC(=O)CH<sub>2</sub>SC(=S)OR, the compounds, in which two (photo)chemically active groups are connected by a photolabile

Scheme 4. Synthesis of 1



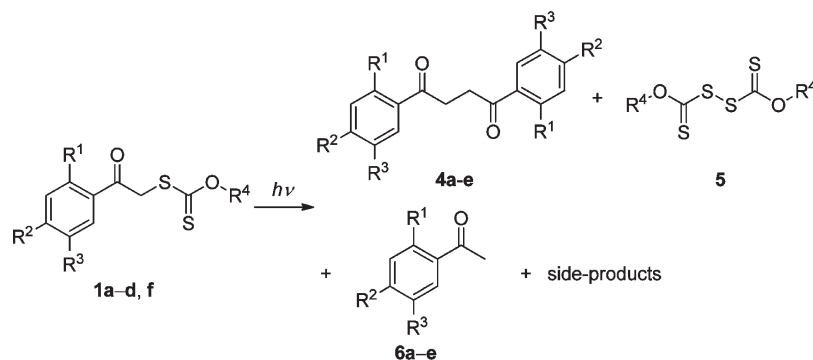
single C–S bond. A series of experiments and DFT-based quantum chemical calculations were performed to determine the primary photochemical processes and to understand the effects that are associated with a RAFT/MADIX mechanism involved in the subsequent steps. Here we discuss the synthetic applications of S-phenacyl xanthates and their potential use as photoinitiators, RAFT agents in polymerization reactions, and photoremovable protecting groups. The photophysical properties of S-phenacyl xanthates, not covered in this study, are currently under investigation in our laboratory.

## RESULTS AND DISCUSSION

**Synthesis of the Starting Compounds.** The S-phenacyl xanthates 1a–i were synthesized from readily accessible substituted phenacyl bromides and the corresponding sodium or potassium salt of the alkyl xanthogenates 3 in one step in high chemical yields (85–98%) and purity (Scheme 4).

**Steady-State Photochemistry.** Degassed solutions of 1 in acetonitrile (Scheme 5, Table 1) or propan-2-ol (Scheme 6, Table 2) were irradiated at  $\lambda > 300$  nm. Formation of the major photoproducts, 1,4-diketones (4a–e), the xanthogen disulfide 5, acetophenones (6a–e), and alcohols (8a,b), was monitored by HPLC. When necessary, the photoproducts were isolated and fully characterized. Compounds 4a,b and 5 were formed from 1a,b in acetonitrile in good chemical yields at <65% conversion (Table 1). More substituted S-phenacyl xanthates (1c,d) gave a mixture of all three photoproducts (4–6). The diketone 4e was not formed by irradiation of 1f. Other side photoproducts, detected by HPLC only in small amounts, were not identified. A complex mixture of products was always observed after extensive photolysis.

Irradiation of 1c,e,g, in propan-2-ol gave the acetophenone 6 and the corresponding alcohol 8 in 79–89% yields (<95% conversion; Table 2). An anticipated xanthic acid intermediate 7 (vide infra) was not detected by HPLC. Formation of 8 was never observed in acetonitrile. Irradiation of the *o*-methyl-substituted phenacyl derivatives 1d–f did not lead to photoproducts, such

Scheme 5. Photochemistry of **1** in Acetonitrile

compounds	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
<b>1a, 4a, 5, 6a</b>	H	H	H	C <sub>2</sub> H <sub>5</sub>
<b>1b, 4b, 5, 6b</b>	H	CH <sub>3</sub>	H	C <sub>2</sub> H <sub>5</sub>
<b>1c, 4c, 5, 6c</b>	H	OCH <sub>3</sub>	OCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
<b>1d, 4d, 5, 6d</b>	CH <sub>3</sub>	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
<b>1f, 4e, 5, 6e</b>	CH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>

Table 1. Irradiation of **1** in Acetonitrile<sup>a</sup>

irradiated xanthate	% yield ( <b>4</b> ) <sup>b</sup>	% yield ( <b>5</b> ) <sup>b</sup>	% yield ( <b>6</b> ) <sup>b</sup>
<b>1a</b>	70 (74 <sup>c</sup> )	65	<1 <sup>d</sup>
<b>1b</b>	81 (84 <sup>c</sup> )	70	<1 <sup>d</sup>
<b>1c</b>	43 (46 <sup>c</sup> )	61	22
<b>1d</b>	32 (37 <sup>c</sup> )	35	20
<b>1f</b>	<1 <sup>d</sup>	24	30

<sup>a</sup> Irradiated at  $\lambda > 300$  nm to  $\sim 60$ – $65\%$  conversion. <sup>b</sup> Isolated yields; the data are normalized to 100% conversion. <sup>c</sup> HPLC yields. <sup>d</sup> Below the detection limit.

as an indanone<sup>34–36</sup> derived from a photoenol intermediate (Scheme 3d), in any of the solvents used.

The quantum yields of xanthates **1** initial disappearance in acetonitrile, methanol, or propan-2-ol are listed in Table 3. Relatively low values ( $\Phi = 0.05$ – $0.11$ ) were found in both acetonitrile and methanol for all derivatives. The quantum yields obtained for **1a** in propan-2-ol and acetonitrile containing thiophenol were higher by several factors compared to that measured in acetonitrile.

Phenacyl halogenides,<sup>19–22</sup> sulfides,<sup>23</sup> and some other  $\alpha$ -substituted derivatives<sup>24–26</sup> mentioned in the introductory paragraph are known to produce phenacyl radicals in the primary homolytic step. Diketones analogous to **4** have been reported as the phenacyl radical recombination products in some cases.<sup>24,25,38</sup> Direct photolysis of *S*-phenacyl xanthates has not been studied much before. Only one study showed that their photolysis gives radical intermediates which were subsequently utilized in the cyclopentane ring-annulation reactions.<sup>39</sup> However, photochemistry of analogous systems, such as dithioester and trithiocarbonate derivatives, has been utilized in photoinduced conjugation of polymers using a RAFT approach.<sup>40</sup> For example, *O*-ethyl-*S*-benzyl xanthate forms the benzyl radical upon irradiation, which was used in the polymerization of methyl

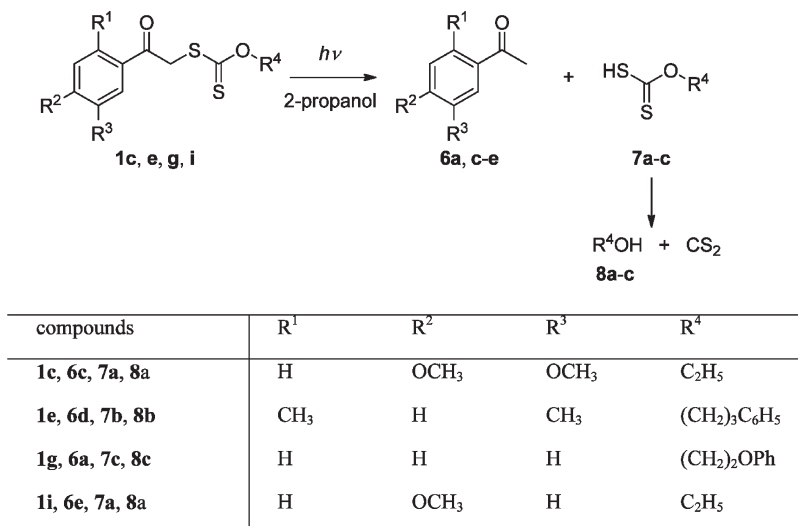
methacrylate.<sup>41</sup> To our knowledge, formation of xanthogen disulfides (**5**) via a photochemical process has not yet been reported.

In order to explain the photochemical behavior of **1** in acetonitrile (as a solvent relatively inert to radicals) shown in Scheme 5, the putative primary radical intermediates formed upon irradiation were chemically trapped. **1a** ( $c = 5 \times 10^{-3}$  M) was irradiated at  $\lambda > 313$  nm in the presence of vinyl acetate (**9**; equimolar amount) to give the major addition product **10** in 55% chemical yield (Scheme 7). We therefore conclude that the phenacyl (**PA**<sup>•</sup>) and xanthic acid (**XAN**<sup>•</sup>) radicals are formed by homolytic cleavage of the C–S bond in the primary photochemical step analogous to the photochemistry of some other phenacyl derivatives mentioned above.

