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# Photochemical transformations of diazocarbonyl compounds: expected and novel reactions

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Photochemical reactions of diazocarbonyl compounds are well positioned in synthetic practice as an efficient method for ring contraction and homologation of carboxylic acids and as a carbene generation method. However, interpretation of the observed transformations of diazo compounds in electronically excited states is incomplete and requires a careful study of the fine mechanisms of these processes specific to different excited states of diazo compounds resorting to modern methods of investigation, including laser technology. The review is devoted to analysis of new data in the chemistry of excited states of diazocarbonyl compounds.
The bibliography includes 155 references.

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## I. Introduction

The energy obtained by a molecule upon electronic excitation can be consumed not only in chemical reactions but also in physical processes such as non-radiative deactivation, luminescence and energy transfer. If these processes are also covered in a discussion of chemical transformations, then, according to A N Terenin,[1] this research area should be called photonics. The present review is devoted to the proper photochemical reactions, in particular, light-induced reactions of diazocarbonyl compounds. According to the views formulated by Turro *et al.*,[2,3] a photochemical transformation can be split into three steps: (i) energy absorption step giving rise to electronically excited states (ES); (ii) primary photochemical processes involving the ES; and (iii) secondary reactions of various chemical compounds formed in the primary processes; these secondary reactions can be both light-independent (thermal) and light-induced if the products formed in the primary process absorb light of the radiation source used (and, hence, they are active under irradiation conditions). Therefore, in the review, we consider some thermal reactions of diazocarbonyl compounds if it is necessary for comparison or explanation of the formation of final transformation products.

Back in the 1960s, Kasha[4,5] demonstrated that the lower singlet and lower triplet ES play the crucial role in the transformations of organic compounds. At approximately the same time, the non-radiative energy transfer[6] and photosensitization[7] were studied and their role in photochemical processes was demonstrated. As has already been noted, this review does not consider the excited state physics,[2] but the Kashi rule is mentioned to put emphasis on those ES and those processes that are important for understanding of the discussed material.

For mechanistic studies of photochemical reactions, of prime importance was the advent of lasers and pulse photolysis technique.[8–10] The development of this method with the use of nanosecond and picosecond laser pulses made it possible to identify intermediates and to study directly the mechanisms and kinetics of photoreactions using various methods (IR, UV/Vis and Raman spectroscopy, mass spectrometry, EPR and so on).

Among light-sensitive organic compounds, diazocarbonyl compounds occupy a special place. As a rule, they are stable and convenient for experimental use. In organic

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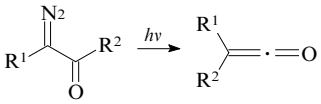
synthesis, they serve for ring contraction, for preparation of acid homologues and, most often, as synthons in the carbene reactions. However, the interpretation of the involved transformations of diazo compounds is often missing.

In recent decade, three reviews on the chemistry [11] and photochemistry of diazocarbonyl compounds [12, 13] were published; they were mainly concerned with the Wolff rearrangement and reactions of photochemically generated carbenes. Our review is devoted to analysis of new data in this area. The transformations of diazocarbonyl compounds with nitrogen elimination include rearrangements and carbene formation. The isomerization to diazirines and reactions with hydrogen donors were assigned to the second group of reactions. The latter reaction is new for the chemistry of the ES of diazo compounds; therefore, it received particular attention.

## II. Wolff rearrangement: use in the organic synthesis and mechanism

The Wolff rearrangement of α-diazoketones, sometimes called the Wolff–Schröter rearrangement, which has been known for more than a century, consists in elimination of a nitrogen molecule and 1,2-nucleophilic migration of the α-substituent at the carbonyl group to the carbon atom that bears the leaving diazo group (the ketene thus formed readily reacts with nucleophilic reagents to give carboxylic acid derivatives) (Scheme 1).[14–17]

**Scheme 1**



Initially, this rearrangement was mainly used to prepare homologues of carboxylic acids; it was the key step of the Arndt–Eistert synthesis.[18–20]

In the 1940–1950s, Süs [21–23] and Horner *et al.*[24, 25] demonstrated the advantages of the photolytic conduction of this reaction and the possibility of its extensive use for ring contraction, despite the relatively low yields of strained four-membered rings.

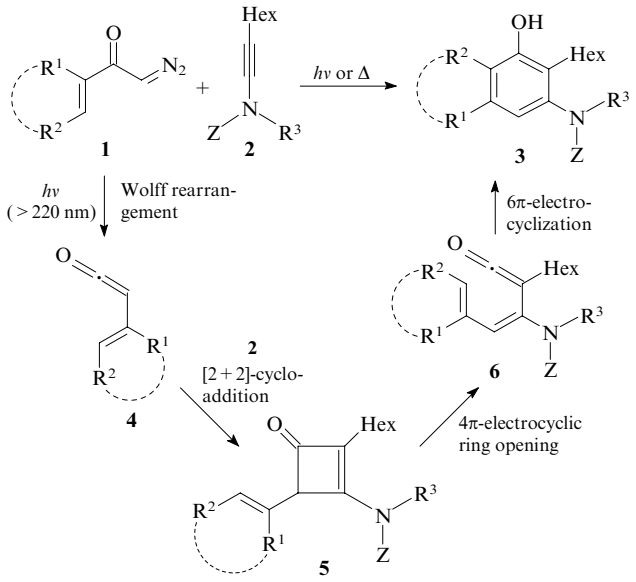
The first review dealing with the Wolff rearrangement [26] published in *Russian Chemical Reviews* in 1967 demonstrated the obvious interest in this process.

In the subsequent decades, the attention to the Wolff rearrangement ever increased.[27] This is caused by the vigorous development of research in the chemistry of diazocarbonyl and diazodicarbonyl compounds, which was stimulated by the extensive use of new catalysts in organic synthesis and by the development of organic photochemistry and ES chemistry as a whole,[28–32] first of all, by the advent of new investigation methods in organic chemistry, in particular, laser techniques.[33, 34]

### II.1. Cascade and tandem reactions comprising the Wolff rearrangement

The use of the benzannulation–cyclization tandem reaction based on the photochemical or thermal Wolff rearrangement of α,β-unsaturated diazoketones enabled the synthesis of a large number of fused nitrogen-containing heterocyclic compounds. For example, diazoketones **1** and ynamides **2** react to give aniline derivatives **3** (Scheme 2).[35]

**Scheme 2**

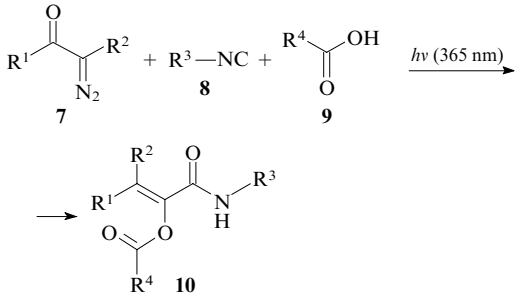


$R^1–R^2 = (CH_2)_4$, benzo; $R^3$ = Me, Bn; Z = $CO_2Me$, $P(O)(OEt)_2$, $SO_2C_6H_4Me$-4; Hex = n-$C_6H_{13}$

On exposure to light ($\lambda$ > 220 nm), diazoketones **1** form vinyl ketenes **4**, which then undergo, under irradiation, the regioselective [2+2]-cycloaddition with ynamides **2**. Under the same conditions, electrocyclic ring opening of the cyclobutenone **5** formed takes place to afford dienyl ketenes **6**, which are finally converted to polysubstituted aniline derivatives **3** upon fast ring closure and tautomerization. Certainly, this benzannulation reaction would smoothly proceed not only with α,β-unsaturated diazoketones of type **1** but also with diazocarbonyl compounds containing aryl and hetaryl moieties.

A multicomponent reaction of ketenes formed upon the photoinduced Wolff rearrangement from diazoketones **7**, isocyanides **8** and carboxylic acids **9** was reported by Basso and co-workers [36] as a preliminary result concerning the synthesis of 2-acyloxyacrylamides **10** (Scheme 3).

**Scheme 3**



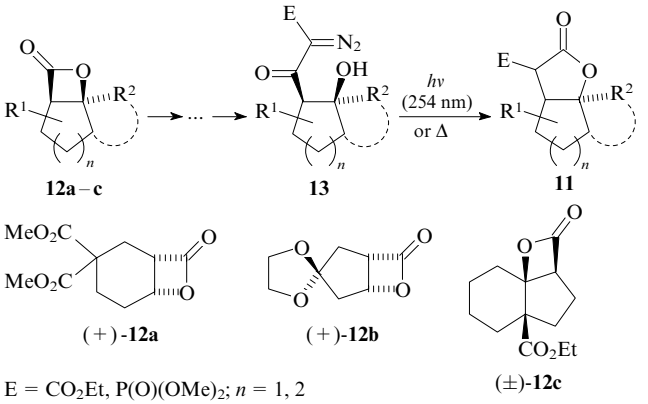
$R^1$ = $CH_2CH_2Cl$, Ph, $C_6H_4Cl$-4, 2-2-thienyl; $R^2$ = H, Me;
$R^3$ = $Bu^n$, $Bu^t$, cyclo-$C_6H_{11}$, $CH_2CH(OMe)_2$;
$R^4$ = Et, $Pr^n$, Bn, $CH_2C_6H_4OMe$-3, penta-1,3-dienyl

For the preparation of ketenes, the authors initially chose a method that implied the use of the metal-catalyzed Wolff rearrangement of the starting aryl diazoketones **7**, in particular, conduction of the multicomponent reaction in the presence of silver benzoate. However, diazoketones **7**

did not react under these conditions. Only UV irradiation ($\lambda$ = 365 nm) of the three-component reaction mixture did result in the desired 2-acyloxyacrylamides **10** in up to 78% yields.

Zhang and Romo [37] reported a two-step modification of the synthesis of γ-lactones **11** from β-lactones **12a – c**, comprising the transformation of the latter into δ-hydroxy-α-diazo-β-ketoesters **13** upon bond cleavage in the starting lactone **12**. The subsequent tandem process comprising the Wolff rearrangement and lactonization of α-diazo intermediate **13** gives *cis*-fused γ-lactones **11** under photolytic ($\lambda$ = 254 nm) or thermal (110 °C) conditions in good yields (Scheme 4).

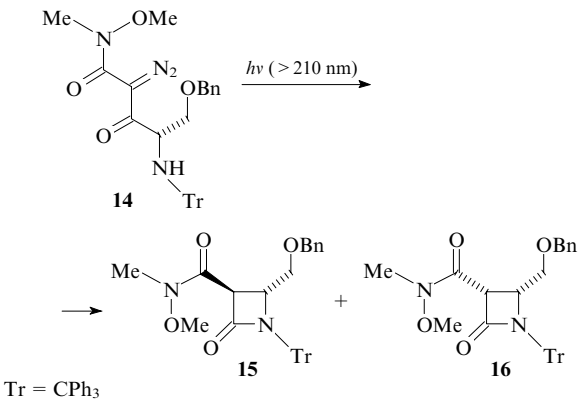
**Scheme 4**




## II.2. The use of the Wolff rearrangement in the stereoselective synthesis and in chemoselective reactions

Photolysis of *N*-methyl-*N*-methoxy-(*S*)-5-(benzyloxy)-2-diazo-3-oxo-4-(tritylamino)pentanamide (**14**), obtained from a derivative of the enantiomerically pure α-amino acid L-serine, on exposure to the light of a medium-pressure mercury lamp ($\lambda$ > 210 nm) or a compact luminescent lamp (100 W) gives the corresponding enantiomerically pure *N*-methyl-*N*-methoxy-(2*R*,3*S*)- (**15**) and *N*-methyl-*N*-methoxy-(2*R*,3*R*)-2-(benzyloxymethyl)-4-oxo-1-tritylazetidine-3-carboxamides (**16**) upon the intramolecular Wolff rearrangement (Scheme 5).[38] This reaction is stereoselective and gives predominantly *trans*-lactam **15** as the thermodynamically more stable product, although the *cis*- and *trans*-product ratio can vary, probably depending on the reaction temperature. It was found that on heating of the diastereomer mixture in toluene, epimerization of β-lactam **16** to *trans*-isomer **15** takes place.

