

# New Synthetic Methods Vol. 4

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Cyclobutanes and

Cyclopropylmethyl Compounds

Phosphinidenes

Bridgehead Olefins

Radical Anion Intermediates

Oxidation-Reduction Condensation

Tertiary Phosphane/Tetrachloromethane

Heteroaromatic Betaines

Verlag Chemie

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**New  
Synthetic  
Methods  
Vol. 4**



# New Synthetic Methods

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## About this book

To synthesize new compounds and to improve the routes leading to known substances have always been and will probably continue to be the major objectives of chemistry. Scientific craftsmanship may be a term suitable to describe the approach that is required in order to ensure success. As in any other craft, then, it is important, if not crucial, to be familiar with the arsenal of available methods and to be able to select from it that method which is most suitable for the task at hand. It is the purpose of this book to aid the chemist in his search for and selection of this method.

The papers collected here describe modern methods of synthetic chemistry in such a way that their advantages, applicability, requirements and limitations become obvious. They do not enumerate each and every publication relevant to the subject matter. Rather, their contents have been critically compiled so as to highlight important recent developments, but all contributions contain adequate references providing the reader with easy access to comprehensive details.

All papers have previously appeared in the International Edition of "Angewandte Chemie". It is the unusual interest which they have aroused among the readers of this journal that has led to their presentation in the form of this book. Divested, as it were, of the material that accompanied them in the pages of the journal they will be more convenient to use. Moreover, the authors have updated their reports such that they reflect the latest state of the art, thus adding considerably to the value of the book.

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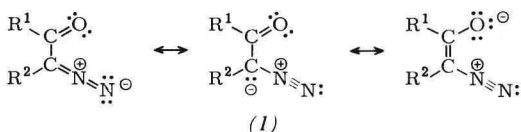
# The Wolff Rearrangement of $\alpha$ -Diazo Carbonyl Compounds

By Herbert Meier and Klaus-Peter Zeller<sup>[\*]</sup>

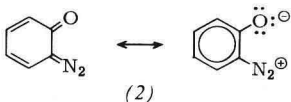
The readily accessible  $\alpha$ -diazo carbonyl compounds are distinguished by their high reactivity, which opens up a variety of preparative applications under modified conditions. Wolff rearrangements of these compounds, induced thermally, photochemically, or catalytically, afford ketenes. Free and complexed carbenes, 1,3-dipoles, 1,3-diradicals, and the anti-aromatic oxirenes have been considered as intermediates or transition states. The present progress report attempts to integrate preparative and theoretical aspects.

## 1. Introduction

$\alpha$ -Diazo carbonyl compounds (1) contain the CO—CN<sub>2</sub> group, which is capable of resonance, as characteristic structural unit.



The C—C bond can be part of a carbon chain or of a cyclic system. If it belongs to an aromatic ring then an inner diazonium phenoxide ("o-quinone diazide") (2) is present.



Key positions in the attached groups may also be occupied

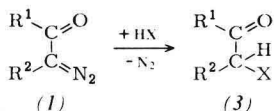
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[\*\*] European Science Exchange Program Fellow.

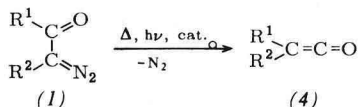
by heteroatoms. In this context, the  $\alpha$ -diazo carboxylic acid derivatives (1),  $R^1 = \text{OR}, \text{NH}_2, \text{NHR}, \text{NR}_2$ , etc., warrant special attention.

Apart from the CO stretching vibration, a simple analytical feature of the open-chain  $\alpha$ -diazo carbonyl structure is the diazo band lying between  $2090$  and  $2190\text{ cm}^{-1}$  (usually at  $2130\text{ cm}^{-1}$ ) in the IR spectrum. Mutual interaction between the diazo and the carbonyl group lowers the CO frequency and raises the  $\text{N}_2$  frequency.

$\alpha$ -Diazo carbonyl compounds are particularly reactive substances. Reactions involving loss of the  $\text{N}_2$  group are generally induced thermally, photochemically, catalytically, or by (Lewis) acids. Whereas the decomposition by acids is applic-



able to all diazoalkanes, in the other three processes one observes a rearrangement that is specific for  $\alpha$ -diazo carbonyl compounds and is known after its discoverer as the Wolff



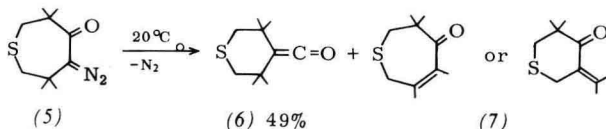
rearrangement<sup>[1, 2]</sup>. The preparative value of the Wolff rearrangement is due to the ready accessibility of the  $\alpha$ -diazo carbonyl compounds<sup>[3]</sup> and to the wide range of reactions of the resulting ketenes (4).

