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Photochemical generation of ketenes from phenanthrene-based cyclobutanones

Alexander D. Roth, Zhazira Koldasbay, Brett H. Ford, Khaidar Kairbek, Heejoon Ahn, Tarini S. Hardikar, Katherine M. Lane, Sarah M. Haynes, Dasan M. Thamattoor *

Department of Chemistry, Colby College, Waterville, ME, 04901, USA

A B S T R A C T

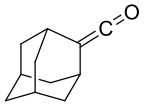
Various 9,10-cyclopropanated phenanthrenes have been shown previously to be viable photochemical precursors to many different types of carbenes. There is also one known example in the literature of a related approach used to generate diphenylketene from a phenanthrene-derived cyclobutanone in a laser flash photolysis study. In an effort to broaden the scope of this promising yet under-utilized method of ketene generation, the synthesis and characterization of several phenanthrene-based cyclobutanones, and their subsequent photolysis to produce a variety of ketenes, are presented in this report. The ketenes are produced, along with phenanthrene, by a formal 2 + 2 cyclo-reversion of the cyclobutanone moiety and have been intercepted by benzyl alcohol and benzyl amine to form the corresponding benzyl esters and amides respectively.

1. Introduction

Cyclopropanated phenanthrenes, exemplified by **1**, **3**, and **5**, have emerged as useful photochemical sources of carbenes **2**, **4**, and **6** respectively (Scheme 1), and provide a viable, less hazardous alternative to nitrogenous precursors such as diazirines and diazo compounds [1]. In each of these cases, the cheletropic extrusion of carbene is accompanied by the concomitant formation of phenanthrene.

Conceptually, one could envision a cyclobutanated phenanthrene undergoing a related 2 + 2 cyclo-reversion to fragment into phenanthrene and another moiety containing a π bond upon photolysis. There are, however, far fewer examples of such transformations reported in the literature. They include a limited number of photofragmentations of phenanthrene-based cyclobutane (**7**) [2,3], cyclobutene (**9**) [3], and cyclobutanone (**11**) [4], to the olefin (**8**), alkyne (**10**), and ketene (**12**) respectively, accompanied by formation of the corresponding phenanthrene byproducts (Scheme 2).

In the course of carrying out an unrelated carbene project, we inadvertently synthesized **11** and (re)discovered that it does, indeed, produce diphenylketene **12** upon photolysis as previously noted in the literature [4]. The formation of **12** from **11** was originally reported as part of a laser flash photolysis study [4] and remains a solitary example of what could be a promising, and broadly applicable, photochemical approach to structurally diverse ketenes with much untapped synthetic potential. Herein, we describe our broader investigation into **11** and analogous precursors to generate **12** and three additional ketenes—adamantylideneketene (**13**), phenylketene (**14**) and cyclopentylideneketene (**15**)—in solution under mild conditions, as well as trapping studies with nucleophiles.



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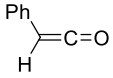

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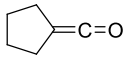

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2. Results and discussion

2.1. Synthesis of precursors

The requisite phenanthrene-based cyclobutanone precursors to ketenes **12** and **13** were prepared as illustrated in Scheme 3. The first step used our optimized procedure [5] to react phenanthrene with dibromocarbene, generated under phase transfer catalyzed conditions, to form the 1,1-dibromocyclopropane derivative **16**. In the next step, a previously reported protocol of Tippmann and Curtis was followed by initially treating **16** with butyllithium at low temperature and subsequently adding benzophenone to obtain precursor **11** [4]. An analogous procedure that used 2-adamantanone (**17**) instead of benzophenone delivered **18**, the desired precursor to ketene **13**. The single crystal X-ray

* Corresponding author.
E-mail address: dmthamat@colby.edu (D.M. Thamattoor).

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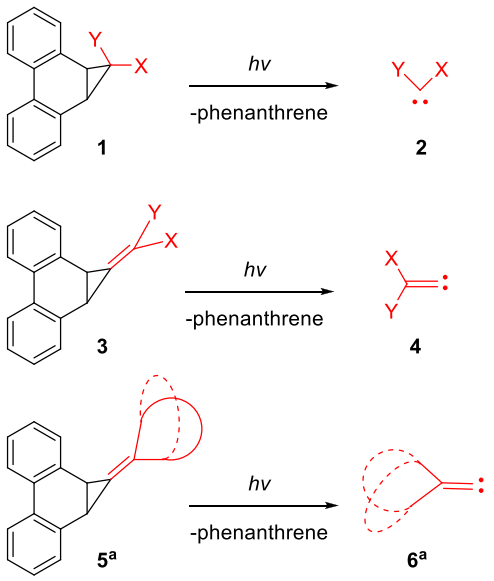
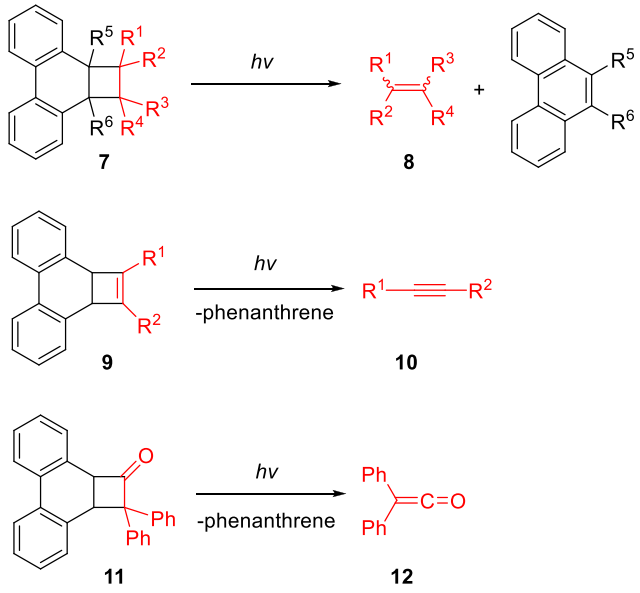


Scheme 1. Photochemical generation of carbenes from cyclopropanated phenanthrenes.



Scheme 2. Photochemical generation of alkene, alkyne, and ketene from cyclobutanated phenanthrenes.

