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Synthesis and photosensitized oxygenation of cyclopropylidenecyclobutenes

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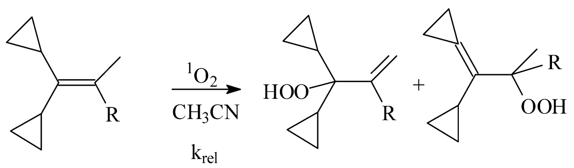
Abstract—Cyclopropylidenecyclobutenes and -cyclobutanes were conveniently prepared using the Petasis titanocene approach. The cyclobutenes were unreactive to singlet oxygen, reacting sluggishly via a photoinitiated free radical autooxidative epoxidation process, to yield the corresponding spiroketones. By contrast, cyclopropylidenecyclobutanes react rapidly with $^1O_2$, via an 'ene' process, initially generating a cyclopropyl hydroperoxide, which proceeds to products via Hock cleavage. The inertness of cyclopropylidenecyclobutenes to a $^1O_2$ 'ene' reaction mode may be attributed to the fact that it would require the formation of the relatively high energy cyclobutadiene moiety.

1. Introduction

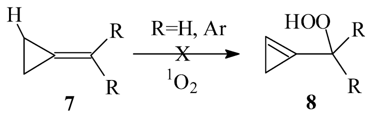
Previous studies carried out in our laboratory have explored the reaction of singlet oxygen with small ring-strained olefins.[1] These studies indicate the following:[1e,l]

(1) The course of the singlet oxygen ene reaction is not determined simply by thermodynamic stability of the resulting hydroperoxy alkenes.[1a,b] Thus, in the singlet oxygen 'ene' reaction of dicyclopropyl olefins **1** and **4** (Scheme 1), allylic hydrogen abstraction occurs both from the methyl group (to give **2** and **5**) and from the three-membered ring (giving **3** and **6**, respectively). This is despite the fact that, in the latter case, the formation of an alkylidenecyclopropane requires an investment of 11.4 kcal of strain energy.[1a,c] This conclusion is consistent with prior evidence that singlet oxygen reactions have very small activation energies (0.5–8 kcal/mol)[2] and that the product-determining transition state is reactant-like and occurs quite early.[3]



Scheme 1. Singlet oxygenation of vinylcyclopropanes **1** and **4**.

(2) The $^1O_2$ 'ene' reaction is dependent on the interatomic distance between the α-olefinic carbon and the γ-allylic hydrogen. The reactive cycloolefins methylenecyclobutane and methylcyclobutene, like isobutylene, all have a C_α–$H_{allylic}$ distance below 3.09 Å, while for those which are unreactive, such as methylenecyclopropane and methylcyclopropene, this value is above 3.24 Å. It may be these crucial 0.15 Å which, in the latter case, place the abstractable γ-allylic hydrogen 'out of reach' of the attacking singlet oxygen molecule which must span this interatomic distance. Thus, in the photosensitized oxygenation of various alkylidenecyclopropane derivatives (Scheme 2), we discovered that the allylic ring hydrogens were inert to ene-reaction, even when no other allylic hydrogens were available for abstraction.[1b,e]



Scheme 2. Singlet oxygenation of alkylidenecyclopropanes **7**.

(3) The $^1O_2$ 'ene' reaction is dependent on the orientation of the adjacent γ-allylic hydrogen. In the $^1O_2$ ene reaction, there is a strong preference for the abstraction of those allylic hydrogens aligned in a 90° dihedral angle with respect to the plane of the double bond in the low energy conformations of the olefin.[1g,3] Similarly, in cyclic systems, the abstraction of pseudo-axial hydrogens are greatly preferred over pseudo-equatorial ones. Thus, the allylic ring hydrogens (H_b) of both cyclopropenes[4] and alkylidenecyclopropanes[5] are displaced ca. 35° from the perpendicular and resist abstraction in a singlet oxygen process (Fig. 1).

Keywords: cyclopropylidenecyclobutenes; cyclopropylidenecyclobutanes; synthesis; oxygen; singlet; autoxidation; epoxidation.
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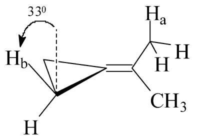
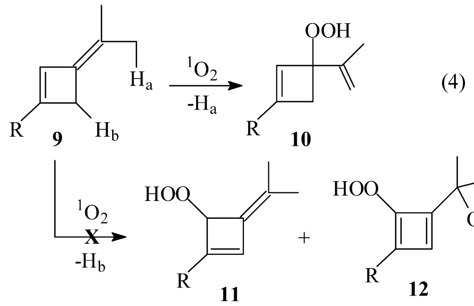


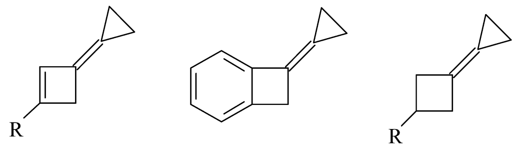
Figure 1. The 33° displacement from the perpendicular of the alkylidenecyclopropane allylic ring hydrogens.

In light of the first observation, we speculated as to whether singlet molecular oxygen reactions could be used to obtain access to the relatively high-energy cyclobutadiene moiety. To this end, Frimer and Weiss[1h] studied the singlet oxygenation of alkylidenecyclobutenes (Scheme 3), and observed exclusive formation of 'ene' reaction product **10**. The latter resulted from oxygen attack at the exocyclic double bond with concomitant abstraction of allylic hydrogen H_a. There was no evidence for abstraction of allylic ring hydrogen H_b accompanied by oxygen attack at either the endo or exocyclic double bonds, which would have yielded cyclobutene **11** or cyclobutadiene **12**, respectively.



Scheme 3. Singlet oxygenation of alkylidenecyclobutene **9**.

In the hope of eliminating competing reaction at H_a, and of forcing the system towards endocyclic proton H_b abstraction, we decided to synthesize cyclopropylidenecyclobutenes **13–15** and, for comparison, saturated analogs **16** (Fig. 2). As noted in observations 2 and 3 above, the cyclopropyl ring protons in **13–16** are unreactive in the $^1O_2$ ene reaction, leaving the cyclobutyl ones as the only protons that might react.



13: R=Bu **14:** R=Ph — **15** — **16a:** R=Bu **16b:** R=Ph

Figure 2. Synthesized cyclopropylidenecyclobutenes and -butanes **13–16**.

2. Results and discussion

2.1. Synthesis of cyclopropylidenecyclobutenes 13–15 and -cyclobutanes 16

The synthesis of the cyclopropylidenecyclobutene system with an unsubstituted cyclopropyl ring is to the best of our knowledge unreported. Because of the ready availability of benzocyclobutenone **17**,[6] we used it in the exploratory studies described below in Scheme 4.

None of the desired product was formed when we used the classic Wittig approach of Utimoto,[7] with or without sonication.[8] These difficulties can be attributed, in part, to the low electrophilicity of the cyclobutenone carbonyl which is not only conjugated, but also has lower p character.[9] This effect of ring strain on hybridization presumably also plays a role in the low nucleophilicity of the cyclopropyl carbanion of Wittig salt **18**, by increasing its s-character. When, however, this reaction was activated by tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1),[10] we recovered a 7% yield of ketone **20** as the only isolable product. The mechanism for this transformation is as yet unknown, but may well involve zwitterion **19** (Scheme 4, approach 1). An alternative strategy involves a Knoevenagel condensation[11] between benzocyclobutanone **17** and diethylmalonate **21** (Scheme 4, approach 2). Unfortunately, this pathway was also blocked by the poor electrophilicity of cyclobutanone **17** which resisted condensation regardless of the Lewis acid utilized (e.g. $TiCl_4$, $BF_3{\cdot}(OEt)_3$).[11] Attempts to obtain **15** by decarboxylation of α-lactone[12] **26** were thwarted because benzocyclobutanone **17** resisted nucleophilic attack by thioester **25** (Scheme 4, approach 3). We also attempted to create the olefinic linkage, prior to cyclopropyl ring formation, by reacting the benzocyclobutyl Wittig reagent **27**[13] with 1,3-dichloroacetone **28** followed by reductive cyclization (Scheme 4, approach 4). Unfortunately, the first step did not proceed as desired; we attribute this to a precedented[14] competing nucleophilic attack of the ylide on the chlorinated α-carbons of **27**.

