APPENDIX ONE

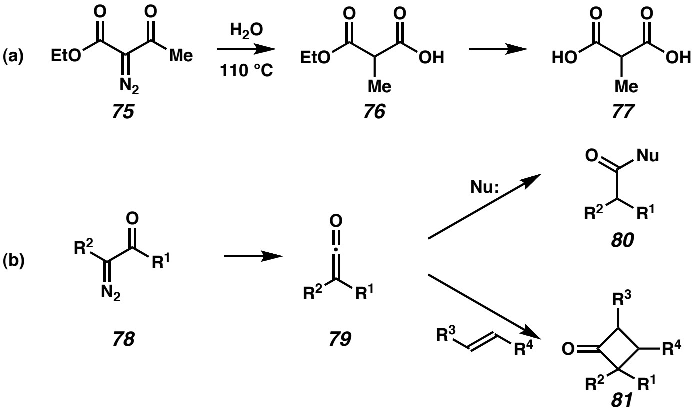
The Wolff Rearrangement

A1.1 The History of the Wolff Rearrangement

In 1902, Ludwig Wolff reported that heating diazoketone **75** with water generated carboxylic acid **77** (Scheme A1.1.1a).[1] At the time, Wolff did not predict the mechanism of this transformation.

We now know that the Wolff rearrangement[2] proceeds from α-diazoketones (e.g., **78**) through a ketene intermediate (e.g., **79**, Scheme A1.1.1b). On loss of nitrogen, a 1,2-shift of ketone substitutent R^1 generates intermediate ketene **79**. Ketene **79** is poised for nucleophilic addition to generate carboxylic acid derivatives, or for a cyclization reaction with an unsaturated system, such as [2+2] addition.

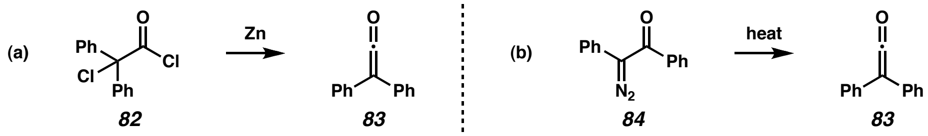
Scheme A1.1.1 The Wolff rearrangement: (a) first, and (b) general reaction



The formation of an intermediate ketene during the Wolff rearrangement only became apparent after Staudinger[3] observed ketenes **83** and Schröter demonstrated that ketene **83** could be formed from a heating of a diazoketone (e.g., **84**, Scheme A1.1.2).[4]

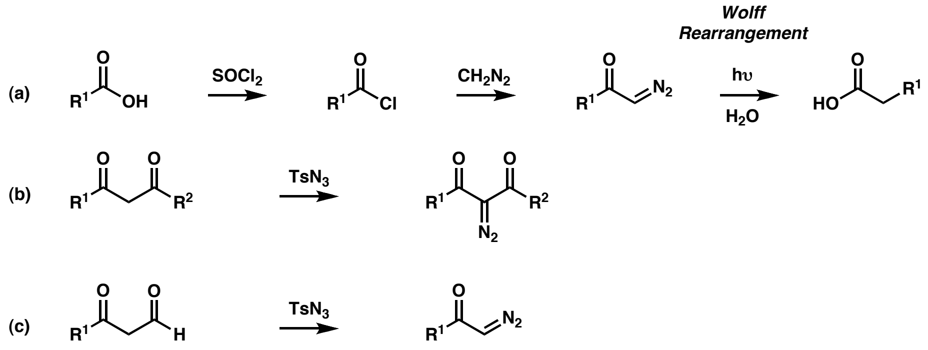
Staudinger reported his initial observation of ketenes,[3] when he determined that dehalogenation of chloride **82** with zinc to formed diphenylketene (**83**). After the discovery of ketenes, Schröter[4] obtained diphenylketene (**83**) by heating diazoketone **84**.

Scheme A1.1.2 Early contributions by (a) Staudinger and (b) Schröter



Without straightforward methods to access α-diazoketones, the Wolff rearrangement was impractical. The rearrangement experienced a renaissance when Arndt and Eistert[5, 2c] disclosed the conversion of carboxylic acids to α-diazoketones (Scheme A1.1.3a). The Arndt-Eistert homologation did not provide access to cyclic α-diazoketones. Fortunately, this limitation was addressed in 1967, when Regitz[6] developed practical diazo transfer techniques (Scheme A1.1.3b, c).

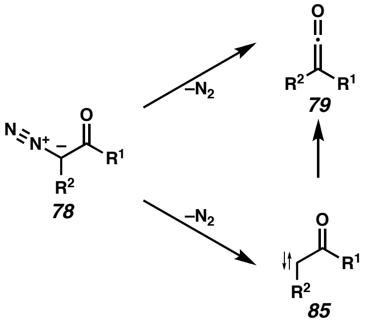
Scheme A1.1.3 (a) The Arndt–Eistert homologation and (b, c) diazo transfer strategies



A1.2 Basic Mechanistic Descriptions of the Wolff Rearrangement

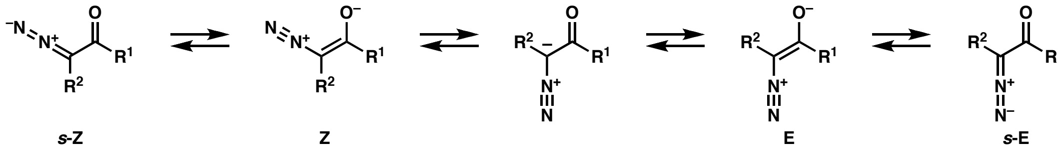
In both photochemical and thermal Wolff rearrangements, there are two operative mechanisms en route to ketene formation: a concerted pathway (e.g., **78** → **79**), and a stepwise pathway (e.g., **78** → **85** → **79**, Scheme A1.2.1). In the concerted pathway, nitrogen extrusion proceeds in concert with a 1,2-shift. In the two-electron stepwise mechanism, nitrogen loss furnishes a singlet carbene intermediate that can undergo group migration.

