

Photochemical methods in metathesis reactions

Freya M. Harvey  and Christian G. Bochet *

Metathesis reactions are one of the most reliable and prevalent ways of creating a C–C bond in synthesis. Photochemical variants exist, and they have proven extremely useful for the construction of complex molecules, from natural products to Möbius rings. A variety of starting materials can undergo photo-metathesis reactions, including alkenes, alkynes, carbonyls, thiocarbonyls, and ketenes. While many of these reactions proceed with UV light and require harsh conditions, a handful of new techniques for visible-light photometathesis reactions have appeared recently. Given the current developments in visible-light photocatalysis, we believe that many more visible light photometathesis reactions await discovery. In this first review on the subject of photometathesis, we have gathered the relevant literature to give the reader an in-depth understanding of the field, and to inspire further development and synthetic application of these fascinating reactions.

Introduction

Metathesis reactions, which involve the exchange of double-bonded partners to create new double-bonded products, are one of the most powerful carbon–carbon bond forming methods in synthesis.¹ Schrock, Grubbs and Chauvin developed and studied active metathesis catalysts in the 1990's, which have since transformed materials science and opened new pathways to complex molecules.² They were awarded the Nobel prize for their work in 2005.

Metathesis reactions with ruthenium catalysts³ to give natural products⁴ or polymers⁵ have been reviewed, as well as alkyne metathesis techniques,⁶ and the recently developed carbonyl–olefin metathesis reactions.⁷ However, photochemical methods in metathesis reactions have only been briefly summarized over three decades ago,⁸ despite a growing number of examples in the literature.

Compared to thermal methods, photochemical processes can overcome large activation barriers, and enable rapid construction of thermodynamically disfavored products. Photochemistry is also generally considered as green and sustainable, because photons are traceless reagents. While most photochemical reactions typically require irradiation with short-wavelength mercury vapor lamps, recent developments in visible-light photoredox catalysis have allowed these reactions (and a range of new ones) to take place with visible light. Removing the need for short-wavelength mercury vapor lamps has made photochemistry much more accessible: more and more research laboratories are using visible-light photochemi-

cal steps in their syntheses.⁹ Industrial laboratories are following suit with new developments in visible-light photocatalysis for the synthesis of pharmaceutical agents,¹⁰ flow photochemistry¹¹ and large-scale solar chemistry.¹² Given the growing popularity of visible-light photochemistry, photochemical metathesis reactions have the potential to be a valuable alternative to the metal-catalyzed reactions often used today.

Photochemical metathesis reactions typically involve the formation of a four-membered ring from the reacting partners, followed by fragmentation of the strained ring system to give new metathesized partners (Fig. 1).

While metathesis reactions are one of the most widely used techniques for creating alkenes, there is still much to be explored in photochemical metathesis reactions. There are a number of examples of UV-light driven photochemical metathesis reactions in the literature, and some visible-light catalyzed reactions have appeared recently. The relevant literature will be summarized in this review to encourage the further development and synthetic application of these reactions. We have organized the different sections according to the type of intermediate four-membered ring.

Cyclobutanes

Early examples in the literature of photochemical alkene metathesis reactions *via* a cyclobutane intermediate can be found in the cycloaddition-fragmentation reactions of natural

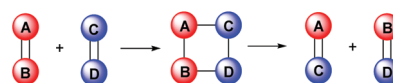
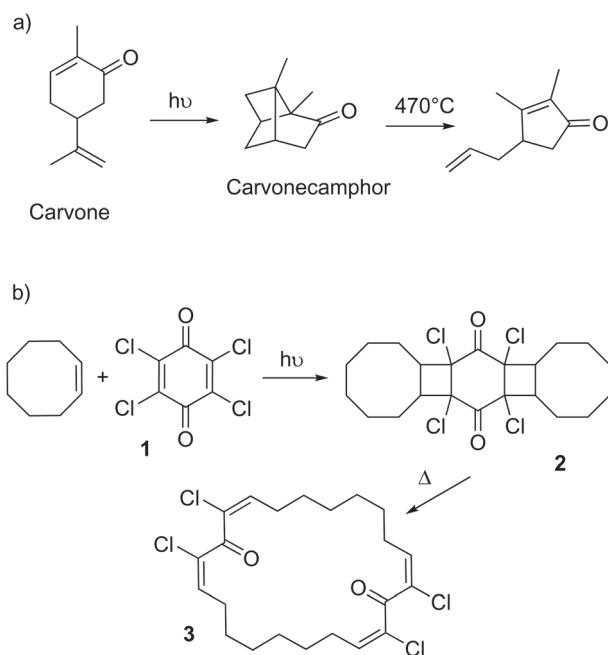


Fig. 1 A photochemical metathesis reaction.

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Scheme 1 Early examples of photometathesis reactions: a) Metathesis of carvone; b) Metathesis of chloranil and cyclooctene.

products. These metathesis sequences were used to elucidate structures, such as carvone camphor by Büchi in 1957¹³ (Scheme 1a). One of the first examples of a metathesis reac-

tion not associated with natural product structure elucidation was by Gilbert in 1964¹⁴ (Scheme 1b): irradiation of chloranil **1** with an excess of cyclooctene gave adduct **2**, which undergoes cycloreversion to metathesized macrocycle **3** upon heating.

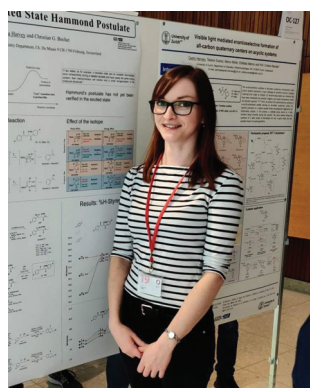
Annulenes

Schröder and co-workers synthesized a variety of annulenes and heteroannulenes using a ring-enlargement metathesis reaction *via* cyclobutanes.¹⁵

Cyclooctatetraene (COT) dimerizes upon heating to cyclobutane **4a**.¹⁶ When irradiated with a high-pressure UV immersion lamp, dimer **4a** cycloreverted to give [16]annulene **5a** (Scheme 2).¹⁷

To study the conformation of the [16]annulene, they synthesized carbomethoxy- and phenyl-substituted [16]annulenes **5b** and **5c** with the same addition-cycloreversion method. COT dimerizes with itself much more efficiently than with substituted COT, giving low yields for the substituted [16]annulenes. NMR studies indicated that there is a fast equilibrium between the different forms (differing number and sequence of *cis* and *trans* double bonds) of the [16]annulene **5a** which is significantly slower for substituted [16]annulenes **5b** and **5c**.¹⁸

They attempted to synthesize [12]annulene **7** from **6**, but only observed products **8** and **9** among other products from thermal reactions (Scheme 3).



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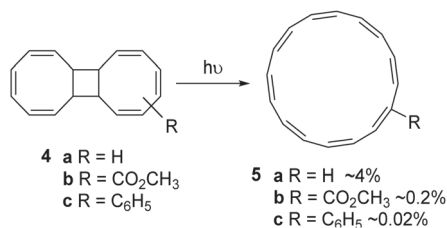
Freya Harvey was born in 1991 in Redhill, UK. She received her BSc in 2013 and her MSc in 2015 at the University of Fribourg, Switzerland. In 2016, she started her PhD studies under the guidance of Professor Christian Bochet at the University of Fribourg. Her research work during her PhD included organic synthesis, photochemistry, and computational chemistry. She submitted her thesis in September



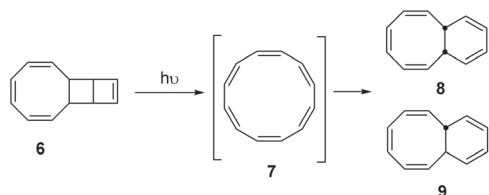
Christian G. Bochet

stay at Stanford University with Prof. Barry M. Trost, where he worked on transition metal catalysis applied to the synthesis of natural products, he returned to the University of Geneva, setting up an independent research group in organic photochemistry. In 2002, he was awarded a SNF-professorship by the Swiss National Science Foundation, and moved to the University of Fribourg, where he became full professor in 2006. He chaired the department of chemistry from 2008 to 2010, and was Dean of the faculty of science from 2016 to 2019. His current interests include reagent-controlled selective reactions, total synthesis of natural products and organic photochemistry. When not doing chemistry, he enjoys playing violin in the Geneva Symphony Orchestra.

Christian Bochet was born in The Netherlands. After attending schools in Paris and Geneva, he started studying chemistry in 1987 at the University of Geneva. He received a BSc degree in 1990, and a MSc in 1991 in inorganic chemistry under the guidance of Prof. Alan Williams. He then joined the group of the late Prof. Wolfgang Oppolzer, and received a Ph.D. in organic chemistry in 1996, focusing on total synthesis of alkaloids. After a postdoctoral



Scheme 2 Access to [16]annulene.

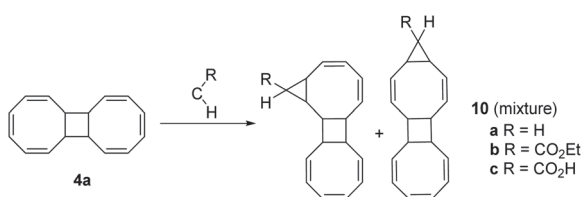


Scheme 3 Spontaneous electrocyclization of [12]annulene.

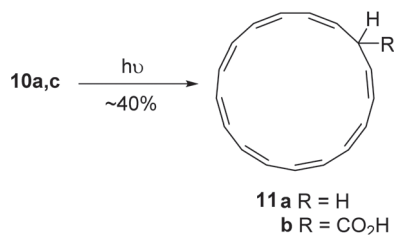
They concluded that [12]annulene does form during the reaction, but it is unstable and undergoes electrocyclization to products **8** and **9**. At $-100\text{ }^{\circ}\text{C}$, the [12]annulene **7** was stable and detected in up to 80% yield. At temperatures above $-70\text{ }^{\circ}\text{C}$, electrocyclization products **8** and **9** formed in close to 70% yield from **7**.¹⁹

Dimer **4a** reacted with carbene precursors methylene iodide or ethyl diazoacetate to give cyclopentanes **10a,b** as a mixture of regio- and stereo-isomers. Acids **10c** were available from **10b** by saponification (Scheme 4). Upon irradiation, **10a** and **10b** ring-opened to give cycloheptadecaoctaenes **11a** or **11b** in fair yield as mixtures of isomers (Scheme 5).²⁰

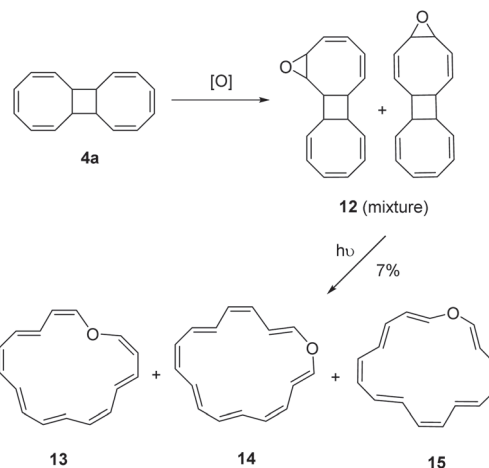
Next, they synthesized a series of heteroannulenes. Epoxidation of cyclooctatetraene dimer **4a** generated the epox-



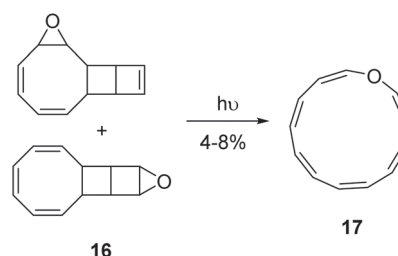
Scheme 4 Synthesis of precursors.



Scheme 5 Synthesis of cycloheptadecaoctaenes.



Scheme 6 Synthesis of oxa[17]annulenes.



Scheme 7 Synthesis of oxa[13]annulenes.

ides **12**, which gave oxa[17]annulene isomers **13**, **14** and **15** upon photolysis with 254 nm light at $10\text{ }^{\circ}\text{C}$ (Scheme 6).

