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Recent developments in photochemical reactions of diazo compounds

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Diazo compounds are among the most important building blocks in organic synthesis. Generally, their photoinitiated, thermal, or transition metal catalyzed decomposition yields the corresponding carbenes or metal carbenoids, which subsequently undergo various transformations. Modern chemistry of diazo compounds is dominated by transition metal catalysis, leaving both catalyzed and non-catalyzed phototransformations of these reagents behind. Recently, photoinitiated reactions of diazo compounds have experienced a revival of interest due to the increased understanding of modern photochemistry. This mini-review covers recently published (year >2000) reports on the reactivity of diazo compounds under light irradiation.

1. Introduction

Since the first documented preparation of ethyl diazoacetate by Curtius in 1883,[1] diazo compounds have been recognized to be amongst the most versatile reagents in organic synthesis. Aliphatic diazo compounds can be considered to be carbene equivalents as their thermal, photoinduced, or metal catalysed decomposition with the extrusion of dinitrogen leads to either carbenes in triplet or singlet states or to metal carbenoids.[2] Reactive carbene species can subsequently undergo insertion to C–H, O–H, Si–H, N–H, S–H bonds, the Wolff rearrangement, cyclopropanation, or addition to the lone pair of a heteroatom to form an ylide (Scheme 1).[3,4] Diazo compounds can also react in such a way that the diazo moiety is incorporated into the product structure, usually *via* a [3 + 2] cycloaddition reaction.[3b,d]

Aliphatic diazo compounds are generally considered to be reactive and potentially explosive species[5] as, in contrast to aromatic diazonium ions, they are not stabilized by π back donation.[4a] Therefore unstabilized diazo compounds such as diazoalkanes are generally avoided in synthetic procedures, with the exception of diazomethane (CH_2N_2) and aryldiazomethanes ($ArCHN_2$), which are usually generated *in situ* prior the reaction.[5] On the other hand, stabilized diazo compounds are common and fall into three categories: acceptor (EWG), acceptor–acceptor (EWG-EWG), and acceptor–donor

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Katarzyna Rybicka-Jasińska

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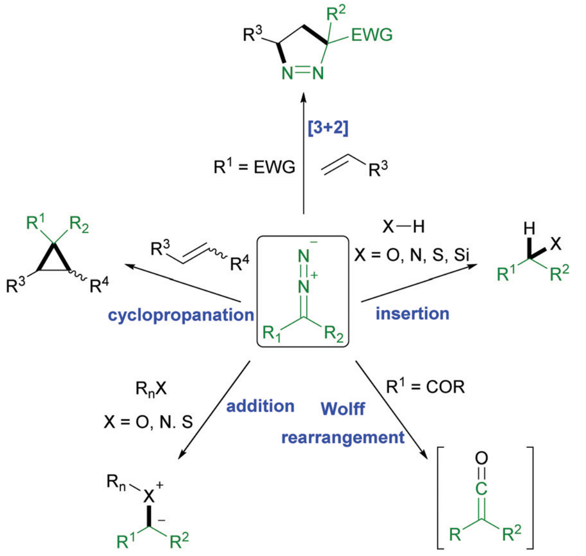


Scheme 1 General reactivity of diazo compounds.

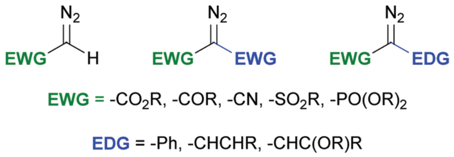


Fig. 1 Classification of substituted diazo compounds.

(EWG-EDG) substituted compounds (Fig. 1). The substitution pattern has a significant influence on the reactivity and stability of carbenes and carbenoids, and this topic is extensively covered in several excellent reviews.[3]

Nowadays transition metal catalysed reactions of diazo compounds are of primary interest due to their high selectivity.[3] However, rapid developments in synthetic organic photochemistry have renewed interest in the photochemistry of diazo compounds. This review mainly focuses on the new photochemical reactions discovered after year 2000, and their relationship with diazo compounds. It is organized into two chapters describing direct, non-catalysed decomposition of diazo compounds and their subsequent transformations and reactions in the presence of a photocatalyst.

Dorota Gryko

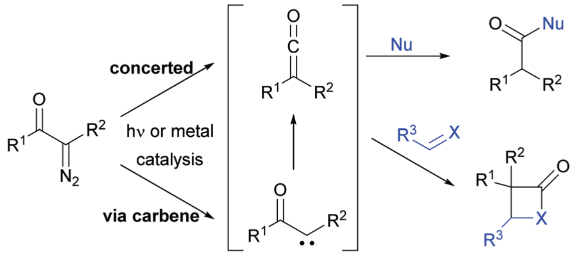
Dorota Gryko obtained a PhD from the Institute of Organic Chemistry at the Polish Academy of Sciences in 1997, under the supervision of Prof. J. Jurczak. After a post-doctoral stay with Prof. J. Lindsey in North Carolina State University (1998–2000), she started an independent career in Poland. In 2009 and 2018, she received the prestigious TEAM grants from the Foundation for Polish Science. Her current research interests are focused on light-induced processes with particular attention being paid to porphyrinoid catalysis as well as on vitamin B$_{12}$ chemistry.

2. Non-catalysed photoreactions of diazo compounds

In general, the direct photoexcitation of a diazo compound generates a singlet carbene which can then undergo a chemical reaction or intersystem crossing (ISC), depending on the singlet–triplet energy gap. In most cases highly energetic UV light is required, though Davis and Jurberg have recently noticed that aryldiazoacetates absorb in the region of 400–500 nm.[6] Dediazoniation of the excited diazo compound is not always the first step of a reaction, in some cases it can proceed simultaneously with a rearrangement or addition, giving the same product as expected by the free carbene pathway (*e.g.* the Wolff rearrangement is known to proceed *via* a carbene or by a concerted rearrangement – dinitrogen elimination process).[4a] Photochemical reactivity of diazo compounds in the absence of a photocatalyst strongly depends not only on the electronic and steric properties of substituents, but also on the character of solvent used. Previous reviews thoroughly describe the influence of a solvent and substituents on the carbene reactivity,[4] therefore this discussion will mainly focus on C–C and C–X bond formation.

2.1. Synthetic applications of the Wolff rearrangement

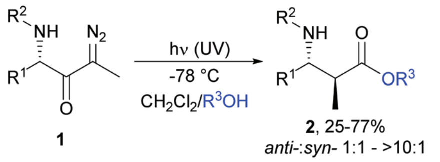
The Wolf rearrangement, discovered in 1902 by Ludwig Wolff,[7] represents one of the most useful and widely studied transformations of α-diazocarbonyl compounds.[8] Nitrogen extrusion and 1,2-rearrangement to a ketene proceeds in either a stepwise, involving a carbene as an intermediate, or concerted manner (Scheme 2). The resulting ketenes are not usually isolated but are directly reacted with various nucleophiles to yield carboxylic acid derivatives or with unsaturated compounds to undergo [2 + 2] cycloaddition reactions.



Scheme 2 General scheme of the Wolff rearrangement and subsequent reactions.

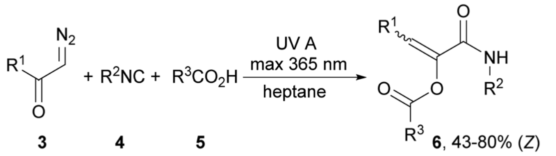
Over the years, the Wolff rearrangement has been extensively applied in organic synthesis for homologation of carboxylic acids or for the preparation of four-membered rings. An excellent, comprehensive review from 2002 by Krimse covers this topic.[8]

2.1.1 UV activation. To the plethora of described transformations, Yang *et al.* added a new photoinduced, diastereoselective process involving the Wolff rearrangement of α-diazoketones **1** in either MeOH or *i*PrOH furnishing α-substituted β-amino acid esters **2** with good diastereoselectivity and decent yields (Scheme 3).[9] Photolysis was performed in a commercially available UV photoreactor at low temperature to ensure high diastereoselectivity. The stereochemistry of this reaction is controlled by the nature of substituent R^1 and the nitrogen protecting group.



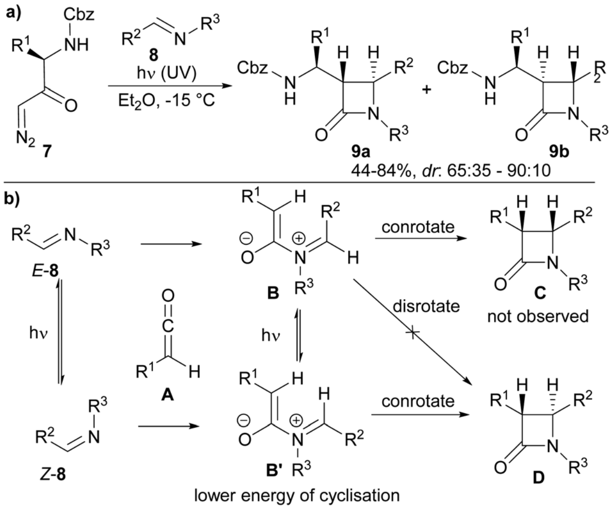
Scheme 3 Synthesis of α-substituted β-amino acid esters by the photoinduced Wolff rearrangement.

Upon irradiation of α-diazoketones **3** with isocyanides **4** and carboxylic acids **5** with a UV A lamp (max 365 nm) corresponding 2-acyloxyacrylamides **6** (valuable synthons in Diels–Alder condensations and 1,3-dipolar cycloadditions) form with *Z*-diastereoselectivity in good yields (Scheme 4).[10] The use of α-diazoketones instead of acyl chlorides as ketene precursors eliminates the need for a base, hence suppressing the formation of a homo-adduct. In fact, photochemical generation of ketenes have proved effective in the preparation of a broad array of substituted olefins. By conducting the process in continuous flow, the formation of the *E* isomer could be suppressed as a consequence of shorter irradiation times.



Scheme 4 Three component, photoinduced synthesis of 2-acyloxyacrylamides.

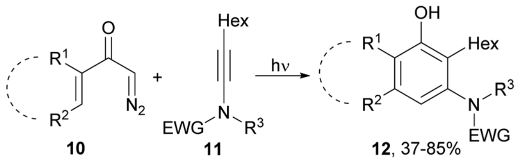
Photochemically generated ketenes react with aromatic imines **8** *via* a formal [2 + 2] cycloaddition reaction (the Staudinger synthesis synthesis), furnishing exclusively *trans*-β-lactam **9** as a mixture of isomers **9a**, **9b** with good yields and diastereoselectivities (Scheme 5a).[11] It is assumed that the selective formation of *trans* diastereoisomers results from the ability of imines and acyclic adducts **B**, **B′** to isomerize upon UV (or MW) irradiation (Scheme 5b).