Scheme 8 illustrates the formation and probable fate of the primary radicals **PA**<sup>•</sup> and **XAN**<sup>•</sup> formed photochemically from **1a** in a *non-hydrogen-donating solvent*. The major products **4a** and **5** (Scheme 5 and Table 1) are evidently formed via recombination (termination) of **PA**<sup>•</sup> and **XAN**<sup>•</sup> radicals, respectively; **6** can be produced from **PA**<sup>•</sup> via hydrogen-atom abstraction (only one example shown). Quantum chemical calculations were performed to estimate the feasibility of various radical reactions occurring after irradiation of **1a** and support our experimental observations. The DFT-calculated enthalpies (at 0 K), shown in the following schemes, serve as a qualified guess.

There are three competing terminal pathways for **PA**<sup>•</sup> according to Scheme 8: formation of **4a** (74% yield), **6a** (Table 1), or the starting material. Formation of **6a** was not observed, although hydrogen-atom abstraction from C <sub>$\alpha$</sub>  of **1a** by **PA**<sup>•</sup> to give **12** is evidently a favorable process according to our DFT calculations ( $\Delta H = -9.8$  kcal mol<sup>-1</sup>). **PA**<sup>•</sup> can also abstract hydrogen from other hydrogen-atom sources, including **6a**, while **6a** itself must be photodegradable (via photoreduction).<sup>43</sup> In the case of **1b, 4b** was obtained in 84% yield.

We have no experimental evidence that the phenacyl carbonyl group of **1** undergoes photoreduction, that is, hydrogen abstraction

Scheme 6. Photochemistry of **1** in Propan-2-olTable 2. Irradiation of **1** in Propan-2-ol<sup>a</sup>

irradiated xanthate	% yield ( <b>6</b> )	% yield ( <b>8</b> )
<b>1c</b>	83	n.e. <sup>b</sup>
<b>1e</b>	79	77
<b>1g</b>	86	84
<b>1i</b>	89	n.e. <sup>b</sup>

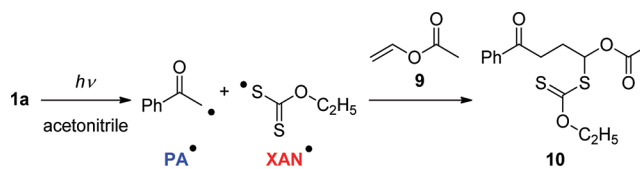
<sup>a</sup> Irradiated at  $\lambda > 300$  nm to  $\sim 95\%$  conversion; HPLC yields. The data are normalized to 100% conversion. <sup>b</sup> **8a** = ethanol; n.e. = not evaluated.

Table 3. Quantum Yields ( $\Phi$ ) of **1**'s Disappearance<sup>a</sup>

xanthate	$\Phi$ (CH <sub>3</sub> CN)	$\Phi$ (CH <sub>3</sub> OH)	$\Phi$ (propan-2-ol)	$\Phi$ (CH <sub>3</sub> CN, TP) <sup>b</sup>
<b>1a</b>	0.081 $\pm$ 0.008	0.096 $\pm$ 0.005	0.32 $\pm$ 0.02	0.43 $\pm$ 0.05
<b>1c</b>	0.053 $\pm$ 0.004	0.078 $\pm$ 0.006	n.d. <sup>c</sup>	n.d. <sup>c</sup>
<b>1d</b>	0.117 $\pm$ 0.009	0.093 $\pm$ 0.006	n.d. <sup>c</sup>	n.d. <sup>c</sup>
<b>1f</b>	0.066 $\pm$ 0.006	0.054 $\pm$ 0.008	n.d. <sup>c</sup>	n.d. <sup>c</sup>

<sup>a</sup> Degassed solutions ( $c \sim 5 \times 10^{-3}$  M) were irradiated at  $\lambda = 313 \pm 5$  nm (optical bench).  $\Phi$  was determined using valerophenone as an actinometer ( $\Phi$  of acetophenone formation = 0.33 in hexane<sup>37</sup>). The values are means and standard deviations from three measurements. <sup>b</sup> In the presence of thiophenol (TP;  $c \sim 1$  M); this number represents the maximum quantum yield of the fragmentation reaction ( $\Phi_{\max}$ ). <sup>c</sup> n.d. = not determined.

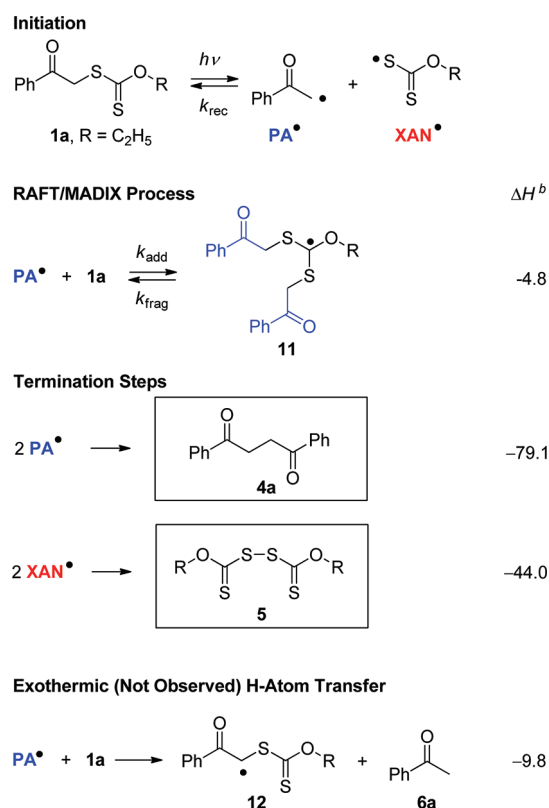
by the excited phenacyl carbonyl group (Scheme 3b) to give the corresponding xanthic acid **7**. The *o*-methylphenacyl xanthates **1d–f** were originally prepared to see whether a photoenolization reaction, i.e., intramolecular hydrogen abstraction (and subsequent formation of an indanone; Scheme 3c), occurs upon irradiation. It is known that when a suitable deuterium donor is present in the solution, the incorporation of deuterium into the *o*-methyl group can be detected by NMR measurements.<sup>44,45</sup> However, irradiation of **1a** in benzene containing D<sub>2</sub>O did not lead to a decrease in the corresponding NMR signal. On the other hand, the presence of an *o*-methyl group in **13** may lead to energetically favorable ( $\Delta H = -4.5$  kcal mol<sup>-1</sup>) formation of the benzyl radical **14** via an

Scheme 7. Radical Trapping by Vinyl Acetate (**9**)

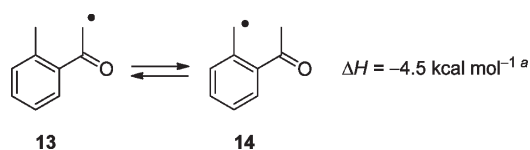
intramolecular hydrogen-atom shift (Scheme 9). Such a process would eventually lead to formation of different side products. Indeed, irradiation of **1d** gave a more complex reaction mixture than irradiation of **1a–c** (Table 1), and the quantum yield of its photodegradation was also slightly higher (Table 3). A complex reaction mixture was also obtained by irradiation of another *o*-methylphenacyl derivative **1f**. In this case, the diketone **4e** was not formed at all.

If no significant termination or degradation reactions other than those shown in Scheme 8 are present, photophysical decay of the excited state and in-cage regeneration of the starting compound **1a** ( $k_{\text{rec}}$  (in cage)) are the only processes that can decrease the observed quantum yield of **4a** production. The anticipated RAFT/MADIX addition/fragmentation equilibrium (formation of **11**) is a nonproductive step which does not affect the quantum yield. All three termination steps are highly exothermic (Scheme 8) and nearly or fully diffusion controlled.<sup>46–48</sup> In a simplified model, in which hydrogen abstraction by PA• is omitted, the rate constant of the recovery step ( $k_{\text{rec}}$ ) competes only with diffusion.