In contrast to the aforementioned carbocyclic annulenes, the configurational isomers **13**, **14** and **15** are not thermally interconvertible and can be isolated pure.²¹

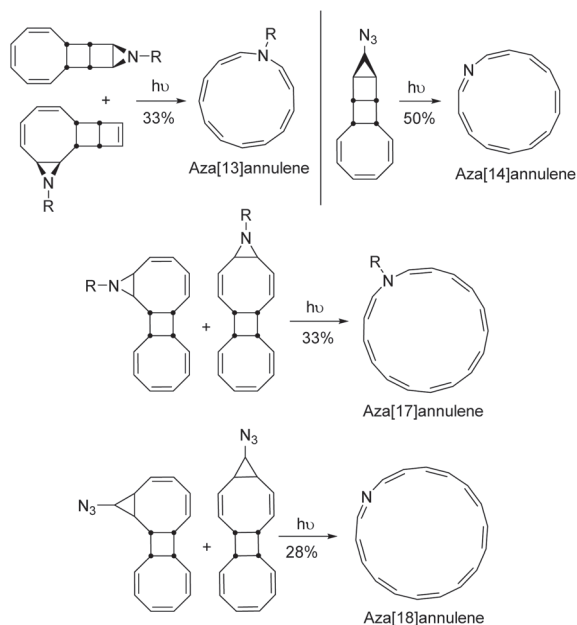
Likewise, oxa[13]annulenes **17** could be synthesized from epoxides **16** as a mixture of isomers of unknown configuration (Scheme 7).²²

Aza[13],²³ aza[14],²⁴ aza[17]²⁵ and aza[18]annulenes²⁶ were synthesized in a similar fashion. The starting materials, annulene products (as mixtures of isomers) and their yields are listed in Scheme 8.

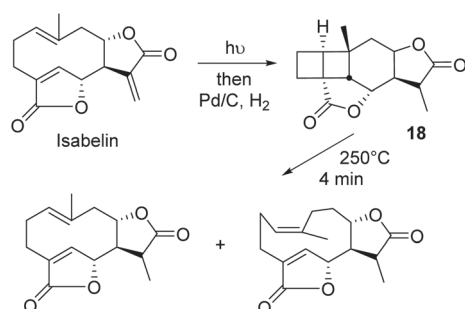
Sesquiterpene natural products

Isabelin is a sesquiterpene of the germacranolide family of natural products with a 1,5-cyclodecadiene skeleton. Upon exposure to UV light, it can undergo [2 + 2] photocycloaddition to give (following hydrogenation) compound **18** (Scheme 9).²⁷ The cyclobutane can be ring-opened by flash pyrolysis to generate two isabelin-type macrocycles.

The synthetic utility of such a transformation was clear: with the appropriate starting alkenes, the bicyclo[2.2.0]hexane core should be accessible by [2 + 2] photocycloaddition. Fragmentation upon heating should then lead to the macrocycle.



Scheme 8 Synthesis of aza[n]annulenes.

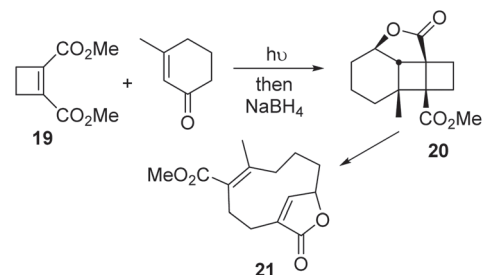


Scheme 9 Photochemistry of isabelin.

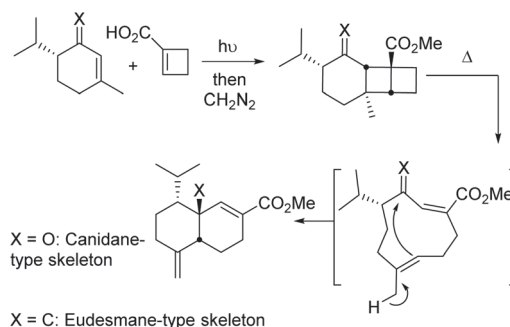
The first report on the synthesis of 1,5-cyclodecadiene skeletons *via* a metathesis sequence was published by the Lange group.²⁸ They used a two-step approach involving a [2 + 2] photocycloaddition of cyclobutene **19** to methyl cyclohexenone to give the strained tricyclic system **20**, followed by reduction with NaBH₄ and cycloreversion in refluxing *m*-xylene to give the desired 1,5-cyclodecadiene **21** (Scheme 10).

Similar reports of photo-thermal metathesis sequences were also made by Wender²⁹ and Wilson.³⁰ Other natural product skeletons accessible with the photo-thermal metathesis include: canidane, eudesmane and eudesmanolide skeletons (Scheme 11), perhydroazulene skeletons (Scheme 12) and guaianolide skeletons (Scheme 13).^{31,32}

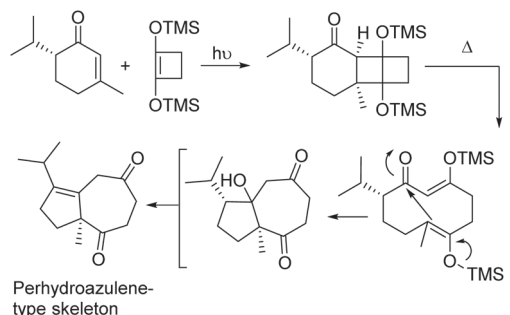
This technique allowed for the synthesis of a large number of natural products and their isomers (Scheme 14), including: isabelin,³³ Aristolactone isomer,³⁴ Daucene,^{31,35} Dihydroreynosin, Maritim, Magnolialide, Santonin,³⁶ Calameon,³⁷ Warburganal,³⁸ Isocalamendiol,³⁹ Zonarene,⁴⁰ and Byssochlamic acid.⁴¹



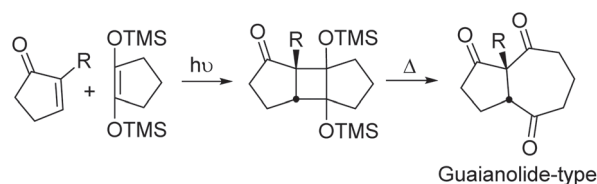
Scheme 10 Access to the 1,5-cyclodecadiene skeleton.



Scheme 11 Access to canidane and eudesmane skeletons.



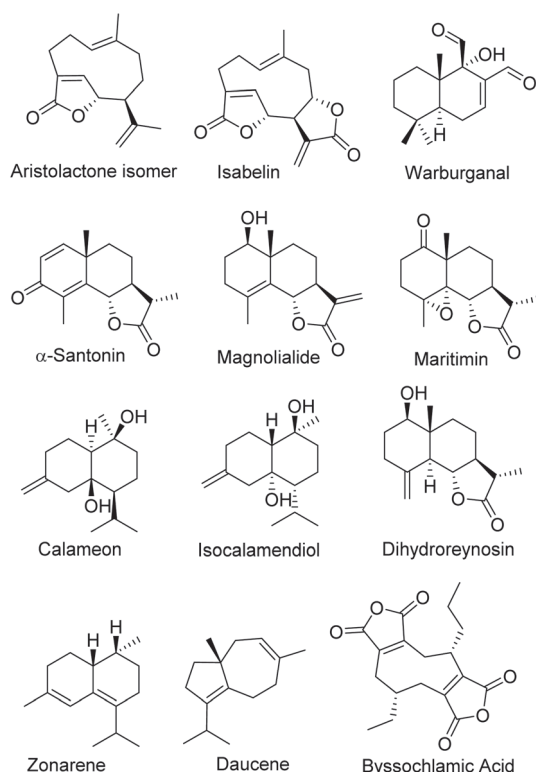
Scheme 12 Access to perhydroazulene skeletons.



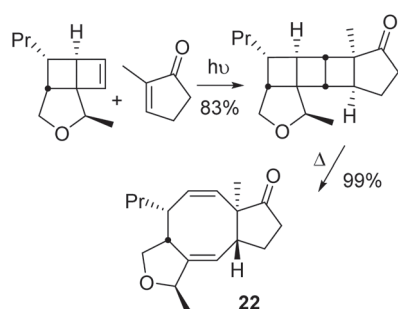
Scheme 13 Access to guaianolide skeletons.

More recently, this method has been used by Snapper and co-workers to synthesize 5–8–5 ring systems **22** in good yields (Scheme 15).⁴²

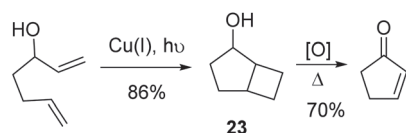
A stepwise metathesis with a copper-catalysed [2 + 2] photocycloaddition was used by Salomon and co-workers to synthesize cyclopentanones (Scheme 16).⁴³



Scheme 14 Natural products synthesized via photo-thermal metathesis.



Scheme 15 Access to 5-8-5 ring systems.



Scheme 16 Metathesis to access cyclopentanones.

Photocyclization of dienols in the presence of copper(I) triflate afforded the bicyclo[3.2.0]heptan-2-ols **23**, which (following oxidation) could be ring-opened upon heating to furnish cyclopentanones.⁴³

Polyquinanes

[2 + 2] photocycloadditions to generate highly strained polycyclic cage compounds have been extensively studied in the

context of light-energy storage.⁴⁴ Cycloreversion of these compounds liberates chemical energy and regenerates the starting alkenes, ready to undergo another cycloaddition-cycloreversion cycle.

During their work with Cookson cage ketones **24**⁴⁵ for light-energy storage purposes, Mehta and co-workers found that cycloreversion upon heating occurred to give a new, metathesized product **25** with a *cis*, *syn*, *cis*-triquinane skeleton.⁴⁶ A variety of substituents were tolerated (Scheme 17).

The starting dienes were readily available from the Diels-Alder reaction of 1,3-cyclopentadienes and *p*-benzoquinones. Mehta and co-workers recognized the synthetic value of their photo-thermal metathesis reaction as an entry to natural products with a triquinane skeleton.

Starting from correctly decorated key intermediates of type **26**, they synthesized a large number of natural products (Scheme 18) including Hirsutene,^{47,48} Coriolin,^{48,49} Capnellene,^{48,50} Precapnelladiene,^{48,51} and the carbocyclic segment of Ikarugamycin.⁵² They carried out model studies on Crinipellin Diterpenes, Magellanine-type and Paniculatine-type Lycopodium Alkaloids,⁵³ and Longipenol's ABD Tricarbo-cyclic Framework.⁵⁴ More recent syntheses include Cucumin E,⁵⁵ (±)-Asterisca-3(15),6-diene,⁵⁶ Isocapnellene,⁵⁷ Pleurotellol and Pleurotellic acid.⁵⁸

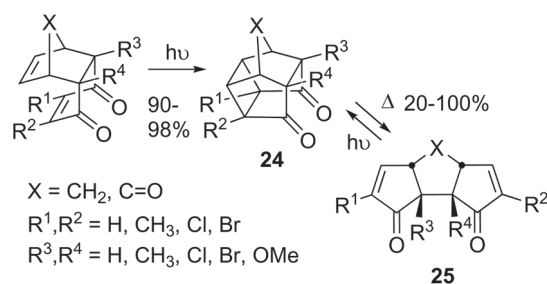
Griesbeck extended the method to the synthesis of tricyclopentanoids **27**, substituted at C7,⁵⁹ and to the synthesis of tetraquinanes **28** (Scheme 19).⁶⁰

Mehta *et al.* also applied the photo-thermal metathesis reaction to the synthesis of polyquinane fragments towards dodecahedrane using three different strategies.