Scheme 5 Photoinduced β-lactam formation *via* formal cycloaddition of ketene to imine.

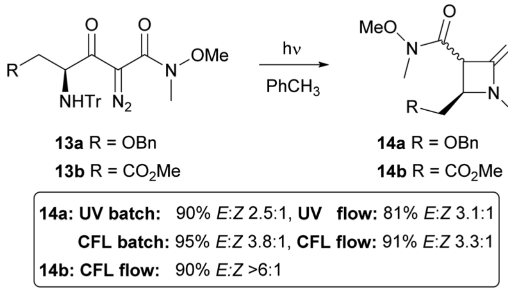
Later, Liang *et al.* revealed that the Woodward-Hoffmann rule is not applicable to the photoinduced Staudinger synthesis and that the cyclization of zwitterionic adduct **B′** occurs only in the conrotatory manner.[12]

Photoinduced [2 + 2] cycloaddition of α,β-unsaturated or aromatic diazoketones **10** with ynamides **11** furnishes highly substituted phenols **12** (medium pressure mercury lamp, spectral lines in the range of 200–600 nm) (Scheme 6). In this reaction, generated cyclobutenones undergo ring opening and subsequent 6e$^-$ electrocyclic ring closure (and tautomerisation) to final products **12**.[13] Undesired dimerization of ketene can be supressed by using continuous flow conditions. Both in batch and under continuous flow conditions products are obtained in comparable yields. Similarly the reaction of *N*-protected-(2-diazoacetyl)-pyrroles or 2-(2-diazoacetyl)-thiophenes produce the corresponding indoles and benzothiophenes in moderate to good yields.



Scheme 6 Photochemical benzannulation *via* reaction of diazo ketones with ynamides.

2.1.2 Visible light induced Wolff rearrangement. In 2010 the Konopelski's group reported photoinduced intramolecular Wolff rearrangement of α-diazo-β-ketoamides **13a–b** – derivatives of trityl-protected aminoacids (Scheme 7).[14] Enantiomerically pure β-lactams **14a–b** form as a mixture of *E* and *Z* diastereoizomers in very good yields. The reaction can be induced by both UV and visible light irradiation (CFL lamp) with the latter providing β-lactam **14a** with slightly higher

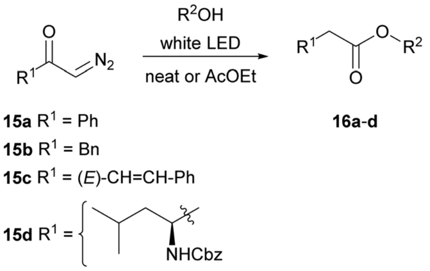


Scheme 7 UV and visible light induced intramolecular Wolff rearrangement of α-diazo-β-keto Weinreb amids.

selectivity, though in a longer time. For both methods continuous flow conditions allowed to increase reaction rates. In this process, the Weinreb amide moiety not only induces favourable conformation of substrate **13** allowing for the visible light activation but also facilitates subsequent modifications of the product.

Visible light (CFL or white LED) also promotes the Wolff rearrangement of α-diazoketones **15a–d** (Scheme 8).[15] The best results were obtained for 18 W LED lamp irradiation of diazo compounds **15a–c** in neat alcohols or water, but with solid nucleophiles ethyl acetate can be used as a solvent.

In addition to its synthetic application, the photoinduced Wolff rearrangement has been widely used in photolithography. Photodecomposition of 2-diazo-2*H*-naphthalen-1-one, a photoactive component of positive photoresists, is usually induced by UV irradiation, however in 2004 Urdabayev *et al.* discovered, that irradiation of a methanolic solution of 2-diazo-2*H*-naphthalen-1-one by a near-infrared (NIR) laser (800 nm) provides the Wolff rearrangement product, due to two photon absorption.[16]

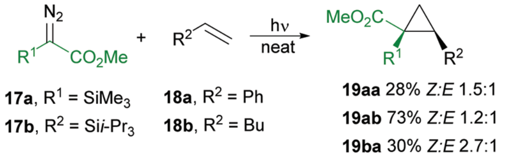


Scheme 8 White LED induced Wolff rearrangement of α-diazoketones **15a–d**.

2.2 C–C bond forming reactions

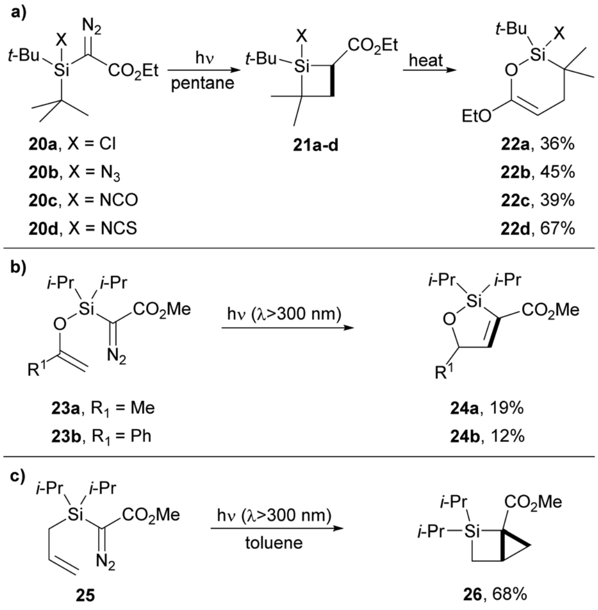
One of the most important reactions of diazo compounds is the cyclopropanation of double bonds. Usually, in the presence of a chiral metal complex the reaction is highly enantio- and diastereoselective.[17] However, due to the inherent bulkiness of employed catalysts, reactions with disubstituted diazo compounds proved challenging.

2.2.1 UV-induced reactions. In 2001 Maas *et al.* reported a method for the photoinduced cyclopropanation of olefins with the sterically hindered methyl 2-trimiethylsilyl-2-diazoacetate **17a** (Scheme 9).[18] In contrast to the metal catalysed cyclopropanation, this photoinduced reaction predominantly yielded *Z* diastereoisomer.



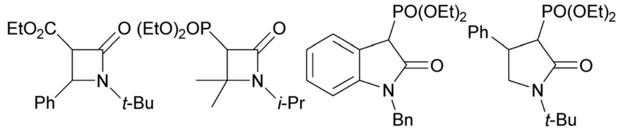
Scheme 9 Photoinduced cyclopropanation of olefins with bulky diazo compounds.

Under light irradiation (λ > 300 nm) α-silyl diazoacetates **20a–d** provide silacyclobutanes **21a–d** as a result of intramolecular carbene insertion to C–H bond of the alkyl substituent at the β-position to the silicon atom (Scheme 10).[19] After heating, ring expansion to the corresponding *O*-silyl ketene acetals **22a–d** occurs. For α-(vinyloxy)silyl-α-diazoacetates **23a,b** the corresponding oxasiloles **24a,b** form, although in low yields (Scheme 10b).[20] Conversely, due to the lower nuclepohilicity of the terminal carbon in the allyl group, structurally related α-(allyl)-silyl-α-diazoacetate **25** gives cyclopropane **26** in good yield instead (Scheme 10c).[21]



Scheme 10 Photolysis of α-silyl diazoacetates.

In 2008 Afonso and co-workers reported the UV photolysis of α-diazoacetamides in water, hexane, and neat (as a film) to form lactams *via* intramolecular C–H insertion of the generated carbenes.[22] The cyclization pathway strongly depends on the nature of the substituent on the nitrogen. For *N*-benzyl-

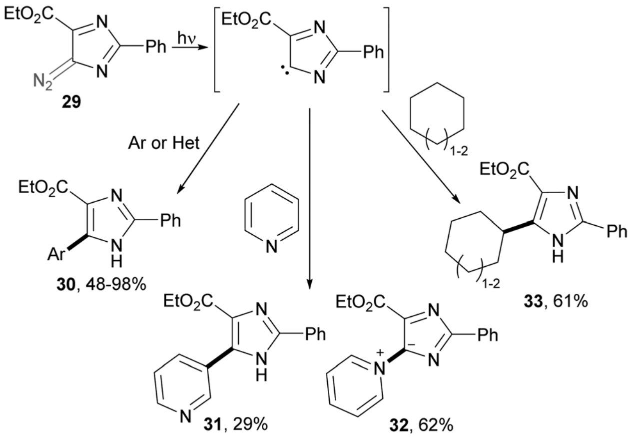


27a, 75% **27b**, 63% **28a**, 90% **28b**, 43%

Fig. 2 Lactams formation *via* C–H insertion of carbenes resulting from irradiation of α-diazo acetamides.

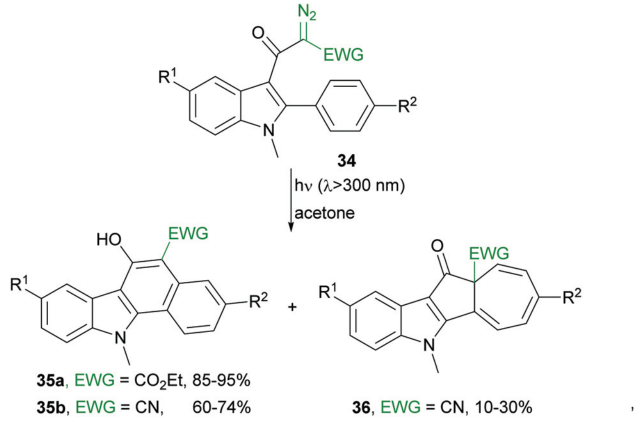
amines formation of β-lactams **27a** is favoured, while *N*-alkyl-, *N*-phenyl, or *N*-(2-phenylethyl)-diazoamides furnish five membered lactams **28a,b** (Fig. 2). The reaction of sterically hindered *N*,*N*-diisopropyl substituted-diazoamides is not selective, yielding a mixture of β and γ-lactams. It was found that the selectivity of the α-diazoacetamide photolysis in water towards C–H insertion is better than in the case of Rh(OAc)$_2$ catalysed processes.