## 2. Methods of Conducting the Reaction

### 2.1. Thermolysis

Thermal energy can induce  $\alpha$ -diazo carbonyl compounds to lose nitrogen and undergo Wolff rearrangement. The decom-

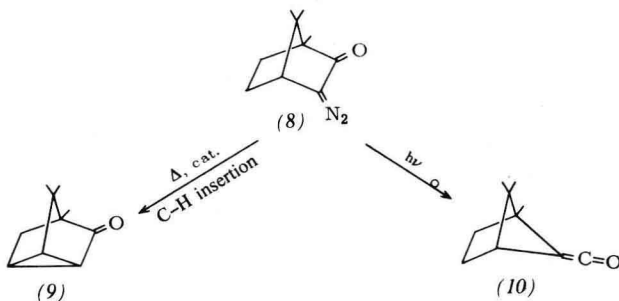
position temperatures range between room temperature and  $750^{\circ}\text{C}$  in gas phase pyrolysis<sup>[4]</sup>. Although generally greater than that of common diazoalkanes, the thermal stability of  $\alpha$ -diazo carbonyl compounds can be reduced by electronic effects<sup>[5, 6]</sup> and even more effectively by steric effects<sup>[7]</sup>. Thus the diazo ketone (5), whose  $-\text{CO}-\text{CN}_2-$  is twisted owing to ring strain, decomposes on formation at room temperature<sup>[7]</sup>.



The tendency to undergo Wolff rearrangement often shows a marked initial increase at the expense of other competing reactions as the thermolysis temperature is raised. Reaction in boiling aniline or boiling benzyl alcohol with addition of tertiary bases such as collidine, isoquinoline, or *N,N*-dimethylaniline has become a proven preparative method.

## 2.2. Photolysis

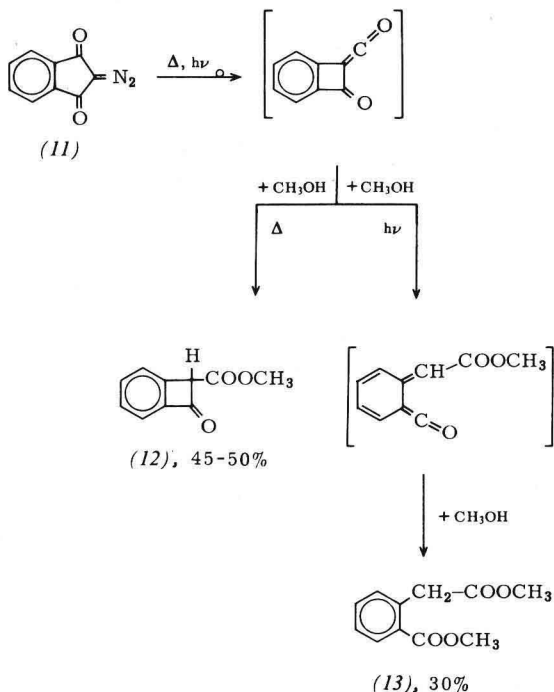
The photochemical variant of the Wolff rearrangement discovered by Horner<sup>[8]</sup> is frequently superior to other methods. It also succeeds when the thermal or catalytic approach merely results in a C—H insertion, as with diazocamphor (8)<sup>[9-11]</sup>.



The limit of the photochemical method is reached when the desired reaction product is itself photolabile under the irradiation.

tion conditions, *e.g.* with 2-diazo-1,3-indandione (11).

The choice of wavelength should be guided by the common photochemical principle: as long as possible, as short as neces-



sary. Decreasing wavelength (increasing energy) of the radiation used leads to increasing amounts of by-products. However, the lowest energy excited singlet state  $S_1$  of diazo ketones, generated by irradiation at the wavelength of a low-intensity forbidden transition in the near UV or visible range, displays only modest reactivity (cf. Section 6).

In the presence of triplet sensitizers, Wolff rearrangement is greatly reduced or completely suppressed in favor of other carbene reactions.

### 2.3. Catalysis

The decomposition temperature of  $\alpha$ -diazo carbonyl compounds can be drastically lowered by metal (ion) catalysts Ag, Ag<sup>+</sup>, Cu, Cu<sup>+</sup>, Cu<sup>2+</sup>, Pt, Pd, Rh, *etc.* Most frequently use is made of freshly precipitated Ag(I) oxide in the presence of alkaline reagents. With the exception of CuI, copper catalysts not only exert an activating effect on nitrogen elimination but also stabilize the resulting carbene (see Section 6.2) by complex formation<sup>[3]</sup>. The same applies to rhodium<sup>[12]</sup> and palladium catalysts<sup>[13]</sup>. As a consequence, Wolff rearrangement no longer occurs or becomes very difficult. Catalysts are sometimes also used during photolysis of  $\alpha$ -diazo carbonyl compounds<sup>[14]</sup> (Table 1).

