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Cascade transformations involving thiocarbonyls: photoassisted access to bicyclic thiiranes and oxapentalenes

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Cascade transformations involving thiocarbonyls: photoassisted access to bicyclic thiiranes and oxapentalenes

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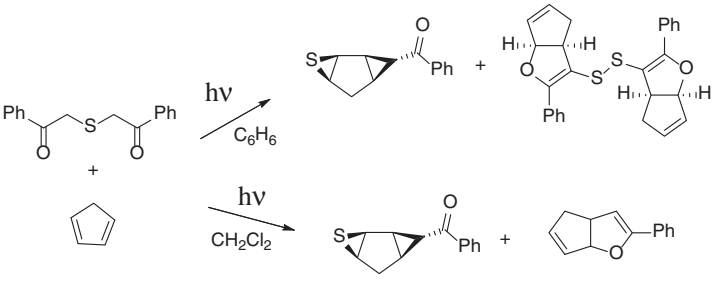
Phenyl(thio)glyoxal, generated via the Norrish type II fragmentation of phenacyl sulfide, undergoes known [4+2] cycloaddition with dienes and the photoactive product is further converted via the interrupted Paternò–Büchi reaction channel into a dihydrofuran derivative possessing the oxapentalene core. The reaction can be carried out in one step as the chromophores are nearly identical and the extended cascade is initiated with the same UV LED source.



Keywords: thiocarbonyl compounds; Bunte salts; phenyl(thio)glyoxal; Norrish II photofragmentation; interrupted Paternò–Büchi reaction; dihydrofuran; oxapentalene

1. Introduction

In 1982, Vedejs noted that thioaldehydes are virtually ignored in synthesis because of their propensity to polymerization. Yet the high intrinsic reactivity and polarizability of the thiocarbonyl group offered a potential tool for the formation of new carbon–carbon bonds with an excellent control of regiochemistry, especially in [4 + 2] cycloadditions with dienes. Traditionally, thioaldehydes are prepared via the elimination of HY from R(R′)CH–SY, where Y can be SO_2ONa (Bunte salts) (*1*), SO_2R (thiosulfonates) (*2*), or N-phthaloyl (sulfonamides) (*3*). Thus generated, they can

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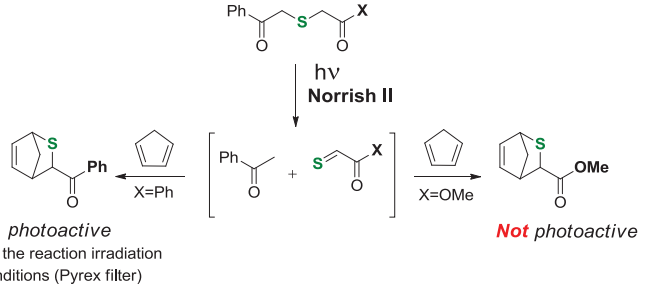
be trapped by reactive dienes, albeit the yields in such reactions were reported to be moderate to low.

To alleviate this deficiency, Vedejs developed a photochemical method for the generation of thioaldehydes via a Norrish type II fragmentation in phenacyl sulfides (see (*4*) and references therein). While the photochemical fragmentation of phenacyl sulfides was known before Vedejs' studies, his photoprecursors were chosen to additionally stabilize the intermediate 1,4-diradical with a carbonyl or a cyano group, which generally improved the selectivity of hydrogen abstraction and the overall yields. For example, phenacyl sulfides shown in Scheme 1 were readily prepared according to existing literature procedures and irradiated to generate thioaldehydes, which underwent [4 + 2] cycloaddition with cyclopentadiene to give the respective thianorbornenes. This worked well for the shown methoxycarbonyl derivative (X=OMe, right). However, the method was not ideal for the photogeneration and cycloadditions of thiacarbonyl compounds conjugated to benzoyl (X=Ph, left), because the same chromophore, the benzoyl group, was incorporated in the resulting Diels–Alder adduct, which, the authors caution, is "destroyed by prolonged irradiation" (*4*(a)).



Scheme 1. Vedejs' photochemical method for the generation of thioaldehydes via a Norrish type II fragmentation.

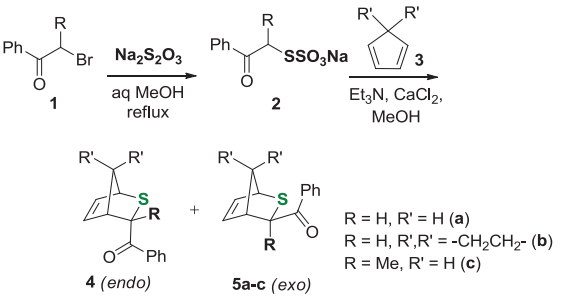
In view of our own interest in Paternò–Büchi reactions in polycyclic systems with subsequent retro-[2 + 2] protolytic ring opening (*5*), we were wondering if this reported "destruction" upon extended irradiation can be, in fact, a useful transformation that the authors simply overlooked.

In this paper, we probe this hypothesis by (i) generating the Diels–Alder adduct of phenyl(thio)glyoxal via non-photochemical means and examining the photochemistry of the adduct and (ii) incorporating the two photochemical steps into a single cascade and carrying out a "one-pot" photochemical generation of the thioaldehyde, its [4 + 2] cycloaddition, and subsequent photo-rearrangement of the [4 + 2] cycloadduct – all starting from bis(phenacyl)sulfide.