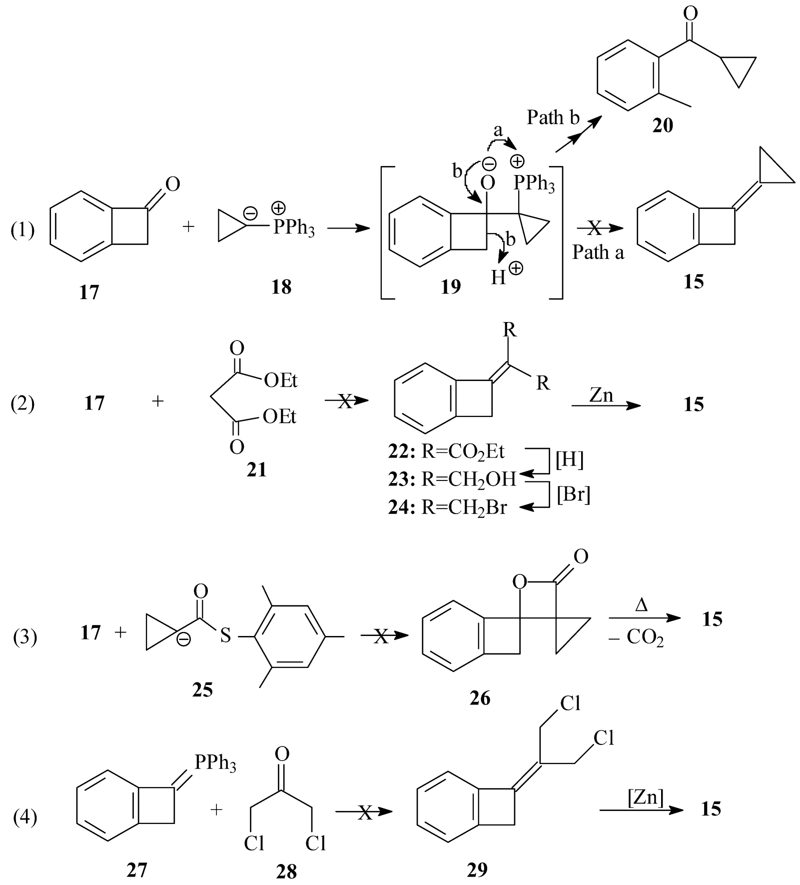
We finally succeeded in developing an easy and convenient synthesis of cyclopropylidenecyclobutenes based on the titanocene approach of Petasis and co-workers.[15] Thus, cyclopropylidenecyclobutenes **13–15** were prepared in low to fair yields (4–39%), and cyclopropylidenecyclobutanes **16** in moderate to good yields (ca. 50–85%), by reacting biscyclopropyltitanocene **34** with the corresponding ketone (Scheme 5).

Interestingly, in the synthesis of **16b**, we succeeded in isolating low yields (<1% each) of two side products, dicyclopropylcyclobutane **35** and cyclopropylidenebutene **36** (Scheme 6). The mechanistic details of these transformations are as yet unclear.

2.2. Photosensitized oxygenation of cyclopropylidenecyclobutenes 13 and 15

Rose Bengal (RB) or methylene blue (MB) photosensitized oxidation of cyclobutenes **13** and **15** in CH_3CN and $CDCl_3$, respectively, proceeded sluggishly (variable O_2 uptake of ca. 0.1 equiv. in 8 h) and was accompanied by sensitizer bleaching.[16] In each case, the only product isolated was the corresponding spiro[3.3]heptenones **39** and **40**, respectively (Scheme 7).

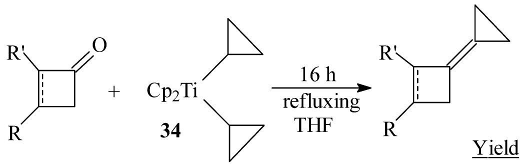
It should be noted that triphenylphosphine is commonly added at the end of $^1O_2$ reactions to reduce any hydroperoxides formed to the more stable alcohols. This Ph_3P reduction of hydroperoxides is typically exothermic. Indeed, instances where release of heat are not observed generally indicate that hydroperoxides are either not formed, or are so labile that they rearrange to non-peroxidic



Scheme 4. Four synthetic approaches to the synthesis of cyclopropylidenebenzocyclobutane **15**.

products prior to Ph_3P treatment.[1b,d,f,g] In the present study, the addition of Ph_3P generated no heat and had little if any effect on the product distribution. Hence, work-up of the present reaction mixtures were carried out without prior addition of Ph_3P.

There is clear evidence in this study to demonstrate that a non-singlet oxygen/free radical mechanism predominates in this photosensitized oxidation. (1) The $^1O_2$-quencher[1g,17] DABCO did not slow the rate or course of the reaction. (2) On the other hand, addition of the free-radical inhibitor 2,6-di-*tert*-butylphenol[1g,18] inhibited the reaction completely. (3) The sensitizer bleaching is a strong indication that the sensitizer is doing more than simply transferring excitation energy; it is chemically involved somehow in initiating a free-radical process.[1d,i,j] In addition, we note that the same spiroketones are formed when the cyclopropylidenecyclobutenes are allowed to undergo autoxidation, by standing for a week in air at room temperature (see Scheme 7).



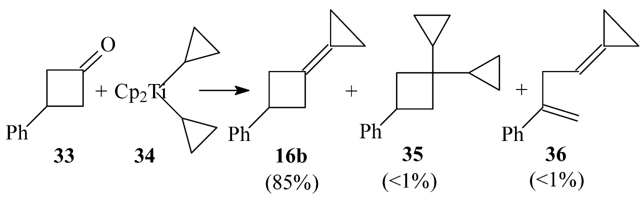
30: R=Bu-n;R'=H	**13**	26 %
31: R=Ph;R'=H	**14**	4 %
17: R,R'=C_4H_4	**15**	39 %
32: R=Bu;R'=H (Saturated)	**16a**	51 %
33: R=Ph;R'=H (Saturated)	**16b**	85 %

Scheme 5. Synthesis of cyclopropylidenecyclobutenes and -butanes.

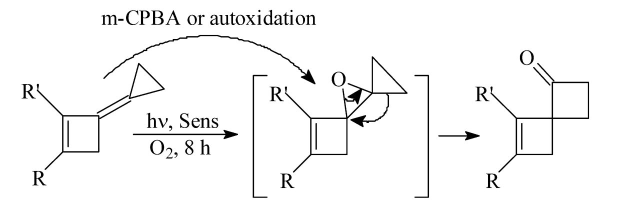
In light of the above, it is clear that the spiro[3.3]heptenones **39** and **40** are formed via epoxides **37** and **38**, generated in a photoinitiated free-radical autoxidation of cyclopropylidenecyclobutenones **13** and **15**. Free-radical autoxidation, in particular short-chain polyperoxidation, is a process in which the formation of epoxides is a well known phenomenon.[19] This rearrangement of epoxides **37** and **38** to the corresponding spiroketones was confirmed by treating cyclopropylidenecyclobutenones **37** and **38** with an equivalent of *m*-chloroperbenzoic acid (see Scheme 7).