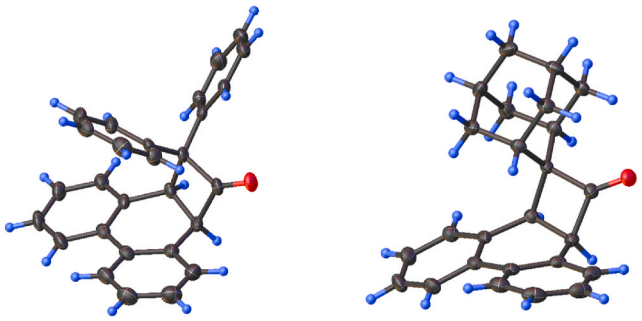


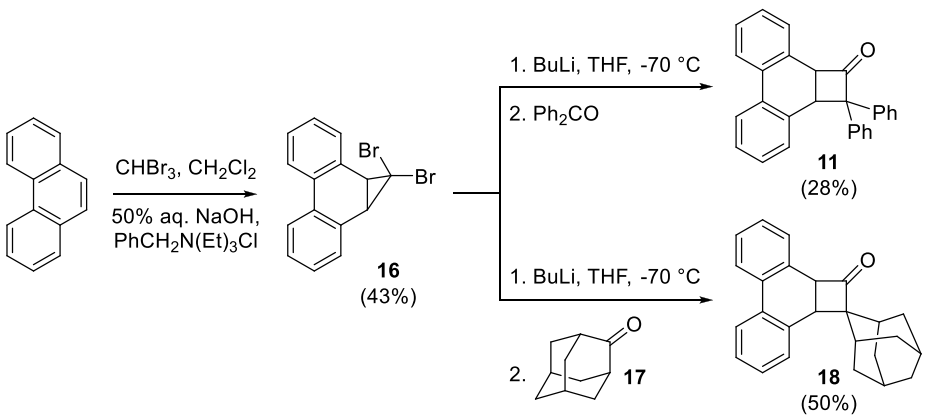
Fig. 1. Single crystal X-ray structures of **11** (left) and **18** (right). Thermal ellipsoids are shown at the 50 % probability level.

structures of **11** and **18** are shown in Fig. 1.

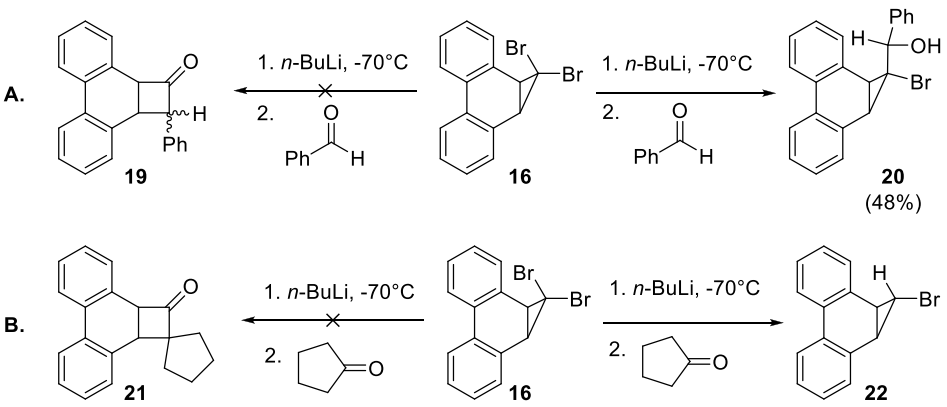
While we attempted to synthesize **19** and **21**, photochemical sources of ketenes **14** and **15** respectively, by the method presented in Scheme 3—using benzaldehyde and cyclopentanone as the corresponding carbonyl reactant in the second step—we were unable to obtain the desired precursors (Scheme 4). The use of benzaldehyde, instead, gave the bromohydrin **20**, presumably by nucleophilic addition of the bromoanion, initially formed by lithium halogen exchange, to the carbonyl group (Scheme 4A). Using cyclopentanone yielded the monobromo derivative **22**, likely by proton abstraction from the enolizable ketone by the bromoanion (Scheme 4B).

We did, however, eventually succeed in synthesizing **19** and **21** using alternative approaches. To prepare **19** we followed the route outlined in Scheme 5. Thus, alkene **24** was first synthesized according to our previously reported procedure [6], wherein **16** was initially reacted with *n*-butyllithium at low temperatures and was subsequently quenched with benzyl bromide to afford the alkyl bromide **23.** The elimination of HBr from **23** using *t*-BuOK provided **24**. We then treated **24** with *m*-CPBA under mildly basic conditions to generate the oxaspiropentanes **25** *in situ*, which rearranged into the desired cyclobutanone **19**. As an oxaspiropentane analogous to **25**, and its subsequent rearrangement into **11**, were previously reported by Tippmann [4], the successful synthesis of **19** was accomplished by devising a different approach to access **25**, namely from **24**. The single crystal X-ray structure of **19** is shown in Fig. 2. While the stereochemistry of **25** remains unknown, it is notable that only the diastereomer in which the phenyl ring is *exo* in **19** was produced. Presumably this is due to the less favorable steric interactions *en route* to the more crowded *endo* isomer of **19**.

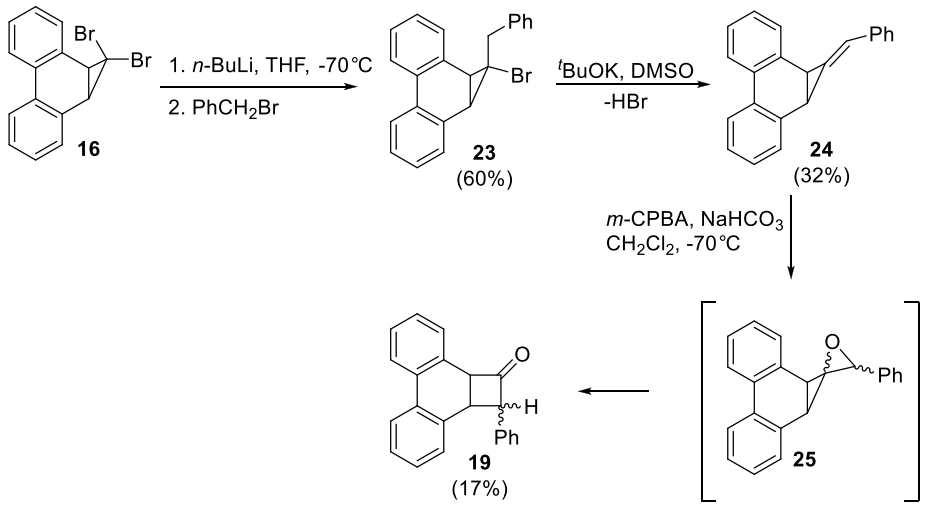
The synthesis of **21** was carried out as depicted in Scheme 6. In this case, we first synthesized alkene **27** in two steps following our previously published procedure [7]. This involved cyclopropanating phenanthrene with dichlorocarbene under phase-transfer catalysis [8] conditions to produce **26** which was then subjected to a Takeda reaction [9] to provide **27**. Treatment of **27** with *m*-CPBA in the presence of sodium bicarbonate directly led to **21** by rearrangement of the putative



Scheme 3. Synthesis of cyclobutanones **11** and **18**, photochemical precursors to ketenes **12** and **13** respectively.