Carbenes derived from diazoimidazolecarboxylate **29** under light irradiation undergo C–H insertions with aromatic compounds and alkanes, or react with pyridine to form ylides (Scheme 11).[23]

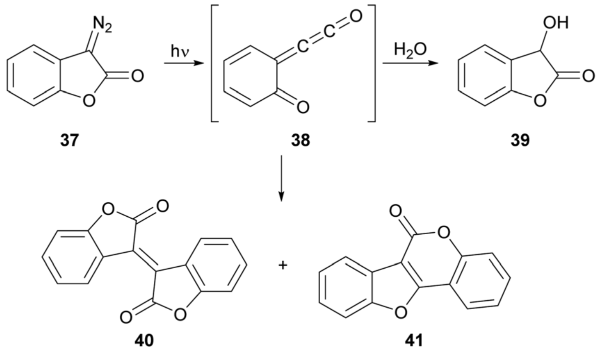


Scheme 11 C–H insertion reactions of photochemically generated carbenes.

Utility of the C–H insertion processes was demonstrated by Zhang, Yu and co-workers who developed an efficient method for the synthesis of benzo[*a*]carbazoles **35a**, **b** involving intramolecular C–H insertion of carbenes (Scheme 12).[24] For α-cyano diazocompounds, side product **36** resulting from the aromatic addition and subsequent tautomerisation, is formed. It is believed that this pathway is feasible because of the low steric hindrance imposed by the cyano group in the intermediate carbene.



Scheme 12 Photochemical synthesis of benzo[*a*]carbazoles form diazo compounds.



Scheme 13 Photoinduced formation of cumulenone **38** and subsequent reactions.

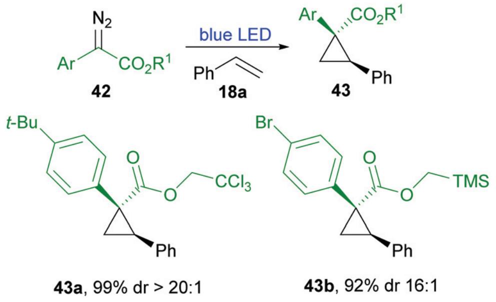
The Wolff rearrangement was proposed for photoinduced dediazoniation of 3-diazo-3*H*-benzofuran-2-one (**37**), however, unexpectedly cumulenone **38** forms as the only product. In the presence of water intermediate **38** hydrolyses to α-hydroxy lactone **39** while in aprotic solvents, dimerizes giving compounds **40** and **41** (Scheme 13).[25] For this process, *ab initio* calculations suggest that the ring opening of an initially formed carbene occurs instead of the expected Wolff rearrangement.

The Shetcher group has studied the photodecomposition of 2-diazoacenapthones. In this case, the reaction does not provide the expected products of the Wolff rearrangement, instead C–H or X–H insertion, ylide formation or cycloaddition reactions with solvent occur.[26]

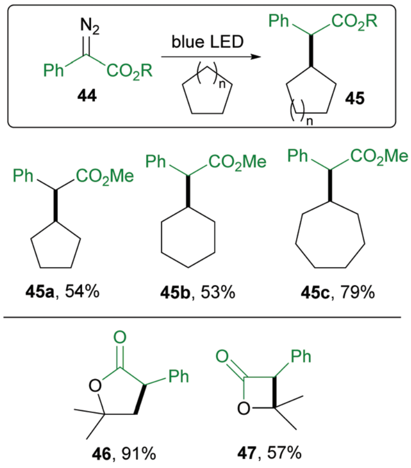
2.2.2 Visible light induced C–C bond formations. Although photocyclopropanation reactions are typically performed under UV irradiation, they can occur at longer wavelengths so long as a suitable diazo compound is used. Jurberg and Davies reported that α-aryldiazoacetates absorb in the 400–500 nm region and generate carbenes. When this photochemical reaction occurs in the presence of styrene (**18a**) the corresponding cyclopropanes **43** form with high *E*-diastereoselectivity in good to excellent yields (Scheme 14).[6] In a similar manner aryldiazoacetates **42** react with *N*-Boc-indole and pyrrole as well as with benzofuranes.

Furthermore, carbenes generated from α-aryldiazoacetates **44** in neat alkanes undergo C–H insertion reactions providing products **45** in moderate yields (Scheme 15).[6]

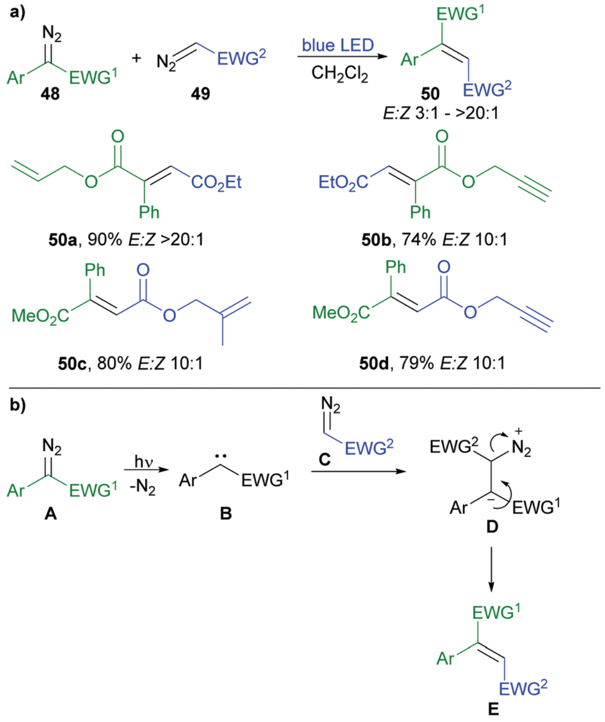
Also electron-rich aromatic compounds, including: 1-methylindole, 1-methylpyrrole and 1,3,5-trimethoxybenzene



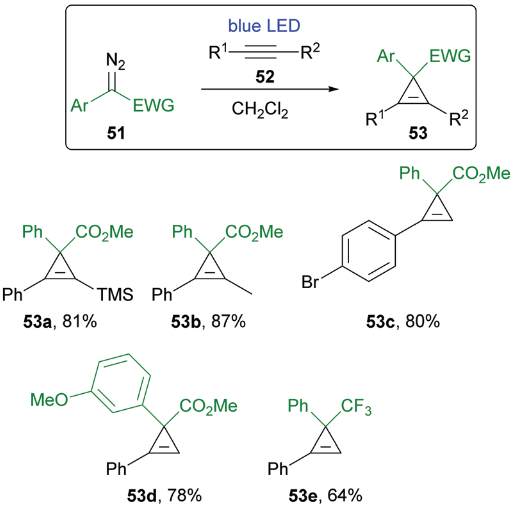
Scheme 14 Blue light induced cyclopropanation of styrenes with α-aryldiazoacetates.



Scheme 15 Inter- and intramolecular C–H insertion of α-aryl diazoacetates.



Scheme 16 Blue light induced cross-coupling of aryl diazoacetates with α-diazocarbonyl compounds.



Scheme 17 Visible light induced cyclopropenation of alkynes (batch conditions).

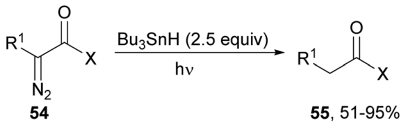
can serve as carbene trapping reagents. Under the same reaction conditions intramolecular cyclization of *tert*-butyl 2-phenyl-2-diazoacetate leads to γ-lactone **46** in excellent yield, for iso-propyl 2-phenyl-2-diazoacetate the yield of the corresponding β-lactone **47** is slightly diminished. The Zhou group took advantage of the fact that aryldiazoacetates **48** display batochromic shifts relative to their unarylated counterparts. Selective excitation with blue light in the presence of only acceptor diazo compounds **49** furnishes cross-coupling products **50** in good to very good yields and excellent *E* selectivity (Scheme 16a).[27] As this reaction occurs at ambient temperature and does not require any catalyst or additive it may find broad application in the synthesis of complex molecules. Scope and limitation studies revealed that the presence of both double or triple bonds and aromatic rings does not affect the reaction course. A plausible mechanism for this involves the photogeneration of electrophilic carbene **B** and its subsequent reaction with diazocarbonyl compound **C** resulting in zwitterionic intermediate **D**, followed by elimination of dinitrogen molecule to yield the desired product **E** (Scheme 16b).

Recently, visible light induced cyclopropenation of alkynes with donor–acceptor diazo compounds has been described (Scheme 17).[28] Cyclopropenes form in good to excellent yields, even TMS-protected alkynes are well tolerated through high excess of the latter (10 equiv.) is required. In a flow set-up, 36-fold increase in productivity over batch conditions was observed.

2.3 C–X bond formation

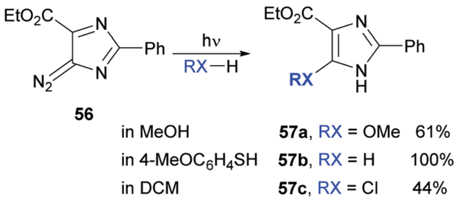
Transition metal-catalysed carbenoid insertion into X–H bonds (X = N, O, S, Si, B) constitute a powerful approach for the construction of C–X bonds. Although a multitude of conditions have been developed for this transformation, the use of milder photochemical conditions may be advantageous.

2.3.1 Reactions under UV light irradiation. The Wang group studied both photochemical and copper catalysed decomposition of α-diazo ketones **54** in the presence of Bu_3SnH providing an efficient route to their corresponding ketones **55** (Scheme 18).[29] It is assumed that initially a Sn–H insertion of the carbene occurs, then the resulting intermediate decomposes to an α-carbonyl radical. After abstraction of hydrogen the desired ketone is formed. This process allows for the synthesis of methyl or ethyl ketones from a carboxylic acid in three steps. Conventionally the same transformation is achieved by converting acids to acyl chlorides and subsequent reaction with organocuprates.[30]



Scheme 18 Photochemical reduction of α-diazoketones.