2.3. Photosensitized oxygenation of 3-phenyl-1-cyclopropylidenecyclobutane 16b

The situation is dramatically different in the photosensitized oxidation of cyclopropylidenecyclobutane **16b** (MB/$CDCl_3$). In this case, the uptake of oxygen was rapid (1 equiv. in 2 h), with essentially no bleaching of the



Scheme 6. Side products in the synthesis of cyclopropylidenecyclobutane **16b**.

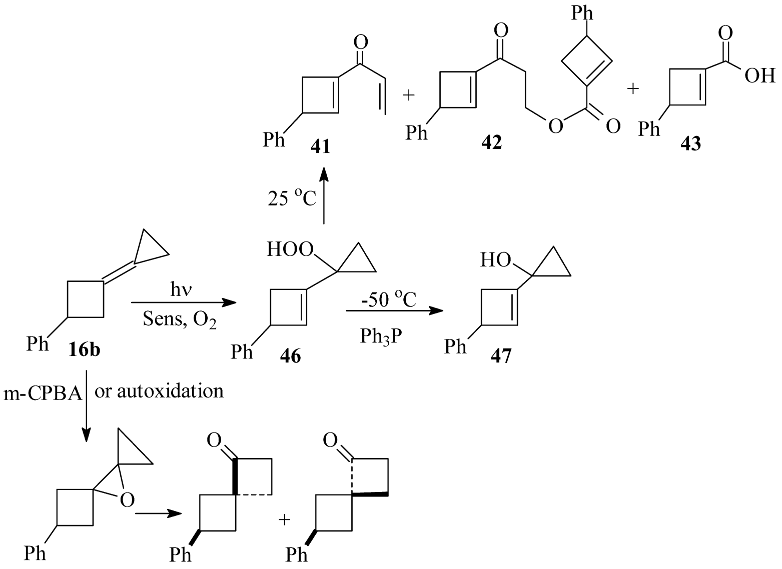


Scheme 7. Photosensitized oxygenation of cyclopropylidenecyclobutenes **13** and **15**.

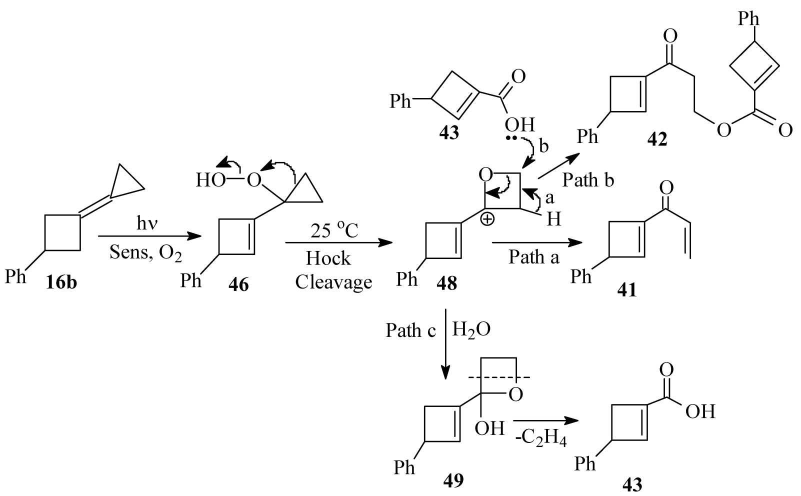
sensitizer. When the photosensitized oxidation was carried out at room temperature, three major products—identified as dienone **41**, ester **42**, and acid **43**—were formed in a 6:1:1 ratio (Scheme 8). In contradistinction to the unsaturated analog **15**, no spiroketone **44b** was observed in the product mixture. The latter could be generated by allowing the starting material to stand under air (autoxidation) or by treating **16b** with *m*-CPBA. Similar treatment of **16a** with *m*-CPBA yields *cis* and *trans*-**44a**.

Turning now to the question of mechanism, we suspected the intermediacy of the labile cyclopropyl hydroperoxide **46**. In the hope of trapping **46**, we repeated the photosensitized oxygenation at −50°C, treating the reaction mixture with triphenylphosphine prior to warming. Indeed, in this case, the isolated product was alcohol **47** exclusively. (Upon standing at room temperature for several days, the latter undergoes a precedented[20] rearrangement to a mixture of *cis* and *trans* cyclobutanone **44b**.) The $^1O_2$-quencher DABCO dramatically slowed the rate of the photooxygenation, while the free-radical inhibitor 2,6-di-*tert*-butylphenol had little, if any, effect on the rate or course of the reaction.

In light of all the above data, it is highly likely that this process involves a $^1O_2$-ene reaction, initially yielding labile hydroperoxide **46** (Scheme 9). Low temperature reduction of the latter generates the corresponding alcohol **47** exclusively. However, at room temperature, the labile hydroperoxide undergoes Hock-cleavage[1f,3c,d,21] passing through a ring-strained oxycarbonium ion, oxetane **48**. In well precedented processes,[3c,d] the latter either loses a



Scheme 8. Reaction of cyclopropylidenecyclobutane **16b** with $^1O_2$ and *m*-CPBA, and under autoxidation.



Scheme 9. Mechanism for the formation of cyclobutenes **41**, **42** and **43**.

proton yielding divinyl ketone **41** (Scheme 9 path a), undergoes nucleophilic attack by acid **43** generating ester **42** (Scheme 9 path b), or adds water generating hemiacetal hydroxyoxetane **49**. Loss of the elements of ethylene from the latter in a retro-Patterno–Buchi reaction[22] gives acid **43**.

The formation of dienone **41**, ester **42** and acid **43** in the photooxidation of cyclopropylidenecyclobutane **16** is highly reminiscent of the formation of the corresponding products **51–53** in the singlet oxygenation of other cyclopropylidenealkanes (i.e. alkylidenecyclopropanes) **50a** and **b** (Scheme 10).[1b] A similar mechanism was invoked in that case as well.

2.4. Is a singlet oxygen approach to cyclobutadiene feasible?

As stated in the Introduction, we initially embarked upon this research in order to get better insight into the role played by the alignment of the allylic ring hydrogen in four membered ring systems in controlling the $^1O_2$ ene reaction. As noted above, this mode of reaction shows a strong preference for those allylic hydrogens aligned in a 90° dihedral angle with respect to the plane of the double bond in the low energy conformations of the olefin.[1g,3] Similarly, in cyclic systems, the abstraction of pseudo-axial hydrogens are greatly preferred over pseudo-equatorial ones.

In this light, we see that alkylidenecyclobutenes **13–15** are four-membered rings containing three trigonal carbons which are constrained to be planar. The remaining ring methylene hydrogens—the only available allylic hydrogens on the ring—are displaced ca. 36° from the perpendicular[23] and there is no way these allylic ring hydrogens can attain anything even approximating a pseudo-axial position.

In previous studies,[1g,h,k,l] we have argued that it is this factor which totally inhibits $^1O_2$-ene reactivity in the alkylidenecyclobutenyl system. We are no longer convinced, however, that this is so. Consider methylenecyclobutane, which is almost planar in its low energy conformation, with at most a 3.8° pucker.[24] Here, too, the allylic ring hydrogens are highly unlikely to attain the proper alignment in the low energy conformations. Nevertheless, when no other choice is available, as in the case of cyclopropylidenecyclobutane **16**, these ring hydrogens do indeed react. The literature[1e] records that the ring hydrogens of methylenecyclobutane,[25] bicyclobutylidene,[26] and cyclopropylmethylenecyclobutane[27] undergo $^1O_2$ ene reaction; but again, these are instances in which the ring hydrogens are the only ones available.