Scheme A1.2.1 Basic concerted and stepwise Wolff rearrangement mechanisms



The geometry of the α-diazoketone is relevant to assigning the operative mechanism of the Wolff reaction (Figure A1.2.1). The concerted Wolff rearrangement requires an α-diazoketone to have access to an *s*-Z conformation for proper orbital overlap. α-Diazoketones are often planar about the O=C–C=N_2 group. The *s*-Z isomer is stabilized by a Coulombic attraction between the partial charges on the oxygen (negative electron density) and the nitrogen (positively charged). The *s*-Z isomer is destabilized by steric repulsion between R^1 and R^2. Therefore, the *s*-Z conformer is favored when either substituent is small (R^1 or R^2 = H). The *s*-E geometry predominates in most other α-diazoketones. An *s*-Z conformation is a necessary, but not sufficient condition for a concerted Wolff rearrangement.

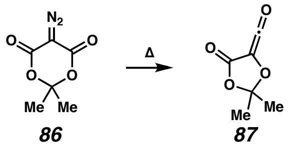
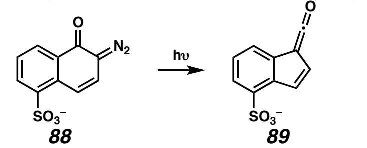
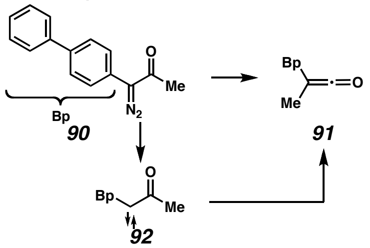
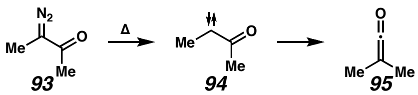
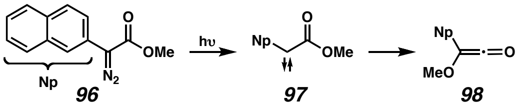
Figure A1.2.1 Geometry of starting α-diazoketones



Additionally, the operative mechanism depends on the reaction conditions. The Wolff rearrangement can be promoted thermally (Section A1.4), photochemically (Section A1.5), or by transition-metal catalysis (Section A1.7).

Table A1.2.1 depicts the general mechanistic trends of the Wolff reaction for representative substrates under either thermal and photochemical conditions. Upon thermal exposure, cyclic substrates predominantly undergo a concerted mechanism, whereas acyclic substrates primarily proceed through a stepwise pathway. Upon photolysis, cyclic substrates predominantly undergo a concerted reaction, while acyclic diazoesters proceed through a stepwise mechanism, and both mechanisms compete on reaction of acyclic diazoketones.

Table A1.2.1 Summary of current predictive guidelines for operative Wolff mechanism

	thermal conditions	**photochemical conditions**
concerted mechanism	**cyclic substrates**  	**cyclic substrates (dominant, not exclusive mechanism)** 
non-concerted and concerted mechanisms are extremely competitive		**acyclic diazoketone precursors** 
non-concerted mechanism	**acyclic substrates**  	**acyclic diazoester precursors** 

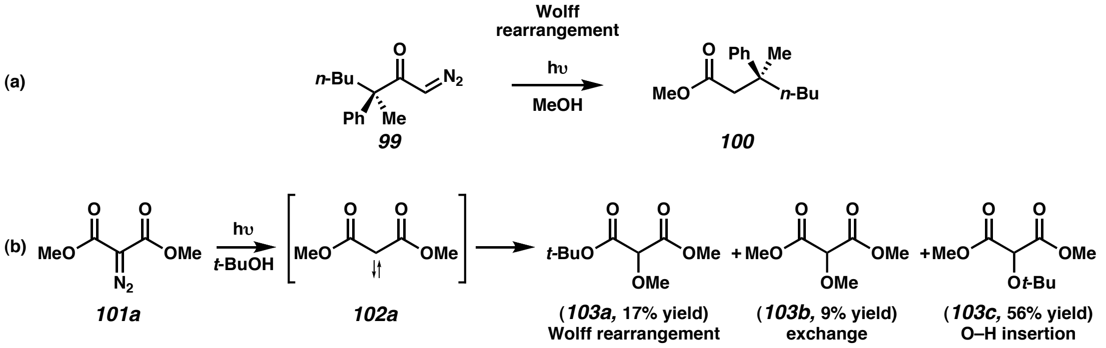
These mechanistic trends have been elucidated experimentally by analyzing product distributions, atom labeling, atom trapping,[7] and observing intermediates spectroscopically. Additionally, calculations map potential energy surfaces to describe thermal rearrangements.

A1.3 Migratory Aptitude and Stereochemical Retention

Retention of stereochemistry has been cited as evidence for a concerted Wolff rearrangement; however, stereochemical fidelity may be maintained in rapid stepwise reactions. Rather, retention of stereochemistry is evidence of an intramolecular Wolff rearrangement.

Kirmse has recently reviewed the stereochemical retention in the Wolff rearrangement.[2a] Generally, the [1,2]-alkyl group migration proceeds with retention of configuration at the migrating stereocenter (Scheme A1.3.1a). By contrast, migration of oxygen and other heteroatoms can occur with some exchange (Scheme A1.3.1b). This exchange indicates a partially dissociative mechanism of the [1,2]-heteroatom migration.

Scheme A1.3.1 (a) stereochemical retention[8] and (b) heteroatom exchange[2a]



Kirmse provided detailed descriptions of the relative migratory aptitudes of Wolff rearrangement precursors[2a] by studying the Wolff rearrangement of 2-diazo-1,3-dicarbonyl compounds (such as **75**, Scheme A1.1.1), in which substitutents undergo a competitive [1,2]-migration. Migratory aptitudes are influenced by the type of migrating group, the substrate conformation, and the mechanism of reaction. The trend for migratory aptitude in thermal rearrangements is H > aryl ≥ alkyl. Heteroatoms do not often migrate in thermal rearrangements. The trend for migratory aptitude in photochemical rearrangements is H > alkyl ≥ aryl > SR > OR ≥ NR. Aryl groups migrate more quickly when they are electron rich. Unfortunately, alkyl groups often impact the geometry of the α-diazoketone, obscuring most migratory trends.