It has been shown that thiocarbonyl compounds can serve as RAFT/MADIX polymerization agents because they can reversibly react with radical species<sup>3,9–15,49–53</sup> (Scheme 2). This reversible and chemically degenerate reaction leads to the equilibrium between the “active” and “dormant” radical species which can be controlled by substrate modifications. Keeping the steady-state concentration of “active” radicals low thus enables control of the overall radical addition transfer process during polymerization. In such cases, chemical or photochemical initiation step gives rise to a very small concentration of radicals, which are scavenged by a xanthate.

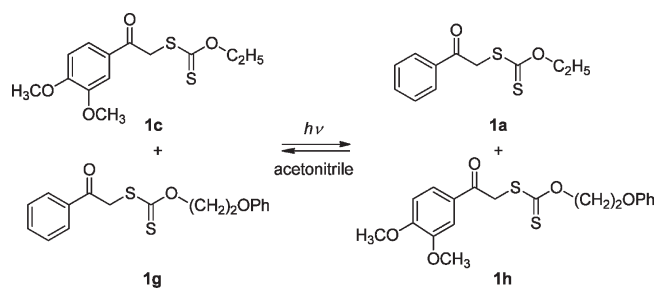
Scheme 8. Chemistry of Primary Radical Intermediates Formed from 1a in Acetonitrile<sup>a,b</sup>

<sup>a</sup>The isolated reaction products are depicted in the boxes. <sup>b</sup>The enthalpies ( $\Delta H$ , kcal mol<sup>-1</sup>; 0 K) were calculated at the UM06-2X/6-311+G(2df,p)//ROB3LYP/6-31+G\* level of theory. The ZPVE was scaled by 0.9857<sup>42</sup>.

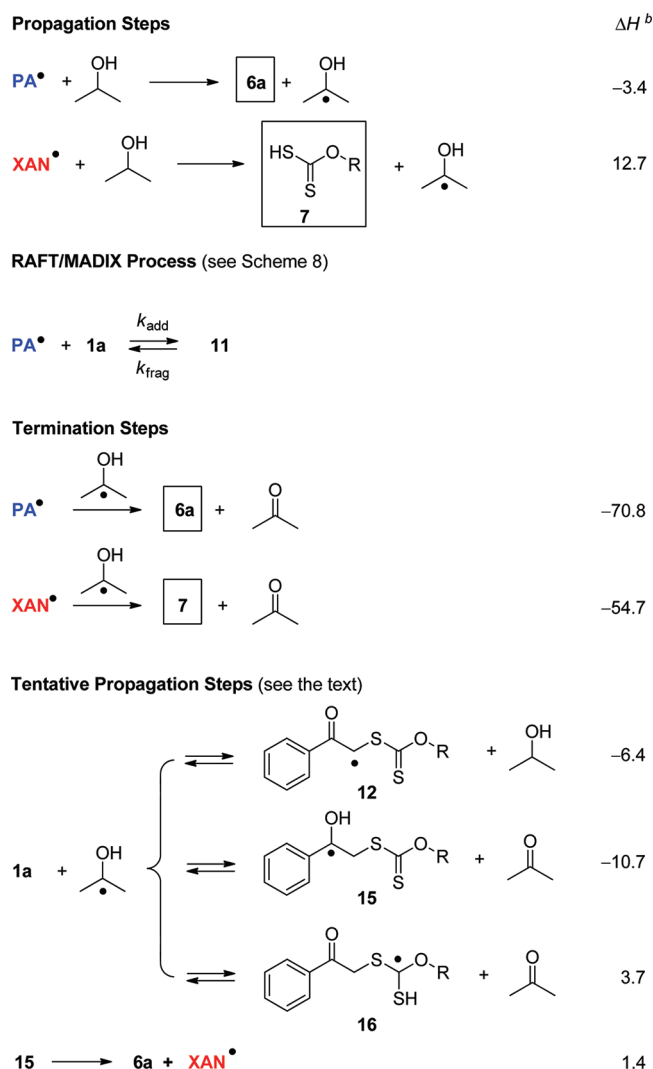
Scheme 9. Intramolecular Hydrogen Abstraction in *o*-Methylacetophenone Radical

<sup>a</sup> See footnote b in Scheme 8.

Scheme 10. Crossover Experiment



The anticipated reversible addition of PA<sup>•</sup> to 1a (Scheme 8) was evidenced by a crossover experiment. An equimolar mixture of 1c and 1g ( $c = 5 \times 10^{-3}$  M) was irradiated in acetonitrile at  $\lambda > 300$  nm (Scheme 10). Photostationary state concentrations of 1a

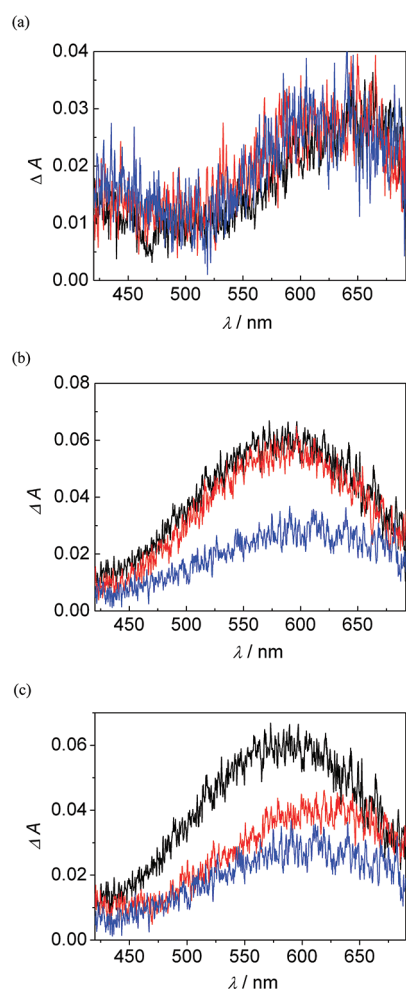
Scheme 11. Chemistry of Radical Intermediates Formed from 1a in Propan-2-ol<sup>a,b</sup>

<sup>a</sup> See footnote a in Scheme 8. <sup>b</sup> See footnote b in Scheme 8.

and 1h, and the parent compounds 1c and 1g, were reached before formation of any of the products 4 or 5 was detected by HPLC. We therefore assume that the RAFT-type radical 11 is a precursor to 1a and h. The xanthate 1 thus serves simultaneously as a source of the primary radicals and a radical scavenger.

When 1 was photolyzed in a *hydrogen-atom donating solvent* (propan-2-ol), 6 and 8 were the sole products (Table 2, Scheme 11). The alcohol 8 was formed along with CS<sub>2</sub> (HPLC) obviously by thermal fragmentation of the xanthic acid<sup>54</sup> 7 (Scheme 6), which was not detected in the reaction mixture. The solvent acted as a scavenger of the ground state PA<sup>•</sup> and XAN<sup>•</sup> radicals. The quantum yield of xanthate photodegradation in propan-2-ol was found to be higher than that in acetonitrile by a factor of 4 (Table 3). The quantum yield  $\Phi = 0.43$  of the same process was obtained in acetonitrile containing a high concentration of thiophenol. Thiophenol is a better H-atom donor (BDE = 79.1 kcal mol<sup>-1</sup><sup>55</sup>) than propan-2-ol (BDE = 90.9 kcal mol<sup>-1</sup><sup>18</sup>); this value thus represents the maximum quantum yield  $\Phi_{\text{max}}$  of the out-of-cage formation of PA<sup>•</sup>.<sup>23</sup>





**Figure 1.** Transient absorption spectra of (a) **1a**, (b) **1c**, and (c) **1i** in acetonitrile (black), 2 M propan-2-ol solution in acetonitrile (red), and neat propan-2-ol (blue) recorded  $400 \pm 30$  ns after a 355 nm flash.