2. Results and discussion

Our first objective was to generate a potentially photoactive [4 + 2] cycloadduct of a thioaldehyde and a diene via a non-photochemical route to avoid premature secondary phototransformation of the cycloadduct. For this reason, we chose Kirby's Bunte salts-based method for the generation of phenyl(thio)glyoxal, which was produced by base-catalyzed sulfite elimination in the presence of cyclopentadiene or *sprio*-2,4-heptadiene to yield thiabicyclo/tricyclo alkenes, possessing a photoactive benzoyl pendant, as shown in Scheme 2. The *endo*/*exo* ratio in the case of cyclopentadiene was 4.1:1, slightly higher than that reported by Vedejs (3:1) (*4*(a)). The Bunte salts were

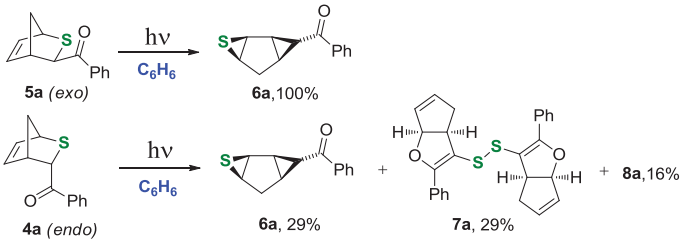
prepared according to literature procedures by treating phenacyl bromides with sodium thiosulfate in aqueous methanol.



Scheme 2. Synthesis of thiabicycloheptenes **4** (*endo*) and **5** (*exo*).

It is easy to see that only one photoreactivity mode is available to *exo*-thianorbornenes **5**, that is, the C–S bond fragmentation, because the α-sulfide bridgehead hydrogen is not accessible for abstraction and the double bond is not accessible for the *exo*-benzoyl group either. The excited carbonyl group in *endo*-isomers **4**, while can also expel the sulfanyl radical, has another option – to attack the double bond as in the Paternò–Büchi cycloaddition.

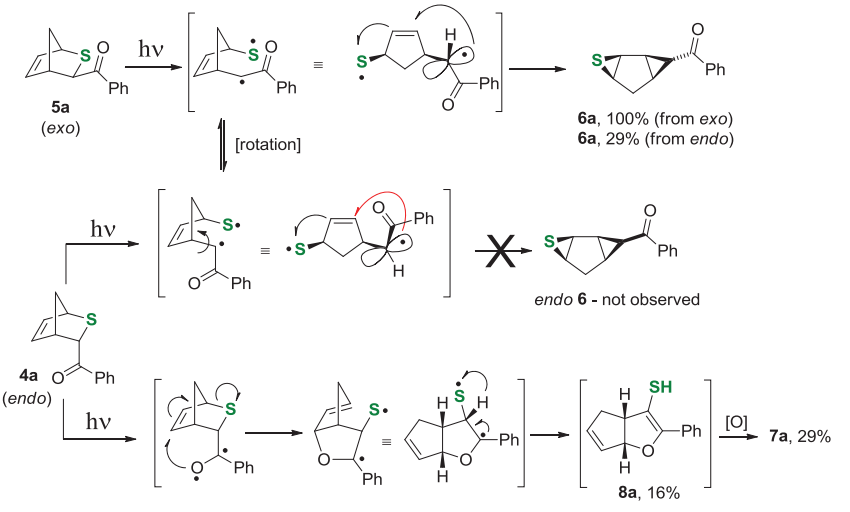
Irradiation experiments in benzene with a UV source (Rayonet, RPR-3500, broadband 300–400-nm or 365-nm UV LEDs) confirmed this hypothesis. Upon irradiation *in benzene*, e*xo*-photoprecursor **5a** yielded tricyclic thiirane **6** nearly quantitatively, whereas *endo*-precursor **4a** exhibited dual photoreactivity, furnishing both thiirane **6a** and disulfide **7a** (Scheme 3).



Scheme 3. Photoreactivity of the *exo*- and *endo*-cycloadducts **5a** and **4a** in benzene.

Our rationale for the formation of thiirane **6a** involves photoinduced BzC–S homolytic bond fragmentation followed by radical addition to the *endo*-cyclic double bond (Scheme 4), which probably occurs stepwise or, at least, asynchronously. Before the phenacyl radical reacts, it apparently has time to rotate, so both the *endo*-isomer and the *exo*-isomer produce the same *exo*-benzoyl-thiirane **6a**.

The mechanistic rationale for the oxapentalene channel starting from *endo*-isomer **4a** involves an interrupted Paternò–Büchi reaction, where the expulsion of the sulfanyl radical from the initially generated 1,4-diradical occurs faster than radical recombination forming the oxetane ring. Subsequent hydrogen migration, which amounts to disproportionation in the 1,3-diradical, yields the thiol and the disulfide. Alternatively, this disproportionation can involve intermolecular hydrogen transfer. The disulfide is formed in the presence of air, which is common for photochemical reactions of thiols. The NMR spectra at lower conversions show the formation of an intermediate possessing an H–C–O broad doublet similar to that of disulfide **7a**. We assume this intermediate



Scheme 4. Mechanistic rationale for photoinduced transformations of **4a** and **5a**.

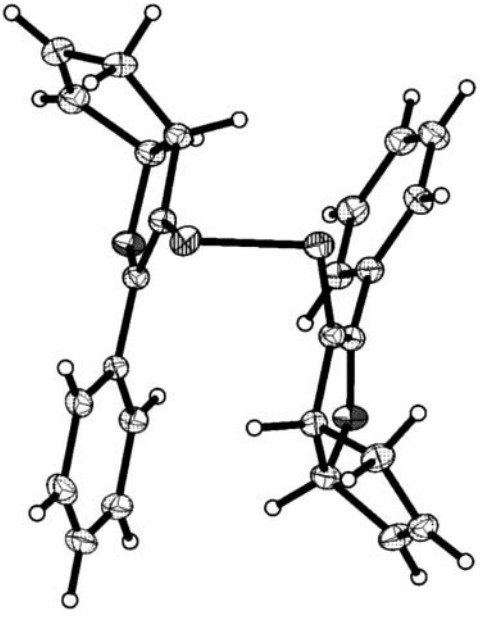


Figure 1. The ORTEP drawing of the X-ray structure of disulfide **7a**.

to be vinyl thiol **8a** (or its thioketone form), which is oxidized into disulfide **7a** under the reaction conditions.