Yet, as just noted, the ring methylene hydrogens of alkylidenecyclobutenes are inert to $^1O_2$. Perhaps, Conia was correct after all when he first suggested[28] that it is the incipient formation of the cyclobutadiene moiety in the product which is the underlying inhibiting factor.

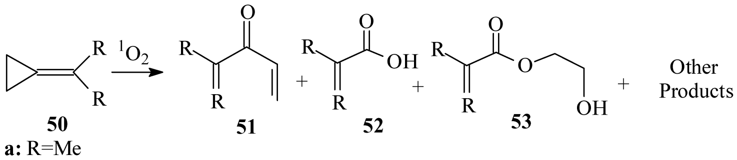
3. Experimental

3.1. General

NMR spectra were obtained on Bruker DMX-600, DPX-300 and AC-200 Fourier transform spectrometers. Assignments were facilitated with DEPT (DPX-300), by correlating proton and carbon chemical shifts through analysis of residual couplings in off-resonance decoupled spectra (AC-200), and via long range hetero COSY and NOESY experiments (DMX-600) as needed. In all cases, TMS served as the internal standard. FTIR spectra were measured with a Nicolet Impact 400D FTIR spectrometer. The samples were neat liquids on a KBr disk. EI and CI (NH_3, CH_4 or *i*-butane) mass spectra were run on a Finnigan-4021 GC/MS machine (at 70 eV, unless otherwise indicated); high resolution mass spectral (HRMS) were performed on a VG-Fison AutoSpecE High Resolution Spectrometer. We note that CI mass spectra run using *i*-butane quite often give an M^+ peak rather than the expected MH^+ peak. Column chromatography separation was carried out using Merck silica gel 230–400 mesh. It should be noted that in the case of butylspiroketones **39** and **44a**, the TLC plates yielded no observable product spots when developed using iodine, vanillin or $KMnO_4$. We discovered, however, that an anisaldehyde-based developing solution was very effective.[29] The solution we used was comprised of anisaldehyde (6.25 mL), ethanol (225 mL), acetic acid (2.5 mL) and conc. sulfuric acid (8.75 mL). The TLC plate was briefly immersed into this developing solution, drained and then dried with a heating fan. The product spots are purple in color. Cyclobutyl ketones **17**,[30] **30**,[31] **31**,[32] **32**[1h] and **33**[33] were prepared according to literature procedures. The compounds synthesized or isolated were numbered as shown below (Fig. 3).

3.2. General procedure for the preparation of cyclopropylidenecyclobutenes and cyclobutanes

A flame dried two necked flask equipped with an argon inlet adapter and glass stopper, was charged with a magnetically stirred suspension of biscyclopropyltitanocene[15] (**34**, 2.5 equiv.) in dried THF (approximately 65 mL per 1 g of cylobutyl ketone).[34] Cyclobutyl ketone (1 equiv—exact quantities are given below for each substrate) was added in one portion and the red orange solution was allowed to reflux overnight. A black–brown solution was obtained which was evaporated down to a black residue. Stirring the residue under argon in *n*-hexane (ca. 60 mL of hexane in



Scheme 10. Photosensitized oxygenation of alkylidenecyclopropanes **50**.

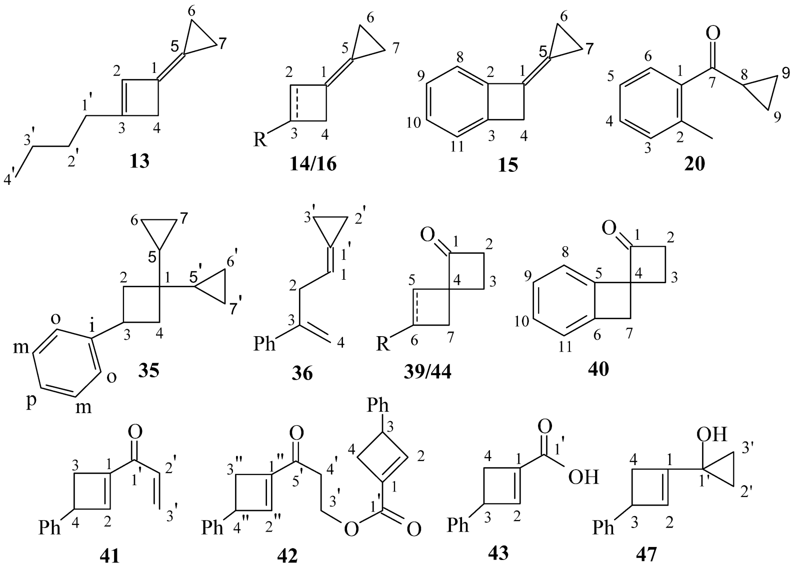


Figure 3. Numbering of the carbons used in the NMR spectral data.

three portions per 1 g of residue) liberated a yellow suspension. The latter was purified on a short silica pad which yielded the cyclopropylidene after solvent removal (which was the above 60 mL of the yellow suspension plus 15% more to was the pad).

3.2.1. 1-Cyclopropylidene-3-*n*-butyl-2-cyclobutene (13). 3-*n*-Butyl-2-cyclobutene-1-one[31] (**30**, 2 g, 16.1 mmol) was reacted with biscyclopropyltitanocene (**34**) according to the above general procedure yielding cyclopropylidenecyclobutene **13** as a colorless liquid (607 mg, 4.1 mmol, 26% yield).

Compound **13**: δ_H (300 MHz, $CDCl_3$) 6.12 (1H, s, H_2), 2.89 (2H, s, H_4), 2.26 (2H, t, J=7 Hz, $H_{1'}$), 1.47 (2H, m, $H_{2'}$), 1.36 (2H, m, $H_{13'}$), 1.09 (4H, bs, H_6 and H_7), 0.92 (3H, t, J=6.8 Hz, $H_{4'}$); δ_C (75.5 MHz, $CDCl_3$) 156.0 (C_3), 129.2 (C_2), 127.3 (C_1), 102.8 (C_5), 38.3 (C_4), 30.7 ($C_{1'}$), 29.1 ($C_{2'}$), 22.5 ($C_{3'}$), 13.9 ($C_{4'}$), 2.5 and 1.7 (C_6 and C_7); ν_{max} (KBr) 3083, 3006, 2958, 2928, 2859, 1630, 1589, 1427, 1023, 892 cm^{-1}; *m/z* (CI, CH_4) 149 (MH^+, 13%), 148 (M, 45%), 133 ($M-CH_3$, 20%), 121 ($MH^+-C_2H_4$, 16%), 105 ($M-C_3H_7$, 73%), 91 ($M-C_4H_9$, 100%); HRMS (CI, CH_4): MH^+, found 149.1319. $C_{11}H_{17}$ requires 149.1330.

3.2.2. 1-Cyclopropylidene-3-phenyl-2-cyclobutene (14).[35] 3-Phenyl-2-cyclobutene-1-one[32] (**31**, 2 g, 13.8 mmol) was reacted with biscyclopropyltitanocene (**34**) according to the above general procedure yielding cyclopropylidenecyclobutene **14** as a pale yellow liquid (100 mg, 0.6 mmol, 4% yield).

Compound **14**: δ_H (300 MHz, $CDCl_3$) 7.46–7.24 (5H, m, aryl), 6.68 (1H, s, H_2), 3.28 (2H, s, H_4), 1.12 (4H, s, H_6 and H_7).

3.2.3. 1-Cyclopropylidenebenzocyclobutane (15). Benzocyclobutanone[30] (**17**, 2 g, 16.9 mmol) was reacted with biscyclopropyltitanocene (**34**) according to the above general procedure yielding cyclopropylidenebenzocyclobutane **15** as a colorless liquid (923 mg, 6.5 mmol, 39% yield).