Scheme 4. Unsuccessful attempts at preparing cyclobutanones **19** and **21**, photochemical precursors to ketenes **14** and **15** respectively, by methods shown in Scheme 3.



Scheme 5. Synthesis of precursor **19** from rearrangement of oxaspiropentane **25**.

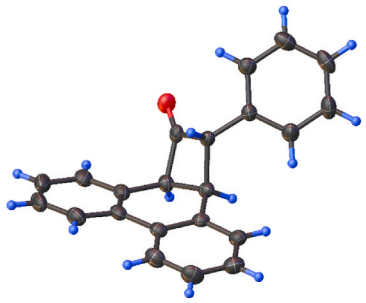


Fig. 2. Single crystal X-ray structure of **19**. Thermal ellipsoids are shown at the 50 % probability level.

oxaspiropentane **28** which is initially formed (*vide supra*).

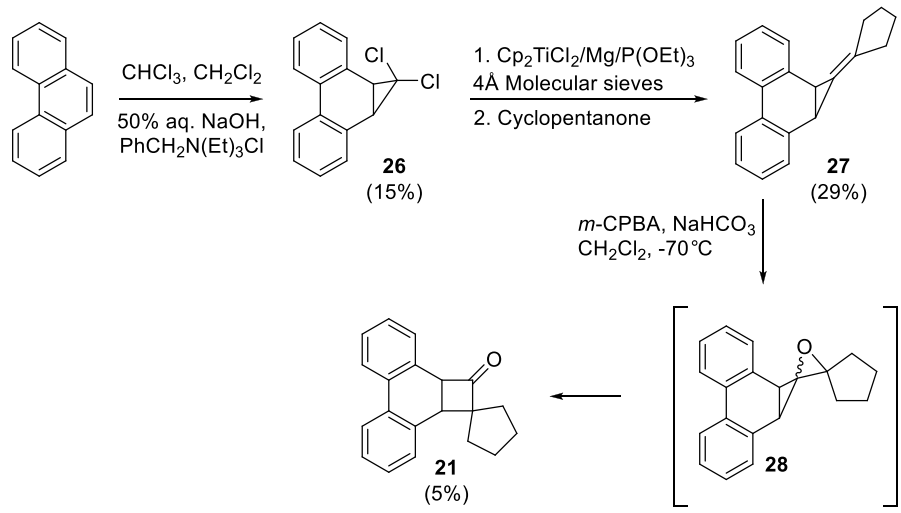
2.2. Photochemical Experiments

The ketene precursors **11**, **18**, **19**, and **21** were photolyzed (Hg–Xe lamp with 280–400 nm dichroic) in the presence of benzyl alcohol and benzylamine in benzene-d6 (Scheme 7). In all cases, photolysis generated phenanthrene and the corresponding ketene, with the latter reacting with the nucleophiles present to afford the appropriate esters (**29a-32a**) or amides (**29b-32b**).

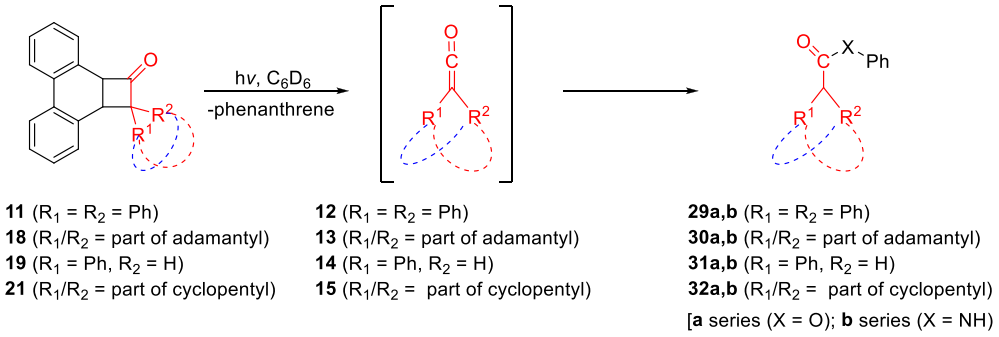
We have previously observed that cyclopropanated phenanthrenes sometimes undergo photochemical rearrangements [1,10,11], in addition to extruding the carbenes, during photolysis. In contrast, all four ketene precursors—**11**, **18**, **19**, and **21**—gave nearly quantitative yields of phenanthrene, determined by NMR using an internal standard. Further, while photolysis with benzyl alcohol typically afforded the expected esters, **29a-32a**, in fair to modest yields, almost complete conversion to the corresponding amides, **29b**–**32b**, was observed when benzylamine was used as the nucleophile. Table 1 shows the yield of both the trapped ketene and phenanthrene for the photolysis of each ketene precursor in both nucleophiles.

Confirmation of the identities of ketene-derived esters and amides, **29a,b** through **32a,b**, was accomplished by obtaining authentic samples and comparing them to the products of photolysis. While all esters (**29a-32a**) and amides (**29b**–**32b**) discussed herein were known in the literature, only ester **31a** was readily available commercially. Therefore, we adapted the procedure of Chen and coworkers [12] to execute a one-pot synthesis of authentic samples of the remaining esters and amides as shown in Scheme 8. Thus, the corresponding carboxylic acid (**33**–**36**), either benzyl alcohol or benzylamine, triethylamine, and DMAP were all dissolved together in CH_2Cl_2. Then, phosphorus oxychloride was slowly added to the reaction which, after 1 h, provided the desired esters or amides in (typically) fair to good yields (Scheme 8).

It is noteworthy that adamantylideneketene (**13**), first observed directly in a cryogenic argon matrix by Bally and coworkers [13], appeared to be remarkably stable in solution when generated by photolysis of precursor **18** in argon-purged C_6D_6 in an NMR tube,



Scheme 6. Synthesis of precursor **21** from rearrangement of oxaspiropentane **28**.