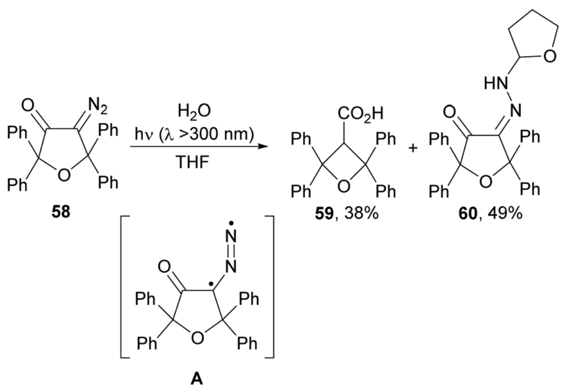
Under light irradiation diazoimidazolecarboxylate **56** undergo X–H insertion with alcohols and amines, but in the presence of good H-donors reduction may predominate. For example photodecomposition of diazoimidazole **56** in methanol affords 5-methoxyimidazole **57a** in 61% yield while in the presence of 4-methoxybenzenethiol hydrogen abstraction occurs (Scheme 19).[31] Interestingly, in DCM the chloro-derivative **57c** forms as a result of the initial attack of the carbene on the chlorine of the solvent.



Scheme 19 Photodecomposition of **56** in MeOH, thiol and DCM.

Zhang *et al.* studied the UV photolysis of substituted diazodihydronaphthalenones in cyclic ethers. For nitro-derivative a 1 : 1 copolymer forms predominantly as a result of C–O insertion, however, for 2-methyl substituted derivative a 1 : 1 copolymer forms predominantly as a result of C–O insertion, for 2-methyl substituted diazonapthalenone a complex mixture of C–H and C–O insertion products formed.[32]

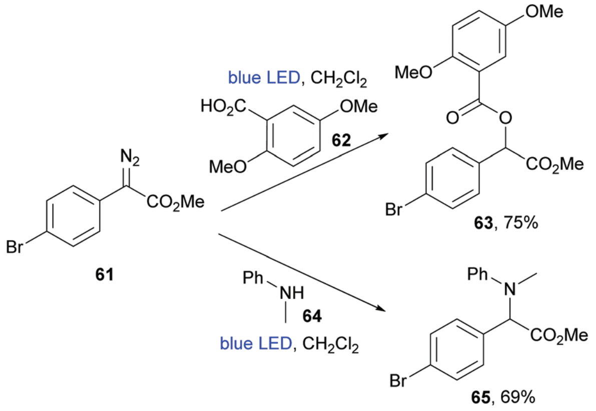
Short wavelength (254 nm) photolysis of diazofuranones in the presence of nucleophiles usually leads to the corresponding carboxylic acid derivatives *via* the Wolff rearrangement and subsequent reaction with water. Interestingly, irradiation of tetraphenyl diazofuranone **58** in the presence of water with less energetic light (λ > 300 nm) yields a mixture of carboxylic acid **59** and hydrazone **60** (Scheme 20).[33]



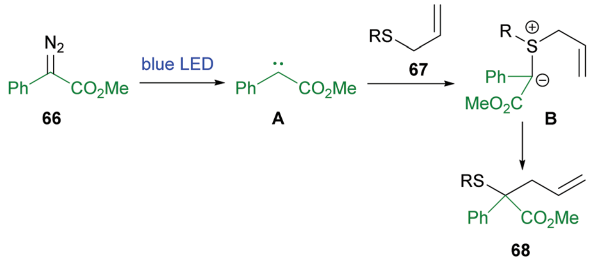
Scheme 20 Hydrazone formation by UVB irradiation of diazofuranone **58** in THF.

It is assumed that initially diradical **A** forms upon irradiation of furanone **58**, which then abstracts a hydrogen atom from THF, followed by coupling of the resulting radicals gives the product. The ratio of products also depends on the nucleophile used and is 1 : 1 for H_2O and 2.5 : 1 for Et_2NH. For tetramethyl substituted diazo furanone carboxylic acid of type **59** forms as a sole product, presumably due to the lower stability of assumed diradical.

2.3.2 Visible light induced C–X bond formation. The shift in absorption observed for aryldiazoacetates is inherently related to a smaller energy difference between a parent diazo compound and its corresponding carbene, which might suggest increased stability. Under blue light irradiation α-(4-bromophenyl)diazoacetate (**61**) undergo X–H insertion reactions with carboxylic acids and amines giving α-acyloxy ester **63** and α-amino esters **65** in good to excellent yields (Scheme 21).[6] For stronger carboxylic acids the reaction does not require light hence it presumably involves protonation of the diazo compound followed by S_N2 displacement of N_2. A variety of substituents are tolerated in both O–H and N–H insertions including electron-rich and -poor aromatic rings as well as double and triple bonds.



Scheme 21 O–H and N–H insertion of EWG-EDG substituted carbenes.



Scheme 22 Visible light induced Doyle-Krimse reaction.

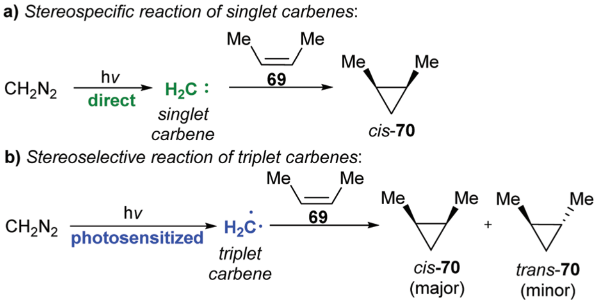
In 2018 the Koenigs group reported visible light induced, catalyst-free approach to the Doyle-Krimse reaction.[28] Under blue light irradiation methyl α-phenyldiazoactate (**66**) decomposes to carbene **A**, which in presence of allylic sulfides **67** forms ylide **B**, subsequent [2,3]-sigmatropic rearrangement yields homoallylic sulfides **68** in high yields (Scheme 22).

3. Photocatalysed reactions of diazo compounds

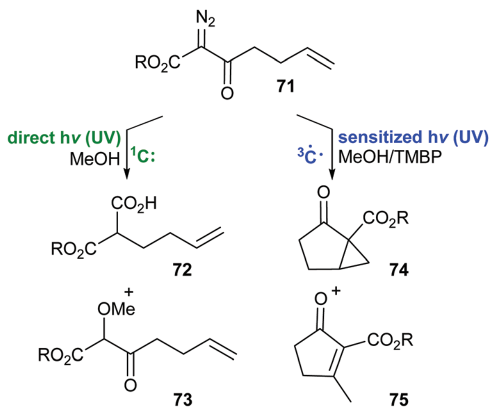
In recent years, photocatalysis has come to the forefront in organic chemistry as a powerful strategy for the activation of small molecules. It is no wonder that it has also been applied for the decomposition and conversion of such important feedstocks as diazo compounds. With the development of new photocatalytic systems for their decomposition under light irradiation, these highly reactive compounds can be used in a controlled way to generate new C–C and C–X bonds. In such transformations diazo reagents can act as free carbenes, radical precursors or radical acceptors, and nucleophiles.

3.1 C–C bond forming reactions

3.1.1 Diazo reagents as carbene precursors. The most important reactions of diazo compounds are those proceeding with the loss of nitrogen, which can be brought about thermally, catalytically, or photochemically. The nitrogen extrusion acts as an entropically driven process which is useful for many applications in organic synthesis.[3g] Over past decades, many photodecomposition reactions of diazo compounds to generate carbenes with or without use of a photosensitizer have been developed.[4] It is commonly accepted that direct UV-irradiation (with no photocatalyst added) of diazo compounds gives singlet carbenes, whereas photosensitization generates carbenes in the triplet state.[34] However, it is important to note that these can interconvert depending on the reaction conditions. The existence of two spin states explains the differences in reactivity of singlet and triplet carbenes. For example, their reactions with olefins afford *cis*- (singlet carbene) or a mixture of *cis*- and *trans*-cyclopropanes (triplet carbene) respectively (Scheme 23).[35]



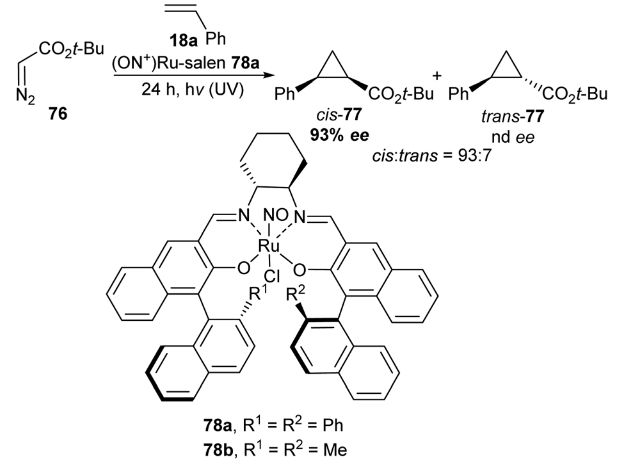
Scheme 23 Reactivity of diazo compounds towards olefins under UV-light.



Scheme 24 Reactivity of alkyl 2-diazo-3-oxoalkenoates under UV-light in the presence/absence of photosensitizer.

Reactions of simple olefins with singlet and triplet carbenes are well developed, but reactions of functionalized unsaturated diazo carbonyl compounds under direct and photosensitized irradiation are more complex (Scheme 24).[36] Under direct UV irradiation compound **71** gives singlet carbenes, which undergo both the expected Wolf rearrangement (**72**) or C–H insertion (**73**) in the presence of a nucleophile (MeOH). On the other hand, in the presence of 2,2′,4,4′-tetramethoxybenzophenone (TMBP), as an efficient triplet photosensitizer, triplet carbene is generated furnishing cyclopropane **74** (major product 86% yield) and unsaturated ketone **75** (minor product). It was assumed that both products **74** and **75** are formed in the triplet- sensitized process as compound **74** cannot be converted into ketone **75**. However, when the concentration of the photosensitizer was decreased, ketone **75** was still present in the reaction mixture, therefore it has to form both upon direct excitation of its precursor **71** and in the triplet-sensitized process.

The enantioselective cyclopropanation of alkenes with diazo compounds is one of the most extensively studied transformations in organic chemistry.[15] This reaction occurs predominantly *via* metal-carbenoids formed from diazo compounds and a chiral metal complex (carbene transfer reactions) leading to optically active cyclopropanes. There are however, also some examples of cyclopropanation performed under light irradiation. Katsuki showed that the chiral (ON^+)Ru-salen complex **78** is effective at catalyzing asymmetric cyclopropana-

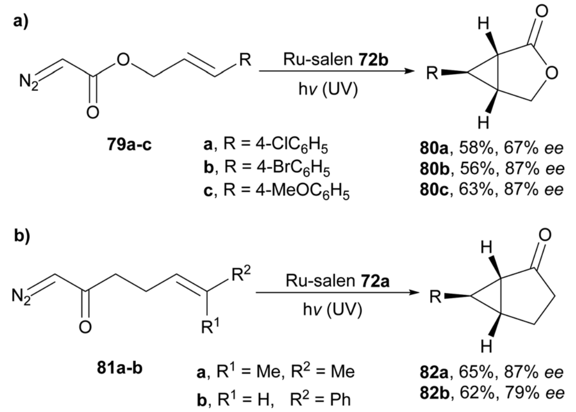


Scheme 25 Cyclopropanation catalyzed by (ON+)Ru-salen complex.