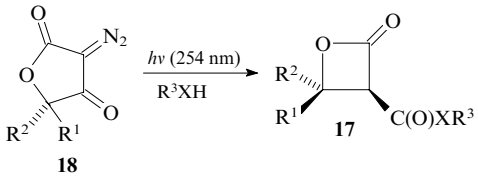
**Scheme 5**




The transformations observed here might start on the potential surface of the ES and then involve the upper vibrational levels of the ground state, *i.e.*, these are diabatic processes. This is indirectly supported [39] by examples of similar transformations accomplished thermally. A convenient method for the preparation of adamantyl-substituted β-lactams by the Staudinger reaction from various imines and adamantyl ketenes (the latter are generated from appropriate diazoketones by the thermal Wolff rearrangement) was reported.[40] The reaction mainly gives more stable *trans*-isomers.

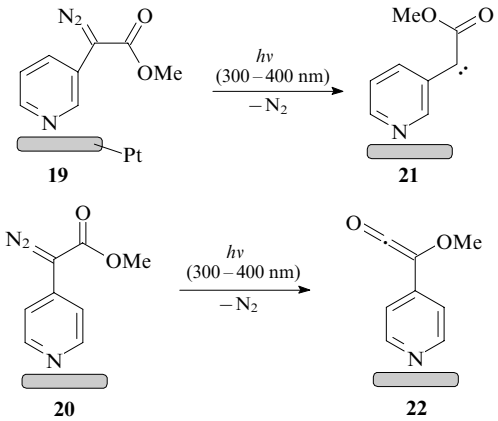
Beneke and Schobert [41] proposed a convenient method for the preparation of *trans*-3,4-disubstituted β-lactones **17**. They demonstrated that on short-wavelength irradiation, 3-diazofuran-2,4(3*H*,5*H*)-diones **18** rearrange with retention of the configuration of the migrating carbon atom. In the presence of alcohols or thiols, this gives 3-(alkoxycarbonyl)- or 3-[(alkylsulfanyl)carbonyl]-β-lactones exclusively in the *trans*-configuration (Scheme 6).

**Scheme 6**




An interesting article dealing with the chemoselective photochemical Wolff rearrangement on the platinum surface was published by Workentin and co-workers [42] (Scheme 7). The irradiation of saturated monolayers of methyl 2-diazo-2-(3-pyridyl)acetate (**19**) and 2-diazo-2-(4-pyridyl)acetate (**20**) on a single-crystalline platinum surface affords either the corresponding reactive (3-pyridyl)methoxycarbonylcarbene (**21**) or a stable intermediate — 2-methoxy-2-(4-pyridyl)ethen-1-one (**22**). The chemoselectivity of the reaction is determined by the position of the photosensitive substituent in the pyridine ring.

**Scheme 7**

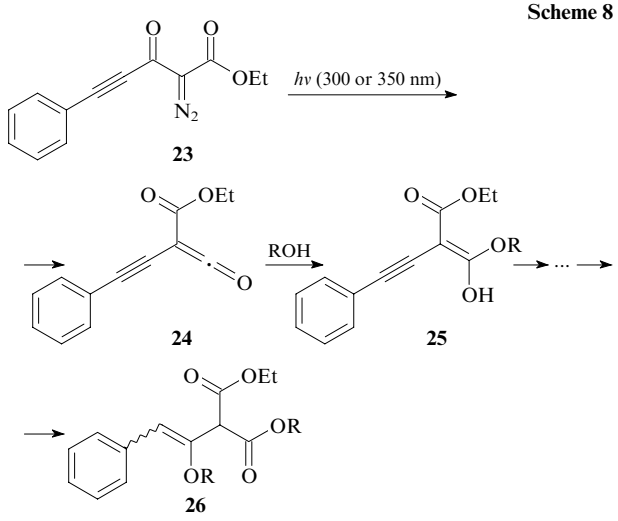


Under the experimental conditions, photolysis of a saturated monolayer of compound **19** affords carbene **21**, which then reacts with either another molecule of diazoester **19** or similar carbene **21** to give azine or alkene. The stereochemistry of the carbene derived from compound **20** precludes a bimolecular reaction within the monolayer; therefore, although unfavourable, the Wolff rearrangement

takes place as migration of the methoxy group to give ketene **22**. The authors note that it is the platinum surface that allows detection of these reactive intermediates, which can usually be detected only in Ar matrices.

Exposure of ethyl 2-diazo-3-oxo-5-phenylpent-4-ynoate (**23**) to light at 300 or 350 nm induces the efficient and regioselective Wolff rearrangement to give the only product resulting from alkynyl group migration — ethyl 2-oxomethylidene-4-phenylbut-3-ynoate (**24**) (Scheme 8).[43] When an alcohol is added to the reaction mixture, ketene **24** is converted to ethyl (*Z*)-2-[alkoxy(hydroxy)methylidene]-4-phenylbut-3-ynoate (**25**), which tautomerizes and reacts with a second alcohol molecule to give the final product, 2-(1-alkoxy-2-phenylvinyl)malonic ester (**26**).

**Scheme 8**




R = Me, Et, Pr$^i$

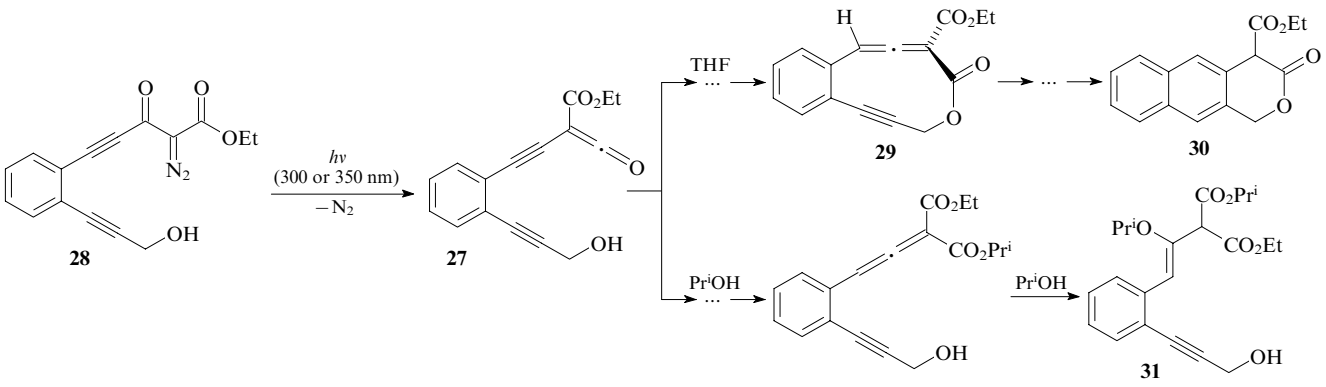
The intramolecular version of this reaction was used for cyclization of ethyl 4-[2-(3-hydroxyprop-1-yn-1-yl)phenyl]-2-oxomethylidenebut-3-ynoate (**27**), which arises upon irradiation of the starting ethyl 2-diazo-5-[2-(3-hydroxyprop-1-yn-1-yl)phenyl]-3-oxopent-4-ynoate (**28**) (Scheme 9). The cyclization occurs as the intramolecular reaction between the hydroxyl group and the ketene group of diacetylene **27** and gives highly reactive enyne-allene **29**. The Myers – Saito cyclization of **29** furnishes the final product — ethyl 3-oxo-3,4-dihydro-1*H*-benzo[*g*]isochromene-4-carboxylate (**30**).

Whereas this synthetic strategy performs well in aprotic media (THF or a THF – hexane mixture), in protic solvents (water, alcohols), the intramolecular reaction of ketene **27** competes with the nucleophilic addition of a solvent molecule, resulting, for example, in 3-isopropyl 1-ethyl 2-{2-[2-(3-hydroxyprop-1-yn-1-yl)phenyl]-1-isopropoxyvinyl}malonate (**31**) (see Scheme 9).[43]

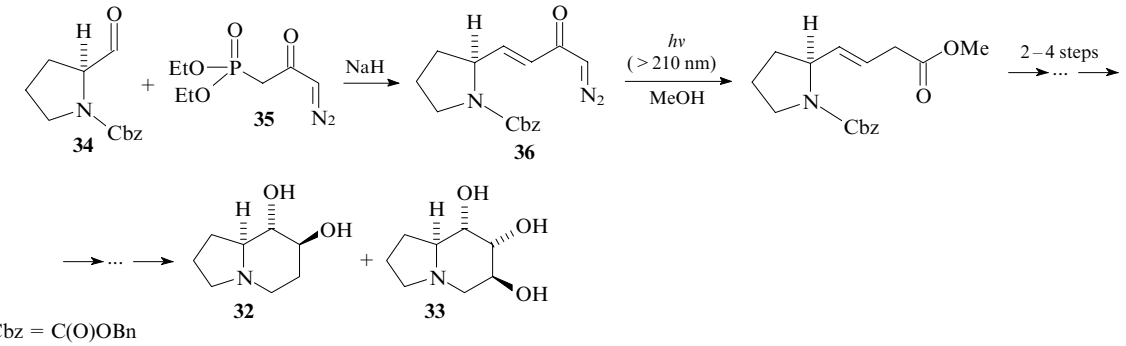
## II.3. Wolff rearrangement as a key step in the total synthesis of natural products

The photochemical Wolff rearrangement has found use in the total syntheses of some alkaloids and in the syntheses of many other biologically active compounds. Burtoloso and co-workers[44, 45] presented a versatile approach to the stereoselective synthesis of di- and trihydroxylated indolizidines, (7*S*,8*S*,8a*S*)-octahydroindolizine-7,8-diol (**32**) and (6*S*,7*R*,8*S*,8a*S*)-octahydroindolizine-6,7,8-triol (**33**), potential α- and β-glycosidase inhibitors, from benzyl (2*R*)-2-formylpyrrolidine-1-carboxylate (**34**) and diethyl (3-diazo-2-oxopropyl)phosphonate (**35**) (Scheme 10). The Wolff rearrangement of benzyl (*S*,*E*)-2-(4-diazo-3-oxobut-1-en-1-yl)pyrrolidine-1-carboxylate (**36**) is the key step of the synthesis, which is followed by dihydroxylation and epoxidation steps.

**Scheme 9**

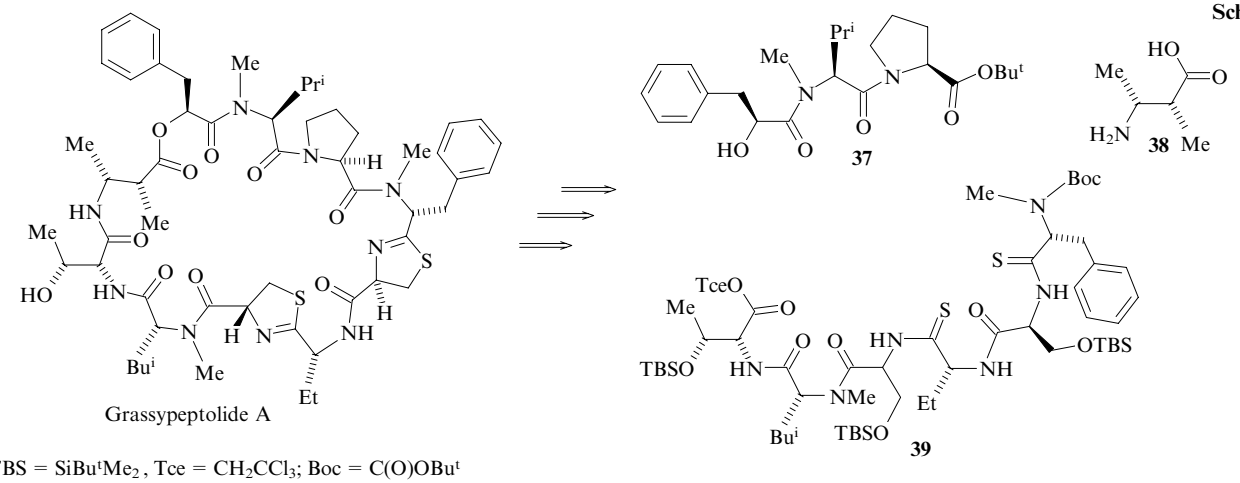



**Scheme 10**




Cbz = C(O)OBn

**Scheme 11**




TBS = $SiBu^tMe_2$, Tce = $CH_2CCl_3$; Boc = $C(O)OBu^t$

Mascitti and Corey[46, 47] carried out a six-step synthesis of (±)-pentacycloanammoxic acid — the principal component of the membranes of anaerobic ammonia oxidizing bacteria. One of the stages of this process was the photoinduced Wolff rearrangement of ladderane containing a diazocarbonyl group. The reaction was carried out in methanol in the presence of triethylamine. The mixture of *exo*- and *endo*-methyl esters thus formed was then converted to the corresponding aldehyde, which was subjected to further transformations. In another paper, Snyder and Corey[48] proposed an efficient method for the preparation of biologically active marine natural products of the dolabellane type, namely, β-araneosene, dolabellatrienone and palominol. The key step of this synthesis was ring contraction, which took place on irradiation of α,β-unsaturated diazoketone in alcohol.