Table 1. Catalysts for Wolff rearrangement of  $\alpha$ -diazo ketones.

Catalyst	Ref.
Ag <sub>2</sub> O/Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	[1]
Ag <sub>2</sub> O/Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub>	[15]
AgNO <sub>3</sub>	[16]
C <sub>6</sub> H <sub>5</sub> —CO <sub>2</sub> Ag/tertiary base	[17]
CF <sub>3</sub> —CO <sub>2</sub> Ag	[17]
colloidal Ag from Ag <sub>2</sub> O + H <sub>2</sub> CO	[18]
CuO	[19]
CuI/acetonitrile	[20]
Cu/acetonitrile	[19]
platinum	[21]

### 3. Secondary Reactions of Ketene Products

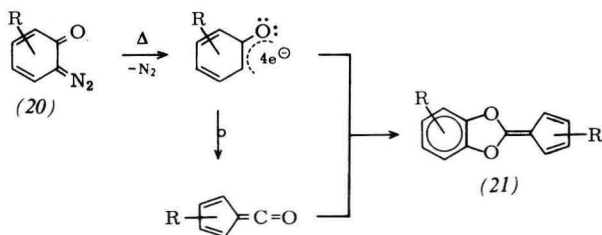
The ketenes (4) are generally not isolated after a Wolff rearrangement; instead their reaction products are obtained.

#### 3.1. Addition of Nucleophiles

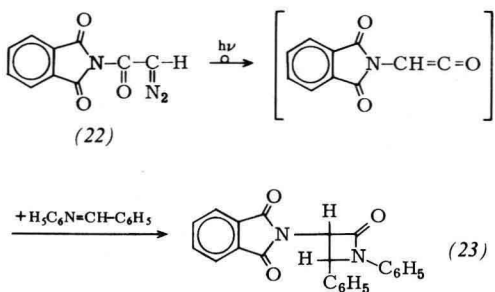
If the Wolff rearrangement is conducted in the presence of nucleophilic reagents whose proton activity is not excessively high, then the ketene intermediates yield carboxylic acids (14) or their derivatives<sup>[3, 22, 22a]</sup>.



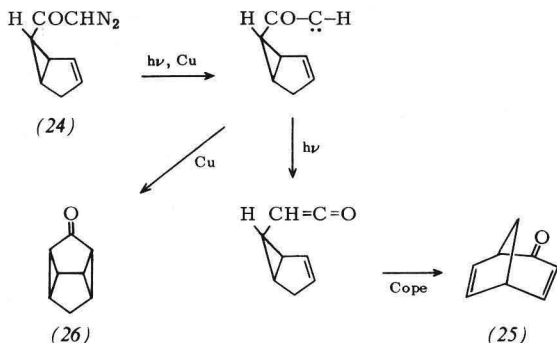
Nearly all *o*-quinone diazides behave in this manner on thermolysis<sup>[28a]</sup>. The resulting ketene reacts with unrearranged primary fragments (carbenes), yielding compounds of type (21).



The ketenes formed “*in situ*” in the Wolff rearrangement have frequently been subjected to cycloadditions with  $C=C$ ,  $C=N$ , and  $N=N$  double bonds or with *o*-quinones<sup>[29–35]</sup>. The trapping of an unstable aminoketene to give the  $\alpha$ -amino  $\beta$ -lactam (23) should be cited as an example<sup>[36]</sup>.



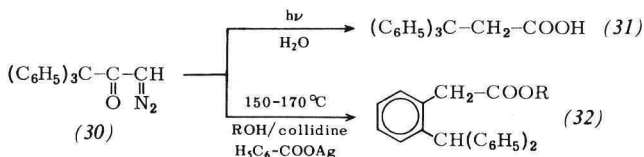
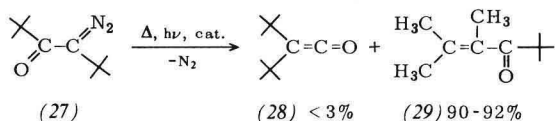
The scope of this cycloaddition is limited above all by reaction of the starting compound itself or its primary fragments (carbenes) prior to rearrangement. The case of the diazo ketone (24) is interesting because intramolecular cycloadditions occur preferentially at the ketene stage in the photochemical reaction<sup>[37]</sup> but at the carbene stage in the catalytic process<sup>[38]</sup>.