A1.4 Basic Mechanistic Descriptions of the Thermal Wolff Rearrangement[i]

Popik employed B3LYP/6-31+G(d,p) level energy calculations to map the potential energy surfaces for four diazocarbonyl compounds as they proceeded through thermal Wolff rearrangements.[9] Due to conformational constraints, *thermal* Wolff rearrangements are stepwise for acyclic diazocarbonyl compounds, but concerted with cyclic diazocarbonyl precursors.

A1.4.1 Thermal Wolff Rearrangement of Acyclic Substrates: A Stepwise Reaction

In computational studies, Popik found that acyclic diazocarbonyl compounds have conformational access to more stable singlet carbene intermediates, and so proceed through a stepwise thermal Wolff rearrangement.[9] When structurally accessible, carbene intermediates adopt conformations with the π-system of the carbonyl in conjugation with the lone pair of the singlet carbene. In these intermediates, the plane of the carbonyl π-system is approximately 81° skewed from the plane defined by the carbonyl carbon, the carbene carbon and the migrating atom (Figure A1.4.1). This perpendicular conformation renders these singlet carbenes more stable, and favored asynchronous Wolff

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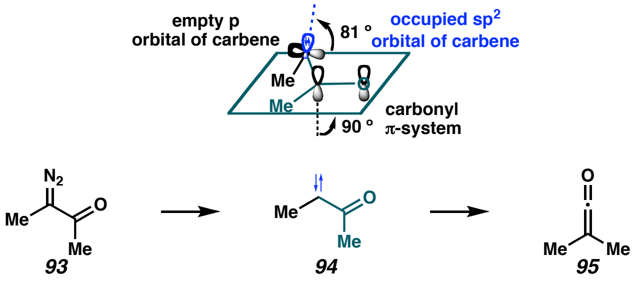
[i] This section is dedicated to Professor John Bercaw, who consistently asks about the mechanism of the Wolff rearrangement.

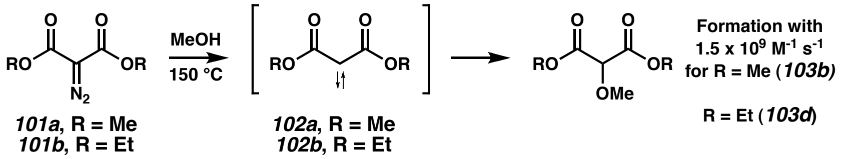
rearrangements. This perpendicular conformation is only accessible to the evaluated acyclic carbene precursors, namely 3-diazo-2-butanone (**93**) and methyl diazomalonate (**101a**).

Figure A1.4.1 Calculated geometry of singlet carbene formed from 3-diazo-2-butanone



As support for a stepwise thermal mechanism in acyclic substrates, Popik[10] demonstrated that during thermal Wolff rearrangement of ethyl diazomalonate (**101b**, 150 °C, MeOH), the intermediate carbene can be intercepted by MeOH through apparent O–H insertion (Scheme A1.4.1). Popik found that O–H insertion by methanol into dicarbomethoxycarbene (**101a**) proceeded in 1.5 x 10^9 M^{-1} s^{-1}.[11]

Scheme A1.4.1 Thermal O–H insertions attempted by Popik

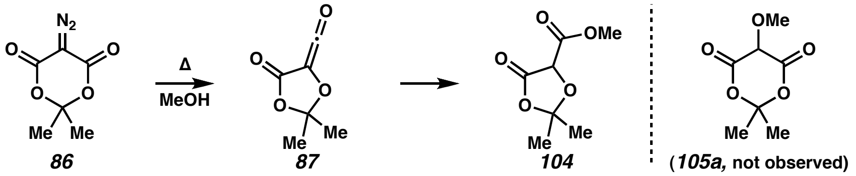


A1.4.2 Thermal Wolff Rearrangement of Cyclic Substrates: A Concerted Reaction

By contrast, Popik[9] found that cyclic analogues proceed through these thermal Wolff rearrangements in a concerted fashion. The thermally stable perpendicular carbene conformation (e.g., **94**, Figure A1.4.1) is inaccessible and so the local energy minimum for their dicarboyl carbene is shallow (<1 kcal/mol).[12]

Popik[13,10] also undertook photochemical and thermal experiments to demonstrate that diazo Meldrum's acid (**86**) probably undergoes a concerted Wolff rearrangement. Popik found that diazo Meldrum's acid undergoes Wolff reaction without formation of O–H insertion products (such as **105a**), which would be available through interception of any intermediate singlet carbene (Scheme A1.4.2). Given trapping timescales with dicarbomethoxycarbene, rearrangement of diazo Meldrum's acid likely occurs faster than 10^9 M^{-1} s^{-1}, and is likely concerted.

Scheme A1.4.2 Popik did not observe thermal O–H insertion with cyclic diazo precursors



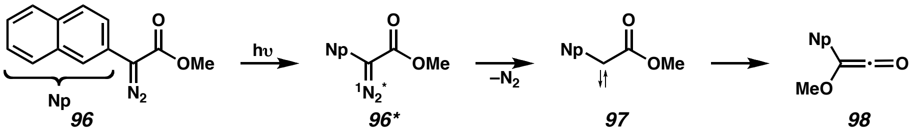
A1.5 Basic Mechanistic Descriptions of the Photochemical Wolff Rearrangement

As is true for thermal Wolff rearrangements, cyclic substrates primarily participate in concerted reactions. For linear diazocarbonyl compounds, the mechanism of the rearrangement is more substrate dependent. Photolysis induces a stepwise Wolff rearrangement for linear diazoesters, whereas both the stepwise and concerted mechanisms compete for Wolff rearrangements of linear diazoketones. Platz postulated that relative to diazoesters, diazoketones undergo a Wolff rearrangement in a more concerted fashion because the ketone has less resonance stabilization.[15] Decreased resonance stabilization increases the energy of the starting ketone, and the ketone excited state. A higher energy excited state will result in a more exothermic, and consequently faster rearrangement of the ketone.