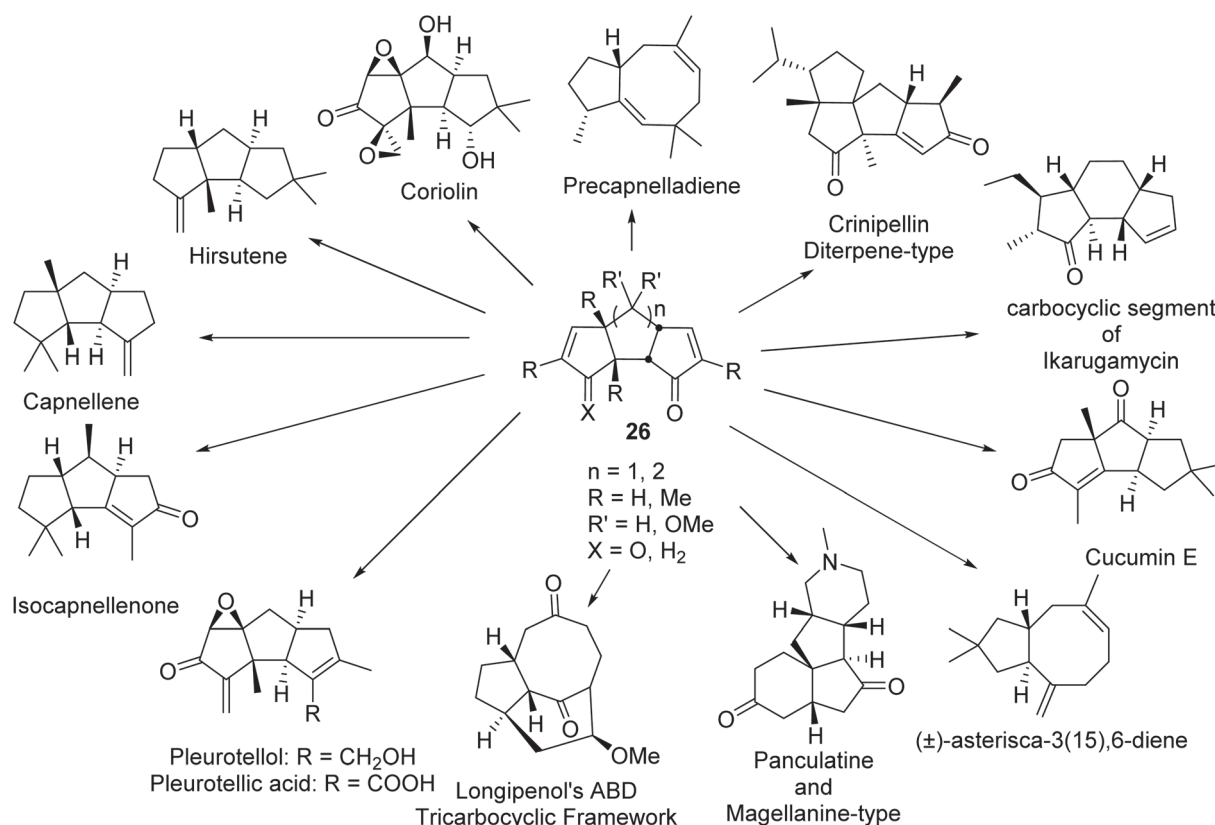
The first strategy consisted of the synthesis of oxa-hexaquinane dione **31**, an advanced intermediate *en route* to dodecahedrane. **31** could be obtained starting from hexacyclic ether **29**, which underwent flash vacuum pyrolysis (FVP) to give **30** (Scheme 20).⁶¹

Their second strategy was the synthesis of key intermediate tetraquinanedione **36** (Scheme 21). Starting from Diels-Alder adduct **32**, they performed the photocycloaddition reaction to obtain product **33**, which could be elaborated to diketone **34**. Cycloreversion of **34** gave the desired tetraquinanedione **35**.⁶² **35** could be further elaborated to all-*cis* C₂₀-hexaquinane **36**, a close precursor to dodecahedrane.⁶³

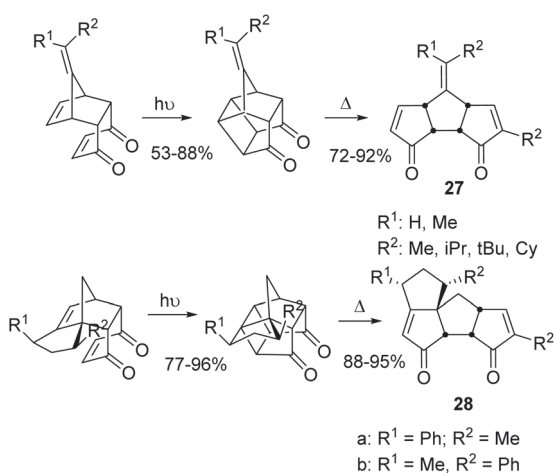
A similar intermediate **38** was synthesized using photo-thermal metathesis of **37** by Prinzbach and co-workers⁶⁴ to test



Scheme 17 Synthesis of triquinanes.



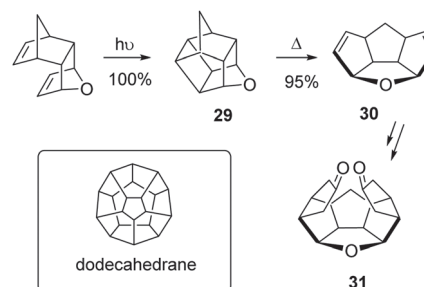
Scheme 18 Natural products starting from triquinanes 26.



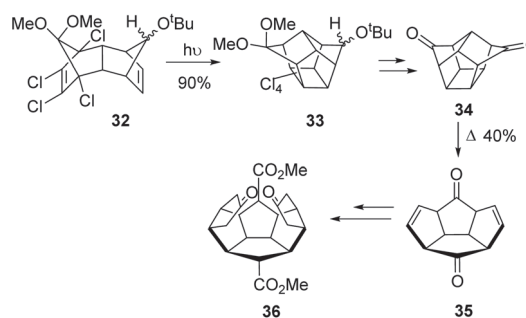
Scheme 19 Synthesis of tricyclopentanoids and tetraquinanes.

whether the ring-opening of pagodane's central cyclobutane *en route* to dodecahedrane was feasible. While the photometa-thesis of 37 worked, the pagodane version decomposed to naphthalene (Scheme 22).

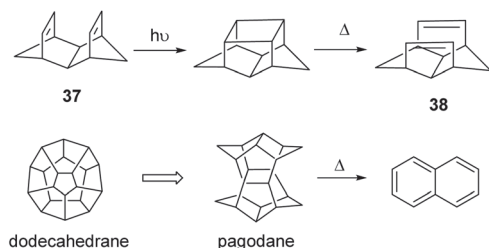
Mehta's third strategy involved the synthesis of roofed poly-quinane 41 as an advanced intermediate (Scheme 23).⁶⁵ Roofed polyquinane 40 was readily available from diels-alder adduct 39 *via* a photo-thermal metathesis sequence.⁶⁶



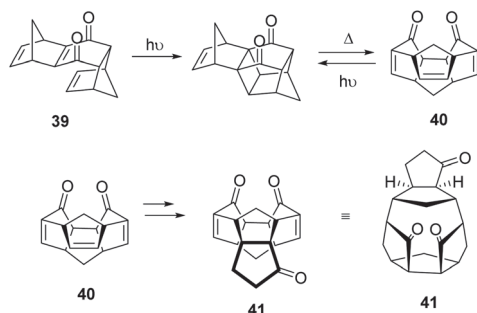
Scheme 20 Efforts towards dodecahedrane *via* X.



Scheme 21 Efforts towards dodecahedrane *via* 35.



Scheme 22 Efforts towards dodecahedrane via pagodane.

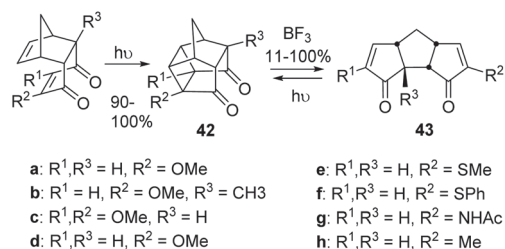


Scheme 23 Efforts towards dodecahedrane via 40.

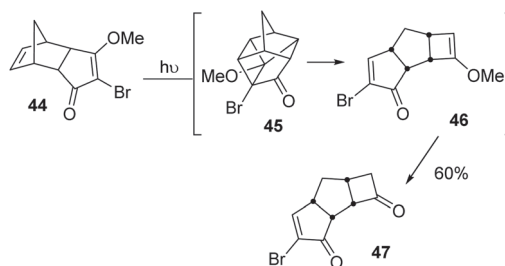
Cyclopentannulation followed by hydrogenation of the double bonds gave hexacyclic system **41**, but efforts to project the five-membered ring within the polyquinane hemisphere were unsuccessful.

Cage Cookson ketones could only be cycloreverted at high temperatures under flash-vacuum pyrolysis conditions, generally between 500–600 °C. As part of their work on model systems for light-energy conversion,⁶⁷ Mehta and co-workers sought to chemically derivatize the cage ketones so that the cycloreversion could proceed at ambient temperature. They synthesized 'push-pull' pentacyclic diones **42a** and **42b** (Scheme 24), which cycloreverted at ambient temperature in presence of a Lewis acid ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) to triquinanes **43a** and **43b**.⁶⁸

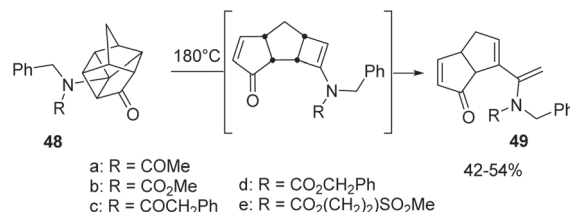
Other authors⁶⁹ also found that adding electron density to the system facilitated the cycloreversion reaction in presence of various Lewis acids at room temperature (**42c–42h** to give **43c–43h**; the best results were obtained with $\text{BF}_3 \cdot \text{OEt}_2$). The cycloaddition and Lewis acid-catalyzed cycloreversion pro-



Scheme 24 Cycloreversion with Lewis acids under mild conditions.



Scheme 25 One-pot access to cyclobutanone 47.



Scheme 26 One-pot access to functionalized cyclopentanone 49.

ceeded in high yields. Kanematsu *et al.* explained this as a synergetic capto-dative stabilization of the 1,4-diradical.⁷⁰

Zwanenburg *et al.* synthesized enol bromide **44** which, upon irradiation, directly gave the metathesized and hydrolyzed product **47** (Scheme 25). Neither bis-homocubanonone **45** nor methyl enol ether **46** could be isolated.

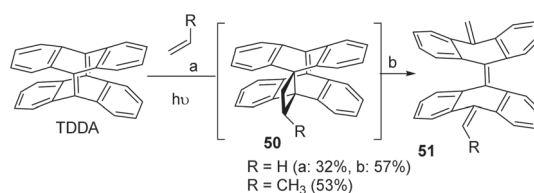
Conversely, the 4-amino substituted 1,3-bishomocubanonone **48** could be isolated (Scheme 26). Upon heating, **48** underwent cycloreversion followed by 1,3-hydrogen shift and ring-opening to give **49** as the major product.⁷¹

Recent uses of photo-thermal metathesis towards caged polyquinanes have been reported by Kotha *et al.*⁷² They found that microwave irradiation conditions are an efficient alternative to flash-vacuum pyrolysis for the cycloreversion step.⁷³

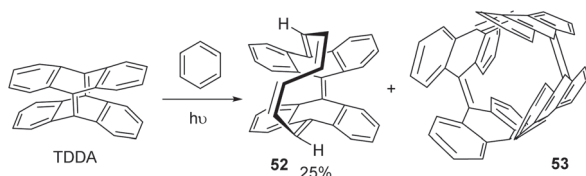
Polyaromatic systems

Herges *et al.* discovered that cyclobutane **50** (formed by [2 + 2] photocycloaddition of ethene and tetradecahydrodianthracene (TDDA)) undergoes, upon heating, a metathetic cycloreversion reaction to generate **51** (Scheme 27).⁷⁴

If propene is used instead of ethene, the cycloreversion reaction proceeds so quickly that the cyclobutane intermediate cannot be isolated, and the metathesis products are obtained directly. Indeed, the cycloreversion of cyclobutanes is accel-



Scheme 27 Metathesis reactions of TDDA.



Scheme 28 Photochemistry of TDDA in benzene.

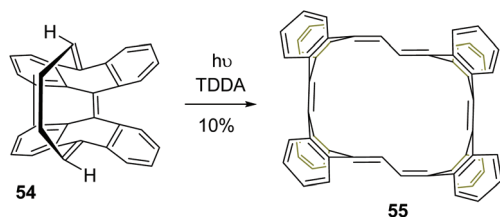
ated by alkyl substituents. They found that the photometathesis reaction also proceeds with cyclic alkenes (good yields were obtained with cyclooctene) and even benzene underwent addition and ring opening to produce macrocyclic polyene **52** (Scheme 28). Irradiation in benzene gave, along with the major benzene metathesized product **52**, small amounts of picotube **53** resulting from dimerization and metathesis of TDDA with itself.⁷⁵ Thus, the group became interested in the synthesis of extended polyaromatic systems, including belt-like and tube-like molecules.

Their first synthesis of a belt-like molecule was that of **55**. Starting from **54**, they performed a photochemical metathesis reaction with TDDA to obtain **55**, a fully conjugated belt-like molecule with 20 carbon atoms in its perimeter (Scheme 29).⁷⁶

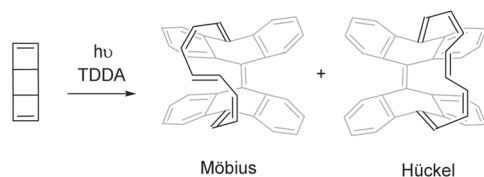
Using their refined photometathesis technique, the Herges group were then able to synthesize the first stable aromatic Möbius compound. Möbius compounds were predicted by Heilbröner in 1964 to be aromatic if they contain $4n$, rather than $4n + 2$, π electrons.⁷⁷ Irradiation of TDDA and *syn*-tricyclooctadiene (TCOD) in benzene gave five isomers of fully ring-opened product, one of which exhibited Hückel topology, and one which had Möbius topology and was significantly conjugated (Scheme 30).⁷⁸ This confirmed Heilbröner's prediction for Möbius twisted $[4n]$ annulenes.