A difference in the quantum yields of **1a** initial disappearance in acetonitrile (0.08) and  $\Phi_{\max}$  in the presence of thiophenol is essentially related to the efficiency of  $\text{PA}^\bullet$  and  $\text{XAN}^\bullet$  out-of-cage recombination regenerating **1** under the given experimental conditions. A relatively low  $\Phi$  in propan-2-ol (0.32) precludes the involvement of any efficient radical chain mechanism as observed, for instance, in the photochemistry of phenacyl bromides<sup>20</sup> or phenacyl acetates.<sup>43</sup> For example, **6** was found to be formed via  $\beta$ -cleavage of phenacyl bromides in propan-2-ol with the chain length of  $\geq 70$  and  $\Phi \geq 35$ .<sup>22</sup> Compared to a very endothermic termination reaction of  $\text{XAN}^\bullet$  with propan-2-ol in our system (Scheme 11), the analogous reaction of  $\text{Br}^\bullet$  is exothermic by  $5.2 \text{ kcal mol}^{-1}$  (our DFT estimate). We thus assume that **7** must rather be formed from  $\text{XAN}^\bullet$  via a termination step with the ketyl radical.

We analyzed the possibility that  $\text{PA}^\bullet$  undergoes the same reversible addition to **1** as observed in acetonitrile. The DFT calculations showed that hydrogen abstraction from propan-2-ol by phenacyl radical is similarly favorable as  $\text{PA}^\bullet$  addition to **1a** (the  $\Delta H$  values are shown in Schemes 8 and 11), whereas H-atom abstraction by  $\text{XAN}^\bullet$  is very endothermic ( $\Delta H = 12.7 \text{ kcal mol}^{-1}$ ). Strongly exothermic termination reactions of both

$\text{PA}^\bullet$  and  $\text{XAN}^\bullet$  with the ketyl radical  $(\text{CH}_3)_2\text{C}^\bullet\text{OH}$  (formed in the propagation steps) also give the products **6** and (ultimately) **8** and could represent an important decay channel.

Similarly to the crossover experiment shown in Scheme 10, an equimolar mixture of **1c** and **1g** ( $c = 5 \times 10^{-3} \text{ M}$ ) was irradiated in a propan-2-ol/acetonitrile (10:1) mixture at  $\lambda > 300 \text{ nm}$ . The crossover products **1a** and **1h** were formed together with acetophenones **6a** and **6c**. When the same concentration of all four xanthates (**1a,c,g,h**) was reached, the molar concentration ratio  $[\mathbf{6}]/[\mathbf{1}]$  was  $\sim 1.3$  for any pair of the compounds. This must mean that the RAFT/MADIX (formation of **11**) is a more efficient process compared to  $\text{PA}^\bullet$  scavenging steps. Extensive photolysis, then, only led to increasing concentrations of acetophenones.

In addition, we considered involvement of the ketyl radical  $(\text{CH}_3)_2\text{C}^\bullet\text{OH}$  as a potential hydrogen atom donor.<sup>56</sup> Formation of the radical intermediates **12** and **15** (Scheme 11) was found to be energetically more favorable than formation of **16** by our DFT calculations. We could not rule out these propagation steps; however, the absence of the corresponding products formed from **12** and **16** and the low quantum yields (Table 3) do not indicate the presence of a free radical chain process (as discussed above), which was observed in the case of phenacyl bromide.<sup>22</sup> Compound **15** could also (endothermically) fragment to give **6a** and  $\text{XAN}^\bullet$ . In order to study more the RAFT/MADIX mechanism contribution in the photochemistry of **1**, flash photolysis was used to monitor the kinetics of the radical intermediates formed in both acetonitrile and propan-2-ol.

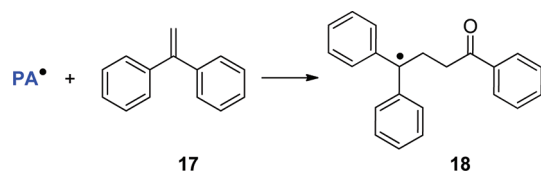
**Kinetic Flash Photolysis.** Long-lived ( $\tau$  in the order of  $10 \mu\text{s}$ ) transient signals at  $\lambda > 500 \text{ nm}$  were followed after irradiation of **1a**, **1c**, and **1i** ( $c \sim 10^{-3} \text{ M}$ ) in acetonitrile, 2 M propan-2-ol solution, or neat propan-2-ol by a 355 nm laser pulse ( $\leq 700 \text{ ps}$  duration; Figure 1a–c). The observed broad band consists of the absorption of two overlapping transient spectra. The first band, kinetically resolved below 600 nm, is assigned to the corresponding phenacyl radical. The other transient that absorbs principally at  $> 550 \text{ nm}$  is assigned to the xanthic acid radical.<sup>7,57</sup> Substituted phenacyl radicals are known to be readily detectable.<sup>19</sup> To the best of our knowledge, the transient absorption of unsubstituted phenacyl radical ( $\text{PA}^\bullet$ ) has not been reported before. Therefore, a solution of phenacyl bromide in acetonitrile was photolyzed for comparison, and the band at  $\lambda_{\max} = 410 \text{ nm}$  was assigned to  $\text{PA}^\bullet$  (Supporting Information, Figure S21). The radical decays with  $k_{\text{obs}} = (7 \pm 4) \times 10^4 \text{ s}^{-1}$ . In addition, we simulated the electronic transition spectra of  $\text{PA}^\bullet$  (and  $\text{XAN}^\bullet$ ; vide supra) radicals by the TD-DFT methodology combined with a linearized harmonic reflection principle to account for vibrational broadening. The calculated spectra further confirm our assignments (Figure S22, Supporting Information).

We were unable to detect any transient absorption signal which would correspond to formation of the ketyl radical **15** in degassed propan-2-ol solutions using either 266 or 355 nm excitation. Such ketyl radicals of various acetophenones are known to absorb with a maximum at  $\sim 370 \text{ nm}$ .<sup>58</sup> A typical decay rate constant for various substituted ketyl radicals derived from acetophenones are in the order of  $10^6 \text{ s}^{-1}$ .<sup>59</sup> This was also supported by our observation that the inter/intramolecular hydrogen atom transfer, typical for triplet acetophenones,<sup>18</sup> does not occur in our systems (vide supra). An alternative (exothermic) formation of the ketyl radical **15** has been excluded even in neat propan-2-ol because a slow reaction of  $\text{PA}^\bullet$  with propan-2-ol ( $k = 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>19</sup> should not provide a

Table 4. Observed Rate Constants ( $k_{\text{dec}}$ ) of  $\text{PA}^\bullet$  and  $\text{XAN}^\bullet$  Decay<sup>a</sup>

xanthate	$10^4 k_{\text{dec}}/\text{s}^{-1b}$					
	$\text{PA}^\bullet$			$\text{XAN}^\bullet$		
	MeCN	2-M IPA	IPA	MeCN	2-M IPA	IPA
<b>1a</b>	$6.2 \pm 2.7$ (4)	$5.0 \pm 0.9$ (3)	$4.5 \pm 0.5$ (3)	$5.6 \pm 1.7$ (4)	$5.4 \pm 1.0$ (2)	$4.2 \pm 0.4$ (2)
<b>1c</b>	$4.2 \pm 1.4$ (3)	$3.7 \pm 1.2$ (3)	$3.6 \pm 0.4$ (2)	$5.6 \pm 1.8$ (3)	$4.2 \pm 0.4$ (3)	$3.6 \pm 0.1$ (3)
<b>1i</b>	$3.5 \pm 1.0$ (2)	$3.5 \pm 0.2$ (2)	$4.4 \pm 1.4$ (2)	$4.0 \pm 1.0$ (2)	$3.3 \pm 0.5$ (2)	$3.2 \pm 0.4$ (2)

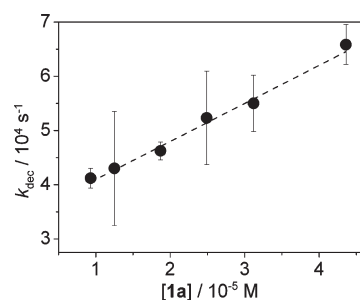
<sup>a</sup> The decay of the signal following 355 nm excitation of **1** ( $c \sim 3 \times 10^{-3}$  M) in the solvents given (IPA = propan-2-ol).  $\lambda = 550$  and 670 nm was used to follow the kinetic traces of  $\text{PA}^\bullet$  and  $\text{XAN}^\bullet$ , respectively. <sup>b</sup> Data are the mean and standard deviations (the number of measurements is given in parentheses).

