Oxirene Participation in the Photochemical Wolff Rearrangement[a]

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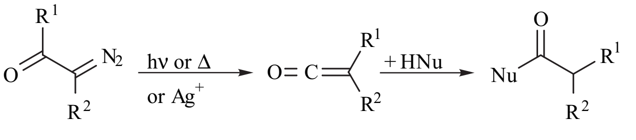
Abstract: Evidence obtained by carbon labelling and carbene-scavenging techniques for the establishment of an α-oxocarbene-oxirene interconversion in the photolysis of acyclic α-diazoketones is summarised. Normal-sized alicyclic α-diazoketones and *o*-quinone diazides react without intervention of the oxirene route, whereas the 12-membered ring system behaves like the acyclic counterparts. The oxirene participation is discussed with reference to stereochemical features of the α-diazoketones and predictions derived from high-level theory.

Keywords: α-diazo carbonyl compounds, ^{13}C-labelling, oxirenes, α-oxocarbenes, photochemistry, rearrangement mechanisms

INTRODUCTION

The first report on the Wolff rearrangement (*i.e.* the thermal, photochemical or catalytic transformation of α-diazoketones **1** into carboxylic acids or acid derivatives **3** *via* ketenes **2**) (Scheme **1**) dates back to the year 1902 [1]. The centenary of this event has been commemorated recently by Kirmse in a brilliant review covering all aspects of the Wolff rearrangement [2]. In the present article the intervention of oxirenes in the photochemical Wolff rearrangement is emphasised.



1 **2** **3**

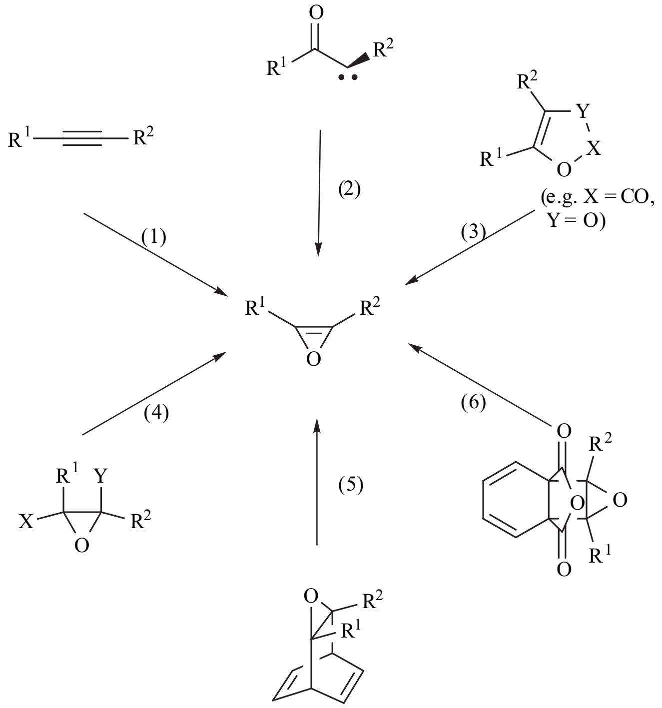
Scheme 1. Wolff rearrangement of α-diazoketones.

With the introduction of Breslow's antiaromaticity concept [3] the interest in oxirenes as potentially anti-heteroaromatic analogues of cyclopropenyl anions has enormously increased and made these species a challenge of both theoretical and experimental investigations.

Numerous attempts to prepare oxirenes by a variety of reactions and techniques indicate that these three-membered ring compounds are extremely elusive species, at best existing as reactive intermediates. The most important approaches attempted to generate oxirenes are summarised in Scheme **2** (for details see ref. [4,5]).

MECHANISM OF THE WOLFF REARRANGEMENT

Schroeter [6] rationalised the rearrangement of α-diazoketones into ketenes by introducing divalent carbon species (in modern terms α-oxocarbenes or carbonyl carbenes). This concept was later incorporated by Eistert [7] into a mechanistic picture based on early electronic theory. Furthermore, in this discussion the hypothetical isomerisation of α-oxocarbenes into oxirenes (conversion (2) in Scheme **2**) was addressed for the first time.



Scheme 2. Potential routes to oxirenes: (1) oxidation of alkynes, (2) isomerisation of α-oxocarbenes, (3) cyclo-elimination from unsaturated five-membered heterocycles, (4) β-elimination from oxiranes, (5) retro-Diels-Alder reaction, (6) retro-[2+2]cycloaddition.

The mechanism of the Wolff rearrangement has been discussed in several reviews [8]. In principle, the formation of ketenes from α-diazocarbonyl compounds can proceed in a concerted or step-wise manner (Scheme **3**). The dichotomy of concerted *vs.* step-wise mechanism has been carefully considered by Kirmse [2].

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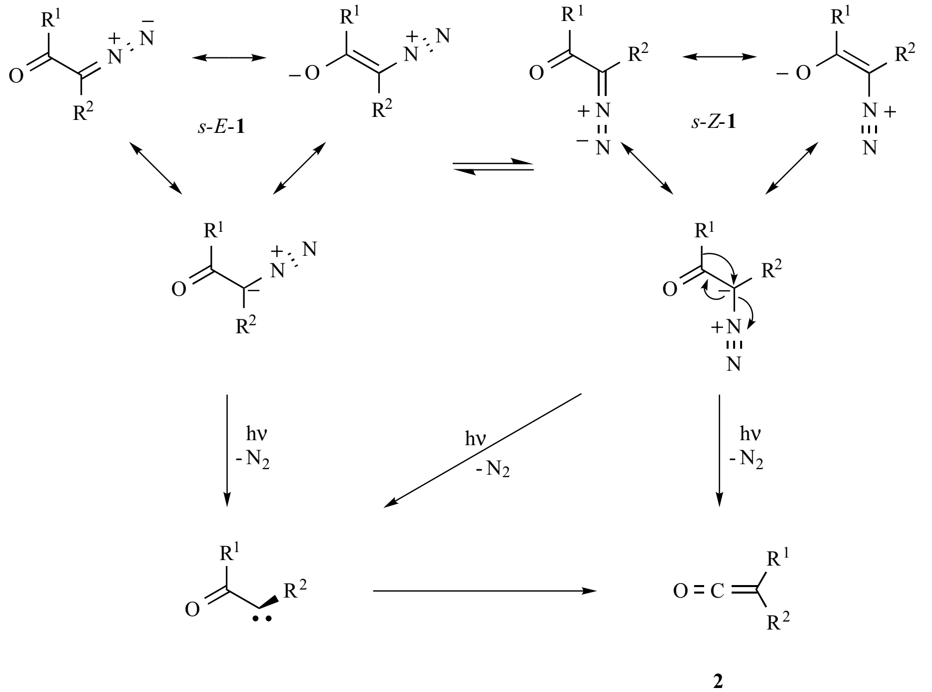


Scheme 3. Conformational equilibrium in α-diazoketones and concerted *vs.* step-wise mechanism of the Wolff rearrangement.

The stereochemistry of α-diazo carbonyl compounds has been concisely reviewed in ref [2]. The *s-Z* conformation is stabilised by Coulomb attraction between the negatively charged oxygen and the positively charged nitrogen and destabilised by steric repulsion of R^1 and R^2. For R^2 = H, *s-Z* has been shown to predominate and the same may be assumed for R^1 = H. In α-diazoketones with R^1, $R^2 \neq$ H *s-E* is the favoured conformation.

The simultaneous extrusion of dinitrogen and migration of R^1 demands an anti-periplanar geometry as realised in the *s-Z* conformation of α-diazoketones. The step-wise mechanism *via* intermediate α-oxocarbenes should be possible starting from both the *s-Z* and the *s-E* conformation. In accordance with a concerted mechanism cyclic, *s-Z* locked α-diazoketones usually readily react to ketenes. On the other hand many representatives of acyclic α-diazoketones with a preferred *s-E* conformation are reluctant to rearrange into ketenes and escape into other reaction channels. This has often been quoted as evidence for a concerted mechanism of the Wolff rearrangement. There are, however, prominent examples of α-diazoketones existing as *s-E* conformers, which readily undergo Wolff rearrangement. Thus, as Kirmse [2] summarised, "the stereochemical argument for concertedness is suggestive rather than conclusive".

As discussed later in some detail, the photo-Wolff rearrangement products of acyclic α-diazoketones exhibit to varying extents partial oxygen shift indicating the intervention of oxirenes, which, in turn, provides evidence for the intermediate existence of singlet α-oxocarbenes. The detected involvement of an α-oxocarbene-oxirene interconversion, as well as other intra- and intermolecular scavenging reaction of α-oxocarbenes, cannot, of course, exclude the presence of a mixed mechanism with parallel formation of ketenes in a concerted and step-wise fashion.

Formylmethylene (**4**), the parent carbonyl carbene, is part of the C_2H_2O potential energy surface and has been subject to theoretical calculation at all stages of sophistication [5,9]. More recent calculations at a high-level of theory [9] predict a triplet ground state of planar *s-Z* geometry, whereas the lowest singlet state is non-planar with the carbene-hydrogen bond nearly perpendicular to the plane of the carbonyl group. In this geometry, the singlet carbene is stabilised by donation from the in-plane lone pair at the carbonyl oxygen to the vacant p-orbital centred at the carbene carbon and interaction between the sp^2-like lone pair at the carbene with the C=O π*-orbital [9d].

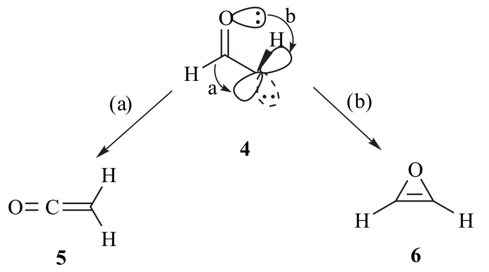
The triplet ground state of many α-oxocarbenes could be detected by ESR spectroscopy after irradiation of the diazo precursors in cryogenic matrices, organic glasses and as powder samples (for reviews see ref [2,10]). In some cases two sets of signals are obtained, indicating that both the *s-Z* and the *s-E* conformer are produced on photolysis. In general, the very efficient Wolff rearrangement prevents the build-up of α-oxocarbene concentrations sufficiently high for IR or UV detection [10,11].

OXIRENE PARTICIPATION

Acyclic α-diazoketones

The described geometry of singlet formylmethylene (**4**) allows favourable orbital interactions leading to both ketene (**5**) and oxirene (**6**) formation (Scheme **4**).

The problematic nature of the C_{2v} stationary point of oxirene has been extensively examined by MO theory. Depending on the choice of the theoretical model, oxirene is predicted to be either a minimum on the potential energy surface or a transition state structure [9]. With the most elaborate (CSDCT) method [12] and density functional theory in combination with the hybrid functional PBEO oxirene is predicted to be a minimum with a ring opening frequency of ca. 150 cm^{-1}.

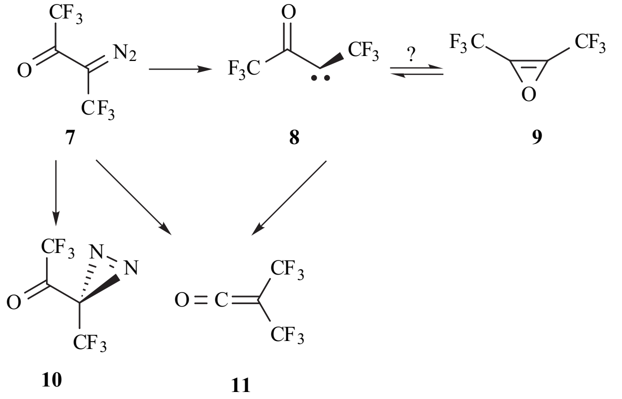


Scheme 4. Formation of ketene (a) and oxirene (b) from formylmethylene.

According to theory, dimethyl substitution has a stabilising effect on the oxirene system [9c]. In contrast, substituted oxirenes C_2X_2O with X=BH_2, NH_2, OH and F are characterised as transition states [9c]. Intuitively, it might be expected that push-pull substitution of oxirene should diminish its antiaromaticity and thus lead to stabilisation. However, AM1 and *ab initio* calculations on amino-formyloxirene came to the conclusion that this species is merely a transition state linking the two corresponding carbonyl carbenes [13].