Compound **15**: δ_H (300 MHz, $CDCl_3$) 7.20–7.15 (4H, m, aryl), 3.68 (2H, s, H_4), 1.30–1.22 (4H, m, H_6 and H_7); δ_C (75.5 MHz, $CDCl_3$) 145.8 and 145.5 (C_2 and C_3), 127.8 and 127.4 (C_9 and C_{10}), 126.6 (C_1), 122.8 (C_{11}), 118.2 (C_8), 112.2 (C_5), 38.8 (C_4), 3.4 and 2.2 (C_6 and C_7); ν_{max} (KBr) 3063, 2976, 2952, 1459, 1447, 1335, 749 cm^{-1}; *m/z* (CI, NH_3) 176 ($M+N_2H_6$, 100%), 159 ($M+NH_3$, 48%), 143 (MH^+, 17%), 116 ($M-C_2H_2$, 36%); HRMS (CI, NH_3): MH^+, found 143.0856. $C_{11}H_{11}$ requires 143.0861.

3.2.4. 1-Cyclopropylidene-3-butylcyclobutane (16a). 3-Butylcyclobutanone[33] (**31**, 1.72 g, 13.6 mmol) was reacted with biscyclopropyltitanocene according to the above general procedure yielding cyclopropylidenecyclobutane **16a** as a colorless liquid with a strong odor (1.03 g, 6.9 mmol, 51% yield).

Compound **16a**: δ_H (300 MHz, $CDCl_3$) 2.89 (1H, m, H_3), 2.33 (2H, m, H_2 and H_4), 2.29 (2H, dt, J=7.0, 1.5 Hz, $H_{2'}$ and $H_{4'}$), 1.47 (2H, m, $H_{1'}$), 1.39–1.21 (8H, m, $H_{2'}$ and $H_{3'}$, and H_6 and H_7), 0.89 (3H, t, J=7.2 Hz, $H_{4'}$); δ_C (75.5 MHz, $CDCl_3$) 127.3 (C_1), 110.5 (C_5), 36.9 (C_2 and C_4), 36.6 ($C_{1'}$), 31.2 (C_3), 29.8 ($C_{2'}$), 22.7 ($C_{3'}$), 14.2 ($C_{4'}$), 1.9 (C_6 and C_7); ν_{max} (KBr) 2957, 2925, 2855, 1465, 1260, 1017 cm^{-1}; *m/z* (CI, *i*-butane) 151 (MH^+, 58%), 137 (MH^+-CH_2, 51%), 123 ($MH^+-C_2H_4$, 15%), 111 ($MH^+-C_3H_4$, 39%), 85 ($MH^+-C_5H_6$, 100%); HRMS (CI, *i*-butane): MH^+, found 151.1474. $C_{11}H_{19}$ requires 151.1487.

3.2.5. 1-Cyclopropylidene-3-phenylcyclobutane (16b). 3-Phenylcyclobutanone[33] (**33**, 2 g, 13.7 mmol) was reacted with biscyclopropyltitanocene (**34**) according to the above general procedure yielding cyclopropylidenecyclobutane **16b** as a colorless liquid (1.99 g, 11.7 mmol, 85% yield). This sample was slightly contaminated by two side products, 1,1-dicyclopropyl-3-phenylcyclobutane (**35**) and 1-cyclopropylidene-3-phenyl-3-butene (**36**), which were present in less than 1% each. A mixture of **35** and **36** was isolated and characterized following the photooxidation of **16b** (vide infra, Section 3.4.2).

Compound **16b**: δ_H (300 MHz, $CDCl_3$) 7.28–7.26 (3H, m, *meta* and *para*), 7.16 (2H, m, *ortho*), 3.56 (1H, quint, J=8.3 Hz, H_3), 3.17 (2H, m, H_2 and H_4), 2.94 (2H, m, H_2 and H_4), 1.02 (4H, bd, J=0.8 Hz, H_6 and H_7); δ_C (75.5 MHz, $CDCl_3$) 146.1 (*ipso*), 128.3 (*meta*), 126.4 (*para*), 125.9 (*ortho*), 124.1 (C_1), 111.1 (C_5), 39.0 (C_2 and C_4), 35.7 (C_3), 2.1 (C_6 and C_7); ν_{max} (KBr) 3061, 3027, 2977, 2951, 2912, 1605, 1495, 1454, 747, 697 cm^{-1}; *m/z* (CI, CH_4) 171 (MH^+, 24%), 143 ($MH^+-C_2H_4$, 42%), 129 ($MH^+-C_3H_6$, 100%), 117 ($MH^+-C_4H_6$, 17%); HRMS (CI, CH_4): MH^+, found 171.1130. $C_{13}H_{15}$ requires 171.1174.

Compound **35**: δ_H (600 MHz, $CDCl_3$) 7.35–7.15 (5H, m, aryl), 3.34 (1H, quint, J=9.0 Hz, H_3), 1.9 (2H, dddd, J=12.0, 9.0, 4.0, 1.0 Hz, H_2 and H_4), 1.72 (2H, dddd, J=12.0, 9.0, 3.0, 1 Hz, H_2 and H_4), 1.02 (1H, m, H_5), 0.85 (1H, tt, J=8.5, 5.5 Hz, $H_{5'}$), 0.49 (2H, ddd, J=8.0, 6.0, 4.0 Hz, H_6 and H_7), 0.36 (2H, ddd, J=6.0, 5.0, 4.0 Hz, H_6 and H_7), 0.33 (2H, ddd, J=8.0, 5.5, 4.0 Hz, $H_{6'}$ and $H_{7'}$), 0.21 (2H, dt, J=4.0, 6.0 Hz, $H_{6'}$ and $H_{7'}$); δ_C (150 MHz, $CDCl_3$) 146.50 (*ipso*), 128–125 (aromatic), 36.9 (C_1), 34.5 (C_2 and C_4), 33.9 (C_3), 19.6 ($C_{5'}$), 19.2 (C_5), 1.0 (C_6 and C_7), 0.6 ($C_{6'}$ and $C_{7'}$); *m/z* (CI, *i*-butane) 211 (M^+-H, 4%), 184 ($M-C_2H_2$, 8%), 156 ($M-C_4H_4$, 4%); HRMS (CI, *i*-butane): M^+-H, found 211.1472. $C_{16}H_{19}$ requires 211.1487.

Compound **36**: δ_H (600 MHz, $CDCl_3$) 7.46 (2H, dd, J=8.5, 1.0 Hz, *ortho*), 7.31 (2H, m, *meta*), 7.19 (1H, m, *para*), 5.84 (1H, tquint, J=6.5, 2.0 Hz, H_1), 5.36 (1H, d, J=1.0 Hz, H_4), 5.11 (1H, q, J=1.5 Hz, H_4), 3.38 (2H, dd, J=4.0, 1.5 Hz, H_2), 1.05 (2H, m, $H_{2'}$), 1.02 (2H, m, $H_{3'}$); δ_C (150 MHz, $CDCl_3$) 147.1 (C_3), 141.1 (*ipso*), 126.0 (*ortho*), 125–123 (*meta* and *para*), 123.4 ($C_{1'}$), 115.8 (C_1), 112.5 (C_4), 37.8 (C_2), 2.5 ($C_{2'}$), 1.8 ($C_{3'}$); *m/z* (CI, *i*-butane) 170 (M^+, 4%), 141 ($M-H-C_2H_2$, 36%), 130 ($M-C_3H_4$, 69%); HRMS (CI, *i*-butane): M^+, found 170.1091. $C_{13}H_{14}$ requires 170.1095.