Metathesis reactions of nitrogen heterocycles

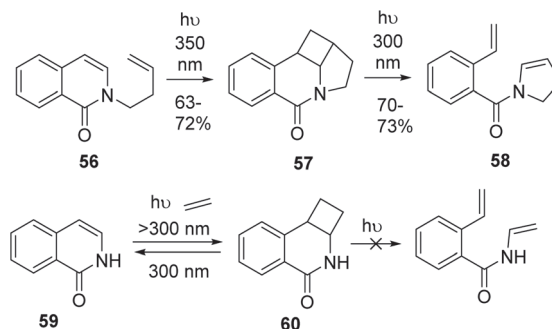
Kaneko and co-workers reported the fully photochemical metathesis of 2-(ω -alkenyl)isoquinolin-1(2*H*)-ones **56** to afford



Scheme 29 Synthesis of a fully conjugated belt-like molecule.



Scheme 30 Synthesis of an aromatic Möbius compound.

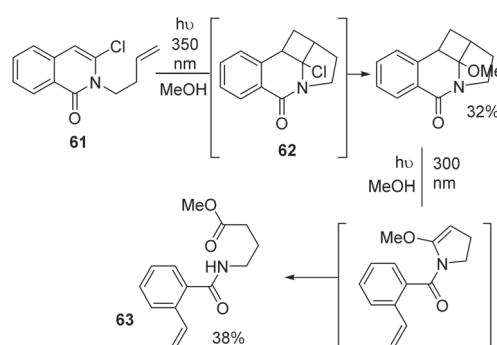


Scheme 31 Photometathesis of 2-(ω -alkenyl)isoquinolin-1(2*H*)-ones.

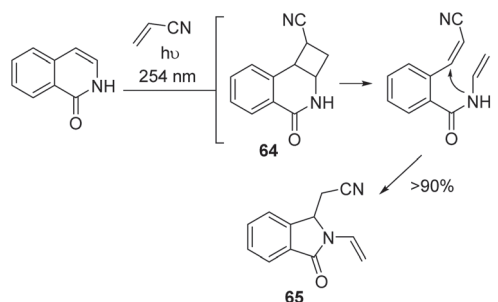
o-vinylbenzamide derivatives.⁷⁹ Upon irradiation at 350 nm, cyclobutane **57** could be isolated, and continued irradiation at 300 nm gave the metathesized product **58** (Scheme 31). However, cyclobutane **60** gave back starting alkene **59** upon prolonged irradiation, indicating that the presence of the methylene bridge is essential for the metathesis reaction.

Irradiation of chlorinated **61** in methanol gave the methoxy-cyclobutane **62**, which underwent cycloreversion and enamine hydrolysis to give ester **63** (Scheme 32).⁸⁰

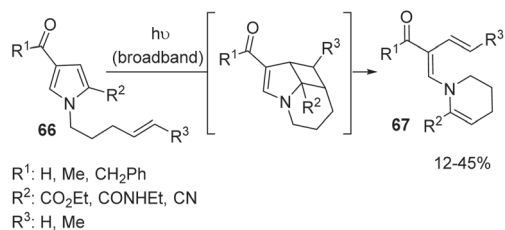
Gilbert and co-workers irradiated isoquinolin-1-one at short wavelengths (254 nm) in presence of acrylonitrile and obtained isoindoline **65** in excellent yield (Scheme 33).⁸¹ Isoindoline **65** arises from the metathetic cycloreversion of cyclobutane **64** and addition of the amide onto the new alkene.⁸²



Scheme 32 Access to esters of type **63**.



Scheme 33 Access to isoindolines.



Scheme 34 Metathesis reactions of pyrroles.

Booker-Milburn and co-workers reported the synthesis of enamine-enones **67** by the fully photochemical intramolecular metathesis of pyrroles **66** (Scheme 34). As seen with isoquinolones, the [2 + 2] cycloaddition and cycloreversion could be carried out at different wavelengths (such that a cyclobutane could be isolated), and when they used a broadband UV lamp, sequential cycloaddition and ring-opening occurred in good yields.⁸³ They examined the scope of the reaction and found that electron-withdrawing groups were necessary at the 2- and 4-position of the pyrrole. The 4-position required a ketone or aldehyde specifically, and the 2-position tolerated ester, amide or nitrile groups.

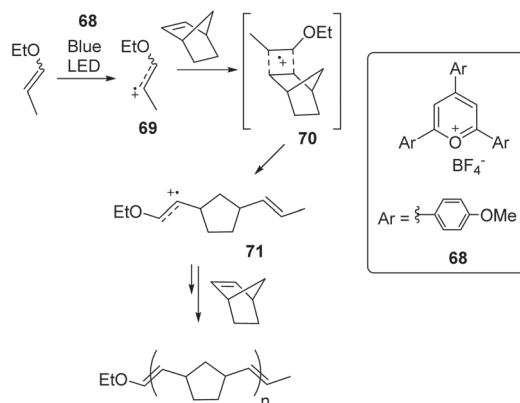
Metal-free ROMP

In the preceding examples, we have seen that cyclobutanes can be cycloreverted by direct irradiation, sensitized irradiation or upon heating. There are several examples in the literature of the cycloreversion of cyclobutanes using photooxidants such as cyanoarenes, pyrylium salts, trityl salts and flavinium salts.⁸⁴ Cyclobutanes can also be synthesized by photoreduction (with a ruthenium complex)⁸⁵ or photooxidation (with pyrylium salts, flavins or ruthenium complexes).⁸⁶ Despite their ability to create and ring-open cyclobutanes, these photocatalysts have rarely been applied to metathesis reactions of alkenes.

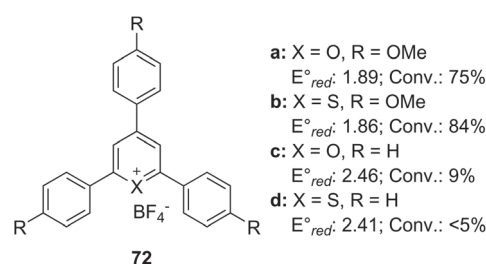
One example is the work of the Boydston group, who have used photoelectron transfer to carry out metal-free ring-opening metathesis polymerization of alkenes. When Chiba published his work on electrochemical cross-metathesis using enol ethers in electrolyte solutions,⁸⁷ the Boydston group recognized that metathesis reactions may be possible with photoelectron transfer catalysts.⁸⁸

With norbornene as the monomer, **68** as the photooxidant and a variety of vinyl ether initiators under blue light irradiation, the polymerization reaction proceeded smoothly and with high conversion (Scheme 35). The vinyl ether initiator is first oxidized to give activated radical cation **69**, which reacts with an alkene monomer to give a radical cation cyclobutane **70**. Rapid ring-opening to release ring strain out-competes reduction and gives new metathesized alkenes **71**. The regenerated vinyl ether ensures propagation of the polymer chain. This was the first protocol for a metal-free ring-opening metathesis polymerization (MF-ROMP).

A comparison of different photooxidants showed that thia-pyrylium salts with relatively low oxidation potentials such as



Scheme 35 Metal-free ring-opening metathesis polymerization.

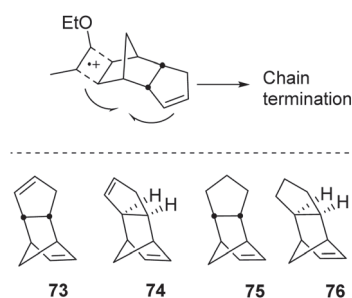


Scheme 36 Comparison of photocatalysts.

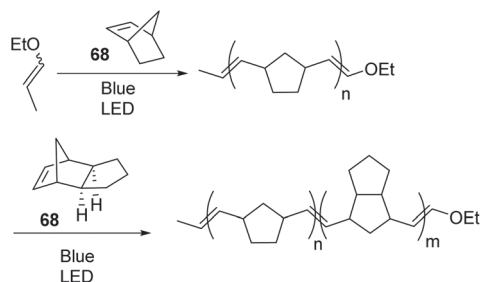
72a gave the highest polymer conversions (Scheme 36). Catalysts with higher oxidation potentials (such as **72c** and **72d**) gave smaller conversions, which the authors attributed to nonselective and deleterious pathways.⁸⁹

Next, they sought to extend their MF-ROMP reaction to the *endo*-dicyclopentadiene (DCPD) monomer **73**, a common ROMP monomer. Unfortunately, the conversion was low with DCPD. This was due to intramolecular reaction of the radical cation with the second alkene on DCPD rather than with a new monomer, resulting in termination of the polymerization (Scheme 37). They found that using two partially hydrogenated monomers (**75** and **76**) gave high conversions.⁹⁰

MF-ROMP also proved useful for the synthesis of copolymers. Boydston and co-workers were able to synthesize diblock copolymers of norbornene and **76** by sequentially adding the monomers to the growing polymer (Scheme 38).⁹¹



Scheme 37 DCPD and hydrogenated monomers.



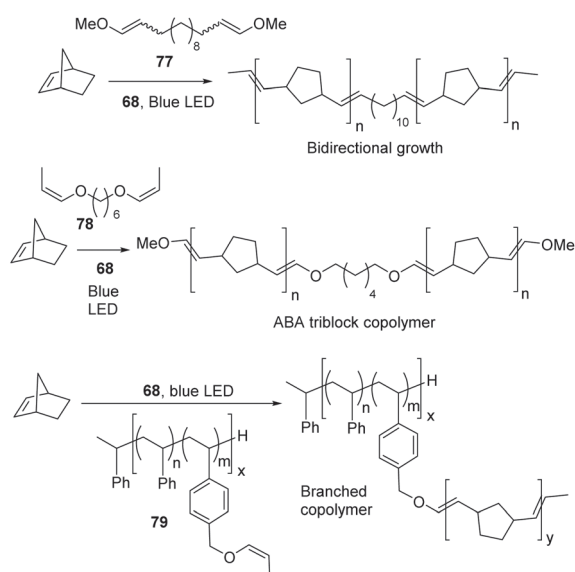
Scheme 38 Synthesis of diblock copolymers.

Starting from bifunctional initiator **77**, they could grow the polymer in both directions (Scheme 39).⁹² With polymer **78** as the macroinitiator, they could create ABA type triblock copolymers, and with macroinitiator **79**, they could generate a branched block copolymer.

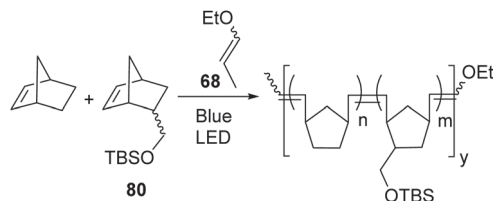
Next, they examined the functional group tolerance of MF-ROMP in the presence of a variety of nucleophiles suspected to react with the radical cation. Water and alcohols had a negative impact on the reaction, but carrying out the reaction under ambient conditions improved the conversion.⁹³ Protected alcohol **80** underwent successful homopolymerization and co-polymerization with norbornene, and they could cleave the TBS group on the polymer to afford an alcohol for further functionalization (Scheme 40).

They could also make block copolymers using MF-ROMP and a different polymerization method (ROP) starting from a bifunctional initiator **81**. First, they could grow the ROP polymer on the alcohol side of the initiator, then the MF-ROMP polymer on the enol ether side of the initiator, effectively creating a diblock copolymer in a one-pot reaction (Scheme 41).⁹⁴

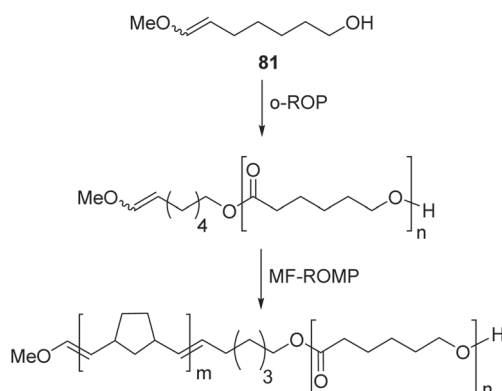
When the MF-ROMP reaction with norbornene is performed in the presence of methyl methacrylate (MMA), they



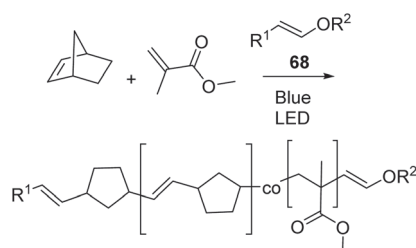
Scheme 39 Synthesis of triblock and branched copolymers.