The structure of disulfide **7a** was determined by X-ray (Figure 1).

The structure of thiirane **6a** was elucidated by NMR. The connectivities are supported by the COSY spectrum. The *exo*-stereochemistry of the benzyl group was determined based on the vicinal spin–spin coupling constants. Figure 2 shows the experimental and calculated proton spectra of **6a** for the two thiirane protons (3.77 and 3.58 ppm) and the α-benzoyl proton (3.19 ppm). The calculated values for the *trans*-vicinal spin–spin coupling constants involving the H–C–Bz proton and the other two protons in the cyclopropane ring in the *exo*-benzoyl-isomer are 3.9 and 3.0 Hz,

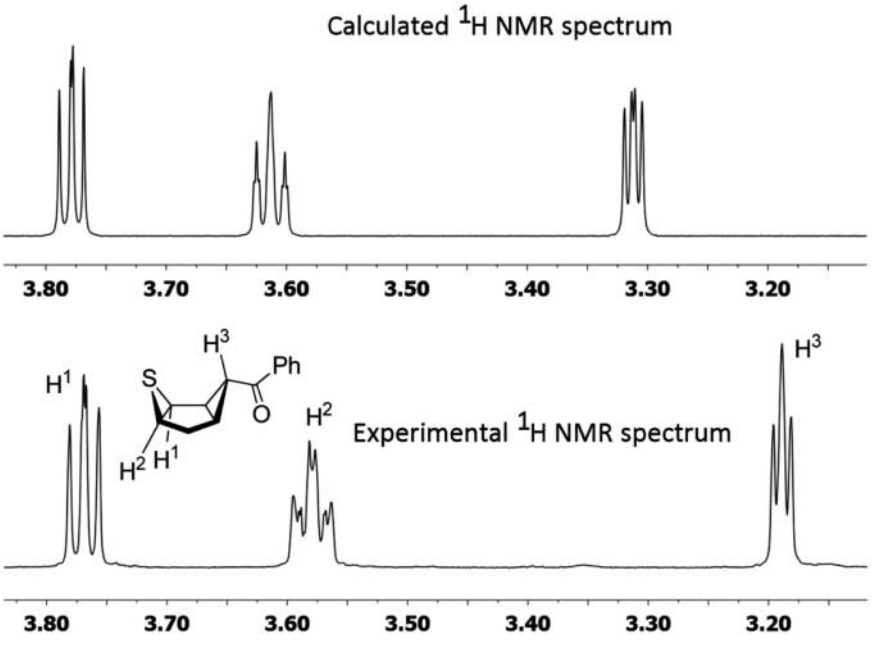
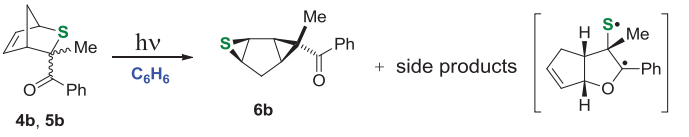


Figure 2. Experimental and calculated ^{1}H NMR spectra of **6a**.

whereas these calculated values for the *endo*-benzoyl-isomer are 8.9 and 9.2 Hz (*i.e.* vicinal *cis*-constants). Since the experimental vicinal constants of the α-benzoyl proton are approximately 3 Hz, we assigned *exo*-stereochemistry for the benzoyl group.

The structures were calculated at the B3LYP/6-311+G(d,p) level of theory. The isotropic components of the SCF GIAO magnetic shielding tensor were calculated at the mPW1PW91/6-311+G(d,p) level of theory and linearly corrected using the experimental values. The spin–spin coupling constants were computed using the Fermi contact terms as suggested by Bally and Rablen (*6*). However, these terms were scaled using our own parameterization scheme, obtained on a training set of approximately 200 experimental spin–spin coupling constants, which will be reported elsewhere. The RMSD for the predicted coupling constants in the training set was improved to 0.235 Hz, which allows for an unambiguous assignment of stereochemistry in the majority of cases.

Thioketones also undergo [4+2] cycloaddition to cyclopentadiene. For example, the reaction of the diene with 1-phenyl-2-thioxo-propan-1-one produces a mixture of *exo*-**5b** and *endo*-**4b** stereoisomers, which were irradiated under the same conditions as described above.

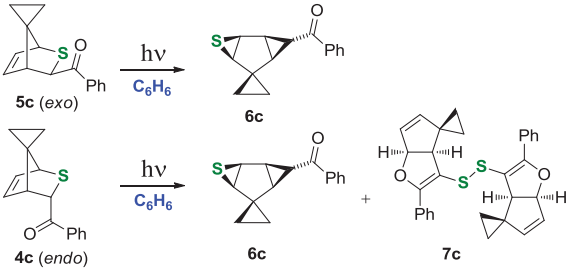


Scheme 5. Photochemistry of methyl derivatives **4b** and **5b**.