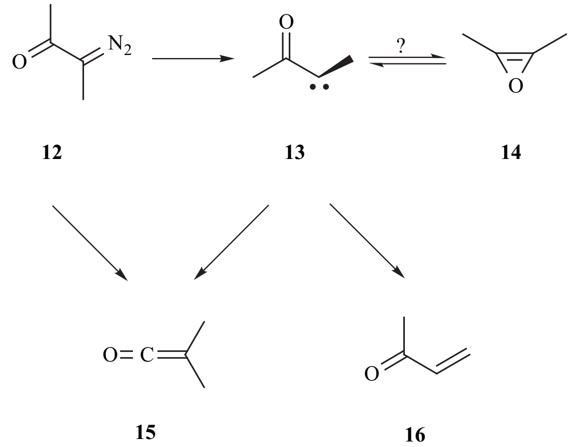
Several attempts to characterise oxirenes by matrix isolation failed [10a,11,14-16]. In retrospect this is not surprising. As outlined above, theory predicts that oxirenes are at best relative minima on the potential energy surface with barriers small enough to enable ring opening even under cryogenic matrix conditions.

In two cases, however, the matrix isolation of oxirenes has been claimed [17,18]. On photolysis of hexafluoro-2-diazo-3-oxobutane (**7**) in argon matrix two species could be observed by IR-spectroscopy [18] in addition to the corresponding ketene **11** (Scheme **5**). One set of bands, which on subsequent irradiation disappeared with a concomitant increase in the ketene spectrum, was assigned to the α-oxocarbene **8**. Further IR absorptions were attributed to bis-(trifluoromethyl)oxirene (**9**). Later, it turned out that the IR spectrum assigned to the α-oxocarbene was in fact caused by isomerisation of the diazo compound to the corresponding diazirene **10** [19]. The spectrum indexed to the oxirene species could not be observed in this matrix isolation study.



Scheme 5. Photolysis of hexafluoro-2-diazo-3-oxobutane (**17**) in a cryogenic argon matrix.

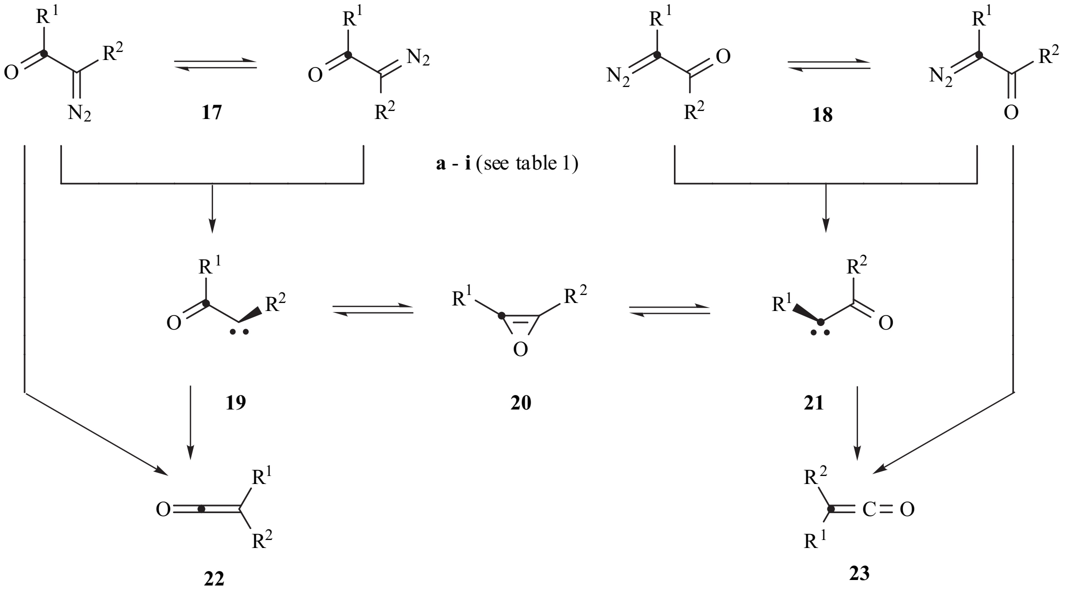
The formation of dimethyloxirene (**14**) as a minor product of the matrix photolysis of 2-diazo-3-oxobutane (**12**) and its perdeuterated analogue was reported [17]. The main products are the IR-spectroscopically well-defined dimethylketene (**15**) and the corresponding enone **16** (Scheme **6**). The assignment of the IR frequency at 2137 cm^{-1} (2128 cm^{-1} in case of perdeuterated diazoketone precursor) to dimethyloxirene has been disputed [20]. It has been argued [20b] that the positive identification of dimethyloxirene (**14**) awaits substantiation by ^{13}C and ^{18}O isotope frequency shifts because this absorption lies in a spectral region where multiple sites of the ketene products absorb and because theory predicts that the ν(C=C) mode of oxirenes is of weak intensity. Furthermore, the detection of **14** failed in the red light mediated oxygen transfer from NO_2 to dimethylethyne in solid argon [20b], although, under these conditions the least amount of excess energy is involved.



Scheme 6. Photolysis of 2-diazo-3oxobutane (**12**) in a cryogenic matrix.

State-of-the-art mass spectrometric techniques have been applied to examine the existence of oxirenes in the gas phase [21]. Neutralisation-reionisation ($^+NR^+$) mass spectrometry on the stable radical cations of oxirene [21a] and methyloxirene [21b] shows that the neutral oxirenes are unstable and rearrange within the μsec time scale of these experiments. Charge reversal ($^-CR^+$) mass spectra of the stable radical anions of formylcarbene [21c], formylmethylcarbene [21d] and acetylcarbene [21d] produce the corresponding radical cations which, depending on their internal energy, either decompose or isomerise to the radical cations of the oxirenes. In contrast, the collisional activation mass spectra of the radical cations produced from the radical anions by neutralisation-reionisation ($^-NR^+$) are identical with the spectra of the radical cations of the corresponding ketenes. This, again, indicates that the neutral α-oxocarbenes and oxirenes are unstable towards rearrangement within the mass spectrometric time scale.

If the interconversion of an α-oxocarbene to a transient oxirene is able to compete with ketene formation, this should give rise to the establishment of an α-oxocarbene-α-oxocarbene rearrangement since the reopening of oxirenes should be possible to both sides. Provided that $R^1 \neq R^2$, two isomeric carbenes could consequently act as ketene precursors. The migration of the carbonyl oxygen to the position originally diazo substituted can be unravelled by



Scheme 7. Detection of an α-oxocarbene-oxirene interconversion by photolysis of ^{13}C-labelled α-diazoketones **17**, **18**. The symbol • signifies carbon labelling. In some of the examples listed in Table 1 the carbon label has been introduced adjacent to the position indicated above. This is, of course, of no influence to the extent of migrated oxygen.

replacing one of the two involved carbon atoms in the starting α-diazoketone by isotopic carbon. The intervention of oxirene would result in a distribution of the label over both ketene carbon positions. Indeed, several decades after the first suggestion of an oxirene participation in the Wolff rearrangement, the involvement of a species having oxirene symmetry has been detected by means of appropriate ^{13}C-labelling experiments [22,23] (Scheme **7**, Table **1**).

The photolysis of [carbonyl-^{13}C]diazoacetic aldehyde (**17a**) represents the simplest case of investigation of an oxirene participation. Irradiation ($\lambda > 290$ nm) in ether, containing 5 vol% benzylic alcohol to trap the ketene formed, yields a Wolff rearrangement product with 8% labelling shift [24]. This indicates 16% of oxirene participation. Thus, the majority of the product originates from a route by-passing the oxirene. Originally this was explained with the high tendency of hydrogen to migrate, so that in the primarily formed formylcarbene (**19a**) the oxirene pathway had little chances to compete with the ketene formation. However, in the light of high-level computational results on the cut-out of the C_2H_2O potential energy surface relevant to the Wolff rearrangement, this interpretation cannot be maintained. The barrier separating formylmethylene (**19a**) from oxirene (**20a**) is extremely small compared to the barrier separating formylmethylene from ketene (21-23 kJ mol^{-1}) [9]. Thus, an equal distribution of the label (**22a** : **23a** = 1 : 1) should be expected in ketene formed *via* formylmethylene. Therefore, it may be concluded that 84% of the ketene are produced in a concerted one-step process from the *s-Z* conformer of the diazoacetic aldehyde.*)

Other symmetrically substituted α-diazoketones studied by the labelling technique are 2-diazo-3-oxobutane (**17b**) and azibenzil (**17c**) exhibiting an oxirene participation of 62% [22c] and 22% [23], respectively, when photolysed in dioxane/water (1 : 1). No label scrambling has been observed for the thermal Wolff rearrangement of azibenzil (**17c**).

Table 1. Labelling Migration in the Photolysis Products of α-Diazoketones 17 and 18 (Scheme 7)

17 / 18	**R^1**	**R^2**	**Phase**	**Migrated label % [a] / % [b]**
a	H	H	Et_2O /$PhCH_2OH$ (95 : 5)	8 [c,d]
b	CH_3	CH_3	vapor *c*-C_5H_{10} dioxane / H_2O (1 : 1)	50 [e] 35 [f] 31 [f]
c	Ph	Ph	dioxane / H_2O (13 : 2) dioxane / H_2O (1 : 1) *c*-C_5H_{10}	15 [d,f] 11 [d,g] 32 [f]
d	CH_3	H	vapor Et_2O /$PhCH_2OH$ (95 : 5) CH_3OH	21 [e,h] / 19 [e] / 4 [i] 7 [h,j] / 5 [h]
e	Ph	H	dioxane / H_2O CH_3OH *c*-C_5H_{10}	18 [d,k] / ~0 [k] 8 [h] 31 [h]
f	Ph	CH_3	dioxane / H_2O (13 : 2) CH_3OH *c*-C_5H_{10}	61 [d,l] / 3 [d,l] 35 [h] 83 [h] / 12 [h]
g	*p*-$NO_2C_6H_4$	CH_3	dioxane / H_2O	69 [d] / 2 [d]
h	*p*-$CH_3OC_6H_4$	CH_3	dioxane / H_2O	26 [d] / 6 [d]
i	CF_3	H	Et_2O / H_2O	7 [m]

[a] In the product from **17**; [b] In the product from **18**; [c] ref [24]; [d] ref [28]; [e] ref [22a]; [f] ref [22c]; [g] ref [23]; [h] ref [8d]; [i] ref [27]; [j] A much higher value has been reported for solution photolysis of **17d** in ref [27]. However, this result is questionable due to sources of error in the labelling technique (^{13}C-depletion) applied; [k] Haiss, P.; Zeller, K.-P., unpublished results; [l] ref [26]; [m] ref [30]

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*) The preferred formation of ketenes from *s-Z* α-diazo carbonyl compounds by a concerted route has also been suggested to rationalise laser flash photolysis experiments [25].

It should be noted that for the unsymmetrically substituted α-diazoketones the extent of oxygen migration derived from the isotopic distribution in the products does not reflect the amount of oxirene participation. In this case the reopening of the oxirene species creates two isomeric α-oxocarbenes with different enthalpies of formation. The two species therefore contribute different amounts to the α-oxocarbene-α-oxocarbene equilibrium. The measured value of oxygen migration represents the lower limit of oxirene participation, which is obtained for the extreme case that the oxirene is exclusively opened to the α-oxocarbene with migrated oxygen.

To illustrate the wide range in degree of oxygen migration, that has been found, the photolysis (λ > 290 nm) of the isomeric pair [1-^{13}C]2-diazo-1-oxo-1-phenylpropane (**17f**) and [2-^{13}C]1-diazo-2-oxo-1-phenylpropane (**18f**) in dioxane/water may be quoted as an example [26-28]. Whereas the product of **17f** shows 61% of labelling migration only 3% could be detected with **18f**. If it is assumed that in both isomeric α-diazoketones the *s-Z* conformer favourable for a concerted mechanism with the retention of the label is of minor importance (p. 292), the two ratios should reflect to a large degree the share of the two interconverting α-oxocarbenes. From this it follows that starting from both α-diazoketones, acetyl-phenylcarbene contributes mainly to product formation.