A1.5.1 Photochemical Wolff Rearrangement of Linear Diazoesters: A Stepwise Reaction

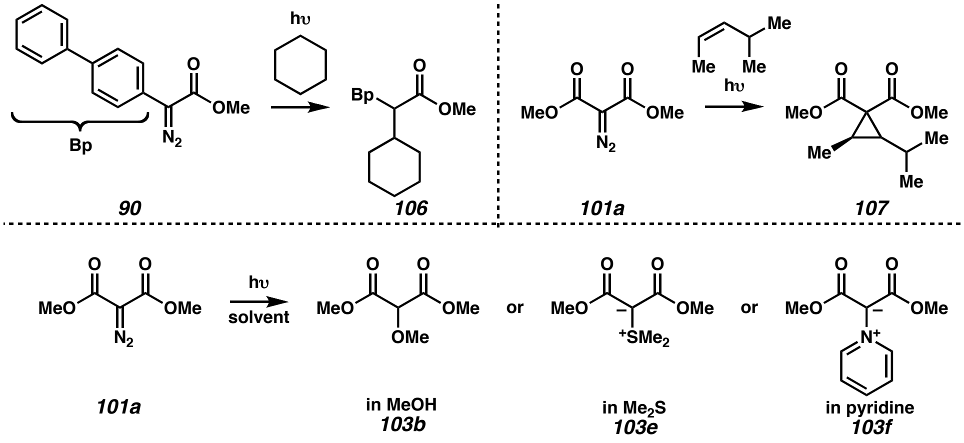
Upon photolysis, linear diazoesters undergo stepwise Wolff rearrangements with singlet carbene intermediates. Using ns time-resolved IR spectroscopy, Toscano found that 2-$NpCN_2CO_2CH_3$ (**96**) forms the ketene **98** solely by a stepwise process with a singlet carbene intermediate (Scheme A1.5.1).[14]

Scheme A1.5.1 Toscano observed stepwise Wolff rearrangement of 2-$NpCN_2CO_2CH_3$



Carbene trapping experiments demonstrate efficient formation of carbenes from acyclic diazoesters through photolysis (Scheme A1.5.2). Platz demonstrated that *p*-biphenyldiazoester (**90**) undergoes primarily C–H insertion on photolysis in cyclohexane.[15] Jones showed that diazomethylmalonate (**101a**) reacts with *cis*-4-methyl-2-pentene to furnish 40% yield of cyclopropane, and provided good evidence for a carbene intermediate.[21] Nikolaev and Platz reported efficient carbene trapping of diazomethylmalonate (**101a**) on photolysis in or with methanol, to generate methyl ethers (e.g., **103b**), and in or with dimethyl sulfide, to form sulfur ylides (e.g., **103e**), and in or with pyridine, to form pyridinium salts (e.g., **103f**).[22c]

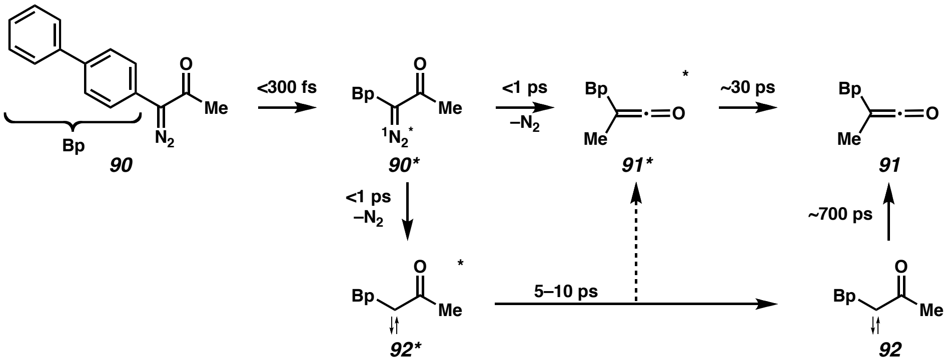
Scheme A1.5.2 Reported trapping studies with linear diazoesters



A1.5.2 Photolysis of Linear Diazoketones Induces Competitively Concerted and Stepwise Wolff Rearrangements

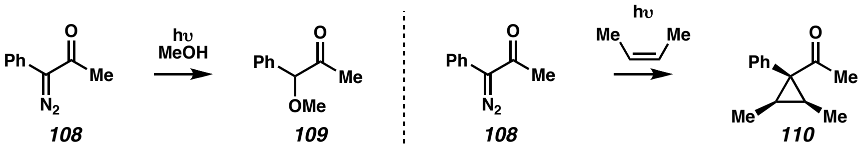
On photolysis, linear diazoketones likely undergo competitive stepwise and concerted Wolff rearrangements. Using ns laser flash photolysis, Burdzinski and Platz determined that *p*-biphenyldiazoketone (**90**) forms ketene **91** by a combination of concerted and stepwise processes (Scheme A1.5.3).[16,15] They observed ketene formation on two time scales: a rapid concerted Wolff rearrangement via a hot ketene (**91***) that undergoes vibrational cooling, and a slower stepwise process involving a singlet carbene.