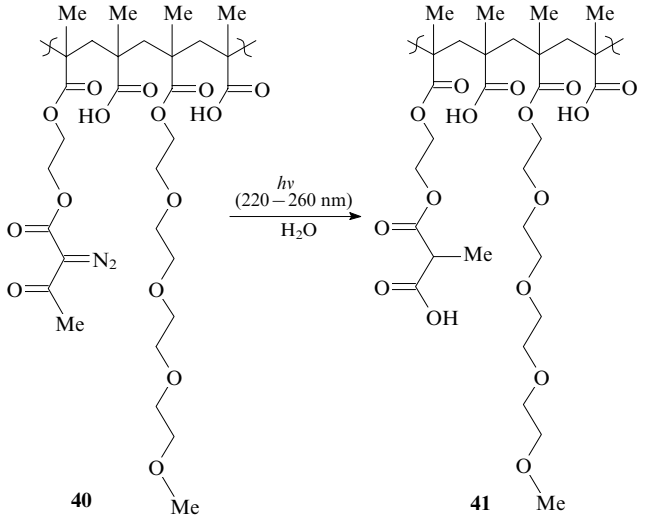
One cannot but mention the 17-step method reported quite recently for the synthesis of Grassypeptolide A, a potential anticancer cyclodepsipeptide (Scheme 11).[49] Grassypeptolide A consists of a number of unique, non-proteinogenic amino acid residues such as 3-amino-2-methylbutyric acid, 2-aminobutyric acid and several D-amino acids and N-methylated amino acids. The final product was synthesized from three initial compounds — the *tert*-butyl ester of *N*-[(*S*)-2-hydroxy-3-phenylpropanoyl]-*N*-methyl-L-valyl-L-proline (**37**), (2*R*,3*R*)-3-amino-2-methylbutyric acid (**38**) and compound **39**. Amino acid **38** was prepared from *N*-Cbz-D-alanine *via* a sequence of three reactions — direct diazo transfer, Wolff rearrangement under UV irradiation and stereoselective methylation.

Other examples of using the photochemical Wolff rearrangement in the total synthesis of natural and biologically active compounds are the 19-step synthesis of the antibiotic (+)-Acanthodoral[50] and the preparation of the marine cytotoxic cyclic depsipeptide Obyanamide[51] and tetracyclic β-carboline alkaloid (*R*)-(+)-Harmicine.[52, 53]

## II.4. Applied aspects of using the Wolff rearrangement

Kim and co-workers[54] reported on the biocompatible and pH-sensitive photoresist **40** containing diazoketo-functionalized methacrylate, methacrylic acid and poly(ethylene glycol)methacrylate monomers for the photolithographic process with a minimum denaturation of biomolecules (Scheme 12). The polymer is poorly soluble in acidic solutions at pH ⩽ 6.4 but is readily soluble in alkaline solutions at pH ⩾ 7.9.

**Scheme 12**

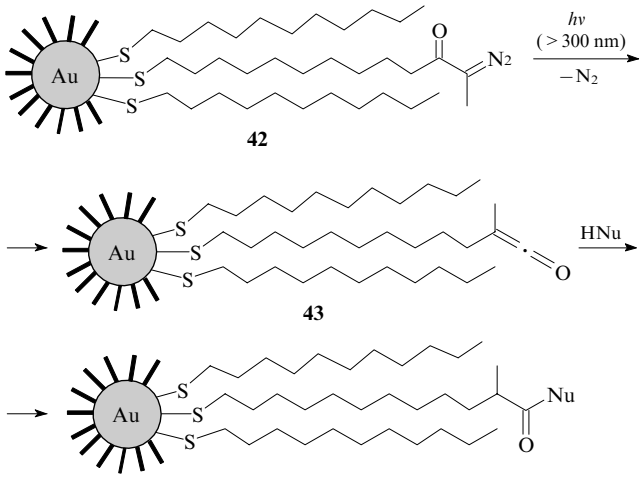



Upon UV radiation, the Wolff rearrangement gives rise to a carboxyl group instead of the diazoketo group, which makes new polymer **41** readily soluble also at pH 6.4. The resulting photoresist system does not release potentially hazardous side products upon photolysis, has high light sensitivity and pH-switching ability, so it is promising for the use in biology.

One more potential photoresist is the photoactive polymer containing aryl-substituted diazoketo groups.[55] Upon irradiation at 365 nm, as in the previous case, the diazocarbonyl moieties undergo the Wolff rearrangement to give intermediate ketenes, which then react with water to give carboxylic acids.

Gold nanoparticles (Au-NP) **42** modified with diazocarbonyl compounds serve as stable precursors for the preparation of the reactive 'surface ketene – Au-NP' phase transfer system **43**, which is formed in a quantitative yield upon the Wolff rearrangement under UV activation (Scheme 13).[56]

**Scheme 13**




The subsequent reaction of ketene **43** with nucleophiles (Nu) can serve for functionalization of Au-NP and, as a consequence, for inclusion of many biological substrates into its structure. The same strategy can be used for modification of surfaces of other nanoparticles with diazoketones — ketene precursors.

In another case,[57] both photolysis and thermolysis of polymers attached to the $SiO_2$ surface and containing α-diazoesters give carbenes rather than ketenes; when the carbenes insert into C—H bonds of neighbouring polymer chains. Polymer cross-linking gives surface-grafted polymer networks, which can possess various physical and chemical properties depending on the nature of the initial substrates.

Thus, the presented data illustrate various practical applications of the Wolff rearrangement: the synthesis of lactones of various types and a broad range of nitrogen-containing heterocyclic structures. The final products are often formed in light-independent (dark) reactions, although ketenes, which are the starting compounds of these reactions, are produced in light-induced reactions.

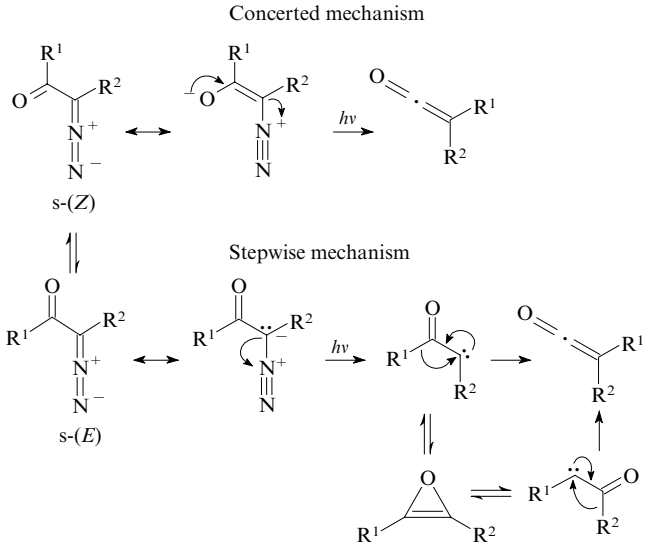
It is noteworthy that the use of photolysis is especially promising for stereoselective transformations, first of all, for the synthesis of natural and biologically active compounds. The success of practical application of the Wolff rearrangement in photolithography has been known for a long time. In recent years, the diazocarbonyl compounds have started to be widely used for surface modification of gold nanoparticles and polymeric materials.

## II.5. Mechanism of the Wolff rearrangement

The mechanism of the rearrangement discovered more than a hundred years ago by Wolff[14,15] and later implemented by Schröter[16,17] is still the subject of numerous debates. Depending on the molecular and spatial structure of diazocarbonyl compounds, the concerted and stepwise mechanisms can compete with each other.[26,27,29,30,58,59]

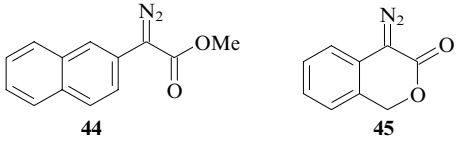
Open-chain (acyclic) α-diazocarbonyl compounds exist as equilibrium mixtures of two conformers, s-(*Z*) and s-(*E*), the contribution of which can considerably affect the reaction pathway. In 1966, Kaplan and Meloy[60] found that during the photolysis of diazo compounds with s-(*Z*)-configuration (*e.g.*, in the case of cyclic diazocarbonyl compounds), the concerted Wolff rearrangement takes place owing to the antiperiplanar arrangement of the leaving and migrating groups, whereas s-(*E*)-configured compounds (open-chain analogues) do not rearrange but decompose in several steps with intermediate formation of carbenes and/or oxirenes (Scheme 14).

**Scheme 14**




For identification of ketenes formed upon the Wolff rearrangement, Toscano and co-workers[61,62] used nanosecond time-resolved IR spectroscopy. While analyzing the reaction mixtures obtained upon photolysis of $^{15}N$-labelled methyl 2-diazo-(2-naphthyl)acetate (**44**) and 4-diazoisochroman-3-one (**45**), they detected strong absorption bands at 2100 $cm^{-1}$ (ketene stretching modes $\nu_{C=C=O}$).

**Structures 44, 45**



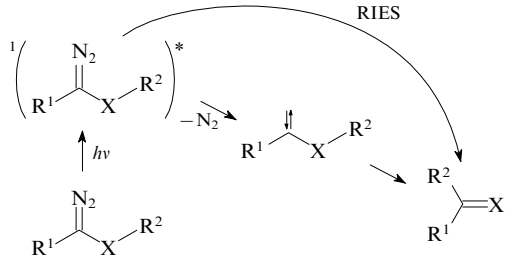

The photoexcitation of diazoester **44** induces its decomposition by a stepwise mechanism, as indicated by an absorption band for singlet carbene (1650 $cm^{-1}$) appearing in the IR spectrum; the intensity of this band decreases on long-term irradiation in direct proportion with the increase in the intensity of the ketene absorption band (2096 $cm^{-1}$). This result is in good agreement with Kaplan's rule, because quantum chemical calculations indicate that ester **44** exists almost entirely (by 99%) in the s-(*E*)-configuration.[63]

In the case of cyclic analogue **45** possessing fixed s-(*Z*)-configuration, pulse nanosecond photolysis induces a sharp increase in the ketene absorption band (2116 $cm^{-1}$) in the IR spectrum. The authors[62] suggest that the ketene is formed by a concerted mechanism from the singlet ES of diazoester **45**.

However, modern femtosecond time-resolved UV and IR spectroscopic measurements demonstrate that unambiguous determination of the Wolff rearrangement mechanism relying on the substrate structure alone is impossible. A number of experimental[64–70] and theoretical[71–73] studies were devoted to the Wolff rearrangement mechanism of cyclic diazoketones, particularly, diazonaphthoquinones (DNQ), which are used in photoresists for photolithogra-

phy. The results confirm the coexistence of the concerted and stepwise processes, including the intermediate carbene formation.[70] Indeed, carbene generation was detected 8 ps after the start of the excitation and was confirmed by reactions with traps (alcohols), which attests in favour of a stepwise mechanism.[74] However, in a recent femtosecond time-resolved spectroscopic study,[70] the IR spectrum was shown to exhibit an absorption band for ketene, which was formed 300 fs after the onset of irradiation ($\lambda$ = 400 nm) upon the Wolff rearrangement of the starting DNQ in the excited state (RIES)[75] (Scheme 15).