Scheme 12. Addition of  $\text{PA}^\bullet$  to 1,1-Diphenylethylene

sufficient concentration of the ketyl radical  $(\text{CH}_3)_2\text{C}^\bullet\text{OH}$  (entry 1, Scheme 11).

We selected the wavelengths of 550 and 670 nm to follow the kinetic traces of  $\text{PA}^\bullet$  and  $\text{XAN}^\bullet$ , respectively. The rise of both the 550 nm and 670 nm signals was faster than our apparatus response time (<5 ns; Figure S23a, Supporting Information). Therefore, it could not be mathematically reconciled with confidence. No additional slower rise of these signals could be resolved. This suggests that the C–S bond cleavage is either of the excited singlet or very short-lived triplet state origin. Such experimental findings are in agreement with those of Scaiano and co-workers who showed that triplet decay of 4-methoxy- $\alpha$ -bromoacetophenones does not contribute to formation of a 4-methoxyphenacyl radical.<sup>19</sup> The decays at both 550 and 670 nm were fitted with monoexponential functions (Figure S23b, Supporting Information). The corresponding rate constants ( $k_{\text{dec}}$ ) are summarized in Table 4. In the case of  $\text{PA}^\bullet$ , their magnitude is similar to that of 4-methoxy-substituted phenacyl radicals in the same solvents.<sup>19</sup> A rather different system, *S*-benzoyl *O*-ethyl xanthate, was investigated by Ajayaghosh and co-workers who have reported that two transients with the second-order decay rate constants, monitored at  $\lambda = 650$  nm and expressed as  $2k/\varepsilon = 7.9 \times 10^6$  and  $4.0 \times 10^7$  cm s<sup>-1</sup>, respectively, are insensitive to the presence of the triplet quenchers, such as 2,5-dimethyl-2,4-hexadiene, azulene, or ferrocene, but are affected by the presence of a radical trapping agent TEMPO.<sup>60</sup> The rate constant magnitudes were also found to be dependent on the type of the substituents. Plyusnin and co-workers have also detected the transient absorption spectra of the xanthic acid radical in the same region ( $\lambda_{\text{max}} = 650$  nm).<sup>48</sup> Our calculation further supports this experimental observation (Figure S22, Supporting Information). In this work, the observed decay rate constants, summarized in Table 4, were found to be independent of the oxygen concentration, the presence of propan-2-ol, or the phenyl ring substitution.

In addition to the experiments with vinyl acetate (Scheme 7), 1,1-diphenylethylene (**17**) was used as an excellent radical



**Figure 2.** Plot of the  $\text{PA}^\bullet$  decay rate constants (monitored at 550 nm) against the concentration of **1a** in degassed acetonitrile with a laser excitation at 266 nm. The standard deviation from three independent measurements is given for each point. The line is a weighted linear fit to the experimental data described by the equation  $y = (3.2 \pm 0.3) \times 10^4 + (7 \pm 1) \times 10^8 \times x$ .

scavenger of  $\text{PA}^\bullet$  generated from **1a**; in this case, with the aim of obtaining the rate constant of addition to an olefinic double bond (Scheme 12). Such a radical addition leads to a resonance-stabilized and readily detectable radical **18** with two characteristic intense absorption bands ( $\lambda \sim 330$  and  $\sim 500$  nm).<sup>19</sup> The addition process was monitored by the decay of  $\text{PA}^\bullet$  at 550 nm. An inherent decay rate of  $\text{PA}^\bullet$  in a given solvent ( $k_0$ ) and a bimolecular rate constant of addition ( $k_{\text{add}}$ ) of  $\text{PA}^\bullet$  to **17** is extracted from a linear dependence of  $k_{\text{dec}}$  of  $\text{PA}^\bullet$  (at 550 nm) on the concentration of **17** ( $k_{\text{dec}} = k_0 + k_{\text{add}} [\text{17}]$ ). A plot of the decay rate constants of  $\text{PA}^\bullet$  formed from **1a** ( $k_{\text{dec}}$ ) against the concentration of **17** (giving the addition rate constant of the process) can be found in the Supporting Information (Figure S24). The values of  $k_0 = (5.6 \pm 0.4) \times 10^4 \text{ s}^{-1}$  and  $k_{\text{add}} = (1.1 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  were obtained in acetonitrile, whereas  $k_0 = (2.6 \pm 0.3) \times 10^4 \text{ s}^{-1}$  and  $k_{\text{add}} = (5.5 \pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  were obtained in propan-2-ol using weighted linear regression. This is in a good agreement with  $k_{\text{add}} = 9.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  found for *p*-methoxyphenacyl radical addition to **17** in acetonitrile.<sup>19</sup> The decay rate constants observed at 550 nm corresponds reasonably well with that of a rise of the 500 nm signal associated with formation of **18**.

A plot of the decay rate constant ( $k_{\text{dec}}$ ) of  $\text{PA}^\bullet$  formed by photolysis of **1a** against the **1a** concentration in acetonitrile gave a linear dependence (Figure 2). Linear ( $k_{\text{dec}} = k_0 + k_{\text{add}} [\text{1a}]$ ) regression of the experimental data then provided the rate constants values for  $\text{PA}^\bullet$  addition to **1a**,  $k_{\text{add}} = (7 \pm 1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , and  $\text{PA}^\bullet$  decay in pure acetonitrile,  $k_0 = (3.2 \pm 0.3) \times 10^4 \text{ s}^{-1}$ . Because acetophenone was not produced in the irradiated **1a** acetonitrile

solution (Table 1), we assume that the only productive reaction of  $\text{PA}^\bullet$  with **1a** is the addition to the C=S bond.

Interestingly, the decay rate constants obtained by flash photolysis (Table 4) are independent of the propan-2-ol concentration. This is not surprising for  $\text{XAN}^\bullet$ , which reacts with propan-2-ol endothermically (entry 2, Scheme 11), provided that it does not participate in the RAFT process. From the perspective of this process involving **1**, the scavenging of the phenacyl radicals by propan-2-ol, associated with increased reaction quantum yields, must be slower than  $\text{PA}^\bullet$  addition to **1** (Schemes 8 and 11). Indeed, the rate constant of the H-atom abstraction of 4-methoxyphenacyl radical from propan-2-ol was reported to be  $k = 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>19</sup> whereas the addition reaction of  $\text{PA}^\bullet$  to **1a** is  $(7 \pm 1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (vide supra). This is also in accord with our observation that cross-coupling products (Scheme 10) are formed nearly as efficiently as acetophenones in propan-2-ol. Since a RAFT process keeps very low  $\text{PA}^\bullet$  concentrations in the solution,  $k_0$  should, in fact, represent the upper-bound out-of-cage recombination rate constant,  $k_{\text{rec}}$  (Scheme 8), the process occurring with the quantum yield of  $\Phi_0 = \Phi_{\text{max}} - \Phi_{\text{dis}} = 0.35$ , where  $\Phi_{\text{max}}$  is the maximum quantum yield in the presence of thiophenol and  $\Phi_{\text{dis}}$  is the disappearance quantum yield of **1a** in acetonitrile (Table 1).