Scheme 40 Polymerization with functionalized norbornene.



Scheme 41 Sequential ROP and MF-ROMP.



Scheme 42 Hybrid copolymerization of norbornene and methyl methacrylate.

found that MMA units were incorporated into the norbornene polymer. With (2-methoxyvinyl)cyclohexane as the initiator, they obtained a polymer containing 90% norbornene and 10% methyl methacrylate *via* a hybrid copolymerization mechanism (Scheme 42).⁹⁵

Oxetanes

Carbonyl-olefin metathesis, a term coined by Jones in 1973,⁹⁶ refers to the cycloaddition of a carbonyl-alkene pair to give an intermediate oxetane, which then fragments to a new carbonyl-alkene pair. This reaction is perhaps best known from the ground-breaking work of the Schindler group with iron catalysis.⁹⁷ However, oxetanes are readily synthesized by a [2 + 2] photocycloaddition of the metathesis partners, and the first carbonyl-olefin metathesis reactions were carried out photochemically. Once formed, the oxetane can be fragmented

using different methods: heat-induced (pyrolytic), acid-induced (protolytic) or light-induced (photolytic). We will separate the different metathesis examples according to these methods.

Photopyrolytic oxametathesis

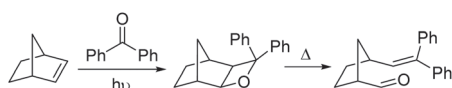
Oxetanes obtained from a [2 + 2] photocycloaddition of an alkene and a carbonyl, can be ring-opened pyrolytically.⁹⁶ Initially intended as a study of the structure–reactivity factors governing the decomposition of oxetanes, Jones saw the synthetic potential of the transformation as a metathesis reaction (Scheme 43).

He and Carless studied the mechanism and stereochemistry of the pyrolysis. Jones⁹⁸ found that the ring-opening was quite stereoselective, whereas Carless⁹⁹ observed considerable loss of stereochemical configuration in going from oxetane to alkene. The fragmentation pattern is dependent on the substituents.¹⁰⁰

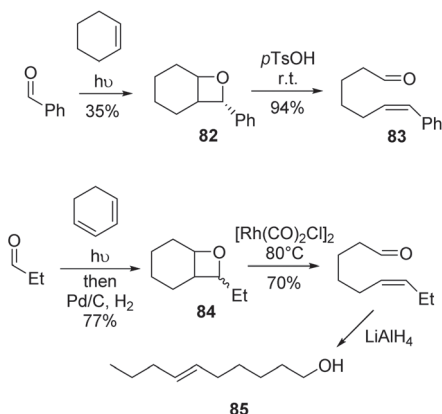
The high temperatures needed for the oxetane pyrolysis limited the scope of the reaction, so other ways to open the oxetane to metathesized products were developed, including acid catalysis (photopyrolytic oxametathesis) and photochemical methods (photo-photo oxametathesis).

Photoprotolytic oxametathesis

Oxetanes can be ring-opened by Brønsted or Lewis acids. In contrast to pyrolysis, acid-catalyzed ring-opening proceeds *via* a carbocation intermediate. Jones synthesized long-chain enal **83** from photogenerated oxetane **82** cycloreverted with *p*-Toluenesulfonic acid. Fruitfly pheromone **85** could be obtained from oxetane **84** with rhodium carbonyl chloride as a Lewis acid (Scheme 44).¹⁰¹



Scheme 43 Carbonyl–olefin photometathesis.



Scheme 44 Acid-catalyzed cycloreversion.

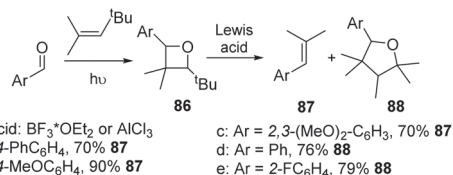
A study by Carless on the reactions of oxetanes **86** with Lewis acids showed that either metathesis to a new alkene **87** or ring expansion to a tetrahydrofuran derivative **88** can occur, depending on the oxetane's substituents.¹⁰² Electron-rich substituents stabilize the intermediate carbocation and favor the ring-opening metathesis reaction, whereas electron-poor substituents destabilize the cation, and 1,2-methyl shift and ring expansion occurs instead (Scheme 45).

Kutateladze and co-workers used photoprotolytic oxametathesis as part of a series of reactions to create complex polycyclic frameworks.¹⁰³ Starting from α -aryl or α -heteroaryl ketones, they found that the cycloaddition to form the oxetane proceeded in excellent yields, and it could be ring-opened in a one-pot reaction with catalytic amounts of a Brønsted or Lewis acid to give the metathesis product **89** or its (hemi)acetal **90** (Scheme 46). The ring-strain in the polycyclic framework was key for the mild retrocycloaddition to take place. They found that Lewis acids (such as $\text{BF}_3 \cdot \text{OEt}_2$) gave aldehydes **89**, whereas protic acids (such as HCl) in the presence of water gave hemiacetals **90**. These one-pot transformations were general, clean and high-yielding, with the best yields obtained when R^1 (which stabilizes the carbocation) is electron-rich.

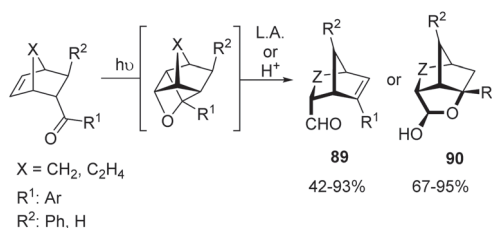
They also isolated the unusual formylcyclopropane **91**, which arose from addition of the enol moiety to the double bond (Scheme 47).

With polycyclic frames of type **92**, they could consistently obtain formylcyclopropanes **94**.¹⁰⁴ Starting from cage compounds **92**, irradiation with broadband UV light gave oxetanes **93** in good yields. When treated with a small amount of HCl, a carbonyl–olefin metathesis reaction occurred to give aldehydes. With excess HCl or a Lewis acid ($\text{BF}_3 \cdot \text{OEt}_2$), they obtained formylcyclopropanes **94** (Scheme 48).

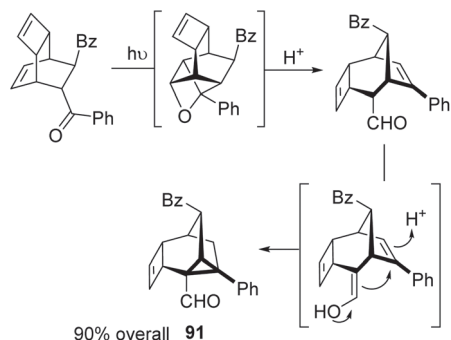
Running the metathesis reaction in presence of ethylene glycol gave acetals **95**. The reaction can be performed one-pot in excellent yield (Scheme 49).



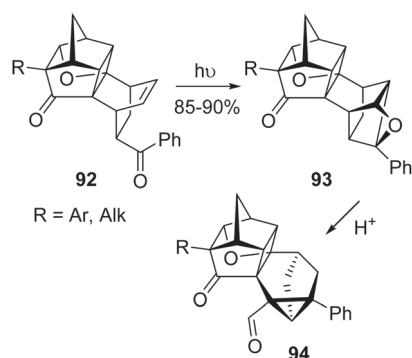
Scheme 45 Metathesis or ring-expansion of oxetanes.



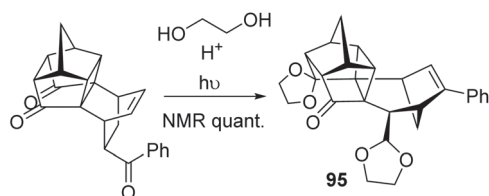
Scheme 46 Photometathesis towards polycyclic frameworks.



Scheme 47 Access to formylcyclopropanes.



Scheme 48 Formylcyclopropanes from cage compounds.

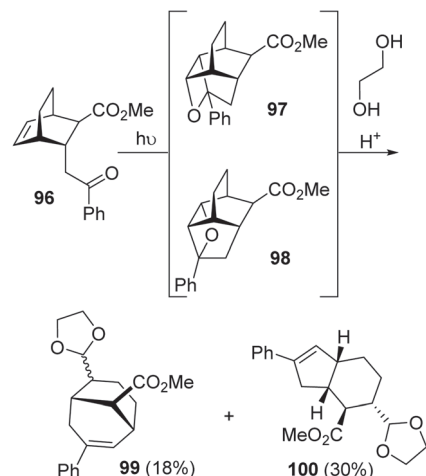


Scheme 49 One-pot metathesis and acetalization.

Kutateladze and co-workers then examined the topological and stereochemical effects on the oxametathesis reaction by using a more flexible tether containing an extra methylene group on the benzoyl chromophore **96**. This way, the initial Paternò-Büchi step can potentially yield both regioisomeric oxetanes, **97** and **98**, and the resulting cycloreversion products in these systems possess either [3.*n*.1] or [*n*.3.0] bicyclic topology (Scheme 50).¹⁰⁵ Oxetanes **97** and **98** form in a nearly 1 : 1 ratio, indicating that in these systems there is no intrinsic bias for cyclization associated with the tether. The metathesis reaction can be carried out one-pot in the presence of ethylene glycol and HCl to furnish the dioxolanes **99** and **100** in modest yields.

Photo-photo oxametathesis

Oxetanes can undergo light-induced ring-opening reactions, either by direct excitation of their own chromophores, or by

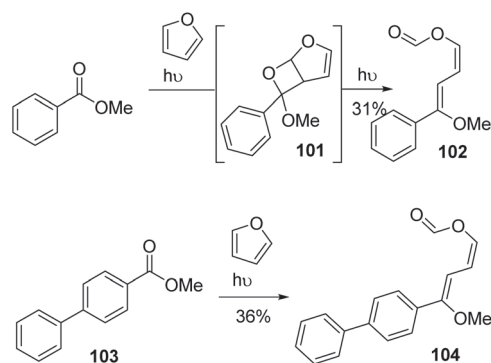


Scheme 50 Access to dioxolanes **99** and **100**.

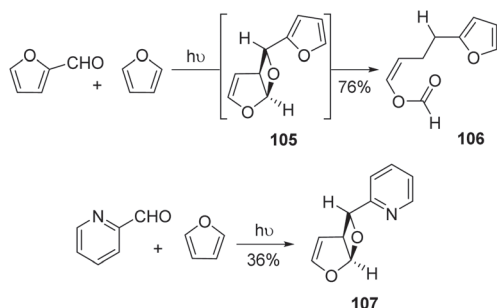
oxidative or reductive cycloreversion using photoinduced electron transfer (PET).

Direct excitation. Metathetic ring-opening of oxetanes by excitation of their own chromophores was observed by Cantrell and co-workers during their investigations of photoreactions of arenecarboxylate with furan. Upon prolonged irradiation, oxetane **101** cycloreverted to diene **102** (Scheme 51). They theorized that the photocycloreversion could result from internal photosensitization of the aromatic chromophore on oxetane **101**. This was further supported by the irradiation of **103** and furan, which gave only **104**. No oxetane was detected, presumably due to the efficient internal photosensitization by the strongly absorbing biphenyl chromophore.¹⁰⁶

During their efforts to synthesize *exo* oxetane **105**, D'Auria and co-workers were only able to isolate cycloreverted compound **106** (Scheme 52).¹⁰⁷ They observed the same cycloreversion reaction in a series of similar substrates. However, when they used 3-substituted heterocyclic aldehydes instead of 2-substituted heterocyclic aldehydes for the Paternò-Büchi reaction, they could isolate the oxetanes **107** and cycloreversion did not occur. They explained that the difference in stability of the oxetanes could be due to the positioning of the π



Scheme 51 Photo-photometathesis by chromophore excitation.



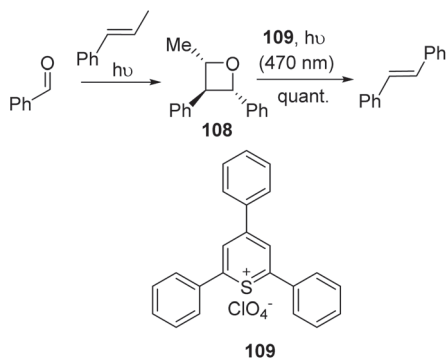
Scheme 52 Metathesis with orbital participation.

system in the heterocyclic ring; if it is orthogonal to the C–O bond (as is the case for **107**), overlapping of the π -system with the developing π orbitals from the C–O bond cleavage could favor the metathesis product.