## 4. Substrates Capable of Rearrangement

### 4.1. Open-Chain $\alpha$ -Diazo Ketones

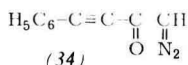
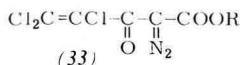
Whereas little is known about the Wolff rearrangement of  $\alpha$ -diazo aldehydes<sup>[39-41]</sup>, numerous publications have appeared on the fragmentation of open-chain  $\alpha$ -diazo ketones<sup>[3]</sup>. In principle, alkyl, aryl, and aralkyl groups can migrate. The *tert*-butyl group in (27)<sup>[42]</sup> and the triphenylmethyl group in (30)<sup>[43]</sup> qualify as borderline cases.



While the *tert*-butyl group of (27) invariably displays only a limited proclivity to migrate, the triphenylmethyl group undergoes clean photochemical reaction. In the catalytic pro-

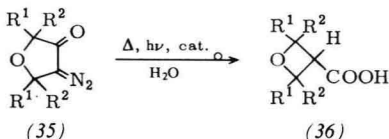
cess, however, anomalous attack at the *ortho* position of a phenyl ring occurs in compound (30). 9-Diazoacetylfluorene behaves similarly to triphenyldiazoacetylmethane (30)<sup>[43]</sup>.

The presence of additional functional groups, particularly in  $\alpha$  position to the CO group, can interfere with the Wolff rearrangement or lead to secondary reactions. Studies on the influence of, for example, halo<sup>[44-53]</sup>, substituted hydroxyl<sup>[54, 55]</sup>, free and substituted amino<sup>[56-64]</sup>, cyclopropyl<sup>[65]</sup>, and cyclopropenyl groups<sup>[35, 66-71]</sup> have been reported. Incorporation of double or triple bonds into the  $\alpha\beta$  position to the CO group<sup>[78]</sup>, suppresses the Wolff rearrangement either completely or partially<sup>[34, 37, 38, 72-78]</sup>. The Wolff rearrangement is known to occur with the  $\alpha,\beta$ -unsaturated diazo carbonyl compounds (33)<sup>[79]</sup> and (34)<sup>[80]</sup>.



## 4.2. Cyclic $\alpha$ -Diazo Ketones

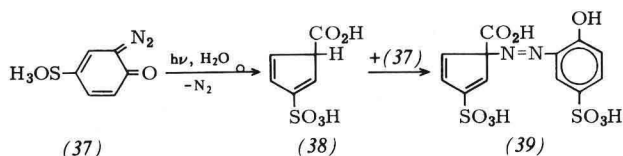
Apart from the Arndt-Eistert homologization<sup>[81, 82]</sup>, ring contraction is the main application of the Wolff rearrangement. Above all the photochemical variant proves suitable for producing strained systems (bicyclics<sup>[10, 83-99]</sup>, polycyclics<sup>[85, 87, 100-103]</sup>, paracyclophanes<sup>[104-106]</sup>, steroids<sup>[107-112]</sup>). The formation of the oxetane (36) can be considered as an example<sup>[113, 114]</sup>.



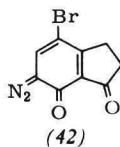
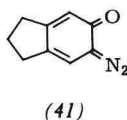
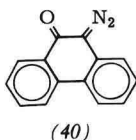
2-Diazo-1-oxoacenaphthene is a negative example—it fails to undergo ring contraction<sup>[115]</sup>.

### 4.3. *o*-Quinone Diazides

As originally demonstrated by O. Süss<sup>[116, 117, 117a]</sup>, the Wolff rearrangement can also be implemented with *o*-quinone diazides. In this case the rearrangement involves ring contraction, thus providing access to the cyclopentadiene series (Süs reaction). This reaction is exploited in a photocopying process (Diazotype, offset process)<sup>[116-118]</sup> in which an increase in pH promotes coupling of rearrangement products with unreacted *o*-quinone diazide, *e.g.* (38) with (37), to yield the azo dye (39).



Coupling reactions can be avoided by working in acid media. Thus irradiation of derivatives of 1-diazo-2-oxo-1,2-dihydronaphthalene and 2-diazo-1-oxo-1,2-dihydronaphthalene leads to the corresponding derivatives of 1-indenecarboxylic acid<sup>[116, 119, 120]</sup> [see formula (19) in Section 3.2]. Application to the pyridine and quinoline series<sup>[119-121]</sup> permits synthesis of pyrrole- and indolecarboxylic acids. Photochemical transformation of 3-diazo-2-oxo-2,3-dihydropyridine to 2-pyrrolecarboxylic acid is a remarkable reaction because it involves migration of an sp<sup>2</sup> nitrogen<sup>[120]</sup>. Whereas (40)<sup>[122, 123]</sup>, (41)<sup>[120]</sup>, and (42)<sup>[124]</sup> undergo smooth Wolff rearrangement,



only 2% ring contraction occurs with (43)<sup>[125]</sup>, presumably owing to an increase of *ca.* 50 kcal/mol in strain energy<sup>[123]</sup>.