Scheme A1.5.3 Concerted and stepwise pathways, as described by Platz and Burdzinski[16]



Indeed, trapping experiments verified the presence of a carbene intermediate during Wolff rearrangements of linear diazoketones (Scheme A1.5.4). Tomioka observed O–H insertion products (e.g., **109**) and Wolff rearrangement products on photolysis of diazoketone **108** in MeOH (at room temperature, or –196 °C).[17] Further, upon reaction with *cis*-2-butene, diazoketone **108** formed primarily cyclopropane **110**.[17]

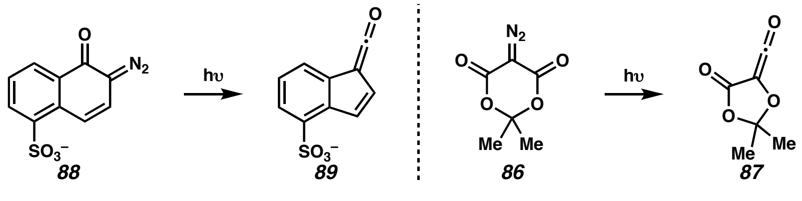
Scheme A1.5.4 Reported trapping studies with linear diazoketones



A1.5.3 Photolytic Wolff Rearrangement of Cyclic Substrates Through a Primarily Concerted Pathway

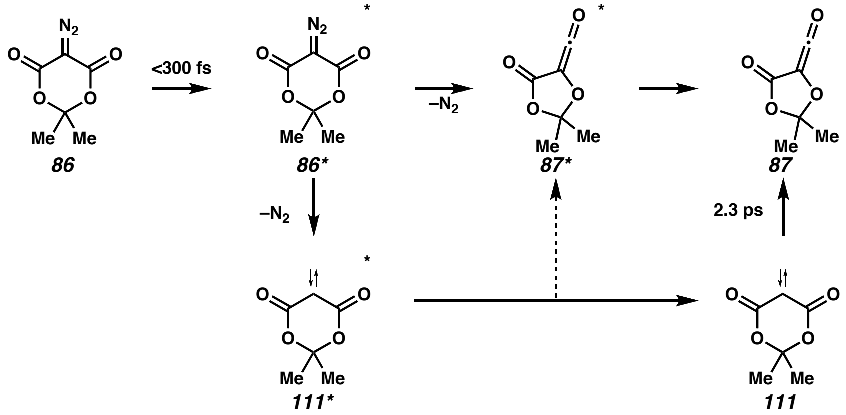
Alicyclic precursors undergo photochemical Wolff rearrangements primarily by a concerted process. Brixner studied the photochemistry of a diazonaphthoquinone (e.g., **88**) by fs time-resolved IR spectroscopy, using DFT calculations to support their spectral assignments (Scheme A1.5.5).[18] They concluded that the primary mode of reaction is concerted, though they cannot rule out stepwise Wolff rearrangement as a minor process. Similarly, Platz and Burdzinski studied the photochemistry of diazo Meldrum's acid (**86**) by fs time-resolved UV–vis and IR spectroscopy. They identified intermediates, and concluded that the stepwise mode of Wolff rearrangement was minor, relative to the concerted process.[19]

Scheme A1.5.5 The concerted Wolff rearrangement of alicyclic compounds



Platz and Burdzinski specified that upon photolysis, diazo Meldrum's acid (**86**) entered the S_5 and S_7 excited states, which rapidly converts to the S_2 state (<100 fs, Scheme A1.5.6). From the S_2 state, direct Wolff rearrangement formed a vibrationally excited ketene, which relaxes in 9 ps,[19] or the S_2 state relaxes to the S_1 state (<300 fs). In turn, the S_1 state relaxed to the ground state, isomerized to diazirine, or fragments to form an intermediate assigned as a singlet carbene. This intermediate underwent Wolff rearrangement, or decomposed to other products.

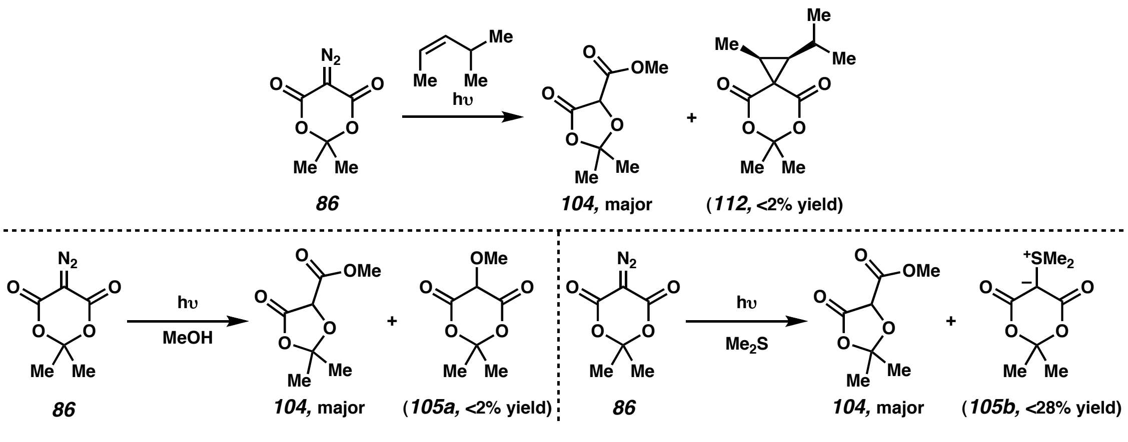
Scheme A1.5.6 Concerted and stepwise pathways, as described by Platz and Burdzinski



Platz and Burdzinski assigned the intermediate as a singlet carbene[20] due to features in the transient absorption spectrum, as well as intermediate lifetime (Scheme A1.5.6). TD-DFT calculations predict that the carbene dilactone has significant oscillator strength above 300 nm, as is observed for the 305 nm absorbance. Also, when formed in CH_3CN or $CHCl_3$, this intermediate has a 2.3 ps lifetime, the shortest measured lifetime of any carbene to date. This, in accord with Popik's potential energy surface calculations,[9–13] would predict that this singlet carbene is blocked from a perpendicular geometry that would involve more stabilizing orbital overlap.