The rate constant,  $k_{\text{add}} = 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , of the addition of *tert*-butyl radical to *tert*-butyl dithiobenzoate has recently been determined by Chernikova and co-workers using EPR spectroscopy.<sup>61</sup> Buback and co-workers studied the kinetics of polymerization process using ethyl *S*-thiobenzoate-2-thiopropionate as the RAFT agent by time-resolved EPR spectroscopy.<sup>62</sup> Predici simulation of experimental data gave the rate constants  $k_{\text{add}}$  and  $k_{\text{fr}}$  with the values of  $1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $4.7 \text{ s}^{-1}$ , respectively, at  $-40^\circ \text{C}$ . Estimation of the fragmentation rate constant at  $60^\circ \text{C}$  resulted in a fast fragmentation step with  $k_{\text{fr}} \sim 10^4 \text{ s}^{-1}$ . However, Chernikova showed that fragmentation is very slow ( $k_{\text{frag}} = 8 \times 10^{-3} \text{ s}^{-1}$ ) at pre-equilibrium conditions at  $20^\circ \text{C}$ .<sup>61</sup> In addition, there is much simulation data available which supports either the slow or fast fragmentation steps.<sup>63,64</sup> Quantum chemical calculations showed that the rate of this step is strongly affected by the structure of a RAFT agent possessing good radical stabilizing groups (to slow down the fragmentation).<sup>63,65,66</sup> This motivated us to attempt to measure the fragmentation step rate for our system; unfortunately, we have been unable to detect any signal corresponding to **11**, which would allow us to determine  $k_{\text{fr}}$ .

**S-Phenacyl Xanthates as Polymerization Photoinitiators.** Xanthates have already been proven to be very useful in the synthesis of block polymers through a controlled radical polymerization.<sup>3,9–15,49–51,67,68</sup> Here we carried out a preliminary experiment to show that *S*-phenacyl xanthates can also serve as photoinitiators in polymerization reactions. In the first experiment, a solution of methyl methacrylate (**19**; a 5 M solution in benzene) containing the xanthate **1i** ( $5 \times 10^{-3} \text{ M}$ ) was photolyzed at  $\lambda > 290 \text{ nm}$  (Scheme 13). The polymerization was monitored by  $^1\text{H}$  NMR (peak broadening; Figure S20, Supporting Information). The presence of the thiocarbonylthiyl group in the polymer was evident from weak resonance signals observed at  $\delta = 4.65$  and  $1.46 \text{ ppm}$ , while the phenacyl-group aromatic signals were found at  $\delta = 6.97$  and  $7.93 \text{ ppm}$  along with  $\delta = 3.91 \text{ ppm}$  of the *p*-methoxy group. These results demonstrate that the phenacyl radicals produced from **1i** upon irradiation add to the double bond of **19** to initiate the polymerization. The inability of  $\text{XAN}^\bullet$  to initiate polymerization and its high tendency to participate in bimolecular termination reactions have already

### Scheme 13. **1i** as a Polymerization Photoinitiator

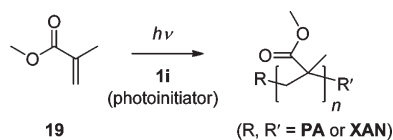


Table 5. Photopolymerization of Methyl Methacrylate<sup>a</sup>

initiator	[initiator] <sup>b</sup> /M	$M_n^c$	$M_w/M_n^c$
<b>1i</b>	0.01	3800	1.32
<b>1i</b>	0.02	2180	1.38
phenacyl bromide	0.02	1600	1.43

<sup>a</sup> Solution of methyl methacrylate (5 M) in benzene irradiated at  $\lambda > 290 \text{ nm}$ . <sup>b</sup> Initiator concentration. <sup>c</sup> Determined by MALDI-TOF.

been explained in the literature.<sup>69,70</sup> It can act as a scavenger for primary radicals, and thus control over the molecular-weight distribution of the resulting polymer. Alternatively, one can anticipate the involvement of an active RAFT process in the polymerization. Such a complex process will thus produce an end-capped polymers with the terminal thiocarbonylthiyl groups, similar to those synthesized using a *S*-benzoyl *O*-ethyl xanthate initiator by Zard and co-workers before.<sup>3,5</sup> Indeed, this type of polymer was determined in our NMR experiment (Scheme 13).

Polydispersed poly(methyl methacrylate) was then synthesized using either **1i** or phenacyl bromide as a photoinitiator (Table 5), and the MALDI-TOF MS spectra (Figure S25, Supporting Information) of the polymer were obtained according to the method described by Becer and co-workers.<sup>71</sup> The polydispersity index was found to be independent of initiator **1i** concentration in the range of 0.01–0.02 M ( $M_w/M_n \sim 1.35$ ), and its value is comparable to that reported by Ajayaghosh and Francis who used *S*-methacryloyl *O*-ethyl xanthate as an initiator of the polymerization of methyl methacrylate.<sup>67,68</sup> This number is below the theoretical value for a conventional free radical polymerization (i.e.,  $M_w/M_n < 1.5$ ).<sup>67</sup> In the case of phenacyl bromide, the index  $M_w/M_n = 1.43$  is only a little higher. These results are preliminary and need to be confirmed by additional studies.

## CONCLUSIONS

*S*-Phenacyl xanthates are photochemically active compounds which undergo homolytic scission of the C–S bond in the primary step. The radical fragments can recombine to form symmetrical 1,4-diketones and xanthogen disulfides in high to moderate chemical yields in chemically inert solvents. On the other hand, the radicals are efficiently trapped by hydrogen-atom donors to form acetophenones along with xanthic acids, which are in situ converted to the corresponding alcohols in high chemical yields. As a result, *S*-phenacyl xanthates can be synthesized from readily accessible material and be utilized as photo-removable protecting groups for alcohols analogously to phenacyl carbonates.<sup>72</sup> It is shown that the phenacyl radical fragments add to the thiocarbonyl group of the parent xanthate. This addition is reversible; the intermediate can fragment to form the same radical because the radical intermediate is a symmetrical molecule. *S*-Phenacyl xanthates can thus serve as photoinitiators and RAFT/MADIX agents in polymerization reactions at the



same time. The primary photophysical steps occurring after excitation of *S*-phenacyl xanthates are currently under investigation in our laboratory.

## EXPERIMENTAL SECTION

**Materials and Methods.** The reagents and solvents of the highest purity available were used as purchased or purified/dried by standard procedures when necessary. Phenacyl bromide and its derivatives were prepared according to the literature.<sup>73,74</sup> 1,4-Diketones were prepared according to a known procedure,<sup>75</sup> and were used as analytical standards. Organic solvents were purified by distillation through a vacuum-sealed column (70 cm) packed with glass detritus.

NMR spectra were recorded on a 300 MHz spectrometer and were calibrated to the residual peak of a solvent. Mass spectra were recorded on a GC-coupled (30-m DB-XLB column) mass spectrometer in a positive mode with EI. HRMS data were obtained on a UPLC/MS-TOF apparatus equipped with an ESI interface and a C-18 (1.7  $\mu\text{m}$ , 2.1  $\times$  50 mm) column, using an ammonium carbonate (0.005 M)/methanol mobile phase. High-performance liquid chromatography was performed on a chromatograph equipped with a C-18 column and a UV-vis detector. UV spectra were obtained with matched 1.0 cm quartz cells. Preparative column chromatography procedures were performed on silica. MALDI-TOF mass spectra measurements were carried out with an instrument operating in a linear positive arrangement with 25 kV acceleration voltage.

**Synthesis of Sodium *O*-(3-Phenylpropyl) Carbonodithioate (3b) and Sodium *O*-(2-Phenoxyethyl) Carbonodithioate (3c).** 3-Phenylpropan-1-ol (10 g, 72.5 mmol) or 2-phenoxyethanol (10 g, 65.79 mmol) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in oil, 2.9 g, 72.5 mmol) in dry diethyl ether (100 mL) over a period of 10 min. After the hydrogen evolution was complete, CS<sub>2</sub> (9.6 mL, 152.17 mmol) was added dropwise over a period of 15 min, and the reaction mixture was stirred for 45 min at 20 °C. A white precipitate was filtered out, dried, and used in the synthesis of the corresponding xanthates **1** without further purification. Note: **3a** (potassium ethyl xanthogenate) was purchased; **3b,c** are known compounds.<sup>76</sup> They were used in the subsequent synthesis without purification.