3.2.6. Cyclopropyl-*o*-tolylmethanone (20). Benzocyclobutanone (**17**, 780 mg, 6.6 mmol) was reacted with the cyclopropyl Wittig reagent prepared via the method of Utimoto[7] using TDA-1 as catalyst.[10] The reaction was allowed to proceed for 6 days, at which time TLC (5% ethyl acetate in hexane) revealed that all the starting material had disappeared. Silica gel chromatography, eluting with a gradient of 0–50% ethyl acetate in hexane, yielded the title compound as a yellowish liquid (74 mg, 0.46 mmol, 7% yield).

Compound **20**: δ_H (600 MHz, $CDCl_3$) 7.70 (1H, dd, J=7.7, 1.5 Hz, H_6), 7.35 (1H, dt, J=7.7, 1.5 Hz, H_4), 7.26 (2H, m, H_5 and H_3), 2.47 (3H, s, methyl), 2.42 (1H, dt, J=7.8, 4.6 Hz, H_8), 1.24 (2H, m, H_9), 1.03 (2H, m, H_9); δ_C (150 MHz, $CDCl_3$) 205.0 (C_7), 139.7 (C_1), 136.8 (C_2), 131.4 (C_3), 130.7 (C_4), 128.2 (C_6), 125.5 (C_5), 20.7 (C_8), 20.6 (methyl), 11.81 (C_9); ν_{max} (KBr) 3062, 3009, 2928, 1672, 1378, 1220, 987, 737 cm^{-1}; *m/z* (CI, CH_4) 161 (MH^+, 100%), 135 ($MH^+-C_2H_2$, 25%), 119 ($MH^+-C_3H_6$, 50%); HRMS (CI, CH_4): MH^+, found 161.0987. $C_{11}H_{13}O$ requires 161.0966.

3.3. General epoxidation procedure

m-CPBA (1 equiv.) was added to a magnetically stirred CH_2Cl_2 solution (30 mL/mmol of substrate) of cyclopropylidenecyclobutene (1 equiv.—exact quantities are given below for each substrate), and the colorless solution was allowed to stir at room temperature overnight. The solution was transferred to separatory funnel, extracted successively with two 40 mL/mmol portions of 10% bisulfite solution, two 40 mL/mmol portions of saturated bicarbonate solution and one 40 mL/mmol portion of saturated sodium chloride solution, dried over magnesium sulfate and the solvent was removed in vacuo.

3.3.1. 6-Butylspiro[3.3]hept-5-en-1-one (39). 1-Cyclopropylidene-3-*n*-butyl-2-cyclobutene (**13**, 0.15 g, 1.01 mmol) was reacted with *m*-CPBA according to the above general procedure. Chromatographic separation, eluting with 20% ethyl acetate in petroleum ether, yielded spiroketone **39** (R_f=0.52) as a colorless liquid (106 mg, 0.646 mmol, 64% yield). The TLC plates were developed using the aforementioned[29] anisaldehyde-based developing solution.

Compound **39**: δ_H (300 MHz, $CDCl_3$) 5.78 (1H, s, H_5), 2.92 (2H, m, H_2), 2.71 (1H, dt, J=12.5, 0.8 Hz, H_7), 2.54 (1H, dd, J=12.5, 0.9 Hz, H_7), 2.21 (2H, t, J=8 Hz, $H_{1'}$), 2.03 (2H, tt, J=2.5, 1.0 Hz, H_3), 1.45–1.30 (4H, m, $H_{2'}$ and $H_{3'}$), 0.87 (3H, t, J=3.5 Hz, $H_{4'}$); δ_C (75.5 MHz, $CDCl_3$) 214.6 (C_1), 152.0 (C_6), 128.0 (C_5), 66.8 (C_4), 42.88 (C_2), 41.39 (C_7), 31.53 ($C_{1'}$), 30.27 ($C_{2'}$), 28.34 (C_3), 22.35 ($C_{3'}$), 14.05 ($C_{4'}$); ν_{max} (KBr) 2957, 2928, 2873, 1781, 1630, 1466, 1262, 1045 cm^{-1}; *m/z* (CI, *i*-butane) 163 (M^+-H, 16%), 140 (MH^+-CH_3, 100%), 136 (MH^+-CO, 26%), 107 ($MH^+-C_4H_9$, 39%), 95 ($M-C_4H_5O$, 50%); HRMS (CI, *i*-butane): M^+-H, found 163.1118. $C_{11}H_{15}O$ requires 163.1123.

3.3.2. 5,6-Benzospiro[3.3]heptan-1-one (40). 1-Cyclopropylidenebenzocyclobutene **15** (0.22 g, 1.55 mmol) was reacted with *m*-CPBA according to the above general procedure. Chromatographic separation, eluting with 20% acetone in hexane, yielded the spiroketone **40** (R_f=0.37) as a yellowish liquid (160 mg, 1.01 mmol, 65% yield).

Compound **40**: δ_H (300 MHz, $CDCl_3$) 7.23 (2H, m, H_8 and H_{11}), 7.08 (2H, m, H_9 and H_{10}), 3.58 (1H, d, J=13.5 Hz, H_7), 3.24 (1H, d, J=13.5 Hz, H_7), 3.16 (2H, m, H_2), 2.49 (2H, m, H_3); δ_C (75.5 MHz, $CDCl_3$) 210.0 (C_1), 145.1 (C_6), 141.8 (C_5), 128.5 (C_8), 127.4 and 123.1 (C_9 and C_{10}), 120.7 (C_{11}), 70.2 (C_4), 44.3 (C_2), 40.0 (C_7), 22.6 (C_3); ν_{max} (KBr) 3070, 2956, 2923, 1778, 1455, 1063, 759, 735 cm^{-1}; *m/z* (CI, *i*-butane) 158 (M^+, 14%), 129 ($M-CHO$, 17%), 116 ($M-C_2H_2O$, 100%); HRMS (CI, *i*-butane): M^+, found 158.0736. $C_{11}H_{10}O$ requires 158.0732.

3.3.3. 6-Butylspiro[3.3]heptan-1-one (44a). 1-Cyclopropylidene-3-butylcyclobutane **16a** (150 mg, 1 mmol) was reacted with *m*-CPBA according to the above general procedure. Chromatographic separation, using a gradient 5–20% ethyl acetate in petroleum ether, yielded spiroketone **44a** as a pale yellow liquid (106 mg, 0.64 mmol, 64% yield). The TLC plates were developed using the aforementioned[29] anisaldehyde-based developing solution. NMR analysis of the product revealed it to be a 1:1 mixture of two isomers with the assignments readily elucidated with the use of NOESY.

Compound trans-**44a**: δ_H (600 MHz, $CDCl_3$) 2.90 (2H, t, J=8.5 Hz, H_2), 2.49 (2H, m, H_5 and H_7), 2.28 (1H, quint, J=8.5 Hz, H_6), 1.96 (2H, t, J=8.5 Hz, H_3), 1.65 (2H, dt, J=8.5, 3 Hz, H_5 and H_7), 1.32 (2H, q, J=7.5 Hz, $H_{1'}$), 1.26 (2H, q, J=7.5 Hz, $H_{3'}$), 1.16 (2H, q, J=7.5 Hz, $H_{2'}$), 0.87 (3H, t, J=7.5 Hz, $H_{4'}$); δ_C (150 MHz, $CDCl_3$) 215.2 (C_1), 60.9 (C_4), 42.6 (C_2), 36.9 ($C_{1'}$), 36.3 (C_5 and C_7), 30.2 (C_6), 29.0 ($C_{2'}$), 24.7 (C_3), 22.6 ($C_{3'}$), 14.0 ($C_{4'}$).