Carbene trapping experiments demonstrated minimal formation of carbenes from cyclic diazo Meldrum's acid through photolysis (Scheme A1.5.7). Jones found that on reaction with *cis*-4-methyl-2-pentene, diazo Meldrum's acid formed only 1–2% of cyclopropane, indicating that the only a modest amount of diazo Meldrum's acid generated carbene with a long enough lifetime to undergo cyclopropanation.[21] Nikolaev and Platz explored carbene trapping of 2,2-dialkyl-5-diazo-1,3-dioxane-4,6-diones on photolysis in or with methanol, to generate methyl ethers, and in or with dimethyl sulfide, to form sulfur ylides.[22] In all cases, these reactions furnished primarily Wolff rearrangement products. Nevertheless, trace amounts of OH–insertion product were detected following reaction in MeOH. Long-wave UV-irradiation provided <28% of the sulfonium ylide, upon reaction in Me_2S or Me_2S–MeOH. Schuster[23] and Kirmse[24] looked for OH–insertion products, without success.

Scheme A1.5.7 Reported trapping studies with alicyclic diazo precursors



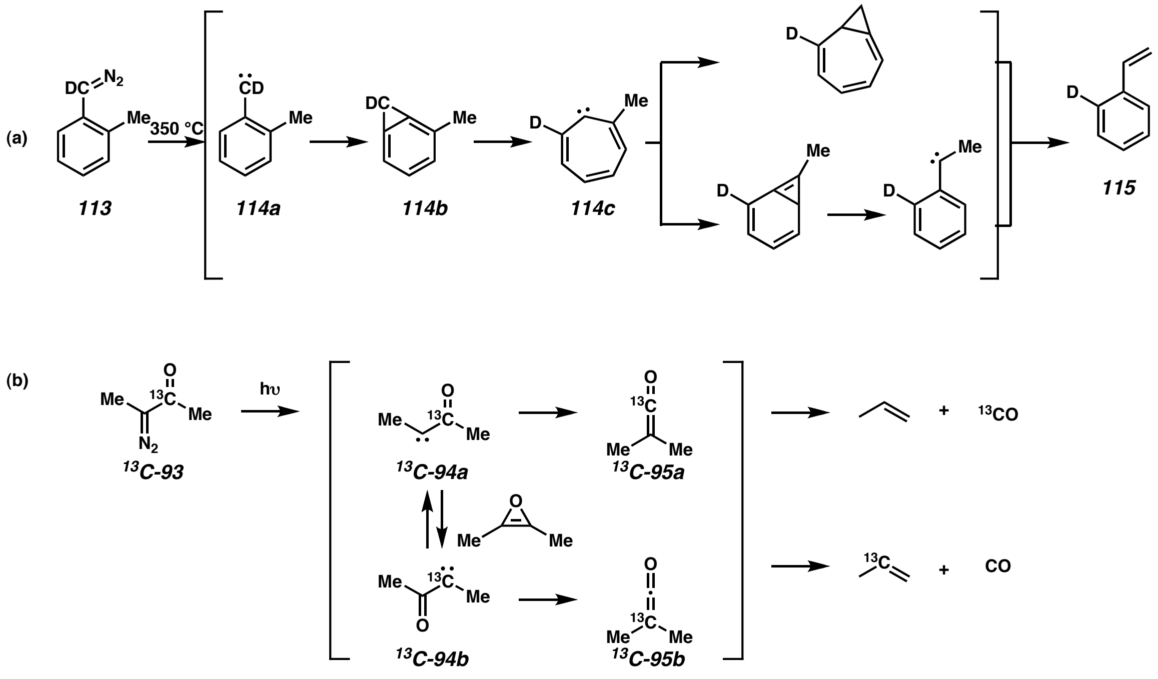
A1.6 α-Oxocarbene Interconversion In Stepwise Wolff Rearrangements

A more subtle mechanistic dispute involves the mechanism of α-oxocarbene-α-oxocarbene interconversions observed during stepwise Wolff rearrangements (Scheme A1.6.1b). The data for α-oxocarbene-α-oxocarbene interconversion is often interpreted to favor an oxirene intermediate, which has not been conclusively demonstrated. An oxirene is often calculated as a minimum, or intermediate, between isomeric carbenes. The evidence, though suggestive, does not conclusively prove the existence of an oxirene intermediate.

A1.6.1 Historical Understanding of α-Oxocarbene Interconversion In Stepwise Wolff Rearrangements

In 1972, Shechter reported the carbene–carbene interconversion of 2-methylbenzylidenes (Scheme A1.6.1a).[25] Strausz demonstrated that the ketocarbene–ketocarbene rearrangement was operative in the decomposition of α-diazo ketones, and postulated the intermediacy of an oxirene to facilitate α-oxocarbene-α-oxocarbene interconversions during stepwise Wolff rearrangements (Scheme A1.6.1b).[26,29a,b,d,27]

Scheme A1.6.1 (a) Shechter and (b) Strausz reported carbene-carbene interconversions



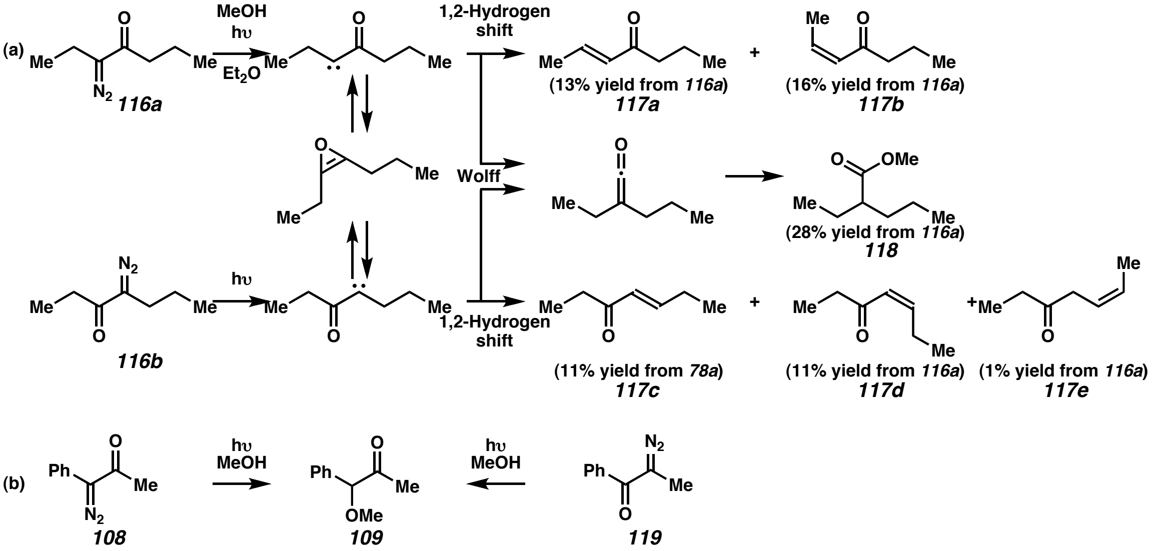
A1.6.2 Evidence for α-Oxocarbene Interconversion In Stepwise Wolff Rearrangements