PET-induced cycloreversion. Oxetanes can be fragmented both by photooxidation (generation of an oxetane radical cation) and photoreduction (generation of an oxetane radical anion). Calculations have shown that fragmentation of a radical anion is more exothermic.¹⁰⁸ There are many examples in the literature of oxetane cycloreversion using photoredox chemistry, as this reaction has been extensively studied in the context of DNA (6–4) lesion repair.¹⁰⁹ Only the examples which result in metathesis products will be discussed here.

Oxidative photocycloreversion. The metathetic cycloreversion of oxetanes has been studied with (thia)pyrylium salt **109** as electron transfer photosensitizers by Miranda and co-workers (Scheme 53).¹¹⁰ Oxetane **108** fragmented exclusively to stilbene and acetaldehyde in excellent yield. Other pyrylium salts showed little to no conversion.

A laser flash photolysis (LFP) study showed a transient with an absorption maximum consistent with that of radical cationic trans-stilbene, confirming that photocycloreversion proceeds by the one-electron oxidation of oxetane by thiapyrylium salt **109** to give a radical cation. The reaction takes place from the excited triplet state of the photosensitizers.¹¹¹ In further work, they confirmed that the cycloreversion is a stepwise process, and that the fragmentation pattern depends on the oxetane's substituents.¹¹² The photosensitizer also plays a key



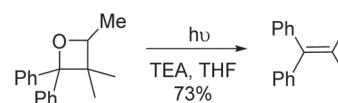
Scheme 53 Photocycloreversion with thiapyrylium salt **109**.

role in the fragmentation pattern: photooxidation of oxetane **x** with chloranil regenerated the starting alkene–carbonyl pair rather than stilbene.¹¹³

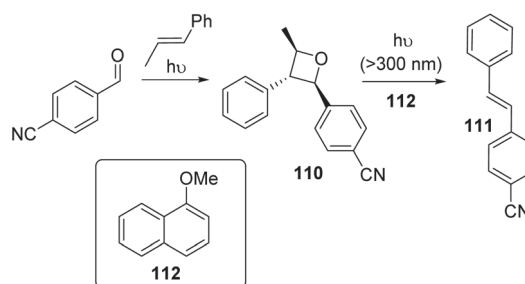
Reductive photocycloreversion. Shima and co-workers studied the metathetic reductive cycloreversion of oxetanes with tertiary amines as electron donors.¹¹⁴ In the presence of triethylamine (TEA) at 254 nm irradiation, they found that oxetanes cleave regioselectively to a new alkene product (Scheme 54). (This contrasts with their previous study on oxidative cycloreversion using cyanoarenes as electron acceptors, where only the starting alkene and carbonyl were observed.)¹¹⁵

According to their mechanistic investigations, an exciplex is formed between the amine and the oxetane, and a proton and an electron are transferred from the amine to the oxetane. The reaction proceeds well in apolar solvents and poorly in polar solvents due to dissociation of the exciplex. Miranda and co-workers¹¹⁶ studied the reductive PET cycloreversion of oxetane **110** using 1-methoxynaphthalene **112** as the electron-transfer photosensitizer. The oxetane cycloreverted to alkene **111** (Scheme 55).

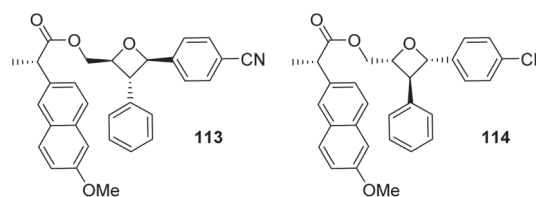
Next, they investigated the analogous intramolecular process in oxetanes **113** and **114**, which contain a chiral methoxynaphthalene linked to the oxetane ring (Scheme 56).¹¹⁷ When irradiated in chloroform, they observed stereodifferentiation: **114** cycloreverted to stilbene much faster than **113**. They attributed the stereodifferentiation to the folded confor-



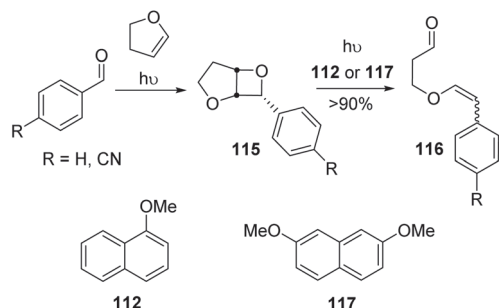
Scheme 54 Reductive cycloreversion with TEA.



Scheme 55 Reductive cycloreversion with 1-methoxynaphthalene.



Scheme 56 Oxetanes and stereodifferentiation.



Scheme 57 Reductive photo-photometathesis.

mation of **114**: the naphthalene ring in **114** is oriented towards the oxetane, facilitating the intramolecular electron transfer. Griesbeck, Miranda and co-workers applied their findings to a photo-photo metathesis reaction:¹¹⁸ oxetanes **115** were cycloreverted to **116** in presence of methoxynaphthalene **112** or dimethoxynaphthalene **117** as electron-donor photosensitizers (Scheme 57). On a preparative scale, >90% conversion to carbonyl-ene pairs was observed.

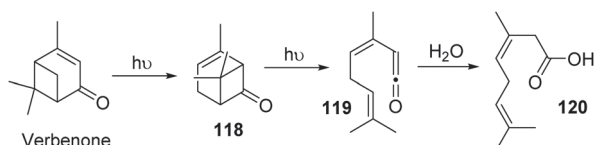
Cyclobutanones

Cyclobutanones, typically made by the cycloaddition of a ketene and an alkene, can be ring-opened by direct irradiation or with sensitizers to give a new metathesized alkene-ketene pair.¹¹⁹ Cycloaddition of ketenes typically proceeds with high regio- and stereospecificity, and photocleavage also proceeds stereospecifically.

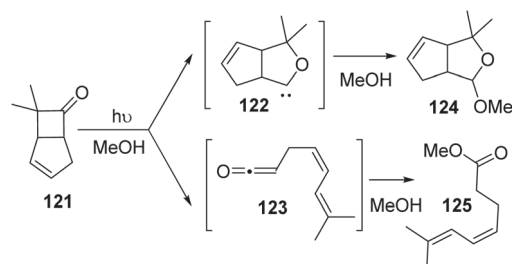
One of the first examples of the ring-opening of cyclobutanones to give a ketene was observed in the photochemistry of verbenone.¹²⁰ Upon exposure to UV light, verbenone isomerizes to chrysanthene **118**, which can fragment upon further irradiation to acid **120**. Acid **120** arises from the reaction of intermediate ketene **119** with water (Scheme 58).

The photolysis of simple cyclobutanones such as **121** (made from the cycloaddition of ketene to cyclopentadiene)¹²¹ in methanol gives two main products, **124** and **125**. Cyclic acetal **124** arises from carbene **122** after reaction with the solvent, and ester **125** arises from ketene **123** *via* a metathesis-type reaction and trapping of the solvent (Scheme 59).¹²²

The synthetic value of this transformation was recognized as a possible thermal-photochemical metathesis reaction in 1983 by Lee-Ruff and co-workers.¹²³ They found that by irradiating the cyclobutanone in benzene with trace amounts of methanol, they could favor the formation of the ketene over



Scheme 58 Photochemistry of verbenone *via* chrysanthene.



Scheme 59 Ring expansion or cycloreversion of cyclobutanones.

the carbene. Esters **126** and **127** were obtained in high yields (Scheme 60).

Later studies showed that the temperature and the size of the adjacent fused ring play important roles in this reaction.¹²⁴

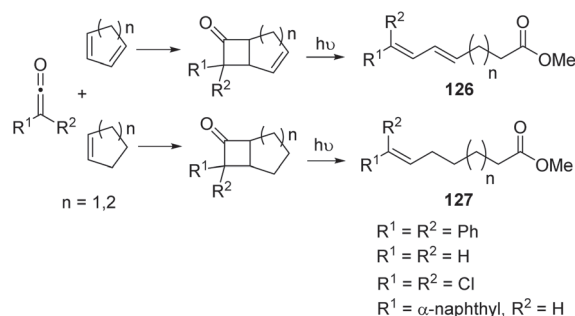
Wakefield and co-workers found that a strategically placed nucleophile (epoxide) on the cyclobutanone could trap the photogenerated ketene. Photolysis of **128** in benzene gave lactone **129** in fair yield (Scheme 61).¹²⁵

Lactone **129** was later used by Roberts and co-workers to synthesize carbocyclic nucleosides.¹²⁶

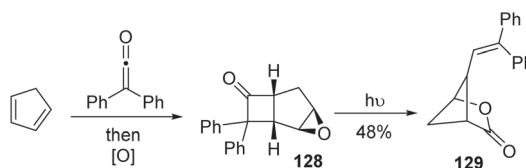
Diol **130** also underwent photolysis in benzene to lactone **131** in 66% yield, and photolysis of amine **132** gave lactam **133** in 45% yield (Scheme 62).¹²⁷

They used this strategy to synthesize natural products (+)-Eldanolide and (+)-Leukotriene B₄ (Scheme 63).^{127,128} Cyclobutanones **134** and **136** were photolyzed *via* the ketenes to lactones **135** and **137**, which were elaborated to the target compounds.

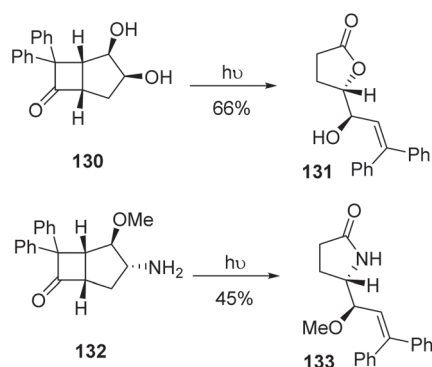
Other natural products synthesized with this method are Goniotalamin, Argentilactone, Streptomyces L-factor, and (+)-20R-Dihydrocleavamine (Scheme 64).^{127,129}



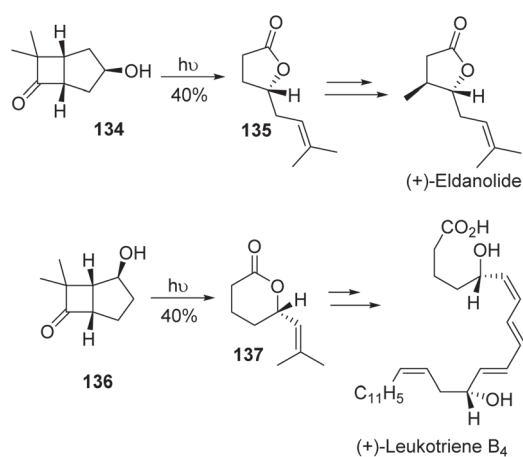
Scheme 60 Metathesis to obtain esters **126** and **127**.



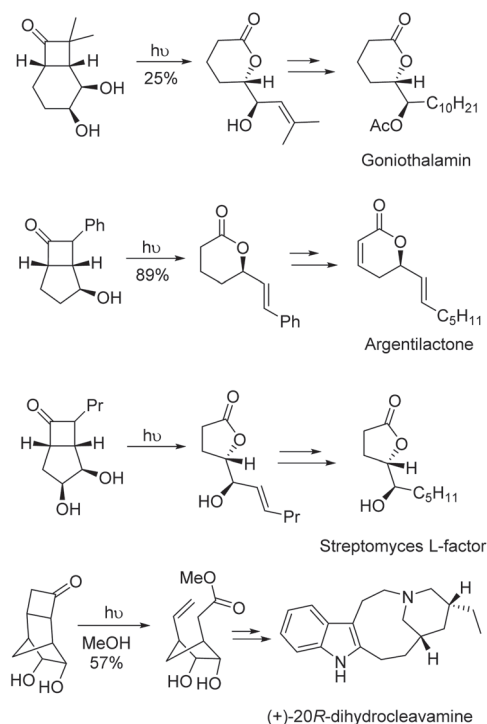
Scheme 61 Synthesis of lactone **129**.



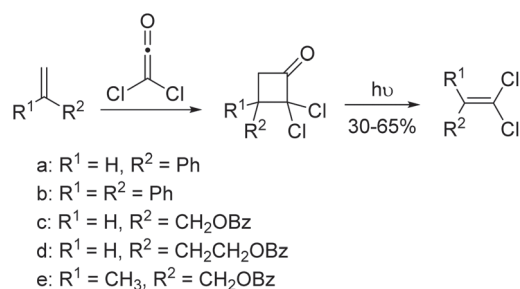
Scheme 62 Trapping with alcohols and amines.



Scheme 63 Synthesis of (+)-Eldanolide and (+)-Leukotriene B₄.



Scheme 64 Total syntheses via metathesis of cyclobutanones.