Table 1 Scope of the cyclopropanation catalyzed by (ON+)Ru-salen complex

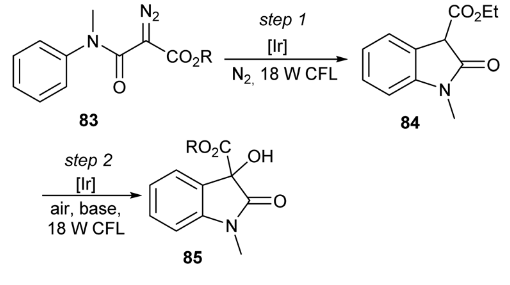
Entry	Olefin	Yield/%	*cis* : *trans*	ee$_{cis}$/%	ee$_{trans}$/%
1	Styrene	33	97 : 3	97	nd
2	4-Chlorostyrene	53	84 : 16	88	50
3	4-Methoxystyrene	51	94 : 6	93	24
4	α-Methylstyrene	61	73 : 28	90	nd

tion of styrenes with diazoesters under light irradiation (Scheme 25, Table 1).[37] Typically, such catalysts have a vacant coordination site on the ruthenium ion available for binding of a diazo compound. In the case of (ON$^+$)Ru-salen **78a** the site is blocked, therefore photo-irradiation was considered to promote the dissociation of one of its apical ligands and it is used only for an activation of the catalyst. The use of blue light (440 nm) efficiently accelerates the desired dissociation of the apical ligand without promoting the undesired photodecomposition of diazoacetate (33% yield, up to 97% ee for *cis* isomer) (Table 1, entry 1). In the dark this reaction is slow and less enantioselective (6% yield, up to 71% ee for *cis* isomer), however, irradiation with more energetic UV light (390 nm) suffers from slightly lower enantioselectivities probably due to photocatalyzed decomposition of diazoacetate (11% yield, up to 91% ee for *cis* isomer). On the other hand, irradiation with the green light (500 nm) promotes neither decomposition of diazoacetate nor the formation of the desired product (3% yield, up to 79% ee for the *cis* isomer). These results suggest that the electron-transfer from the ruthenium ion to the ligand and subsequent ligand dissociation is responsible for this photoacceleration. The scope of the reaction is quite limited, and only investigated the bulky *tert*-butyl diazoacetate (**76**) with a few different styrenes. Although the yields are moderate, very good diastereo- and enantioselectivities are observed (ee up to 92% for *cis* diastereoisomer). Subsequently, using slightly modified (ON$^+$)Ru-Salen complexes this methodology was further expanded to intramolecular cyclopropanation of alkenyl diazo esters **79a–c** (Scheme 26a)[38] and alkenyl diazo ketones **81a–b** (Scheme 24b).[39] Reactions of diazoesters **79a–c** and diazoketones **81a–b** proceed with good yields and enantioselectivities (alkenyl diazoketones: yields up to 82%, ee up to 94%; alkenyl diazoesters: yields up to 63%, ee up to 87%). The stereoselectivity of the intramolecular cyclopropanation strongly depends on the structure of the chiral (NO$^+$)Ru-Salen complex.



Scheme 26 Photocatalytic cyclopropanation of alkenyl diazo esters (**79a–c**) and diazo ketones (**81a–b**).

Aromatic substitution of diazocarbonyl compounds is a powerful synthetic tool for the formation of C–C bonds between two sp^2-hybridized carbons under relatively mild conditions. Traditionally, these reactions are carried out in the presence of a transition-metal catalyst (*e.g.* Rh, Cu) and they are assumed to involve the formation of a zwitterionic intermediate resulting from the electrophilic addition of a metal carbene to the aromatic ring and subsequent rapid proton transfer.[3g] Photocatalytic intramolecular aromatic substitution of disubstituted (EWG-EWG) diazo compounds was reported by Xiao *et al.* in a photo-tandem cyclization reaction consisting of two catalytic cycles involving iridium catalyzed photocatalytic energy transfer with the carbene formation (ET – step 1) and single electron transfer (SET – step 2) (Scheme 27).[40] This iridium-catalysed transformation of diazo amides **83** allows for the synthesis of alkyl 3-hydroxy-2-oxoindoline-3-carboxylate derivatives **85** in a two-step, one pot protocol. Various electron-poor (*e.g.* F, Br, CN, CO_2Et, CF_3) and electron-donating (*e.g.* OMe, Me) groups on the aromatic ring of



Scheme 27 Tadem cyclization of diazoamides.

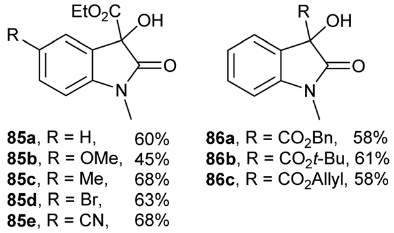
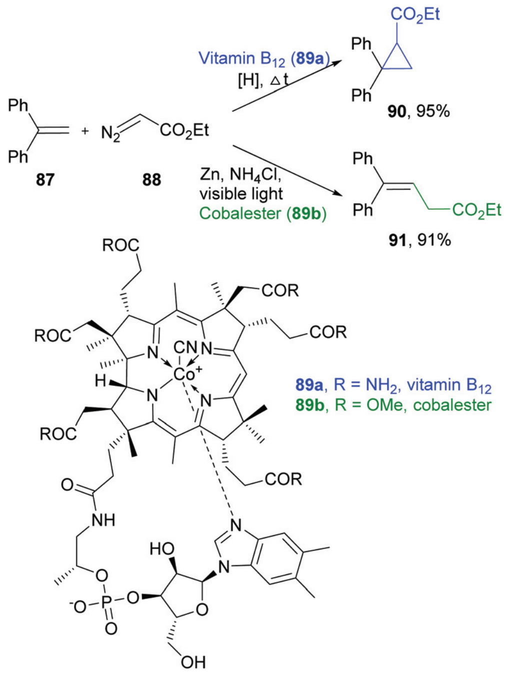


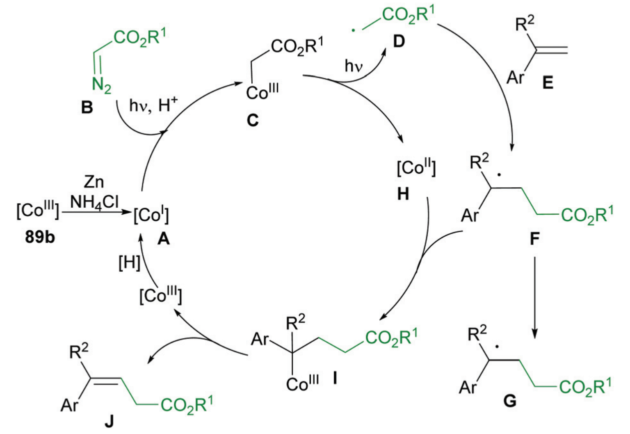
Fig. 3 Tadem cyclization of diazoamides – scope of the reaction.

N-phenyl diazo amides **83** are well tolerated in this reaction (yields of 48–86%), as well as different ester groups (58–61%) (Fig. 3).

3.1.2 Diazo reagents as radical precursors. Under light irradiatoion diazo compounds can serve as a source of radicals. For photocatalyzed reactions of diazo compounds the choice of a catalyst has a large impact on the course of the process. In 2004 Chen and Zhang reported that the reaction of styrenes with ethyl diazoacetate **88** catalyzed by vitamin B_{12} [(Co^{III}), **89a**] furnishes cyclopropanes (Scheme 28).[41] When native vitamin B_{12} (**89a**) is changed to cobalester (**89b**) – a vitamin B_{12} derivative C–H insertion product **91** forms instead of the expected cyclopropane (Scheme 28).[42] In this case, the proposed reaction pathway proceeds *via* a carbene transfer mechanism involving a Co(I) species, contrary to a previous report postulating (Co^{II}) intermediate (Scheme 29). Here, the cobalt ion within the macrocyclic ring (Co^{III}) is reduced to a nucleophilic Co^{I} form **A** and as such reacts with ethyl diazoacetate **B** (radical precursor) so that after protonation gives intermediate **C**. Upon light irradiation, homolytic bond cleavage generates radical **D** which subsequently reacts with an electron-rich olefin **E** to form radical **F**. The newly formed radical **F** recombines with a Co^{II} species, which after dehydrocobaltation gives desired product **J**. Experimental data corroborates that the reaction proceed *via* a radical pathway and the applied catalyst acts as a reversible carrier for an alkyl group for C–H insertion.

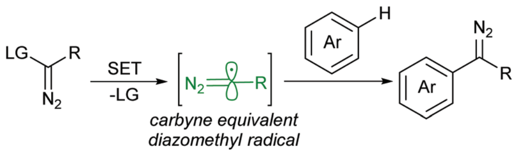


Scheme 28 C–H functionalization of olefins with diazo esters.



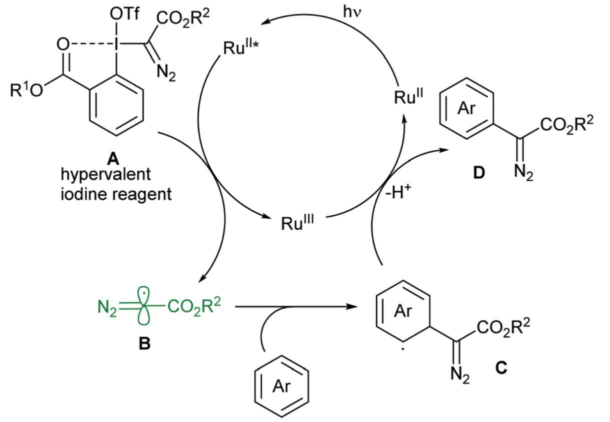
Scheme 29 C–H functionalization of olefins with diazo esters – a proposed mechanism.

Typically, light irradiation or combined irradiation and action of a catalyst on diazo compounds induces controlled decomposition with the loss of dinitrogen. However, an excellent example with the retention of the diazo functionality was presented by Suero.[43] In this case, light irradiation of diazo compounds containing a hypervalent iodine leaving group in the presence of an arene substrate furnish C–H arylated products (Scheme 30).