**Scheme 15**



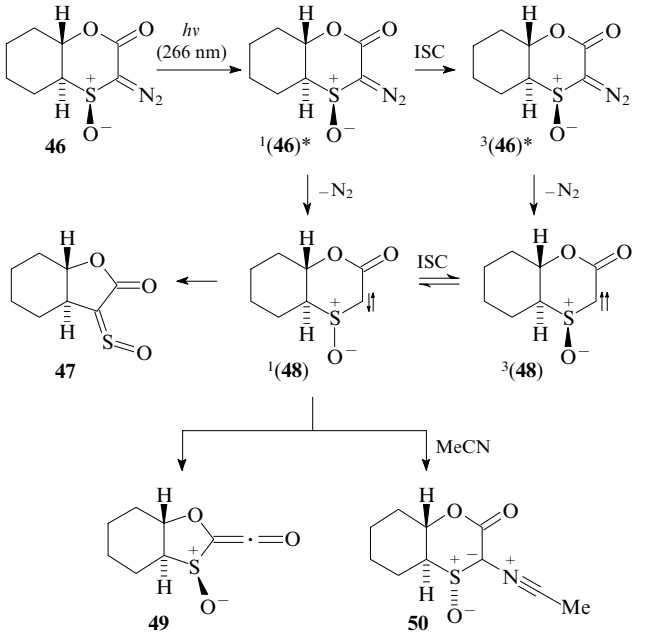

Similar results indicating the coexistence of two mechanisms of the Wolff rearrangement were also obtained for the non-fused DNQ analogue — diazocyclohexadienone.[76]

Most of detailed studies were carried out for the transformations of another diazoester — 5-diazo-2,2-dimethyl-4,6-dioxo-1,3-dioxane (diazo Meldrum's acid, DMA), in the ES. For DMA, thermolysis and photolysis experiments in various media[77–85] and matrix photoreactivity measurements[86,87] were carried out. Laser ablation of DMA-doped polymers was performed.[88,89] Popik and co-workers[81,82,90] elucidated the potential energy surfaces, while Platz, Burdzinski and co-workers[91–94] investigated the dynamics of ultrafast processes in the liquid phase, for which Nuernberger, Brixner and co-workers[95,96] considered later the consecutive reactions involving the solvent molecules. However, it was only recently[95] that the data indicating the coexistence of the stepwise and concerted mechanisms of the Wolff rearrangement for this diazodiester were obtained.

Equally ambiguous conclusions on the mechanism of this rearrangement were also made for some acyclic diazoketones, diazoesters and diazoacetamides. Photolysis of diazoacetone,[92] *N*-(diazoacetyl)azetidine and *N*-(diazoacetyl)pyrrolidine[97] gives ketenes by a concerted mechanism and gives methyl α-biphenyl-α-diazoacetate[94,98] by the stepwise mechanism, and upon irradiation of azibenzil[92] and α-biphenyl-α-diazoacetone,[93] the reaction follows two parallel pathways.

An interesting example of the stepwise hetero-Wolff rearrangement involving the intermediate formation of carbenes was reported by Buche and co-workers,[99] who studied the photochemistry of (4a*S*,8a*S*)-3-diazo-4-($\lambda^1$-oxidanyl)octahydro-2*H*-4$\lambda^3$-benzo[*b*][1,4]oxathiin-2-one (**46**) using nanosecond time-resolved laser flash photolysis and resorting to quantum chemical calculations (Scheme 16). The spectroscopic results obtained attest to the very rapid (unresolvable) formation of (3a*S*,7a*S*)-3-(oxo-$\lambda^4$-sulfanylidene)hexahydrobenzofuran-2(3*H*)-one (**47**) (90%) and the triplet carbene $^3$(**48**) (10%). According to calculations, the latter undergoes intersystem crossing (ISC) to singlet carbene $^1$(**48**), which subsequently either rearranges to sulfine **47** or to [(3*S*,3a*S*,7a*S*)-3-oxidohexahydro-2*H*-benzo[*d*][1,3]-oxathiol-2-yidene]methanone (**49**) or reacts with an acetonitrile molecule to give *N*-{(4a*S*,8a*S*)-4-($\lambda^1$-oxidanyl)-2-oxohexahydro-2*H*-4$\lambda^3$-benzo[*b*][1,4]oxathiin-3(4*H*)-ylidene}-ethan-1-ideiminium (**50**) (see Scheme 16).

**Scheme 16**




Thus, the available data concerning the Wolff rearrangement mechanism provide the conclusion that both reaction pathways coexist: some molecules of diazo compounds rearrange without formation of intermediates, while the other molecules undergo a two-step transformation to give initially keto carbene, which actually rearranges.

However, this is only one side of the problem. The other side, which is equally significant, concerns the possible complication of the whole picture. Indeed, the initial diazo compound can isomerize to diazirine upon irradiation. This brings about the question of the possible rearrangement of this diazirine to the same ketene.

This has remained an open question until recently. However, mention may be made of the deliberate experiments carried out at the Saint Petersburg State University for cyclic diazodiketones[100] and THF-derived diazoketones,[101] which are considered in Section V.

## III. Formation of carbenes

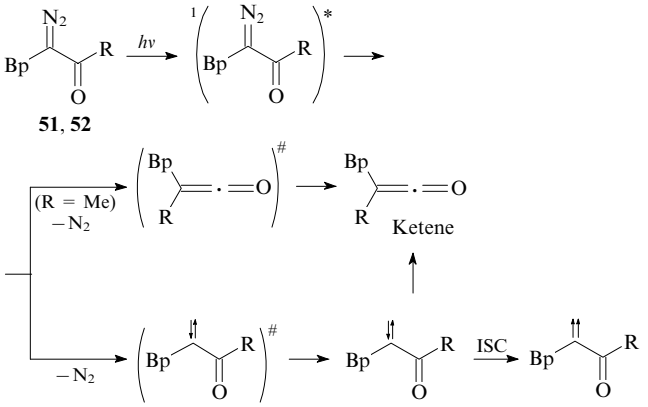
A recent review[102] of Matthew Platz, a prominent expert in the chemistry of reactive intermediates — carbenes and nitrenes[103] — integrates the accumulated data on mechanistic carbene chemistry and outlines the prospects of further research along this line. We will not dwell in detail on the results cited by the author and will consider only the most significant data concerning superfast investigation techniques of keto and alkoxycarbonyl carbenes.

Generally, photochemical decomposition of diazo compounds is one of the most general and popular methods for carbene generation. This process has been considered in detail in many fundamental monographs (see, for example, Refs 30 and 31). The 'hot' carbenes thus formed often

possess excess vibration energy (designated by #), which they lose upon collisions with solvent molecules. This process has a time constant of 5–30 ps and is called 'vibrational cooling'.[104] The narrowing down of the carbene absorption band (both in UV and IR spectra) and the blue shift of the absorption maximum are indicative of the 'vibrational cooling' of the vibrationally excited intermediates.[104]

In the ultrafast photolysis of 1-(biphenyl-4-yl)-1-diazopropan-2-one (**51**) ($\lambda$ = 270 nm), the expected ketene (2020 $cm^{-1}$) is formed both upon a fast process ($\tau$ < 0.4 ps) directly from the ES of diazoketone $^1$(**51**)* and upon a slower process ($\tau \sim$ 700 ps) from the relaxed singlet keto carbene (Scheme 17).[93] The 'vibrational cooling' of the ketene is confirmed by narrowing down of the characteristic absorption band and blue shift of this band to 2110 $cm^{-1}$. The 'hot' ketene is formed from the singlet ES of diazoketone $^1$(**51**)*, which decomposes in parallel to give the singlet carbene, as indicated by increasing intensity of the absorption band at 380 nm.

**Scheme 17**




R = Me (**51**), OMe (**52**); Bp is biphenyl-4-yl

Meanwhile, irradiation of methyl 2-(biphenyl-4-yl)-2-diazoacetate (**52**) ($\lambda$ = 308 nm) results exclusively in carbene generation, no fast formation of ketene from the ES of diazoester $^1$(**52**)* being detected (see Scheme 17).[98] What is the reason for this difference?

According to quantum chemical calculations, the barrier for the Wolff rearrangement of biphenyl-substituted diazoketone, which involves the intermediate formation of the singlet keto carbene, is 4.4 kcal $mol^{-1}$, while in the case of diazoester that forms alkoxycarbonyl carbene as the intermediate, this barrier is 8.9 kcal $mol^{-1}$. This fact is related to the loss of so-called 'resonance stabilization' in the ester moiety of the diazoester ES in the case of the concerted rearrangement, which decreases the heat evolution and decelerates the reaction.[105]

This is why it is more favourable for the ES $^1$[BpC($N_2$)$CO_2$Me]* to give off a nitrogen molecule to be converted to a singlet carbene ester than to undergo bond cleavage and 1,2-migration of the substituent to the carbon atom bearing the diazo leaving group, *i.e.*, the concerted rearrangement is preferred. As a consequence, diazoester **52** forms the singlet carbene with a much higher quantum yield than diazoketone **51**, exactly because of the Wolff rearrangement of the diazoketone ES $^1$[BpC($N_2$)C(O)Me]* occurring in parallel.

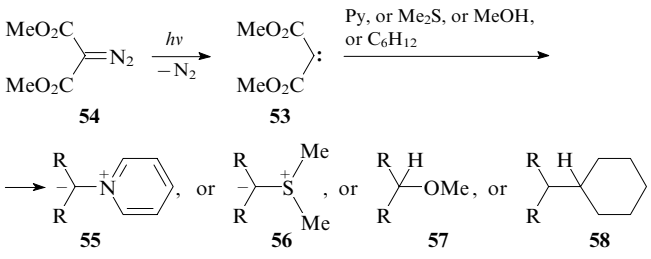
The multiplicity of methoxycarbonyl-2-naphthylcarbene (2-NaphC̈$CO_2$Me) was the subject of a number of studies carried out by research teams headed by Bally,[63] Toscano,[61] Kohler[106] and Platz.[106, 107] In the most recent works using ultrafast optical and IR spectroscopy in various solvents,[105] it was concluded that this carbene exists in the singlet ground state in acetonitrile ($\tau$ = 700 ± 30 ps) and dichloromethane ($\tau$ = 770 ± 40 ps) and in the triplet state in cyclohexane ($\tau \sim$ 2 ns); in cyclohexane, the lifetime of the singlet state is controlled by ISC. The singlet–triplet gap for 2-NaphC̈$CO_2$Me in cyclohexane is virtually zero, and, at 298 K, the two spin states exist as an equilibrium mixture in which the proportions of the components are 16% and 84%. (The ISC rate in this solvent is very low, as the singlet carbene should first transform into the conformation with higher energy, which can undergo relaxation to the triplet state.)