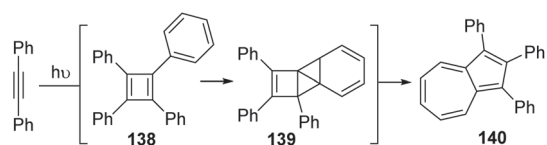
Scheme 65 Synthesis of dichloroalkenes.

The photocycloreversion of dichlorocyclobutanones (made from the addition of dichloroketene to an alkene) gives dichloroalkenes, which are useful synthetic intermediates (Scheme 65).¹³⁰ A wide range of alkenes add to dichloroketene, which allows access to a variety of dichloroalkenes. Yields were fair to high.

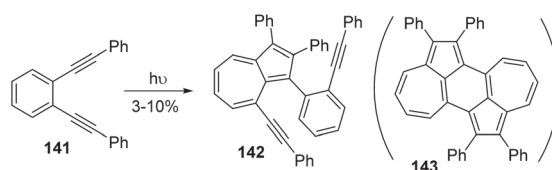
Bicyclobutanes

During their attempts to synthesize cyclobutadienes, a meta-thesis-type reaction was observed by Büchi and co-workers when they investigated the photochemistry of diphenylacetylene (Scheme 66). Upon UV irradiation, diphenylacetylene undergoes a [2 + 2] cycloaddition to give a cyclobutadiene derivative **138**. This cyclobutadiene product is unstable and adds onto one of the aromatic rings to give bicyclobutane intermediate **139**. The bicyclobutane then cycloreverts to azulene **140**.¹³¹

Müller and co-workers also synthesized an azulene while attempting to make cyclobutadienes.¹³² Starting from *o*-diacetylene **141**, they obtained a dimeric bright green hydrocarbon in low yield (3–10%), which they named *Verdene* after its color (Scheme 67). Its structure was at first thought to be **143**,¹³³ but was corrected to **142** following an X-ray structural analysis.¹³⁴



Scheme 66 Photochemistry of diphenylacetylene.



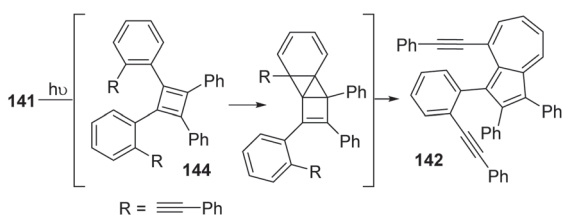
Scheme 67 Structure of Verdene.

Based on Büchi's hypothesis, they suggested that **142** may result from unstable cyclobutadiene **144** via a metathesis-type reaction with the phenyl rings (Scheme 68).

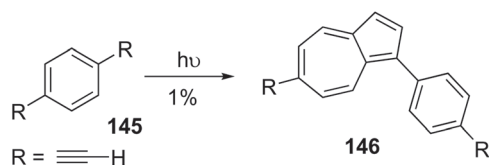
Further proof of the mechanism and structure came from Ried and co-workers, who synthesized azulene **146** from **145** (Scheme 69).¹³⁵

Müller and co-workers synthesized a series of derivatives and found that electron-withdrawing groups on the alkyne gave higher yields than electron-donating groups, and if R = H, the azulene products were unstable (Scheme 70).¹³⁶

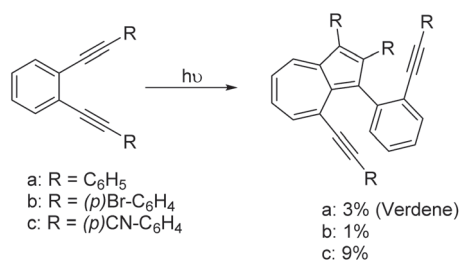
Irradiation of **147** gave tetrahydroazulene **148**, showing that the aromatic ring was not required for the reaction to take place (Scheme 71).¹³⁷



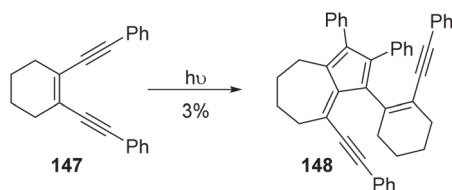
Scheme 68 Mechanism of formation of Verdene.



Scheme 69 Synthesis of azulenes from 1,4-dialkynylarenes.



Scheme 70 Electronic effects on the synthesis of azulenes.



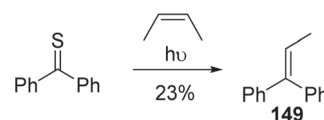
Scheme 71 Synthesis of tetrahydroazulene.

Thietanes

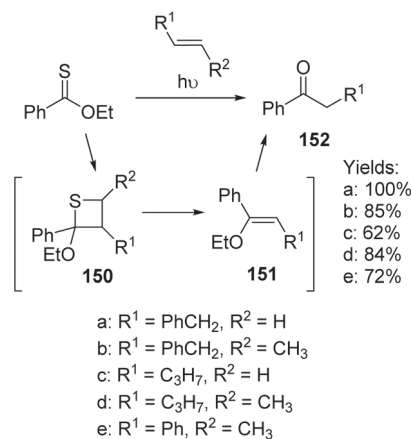
The first investigations into the photoreactivity of thioketones with alkenes were carried out by Kaiser and co-workers. They found that irradiating thiobenzophenone with wavelengths between 210–280 nm in presence of *cis*-2-butene gave a new metathesized alkene product **149** (Scheme 72).¹³⁸

Irradiation of *o*-alkyl thiobenzoates with alkenes afforded ketones in good yields, albeit with an irradiation time of more than 10 days to reach reaction completion (selected examples in Scheme 73). The ketones **152** result from fragmentation of the intermediate thietane **150** to enol ether **151**, which hydrolyses during purification. The thietanes could sometimes be isolated.¹³⁹

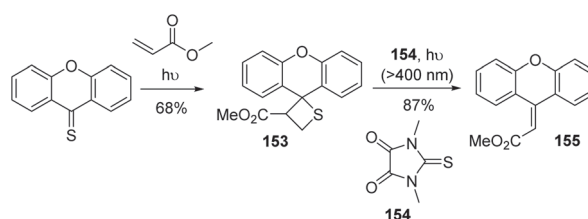
Gotthard and co-workers found that spirothietane **153**, generated from the photocycloaddition of xanthione to methyl acrylate, cycloreverted to the metathesized alkene product **155** in 44% yield.¹⁴⁰ Upon sensitization with **154** and visible light, the yield of **155** rose to 87% (Scheme 74).¹⁴¹



Scheme 72 Metathesis via a thietane.



Scheme 73 Access to aryl ketones from aryl thiobenzoates.



Scheme 74 Sensitization in thietane metathesis.

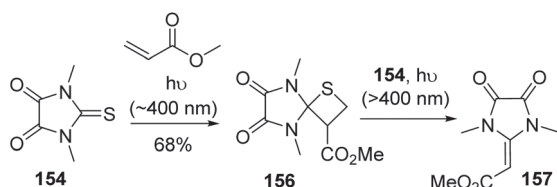
Photocycloaddition of a variety of alkenes to sensitizer **154** gave thietanes **156** in high yield (Scheme 75).¹⁴² The thietane could be ring-opened to a new alkene **157** upon irradiation with visible light and sensitization with **154**.

Irradiating an excess of sensitizer **154** in presence of methyl acrylate gave the metathesis product **157** directly from **154** in 56% yield.¹⁴¹

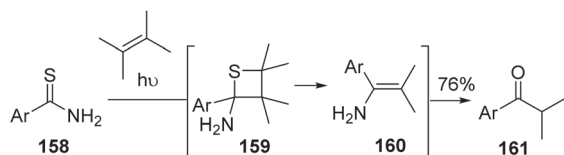
The Machida group reported on the photoreactivity of arylcarbothioamides **158** with alkenes. Under inert atmosphere, an intermediate thietane **159** is formed, which fragments to imine **160**. Imine **160** hydrolyses to aryl ketone **161** in an overall yield of 76% (Scheme 76).¹⁴³

Coyle and co-workers studied the photochemistry of thioimide compounds, namely thiophthalimide **162**, with alkenes and ketenes. Upon exposure to UV light, various alkenes reacted exclusively with the thioamide function to give thietanes. When diphenylethene was used, the metathesis product **163** was obtained directly (Scheme 77).¹⁴⁴ With ketenes, exclusive reactivity at the thioamide moiety was again observed.¹⁴⁵ Irradiation of a solution of **162** and diphenylketene gave the spirothietanone **164** and the metathesis product **165** (Scheme 78). Irradiation of purified **164** gave **165** cleanly *via* loss of COS. Similar results were observed for the reaction of *N*-methylthiophthalimide with diphenylketene.

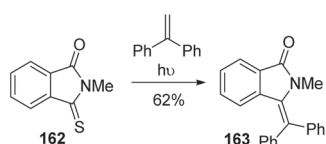
Thietanes can also be ring-opened by photoelectron transfer.¹⁴⁶ Shima and co-workers synthesized 3-cyano-2,2-diphenylthietane **166a** from the photocycloaddition thiobenzophenone and acrylonitrile, and upon 366 nm irradiation in the presence of photooxidant dicyanoanthracene **167** (DCA), they



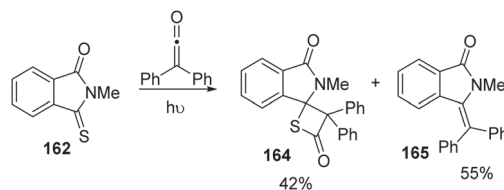
Scheme 75 Metathesis chemistry of **154**.



Scheme 76 Synthesis of ketones from arylcarbothioamides.



Scheme 77 Photochemistry of thiophthalimide.

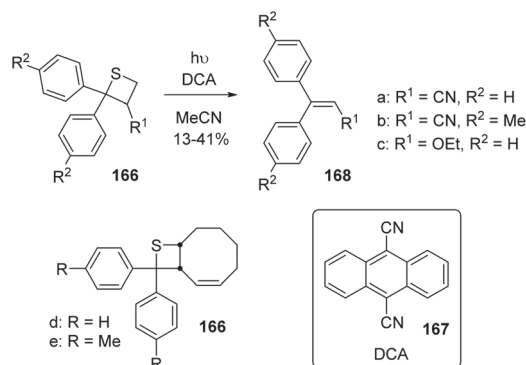


Scheme 78 Photochemistry of thiophthalimide with ketene.

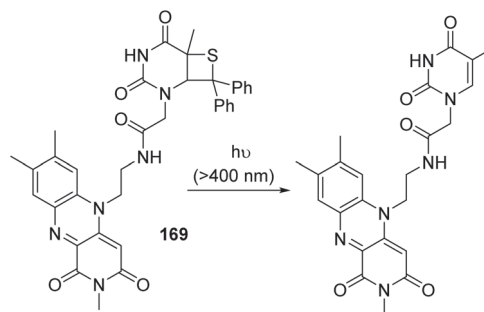
obtained metathesized alkene **168a** (Scheme 79). Similarly, irradiation of **166b** and **166c** in the presence of DCA gave **168b** and **168c**. Ring splitting of **166a** also occurred without DCA by direct irradiation at 313 nm. Bicyclic thietanes **166d** and **166e** were unreactive. They concluded that the ring-splitting takes place *via* the one-electron oxidation of the thietane ring by the photocatalyst.¹⁴⁷

Thietanes and their cycloreversion have been extensively studied in the context of DNA repair of (6–4) photoproducts.¹⁰⁹ They are more stable than their oxetane counterparts, making them convenient for model studies.¹⁴⁶ Although this work was not carried out in the goal of a metathesis reaction, it is noteworthy that Carell and co-workers were able to cyclorevert thietane **169** by one-electron photoreduction from a linked flavin moiety upon irradiation with visible light (Scheme 80).¹⁴⁸

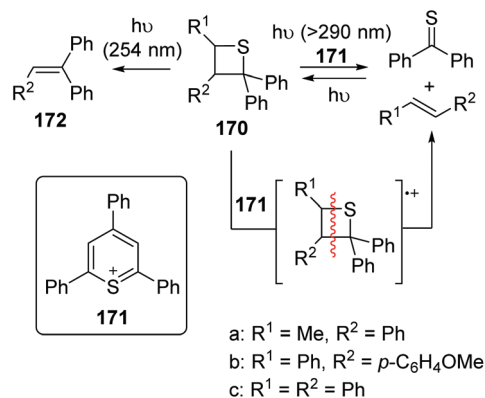
Miranda *et al.* found that photooxidation of thietanes **170** with thiapyrylium salt **171** gave the starting alkene and thio-benzophenone (or other products), but direct irradiation with



Scheme 79 PET ring-splitting of thietane.