1-Diazo-2-oxopropane (**17d**) and 2-diazopropanal (**18d**), both labelled in position C1, represent another pair of isomeric α-diazo carbonyl compounds. However, in this case only small amounts of labelling migration have been reported for solution photolysis of both precursors [8d,27]. Gas phase photolysis leads to a higher degree of scrambling [8d,22a]. Compounds **17d** and **18d** are examples of hydrogen substituted α-diazo carbonyl compounds and, therefore, prefer the *s-Z* conformation. In line with this, it may be assumed that both tend to by-pass the oxirene route in solution photolysis and undergo a concerted Wolff rearrangement as major contribution to the overall process.

More information on the factors ruling the extent of oxygen shift may be expected by entering the α-oxocarbene-α-oxocarbene equilibrium not only through the two participating carbenes but also by direct generation of the oxirene species linking both. Oxidation of alkynes by dimethyldioxirane has been extensively tested as a source for intermediate oxirenes [4]. This approach has been realised with ^{13}C-labelled diazoacetophenone (**17e**), 1-diazo-1-phenylacetic aldehyde (**18e**) and phenylethyne (**24**) as precursors.

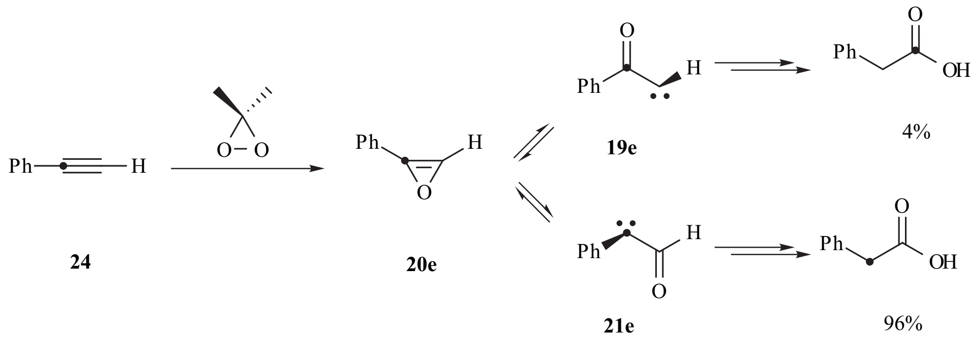
Oxidation of [1-^{13}C]phenylethyne (**24**) with *in situ* generated dimethyldioxirane at 10°C yields phenylacetic acid in which 96% of the label is found in the phenyl substituted carbon position (Scheme **8**).*)

This indicates that the majority of product is formed *via* formyl-phenylcarbene (**21e**). If the ratio of the two isotopomeric acids is taken as a measure for the ratio of the two carbenes, it follows that the standard free enthalpy of formation of formyl-phenylcarbene is smaller by ca. 7.5 kJ mol^{-1} compared to the isomeric benzoylmethylene.

Starting from [1-^{13}C]diazoacetophenone (**17e**) the phenylacetic acid obtained exhibit 18% migration of the label (Scheme **7**, Table **1**). Provided that in the step-wise mechanism the carbene-carbene equilibrium is complete before rearrangement into ketene, this would require that a much larger part should be formed with concomitant oxygen shift. Therefore, the experimentally detected labelling migration of 18% points to a portion of **17e** of more than 80% reacting in a concerted fashion. The phenylacetic acid obtained from precursor **18e** shows practically complete retention of the label indicating a large degree of concerted Wolff rearrangement. Due to the limits of error in determination of labelling distribution (ca. ±2%) some contribution of a step-wise mechanism cannot be excluded. The predominance of the concerted processes in this example is in accordance with the preferred *s-Z* conformation attained in **17e** and **18e** (Scheme **7**).

The trifluormethyl substituent is considered to be a group with a low migration tendency in anionotropic rearrangements. In accordance with this, ethyl 2-diazo-4,4,4-trifluoroacetoacetate (**25a**) does not yield the Wolff rearrangement product when photolysed in alcoholic solutions. Instead, ethyl 4,4,4-trifluoroacetoacetate is obtained as hydrogen abstraction product [29a]. In puzzling contrast, photolysis of 3-diazo-1,1,1-trifluoro-2-oxopropane (**25b**) proceeds in a smooth reaction to the rearrangement product [29b] (Scheme **9**).

Because hydrogen is the substituent on the diazo substituted carbon, compound **25b** should preferentially exist as *s-Z* conformer, by way of analogy [2], it may be



Scheme 8. Oxidation of [1-^{13}C]phenylethyne (**24**) with dimethyldioxirane.

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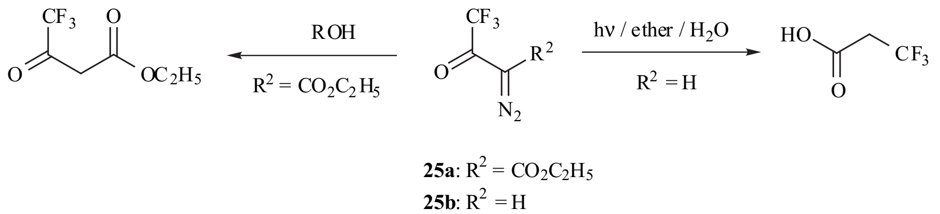
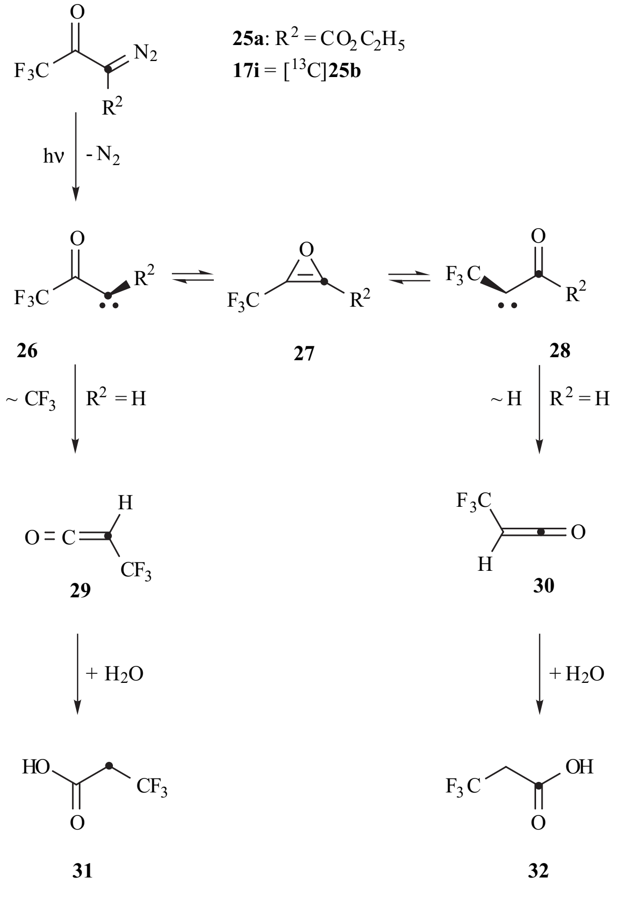
*) P. Haiss, K.-P. Zeller, unpublished results.



Scheme 9. Photolysis of ethyl 2-diazo-4,4,4-trifluoroacetoacetate (**25a**) and 3-diazo-1,1,1-trifluoro-2-oxopropane (**25b**).

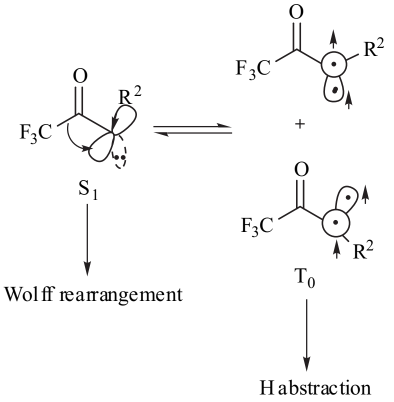
expected that the conformational equilibrium of **25a** should be dominated by the *s-Z,s-Z* and the *s-Z,s-E* conformations presenting the CF$_3$ group and the diazo group in an *anti*-position.

Therefore, a different stereochemical starting point in the two α-diazoketones enabling **25b**, but not **25a** to undergo a concerted Wolff rearrangement seems unlikely. Oxirene participation in the step-wise mechanism, however, offers an attractive explanation of the deviating behaviour of the two α-diazoketones. With **25b** as starting compound, the oxirene route would include the occurrence of an isomeric α-oxocarbene **28b** with a hydrogen in the position capable of migration, whereas starting from **25a** this site would be occupied by an ethoxycarbonyl group of poor migratory aptitude (Scheme **10**). It is generally agreed that hydrogen surpasses all other substituents in their capability to migrate in the Wolff rearrangement. Thus, the detour *via* **28b** would be as a plausible explanation for the contrasting behaviour of **25a** and **25b** in solution photolysis. However, photolysis of ^{13}C-labelled **25b** unequivocally shows that only 6.5% of the Wolff rearrangement product is formed from the isomeric carbene **28** [30]. Furthermore, the assertion that the trifluoro substituent in **25a** resists the rearrangement is only valid for the photolysis in solution. The homologous methyl ester of **25a** embedded in an argon matrix at 10K reacts completely to the corresponding ketene on UV irradiation [15].



Scheme 10. Photolysis of [3-^{13}C]3-diazo-1,1,1-trifluoro-2-oxopropane (**17i** = [^{13}C]**25b**).

The striking difference between solution and matrix photolysis of **25a** may be due to competing reactions on the singlet and triplet surface, respectively.

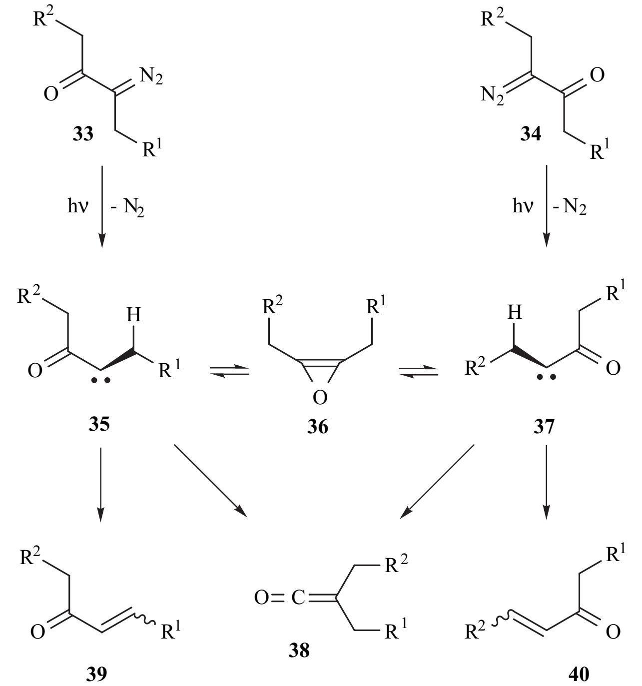


Scheme 11. Spin equilibration in carbenes **26a**,**b** and competing singlet and triplet reactions.

The hydrogen abstraction is considered as a typical triplet reaction, whereas the Wolff rearrangement must proceed through the singlet state (Scheme **11**). This would require that in the solution photolysis the triplet state of carbene **26a** accounts for the only isolated product, however, under matrix conditions the Wolff rearrangement product is obtained through singlet **26a**. On the other hand, the experimental observation that **25b** behaves as an ordinary precursor for the Wolff rearrangement product in solution photolysis, indicates that the primarily formed singlet **26b** is less efficiently converted to the triplet state and can enter the intramolecular reaction path leading to ketene.

In carbonyl carbenes the difference in energy between the perpendicular singlet and the planar triplet ground state is much lower than in methylene [9d]. In **26a** the divalent carbon is flanked by two carbonyl groups, which suggest enhanced stabilisation of the lowest singlet, and, thus, increased efficiency of the singlet-triplet equilibration. In solution the triplet species is scavenged by intermolecular hydrogen abstraction, whereas in a cryogenic matrix the only reaction path accessible after spin equilibration is the intramolecular migration of the CF$_3$ group in singlet **26b**. Due to the larger S-T splitting expected for the carbene **26b**, the singlet-triplet interconversion is less efficient and the rearrangement into **29b** and to a smaller extent the ring closure to oxirene **27b** can compete as singlet reactions under the conditions of the solution photolysis.