11 (R_1 = R_2 = Ph)
18 (R_1/R_2 = part of adamantyl)
19 (R_1 = Ph, R_2 = H)
21 (R_1/R_2 = part of cyclopentyl)

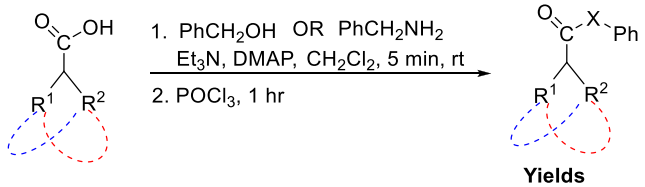
12 (R_1 = R_2 = Ph)
13 (R_1/R_2 = part of adamantyl)
14 (R_1 = Ph, R_2 = H)
15 (R_1/R_2 = part of cyclopentyl)

29a,b (R_1 = R_2 = Ph)
30a,b (R_1/R_2 = part of adamantyl)
31a,b (R_1 = Ph, R_2 = H)
32a,b (R_1/R_2 = part of cyclopentyl)
[**a** series (X = O); **b** series (X = NH)

Scheme 7. Photolysis of phenanthrene-based ketene precursors in C_6D_6 and the trapping of generated ketenes with either benzyl alcohol or benzylamine to give the corresponding esters or amides respectively.

Table 1
Yields of esters and amides from the photolysis of ketene precursors.

		From **11**	From **18**	From **19**	From **21**
Benzyl alcohol	Esters	**29a** (41 %)	**30a** (33 %)	**31a** (63 %)	**32a** (34 %)
	Phenanthrene	92 %	94 %	95 %	94 %
Benzylamine	Amides	**29b** (88 %)	**30b** (95 %)	**31b** (97 %)	**32b** (92 %)
	Phenanthrene	92 %	96 %	98 %	92 %



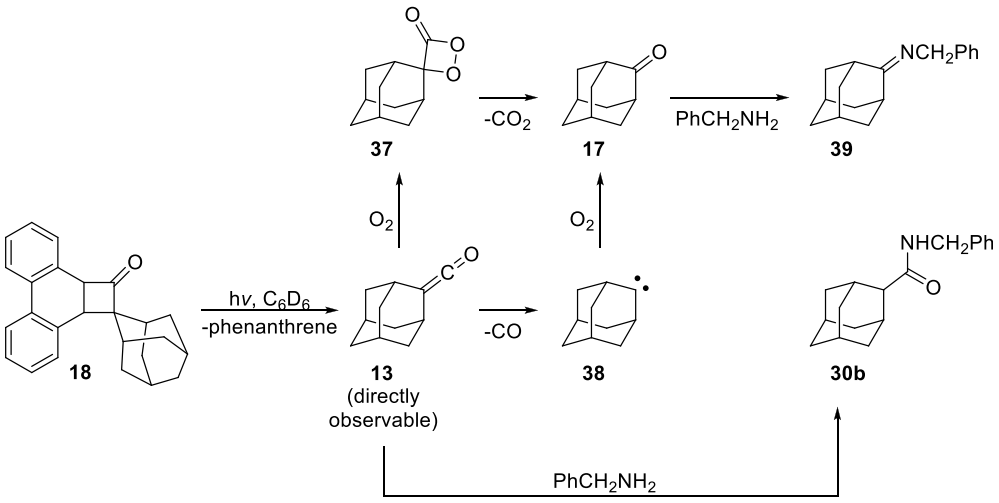
33 (R_1 = R_2 = Ph)
34 (R_1/R_2 = part of adamantyl)
35 (R_1 = Ph, R_2 = H)
36 (R_1/R_2 = part of cyclopentyl)

Yields

	29	**30**	**31**	**32**
a (X = O)	64%	56%	N/A	12%
b (X = NH)	38%	70%	59%	80%

Scheme 8. Conversion of commercially available carboxylic acids **33**–**36** into authentic samples of benzyl esters and amides using the procedure developed by Chen et al. [12].

without any added nucleophiles (Scheme 9). Monitoring the photolysis hourly with NMR showed peaks attributable to **13** throughout the 4 h of photolysis (62 %), along with 2-adamantanone (**17**) (16 %) and phenanthrene (98 %) (see Experimental Methods; Photolysis Bv). Subsequent addition of excess benzylamine and analysis by NMR showed that all **13** had been converted to amide **31b**, and the imine **39** was presumably produced from **17**. Photolysis of **18** in benzene and monitoring with GC-MS provided further evidence for the stability of **13**, where a peak



Scheme 9. Photolysis of **18** without added nucleophiles gives ketene **13**, which is observable both by NMR and GC-MS. **17** is likely formed by the slow reaction of **13** or carbene **38** with adventitious oxygen. Subsequent addition of benzylamine converts **13** into amide **30b** and **17** into imine **39**.

with mass 162 *m/z* persisted throughout the 7 h of photolysis. **17** and trace amounts of 2-adamantanecarboxylic acid (**34**), likely arising from the reaction of **13** with water, were also observed. Subsequent addition of benzylamine resulted in the complete disappearance of the 162 *m/z* peak and the formation of amide **30b** along with imine **39** (see Experimental Methods; Photolysis Biv).

The origin of **17** may be attributable to at least two pathways. In one, the reaction of **13** with adventitious oxygen could give the *spiro*-adamantyl-1,2-dioxetanone (**37**) [14], which is known to fragment into **17** and carbon dioxide [15]. A second possibility is the loss of CO from **13** to form adamantylidene **38** [16]. The known reaction of carbene **38** with oxygen could then give **17** [17].

3. Conclusions

Herein, we report the direct, photochemical generation of diphenylketene (**12**), adamantylideneketene (**13**), monophenylketene (**14**), and cyclopentylideneketene (**15**) each from their respective phenanthrene-based cyclobutanone precursors (**11**, **18**, **19**, and **21**). Photolysis of the precursors in the presence of benzyl alcohol and benzylamine gave the expected esters and amides in fair or high yields respectively. The yield of phenanthrene by product was near-quantitative in all cases. In the absence of nucleophiles, ketene **13** was found to be quite stable, persisting in C_6D_6 for at least 7 h, and being observable by both NMR and GC-MS methods. The presence of 2-adamantanone points to secondary products issuing from ketene **13** either *via* a spiro-1,2-dioxetanone **37** and/or adamantylidene **38**, with residual oxygen participating in these two pathways. It is conceivable that these cyclobutanone precursors could be potentially tapped as efficient photochemical routes to generate reactive ketenes, thus rendering them particularly strong candidates for matrix isolation spectroscopy and laser flash photolysis studies. These investigations are currently underway in our laboratory and their results will be disseminated in due course.