Scheme 80 Visible-light PET ring-splitting of thietane.



Scheme 81 PET cycloreversion of thietanes with thiapyrylium salt **171**.

short wavelength light gave the metathesized product **172** (Scheme 81).¹⁴⁹

Photochemically initiated transition-metal complexes

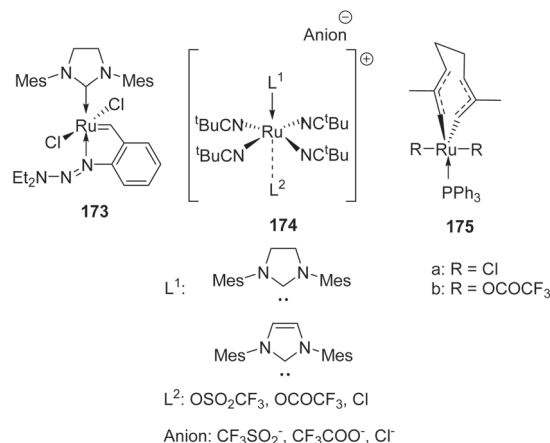
Several excellent reviews¹⁵⁰ have been written recently on this subject, so we will give only a brief summary here of this field and its latest developments. We encourage the reader to refer to the aforementioned reviews for more information.

Transition-metal catalysts for metathesis reactions (such as those developed by Grubbs and Schrock)¹⁵¹ are widely used in synthetic chemistry, especially in polymer chemistry. By tuning the ligand sphere, researchers found that they could create metathesis catalysts which are inert until activated by irradiation with (usually UV) light. Activation of a catalyst on demand allows for spatial and temporal control of the metathesis reaction, which is enormously useful for materials technologies (for example, photolithography, 3D-printing, etc.). The light-activation step typically involves photodissociation of a ligand from the metal to give the active metathesis catalyst. Other photoactivation methods have been developed, including (but not limited to): the generation of a photoacid which protonates a labile ligand to give the active catalyst,¹⁵² and the photolysis of microcapsules to liberate a metathesis catalyst.¹⁵³

The Buchmeiser group have developed a range of light-activated catalysts for metathesis reactions (Scheme 82).¹⁵⁴

Their recent focus has been the photochemical rupture of Ru–N bonds, either with triazene or nitrile (^tBuCN) ligands. Triazene slowly decomposes upon irradiation to release N₂.

Polymerizations with the catalysts shown in Scheme 82 upon irradiation with 254 nm light are quick and give high conversions. For example, in the dark, triazene catalyst **173** showed no polymerization of ROMP monomer cycloocta-1,5-diene (COD), even upon heating to 50 °C for 24 hours. But when the mixture was irradiated with 254 nm light, polymerization of COD occurred with 95% conversion.



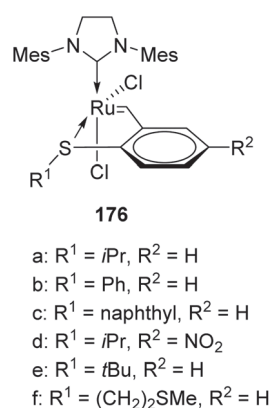
Scheme 82 Light-activated catalysts for metathesis reactions.

A variety of ROMP monomers could be polymerized for catalysts **174**, but catalysts **175a** and **175b** polymerized norbornene exclusively. This is because, once coordinated to the catalyst, norbornene undergoes a sigmatropic [1,2-*H*] rearrangement to generate the ROMP-active species. Other monomers do not undergo sigmatropic [1,2-*H*] rearrangement so easily.^{154b}

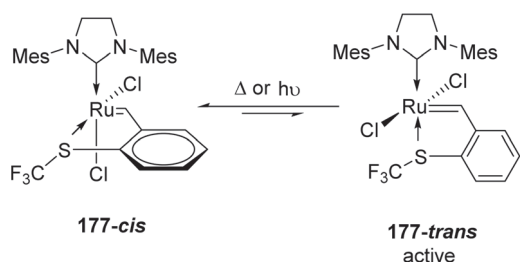
The Lemcoff group focused on sulfur-chelated Hoveyda-Grubbs-type catalysts **176**. Some examples are shown in Scheme 83. The latent catalysts are in the *cis*-dichloro configuration, and they isomerize to the active *trans* form upon irradiation.¹⁵⁵ The inactive *cis* form can be regenerated by heating to 80 °C for a short period (five minutes), making it a system that they could effectively switch on and off.

Catalysts **177** with an electron-withdrawing trifluoromethyl group on the sulfur atom showed improved activity (Scheme 84). The catalyst could be left in a solution of cyclooctene (COE) monomer for over a week with almost no polymerization, and upon irradiation with 350 nm light in a Rayonet photoreactor, quantitative conversion of the monomer was obtained within 1 hour.¹⁵⁶

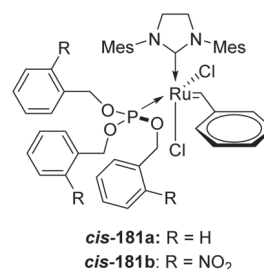
They found that the sulfur-chelated catalysts did not isomerize to the active *trans* form upon irradiation with 254 nm



Scheme 83 Sulfur-chelated Hoveyda-Grubbs-type catalysts.



Scheme 84 Sulfur-chelated catalyst with improved activity.



Scheme 86 Ruthenium benzylidene phosphite complexes.

light. This allowed them to develop a chromatic orthogonal system shown in Scheme 85:¹⁵⁷ irradiation of **178** in presence of **176c** with 350 nm light induced a metathesis reaction, and irradiation with 254 nm light cleaved a silyl protecting group.¹⁵⁸ Sequential irradiation following path A gave dihydrofuran **180**, and following path B gave dihydropyran **179** in excellent selectivity.

Recently, the Lemcoff group developed ruthenium benzylidene phosphite complexes **181a** and **181b**, which can be activated using visible light (420 nm lamps or blue LEDs). These complexes have a latent *cis*-dichloro configuration. Complex **181b** was equipped with 2-nitrobenzyl groups, which can cleave on exposure to UV-C light, acting as a chromatic orthogonal “kill switch” for the catalyst (Scheme 86). Both complexes efficiently catalyzed the RCM and ROMP reactions of a variety of monomers.

The Rovis group recently reported the first metathesis catalyst **182** activated by visible light photoredox catalysis. Photocatalyst 2,4,6-triphenylpyrylium tetrafluoroborate **72c** oxidizes the ruthenium catalyst **182**, and one of the NHC ligands dissociates to give the active catalyst **183** and an IMes radical cation. Standard metathesis reactions and ROMP of a variety of monomers were successfully carried out with this two-catalyst system (Scheme 87).¹⁵⁹



Scheme 87 Visible-light-controlled ruthenium-catalyzed olefin metathesis.

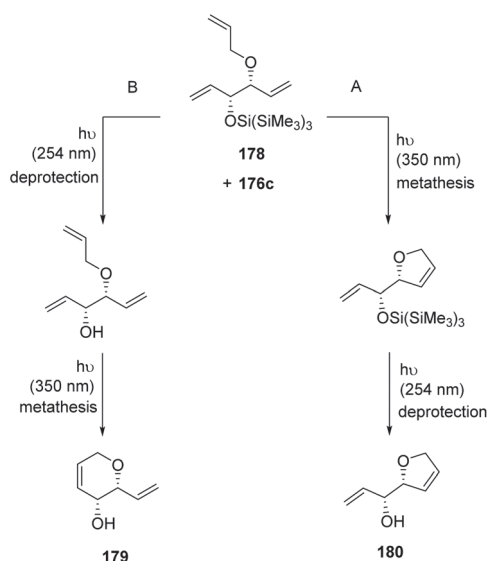
One feature of this reaction was that the IMes radical cation was reversibly trapped by the photocatalyst. In the absence of light, it returned to the ruthenium catalyst, deactivating it and regenerating the photocatalyst. Thus, they were able to switch the metathesis reaction on and off by turning the light on and off, making the reaction spatially and temporally controllable. They illustrated this with a series of polymer patterning experiments using visible light.

Novel methods with visible-light photoredox catalysis

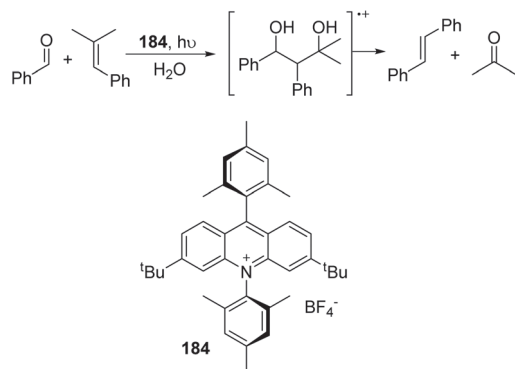
Current developments in photoredox catalysis have given chemists a new set of techniques to access their synthetic targets. Two interesting reports of metathesis-type reactions using photoredox chemistry have appeared recently.

Glorius and co-workers envisioned a cross carbonyl-olefin metathesis reaction *via* a 1,3-diol and an acid-induced Grob fragmentation, rather than *via* an oxetane (Scheme 88). They used **184** as a robust photocatalyst which tolerated the aqueous reaction medium, with aromatic alkenes and aldehydes as metathesis partners.¹⁶⁰ The reaction proceeds in high yields when the aldehyde partner is electron-rich, and alkenes are afforded with high *E* selectivity.

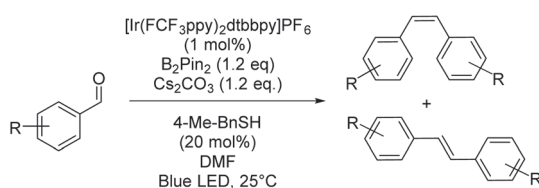
The König group described a carbonyl-carbonyl metathesis reaction using visible light and an iridium catalyst to generate an alkene from an aldehyde pair.¹⁶¹ They envisioned a McMurry-type reaction where the carbonyl groups could be activated by a diboronate compound to drive the deoxygenation process (Scheme 89). The thiol acts as a co-catalyst: after deprotonation by cesium carbonate, the sulfur anion reduces the photoexcited iridium catalyst. Then, single electron trans-



Scheme 85 A chromatic orthogonal system.



Scheme 88 Carbonyl–olefin metathesis via a 1,3-diol.



Scheme 89 Carbonyl–carbonyl metathesis.

fer from the Ir(III) species to benzaldehyde starts a catalytic cycle involving B_2Pin_2 and regenerating the thiol. The oxygen atoms from two benzaldehyde molecules are transferred to boron over several steps to give the alkene product. Many co-catalysts were tested, and they found that 4-methylbenzyl mercaptan (4-Me-BnSH) gave the best results.

The reaction has broad functional group tolerance, and it can be used for homocoupling and cross-coupling reactions of aldehydes to generate the alkenes.

Conclusion

Photochemical metathesis reactions can be carried out with a wide array of starting materials (alkenes, carbonyl groups, thio-carbonyl groups, ketenes,...) for the formation of a new double-bonded species. The technique has proven extremely useful for synthesizing biologically active natural products, and it has allowed chemists to build intriguing structures, from azulenes to Möbius rings. Often, a reaction cascade occurs after the initial [2 + 2] cycloaddition, yielding complex products in a single step that are very different from the starting material.

We have seen in this review that the outcome of a photometathesis reaction is highly dependent on the photocatalyst, the light wavelength, and the nature of the double-bonded partners. When strained intermediates are formed after a [2 + 2] cycloaddition, ring-opening to new product(s) is typically clean and high-yielding. Ring-opening is also favorable if the new alkene is conjugated and/or contained within a five-membered ring.

Photometathesis has undoubtedly proven its worth in synthesis, but there is still much progress to be made in this area. Many of the reactions we have shown proceed in a step-wise fashion, often requiring short-wavelength light for the intermediate four-membered ring formation, and high temperatures or acidic conditions to fragment the ring and complete the metathesis. Ideally, the transformation would proceed in a single step with visible light under mild conditions. Recently, scattered examples of one-pot photochemical metathesis reactions using visible light that have appeared. Given these developments and the importance of metathesis reactions in synthesis, we believe that there is great potential for the elaboration of new photometathesis techniques. We hope that the examples we have shown here will inspire the reader and give them an in-depth understanding of this nascent research area.

In his 1912 *Science* paper,¹⁶² the renowned photochemist Giacomo Ciamician said: “On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is”. With each newly developed visible-light photochemical reaction, we come closer to this ideal.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The support of the Swiss National Science Foundation is gratefully acknowledged.

Notes and references

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