**General Procedure for the Synthesis of 1.** NaI (1.5 g, 10 mmol) was added to a stirred solution of phenacyl bromide (**2a-f**; 10 mmol) in dry acetone (15 mL) at 20 °C, and the mixture was stirred for 10 min. Then the corresponding xanthogenate **3** (12 mmol) was added in small portions over a period of 5 min. The resulting mixture was stirred at 20 °C for approximately 20 min (the reaction completion was followed by TLC). Acetone was evaporated and the residue was extracted with dichloromethane (3  $\times$  30 mL), washed with brine, and the solution was dried over Na<sub>2</sub>SO<sub>4</sub>. Dichloromethane was evaporated under reduced pressure to give the title product in good chemical yields (88–95%). The xanthogenates **1** were recrystallized from hot ethanol or methanol prior to their use in the laser flash studies. The compounds **1a**, **b**, and **i**<sup>77</sup> and **3**<sup>73,74</sup> have been characterized previously.

**S-(2-(3,4-Dimethoxyphenyl)-2-oxoethyl) *O*-Ethyl Carbonodithioate (1c).** Yield: 90%. White solid. Mp: 73–74 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.40 (t, 3H,  $J = 7.1$  Hz), 3.93 (s, 3H), 3.96 (s, 3H), 4.63 (s, 2H), 4.61–4.68 (q, 2H), 6.92 (d, 1H,  $J = 8.4$  Hz), 7.55 (d, 1H,  $J = 2.0$  Hz), 7.68 (dd, 1H,  $J_1 = 2.0$  Hz,  $J_2 = 8.4$  Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 13.9, 43.4, 56.3, 56.3, 70.8, 110.4, 110.8, 123.5, 129.2, 149.4, 154.1, 191.1, 213.7. HRMS (APCI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M + H<sup>+</sup>) 301.0563, found 301.0560. UV–VIS:  $\epsilon_{313}$  (acetonitrile) = 7780.32 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>,  $\epsilon_{313}$  (CH<sub>3</sub>OH) = 8608.92 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**S-(2-(2,5-Dimethylphenyl)-2-oxoethyl) *O*-Ethyl Carbonodithioate (1d).** Yield: 92%. White crystalline solid. Mp: 63–64 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.40 (t, 3H,  $J = 7.1$  Hz), 2.40 (s, 3H), 2.46 (s, 3H), 4.57 (s, 2H), 4.65 (q, 2H,  $J = 7.1$  Hz), 7.17 (d, 1H,  $J = 7.8$  Hz), 7.24 (d, 1H,  $J = 7.9$  Hz), 7.57 (s, 1H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.9, 20.9, 21.1, 45.9, 70.8, 129.4, 132.2, 132.9, 135.4, 135.9, 136.5, 195.7, 213.7. HRMS (APCI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>17</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> (M + H<sup>+</sup>) 269.0664, found 269.0661. UV–VIS:  $\epsilon_{313}$  (acetonitrile) = 780 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>,  $\epsilon_{313}$  (CH<sub>3</sub>OH) = 813 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**S-(2-(2,5-Dimethylphenyl)-2-oxoethyl) *O*-(3-Phenylpropyl) Carbonodithioate (1e).** Yield: 88%. White crystalline solid. Mp: 40–41 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 2.11–2.21 (m, 2H), 2.42 (s, 3H), 2.50 (s, 3H), 2.77 (t, 3H), 4.60 (s, 2H), 4.64 (t, 2H,  $J = 6.5$  Hz), 7.19–7.35 (m, 7H), 7.60 (s, 1H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 20.8, 20.9, 29.8, 32.1, 45.8, 73.9, 126.1, 128.4, 128.5, 129.3, 132.1, 132.8, 135.3, 135.8, 136.3, 140.8, 195.5, 213.6. HRMS (APCI<sup>+</sup>): calcd for C<sub>20</sub>H<sub>23</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> (M + H<sup>+</sup>) 359.1134, found 359.1136.

**S-(2-(4,5-Dimethoxy-2-methylphenyl)-2-oxoethyl) *O*-Ethyl Carbonodithioate (1f).** Yield: 89%. White solid. Mp: 85–86 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.40 (t, 3H,  $J = 7.1$  Hz), 2.50 (s, 3H), 3.92 (2s, 6H), 4.57 (s, 2H), 4.64 (q, 2H,  $J = 7.1$  Hz), 6.75 (s, 1H), 7.35 (s, 1H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.7, 21.6, 45.7, 55.9, 56.4, 70.7, 112.8, 114.8, 127.9, 134.4, 146.4, 152.1, 193.5, 213.9. HRMS (APCI<sup>+</sup>): calcd for C<sub>14</sub>H<sub>19</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup> (M + H<sup>+</sup>) 315.0719, found 315.0716. UV–VIS:  $\epsilon_{313}$  (acetonitrile) = 7675 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>,  $\epsilon_{313}$  (CH<sub>3</sub>OH) = 8272 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**S-(2-Oxo-2-phenylethyl) *O*-(2-Phenoxyethyl) Carbonodithioate (1g).** Yield: 92%. Pale white solid. Mp: 56–57 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 4.32 (t, 2H), 4.70 (s, 2H), 4.95 (t, 2H), 6.93 (d, 2H,  $J = 8.0$  Hz), 7.02 (t, 1H,  $J = 7.3$  Hz), 7.33 (m, 2H), 7.50 (t, 2H,  $J = 7.6$  Hz), 7.63 (t, 1H,  $J = 7.3$  Hz), 8.03 (d, 2H,  $J = 7.4$  Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 43.5, 65.1, 72.1, 114.6, 121.3, 128.4, 128.8, 129.5, 133.7, 135.7, 158.3, 192.1, 213.1. HRMS (APCI<sup>+</sup>): calcd for C<sub>17</sub>H<sub>17</sub>O<sub>3</sub>S<sub>2</sub><sup>+</sup> (M + H<sup>+</sup>) 333.0614, found 333.0612.

**S-(2-(3,4-Dimethoxyphenyl)-2-oxoethyl) *O*-(2-Phenoxyethyl) Carbonodithioate (1h).** Yield: 83%. Pale white solid. Mp: 103–104 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.94 (s, 3H), 3.96 (s, 3H), 4.34 (t, 2H), 4.65 (s, 2H), 4.94 (t, 3H), 6.90 (m, 3H), 7.01 (t, 1H,  $J = 7.4$  Hz), 7.31 (m, 2H), 7.56 (d, 1H,  $J = 2.0$  Hz), 7.67 (dd, 1H,  $J_1 = 2.0$  Hz,  $J_2 = 8.4$  Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 43.0, 56.0, 56.1, 65.1, 72.1, 110.1, 110.4, 114.6, 121.3, 123.3, 128.8, 129.5, 149.2, 153.9, 158.3, 190.6, 213.2. HRMS (APCI<sup>+</sup>): calcd for C<sub>19</sub>H<sub>21</sub>O<sub>5</sub>S<sub>2</sub><sup>+</sup> (M + H<sup>+</sup>) 393.0830, found 393.0830.

**Preparative Irradiation of 1.** A solution of **1a-f** ( $c = 10^{-2}$  M) in dry acetonitrile or propan-2-ol (100 mL) was degassed by purging with argon for 15 min and then irradiated with a 450-W medium pressure lamp through a Pyrex glass sleeve ( $\lambda > 290$  nm) for ~15 h. The irradiation was stopped when the conversion reached 60–65% (HPLC). The solvent was removed under reduced pressure and the crude mixture was subjected to column chromatography (*n*-hexane/ethyl acetate) to obtain the products (**4a-e**, **5**, and **6a-e**). Unreacted starting material was recycled for further use. The compounds **4a**,<sup>78</sup> **b**,<sup>79</sup> and **5**,<sup>80</sup> have been characterized previously. The ketones **6a-e** are commercially available compounds.