4. Experimental Methods

General experimental procedures. Tetrahydrofuran was degassed by purging with nitrogen and dried by passage through two activated alumina columns (2 ft × 4 in). Other solvents and reagents were used as obtained from commercial sources. Previously, we have reported procedures for preparing 1,1-dibromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**16**) [5], 1-benzylidene-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (**24**) [6], and 1-cyclopentylidene-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (**27**) [7]. Medium pressure flash chromatography was performed on an automated system using pre-packed silica gel columns (70–230 mesh) with the indicated eluents. Proton (^{1}H) and proton-decoupled carbon (^{13}C) NMR spectra were recorded in $CDCl_3$ or C_6D_6 at 500 MHz and 126 MHz respectively. The chemical shifts are reported in δ ppm, with tetramethylsilane set to 0 ppm. Infrared spectra (resolution 4 cm^{-1}) were acquired on solid samples with an FTIR instrument equipped with an attenuated total reflectance (ATR) accessory and were processed with SpectraGryph [18]. GC/MS data were obtained with a capillary gas chromatograph interfaced with a quadrupole, triple-axis mass selective detector operating in the electron impact (EI) mode. High resolution mass spectra were acquired on an LC-ToF-MS system. Melting points are uncorrected. Single crystals suitable for X-ray crystallography were either obtained by slow evaporation of the hexanes from column fractions or from vapor diffusion using a binary solvent system (DCM/pentanes). UV–vis absorption spectra were obtained at room temperature using an Agilent Cary 60 UV–Vis spectrophotometer, with samples prepared in acetonitrile.

Photolyses were performed in benzene in a long-necked quartz cuvette or in benzene-d6 in a quartz NMR tube and were monitored using GC-MS and NMR respectively. A medium pressure Hg–Xe lamp (equipped with a 280–400 nm dichroic) at ambient temperature was used for photolysis. X-ray crystallography equipment and procedures have been recently described [19].

*2,2-diphenyl-2a,10b-dihydrocyclobuta[l]phenanthren-1(2H)-one (**11**).* First synthesized by Tippmann [4], but our detailed procedure is described below. The dibromo compound **16** (3.542 g, 10 mmol) was dissolved in THF (40 mL) in a 100 mL three-necked flask under an argon atmosphere with a magnetic stir bar. The reaction mixture was cooled to −70 °C, and *n*-butyllithium (4.2 mL, 2.5 M in hexanes) was slowly added over 30 min. After 40 min of stirring at −70 °C, benzophenone (1.826 g, 10 mmol) was added. The solution was allowed to stir at −70 °C for another hour, then it was removed from the ice bath and allowed to stir for 30 min. The reaction was then quenched with H_2O (30 mL), the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were then washed with H_2O (2 × 50 mL) and brine (3 × 50 mL). The solid obtained after rotary evaporation was recrystallized in hexanes and minimal ethyl acetate. The final yield was 1.049 g (28 %); mp 144–145 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73–7.66 (m, 2H), 7.66–7.63 (m, 2H), 7.43 (dd, J = 8.4, 7.1 Hz, 2H), 7.38 (dt, J = 7.5, 1.4 Hz, 1H), 7.35–7.26 (m, 2H), 7.26–7.21 (m, 2H), 7.18 (td, J = 7.6, 1.6 Hz, 1H), 7.13 (td, J = 7.3, 1.4 Hz, 1H), 6.90–6.81 (m, 1H), 6.81–6.70 (m, 2H), 6.50–6.36 (m, 2H), 4.92 (d, J = 10.6 Hz, 1H), 4.79 (dt, J = 10.6, 0.9 Hz, 1H). ^{13}C NMR (126 MHz,

$CDCl_3$): δ 207.5, 140.9, 138.7, 132.6, 131.9, 131.4, 130.8, 128.8, 128.7, 128.3, 128.1, 127.7, 127.6, 127.4, 127.2 (2 carbon resonances), 127.1, 126.3, 123.3, 123.1, 85.9, 58.2, 39.9. FTIR: ν 3059.5, 3020.2, 2960.1, 1770.6, 1597, 1489.1, 1443.3 cm^{-1}. UV–Vis (MeCN): λ_{max} = 277 nm.

2a,10b-dihydro-2H-spiro[adamantane-2,1-cyclobuta[l]phenanthren]-2-one ***(18)***. Dibromo compound **16** (2.33 g, 6.6 mmol) was dissolved in THF (120 mL) in a 250 mL three-necked flask under argon atmosphere with stirring. The reaction mixture was cooled to −70 °C, and *n*-butyllithium (2.6 mL, 2.5 M in hexanes, 6.5 mmol) was slowly added. The reaction was allowed to stir for 1 h at this temperature, and adamantan-2-one (0.911 g, 6.1 mmol) dissolved in THF (10 mL) was slowly added. The temperature was maintained at −70 °C for another hour, after which the mixture was allowed to warm to room temperature. After stirring overnight, the reaction was quenched with H_2O, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with H_2O (2 × 30 mL), brine (1 × 30 mL), and dried over sodium sulfate. Crude **16** was purified using silica-gel flash column chromatography (0:100 → 10:90 ethyl acetate:hexanes) and isolated as a white solid. The final yield was 1.045 g (50 %); mp: 149–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (ddd, *J* = 7.9, 3.2, 1.6 Hz, 2H), 7.48 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.39–7.32 (m, 2H), 7.28 (td, *J* = 8.1, 7.6, 2.1 Hz, 3H), 4.48 (d, *J* = 9.7 Hz, 1H), 3.77 (d, *J* = 9.8 Hz, 1H), 2.51 (dddd, *J* = 12.6, 5.7, 3.3, 2.3 Hz, 1H), 2.26 (d, *J* = 3.7 Hz, 1H), 2.21–2.14 (m, 1H), 1.90 (dp, *J* = 12.7, 2.9 Hz, 1H), 1.82–1.59 (m, 6H), 1.53 (td, *J* = 6.3, 5.4, 2.7 Hz, 1H), 1.32 (dq, *J* = 12.9, 2.8 Hz, 1H), 1.24 (dq, *J* = 12.8, 2.9 Hz, 1H), 1.04 (dq, *J* = 13.0, 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 211.8, 132.7, 132.3, 132.2, 132.0, 128.8, 128.4, 128.3, 127.6 (2 carbon resonances), 127.4, 123.9, 123.1, 78.8, 56.1, 42.7, 37.4, 36.6, 34.4, 34.3, 33.0, 32.6, 32.2, 27.0, 26.9. FTIR: ν 3058.6, 2899.6, 2847.8, 1757.7, 1596.5, 1486.6, 1448.5 cm^{-1}. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{25}O$ 341.1905; Found 341.1896. UV–Vis (MeCN): λ_{max} = 209, 277 nm.