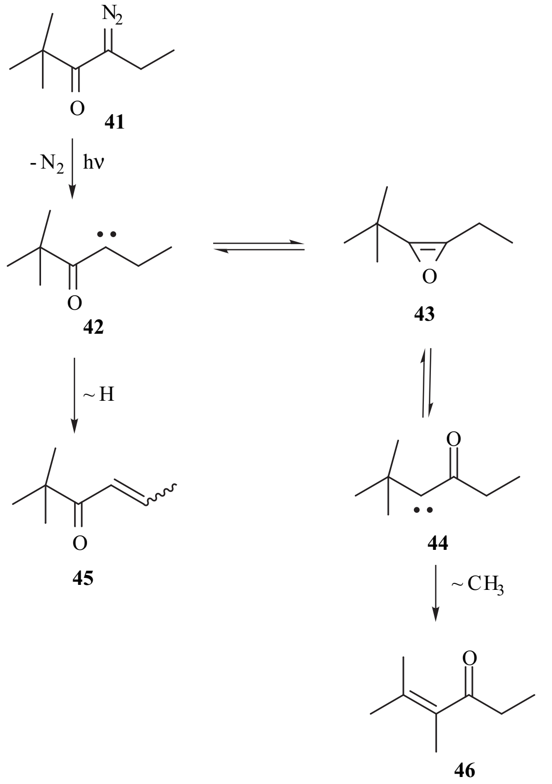
Evidence of oxirene-mediated α-oxocarbene-α-oxocarbene interconversions has also been obtained by intramolecular and intermolecular trapping reactions. α-Diazoketones with primary or secondary alkyl substituents on both, the carbonyl and the diazo carbon are denitrogenated to α-oxocarbene in which a CH bond is positioned next to the carbenic center. Apart from the formation of ketenes such species possess the option of a 1,2-hydrogen shift as further possibilities to be transformed into a stable molecule. The establishment of an α-oxocarbene-oxirene equilibrium would involve a dissimilar alkyl substituted oxirene and two regioisomeric α-oxocarbenes. Consequently, two regioisomeric enones should be formed (Scheme **12**) [31,32]. The oxirene may be called pseudosymmetrical in the sense, that two different alkyl substituents should not influence the two possibilities of ring opening to a larger extent, thus, an approximate 1 : 1 ratio for the two regioisomeric enones may be assumed*).



Scheme 12. Oxirene participation in the photolysis of alkyl substituted α-diazoketones, indicated by formation of regioisomeric enones.

Photolysis (λ = 300 nm, diethyl ether) of 3-diazo-4-oxoheptane (**33**, $R^1 = CH_3$, $R^2 = C_2H_5$) yields apart from products of secondary photolysis *trans*- and *cis*-4-oxo-2-heptene (**39**) (29%) *trans*- and *cis*-5-oxo-3-heptene (**40**) (23%) and ethyl-propylketene (**38**) (28%) [32a]. Since the formation of the *cis-trans*-isomeric enones **40** requires oxygen migration, the intervention of oxirene **36** is clearly implicated by these results. Provided that the two ring opening modes proceed unbiassed, the degree of oxirene participation is calculated as 88%. In a similar experiment with the isomeric 4-diazo-3-oxoheptane (**34**) an oxirene participation of 83% has been estimated [32b].

The photolysis of 3-diazo-5,5,-dimethyl-4-oxohexane (**41**) also indicates oxirene intervention [31]. In this case the rearranged carbene **44** reacts by 1,2-methyl shift to **46**, whereas the primarily formed carbene **42** shows 1,2-hydrogen shift leading to **45** (Scheme **13**). The products from hydrogen migration prevail.



Scheme 13. Oxirene participation in the photolysis of 3-diazo-5,5-dimethyl-4-oxohexane (**41**).

It is interesting to note that the formation of the isomeric enones involving oxygen shift has also been reported for the thermolysis of the corresponding dialkyl substituted α-diazoketones. The degree of oxygen shift is, however, markedly decreased compared to photolysis. This may provoke the interpretation that the α-oxocarbene-oxirene isomerisation requires a vibrationally excited α-oxocarbene, which would be accessible to a larger extent by photolysis (through internal conversion of higher electronic singlet states of the carbene) than by thermolysis. However, this is not the only interpretation possible. The apparent preference of product formation from the α-oxocarbene without oxygen shift under thermal reaction conditions could be simulated by a large contribution of a mechanism with concerted 1,2-hydrogen shift in the starting material.

The photochemical decomposition of the chiral α-diazo-α'-hydroxyketone **47** in methanol affords an epimeric 1 : 1 mixture of the β-hydroxy ester **53** (55%) as Wolff rearrangement product and the β-diketone **54** (45%) [34]. The concomitant formation of **54** requires a preceding oxygen migration *via* the transient oxirene **49** followed by 1,2-

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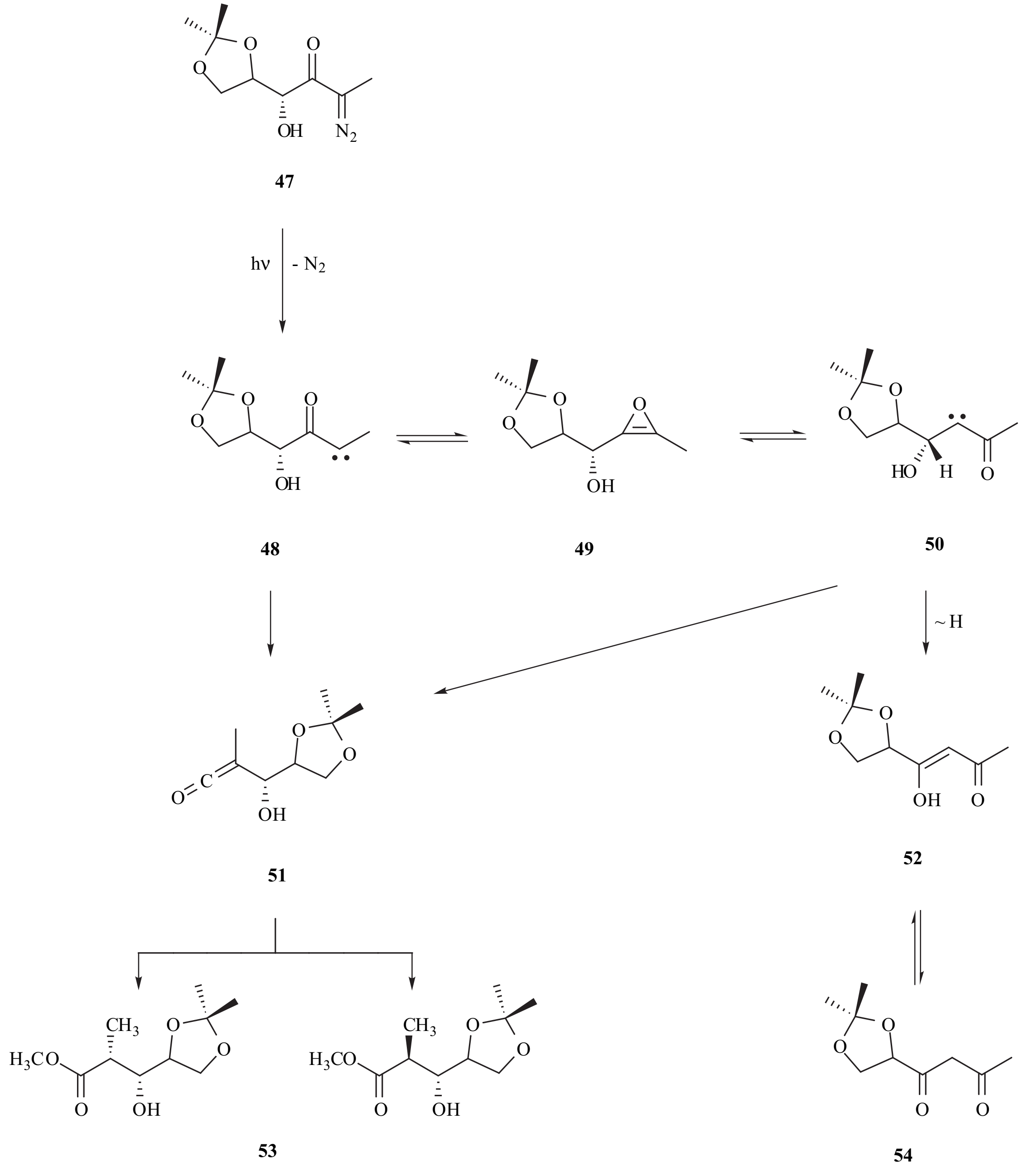
*) It should be kept in mind, that the enone with intact skeleton (no oxygen migration) could also be formed to some extent by a carbene-free route *via* synchronous 1,2-H shift in the excited state of the α-diazo ketone. In ref [33] evidence for the formation of alkenes from electronic excited diazo compounds by a concerted process is summarised.

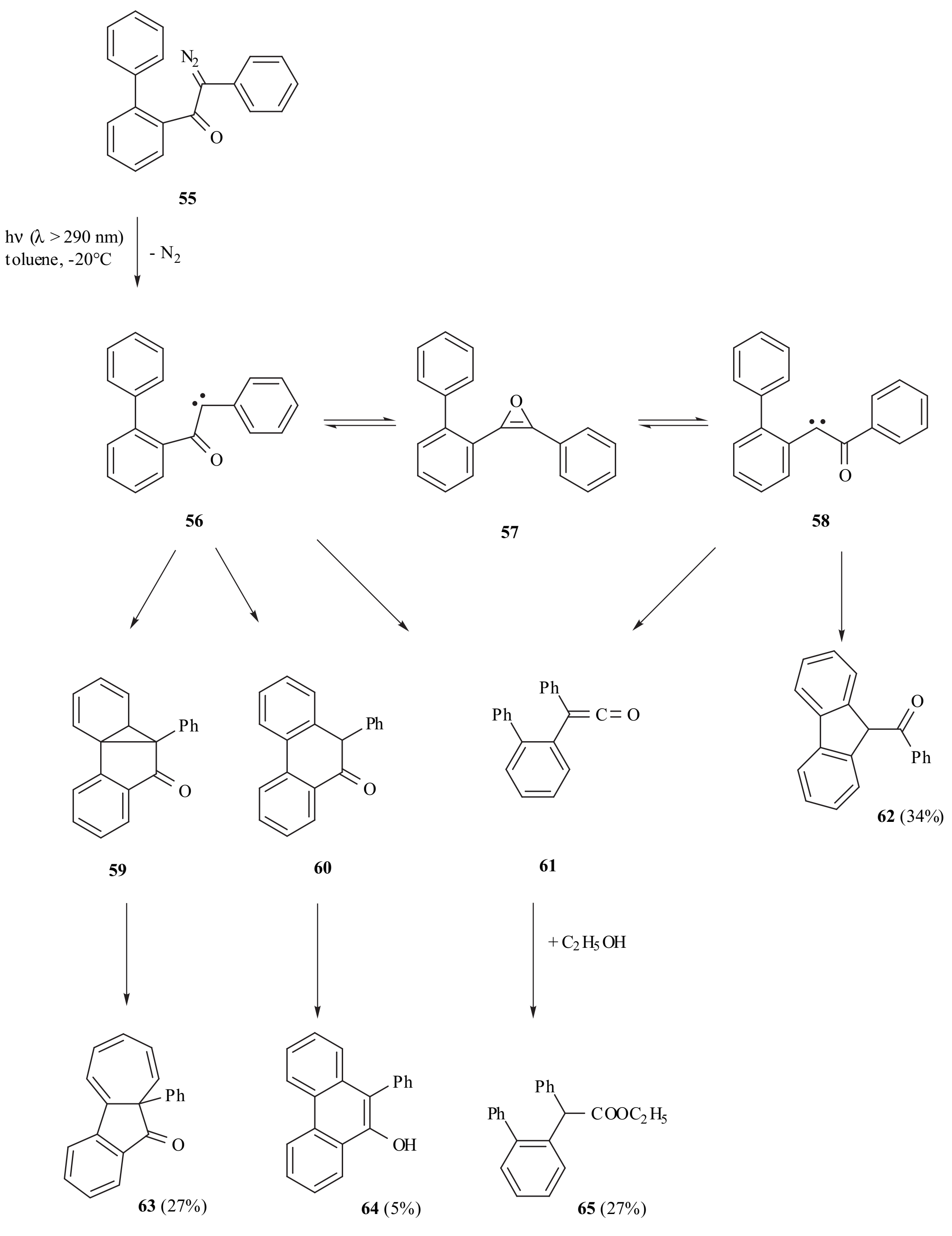


Scheme 14. Oxirene participation in the photolysis of (*S*)-2-diazo-4-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-hydroxy-3-oxobutane (**47**).

hydrogen shift in the isomeric α-oxocarbene **50** (Scheme **14**).