There is extensive evidence for α-oxocarbene-α-oxocarbene interconversions during stepwise Wolff rearrangements.[28] The carbonyl and diazotized carbons switch places during some Wolff rearrangements.

Strausz and Zeller studied α-oxocarbene-α-oxocarbene interconversions by using photochemical isotopic labeling experiments involving linear α-diazoketones (e.g., Scheme A1.6.1b). In linear α-diazoketones, when either the carbonyl or diazotized carbon was ^{13}C-labeled, this label was distributed over both carbons of the ketene.[29]

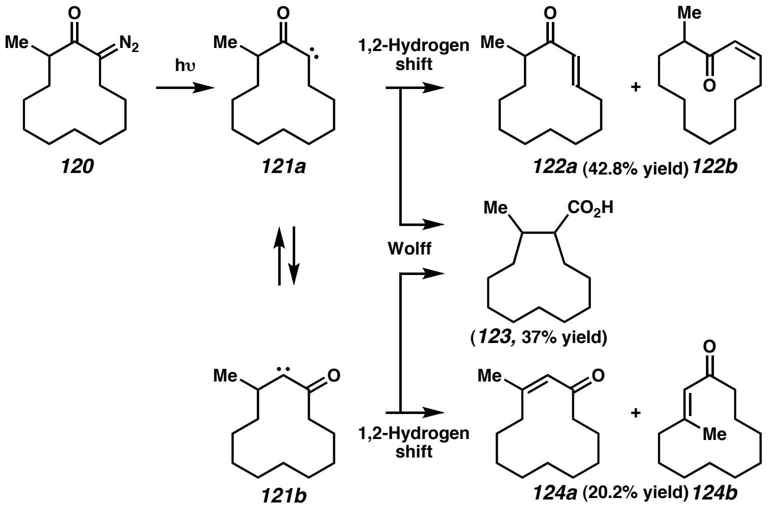
In addition to labeling experiments, photolytic reactions of α-diazoketones provided support for α-oxocarbene-α-oxocarbene interconversions (Scheme A1.6.2).[30] Photolysis of 3-diazo-4-heptanone (**116a**) provided the Wolff rearranged methyl ester via a carbene in 28% yield, in addition to enones **117**.[30b] Mechanistically, enones **117a** and **b** arose from the directly generated carbene through 1,2-hydrogen shifts. Enones **117c–e** were also available by 1,2-hydrogen shifts; however, their direct precursor was an isomeric α-oxocarbene, which was proposed to form via an oxirene intermediate. Similar product mixtures were achieved with 4-diazo-3-heptanone (**116b**) as the starting material. A similar equilibration was implicated when Tomioko demonstrated that both α-diazopropiophenone and its isomer generate the same Wolff and O–H insertion products.[17]

Scheme A1.6.2 Product analysis demonstrated carbene-carbene interconversion



Larger carbocycles, with more than 12-carbons, have conformational flexibility, and likely undergo α-oxocarbene-α-oxocarbene interconversions (Scheme A1.6.3). On photolysis (λ>290 nm, dioxane:water 10:1), diazoketone **120** formed the Wolff rearrangement product, as well as isomeric enones **122** and **124**.[31] Notably, enones **124** incorporated oxygenation at the previously diazotized position, which supported a α-oxocarbene-α-oxocarbene interconversion in this larger carbocycle.

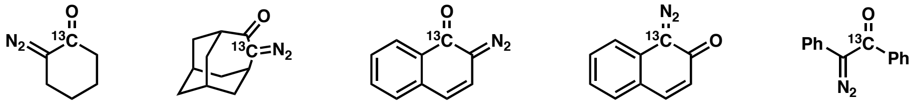
Scheme A1.6.3 Larger carbocycles exhibited carbene-carbene interconversion



A1.6.3 α-Oxocarbene Interconversions Are Not Apparent in Conformationally Constrained Compounds that Seem to Undergo Concerted Wolff Rearrangements

α-Oxocarbene-α-oxocarbene interconversions were not apparent during photochemical Wolff rearrangements of conformationally constrained carbocycles, in agreement with of a concerted rearrangement pathway. The ^{13}C-label was not scrambled in photochemical experiments with alicyclic α-diazoketones **125a–d**,[32,33,34] or in thermal Wolff rearrangement of linear α-diazoketone **125e** (Figure A1.6.1).[28]

Figure A1.6.1 Carbocycles that did not demonstrate carbene-carbene interconversion