2-phenyl-2a,10b-dihydrocyclobuta[l]phenanthren-1(2H)-one ***(19)***. $NaHCO_3$ was added to DCM (20 mL) in a 50 mL three-necked flask under argon atmosphere with stirring, and **24** (0.28 g, 1.0 mmol) was added to the suspension. The mixture was cooled to −70 °C, *m*CPBA (0.21 g, 1.3 mmol) was added to the solution, and the solution stirred for 1 h. Then, the mixture was warmed to room temperature, where it stirred overnight. H_2O (20 mL) was added to the reaction vessel, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic layers were washed with brine (1 × 20 mL) and dried over sodium sulfate. **19** was purified using silica-gel flash column chromatography (0:100 → 3:97 ethyl acetate:hexanes) and isolated as a white solid. The final yield was 50 mg (17 %); mp: 136–139 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (ddd, *J* = 10.5, 7.9, 1.4 Hz, 2H), 7.44 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.42–7.33 (m, 5H), 7.33–7.26 (m, 4H), 7.24 (dd, *J* = 7.5, 1.6 Hz, 1H), 4.73 (dt, *J* = 9.7, 1.8 Hz, 1H), 4.69 (dd, *J* = 8.7, 2.7 Hz, 1H), 4.01 (t, *J* = 9.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 204.3, 135.3, 134.1, 130.9, 130.5, 129.3, 129.2, 128.9, 128.5, 128.3, 127.9, 127.8, 127.5, 127.3, 127.0, 123.9, 123.6, 73.9, 58.9, 36.1. FTIR: ν 3066.1, 3028, 2922.6, 2857.1, 1774.7, 1648.6, 1603.2, 1495.2, 1437.7 cm^{-1}. UV–Vis (MeCN): λ_{max} = 274 nm.

2a,10b-dihydro-2H-spiro[cyclobuta[l]phenanthrene-1,1′-cyclopentan]-2-one ***(21)***. $NaHCO_3$ (0.84 g) was added to DCM (20 mL) in a 50 mL three-necked flask under argon atmosphere with stirring, and **27** was added to the suspension (0.258 mg, 1 mmol). The mixture was cooled to −70 °C, *m*CPBA (0.21 g, 1.3 mmol) was added to the solution, the reaction was stirred for an hour, and then it was warmed to room temperature, where it stirred overnight. The reaction was quenched with H_2O, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were then washed with H_2O (2 × 10 mL) and brine (3 × 10 mL) and dried over sodium sulfate. **21** was purified using silica-gel flash column chromatography (0:100 → 5:95 ethyl acetate:hexanes) and isolated as a colorless oil. The final yield was 14 mg (5 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.88 (m, 2H), 7.36–7.30 (m, 2H), 7.30–7.26 (m, 3H), 7.16–7.12 (m, 1H), 4.61 (dd, *J* = 10.2, 0.9 Hz, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 2.27 (ddd, *J* = 13.3, 8.1, 6.9 Hz, 1H), 1.97 (ddd, *J* = 13.3, 8.2, 6.2 Hz, 1H), 1.79–1.60 (m, 2H), 1.55–1.43 (m, 1H), 1.42–1.18 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 213.5, 132.3, 131.9, 131.2, 130.1, 128.9, 128.4, 128.0 (2 carbon resonances), 127.5 (2 carbon resonances), 123.4, 123.3, 78.3, 57.4, 39.8, 36.8, 31.4, 25.6, 25.5. FTIR: ν 3067.3, 3020.5, 2949.5, 2867.4, 1767.7, 1600.8, 1485.9, 1448.9 cm^{-1}. UV–Vis (MeCN): λ_{max} = 207, 275 nm.

*(1-bromo-1a,9b-dihydro-1H-cyclopropa[l]phenanthren-*1-yl*)(phenyl)methanol* ***(20)***. Dibromo compound **16** (1.77 g, 5.00 mmol) was dissolved in THF (50 mL) in a 100 mL three-necked flask under argon atmosphere with stirring. The mixture was cooled to −70 °C, and *n*-butyllithium (2.3 mL, 2.5 M in hexanes, 5 mmol) was slowly added over 15 min. After stirring at low temperature for 1 h, benzaldehyde (0.53 mL, 5 mmol) was added to the solution. The mixture was allowed to stir for one more hour at −70 °C before heating to room temperature and stirring overnight. The reaction was quenched with H_2O (25 mL), the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were washed with water (2 × 20 mL), brine (1 × 25 mL), and dried over sodium sulfate. Alcohol **20** was purified and isolated using silica-gel flash column chromatography (0:100 → 6:94 ethyl acetate:hexanes) as a white solid. The final yield was 900 mg (48 %); mp: 144–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05–7.99 (m, 2H), 7.68–7.63 (m, 1H), 7.50 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.43–7.31 (m, 4H), 7.21–7.14 (m, 3H), 6.96–6.89 (m, 2H), 4.20–4.15 (m, 1H), 3.47 (d, *J* = 9.4 Hz, 1H), 3.42 (d, *J* = 9.6 Hz, 1H), 1.77 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.6, 131.6, 130.9 (2 carbon resonances), 130.8, 129.5, 129.2, 128.7, 128.5, 128.0, 127.7, 127.4, 126.3, 123.3, 123.2, 70.1, 46.2, 35.6, 34.3. FTIR: ν 3290.2, 3060.6, 3026.6, 1601.9, 1562.6, 1487.4, 1449.5 cm^{-1}.

General Procedure for Ester/Amide Synthesis. Adapted from the work of Chen et al. [12] A solution of the appropriate carboxylic acid (5.00 mmol; **33**–**36**) was dissolved in CH_2Cl_2 (20 mL) in a 100 mL three-necked flask under argon atmosphere with stirring. Either benzyl alcohol or benzylamine (6.00 mmol) was added to the mixture, followed by triethylamine (12.0 mmol, 1.7 mL) and 4-(dimethylamino)pyridine (1.64 mmol, 0.200 g). After 5 min of stirring, $POCl_3$ (5.35 mmol, 0.500 mL) in DCM (10 mL) was gradually added to the mixture, resulting in fuming and the evolution of heat. After 1 h of stirring, the reaction was quenched with H_2O (30 mL), the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (1 × 30 mL) and dried over sodium sulfate. The ester/amide was purified and isolated using silica-gel flash column chromatography. Esters typically eluted around 10:90 ethyl acetate:hexanes, while amides eluted around 70:30 ethyl acetate: hexanes.

Benzyl 2,2-diphenylacetate ***(29a)***. Viscous, colorless oil. 980 mg (64 %). ^{1}H NMR (500 MHz, C_6D_6): δ 7.38–7.27 (m, 4H), 7.12–6.95 (m, 11H), 5.03 (s, 1H), 4.96 (s, 2H). Other characterization data and means of synthesis can be readily found in the literature [20].