Unlike the alkoxycarbonyl carbene 2-NaphC̈$CO_2$Me, the situation for the phenylvinyl carbene PhCH=CHC̈$CO_2$Me is exactly the opposite. In cyclohexane, the triplet vinyl carbene does not occur in equilibration with the singlet carbene because of pronounced energy difference between them. The intramolecular cyclization of the singlet carbene to give cyclopropene derivative is a more preferable process than ISC to the triplet carbene.[108]

The intermediate carbenes can be identified not only by spectral methods. The carbene formation in the photolysis of diazo compounds can be detected by adding traps into the reaction mixture and by isolation of ylides formed upon reactions with these traps. Nikolaev and co-workers[83, 84, 109] published a number of papers dealing with the search for cyclic and acyclic dioxocarbenes and the best traps for them. It was found that under irradiation in the presence of pyridine, methanol or dimethyl sulfide (as carbene traps), 2,2-dialkyl-5-diazo-1,3-dioxane-4,6-diones mainly undergo the concerted Wolff rearrangement. The contribution of the carbene processes to the photochemical reactions of these diazodiketones depends considerably on the irradiation wavelength and on the nature of the solvent and the trap. The highest yields of the carbene-derived products — sulfonium ylides and dioxodioxanes — were obtained at $\lambda$ > 310 nm with a dimethyl sulfide trap.[83, 84]

The efficiency and the ability of various chemical molecules to function as traps for bis(methoxycarbonyl)carbene (**53**) are affected by conditions of formation of this carbene.[109] In the case of UV irradiation of dimethyl diazomalonate (**54**) at $\lambda$ > 290 nm (Pyrex filter), out of pyridine, dimethyl sulfide, methanol and cyclohexane (adducts **55**–**58**), cyclohexane proved to be the best trap (Scheme 18). On short-wavelength irradiation ($\lambda$ >

**Scheme 18**




R = $CO_2$Me; Py is pyridine

210 nm, quartz filter), the best results were found for pyridine and cyclohexane, the adducts they form (**55** and **58**) with carbene **53** being more stable under experimental conditions.

The use of alcohols as bis(methoxycarbonyl)carbene (**53**) traps is justified only when both carbene and oxoketene are formed simultaneously in the photolysis. This is quite understandable: alcohols can trap oxoketenes, yielding finally stable carboxylic acid derivatives.

Thus, the key methods to prove the formation of carbene intermediates in the transformations of diazocarbonyl compounds have now been thoroughly developed. As can be seen by examining recent publications, this is done using not only spectroscopic methods but also a purely chemical trapping technique.

## IV. Reactions of photochemically generated carbenes

According to the generally accepted views, photochemical decomposition of diazocarbonyl compounds **I** to give insertion (**II**) and reduction (**III**) products is regarded as a set of reactions involving intermediate carbenes **IV** and **V** (Scheme 19). The insertion products **II** are regarded as resulting from reactions of singlet carbene **IV**, while the reduction products **III** are attributed to reactions of triplet carbene **V**. The latter reactions are typical of sensitized photolysis.[30]

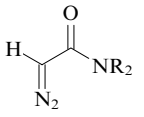
The reactions of singlet carbene are ambiguous. Apart from the formation of the insertion products into the X–H bond (**II**), it can rearrange (the Wolff rearrangement) to give ketene **VI**. [an alternative concerted mechanism of rearrangement *via* the singlet ES of diazo compound $^1$(**I**)* followed by simultaneous elimination of a nitrogen molecule and migration of the substituent at the carbonyl group is not ruled out either.[30]]

Below we consider new examples of typical transformations involving keto carbenes, in particular, 1,2-migration and cyclopropanation.

### IV.1. Formation of insertion products into the X–H bond and 1,2-migration

The results of matrix photolysis and vacuum flash thermolysis of *N*,*N*-dialkyldiazoacetamides (**59a–d**) demonstrated a clear dependence of the reaction pathway on the substrate structure.[97]

**Structures 59**



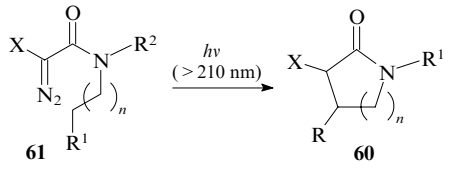
**59a–d**

R = Me (**a**), Et (**b**);
R–R = $(CH_2)_3$ (**c**), $(CH_2)_4$ (**d**)

Acyclic *N*,*N*-dialkyldiazoamides **59a**,**b** are mainly converted to β- and γ-lactams *via* intramolecular insertion of the intermediate carbenes into the C–H bonds of N-alkyl substituents. In the case of diazoamides **59c**,**d**, the inclusion of the amide nitrogen atom into the four- or five-membered ring efficiently suppresses the C–H-insertion reactions (owing to steric hindrance), which results in the formation of only ketenes upon the Wolff rearrangement. It was shown that the rearrangement involves the intermediate formation of carbenes, which react with carbon monoxide present as the carbene trap giving rise to ketenes. In the authors' opinion, this proves that the Wolff rearrangement being discussed follows, at least partly, the carbene mechanism. In our opinion, this way of proving the presence of carbene (potentially formed upon diazo compound decomposition independently of the Wolff rearrangement) is not well-posed, as the reaction with the chosen trap gives the same ketene as is formed upon the rearrangement; meanwhile, the rearrangement can be concerted, *i.e.*, it can involve no intermediate carbene formation.

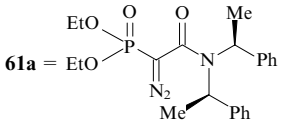
The preparation of similar β- and/or γ-lactams **60** is the subject of a publication [110] dealing with the photochemical decomposition of α-diazoacetamides **61** in hexane, water and films (Scheme 20). It was shown that in the case of

**Scheme 20**



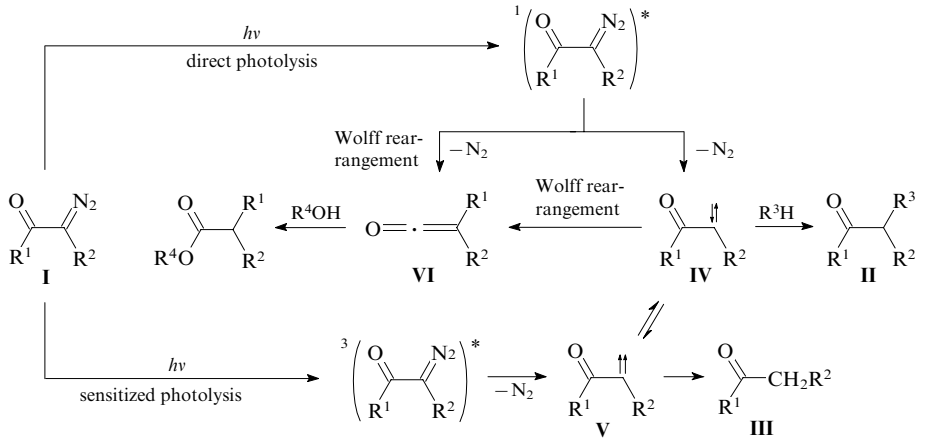
**61** **60**

X = P(O)$(OEt)_2$, $CO_2Et$, $CO_2Me$; $R^1$ = $Pr^i$, Ph, OMe;
$R^2$ = $Pr^i$, $Bu^t$, $(CH_2)_2OMe$, Ph; *n* = 0–2



**61a**

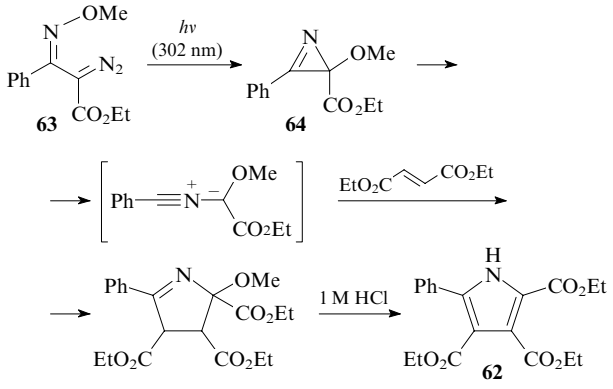
**Scheme 19**



chiral diazo substrate **61a**, intramolecular C–H insertion occurs with retention of the configuration, which rules out the intermediate formation of the triplet carbene.

The intramolecular insertion into the N–O bond, which is rather rare for carbenes generated photochemically, was used in the tandem synthesis of triethyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (**62**) (Scheme 21).[111]

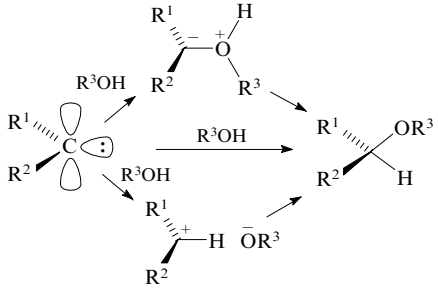
**Scheme 21**



In the first step, the authors irradiated ethyl (*Z*)-2-diazo-3-methoxyimino-3-phenylpropionate (**63**) and isolated ethyl 2-methoxy-3-phenyl-2*H*-azirine-2-carboxylate (**64**) in a high yield [for comparison, the yield of the insertion product into the N–O bond (**64**) upon thermolysis of diazo compound **63** in trifluorotoluene did not exceed 17%, and the attempts at catalytic decomposition of diazo compound **63** completely failed]. Under conditions of photolysis, azirine **64** was converted to nitrile ylide, which reacted with dipolarophiles (*e.g.*, diethyl fumarate) to give 1,3-cycloadducts — 2,3-dihydropyrroles.

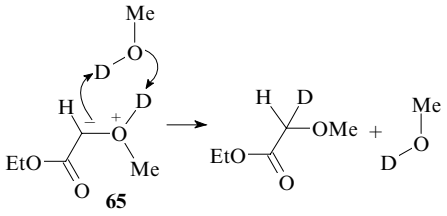
The carbene reactions with O–H substrates, *e.g.*, alcohols, can follow several mechanisms (Scheme 22). Carbenes can abstract protons from solvent molecules to give ion pairs, react with the alcohol oxygen atom to give ylides or can be inserted directly into the O–H bond.[112–114] Platz and co-workers[115] used ethyl diazoacetate and methanol-OD to directly observe for the first time the formation and decomposition of carbene alcohol ylide **65** upon ultrafast photolysis of the starting diazo ester.

**Scheme 22**



The rates of the above processes are directly proportional to the concentration of the methanol-OD molecules in acetonitrile, and the rate constants for the formation and decomposition of ylide **65** correspond to second-order kinetics because both processes involve a second methanol molecule (Scheme 23).

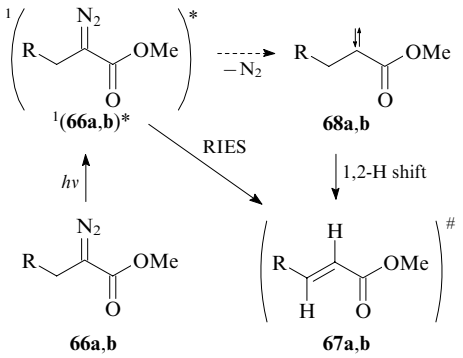
**Scheme 23**



When considering the photochemistry of alkyl-substituted diazo compounds, the mechanism of alkene formation remains unknown. Previously, it was found that the laser flash photolysis of alkylphenyldiazomethanes gives rise to both singlet carbenes and directly 1,2-hydride shift products without the intermediate carbene formation.[116]

Recently, a study of the photochemical transformations of methyl diazopropionate (**66a**) and methyl diazophenylpropionate (**66b**) in chloroform on exposure to light at 266 nm has been reported (Scheme 24).[117]

**Scheme 24**

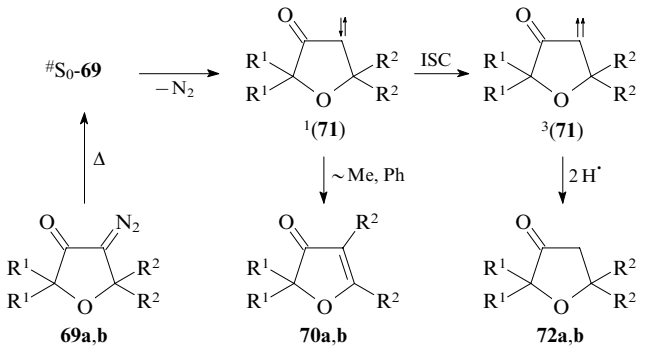


R = H (**a**), Ph (**b**)

Upon UV irradiation, these diazo esters are converted to $S_2$-ES $^1$(**66**)*, which gives off a nitrogen molecule and rearranges in less than 1 ps to alkene (**67**)$^{\#}$. This RIES process is confirmed by the immediate increase in the intensity of the absorption band of alkene **67** in the IR spectrum. The intermediate formation of singlet carbenes **68a**,**b** was not detected experimentally.