The formation of enones is not the only reported intramolecular trapping test to identify the two isomeric carbenes involved in the α-oxocarbene-oxirene interconversion. The photolysis of (2-phenylbenzoyl)-phenyldiazomethane (**55**) yields products originating from intramolecular addition and CH-insertion reactions of two isomeric carbenes **56** and **58** together with the Wolff rearrangement product **65**. The intramolecular trapping reactions of the carbenes **56** and **58** are facilitated by favourably positioned aromatic units [35] (Scheme **15**). The formation of 9-benzoylfluorene (**62**) indicates oxygen migration and, thus, the involvement of 2-biphenyl-phenyloxirene (**57**) (Scheme **15**). Compound **62** is absent when the decomposition is thermally initiated.

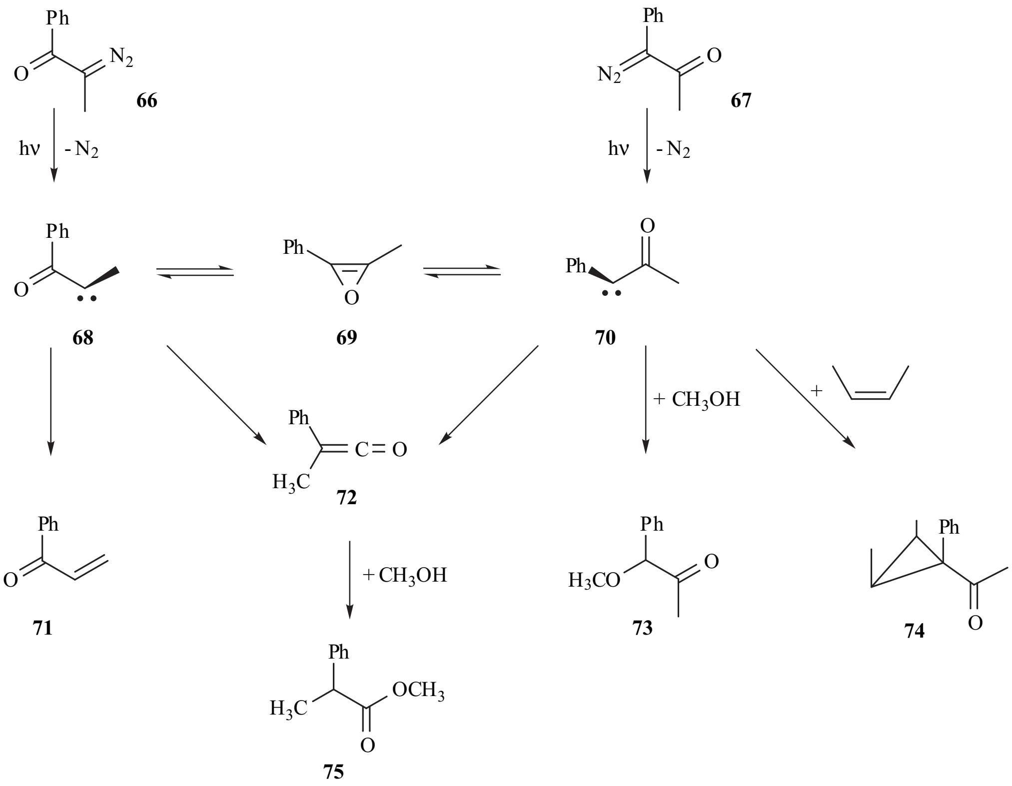
The equilibrium between benzoyl-methylcarbene (**68**) and acetyl-phenylcarbene (**70**) entered *via* both precursors, 2-diazo-1-oxo-1-phenylpropane (**66**) and 1-diazo-2-oxo-1-phenylpropane (**67**) has been studied by intermolecular scavenging of **70** with methanol [36]. Independent from the entrance, the ratio of **75** (Wolff rearrangement) to **73** (OH insertion of **70**) is roughly the same: 52.9% : 39.1% from **66**, 50% : 35% from **67** (Scheme **16**). Only traces of the enone **71** as product of 1,2-hydrogen shift in carbene **68** has been detected. Carbene **70** has also been trapped by stereospecific addition to *cis*-butene. In the presence of *Z*-2-butene the cyclopropane **74** is obtained as main product from **66** and **67** as starting materials [36]. These results point to a



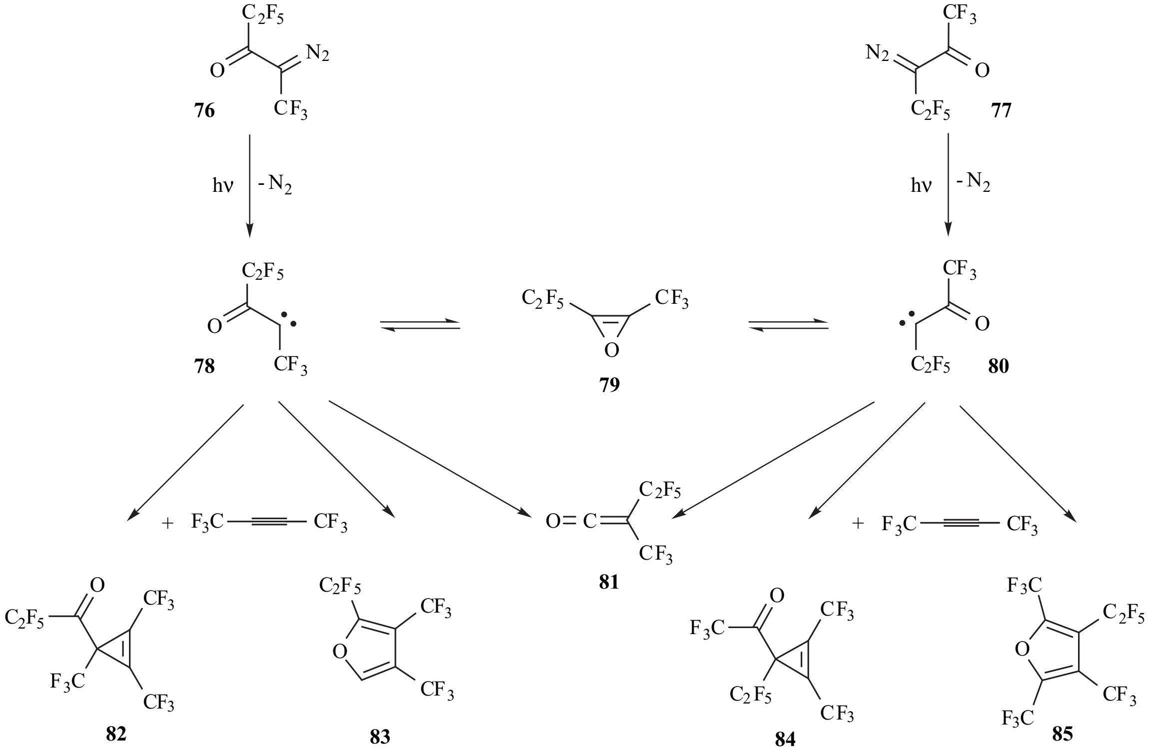
Scheme 15. Carbene-carbene rearrangement in the photolysis of (2-phenylbenzoyl)-phenyldiazomethane (**55**).

predominance of acetyl-phenylcarbene **70**, which is the rearranged carbene starting from **66** and the directly formed carbene starting from **67** (Scheme **16**). This is in qualitative agreement with the labelling study, which demonstrated that this carbene also prevails in the Wolff rearrangement (p. 295).

Intermolecular cycloaddition reactions have been used to detect the interconversion between the two perfluorinated α-oxocarbenes **78** and **80** [18b]. Gas phase photolysis (λ > 335 nm) of either octafluoro-2-diazo-3-oxopentane (**76**) or octafluoro-3-diazo-2-oxopentane (**77**) in the presence of a 400-fold excess of hexafluoro-2-butyne yields in addition to the ketene **81** two sets of cycloaddition products, the cyclopropenes **82** and **84** and the furans **83** and **85**. Identical product ratios **82**/**84** = **83**/**85** = 0.75 have been observed, regardless of which α-oxocarbene, **78** or **80**, has been directly generated. This points to a complete equilibration between both carbenes by way of oxirene **79**, which is in line with a kinetic stabilisation of these species due to the low migratory aptitude of perfluoroalkyl substituents (Scheme **17**).



Scheme 16. Interconversion of benzoyl-methylcarbene (**68**) to acetyl-phenylcarbene (**70**) *via* methyl-phenyloxirene (**69**) in the photolysis of the isomeric α-diazoketones **66** and **67.**



Scheme 17. Interconversion of the perfluorinated α-oxocarbenes **78** and **80**, as detected by cycloaddition trapping reactions.

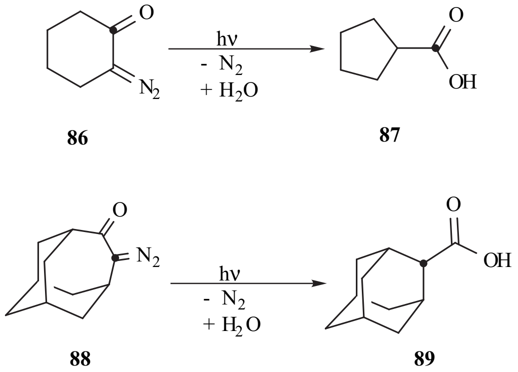
Alicyclic α-diazoketones and *o*-quinone diazides

As discussed above, the lowest singlet state of α-oxocarbenes is predicted by theory to exist in a geometry with a near orthogonal orientation about the C,C bond. In this geometry singlet α-oxocarbenes enjoy electronic stabilisation reflected in a smaller separation from the planar triplet ground states relative to the parent carbene (CH_2). α-Oxocarbenes derived from small or normal-sized cyclic α-diazoketones cannot attain this preferable geometry. On the other hand, in cyclic α-diazoketones the diazo group and the

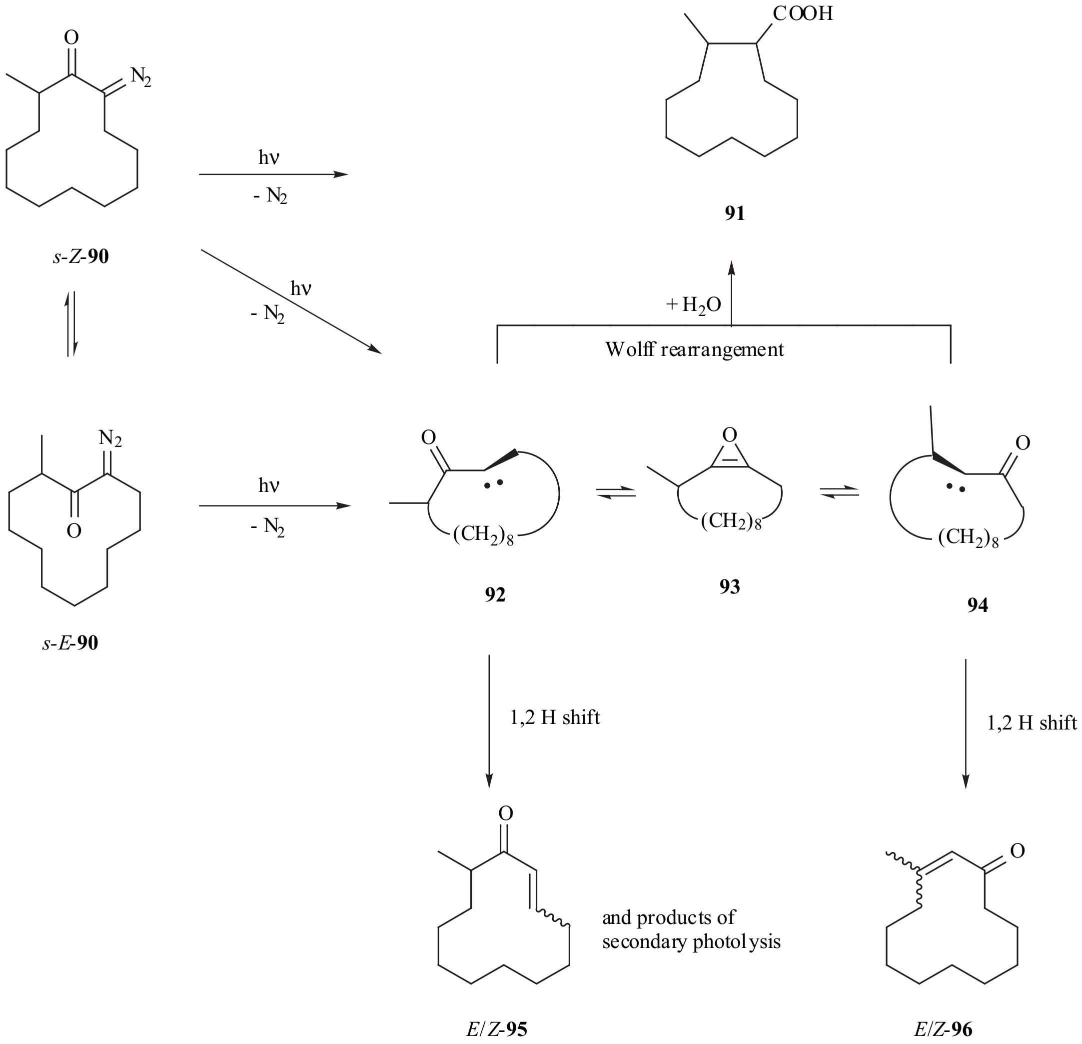
C,C bond migrating in the Wolff rearrangement are fixed in an antiperiplanar geometry.