**1,4-Bis(3,4-dimethoxyphenyl)butane-1,4-dione (4c).** Yield: 43%. White solid. Mp: 178–176 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.41 (s, 4H), 3.93 (s, 6H), 3.95 (s, 6H), 6.91 (d, 2H,  $J = 8.4$  Hz), 7.57 (d, 2H,  $J = 2.0$  Hz), 7.71 (dd, 2H,  $J_1 = 2.0$  Hz,  $J_2 = 8.4$  Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 32.3, 56.0, 56.1, 110.1, 110.3, 122.8, 130.1, 149.0, 153.4, 197.5. HRMS (APCI<sup>+</sup>): calcd for C<sub>20</sub>H<sub>23</sub>O<sub>6</sub><sup>+</sup> (M + H<sup>+</sup>) 359.1489, found 359.1487.

**1,4-Bis(2,5-dimethylphenyl)butane-1,4-dione (4d).** Yield: 32%. White solid. Mp: 82–83 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 2.42 (s, 3H), 2.49 (s, 3H), 3.37 (s, 4H), 7.17 (d, 2H,  $J = 7.7$  Hz), 7.23 (d, 2H,  $J = 7.3$  Hz), 7.61 (s, 2H); NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 20.7, 20.9, 35.6, 129.1, 131.8, 132.0, 134.8, 135.2, 137.8, 202.8. HRMS (APCI<sup>+</sup>): calcd for C<sub>20</sub>H<sub>23</sub>O<sub>2</sub><sup>+</sup> (M + H<sup>+</sup>) 295.1693, found 295.1693.

**Cross-Coupling Experiment.** An equimolar solution of both **1c** and **1g** ( $c = 5 \times 10^{-3}$  M) in acetonitrile (100 mL) or a propan-2-ol/acetonitrile mixture (9:1; 100 mL) was degassed by purging with argon for 15 min and then irradiated through a Pyrex glass sleeve ( $\lambda > 290$  nm). The product formation was followed on HPLC. The compounds **1a** and **1i** started to be formed in the first minutes of irradiation. Continuous irradiation (for >25 min) resulted in equal (photostationary) amounts of all four xanthates (**1a**, **1c**, **1g**, and **1h**).

**Irradiation of 1a with Vinyl Acetate.** A degassed solution of **1a** (500 mg, 2.08 mmol) and vinyl acetate (**9**, 192  $\mu$ L, 2.08 mmol) in dry acetonitrile (20 mL) was irradiated for 2.5 h ( $\lambda_{\text{irr}} > 313$  nm). Irradiation was stopped when the consumption of **1a** reached 70%, and the solvent was removed under reduced pressure. The product **10** was separated from the reaction mixture by column chromatography (*n*-hexane/ethyl acetate) in 55% yield.

**1-((Ethoxycarbonothioyl)thio)-4-oxo-4-phenylbutyl Acetate (10).** Yield: 55%. White liquid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.41 (t, 3H,  $J = 7.1$  Hz), 2.06 (s, 3H), 2.40 (ddd, 2H,  $J_1 = 2.5$  Hz,  $J_2 = 6.9$  Hz,  $J_3 = 9.0$  Hz), 3.14 (dt, 2H,  $J_1 = 2.5$  Hz,  $J_2 = 7.1$  Hz), 4.63 (m, 2H), 6.74 (t, 1H,  $J = 6.4$  Hz), 7.46 (t, 2H,  $J = 7.5$  Hz), 7.57 (t, 2H,  $J = 7.3$  Hz), 7.96 (d, 2H);  $^13\text{C NMR}$  (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 13.6, 20.8, 28.6, 34.2, 70.3, 80.3, 128.0, 128.6, 133.2, 136.6, 169.3, 197.9, 209.9. HRMS (APCI<sup>+</sup>): calcd for  $\text{C}_{15}\text{H}_{19}\text{O}_4\text{S}_2^+$  ( $M + \text{H}^+$ ) 327.0725, found 327.0725.

**Photoinitiated Polymerization of 19.** A solution of methyl methacrylate (5 M) in dry benzene containing **1i** or phenacyl bromide (as a photoinitiator) was degassed by purging with argon for 15 min and irradiated through a Pyrex glass ( $\lambda > 290$  nm) for 1 h. In the case of one sample (utilizing **1i**,  $c = 5 \times 10^{-3}$  M), the reaction mixture was poured into methanol, and the precipitates were collected by filtration, washed with methanol, dried at 40 °C under reduced pressure, and dissolved in  $\text{CDCl}_3$  for an NMR analysis (Figure S20, Supporting Information). The other samples (utilizing either **1i**,  $c = 0.01$  or 0.02 M, or phenacyl bromide,  $c = 0.02$  M) were processed as follows: The irradiated mixture was poured into methanol and the precipitates were collected by filtration, dissolved in chloroform (25 mL), and reprecipitated by addition of methanol (100 mL). The resulting solid was filtered and dried in at 40 °C under reduced pressure. The samples were adjusted according to a procedure described by Becer and co-workers<sup>71</sup> and analyzed by MALDI-TOF.

**Quantum Yield Measurements.** The quantum yields were obtained on an optical bench consisting of a high-pressure 350 W or 450 W UV lamp, a 1/8 m monochromator with 200–1600 nm grating set to 313 nm, and a 1.0-cm matched quartz cell containing a degassed solution purging with argon for 10 min. The light intensity was detected by an Si photodiode detector (UV enhanced) with a multifunction optical power meter. The concentration of the sample solutions, containing methyl benzoate ( $c = 10^{-3}$  M) as an internal standard for HPLC analyses, was approximately  $5 \times 10^{-3}$  M. Valerophenone ( $\Phi$  of acetophenone formation is 0.33 in hexane<sup>37</sup>) was used as an actinometer. The reaction conversions were always kept below 10% to avoid the interference of photoproducts. The relative standard deviations for multiple (at least five) samples were below 10% in all measurements. (**1a**, UV-vis:  $\epsilon_{313}$  (acetonitrile) = 496  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ,  $\epsilon_{313}$  ( $\text{CH}_3\text{OH}$ ) = 479  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ,  $\epsilon_{313}$  (propan-2-ol) = 646  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ).

**Laser Flash Photolysis Studies.** The nanosecond laser flash photolysis (LFP) setup was operated in a right angle arrangement of the pump and probe beams. Laser pulses of  $\leq 700$  ps duration at 355 nm (120–200 mJ) or 266 nm (30–80 mJ) were obtained from a Nd:YAG laser and were dispersed over the 4 cm optical path of the quartz cell by a cylindrical concave lens. The absorbance of the sample solution was adjusted to 0.3–0.5 in a 1 cm cuvette at the wavelength of excitation. A pulsed 75 W xenon lamp was used as the source of probe white light. Kinetic (a photomultiplier) and spectrographic detection (an ICCD camera) of the transient absorption was available. Measurements were

done at ambient temperature ( $22 \pm 2$  °C). Samples were degassed by repeated freeze–thaw cycles under reduced pressure (5 Pa).

**Quantum Chemical Calculations.** The calculations were performed with the Gaussian 09 package (revision A.02) of programs.<sup>81</sup> Geometries were fully optimized at the RB3LYP/6-31+G(d) level of theory. For all stationary points, harmonic vibrational frequencies were computed at RB3LYP/6-31+G(d) to obtain the ZPVE which was scaled by 0.9857.<sup>42</sup> Single-point energies at the B3LYP geometries were computed at the UM06-2X/6-311+G(2df,p) level of theory. The resulting enthalpies are given at 0 K (E + scaled ZPVE). The electronic transitions were calculated using a time-dependent density functional theory (TD-DFT) approach employing the B3LYP functional with the 6-31G(d) basis set. The UV–vis spectra were obtained using a linearized harmonic reflection principle as employed by Slavicek and co-workers.<sup>82</sup>

## ■ ASSOCIATED CONTENT

**Supporting Information.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of new compounds, laser flash photolysis data, theoretical absorption spectra of the radicals, and MALDI-TOF MS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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