In turn, we demonstrated[118] that the thermal decomposition of 5,5-dimethyl-2,2-diphenyl- and 2,2-dimethyl-5,5-diphenyl-4-diazodihydrofuran-3(2*H*)-ones (**69a**,**b**) in protic and aprotic media affords mainly 2,2-dimethyl-

**Scheme 25**



$R^1$ = Me, $R^2$ = Ph (**a**); $R^1$ = Ph, $R^2$ = Me (**b**)

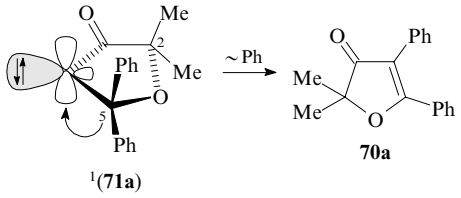
4,5-diphenylfuran-3(2*H*)-one (**70a**) and 4,5-dimethyl-2,2-diphenylfuran-3(2*H*)-one (**70b**), resulting from the 1,2-shift of the phenyl or methyl group, *i.e.*, involves the intermediacy of singlet oxocarbenes $^1$(**71**) (Scheme 25).

Unlike photolysis, thermal transformations of diazoketones **69** occur in 'hot' vibrational levels of the ground state $^{\#}S_0$-**69**,[81, 119] which are much lower in energy than the singlet ES of diazoketone $^1$(**69**)*, generated upon photochemical irradiation. Evidently, this energy of 'hot' levels $^{\#}S_0$ is quite sufficient for the 1,2-shift of a Me or Ph group to give 3(2*H*)-furanones **70** but is apparently insufficient for the Wolff rearrangement to take place. Apart from this, the singlet oxo carbenes $^1$(**71**) formed in the reaction are partly converted to triplet carbenes $^3$(**71**) *via* the ISC, which is evidenced by identification of 2,2-dimethyl-5,5-diphenyl- and 5,5-dimethyl-2,2-diphenyldihydrofuran-3(2*H*)-ones (**72a**,**b**) in the reaction mixtures.

3(2*H*)-Furanones **70** can also potentially arise from diazoketones **69** by a concerted mechanism with simultaneous elimination of the nitrogen molecule and phenyl (methyl) group migration. However, most likely, this process occurs *via* the intermediacy of exactly oxocarbenes $^1$(**71**), as it was shown previously for cyclic diazodiketones.[27, 29, 120]

The stereochemistry of carbene $^1$(**71**) in which the C(5)–Ph bond [or the C(5)–Me bond] of the migrating group is located virtually in the plane of the vacant p-orbital is, evidently, rather favourable for this process (Scheme 26).

**Scheme 26**

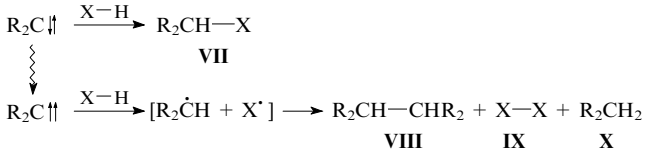



$^1$(**71a**) **70a**

## IV.2. Reductive elimination of nitrogen and cyclopropanation reactions

Triplet carbenes, like radicals, contain a p-orbital with one electron, so they should behave similarly to radical species. Indeed, elimination of a hydrogen atom is the most typical transformation of triplet carbenes. Their reactions with compounds containing X–H bonds are similar to the radical hydrogen atom transfer (Scheme 27).[121]

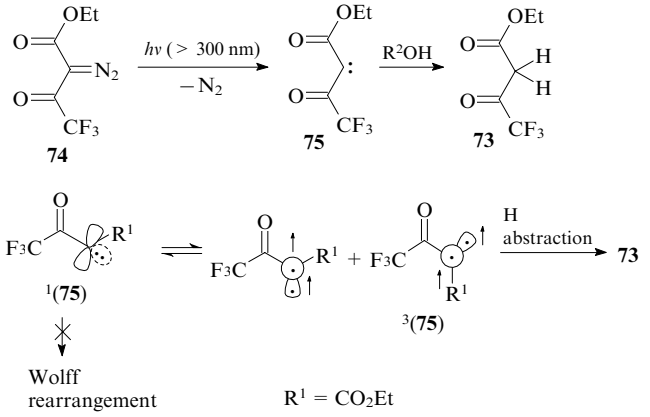
**Scheme 27**




When triplet carbenes are generated in hydrogen-donor solvents, hydrogen abstraction by the carbene takes place. This reaction gives the radical pairs [$R_2C^{\bullet}H + X^{\bullet}$]. In solutions, components of these radical pairs are usually separated to give product mixtures, which comprise the product of formal insertion into the X–H bond (**VII**), radical recombination dimers (**VIII**, **IX**) and the products of 'double' hydrogen atom abstraction (**X**). Thus, the formation of product **X** from the triplet carbene is usually accompanied by the formation of large amounts of side products **VII**–**IX**.

The product of 'double' hydrogen abstraction, ethyl 3-oxo-4,4,4-trifluorobutyrate (**73**), was isolated, instead of the expected Wolff rearrangement product, upon irradiation of ethyl 2-diazo-4,4,4-trifluoroacetoacetate (**74**) in alcohol solution (Scheme 28).[122]

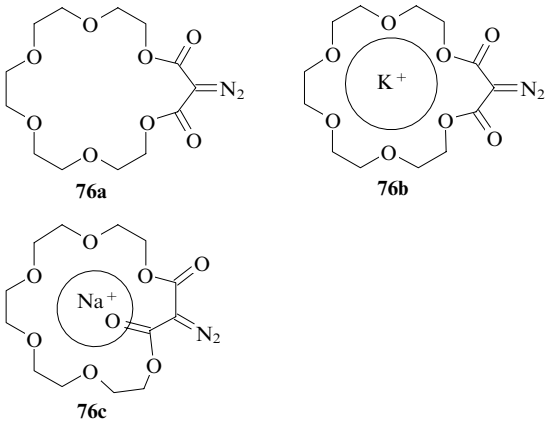
**Scheme 28**




Apparently, triplet carbene $^3$(**75**) arising as a result of an ISC of α-oxocarbene $^1$(**75**) is stabilized upon abstraction of two hydrogen atoms ('double' hydrogen abstraction). Evidently, this process is much faster than the insertion of singlet carbenes.

The most reliable method for generation of triplet carbenes is sensitized photolysis.[123–125] Aromatic ketones characterized by high ISC efficiency (quantum yield $\varphi = 1$) are used, most often, as energy transfer agents. The sensitizer molecule occurring in the triplet ES transfers its excitation energy to the molecules of a diazo compound, which pass at once from the ground state to the triplet state. Popik and co-workers [126] studied the photochemical decomposition of the macrocyclic 3-diazo-2,4-dioxo-19-crown-6 (**76a**) and its complexes **76b**,**c** with potassium and sodium ions.

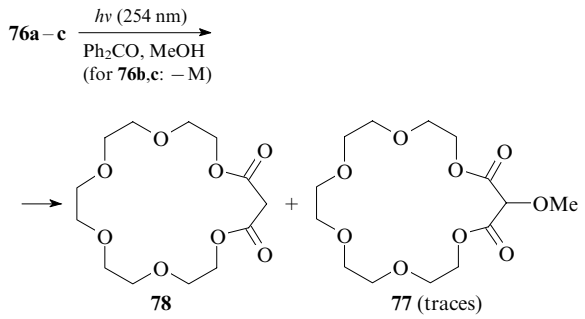
**Structures 76**




Direct photolysis ($\lambda = 254$ nm) of diazo compounds **76a**–**c** in methanol affords 3-methoxy-2,4-dioxo-19-crown-6 (**77**), resulting from insertion of the α,α′-dicarbonyl carbene into the O–H bond of the solvent. Meanwhile, triplet-sensitized photolysis of diazocrown ethers **76a**–**c** affords exclusively diketocrown ether **78** (> 80%),

which is formed, beyond doubt, from the corresponding triplet carbene upon the reaction with the solvent molecules (Scheme 29).

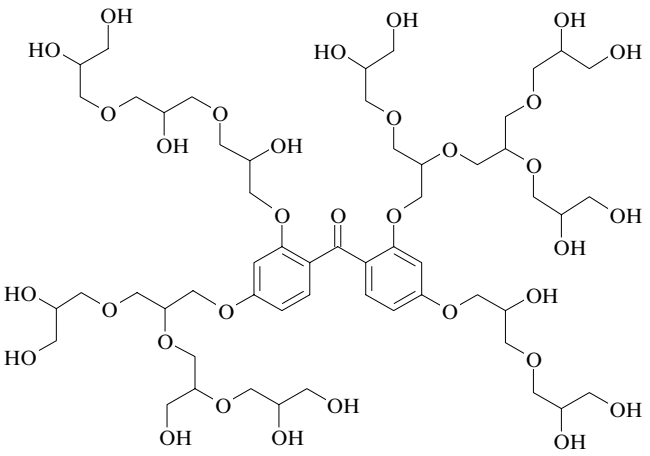
**Scheme 29**

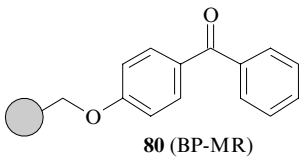



The obtained results are in line with the accepted mechanism of photochemical reduction of α-diazocarbonyl compounds *via* the triplet carbonyl carbene intermediate.[27, 59, 127]

The triplet sensitizers are, most often, regenerated during the reaction. However, in some cases, they can themselves decompose during the photolysis. Stiriba and coworkers[128 – 131] published a series of papers dealing with stabilization methods of a triplet photosensitizer, benzophenone, including icorporation within hyperbranched polyethers (*e.g.*, structure **79**, BP-PG)[130] and grafting to the Merrifield resin (**80**, BP-MR)[131] — spherical particles of benzoylated polystyrene – divinylbenzene copolymer.[132]

**Structures 79, 80**

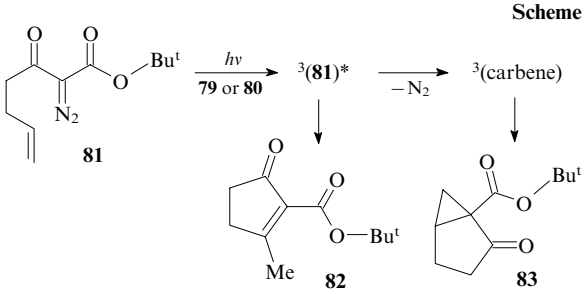



The photocatalytic potential of these systems was evaluated in relation to the sensitized transformations of *tert*-butyl 2-diazo-3-oxohept-6-enoate (**81**) as the model reaction (Scheme 30).

Irrespective of the nature of the solvent used (methanol, acetonitrile), the irradiation wavelength ($\lambda > 300$, $400 > \lambda > 320$ and $\lambda > 350$ nm) and the sensitizer concentration, apart from the minor amount of *tert*-butyl

**Scheme 30**




2-methyl-5-oxocyclopent-1-ene-1-carboxylate (**82**), the photolysis gave *tert*-butyl 2-oxobicyclo[3.1.0]hexane-1-carboxylate (**83**) as the major product. The intramolecular cycloaddition of the triplet carbene to the double bond of the starting diazoketoester **81** is fairly efficient, the cyclopropanation product **83** being formed in up to 90% yield. Furthermore, using these modified sensitizer photocatalysts, it is possible to obtain the same set of products in the same ratio even after five catalytic cycles. The photocatalysts BP-PG and BP-MR are readily regenerated and function for long periods of time.

The carbene reactions considered in this Section are very often cited as convincing evidence for the presence of carbene intermediates in the reaction system. They can also be used for synthetic purposes. Of special interest in this respect are intramolecular processes, in particular, for the preparation of unusual heterocyclic compounds (as a result of insertion into appropriate bonds), for introduction of double bonds into the initial substrate (as a result of 1,2-migration of substituents in the carbene) and for intramolecular cyclopropanation, *i.e.*, introduction of cyclopropane-containing structural units into the substrate.