Scheme 30 Designed carbene source.

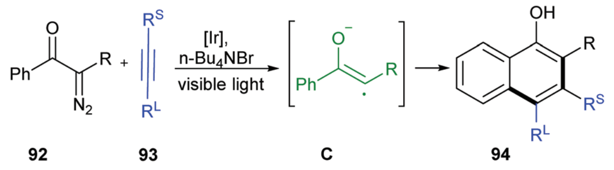
This reaction is catalysed by a ruthenium-tris(2,2′-bipyridyl) complex which in its excited state undergoes single-electron reduction with the hypervalent iodine reagent **A** to produce radical **B** (carbyne equivalent) (Scheme 31). This reactive intermediate reacts with aromatic compounds generating cyclohexadienyl radical **C**, that after reduction affords the diazomethylated product. Scope and limitation studies showed that this process could be successfully applied to a wide range of aromatic hydrocarbons decorated with a variety of useful functional groups (38–96%) and diazo esters (24–96%). In general, the C–H diazomethylation reaction proceeds with high *ortho*-selectivity for arenes substituted with alkyl groups, halogens, amides and carbonyls. Importantly, this methodology is also suitable



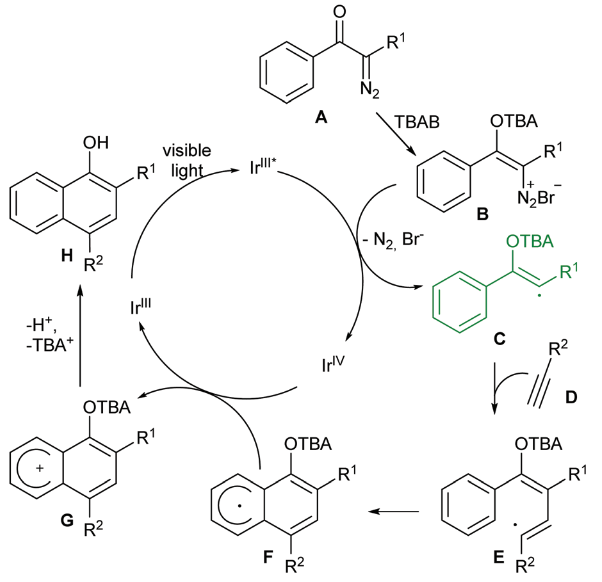
Scheme 31 C–H bond diazomethylation reaction – a mechanistic proposal.

for late-stage diazo-functionalizations of medicinally relevant agents (*e.g.* diazomethylation of estrone, paroxetine, paclitaxel, celecoxib, duloxetine, ibuprofen, indomethacin and caffeine) and diazo diversification reactions (*e.g.* N–H insertion, O–H insertion, C–H insertion, trifluoromethylation). This approach to the synthesis of highly functionalized diazo compounds complements strategies involving palladium-catalyzed cross-couplings or diazo transfer reactions.

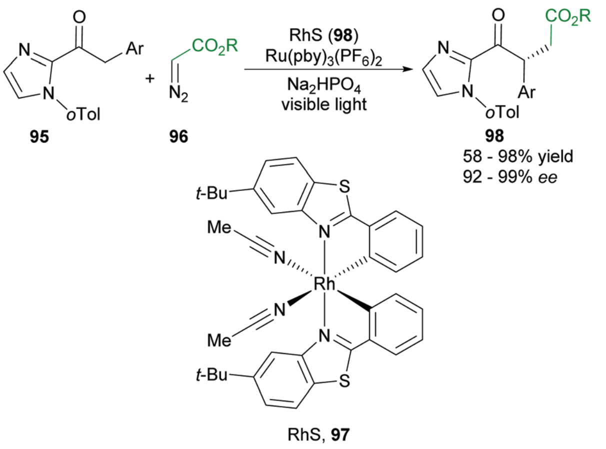
In contrast to the non-photochemical benzannulation of diazoketones **92** and alkynes **93** leading to naphthols **94** *via* carbene intermediates, the photoinduced reaction is radical in nature (Scheme 32).[44] Diazo ketone (**A**) in the presence of TBAB forms diazonium salt **B**, which after reduction with an iridium complex in its excited state to enolated vinyl radical **C**, reacts with phenylacetylene (**D**) (Scheme 33). Subsequently, vinyl radical **E** after homolytic aromatic substitution followed-up by oxidation and protonation gives final product **H**. The mechanistic proposal is well supported by experiments with the addition of radical scavengers and cyclic voltamperometry studies. In this photocatalytic benzoannulation, ketones with various substituents on the aromatic ring (*e.g.* –F, –Cl, –Br, –Me, –OMe) are well tolerated (35–52%) and the reaction is not significantly affected by substituents on the aromatic ring of phenylacetylene (61–73%).



Scheme 32 Photochemical radical benzannulation of diazoketones with alkynes.

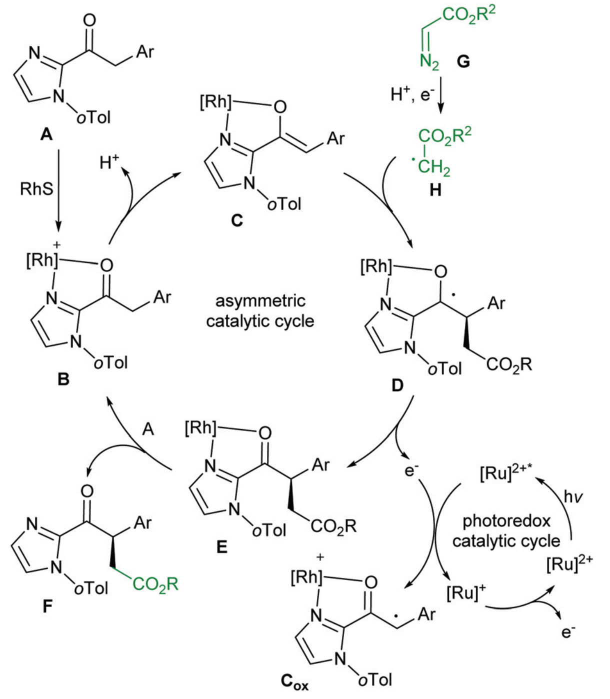


Scheme 33 Photochemical radical benzannulation of diazoketones with alkynes – proposed mechanism.



Scheme 34 Enantioselective alkylation with of diazo esters.

Meggers *et al.* reported that diazoesters can act as radical precursors also in alkylation of ketones.[45] Here, the specifically designed carbonyl compounds 2-acyl imidazoles **95** were shown to react with diazoesters (as the radical precursors) in the presence of a Rh-Lewis acid **96** and ruthenium complex that absorbs light and at the same time is able to activate the carbonyl group (Scheme 34). Though stereoselective and highly yielding, this reaction is limited to certain, specifically designed carbonyl compounds and requires the addition of Rh-cocatalysts. The proposed mechanism for the enantioselective alkylation with diazoesters involves dual activation modes: photoredox and asymmetric catalytic cycles (Scheme 35). Firstly, ketone **A** coordinates to rhodium complex (RhS, **99**) to form intermediate **B.** Subsequent base-induced deprotonation provides electron-rich rhodium enolate **C**, which initially serves as a single electron donor for a photoexcited ruthenium complex. Generated *in situ* [Ru(bpy)$_3^{I}$] transfers an electron to diazo ester **G** affording radical **H** after extrusion of nitrogen and protonation. The following stereoselective addition of electron-poor radical **H** to rhodium enolate **C** leads to Rh-coordinated radical **D.** This reactive intermediate is a strong reducing agent and can either directly reduce the diazo

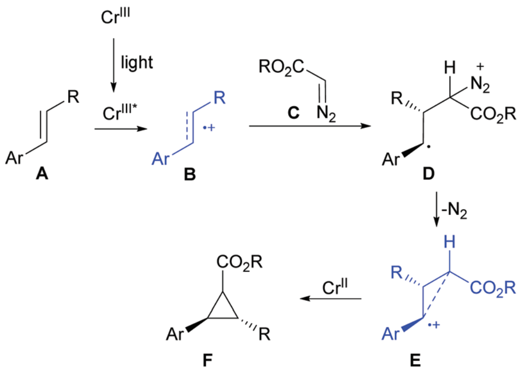


Scheme 35 Enantioselective alkylation with diazo esters – proposed mechanism.

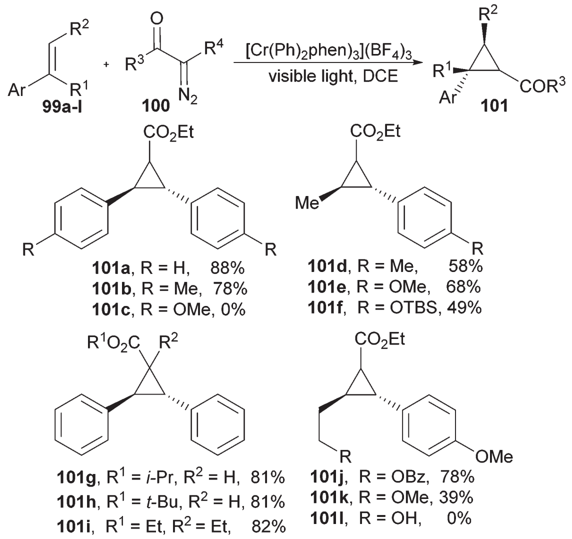
reagent or quench the photoexcited ruthenium complex to produce the reduced photoredox sensitizer [Ru(bpy)$_3^I$]. Product **F** is released after oxidation of radical **D** and recoordination of RhS **97** In agreement with previous reports, cyclopropane formation was also ruled out. The enantioselective alkylation of a variety of 2-acyl imidazoles worked well, providing respective 1,4-dicarbonyl compounds in good to very good yields (up to 99%) and excellent enantioselectivities (up to 98%).