In this reaction, thiirane **6b** was the only dominating product, with no oxapentalene derivatives observed (Scheme 5). This can be explained by both (i) a weaker αC–S bond (expected to fragment much faster) and/or (ii) a methyl-induced less favorable conformation of the benzoyl group in the *endo*-isomer which slows the interrupted Paternò–Büchi channel. It is also conceivable that

the 1,3-diradical, shown in Scheme 5 in square brackets, is not capable of Me migration to sulfur and reverses to the starting material (or degrades). The major photoproduct **6b** is less stable than the parent thiirane **6a** and is degraded significantly upon extended irradiation.

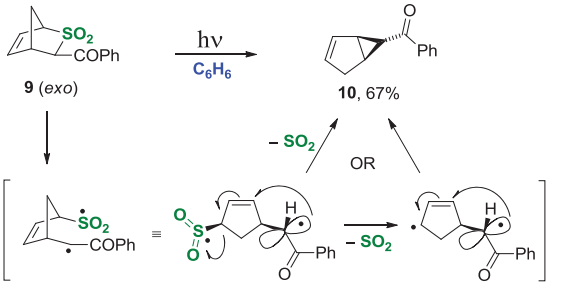
Spiro-photoprecursors **4c** and **5c** were obtained by reacting phenyl(thio)glyoxal, generated from Bunte salt **2**, with *spiro*-heptadiene as shown in Scheme 2. As it is abundantly clear from Scheme 6, their photoreactivity is similar to that of thianorbornenes **4a** and **5a**.



Scheme 6. *Spiro*-photoprecursors **4c** (*endo*) and **5c** (*exo*) exhibiting a similar photoreactivity.

It appears that the interrupted Paternò–Büchi reaction in *endo*-3-benzoyl-2-thianorbornenes is general.

We also explored the photochemistry of the corresponding sulfones, which were obtained by the oxidation of thianorbornenes **4a** and **5a** with *m*CPBA. Regrettably, the acidity of the C(3)-H proton prevented us from obtaining the *endo*-benzoyl epimer due to enolization and rapid conversion of the *endo*-isomer into the *exo-isomer*. The *exo*-isomer **9** undergoes the αC–SO_2 bond scission with subsequent extrusion of SO_2 either (i) assisted by the phenacyl radical via the allylic radical substitution or (ii) a two-step dissociative mechanism (Scheme 7).

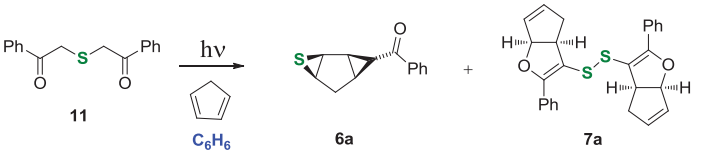


Scheme 7. The αC–SO_2 bond scission with subsequent extrusion of SO_2 in the case of *exo*-**9** isomer.

It is a matter of curiosity that under the irradiation conditions, we did not find any evidence for bicyclo[3.1.0]hexene **10** rearranging into the oxapentalene structure via the cyclopropane ring opening and closure at the oxygen radical center. However, all benzoylcyclopropanes are photoreactive and eventually degrade upon extended irradiation. In this particular case, we were able to drive the conversion to a maximum of 67%. Bicyclic photoproduct **10** was characterized by NMR. As in the case of thiirane **6a**, the *trans*-vicinal spin–spin constants of the H–C–Bz proton in **10** are predicted to be 2.7 Hz (experimental value is 3 Hz). The *cis*-vicinal spin–spin coupling constants for the *endo*-isomer are calculated in the 9 Hz range, which does not match the experimental observation.

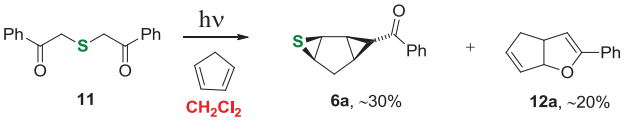
After exploring the photochemistry of adducts **4** and **5** prepared via the ground-state chemistry, that is, non-photochemically, we explored the feasibility of a one-pot integrated procedure for the photogeneration of phenyl(thio)glyoxal from phenacyl sulfide, its [4+2] cycloaddition to cyclopentadiene, and subsequent photoinduced transformation of thianorbornene equipped with the photoactive benzoyl group.

We found that the kinetics of the ground-state phenyl(thio)glyoxal addition to cyclopentadiene is a limiting factor. An excess of cyclopentadiene helps capture the photogenerated thiocarbonyl. In stoichiometric runs, the photogenerated phenyl(thio)glyoxal undergoes secondary transformations. Another distinctive feature of the cascade reaction is that phenyl(thio)glyoxal generation is accompanied by the release of acetophenone, which accumulates in the reaction mixture. The NMR monitoring of the reaction mixture in benzene-d6 or toluene-d8 clearly shows the growth of the [4+2] cycloadducts **4a** (*endo*) and **5a** (*exo*), which over time are converted into the major photoproduct, thiirane **6a**, thiol **8a**, and disulfide **7a** (Scheme 8).



Scheme 8. One-pot cascade photoassisted transformation in benzene.

It was further found that the solvent had a dramatic effect on the formation of disulfide **7a**. For example, running the reaction in dichloromethane (DCM) or chloroform produced thiirane **6a** as the major product, but no disulfide **7a** was formed. Instead, a completely desulfurized oxapentalene **12a** was detected in a 2:3 ratio to thiirane **6a**.



Scheme 9. One-pot cascade phototransformation of phenacyl sulfide **11** in DCM.

The NMR spectrum integration of four characteristic protons found in the reaction mixture (Figure 3, Scheme 9) reveals two photoproducts **6a** and **12a** in a 3:2 ratio, which are readily quantified based on the integrated value of acetophenone peaks as a reference (Me group integrates to 15.7 or 5.2/1H). This amounts to approximately 50% combined yield of **6a** and **12a** based on the photogenerated phenyl(thio)glyoxal.