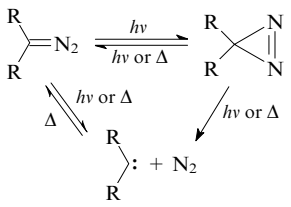
## V. Transformations of diazocarbonyl compounds in the excited state with retention of both nitrogen atoms of diazo group

### V.1. Isomerization to diazirines

The review[133] on the valence isomerization of diazo compounds to diazirines published in 2011 covers this issue rather comprehensively. Therefore, we will briefly consider the development of the views on the nature of this photochemical transformation, namely, what was known 50 years ago about the diazirine synthesis from their diazocarbonyl analogues and what is known today about the mechanism of this reaction relying on the results of modern spectroscopic methods.

The currently known interconversions of diazo compounds and diazirines are summarized in Scheme 31.

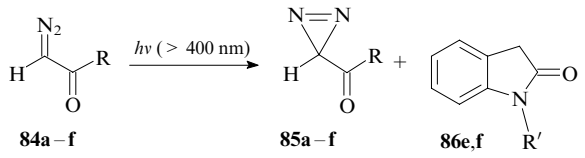
**Scheme 31**




The photochemical isomerization of diazocarbonyl compounds to diazirines was first established experimentally in relation to diazoacetamide (**84a**) and some its derivatives

**84b – f** (Scheme 32).[134, 135] On exposure of diazo compounds **84a – f** to visible light ($\lambda \geqslant 400$ nm), 3-aminocarbonyl-3*H*-diazirines **85a – f** were isolated in moderate yields.

**Scheme 32**



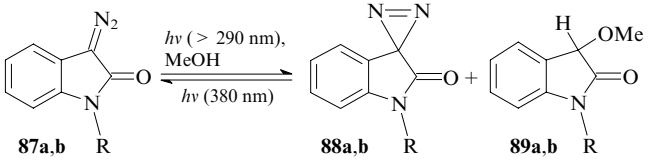

**84**, **85**: R = $NH_2$ (**a**), NHMe (**b**), $NEt_2$ (**c**), NHPh (**d**), NMePh (**e**), $NPh_2$ (**f**); **86**: R′ = Me (**e**), Ph (**f**)

Apart from diazirines **85a – f**, the reaction mixture was found to contain 2-oxoindoles **86e**,**f**, which resulted from the photochemical decomposition of diazoamides **84e**,**f** and subsequent insertion of the intermediate carbenes into the C – H bond of the phenyl group. Furthermore, it was shown that the product ratio in the mixture depends on the excitation wavelength and that exposure of diazirines **85b**,**f** to shorter-wavelength light ($\lambda$ = 312 and 334 nm) induces at least partial reverse isomerization to the starting diazoamides **84b**,**f**.

The attempts to carry out a similar isomerization of diazo compounds of other classes — the esters of diazoacetic and diazomalonic acids or diphenyldiazomethane — were not a success: in all cases, only reactions accompanied by nitrogen evolution took place. These experiments provided the conclusion that in the case of α-diazoacetamides **84a – f**, photochemical dissociation of the C=$N_2$ bond of diazoamides is suppressed owing to interaction of the carbon atom at the diazo group with the amide nitrogen atom.[136]

One more example of transformation of diazoketones to diazirines is isomerization of 3-diazoindol-2(3*H*)-one (**87a**) and 3-diazo-1-methylindol-2(3*H*)-one (**87b**) induced by UV irradiation ($\lambda$ > 290 nm) in methanol (Scheme 33).[137, 138] However, the yields of spiro(diazirine-3,3′-indol)-2′(3′*H*)-one (**88a**) and 1′-methylspiro(diazirine-3,3′-indol)-2′(3′*H*)-one (**88b**) were relatively low (10% – 15%).

**Scheme 33**



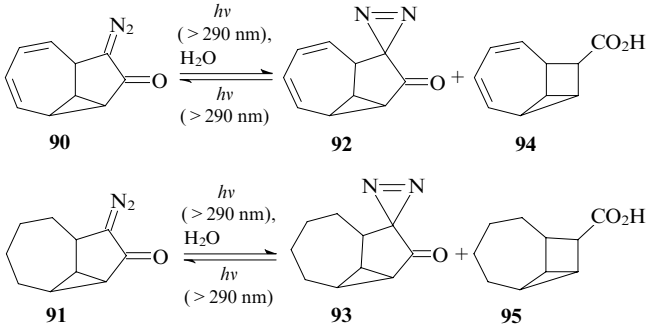

R = H (**a**), Me (**b**)

The reverse reaction, namely, the photochemical opening of diazirine rings with transformation into the starting diazo compounds **87a**,**b** was initiated by UV light at ~380 nm. As in the case of acyclic diazoamides, isomerization under these conditions is accompanied by parallel photolysis of diazoindolines **87a**,**b**, mainly giving rise to typical 'carbene' products — 3-methoxyindol-2(3*H*)-one (**89a**) and 1-methyl-3-methoxyindol-2(3*H*)-one (**89b**).

However, unlike the results of Lowe and co-workers,[134, 135] exposure of diazoindoles **87a**,**b** to long-wavelength light ($\lambda \geqslant 480$ nm) proved inefficient, as no diazirines were isolated under these conditions.[137, 138]

Subsequently, the possibility of isomerization of diazocarbonyl compounds to diazirines was found not only for diazoamides. Indeed, on exposure to UV light through a Pyrex filter ($\lambda$ > 290 nm), (2a*S*,2b*S*)-1-diazo-2a,2a$^1$,2b,6a-tetrahydrocyclopropa[*cd*]azulen-2(1*H*)-one (**90**) and (2a*S*,2b*S*)-1-diazooctahydrocyclopropa[*cd*]azulen-2(1*H*)-one (**91**) are converted to (2a*S*,2b*S*)-2a,2a$^1$,2b,6a-tetrahydro-2*H*-spiro(cyclopropa[*cd*]azulen-1,3′-diazirin)-2-one (**92**) and (2a*S*,2b*S*)-2a,2a$^1$,2b,3,4,5,6,6a-octahydro-2*H*-spiro(cyclopropa[*cd*]azulene-1,3′-diazirin)-2-one (**93**), respectively, in relatively low yields (11% – 17%); under the same irradiation conditions, these products are converted to the initial diazo compounds **90** and **91** (Scheme 34).[139]

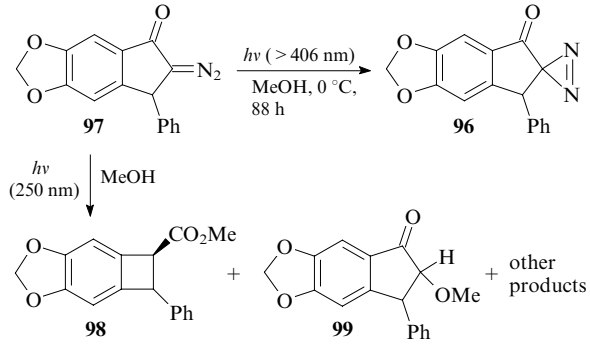
**Scheme 34**




In this case, the diazo compound – diazirine photoisomerization competes with the Wolff rearrangement. Ketenes thus formed readily react with water to give (2*S*,9*S*)-tricyclo[5.2.0.0$^{2,9}$]nona-3,5-diene-8-carboxylic acid (**94**) and (2*S*,9*S*)-tricyclo[5.2.0.0$^{2,9}$]nonane-8-carboxylic acid (**95**).

However, there is an example of formation of 7′-phenylspiro(diazirine-3,6′-indeno[5,6-*d*][1,3]dioxol)-5′(7′*H*)-one (**96**) as the only product (in 60% yield) of the photochemical transformation of 6-diazo-7-phenyl-6,7-dihydro-5*H*-indeno[5,6-*d*][1,3]dioxol-5-one (**97**) induced by long-wavelength irradiation ($\lambda$ > 406 nm) at 0 °C in methanol for 88 h (Scheme 35).[140]

**Scheme 35**

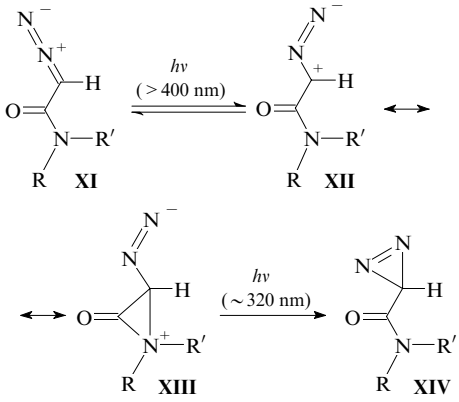



On exposure of the same diazoketone **97** to a shorter-wavelength light ($\lambda$ = 250 nm), no diazirine **96** was identified in the reaction mixture, and the Wolff rearrangement product [methyl (5*S*)-6-phenyl-5,6-dihydrocyclobuta[4,5]-benzo[1,2-*d*][1,3]dioxole-5-carboxylate (**98**), 7% yield] and the product of carbene insertion into the O – H bond of the solvent [6-methoxy-7-phenyl-6,7-dihydro-5*H*-indeno[5,6-*d*]-

[1,3]dioxol-5-one (**99**) (17%)] were isolated as the major reaction products.

The mechanism of formation of diazirines upon irradiation of diazo compounds has not been ultimately elucidated. In the opinion of some authors,[135, 141] the highest contribution to the resonance stabilization of the diazoamide structure **XI** (depicted as canonical structures **XII** and **XIII**) is made by the canonical structure **XII**, which is, most likely, responsible for cyclization to diazirine **XIV**.

**Scheme 36**



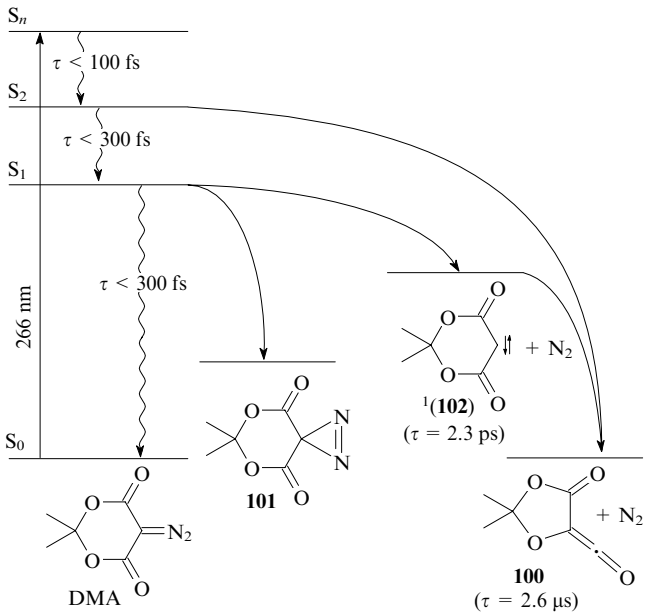

According to other researchers,[137] it is more probable that diazo compound in the ES decomposes to carbene and a nitrogen molecule, which then recombine to give diazirine. However, this assumption is at variance with earlier experiments, which showed that methylene generated from diazomethane in a nitrogen matrix is converted again to a diazomethane rather than to diazirine.[142]

These researchers [137] assume that photoisomerization of diazo compounds to diazirines occurs from the state $S_2$, while in the opinion of other authors, this occurs from the state $S_1$.[81] However, these opinions are hypothetical, and none of them was substantiated. Thus, the mechanism of light-induced transformation of diazo compounds to diazirines has not yet been elucidated.