The expected absence of stabilisation in cyclic α-oxocarbenes disfavours a step-wise mechanism, whereas the *s-Z* constrained geometry of cyclic α-diazoketones encourages a synchronous migration of the corresponding C,C bond and elimination of N_2. In accordance with a concerted mechanism, the cyclic α-diazoketones **86** [37] and **88** [38,39] undergo Wolff rearrangement to **87** and **89** without distribution of the carbon labelling (Scheme **18**).

In large carbocycles with two neighbouring sp^2 carbon atoms the stereochemical situation can be reversed. In cyclododecene [40], 1,2-dioxocyclododecane [41], cylododecan-1,2-semidione [42] the *E* and the *s-E* isomers, respectively are found to be more stable than the *Z* and *s-Z* isomers, respectively. If these compounds are accepted as



Scheme 18. Photochemical Wolff rearrangement of cyclic α-diazoketones without labelling scrambling.



Scheme 19. Oxirene participation in the photolysis of 1-diazo-3-methyl-2-oxocyclododecane (**90**) indicated by formation of regioisomeric enones.

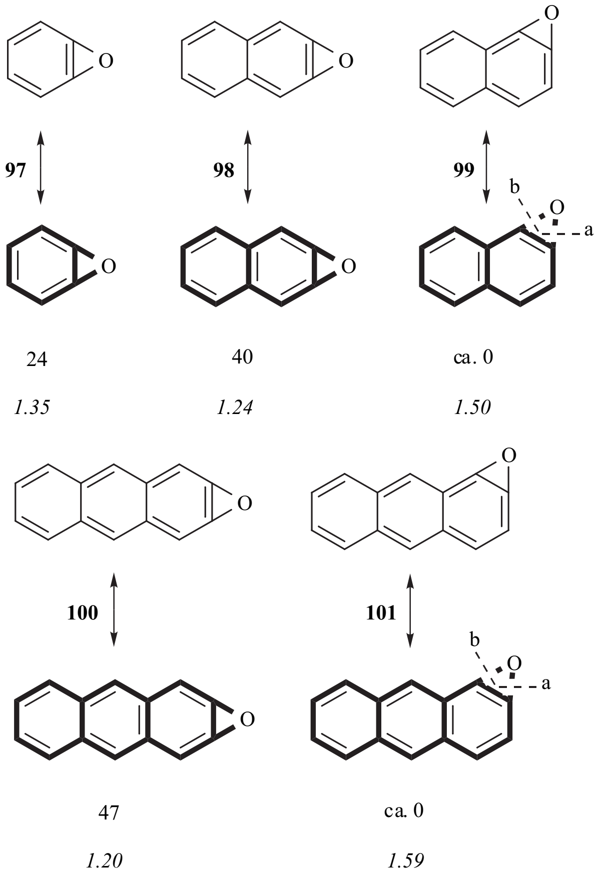
stereochemical models for 1-diazo-2-oxocyclododecane, a preference of the *s-E* conformer*) in the conformational equilibrium can be expected. This should reduce any contribution of a concerted Wolff rearrangement. Furthermore, the large ring size should render this system flexible enough to allow the α-oxocarbene obtained by elimination of nitrogen to adopt the preferred geometry. Both arguments work the same direction and favour a step-wise mechanism and, thus, possible oxirene participation.

The possible intervention of oxirenes in such systems has been investigated with 1-diazo-3-methyl-2-oxocyclododecane (**90**). The methyl substituent next to the carbonyl group is required to utilise the "enone" test for oxirene participation. Photolysis ($\lambda > 290$ nm) of racemic **90** in dioxane/water (10 : 1) yields 2-methylcycloundecanecarboxylic acid (**91**, 37%) as the Wolff rearrangement product in the form of two enantiomeric pairs. Furthermore, two sets of cyclic *cis-trans*-isomeric α,β-unsaturated enones (**95**, 42.8% and **96**, 20.2%) are produced [44]. The appearance of products **96** with shifted oxygen (relative to the methyl substituents) is evidence for the intermediacy of oxirene **93**. From the ratio of products with retained oxygen to products with shifted oxygen (68 : 32) an oxirene participation of 64% is obtained assuming an equal opening of the intermediate oxirene **93** to both sides (Scheme **19**).

The cyclic α-diazoketone **90** is one of the rare examples where oxirene participation under thermal decomposition conditions has be shown. Thermolysis (dioxane/water 10 : 1, reflux) more than doubles the yield of the Wolff rearrangement product **91**. The enone fraction consists to ca. 10% of compounds with migrated oxygen. Thus, the oxirene participation is much less pronounced compared to photolysis.

In contrast to the parent oxirene, which is predicted by high-level theory to be only a shallow well on the potential energy surface, benzooxirene (**97**) seems to reside in a minimum distinctly separated from the corresponding α-oxocarbene by a barrier of ca. 24 kJ mol^{-1} [45,46]. For the linearly annulated naphtho[2,3-*b*] (**98**) and the anthraceno[2,3-*b*]oxirene (**100**) the barrier for ring opening is even larger. On contrast, angular annulation is predicted to create species **99**, **101** with activation energies near zero for both possible ring opening modes (a, b) (Scheme **20**).

An interesting linear correlation has been found empirically between the calculated barriers of ring opening and the bond orders of the oxirene moiety [46]. The angular systems having high bond orders should open easily with virtually no energy of activation, whereas benzooxirene (**97**) and the linearly annulated systems **98** and **100**, characterised by low bond orders, exhibit pronounced barriers for this process. The high-barriers vs. low-barriers series corresponds to the stabilities of the oxirenes or their formal acenes [46]. This essentially signifies that the bold printed resonance structures (Scheme **20**), which decrease the antiaromaticity in benzooxirene and linear higher homologues but not in the angular systems, have higher weights than the other resonance structures (see also ref [47]).



Scheme 20. Resonance structures of areno-annulated oxirenes and activation barriers for ring opening in kJ mol^{-1} obtained by using DFT(pBP/DN*) [46]. The calculated bond orders for the oxirene rings are also given (numbers in italics).

The isomeric α-oxocarbene structures derived by ring opening are predicted by the DFT method not to be stationary points on route to the corresponding ketenes. The only exception is ring opening mode (a) of anthraceno[1,2-*b*]oxirene (**101**). This means, that the corresponding α-oxocarbenes either do not exist as intermediates or, if the DFT methods applied are not precisely enough to detect small relative minima, rearrange with activation barriers near zero into ketenes.**)

The photo-induced Wolff rearrangement of *ortho*-naphthoquinone diazides **102** has been intensively studied by laser flash photolysis with the aim to detect transient species. Two successively formed transients detected by nanosecond laser flash photolysis had been attributed to the corresponding oxirene **104** and ketene **106** [48]. However, the shorter-lived species was later shown to be the ketene **106** and the second intermediate was identified as indenecarboxylic acid enol (ketene hydrate) **107** [49-51]. These assignments are based on the pH dependence of the decay kinetics and solvent isotope effects [50]. It has been concluded that on the nanosecond time scale the ring

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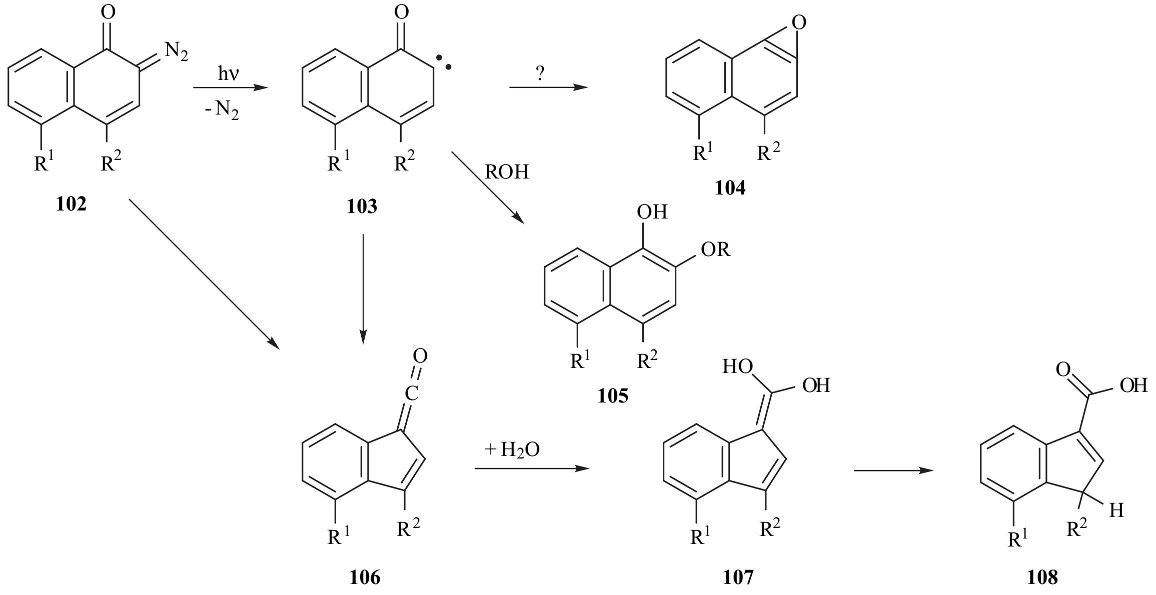
*) It is likely that more than one *s-E* conformation is possible. In case of *trans*-cyclododecene four conformations have been detected by dynamic ^{13}C-NMR spectroscopy [43].

**) Other methods [AM1, HF/6-31G*, MP2(fc)/6-31G*] reproduce stationary points for the involved carbenes. These methods are, however, supposed to overestimate carbene stabilities [46].

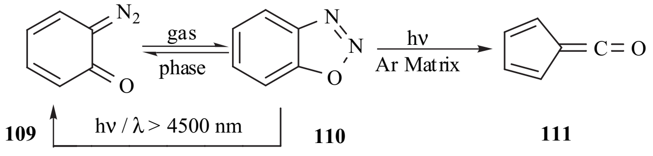


Scheme 21. Laser flash photolysis of 2-diazonaphthalen-1(2*H*)-ones (**102**). The ketenes **106** and the carboxylic acid enoles (ketene hydrates) **107**, but not the carbenes **103** and oxirenes **104**, have been detected in the nanosecond time domain [49-51]. A third transient species with a lifetime ≤ 8 psec has been attributed to the carbenes [52].

contraction of *ortho*-naphthoquinone diazide is a concerted process [49]. Later, by ultrafast spectroscopy, a further, even shorter-lived transient species, arising in the 8 psec time interval between electronic excitation and ketene formation, could be detected [52]. This species has been proposed to be the α-oxocarbene **103** in line with the occurrence of formal OH insertion products **105** as by-products of the photolysis. It should be noted, however, that the claimed detection of **103** seems problematic in view of the theoretical results discussed above.