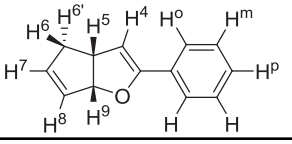
Our hypothesis is that in DCM acetophenone sensitizes this desulfurization, because it does not happen in the absence of acetophenone, that is, when the irradiation of pure adducts **4a** and **5a** is carried out in the same solvent. We were not able to obtain the X-ray structure of oxapentalene **12a**. However, its experimental ^{1}H NMR matches well the calculated spectrum, see Table 1.

The chemical shifts were linearly corrected using the following expression:

$$\delta_{\text{corr}} = -0.989\delta_{\text{DFT}} + 31.48.$$

The spin–spin coupling constants were computed using the Fermi contact terms as suggested by Bally and Rablen. As Table 1 shows, for compound **12a**, we achieved an RMSD of 0.08 ppm for chemical shifts and 0.5 Hz for the spin–spin coupling constants.

Table 1. Experimental and calculated chemical shifts and spin–spin coupling constants for oxapentalene **12a**.



	Experimental values					Calculated values				
	δ_{exp} (ppm)	J_1 (Hz)	J_2 (Hz)	J_3 (Hz)	J_4 (Hz)	δ_{calc} (ppm)	J_1 (Hz)	J_2 (Hz)	J_3 (Hz)	J_4 (Hz)
H^o, 2H	7.47	7.4				7.48	7.8			
H^p, 1H	7.24	7.4	7.3			7.19	7.8	7.3		
H^m, 2H	7.19	7.3	7.3			7.11	7.3	7.2		
H^7,1H	5.96	5.7				6.03	5.6			
H^8, 1H	5.78	5.7				5.99	5.6			
H^9, 1H	5.69	8.8				5.62	9.4			
H^4, 1H	5.19	2.6				5.19	3.2			
H^5, 1H	3.76	8.8	8.0	2.8	1.8	3.70	9.4	7.9	3.2	2.2
H^6, 1H	2.62	17.1	8.0			2.57	17.9	7.9		
$H^{6'}$, 1H	2.32	17.1				2.37	17.9			
				RMSD		0.08 ppm	0.5 Hz			

It is unlikely that oxapentalene **12a** is formed from thiirane **6a**, as their ratio does not change during irradiation in DCM. Irradiation of thiirane **6a** in CD_2Cl_2 for an extended period of time with 365-nm UV LEDs does not produce **10** or **12a**. Under similar experimental conditions, the one-pot cascade transformation is fully complete in 6 – 10 h. Another control experiment showed that desulfurized **10** does partially rearrange into **12a** under irradiation. However, within 2 h of irradiation with 365-nm UV LEDs, a photostationary state is reached, with approximately 15% of **12a** and 85% of **10**. This suggests that **12a** is not formed from **10**, because in the NMR of the reaction mixture, we see only **6a** and **12a** in a 3:2 ratio, and **10** is not detected.

Our hypothesis is that oxapentalene **12a** is produced directly from the sulfur-containing diradical **DR** (Scheme 10). It is plausible that in DCM this oxapentalene diradical intermediate extrudes sulfur instead of converting into thioenol (Scheme 4).

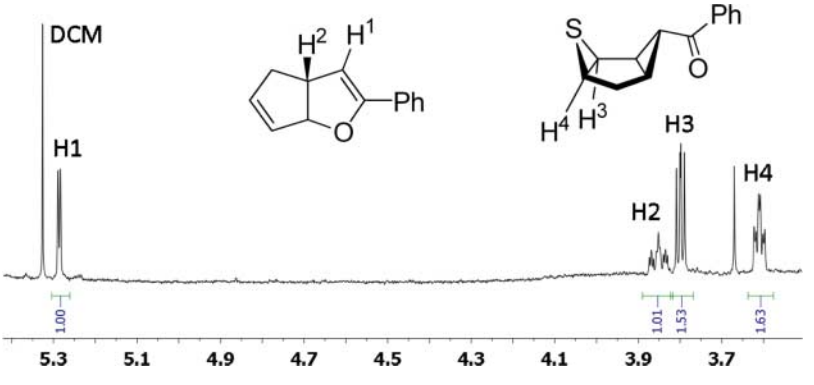
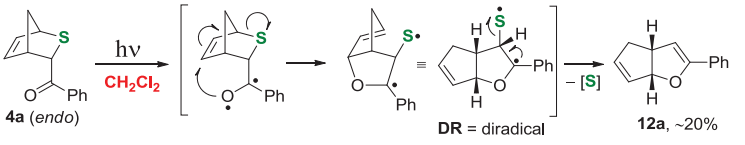


Figure 3. ^{1}H NMR of the reaction mixture presented in Scheme 9.



Scheme 10. A plausible mechanism for oxapentalene **12a** formation in DCM.

3. Conclusion

We have investigated a new photoinduced transformation of thianorbornenes outfitted with a photoactive benozyl pendant. The primary photochemical product is thiirane **6**, which is derived from the homolytic scission of the BzC–S bond upon excitation of the benzoyl chromophore. We have also discovered a novel interrupted Paternò–Büchi channel in these irradiations leading to oxapentalene structures. While the yield of this photochemical transformation is modest (20%, calculated based on the converted phenacyl sulfide **11**, it gives rapid access to fused dihydrofuran derivatives via a one-pot photoassisted reaction starting from readily available materials.