N-benzyl-2,2-diphenylacetamide ***(29b)***. White solid. 581 mg (38 %). ^{1}H NMR (500 MHz, C_6D_6) δ 7.37–7.28 (m, 4H), 7.14–6.99 (m, 9H), 6.99–6.94 (m, 2H), 5.26 (t, *J* = 6.0 Hz, 1H), 4.52 (s, 1H), 4.17 (d, *J* = 5.9 Hz, 2H). Other characterization data and means of synthesis can be readily found in the literature [21].

Benzyl adamantane-2-carboxylate ***(30a)***. Waxy white solid. 755 mg (56 %); mp: 44–45 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.34 (m, 4H), 7.34–7.29 (m, 1H), 5.15 (s, 2H), 2.66 (p, *J* = 2.1 Hz, 1H), 2.37 (q, *J* = 2.9 Hz, 2H), 1.90–1.79 (m, 6H), 1.77–1.72 (m, 4H), 1.62 (dtt, *J* = 12.8, 2.7, 1.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.5, 136.4, 128.5, 128.1, 128.0, 65.8, 49.6, 38.1, 37.4, 33.6, 29.6, 27.5, 27.4. FTIR: ν 3027.2, 2905, 2848.6, 1720.2, 1606.2, 1583.5, 1495.1, 1452 cm^{-1}. This compound is known to the literature [22].

N-benzyladamantane-2-carboxamide ***(30b)***. White solid. 937 mg (70 %); mp: 150–152 °C. **30b** was also isolated from Photolysis Bii (*vide infra*) in 31 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.30 (m, 2H),

7.30–7.25 (m, 3H), 6.11–5.76 (brs, 1H), 4.49 (d, $J = 5.7$ Hz, 2H), 2.51 (t, $J = 2.2$ Hz, 1H), 2.34–2.21 (m, 2H), 1.98 (dd, $J = 12.9$, 3.0 Hz, 2H), 1.94–1.80 (m, 4H), 1.79–1.71 (m, 4H), 1.63 (dq, $J = 12.9$, 2.7, 2.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 138.8, 128.7, 127.8, 127.4, 50.1, 43.5, 38.4, 37.4, 33.4, 30.0, 27.5, 27.4. FTIR: ν 3339.1, 2901, 2860.8, 2844.8, 1628, 1533.2, 1496.6, 1469.7, 1450.1, 1417.5 cm^{-1}. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{24}NO$ 270.1852; Found 270.1859. This compound is known to the literature [23].

*Benzyl phenylacetate (**31a**)*. Purchased from a chemical vendor. ^{1}H NMR (500 MHz, C_6D_6) δ 7.15–7.00 (m, 10H), 4.92 (s, 2H), 3.34 (s, 2H). ^{13}C NMR (126 MHz, C_6D_6) δ 170.4, 136.3, 134.2, 129.3, 128.4, 128.3, 128.1, 126.9, 66.1, 41.1.

*N-benzyl-2-phenylacetamide (**31b**)*. White solid. 659 mg (59 %). ^{1}H NMR (500 MHz, C_6D_6): δ 7.14–6.94 (m, 10H), 5.01 (s, 1H), 4.13 (d, $J = 6.0$ Hz, 2H), 3.21 (s, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 169.8, 139.6, 136.2, 129.8, 129.1, 128.9, 127.6, 127.4, 44.1, 43.7. Other characterization data and methods of synthesis can be readily found in the literature [24].

*Benzyl cyclopentanecarboxylate (**32a**)*. Light yellow oil. 123 mg (12 %). ^{1}H NMR (500 MHz, C_6D_6): δ 7.23–7.18 (m, 2H), 7.12–7.07 (m, 2H), 7.07–7.01 (m, 1H), 5.02 (s, 2H), 2.59 (tt, $J = 8.5$, 7.3 Hz, 1H), 1.92–1.80 (m, 2H), 1.73–1.60 (m, 2H), 1.57–1.45 (m, 2H), 1.33–1.21 (m, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 176.0, 137.3, 128.9, 128.6, 66.2, 44.2, 30.4, 26.2. Other characterization data and methods of synthesis can be readily found in the literature [25].

*N-benzylcyclopentanecarboxamide (**32b**)*. White solid. 814 mg (80 %). ^{1}H NMR (500 MHz, C_6D_6): δ 7.13–7.02 (m, 5H), 4.88 (s, 1H), 4.25 (d, $J = 5.9$ Hz, 2H), 1.98 (p, $J = 7.9$ Hz, 1H), 1.94–1.84 (m, 2H), 1.72–1.54 (m, 4H), 1.45–1.30 (m, 2H). ^{13}C NMR (126 MHz, C_6D_6): 176.0, 137.3, 128.9, 128.6, 66.2, 44.2, 30.4, 26.2. Other characterization data and methods of synthesis can be readily found in the literature [26].

5. Photolysis data

*Ai. Photolysis of **11** with benzyl alcohol and m-xylene:* Precursor **11** (3.3 mg, 0.009 mmol) was dissolved in C_6D_6 (0.75 mL) in a quartz NMR tube. To the solution was added benzyl alcohol (4.3 μL, 5.3 mg, 0.042 mmol) and *m*-xylene as an internal standard (1.5 μL, 1.3 mg, 0.012 mmol). Photolysis was monitored by NMR every hour until all **11** had reacted, or 5 h. Yields of the ester **29a** (1.1 mg, 0.004 mmol, 41 %) and phenanthrene (1.5 mg, 0.008 mmol, 92 %) were thus determined.

*Aii. Photolysis of **11** with benzylamine and m-xylene:* Precursor **11** (6.3 mg, 0.017 mmol) was dissolved in C_6D_6 (0.75 mL) in a quartz NMR tube. To the solution was added benzylamine (3.7 μL, 3.6 mg, 0.034 mmol) and *m*-xylene as an internal standard (2.5 μL, 2.2 mg, 0.020 mmol). Photolysis was monitored by NMR every 30 min until all **11** had reacted, or 2 h. Yields of the amide **29b** (4.5 mg, 0.015 mmol, 88 %) and phenanthrene (2.6 mg, 0.016 mmol, 92 %) were thus determined.