3.1.3 Diazo reagents as nucleophiles. New mechanistic insights into light-induced cyclopropanation of olefins with diazocarbonyl compounds in the presence of a chromium catalyst were reported by Ferreira (Scheme 36).[46] This reaction was proven not to operate *via* a typical metal–carbenoid intermediate, instead a radical cycloaddition of electron-rich alkenes to the diazo reagent (nucleophile) occurs. In this case, the chromium catalyst does not react with a diazo compound to form a carbenoid species but rather to photooxidize an electron-rich olefin **A** to radical cation **B.** Subsequent nucleophilic addition and extrusion of nitrogen followed-by reduction affords cyclopropane **F.** Different diazoesters underwent the reaction smoothly in good to very good yields (up to 88%) (Scheme 37). The reaction proceeds well only for those alkenes, which reduction potentials of oxidation are located in the range between +1.11 V to +1.80 V (*vs.* SCE). Stilbene derivative **99l** due to its low reduction potential of oxidation (0.99 V *vs.* SCE) remains unreactive. It is distinctively different that the reaction catalyzed by the photoredox chromium complex is highly chemoselective – only intermolecular addition product **104** formed, while in the case of Cu-catalyst **106**, an intramolecular reaction additionally occurs (Table 2).

In general, reactions with vinyl and enol diazocarbonyl compounds involve metal carbenoid/carbenoid intermediates, which as electrophilic species can by attacked by nucleophilic

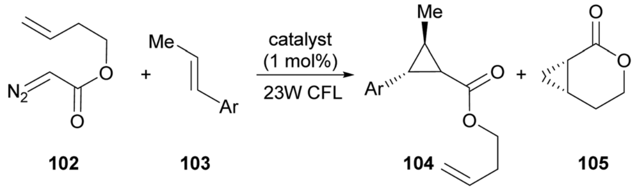


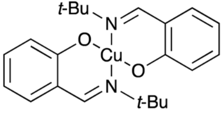
Scheme 36 Proposed mechanism for radical cyclopropanation.



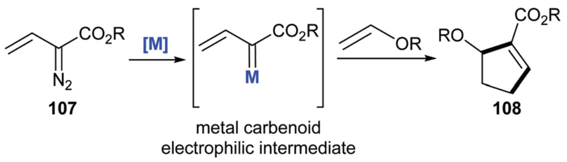
Scheme 37 Radical cation cyclopropanation *via* chromium catalysis.

Table 2 Chemoselectivity of radical cyclopropanation

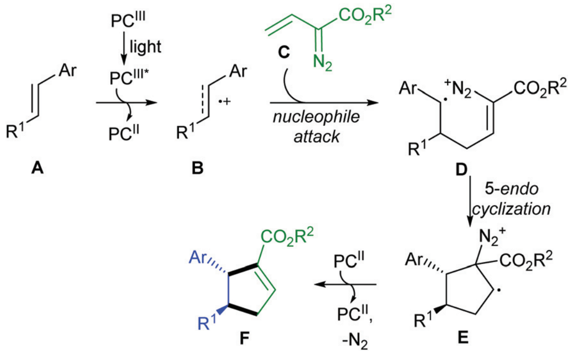


Catalyst, conditions	**82 : 83**
$Cr(Ph_2phen)_3(BF_4)_2$ CFL, 72 h	100 : 0 (53% yield)
 **106**, 105 °C, 6 h	5 9 : 41 (<20% conversion)

double bonds (Scheme 38).[47] But photocatalyzed cyclopentene annulation of alkene and vinyl diazo reagents proceeds *via* a radical cycloaddition reaction (Scheme 39).[48]



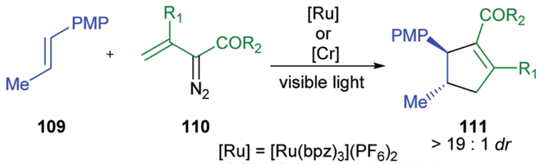
Scheme 38 Cyclopentane formation through metal carbenoid intermediate.



Scheme 39 Proposed mechanism for cyclopentene annulation.

This reaction is catalyzed by both ruthenium and chromium complexes in their excited states which oxidize the alkene to radical cation **B.** At this stage, the vinyl diazo reagent (nucleophile) **C** attacks the electron-poor radical cation **B.** Subsequent reduction and loss of nitrogen affords the observed cyclopentane **F.** Experimental insights confirm a radical cycloaddition instead of a cyclopropanation/rearrangement process. In general, alkenes bearing electron-rich substituents **109**, which facilitate the single-electron oxidation to radical cation more easily, afford desired products **111** in higher yields (Table 3).

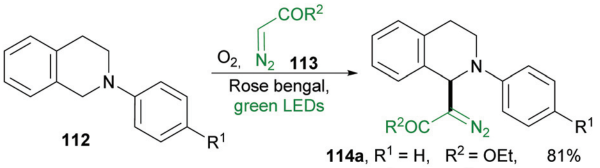
Table 3 Cyclopentane annulation – diazo scope



[Ru] = $[Ru(bpz)_3](PF_6)_2$
[Cr] = $[Cr(Ph_2phen)_3](BF_4)_3$)

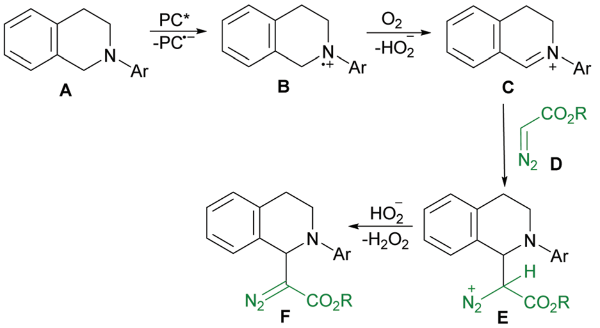
Entry	R^1	R^2	Yield (Cr)/%	Yield (Ru)/%
1	H	O*t*-Bu	94	99
2	H	Ph	<5	61
3	Me	OEt	56	90
4	Ph	OEt	62	92
5	*p*-MeC_6H_5	OEt	34	96
6	*p*-$CF_3C_6H_5$	OEt	<6	68

A typical reaction of diazo compounds with tertiary amines in the presence of a metal catalyst is the direct C–H insertion which proceeds *via* a metal carbenoid intermediate.[49] In the case of an organic dye catalyzed coupling of tertiary amines **112** with α-diazocarbonyl compounds **113**, which act as nucleophile and the reaction occurs without the loss of nitrogen (Scheme 40).[50] Light induced cross-dehydrogenative coupling works well for a variety of tertiary amines and α-diazocarbonyls giving products **114a–e** with good to very good yields. Practical usefulness of the reaction was demonstrated by scaling-up conditions to gram scale – diazo compound **114a** was obtained in 1.2 gram quantities only in slightly diminished yield 71%. The proposed mechanism is depicted in Scheme 41. Initially, Rose Bengal in its excited state photooxidizes *N*-aryl-tetrahydroisochinoline **A** to radical cation **B.** Subsequent hydrogen abstraction by the $O_2^{\bullet -}$ furnishes iminium ion **C** that reacts with nucleophilic diazo reagent **D** to give compound **E.** In the final step, intermediate **E** is deprotonated by hydroperoxide anion leading to α-amino diazo compound **F.** The nitrogen extrusion does not occur under green light irradiation, presumably, because of the fact that tested diazo compounds do not absorb light in that region.



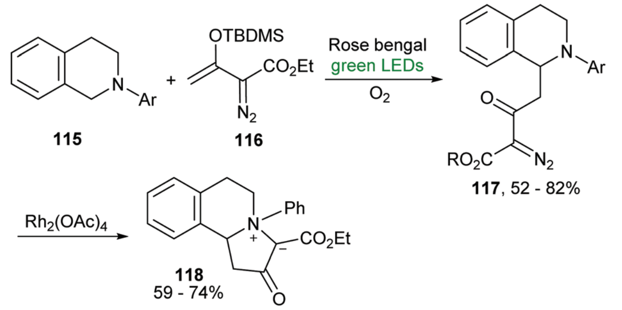
114a, R^1 = H, R^2 = OEt, 81%
114b, R^1 = Me, R^2 = OEt, 87%
114c, R^1 = F, R^2 = OEt, 86%
114d, R^1 = CF_3, R^2 = OEt, 79%
114e, R^1 = H, R^2 = O*i*-Bu, 70%
114e, R^1 = H, R^2 = Ph, 64%

Scheme 40 Photoinduced reaction of tertiary amines and α-diazocarbonyl compounds.



Scheme 41 A proposed mechanism for photoinduced reaction of tertiary amines with α-diazocarbonyl compounds.

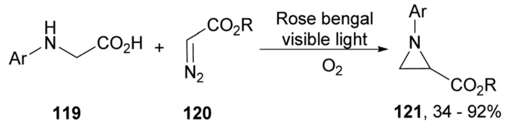
This methodology was further expanded by Rastogi[51] who showed that the visible light induced reaction of tertiary amines **115** with silyl diazoenolates **116** afforded Mannich type products **117** that in the presence of a Rh-complex cyclized to



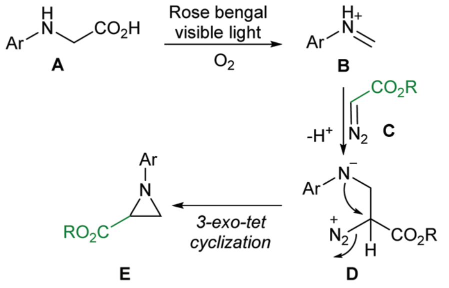
Scheme 42 Photoinduced reaction of tertiary amines with silyl diazoenolates.

stable ammonium ylides **118** in high yields (Scheme 42). *N*-Aryl-tetrahydroisochinolines **115** with different substituents on the aryl ring furnish products in decent yields, but in case of aliphatic tertiary amines, the reaction does not proceed even with high catalyst loading. The plausible reaction mechanism is similar to that proposed by Zhou (see Scheme 41).[50]

Photoinduced process involving nucleophilic addition of diazo compound to the *in situ* generated iminium ion have found an additional application in the synthesis of aziridines **121** *via* the aza-Darzen reaction (Scheme 43).[52] The visible light photoredox-mediated decarboxylation of *N*-aryl glycine **A** affords α-amino radical **B**, which, after oxidation generates an active iminium cation (Scheme 44). Subsequently the nucleophilic addition of diazo reagent **C** followed by 3-*exo*-tet cyclization leads to aziridine **E**.

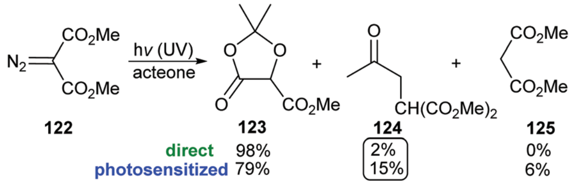


Scheme 43 Visible-light mediated induced decarboxylative cyclization of *N*-aryl glicynes and diazo compounds.