4. Experimental

4.1. *Preparation of Bunte salts (1)*

Bromoacetophenone or 2-bromopropiophenone (1.0 eq) was dissolved in MeOH. Sodium thiosulfate (1.2 eq) was added to the solution followed by 1–2 ml of water. The resulting mixture was then refluxed overnight. MeOH and water were removed on a high-vacuum pump to give the Bunte salt, which was used without further purification.

4.1.1. *Sodium benzoylmethanethiosulfonate (**1a**)*

This was prepared from 2.0 g of bromoacetophenone (0.010 mol) and 1.9 g of $Na_2S_2O_3$ (0.012 mol). ^{1}H NMR (400 MHz, CD_3OD) $\delta = 8.05$ (dd, $J = 8.5, 1.3$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 4.61 (s, 2H).

4.1.2. *Sodium 1-benzoylethanethiosulfonate (**1b**)*

This was prepared from 4 ml of 2-bromopropiophenone (0.026 mol) and 5 g of $Na_2S_2O_3$ (0.032 mol). ^{1}H NMR (400 MHz, CD_3OD) $\delta = 8.16$ (d, $J = 7.3$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 5.14 (q, $J = 6.8$ Hz, 1H), 1.70 (d, $J = 6.8$ Hz, 3H).

4.2. *Preparation of the exo-[S]-based Diels–Alder adducts(4,5).*

General procedure: Triethylamine (10.0 eq) was added slowly with stirring to Bunte salt **1** (1.0 eq) in methanol containing cyclopentadiene (5.0 eq) and calcium chloride (1.0 eq) at room temperature. After 24 h, the mixture was acidified and extracted with DCM. The extract was washed successively with dilute hydrochloric acid, dilute sodium hydroxide, and water and subjected to silica gel chromatography (eluted with hexane/EtOAc = 60:1→40:1) (*1*).

4.2.1. *exo-3-Benzoyl-2-thiabicyclo[2.2.1]hept-5-ene (**5a**)*

This was prepared from 5.5 ml of Et_3N (39.46 mmol), 1.3 g of freshly distilled cyclopentadiene (19.67 mmol), 0.48 g of $CaCl_2$ (4.33 mmol), and 1.0 g of **1a** (3.93 mmol) (hexane/EtOAc gradient 60:1→40:1) : before column purification – a mixture of *exo*- and *endo*-isomers by NMR, 58% and 42%, respectively (mostly the *exo*-adduct was recovered after column purification). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.95$ (d, $J = 7.3$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 6.47 (dd, $J = 5.5$, 2.8 Hz, 1H), 6.09 (dd, $J = 5.5$, 3.2 Hz, 1H), 4.16 (m, 1H), 4.06 (m, 1H), 3.67 (m, 1H), 1.89 (d, $J = 9.5$ Hz, 1H), 1.77 (ddd, $J = 9.5$, 2.2, 2.2 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta =$ 197.91, 138.79, 137.30, 133.48 overlaps with 133.47, 128.80, 128.45, 53.12, 52.43, 49.50, 46.71.

4.2.2. *endo-3-Benzoyl-2-thiabicyclo[2.2.1]hept-5-ene (**4a**)*

^{1}H NMR (400 MHz, $CDCl_3$)$\delta = 7.94$ (m, 2H), 7.55 (m, 1H), 7.45 (m, 2H), 6.38 (dd, $J = 5.5$, 2.9 Hz, 1H), 6.15 (dd, $J = 5.5$, 3.0 Hz, 1H), 5.12 (d, $J = 3.5$ Hz, 1H), 4.08 (m, 1H), 3.79 (m, 1H), 1.79 (m, 2H).

4.2.3. *exo-3-Benzoyl-endo-3-methyl-2-thiabicyclo[2.2.1]hept-5-ene (**5b**)*

This was prepared from 5.5 ml of Et_3N (39.46 mmol), 1.3 g of freshly distilled cyclopentadiene (19.67 mmol), 0.48 g of $CaCl_2$ (4.33 mmol), and 1.0 g of **1b** (3.93 mmol) (hexane/EtOAc gradient 60:1→40:1): a mixture of *exo*-and *endo*-isomers by NMR, 66% and 34%, respectively. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.98$ (m, 2H), 7.51 (m, 1H), 7.43 (m, 2H), 6.58 (d, $J = 5.5$, 2.8 Hz, 1H), 6.07 (d, $J = 5.5$, 3.3 Hz, 1H), 4.08 (m, 1H), 3.88 (m, 1H), 1.79 (ddd, $J = 9.6$, 2.3, 2.3 Hz, 1H), 1.74 (d, $J = 9.6$ Hz, 1H), 1.59 (s, 3H).

4.2.4. *endo-3-Benzoyl-exo-3-methyl-2-thiabicyclo[2.2.1]hept-5-ene (**4b**)*

Attempts to obtain pure *endo*-**4b** failed. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.90$ (m, 2H), 7.50 (m, 1H), 7.40 (m, 2H), 6.26 (d, $J = 5.4$, 2.8 Hz, 1H), 6.20 (d, $J = 5.4$, 3.1 Hz, 1H), 4.07 (m, 1H), 3.52 (m, 1H), 2.02 (s, 3H), 1.98 (d, $J = 9.5$ Hz, 1H), 1.75 (ddd, $J = 9.5$, 2.3, 2.3 Hz, 1H).