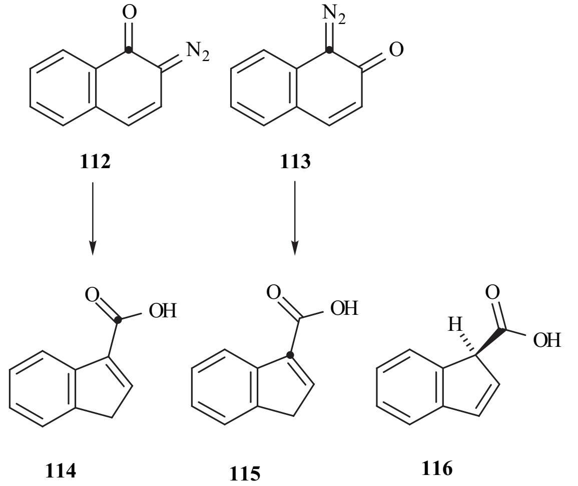
In a laser flash photolysis study combined with IR monitoring the ketene **106** was detected immediately after the laser flash pulse [53] (Scheme **21**). The decay kinetics of ketene does, however, not correspond to the formation of ketene hydrate suggesting the existence of another intermediate (protonated ketene?) between ketene and ketene hydrate.

Ortho-benzoquinone diazide (**109**) undergoes gas phase isomerisation into 1,2,3-benzooxadiazole (**110**), which can be frozen out in a solid argon matrix [54]. IR irradiation (λ > 4500 nm) causes rearrangement back to **109**. UV irradiation leads to elimination of nitrogen and formation of cyclopentadienylidene ketene (**111**), characterised by IR spectroscopy (Scheme **22**). Intermediate precursors of the ketene, including benzooxirene (**97**), could not be detected in the matrix IR experiment. Similar results have been obtained with derivatives bearing various substituents on the benzenoid ring [55].



Scheme 22. Isolation of 1,2,3-benzooxadiazole (**110**) and photolysis in a solid argon matrix.

^{13}C-Labelling studies with 2-diazo[1-^{13}C]naphthalene-1(2*H*)-one (**112**), 1-diazo-[1-^{13}C]naphthalene-2(1*H*)-one (**113**) [56] and naphtho[2,3-*d*]-1,2,3-oxadiazole (**117**) [47] clearly exclude the intermediate existence of naphtho[1,2-*b*]oxirene (**99**) and naphtho[2,3-*b*]oxirene (**98**), respectively.



Scheme 23. Absence of labelling migration in the photolysis of *ortho*-naphthoquinone diazides **112** and **113.**

The two *ortho*-naphthoquinone diazides **112** and **113** on photolysis in dioxane/water give 1*H*-indene-3-carboxylic acid [57]*). The ^{13}C-enrichment in the carbonyl group of **112** completely emerges in the carboxy group (**114**) and the label at the diazo substituted carbon of **113** completely in position 3 (**115**). This excludes naphtho[1,2-*b*]oxirene (**99**)

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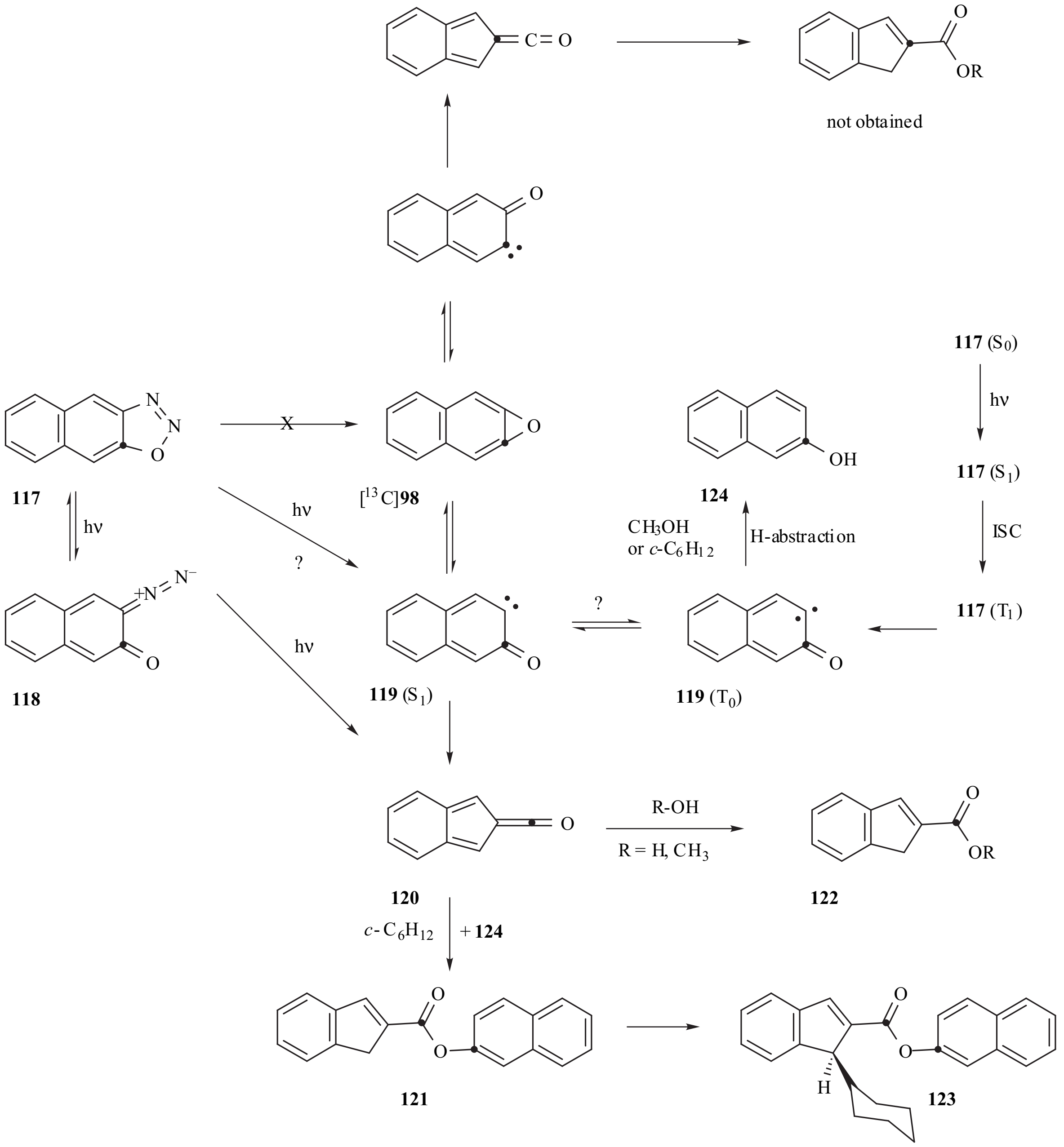
*) In ref [56] the structure of 1*H*-indene-1-carboxylic acid (**116**) was erroneously assigned to the product of photolysis. ^{13}C-NMR data indicate without doubt that, in accordance with other work (*e.g.* ref [57]), the 3-carboxylic acid is in fact obtained (δ [ppm]/Ci: 38.7/C1, 122.5/C4, 123.8/C7, 125.7/C6, 126.8/C5, 135.8/C3, 140.4/C3a, 141.3/C7a, 147.1/C2, 169.4/COOH). The false structural assignment has no influence on the assessment made in ref. [56] with respect to the absence of any labelling scrambling.

as common intermediate in the photolysis of **112** and **113** (Scheme **23**). Although the two ring-opening modes (a, b) of the angular system (Scheme **20**) are principally not equivalent, there should be no discrimination between them, as DFT theory predicts an energy barrier near zero for both. Consequently, labelling distribution should result in any case.

Whereas the ketenes and ketene hydrates have proven to be true intermediates in the photolysis process, the occurrence of the corresponding carbenes is disputed in the literature (see discussion above). Therefore, the concerted N_2 elimination and rearrangement is an attractive alternative to rationalise the ring contraction reaction.

Naphtho[2,3-*d*]1,2,3-oxadiazole (**117**) is one of the rare examples where a 1,2,3-oxadiazole exists as a stable, crystalline compound [47,58,59]. The isomeric 2,3-naphtoquinone diazide (**118**) is destabilised in this case due to its unfavourable π-system [47,58]. Compound **117** should be an ideal precursor of naphtho[2,3-*b*]oxirene (**98**), which, in contrast to the isomeric **99**, would be fully symmetrical and stabilised by bond alternation as discussed above.

To test the formation of **98**, [9a-^{13}C]-labelled **117** [59] has been subjected to photolysis in water, methanol/hexane and cyclohexane [47]. Photolysis in the presence of water or methanol furnishes 1*H*-indene-2-carboxylic acid (**122**, R = H) and the corresponding methyl ester (**122**, R = CH_3), respectively, with the label fully retained in the carbonyl carbon [47]. 2-Naphthol (**124**) is also formed by irradiation in methanol/hexane exhibiting the complete ^{13}C-enrichment at C2. The absence of any labelling distribution excludes the intervention of oxirene **98**. This has also been found for the



Scheme 24. Photolysis of [9a-^{13}C]naphtho[2,3-*b*]1,2,3-oxadiazole (**117**) in H_2O, CH_3OH/*n*-hexane and cyclohexane.

photolysis of **117** in cyclohexane. Under these conditions the 2-indenylidene ketene (**120**) reacts with 2-naphthol (**124**) formed in a parallel reaction to the ester **121**, which is partly further transformed by a radical chain reaction to the cyclohexyl derivative **123**. The labelled positions found in the reaction products are as indicated in Scheme **24**.

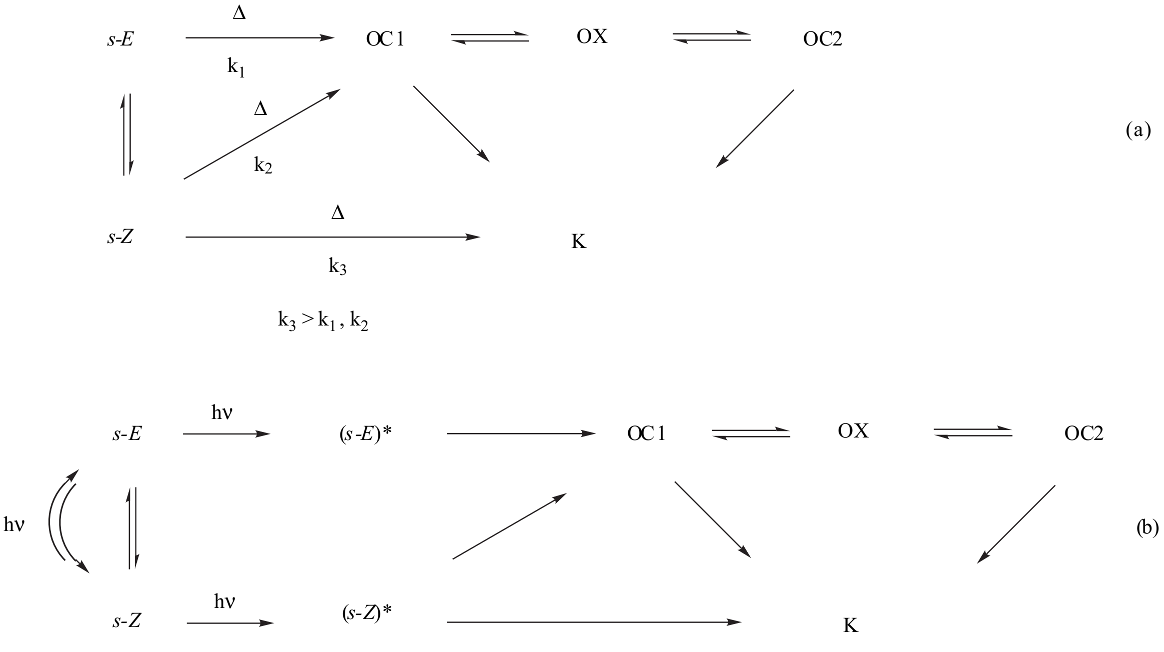
In a matrix experiment, unlabelled **117** has been isolated in solid Ar at 10 - 12K [60]. No diazo band (expected in the range between 2090 - 2190 cm^{-1}) has been found by IR spectroscopy. Thus, no valence isomerisation to **118** intervenes in the vapourisation/condensation sequence. On irradiation of the matrix with 366 nm-light a strong IR absorption at 2127 cm^{-1} appears, which in accordance with ref [61] is assigned to ketene **120**. Additionally, a much smaller IR absorption at 2090/2094 cm^{-1} is observed. Prolonged irradiation results in the decay of the weak double band, whereas, the strong band at 2127 cm^{-1} increases further and remains stable. The weak absorption has been related to small stationary concentration of **118**. The successful matrix isolation of ketene **120** by photolysis of **117** allows the conclusion that this species also intervenes in solution photolysis. The oxirene **98** must clearly be excluded. If it had been formed, either directly or *via* α-oxocarbene **119**, a labelling distribution should have been found in the experiments with [9a-^{13}C] **117**. If theory is taken as a guide, the singlet-α-oxocarbene **119** should also be excluded (no stationary point has been found by DFT [46]). On the other hand, the formation of 2-naphthol (**124**) parallel to the ketene trapping products indicates an intermediate triplet-α-oxocarbene as a precursor. Spin equilibration [**119** (S_1) $\rightleftharpoons$ **119** (T_0)] may be considered as an obvious explanation of the intermediacy of the triplet-α-oxocarbene. However, it cannot be ruled out that this species is generated, without preceding formation of the singlet, *via* intersystem crossing of the singlet-excited naphtha[2,3-*b*]1,2,3-oxadiazole (**117**) followed by N_2 expulsion. If the latter route to **119** (T_0) and finally to 2-naphthol (**124**) is accepted, a concerted process for the Wolff rearrangement into 2-indenylidene ketene (**120**) probably initiated by photoisomerisation of **117** in 2,3-naphtoquinone diazide (**118**) remains as pathway to 1*H*-indene-2-carboxylic acid and its ester derivatives.