*Bi. Photolysis of **18** in benzyl alcohol and m-xylene:* Precursor **18** (13.9 mg, 0.0409 mmol) was dissolved in C_6D_6 (0.5 mL) in a quartz NMR tube. To the solution was added benzyl alcohol (6.63 μL, 6.89 mg, 0.0637 mmol) and *m*-xylene as an internal standard (1.50 μL, 1.29 mg, 0.0122 mmol). Photolysis was monitored by NMR until all **18** had reacted, or 6.5 h. Yields of the ester **30a** (3.61 mg, 0.0134 mmol, 33 %) and phenanthrene (6.80 mg, 0.0382 mmol, 94 %) were thus determined.

*Bii. Photolysis of **18** in benzylamine:* Precursor **18** (150 mg, 0.441 mmol) and benzylamine (92.1 μL, 90.4 mg, 0.845 mmol) were dissolved in benzene (4.5 mL) in a quartz pressure tube. Photolysis was monitored by GC-MS and TLC until all **18** had reacted, or 6 h. The amide (**30b**) was isolated using silica-gel flash column chromatography (0:100 → 50:50 ethyl acetate:hexanes) in a 31 % yield.

*Biii. Photolysis of **18** in benzylamine and m-xylene:* Precursor **18** (13.0 mg, 0.0384 mmol) was dissolved in C_6D_6 (0.5 mL) in a quartz NMR tube. To the solution was added benzylamine (5.60 μL, 5.49 mg, 0.0512 mmol) and *m*-xylene as an internal standard (1.50 μL, 1.29 mg, 0.0122 mmol). Photolysis was monitored by NMR until all **18** had reacted, or 3 h. Yields of the amide **30b** (9.85 mg, 0.0366 mmol, 95 %) and phenanthrene (6.59 mg, 0.0370 mmol, 96 %) were thus determined.

*Biv. Photolysis of **18** without an internal trap:* Precursor **18** (30.0 mg, 0.0881 mmol) was dissolved in benzene (2 mL) in a long-necked quartz cuvette. The solution was photolyzed for 7 h, checking *via* GC-MS once every hour. Ketene **13** was observed, along with a minor amount of 2-adamantanone and trace amounts of 2-adamantylcarboxylic acid. The addition of benzylamine (1 mL) to the photolysate and immediate analysis with GC-MS showed full conversion of **13** into amide **30b**, as well as reaction of 2-adamantanone with the amine to make imine **39**. No yields were determined.

*Bv. Photolysis of **18** with m-xylene but without an internal trap:* In a quartz NMR tube that had been purged with argon for 10 min, **18** (7.6 mg, 0.022 mmol) was dissolved in C_6D_6 (0.75 mL), and *m*-xylene (5.0 μL, 4.3 mg, 0.041 mmol) was added as an internal standard. The solution was photolyzed for 4 h, checking *via* NMR once per hour. Yields of ketene **13** (2.4 mg, 0.015 mmol, 62 %), 2-adamantanone (0.55 mg, 0.0036 mmol, 16 %), and phenanthrene (4.1 mg, 0.023 mmol, 98 %) were thus determined. To further confirm the identity of ketene **13**, benzylamine (10 μL) was subsequently added to the NMR tube, which immediately reacted to form amide **30b**.

*Ci. Photolysis of **19** with benzyl alcohol and m-xylene:* Precursor **19** (2.9 mg, 0.0098 mmol) was dissolved in C_6D_6 (0.75 mL) in a quartz NMR tube. To the solution was added benzyl alcohol (5.4 μL, 5.6 mg, 0.052 mmol) and *m*-xylene as an internal standard (5.0 μL, 4.3 mg, 0.041 mmol). Photolysis was monitored by NMR every 30 min until all **19** had reacted, or 1.5 h. Yields of the ester **31a** (1.4 mg, 0.0062 mmol, 63 %), phenanthrene (1.7 mg, 0.0093 mmol, 95 %), and benzaldehyde (0.099 mg, 0.00093 mmol, 9 %) were thus determined.

*Cii. Photolysis of **19** with benzylamine and m-xylene:* Precursor **19** (5.3 mg, 0.018 mmol) was dissolved in C_6D_6 (0.75 mL) in a quartz NMR tube. To the solution was added benzylamine (5.5 μL, 5.4 mg, 0.050 mmol) and *m*-xylene as an internal standard (2.5 μL, 2.2 mg, 0.020 mmol). Photolysis was monitored by NMR every 30 min until all **19** had reacted, or 1 h. Yields of the amide **31b** (4.1 mg, 0.018 mmol, 97 %) and phenanthrene (3.2 mg, 0.018 mmol, 98 %) were thus determined.

*Di. Photolysis of **21** with benzyl alcohol and m-xylene:* Precursor **21** (4.7 mg, 0.017 mmol) was dissolved in C_6D_6 (0.75 mL) in a quartz NMR tube. To the solution was added benzyl alcohol (5.1 μL, 5.3 mg, 0.049 mmol) and *m*-xylene as an internal standard (5.0 μL, 4.3 mg, 0.041 mmol). Photolysis was monitored by NMR every hour until all **21** had reacted, or 2 h. Yields of the ester **32a** (1.2 mg, 0.0058 mmol, 34 %) and phenanthrene (2.9 mg, 0.016 mmol, 94 %) were thus determined.

*Dii. Photolysis of **21** with benzylamine and m-xylene:* Precursor **21** (3.6 mg, 0.013 mmol) was dissolved in C_6D_6 (0.75 mL) in a quartz NMR tube. To the solution was added benzylamine (4.5 μL, 4.4 mg, 0.041 mmol) and *m*-xylene as an internal standard (2.5 μL, 2.2 mg, 0.020 mmol). Photolysis was monitored by NMR every 30 min until all **21** had reacted, or 1 h. Yields of the amide **32b** (2.4 mg, 0.012 mmol, 92 %) and phenanthrene (2.2 mg, 0.012 mmol, 92 %) were thus determined.

Author contributions

A. D. R. synthesized precursors **18** and **19**, acquired and solved X-ray diffraction data, performed photolysis experiments, conducted trapping studies on ketenes **13**-**15**, and assisted with the writing of the initial manuscript draft and supplementary information; Z. K. synthesized precursors **11**, **18** and **21**, performed their photolysis experiments, conducted trapping studies on ketene **12**, assisted with the writing of the initial manuscript draft and supplementary information, and contributed to the revision of the supplementary information to comply with reviewer comments; B. H. F. and K. M. L. synthesized precursor **19** and the latter investigated its photochemical reactions; K. K. and S. M. H. synthesized **18** and investigated its photochemical decomposition; H. A. and T. S. H. synthesized **11** and investigated its photochemistry; and D. M. T. designed and supervised the projects, and produced the final drafts

of the manuscript and supplementary information, including revisions. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2024.134344.

Data availability

Data will be made available on request.

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