4.2.5. *Spiro[exo-3-benzoyl-2-thiabicyclo[2.2.1]hept-5-ene-7,1′-cyclopropane](**5c**)*

^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.94$ (m, 2H), 7.56 (m, 1H), 7.46 (m, 2H), 6.51 (ddd, $J = 5.6$, 2.8 Hz, 1H), 6.27 (ddd, $J = 5.7$, 3.3, 0.8 Hz, 1H), 4.09 (m, 1H), 3.43 (m, 1H), 3.28 (d, $J = 3.1$ Hz, 1H), 1.04 (ddd, $J = 9.3$, 5.6, 5.6 Hz, 1H), 0.81 (ddd, $J = 9.5$, 6.3, 4.6 Hz, 1H), 0.65 (ddd, $J = 9.9$, 5.8, 4.6 Hz, 1H), 0.56 (ddd, $J = 9.8$, 6.3, 5.5 Hz, 1H).^{13}C NMR (500 MHz, $CDCl_3$) $\delta =$ 196.31, 137.71, 137.36, 134.41, 133.15, 128.53, 128.27, 58.81, 54.92, 49.99, 44.84, 11.14, 9.27. HRMS (ESI) calcd for $C_{15}H_{15}OS^+$ (MH^+) 243.0838, found 243.0836.

4.3. *Preparation of the exo-[SO_2]-based adducts (3)*

General procedure: A solution of *m*CPBA (2.1 eq, 77% max) in DCM was added to a stirring solution of *exo*-adduct **5** (1.0 eq) in DCM at −78°C, which was allowed to cool to room temperature overnight. The solution was washed with a saturated solution of $NaHCO_3$, brine, extracted with DCM, and dried over Na_2SO_4, filtered, and concentrated *in vacuo*, affording the pure product as a pale yellow solid (*7*).

4.3.1. *exo-3-Benzoyl-2,2-dioxo-2-thiabicyclo[2.2.1]hept-5-ene (exo-3-benzoyl-2-thiabicyclo[2.2.1]hept-5-eneS,S-dioxide) (**9a**)*

This was prepared from 0.79 g of *m*CPBA (77 %) (3.53 mmol) and 0.34 g of *exo*-**5a** (1.57 mmol): 0.38 g (97 %). ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 8.05$ (d, $J = 7.4$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 2H), 6.67 (dd, $J = 5.6$, 2.8 Hz, 1H), 6.47 (dd, $J = 5.6$, 3.1 Hz, 1H), 4.22 (d, $J = 2.5$ Hz, 1H), 3.99 (m, 1H), 3.71 (m, 1H), 2.83 (d, $J = 11.6$ Hz, 1H), 2.47 (dddd, $J = 11.6$, 2.7, 2.7, 2.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) $\delta = 191.08$, 141.99, 136.54, 134.30, 131.68, 129.06, 128.68, 66.27, 59.44, 44.39, 44.17.

4.3.2. *exo-3-Benzoyl-endo-3-methyl-2,2-dioxo-2-thiabicyclo[2.2.1]hept-5-ene (**9b**)*

This was prepared from 0.82 g of *m*CPBA (77%) (3.66 mmol) and 0.40 g of *exo*-**5b** (1.74 mmol): 0.45 g (99 %). ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.96$ (m, 2H), 7.56 (m, 1H), 7.48 (m, 2H), 6.60 (dd, $J = 5.7$, 3.0 Hz, 1H), 6.41 (dd, $J = 5.7$, 3.2 Hz, 1H), 4.03 (m, 1H), 3.79 (m, 1H), 2.61 (d, $J = 11.6$ Hz, 1H), 2.41 (ddd, $J = 11.6$, 3.4, 2.3 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) $\delta = 195.32$, 140.77, 134.37, 133.21, 131.53, 130.07, 128.40, 67.53, 64.52, 49.88, 43.38, 23.22.

Photolysis of **4** and **5**: Approximately 0.01−0.1 *M* solution of a precursor **4** or **5** in benzene (or DCM) was irradiated in Pyrex vials in a Rayonet reactor equipped with RPR-3500 UV lamps (broadband 300−400 nm UV source with peak emission at 350 nm) or a UV LED-based illuminator with five 250 mW at 365 nm Nichia chips. The products were separated by silica gel chromatography (eluted with hexane/EtOAc = 40:1→30:1).

4.3.3. *(1R*, 2S*, 4R*, 6R*, 7R*)-7-Benzoyl-3-thiatricyclo[4.1.0.0^{2,4}]heptane (**6a**)*

This was prepared by quantitative conversion from *exo*-**5a** and ∼29% conversion from *endo*-**4a** by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.98$ (m, 2H), 7.57 (m, 1H), 7.47 (m, 2H), 3.77 (dd, $J = 5.5$, 4.2 Hz, 1H), 3.58 (ddd, $J = 5.3$, 2.2, 2.2 Hz, 1H), 3.19 (dd, $J = 2.9$, 2.9 Hz, 1H), 2.52-2.44 (m, 2H), 2.41 (m, 1H), 2.12–2.07 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta = 197.41$, 137.31, 132.96, 128.53, 128.20, 46.20, 44.05, 37.49, 34.32, 31.48, 31.02. HRMS (ESI) calcd for $C_{13}H_{12}NaOS^+$ (MNa^+) 239.0501, found 239.0490.

4.3.4. *Di-(3-phenyl-2-oxabicyclo[3.3.0]octa-3,7-diene-4-yl)disulfide (**7a**)*

This was prepared by ∼29% conversion by NMR from *endo*-**4a** with 29% of **6a**, 16% of thiol **8a**, and 26% of the remaining *endo*-**4a**. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.77$ (m, 2H), 7.40–7.36 (m, 3H), 5.95 (dddd, $J = 5.7$, 2.3, 2.3, 1.1 Hz, 1H), 5.62 (dddd, $J = 5.7$, 2.1, 2.1, 2.1 Hz, 1H), 4.54 (br. d, $J = 9.1$ Hz,1H), 3.07 (ddd, $J = 9.1$, 6.4, 3.4 Hz, 1H), 2.52 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta = 160.44$, 135.70, 129.96, 129.26, 128.93, 128.19, 127.60, 104.54, 89.58, 46.28, 39.44. HRMS (ESI) calcd for $C_{13}H_{12}NaOS^+$ (MNa^+) 239.0501, found 239.0507.