Compound cis-**44a**: δ_H (600 MHz, $CDCl_3$) 2.90 (2H, t, J=8.5 Hz, H_2), 2.20 (1H, quint, J=7.0 Hz, H_6), 2.18 (2H, m, H_5 and H_7), 2.10 (2H, t, J=8.5 Hz, H_3), 2.01 (2H, m, H_5 and H_7), 1.42 (2H, q, J=8.0 Hz, $H_{1'}$), 1.26 (2H, q, J=7.5 Hz, $H_{3'}$), 1.16 (2H, q, J=7.5 Hz, $H_{2'}$), 0.87 (3H, t, J=7.5 Hz, $H_{4'}$); δ_C (150 MHz, $CDCl_3$) 213.41 (C_1), 60.4 (C_4), 42.8 (C_2), 36.2 (C_5 and C_7), 35.4 ($C_{1'}$), 29.2 ($C_{2'}$), 28.9 (C_6), 26.1 (C_3), 22.6 ($C_{3'}$), 14.1 ($C_{4'}$).

Mixture of compounds cis-**44a** *and trans*-**44a**; ν_{max} (KBr) 2957, 2922, 2872, 2853, 1776, 1052 cm^{-1}; *m/z* (CI, *i*-butane) 167 (MH^+, 85%), 166 (M, 26%), 141 ($MH^+-C_2H_2$, 100%), 140 ($M-C_2H_2$, 50.57%); HRMS (CI, *i*-butane): MH^+, found 167.1442. $C_{11}H_{19}O$ requires 167.1436.

3.3.4. 6-Phenylspiro[3.3]heptan-1-one (44b). 1-Cyclopropylidene-3-phenylcyclobutane **16b** (0.20 g, 1.17 mmol) was reacted with *m*-CPBA according to the above general procedure. Chromatographic separation using a gradient 5–20% ethyl acetate in petroleum ether yielded spiroketone **44b** as a yellowish liquid (106 mg, 0.57 mmol, 49% yield). NMR analysis revealed it to be a 1:1 mixture of two isomers, with the assignments readily elucidated with the use of NOESY.

Compound cis-**44b**: δ_H (600 MHz, $CDCl_3$) 7.19 (2H, m, *meta*), 7.08 (3H, m, *ortho* and *para*), 3.52 (1H, quint, J=8.5 Hz, H_6), 2.86 (2H, t, J=9.0 Hz, H_2), 2.66 (2H, dt, J=8.0, 3.5 Hz, H_5 and H_7), 2.13 (2H, dt, J=8.0, 3.5 Hz, H_5 and H_7), 1.91 (2H, t, J=9.0 Hz, H_3); δ_C (150 MHz, $CDCl_3$) 214.8 (C_1), 144.7 (*ipso*), 128.4 (*meta*), 126.3 and 126.2 (*ortho* and *para*), 60.4 (C_4), 42.5 (C_2), 37.5 (C_5 and C_7), 34.7 (C_6), 24.0 (C_3).

Compound trans-**44b**: δ_H (600 MHz, $CDCl_3$) 7.19 (2H, m, *meta*), 7.14 (2H, d, J=8.0 Hz, *ortho*), 7.08 (1H, m, *para*), 3.40 (1H, quint, J=8.5 Hz, H_6), 2.88 (2H, t, J=8.0 Hz, H_2), 2.50 (2H, dt, J=8.0, 3.5 Hz, H_5 and H_7), 2.37 (2H, dt, J=8.0, 3.5 Hz, H_5 and H_7), 2.16 (2H, t, J=8.0 Hz, H_3); δ_C (150 MHz, $CDCl_3$) 212.6 (C_1), 144.3 (*ipso*), 128.4 (*meta*), 126.6 and 126.3 (*ortho* and *para*), 59.5 (C_4), 43.3 (C_2), 38.0 (C_5 and C_7), 33.4 (C_6), 26.2 (C_3).

Mixture of compounds cis-**44b** *and trans*-**44b**; ν_{max} (KBr) 3031, 2933, 1774 cm^{-1}; *m/z* (CI, *i*-butane) 186 (M^+, 15%), 144 ($M-C_2H_2O$, 20%), 129 ($M-C_3H_5O$, 100%), 118 ($M-C_4H_4O$, 23%), 104 ($M-C_5H_6O$, 45%); HRMS (CI, *i*-butane): M^+, found 186.1045. $C_{13}H_{14}O$ requires 186.1045.

3.4. General photooxidation procedure

All photooxidations were carried out in the following system. The light source was comprised of two 650 watt projector lamps placed on either side of the sample. Each lamps was situated within a compressed-air and water cooled well. For water-cooled photooxidations, the sample reactor was a converted reflux condenser whose bottom end was sealed, allowing for agitation of the sample with a small stirring bar and water-cooling at the same time. When the reaction was carried out at low temperature, the reaction vessel was a flat-bottom test tube cooled to the desired temperature in a dry-ice acetone bath. The reactor was centered between the two lamps and light filters (320 nm UV cutoff) were placed between the sample reactor and the lamps to prevent UV light from passing into the sample. A gas burette was connected to an oxygen cylinder and flushed three times with oxygen. The photooxidation vessel equipped with magnetic stirring bar, was flushed with oxygen and charged with olefin (ca. 250 mg) dissolved in 5 mL of $CDCl_3$ or CH_3CN to which was added a spatula tipful of methylene blue ($CDCl_3$) or Rose Bengal (CH_3CN). The photooxidation vessel was capped with a rubber septum. The burette was connected to the reaction vessel via Teflon tubing capped with syringe needle. The volume of the oxygen in the burette was measured at the beginning of the reaction after the system had equilibrated. The sample was irradiated (λ>360 nm) until oxygen uptake essentially ceased. The apparatus was then allowed to cool down and the volume of the oxygen in the burette was measured again after the system had re-equilibrated. It was generally assumed that ca. 22.4 mL was required per mmol of substrate.

3.4.1. Photooxidation of cyclopropylidenecyclobutenes 13 and 15. Rose Bengal (RB) or methylene blue (MB) photosensitized oxidation of cyclobutenes **13** and **15** in CH_3CN and $CDCl_3$, respectively, proceeded sluggishly (variable O_2 uptake of ca. 0.1 equiv. in 8 h) and was accompanied by sensitizer bleaching. In each case, the only product isolated was the corresponding spiro[3.3] heptenones **39** and **40**, respectively—the same products obtained via *m*-CPBA epoxidation (vide supra, Sections 3.3.1 and 3.3.2). The $^1O_2$-quencher DABCO did not slow the rate or course of the reaction. On the other hand, addition of the free-radical inhibitor 2,6-di-*tert*-butylphenol inhibited the reaction completely, clearly indicating that a free radical oxidative process was involved.

3.4.2. The water-cooled photooxidation of cyclobutane 16b; formation of 1-(3-phenylcyclobut-1-enyl)-propenone (41), 3-oxo-3-(3-phenylcyclobut-1-enyl)propyl 3-phenylcyclobut-1-enecarboxylate (42), and 3-phenylcyclobut-1-enecarboxylic acid (43). The water-cooled photooxidation of cyclobutane **16b** (150 mg, 8.8 mmol) in $CDCl_3$ (3 mL) in the presence of a small amount of the radical inhibitor 2,6-di-*tert*-butylphenol proceeded essentially to completion within 2 h. Silica column chromatography, using a 0–20% gradient of ethyl acetate in hexane, yielded three fractions. The first was a mixture (4 mg, ca. 2% total) of **16**, **35**, **36** and 2,6-di-*tert*-butylphenol in a 1:1.5:3:1 ratio respectively. Compounds **35** and **36** were impurities in the starting material (vide supra, Section 3.2.5). This was followed at higher eluent polarity by the unsaturated ketone **41** (109 mg, 5.9 mmol, 67% yield) as a yellow liquid, the ester **42** (37 mg, 1.03 mmol, 12%) as a viscous yellow oil, and the carboxylic acid **43** (21 mg, 1.2 mmol, 14% yield) as a white solid (mp 87°C).