PHOTOCHEMICAL *VS.* THERMAL WOLFF REARRANGEMENT

In the cases where the oxirene participation in the thermal Wolff rearrangement has been studied and compared with the photochemical counter-part no [23,35] or a significantly less expressed contribution [31,44] of the oxirene route has been reported. This behaviour can be rationalised according to Scheme **25**.

Both conformers of α-diazoketones can in principle react to α-oxocarbenes in which the *s-Z*/*s-E* relation is lost due to their orthogonal geometry. However, the concerted N_2 elimination-migration reaction is only possible from the *s-Z*. In thermolysis, the concerted Wolff rearrangement of the *s-Z* form should be favoured over simple N_2 elimination to α-oxocarbenes, because of the anchimeric assistance. Provided that the consumed *s-Z* conformer is supplemented from the conformational equilibrium (*s-E* $\rightleftharpoons$ *s-Z*) rapidly enough, then, in the extreme, the α-diazoketone could be transformed to ketene completely by a concerted rearrangement even in the cases of *s-E* dominance in the thermal equilibrium.

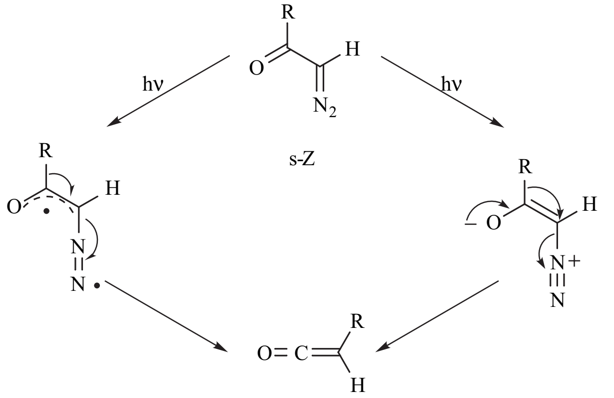
Neglecting any differences in the molar extinction coefficients, photoexcitation should produce (*s-E*)* and (*s-Z*)* α-diazoketones in the ratio as they are present before light absorption. The ratio *s-E*/*s-Z* could be influenced in the photochemical process by superimposition of a light-induced *cis-trans*-like isomerisation. Both excited conformers have more than enough internal energy to undergo elimination of



Scheme 25. Thermal (a) and photochemical Wolff rearrangement (b). OC1 = directly formed α-oxocarbene, OX = oxirene, OC2 = α-oxocarbene obtained by oxygen shift, K = ketene.

N_2 under formation of α-oxocarbenes. In the excited *s-Z* conformation a concerted Wolff rearrangement can compete with the production of α-oxocarbenes. The amount of migrated oxygen increases upon photolysis at shorter wavelength (254 vs. > 290 nm) [28]. This may be explained by an enhanced formation of the α-oxocarbene (precursor of oxirene) from (*s-Z*)* as the higher energy route relative to the concerted rearrangement.

In the valence bond language, the singlet excited state of α-diazoketones may be characterised by a larger adjunct of the more polar resonance structure. In this structure the N_2 unit has diazonium character and, therefore, N_2 elimination is facilitated. It seems within allowed chemical reasoning to assume, that the detachment of N_2 and the backside attack of R possible in the excited *s-Z* conformation occurs to a large extent synchronously to the debit of the α-oxocarbene formation and, thus, the oxirene route. A similar explanation has been put forward including the intervention of diradical structures to account for the excited state rearrangement [33] (Scheme **26**).

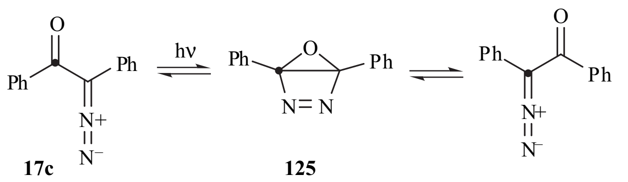


Scheme 26. Concerted rearrangement in singlet excited α-diazoketones.

EXPERIMENTAL EXCLUSION OF ALTERNATIVE MECHANISMS FOR OXYGEN MIGRATION

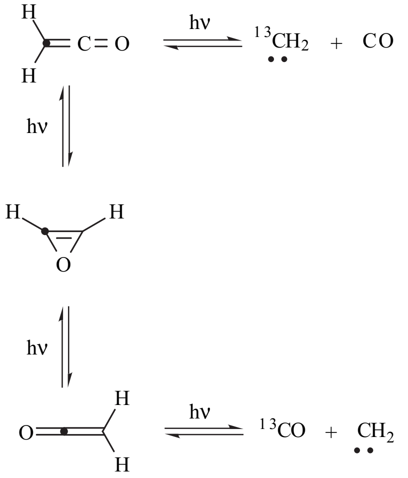
In the foregoing discussions the partial oxygen migration, detected in the Wolff rearrangement product of α-diazoketones and in the scavenging products of the involved carbenes, has been rationalised by an oxirene-mediated carbene-carbene-rearrangement. This interpretation requires a critical examination of possible alternatives for shifting the oxygen of the carbonyl group to the formerly diazo-substituted carbon of the α-diazoketones. Possible alternatives could be seen in the migration of oxygen in the starting materials (α-diazoketones) or products (ketenes) of the Wolff rearrangement and in an intermolecular oxygen transfer.

The hypothetical isomerisation of symmetrically substituted ^{13}C-labelled α-diazoketones by positional exchange of the carbonyl oxygen and the diazo group *via* the bicyclic intermediate **125** should afford labelling scrambling in the recovered starting product (Scheme **27**). This could be excluded for the photolysis of [carbonyl-^{13}C]azibenzil (**17c**) [62]. Similarly, in the case of unsymmetrically substituted α-diazoketones, this reaction sequence should produce the corresponding isomer.

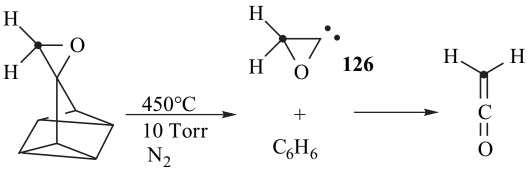


Scheme 27. Hypothetical photo-induced labelling distribution in the photolysis of azibenzil.

In gas phase experiments, it has been demonstrated that labelled ketene suffers from a photo-induced (308, 351 nm) labelling scrambling in competition to photodissociation [63]. Chemically activated ketene, obtained by reaction of singlet methylene with carbon monoxide, gives a similar scrambling [64]. It is supposed that the ketene automerisation involves oxirene as intermediate (Scheme **28**). Oxiranylidene (**126**) can be ruled out as intermediate. Its independent generation results in ketene, which shows no intramolecular carbon atom exchange [65a] (Scheme **29**). Matrix isolation experiments also confirm that **126** rearranges to ketene without intervention of oxirene [65b].



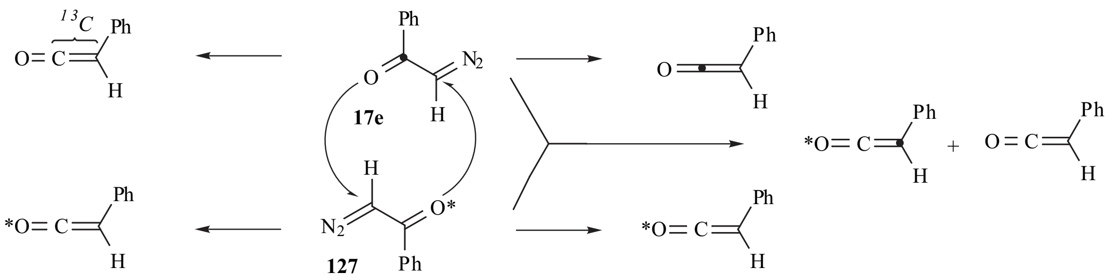
Scheme 28. Gas phase automerisation of ketene.



Scheme 29. Generation and rearrangement of oxiranylidene (**126**).

Ketene automerisation could result in an overestimation of the contribution of a carbene-carbene interconversion, when the carbon-labelling test is applied. The ratios of scavenging products of the isomeric α-oxocarbenes (*e.g.* enones) are, however, not affected by ketene automerisation.

Solution photolysis of a series of labelled, isomeric α-diazoketones shows that scrambling in ketenes cannot contribute to a marked extent under these conditions [28]; *e.g.* from the isomeric pair [1-^{13}C]2-diazo-1-oxo-1-phenylpropane (**17f**) and [2-^{13}C]1-diazo-2-oxo-1-phenylpropane (**18f**) (p 295) labelled methyl-phenylketene is obtained with 61% and 3% scrambling, respectively. From a pronounced degree of scrambling in the ketene stage values situated closer together should be expected. In gas phase



Scheme 30. Labelling distribution to be expected in the photolysis of a mixture of [carbonyl-^{13}C]diazoacetophenone (**17e**) and [^{18}O]diazoacetophenone (**127**) with (right hand side) and without (left hand side) accompanying intermolecular oxygen transfer.

experiments the ketene automerisation process may, however, have some implication.

The tests utilised to unravel partial oxygen migration in the Wolff rearrangement do not differentiate between intra- and intermolecular routes of oxygen transfer. Intermolecular reactions between two α-oxocarbenes can be ruled out, as their life times are in the nanosecond range [66] and, thus, the stationary concentrations of carbenes are extremely low. An intermolecular transfer of the carbonyl oxygen to the formerly diazo substituted carbon of a second α-diazoketone molecule, however, could occur in bimolecular reactions between two α-diazoketones or between an α-oxocarbene and an α-diazoketone. The involvement of such processes can be made visible by a cross-over experiment between isotopomeric ^{13}C-labelled and ^{18}O-labelled α-diazoketones. A corresponding study has been carried out with the isotopomeric pair **17e**/**127** of diazoacetophenone [67] (Scheme **30**).

The careful mass spectrometric analysis of the ketene scavenging product with water (phenylacetic acid) clearly excludes the formation of [^{13}C,^{18}O]phenylketene and a corresponding amount of unlabelled ketene, which exempts us from the troublesome discussion of possible intermolecular mechanisms.

In summary, none of the considered alternatives to the oxirene-mediated α-oxocarbene-α-oxocarbene interconversion endured experimental examination.

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