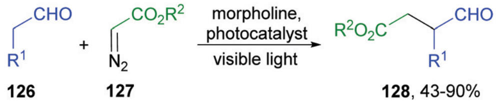
Scheme 44 Photoinduced aza-Darzens reaction pathway.

3.1.4 Diazo reagents as radical acceptors. Over the past decades, the reaction of diazo compounds with olefins under light irradiation has been extensively studied.[4] Jones described direct and photosensitized reactions of dimethyl diazomalonate (**122**) with carbonyl compounds (Scheme 45).[34] According to the proposed mechanism, upon direct irradiation a carbene in the singlet state is formed and as such furnishes predominantly product **123** deriving from an ylide intermediate. In the presence of a photosensitizer, however, a carbene in the triplet state is formed, and the following C–H insertion gives also alkylated malonate **124** in 15% yield.



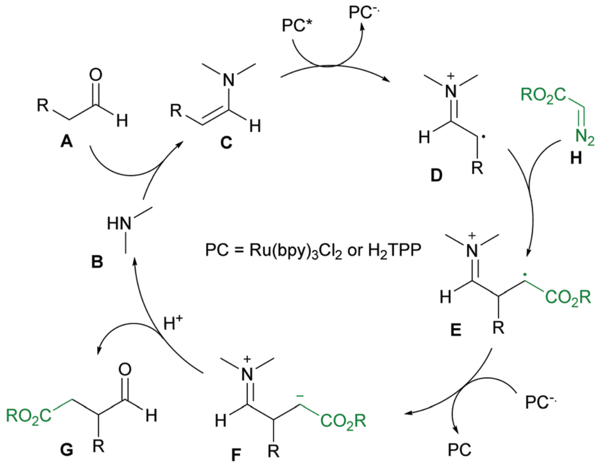
Scheme 45 Direct and sensitized irradiation of dimethyl diazoacetate in acetone.

In 2016 our group showed that diazoesters act as alkylating agents in α-functionalization of aldehydes (Scheme 46). Dual modes of activation – enamine converged with photoredox catalysis ($Ru(bpy)_3Cl_2$ or tetraphenyl porphyrin (H_2TPP) change the reaction pathway from the usual condensation of aldehydes **126** with diazoesters **127** to the C–H functionalization at the α-position.[53]



Scheme 46 Photocatalytic reaction of diazo compounds with aldehydes.

The reported reaction proceeds mainly *via* a radical pathway and requires a dual catalytic system – photocatalysis merged with enamine-iminium catalysis. Experimental analyses provided sufficient data to corroborate the proposed radical mechanism and ruled out the formation of cyclopropane and the subsequent ring-opening (Scheme 47).



Scheme 47 A proposed mechanism for photocatalytic reaction of diazo compounds with aldehydes.

Interestingly, all the experimental evidences suggest a mechanism of this reaction which differing from the one reported by Meggers (see Scheme 35).[45] A photocatalyst (Ru^{III}* or H_2TPP*) in its excited state oxidizes enamine **C** (formed from aldehyde **A** and amine **B**) to radical cation **D** which than reacts with diazo ester **H** with simultaneous extrusion of nitrogen, furnishing new radical **E**. After electron transfer from a photocatalyst (Ru^{II} or $H_2TPP^{\bullet-}$) and protonation, the final product **G** is formed. Subsequently, this methodology was further expanded for α-functionalization of ketones.[54]

The C–H alkylation catalyzed by ruthenium complex or tetraphenylporphyrin is applicable to various aldehydes giving the desired product in decent yields (44–90%). It is noteworthy that unsaturated aldehydes furnish only C–H alkylated compounds **96** with no cyclopropane product being formed (Fig. 4). Furthermore, even sterically hindered diazo esters react equally well (67–80%).

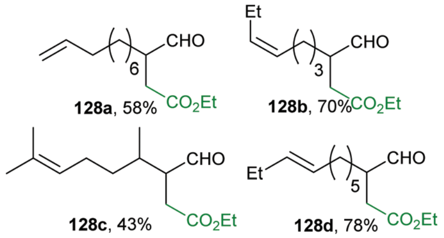
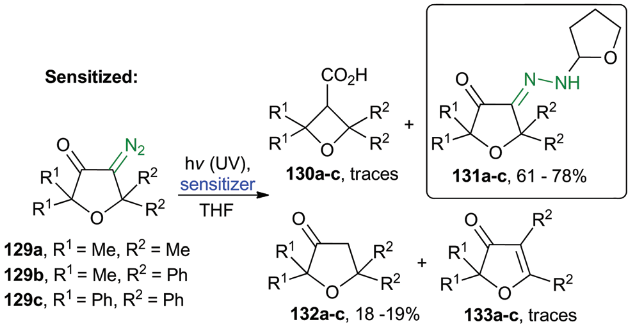


Fig. 4 Photocatalytic reaction of diazo compounds with unsaturated aldehydes.

3.2 C–X bond forming reaction

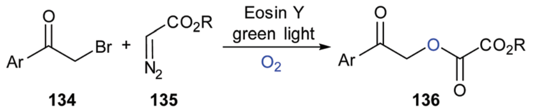
Insertions of diazo compounds into X–H bonds are important synthetic tool by which new C–X bonds can be formed under relatively mild conditions. These reactions have been carried out traditionally in the presence of a transition-metal catalyst and they proceed *via* a carbene intermediate.[4g]

3.2.1 Diazo reagents as carbene precursors. The photosensitized transformation of 4-diazotetrahydrofuran-3(2*H*)-ones **129** in the presence of H-donors such as tetrahydrofuran predominantly leads to *N*-substituted hydrazones **131** (Scheme 48).[55] This unusual photochemical reaction occurs without extrusion of nitrogen under UV irradiation. The comparison of direct and sensitized photoreaction of 4-diazotetrahydrofuran-3(2*H*)-ones **129** in the presence of H-donors revealed that their direct irradiation leads mainly to the Wolff rearrangement and 1,2-alk(aryl)-shifts, while in the presence of a photosensitizer and H-donors (such as THF), diazoketones in 3T excited states are generated and as such afford *N*-substituted hydrazones **131** – insertion products of the diazo terminal N atom into C–H bonds of ethers (yields up 78%).

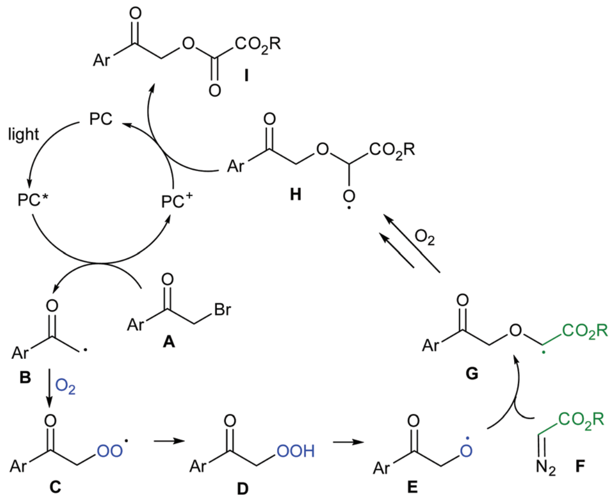


Scheme 48 Photosensitized transformation of 4-diazotetrahydrofuran-3(2*H*)-ones.

3.2.2 Diazo reagents as radical acceptors. Very recently, the possibility of using a photoredox catalysis approach to C–X bond formation in the reactions of diazo compounds has been realized. Wan and coworkers showed that α-bromo-ketones **134** can serve as radical precursors, which after reaction with dioxygen and diazoester **135** gives oxalate ester **136** (Scheme 49).[56] The authors proposed a plausible mechanism for the reaction in which the photocatalyst eosin Y in its excited state reduces α- bromo-ketone **A** to alkyl radical **B**, which upon reaction with molecular oxygen, gives superooxide radical **C** (Scheme 50). After abstraction of a hydrogen atom and homolysis of intermediate **D**, radical **E** is formed. This reactive intermediate reacts with diazo acetate **F** with simultaneous extrusion of nitrogen to form radical species **G**. After subsequent reaction with molecular oxygen, abstraction of hydrogen, homolysis, and photooxidation final product **I** is formed. Stern–Volmer experiments show that only α-bromoacetophenone quenches luminescence of the photocatalyst, which is consistent with proposed mechanism.



Scheme 49 Synthesis of oxalater esters with application of diazo esters.



Scheme 50 Synthesis of oxalate esters – mechanistic proposal.

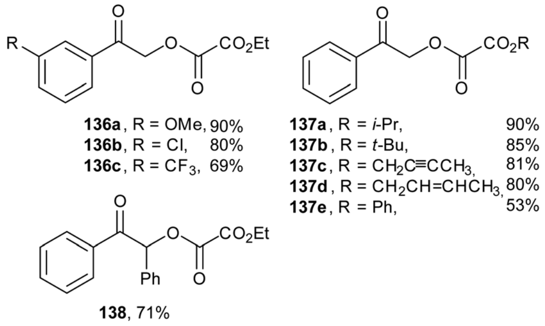


Fig. 5 Synthesis of oxalater esters – scope.

A series of oxalate esters **136–138** containing a variety of functional groups were synthesized using this methodology (Fig. 5). In general, the corresponding products were obtained in good to very good yields (53–88%).

4. Conclusions

Under light irradiation the reactivity of diazo compounds is strongly dominated by the Wolff rearrangement, and the generated ketenes serve as a starting material not only for the preparation of carboxylic acid derivatives but also have been recently used for the synthesis of acyloxy-acrylamides and highly substituted phenols. However, developments in the photochemistry of diazo compounds which allow such reactions as C–H insertion to alkanes or alkenes, and α-alkylation of carbonyl compounds have gained increased significance. Moreover, bathochromic shifts in the absorption of aryl diazoacetates allow for their visible light induced transformations to take place in the absence of a photocatalyst, including C–H, O–H, and N–H insertions as well as their selective cross coupling with diazocarbonyl compounds. Of great importance is also the catalyzed and non-catalyzed photoinduced cyclopropanations of double bonds that can be performed in an enantioselective manner.

Developments described in this review clearly suggest that the photochemistry of diazo compounds still remains an underdeveloped research field, particularly with respect to photocatalyzed reactions under mild reaction conditions. Reactions requiring no transition metal catalysts hold promise for broader application in industry.

Conflicts of interest

There are no conflicts to declare.

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