4.3.5. *(1R*, 2S*, 4R*, 6R*, 7R*)-Spiro[7-benzoyl-3-thiatribicyclo[4.1.0.0^{2,4}] heptane-5,1′-cyclopropane] (**6c**)*

^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.99$ (d, $J = 7.2$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.48 (d, $J = 7.6$ Hz, 2H), 3.91 (dd, $J = 5.5$, 4.6 Hz, 1H), 3.38 (dd, $J = 3.4$, 2.8 Hz, 1H), 3.31 (dd, $J = 5.5$, 1.4 Hz, 1H), 2.59 (ddd, $J = 7.2$, 4.5, 2.7 Hz, 1H), 2.14 (ddd, $J = 7.2$, 3.5, 1.4 Hz, 1H), 1.09–0.99 (m, 2H), 0.96–0.84 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) $\delta = 197.34$, 137.33, 132.97, 128.54,

128.22, 54.54, 44.67, 44.29, 34.03, 32.43, 26.66, 18.96, 10.85. HRMS (ESI) calcd for $C_{15}H_{15}OS^+$ (MH^+) 243.0838, found 243.0833.

4.3.6. *Di(spiro[3-phenyl-2-oxabicyclo[3.3.0]octa-3,7-diene-4-yl-6,1′-cyclopropane]) disulfide (**7c**)*

^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.79$ (m, 2H), 7.41 (m, 2H), 7.36 (m, 1H), 5.56 (dd, $J = 5.6$, 2.2 Hz, 1H), 5.40 (d, $J = 5.6$ Hz, 1H), 4.31 (dd, $J = 9.3$, 2.2 Hz, 1H), 2.71 (d, $J = 9.3$ Hz, 1H), 0.88–0.75 (m, 2H), 0.68–0.64 (m, 1H), 0.59–0.55 (m, 1H). HRMS (ESI) calcd for $C_{15}H_{14}LiOS^+$ (MLi^+) 249.0920, found 249.0912.

4.3.7. *exo-6-Benzylbicyclo[3.1.0]hex-2-ene (**10**)*

This was prepared from sulfone **9a**, max 67% photoconversion (2 h of irradiation) by NMR. ^{1}H NMR (500 MHz, $\underline{C}DCl_3$) $\delta = 7.95$ (d, $J = 7.8$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.46 (dd, $J = 7.8$, 7.5 Hz, 2H), 6.05 (dddd, $J = 5.5$, 2.1, 2.1, 2.1 Hz, 1H), 5.68 (ddd, $J = 5.5$, 3.5, 2.1, 1H), 2.79 (dddd, $J = 19.0$, 6.5, 2.2, 2.2 Hz, 1H), 2.68 (dddd, $J = 6.4$, 2.2, 2.2, 2.2 Hz, 1H), 2.56 (dddd, $J = 19.0$, 2.2, 2.2, 2.2 Hz, 1H), 2.50 (ddd, $J = 6.4$, 6.4, 3.2 Hz, 1H), 2.02 (t, $J = 2.7$ Hz, 1H). ^{1}H NMR (500 MHz, $\underline{C}_6\underline{D}_6$) $\delta = 7.89$ (m, 2H), 7.13 (m, 1H), 7.06 (m, 2H), 5.76 (m, 1H), 5.35 (m, 1H), 2.71 (dddd, $J = 6.3$, 2.2, 2.2, 2.2 Hz, 1H), 2.48 (ddd, $J = 6.4$, 6.4, 3.0 Hz, 1H), 2.39 (dddd, $J = 18.8$, 6.5, 2.2, 2.2 Hz, 1H), 2.14 (dddd, $J = 18.8$, 2.3, 2.3, 2.3 Hz, 1H), 1.84 (t, $J = 2.7$ Hz, 1H).

4.3.8. *Phenacyl sulfide (**11**)*

A solution of 2-bromoacetophenone (1.00 g, 4.92 mmol) in anhydrous DMF (20 ml) was added dropwise to a stirred suspension of anhydrous sodium sulfide (0.268 g, 3.44 mmol) in anhydrous DMF (10 ml). In 3 h, the reaction was complete by NMR. The reaction mixture was poured into cold water (200 ml) and a yellow precipitate was collected and dried to give 0.371 g (56%) of the product. The NMR spectrum of the product matches the literature data (*8*). ^{1}H NMR (500 MHz, $\underline{C}DCl_3$) $\delta = 8.01$ (m, 4H), 7.60 (m, 2H), 7.49 (m, 4H), 4.01 (br. s, 4H).

4.3.9. *3-Phenyl-4-oxabicyclo[3.3.0]octa-2,6-diene (**12a**)*

^{1}H NMR (500 MHz, $\underline{C}DCl_3$) $\delta = 7.47$ (d, $J = 7.3$ Hz, 2H), 7.24 (m, 3H), 5.96 (dm, $J = 5.7$ Hz, 1H), 5.78 (dm, $J = 5.7$ Hz, 1H), 5.69 (br. d, $J = 8.8$ Hz, 1H), 5.2 (d, $J = 2.7$ Hz, 1H), 3.76 (dddd, $J = 8.8$, 8.0, 2.8, 1.8, 1H), 2.62 (br. dd, $J = 17.1$, 8.0 Hz, 1H), 2.32 (br. d, $J = 17.1$ Hz, 1H).

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