Compound **41**: δ_H (300 MHz, $CDCl_3$) 7.32–7.21 (5H, aryl), 6.99 (1H, s, H_2), 6.79 (1H, dd, J=17.0, 12.0 Hz, $H_{2'}$), 6.39 (1H, dd, J=17.0, 1.5 Hz, $H_{3'}$), 5.83 (1H, dd, J=12.0, 1.5 Hz, $H_{3'}$), 4.00 (1H, dd, J=4.5, 1.5 Hz, H_3), 3.27 (1H, dd, J=13.0, 4.5 Hz, H_4), 2.65 (1H, dd, J=13.0, 1.5 Hz, H_4); δ_C (75.5 MHz, $CDCl_3$) 185.8 ($C_{1'}$), 147.5 (C_2), 146.8 (C_1), 140.6 (*ipso*), 131.8 ($C_{2'}$), 128.7 ($C_{3'}$), 128.6 (*meta*), 126.9 (*para*), 126.8 (*ortho*), 43.8 (C_3), 38.4 (C_4); ν_{max} (KBr) 3057, 3027, 2959, 2933, 1728, 1661, 1599, 1403, 751, 697 cm^{-1}; *m/z* (EI) 184 (M^+, 22%), 128 ($M-C_3H_4O$, 100%), 104 ($M-C_5H_3O$, 44%), 92 ($M-C_6H_4O$, 49%), 77 ($M-C_7H_7O$, 41%); HRMS (CI, *i*-butane): M^+, found 184.0880. $C_{13}H_{12}O$ requires 184.0888.

Compound **42**: δ_H (600 MHz, $CDCl_3$) 7.33–7.30 (4H, *meta*), 7.25–7.21 (6H, *ortho* and *para*), 7.11 (1H, s, H_2), 6.99 (1H, s, $H_{2''}$), 3.98 (1H, dd, J=4.0, 2.0 Hz, $H_{3''}$), 3.97 (1H, dd, J=4.0, 2.0 Hz, H_3), 3.96 (2H, t, J=5.0 Hz, $H_{3'}$), 3.25 (1H, dd, J=14.0, 4.0 Hz, H_4), 3.19 (1H, dd, J=14.0, 4.0 Hz, $H_{4''}$), 2.92 (2H, t, J=5.0 Hz, $H_{4'}$), 2.63 (1H, dd, J=14.0, 2.0 Hz, H_4), 2.57 (1H, dd, J=14.0, 2.0 Hz, $H_{4''}$); δ_C (150 MHz, $CDCl_3$) 196.8 ($C_{5'}$), 166.2 ($C_{1'}$), 150.8 (C_2), 147.9 ($C_{2''}$), 146.4 ($C_{1''}$), 140.7 (both the *ipso* carbon), 139.5 (C_1), 128.7–126.8 (other aromatic carbons), 57.9 ($C_{3'}$), 43.8 (C_3), 43.4 ($C_{3''}$), 39.6 ($C_{4'}$), 38.4 (C_4), 37.3 ($C_{4''}$); ν_{max} (KBr) 3060, 3027, 2931, 1712, 1666, 1599, 1490, 1129, 699 cm^{-1}; *m/z* (CI, *i*-butane) 359 (MH^+, 24%), 203 ($MH^+-C_{11}H_8O$, 15%), 157 ($M-C_{13}H_{13}O_2$, 21%), 129 ($M-C_{14}H_{13}O_3$, 100%); HRMS (CI, *i*-butane): MH^+, found 359.1620. $C_{24}H_{23}O_3$ requires 359.1647.

Compound **43**: δ_H (600 MHz, $CDCl_3$) 7.32 (2H, t, J=7.0 Hz, *meta*), 7.23 (3H, m, *ortho* and *para*), 7.14 (1H, dd, J=1.5, 0.5 Hz, H_2), 3.98 (1H, ddd, J=5.0, 2.0, 1.5 Hz, H_3), 3.25 (1H, dd, J=13.5, 5.0 Hz, H_4), 2.65 (1H, ddd, J=13.5, 2.0, 0.5 Hz, H_4); δ_C (150 MHz, $CDCl_3$) 167.2 ($C_{1'}$), 151.4 (C_2), 140.6 (*ipso*), 138.2 (C_1), 128.6 (*meta*), 126.9 (*ortho*), 126.8 (*para*), 43.8 (C_3), 38.4 (C_4); *m/z* (CI, NH_3) 174 (M^+, 16%), 129 ($M-CHO_2$, 100%), 84 ($M-C_7H_6$, 32%); HRMS (CI, *i*-butane): M^+, found 174.0674. $C_{11}H_{10}O_2$ requires 174.0681.

3.4.3. Low temperature photooxidation of cyclobutane 16b; formation of 1-(1′-hydroxycyclopropyl)-3-phenyl-1-cyclobutene (47). 1-Cyclopropylidene-3-phenylcyclobutane **16b** (120 mg, 0.71 mmol) was dissolved in $CDCl_3$ (3 mL) along with a spatula tipful of methylene blue and cooled to ca. −50°C (dry-ice/acetone). The reaction mixture was photooxygenated for 3.5 h until oxygen uptake essentially ceased (0.5 equiv.). Triphenylphosphine (185 mg, 0.71 mmol) dissolved in $CDCl_3$ (1 mL) was syringed into the reaction vessel. The latter was then removed from the dry-ice/acetone bath and stored overnight in the freezer (−18°C). ^1H NMR spectroscopy of the crude reaction mixture revealed the presence of only two components, unreacted starting material **16b** and a new product, in a 1:1 ratio. Silica column chromatography, eluting with a solvent gradient ranging from 5–50% ethyl acetate in petroleum ether, yielded two fractions. The first was the starting material **16b** (48 mg), while the second was a white solid (mp 103°C) which was identified as alcohol **47** (41 mg, 0.245 mmol, 58% yield based on 60% conversion). The latter rearranges upon standing at room temperature to a mixture of *cis* and *trans* **44b**.

Compound **16b**: δ_H (600 MHz, $CDCl_3$) 7.28 (2H, t, J=7 Hz, *meta*), 7.26 (2H, m, *ortho*), 7.20 (1H, bt, J=7.0 Hz, *para*), 6.16 (1H, s, H_2), 3.81 (1H, bd, J=4.0 Hz, H_3), 2.81 (1H, dd, J=12.0, 4.0 Hz, H_4), 2.16 (1H, dd, J=12.0, 2.0 Hz, $H_{4'}$), 1.03 (2H, m, $H_{2'}$ and $H_{3'}$), 0.87 (2H, m, $H_{2'}$ and $H_{3'}$); δ_C (150 MHz, $CDCl_3$) 151.3 (C_1), 143.9 (*ipso*), 128.5 (C_2), 128.3 (*meta*), 126.7 (*ortho*), 126.2 (*para*), 54.9 ($C_{1'}$), 41.9 (C_3), 37.8 (C_4), 14.6 and 14.2 ($C_{2'}$ and $C_{3'}$); ν_{max} (KBr) 3454, 3360, 2955, 2925, 2853, 1602 cm^{-1}; *m/z* (CI, *i*-butane) 187 (MH^+, 12%), 186 (M, 13%), 168 ($M-H_2O$, 25%), 129 ($M-C_3H_5O$, 35%), 105 ($MH^+-C_5H_6O$, 100%), 104 ($M-C_5H_6O$, 61%); HRMS (CI, *i*-butane): MH^+, found 187.1120. $C_{13}H_{15}O$ requires 187.1123.

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