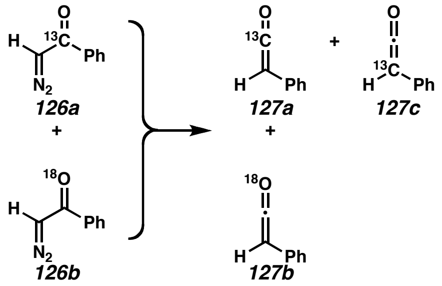


125a ***125b*** ***125c*** ***125d*** ***125e***

A1.6.4 The Mechanism of α-Oxocarbene Interconversions

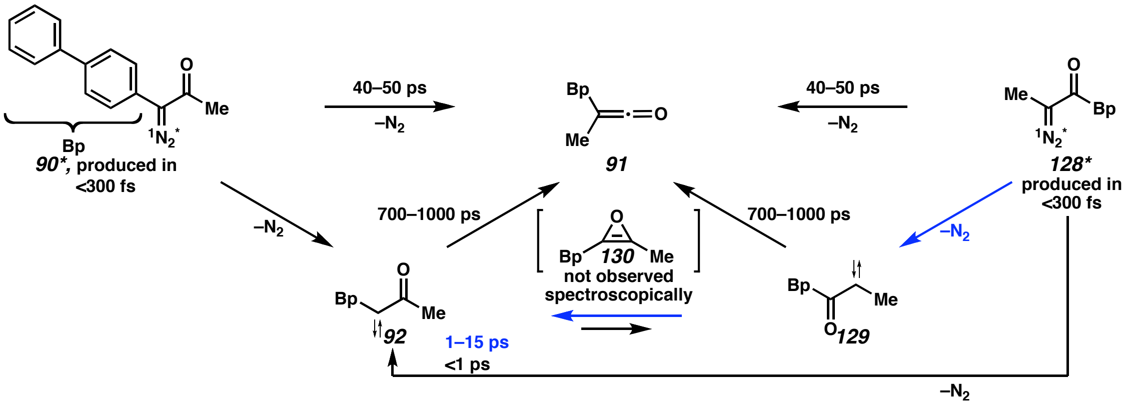
The data for α-oxocarbene-α-oxocarbene interconversions prompts speculation about the mechanisms of these interconversions. It is clear that partial oxygen migration does not proceed through intermolecular pathways. Intermolecular reactions between two α-oxocarbenes are unlikely because their lifetimes are in the nanosecond range,[35] so their local concentration is low. Further, Zeller disclosed that cross-over experiments involving photolysis of singly-^{13}C- and singly-^{18}O-labeled α-diazoacetophenone in the presence of water did not form bis-labeled or unlabeled phenylacetic acid (Scheme A1.6.4).[36]

Scheme A1.6.4 Zeller's cross-over experiments excluded intermolecular interconversion



Platz employed femtosecond laser flash photolysis to study the decay of an excited diazoketone to a ketene by three competing pathways: (1) concerted nitrogen extrusion and Wolff rearrangement, (2) dediazotization to form an intermediate assigned as the singlet carbene, and (3) oxygen migration to form a moiety assigned as the rearranged carbene (Scheme A1.6.5).[37] Using gas phase DFT calculations, Platz did not locate the transition state between the isomeric carbenes, but identified the oxirene as a minimum, 0.7 kcal/mol higher in energy than ^{1}BpCOCMe, such that the activation barrier for carbene interconversion would be close to 0.7 kcal/mol. This activation barrier was consistent with the 1–15 ps delayed observation of rearranged ^{1}BpCCOMe carbene. Nevertheless, Platz did not observe any spectroscopic signals for any proposed oxirenes.

Scheme A1.6.5 Platz observed oxygen migration

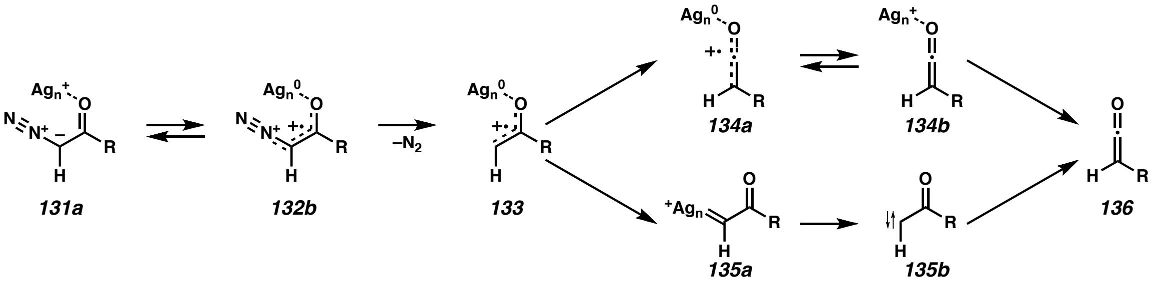


A1.7 Mechanism of Transition-Metal-Mediated Wolff Rearrangements

Finally, Wolff rearrangements may be promoted with silver(I) salts as pre-catalysts. Sudrik and Vijayamohanan identified silver nanoclusters (Ag_n) as the active catalytic species in such Wolff rearrangements (Scheme A1.7.1).[38] They demonstrated that the Ag_n^+/Ag_n^0 redox couple initially extracted an electron from the α-diazoketone, which underwent chemical transformations, and then accepted the electron.[38b,39] They proposed two possible mechanistic pathways to explain their results.

Both mechanisms begin with electron abstraction to generate a radical cation, which undergoes loss of dinitrogen to furnish another radical cation. At this point, the mechanisms diverge. One possibility is that the radical cation undergoes a 1,2-shift to provide a ketenyl radical cation, which upon 1-electron reduction furnishes the Lewis-acid bound ketene. Loss of coordination generated the ketene. Alternatively, the radical cation undergoes initial 1-electron reduction to form a silver nanocluster-bound carbenoid. This carbenoid looses silver to provide a singlet carbene, which rearranges to the ketene. To differentiate between these proposed mechanisms, further experimentation is required.

Scheme A1.7.1 Electron-transfer mechanisms for Ag-mediated Wolff rearrangements



A1.8 Concluding Remarks

The mechanisms of Wolff rearrangements is influenced by the geometry and electronics of starting α-diazoketones and the reaction conditions. Consequently, the Wolff mechanism is controversial. Concerted and stepwise mechanisms operate in photochemical and thermal Wolff rearrangements. Stepwise transformations may be subject to α-oxocarbene-α-oxocarbene interconversions, eliciting speculation about the mechanisms of these interconversions. Investigations have only just begun to identify the pathway for transition-metal-mediated Wolff rearrangements. It is now clear that Wolff rearrangements promoted with silver(I) salts proceed through an electron transfer mechanism.

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