Modern chemical and physical methods and quantum chemical calculations make it possible to conceive which of the ES arising upon irradiation of diazo compounds are responsible for the Wolff rearrangement ($S_2$), which are responsible for isomerization to diazirines ($S_1$) and which are involved in photophysical processes with the loss of the gained energy. Popik's [80, 81] and Nikolaev's [84, 143] research teams demonstrated that on exposure of DMA to light at 254 nm, the effective ($\varphi = 0.34$) photolytic Wolff rearrangement takes place to give 2,2-dimethyl-5-oxomethylidene-1,3-dioxolan-4-one (**100**) (Scheme 37, $\tau$ is the lifetime). However, in the photolysis at $\lambda = 350$ nm, the rearrangement becomes an inefficient ($\varphi = 0.024$) side process, while the formation of 6,6-dimethyl-5,7-dioxa-1,2-diazaspiro[2.5]oct-1-ene-4,8-dione (**101**) is the major pathway. Furthermore, the Wolff rearrangement and the formation of diazirine **101** should occur from different ES of the DMA molecule, and the lifetime of the highest ES, from which ketene **100** is directly formed, was calculated to be $< 1$ ps.[80, 81]

More recently, Burdzinski, Platz and co-workers [91] used the UV/Vis and femtosecond time-resolved IR spectroscopy for detailed description of the mechanism of DMA photodecomposition and photoisomerization. Powerful UV radiation induces the formation of higher ES, for example, $S_5$ and even $S_7$. Fast internal conversion gives the $S_2$ state, which undergoes the Wolff rearrangement to give the vibrationally excited ketene **100**, which relaxes in 9 ps. Upon internal conversion, the state $S_2$ is easily transformed to $S_1$, which either isomerizes to diazirine **101**, or decomposes to give singlet carbene, 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene [$^1$(**102**)], or further relaxes to the DMA ground state. The lifetime of DMA in the states $S_1$ and $S_2$ is $< 300$ fs, and the quantum yield of its decomposition is $\sim 50\%$ in chloroform upon excitation at $\lambda = 266$ nm.

**Scheme 37**



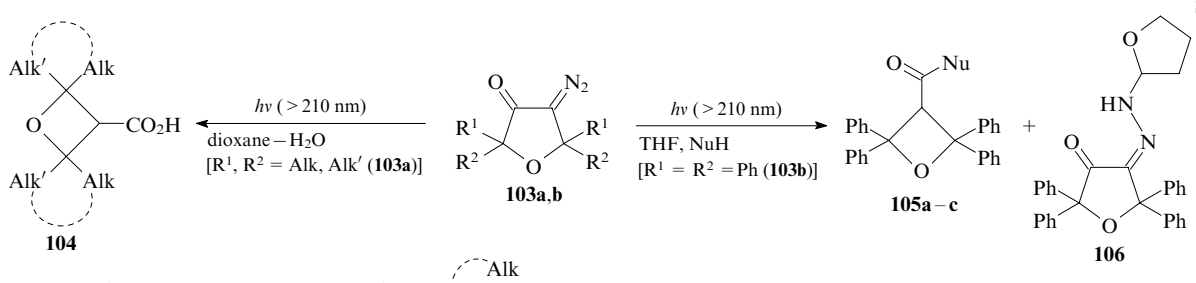

While analyzing the above data, one should put emphasis on the very high role of selectivity of the excitation of initial compounds: by selecting monochromatic radiation, it would be apparently possible to direct the photochemical transformations along a desired pathway.

## V.2. Reactions with hydrogen donors

The key pathway of photolysis of regioisomeric tetrahydrofuran diazoketones is elimination of a nitrogen molecule and formation of the Wolff rearrangement products. Direct photolysis of 2,2,5,5-tetraalkyl-4-diazofuran-3-ones **103a** ($R^1 = R^2 =$ Alk) with short-wavelength UV light ($\lambda > 210$ nm) in aqueous dioxane usually gives 2,2,4,4-tetraalkyloxetane-3-carboxylic acids **104** or their derivatives, the yields of which for the tetramethyl-substituted diazoketone reach 90%–95% (Scheme 38).[144, 145] Irradiation of 4-diazo-2,2,5,5-tetraphenyltetrahydrofuran-3-one **103b** ($R^1 = R^2 =$ Ph) in a benzene–$H_2O$ system also results in 2,2,4,4-tetraphenyloxetane-3-carboxylic acid (**105a**), but the yield is not more than 60%.[145]

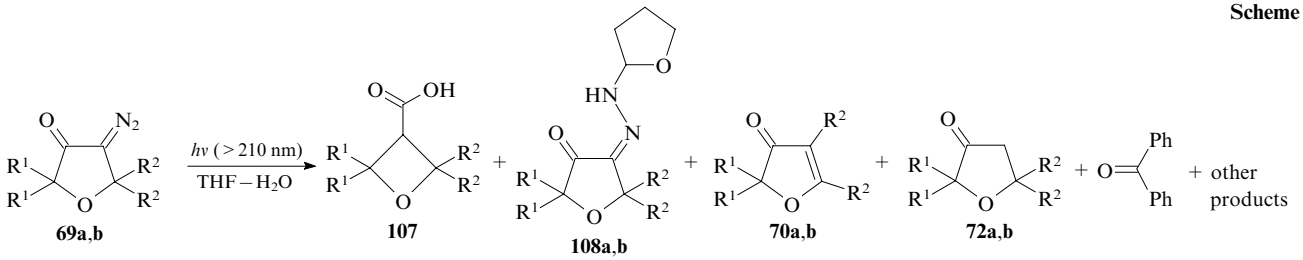
Subsequently, in a study of the photochemical transformations of diazoketone **103b** in THF induced by long-wavelength UV light ($\lambda > 300$ nm), Nikolaev, Rodina and co-workers [146] found that direct photolysis in the presence of various nucleophiles ($H_2O$, MeOH, $Et_2NH$) results in the formation of a mixture of the expected Wolff rearrangement product (**105a–c**) and (*Z*)-4-[2-(tetrahydrofuran-2-yl)hydrazono]-2,2,5,5-tetraphenyldihydrofuran-3(2*H*)-one (**106**) — an unexpected adduct of the initial diazoketone with THF,

**Scheme 38**




**104**: Alk = Alk′ = Me, Et, Pr$^i$; Alk = Me, Alk′ = Et;  = $(CH_2)_4$, $(CH_2)_5$; **105**: Nu = OH (**a**), OMe (**b**), $NEt_2$ (**c**)

**Scheme 39**




$R^1$ = Me, $R^2$ = Ph (**a**); $R^1$ = Ph, $R^2$ = Me (**b**)

which could formally be treated as the product of 'insertion' of the terminal N atom of diazo group into the α-C – H bond of the solvent (see Scheme 38).

This transformation is the first example of intermolecular photochemical reaction of the excited diazo compound occurring with retention of the diazo group nitrogen atoms.

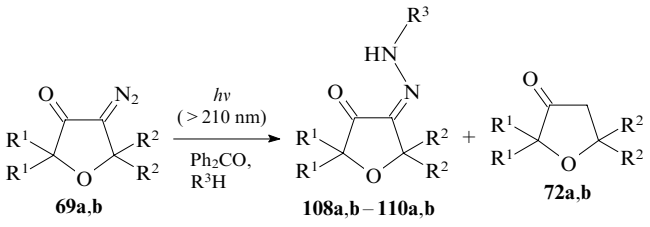
The formation of the named products indicates that this photochemical process involves compounds in electronically excited states with different multiplicity: triplet intermediates should be responsible for the formation of hydrazone **106**, while the Wolff rearrangement may imply the intermediate formation of compounds in singlet excited states.

Comparison of the results of photochemical experiments using regioisomeric diazoketones **69a**,**b** containing phenyl substituents only near the carbonyl group or near the diazo group did not show any noticeable differences in their behaviours. Both regioisomers were converted to the same compounds upon photolysis, namely, 2,2-dimethyl-4,4-diphenyloxetane-3-carboxylic acid (**107**) (⩽62%) and substituted hydrazones (*Z*)-2,2-dimethyl-4-[2-(tetrahydrofuran-2-yl)hydrazono]-5,5-diphenyldihydrofuran-3(2*H*)-one (**108a**) and (*Z*)-5,5-dimethyl-4-[2-(tetrahydrofuran-2-yl)hydrazono]-2,2-diphenyldihydrofuran-3(2*H*)-one (**108b**) (⩽ 14%) (Scheme 39).[147]

Further thorough investigation of the reaction mixtures using gas chromatography – mass spectrometry demonstrated that the primary products of photochemical transformations were unstable and underwent transformations upon irradiation. After the complete disappearance of the starting diazoketones **69**, almost ten reaction products were detected, including unsaturated ketones **70a**,**b** (2% – 8%), ketones **72a**,**b** (4% – 14%), benzophenone (2% – 10%) and so on.[148, 149]

The sensitized photolysis with an excess of benzophenone carried out in various hydrogen donors (THF, dioxane, cyclohexane) furnished adducts **108** and (*Z*)-4-[2-(1,4-dioxan-2-yl)hydrazono]-2,2-dimethyl-5,5-diphenyldihydrofuran-3(2*H*)-one (**109a**), (*Z*)-4-[2-(1,4-dioxan-2-yl)hydrazono]-5,5-dimethyl-2,2-diphenyldihydrofuran-3(2*H*)-one (**109b**), (*Z*)-4-cyclohexylhydrazono-2,2-dimethyl-5,5-diphenyldihydrofuran-3(2*H*)-one (**110a**) or (*Z*)-4-cyclohexylhydrazono-5,5-dimethyl-2,2-diphenyldihydrofuran-3(2*H*)-one (**110b**) in high yields (up to 56%) and ketone **72a**,**b** (9% – 33%) (Scheme 40).[150, 151] Hence, in the presence of a triplet sensitizer, benzophenone, the yields of hydrazones **108** – **110** are especially high, which unambiguously attests in favour of participation of the triplet ES of diazoketones **69** in the reaction.

**Scheme 40**

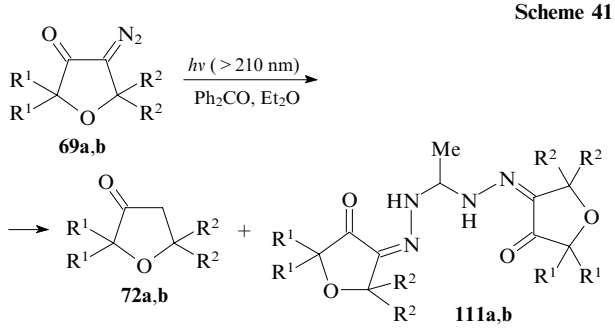



$R^1$ = Me, $R^2$ = Ph (**a**); $R^1$ = Ph, $R^2$ = Me (**b**);
$R^3$ — 2-furyl (**108**), 1,4-dioxan-2-yl (**109**), cyclo-$C_6H_{11}$ (**110**)

While carrying out the reaction in diethyl ether, apart from ketones **72**, we isolated the products of successive 'insertion' of two diazoketone **69** molecules into the C – H bond of the solvent molecule, namely, (4*Z*,4′*Z*)-4,4′-[ethane-1,1-diylbis(hydrazin-2-yl-1-ylidene)]bis(2,2-dimethyl-5,5-diphenyldihydrofuran-3(2*H*)-one) (**111a**) and (4*Z*,4′*Z*)-4,4′-[ethane-1,1-diylbis(hydrazin-2-yl-1-ylidene)]bis(5,5-dimethyl-2,2-diphenyldihydrofuran-3(2*H*)-one) (**111b**) (Scheme 41).[151]

Thus, the obtained results indicate that upon photolysis of di- and tetraphenyl-substituted diazoketones **69a**,**b** and **103b**, benzophenone is formed in the secondary photochemical reactions; this is followed by benzophenone-sensitized transformations, which start with the reaction of diazoketone molecules occurring in the triplet ES $^3$(**69**)*

**Scheme 41**




$R^1$ = Me, $R^2$ = Ph (**a**); $R^1$ = Ph, $R^2$ = Me (**b**)

with solvent molecules at one of the α-CH bonds. This ES transformations give hydrazones **108** – **110** (or bis-hydrazone **111**) and ketones **72**.

Analysis of the accumulation curves of the photolysis products (derived from the $^1$H NMR data for the aliquot portions taken from the reaction mixture with an internal standard) and the consumption curves of the starting diazoketones showed that diazoketones **69** (which serve as the sources of ketene and oxetanecarboxylic acid **107**) disappear, while the product of the Wolff rearrangement **107** continues to accumulate.[152] This indicates unambiguously that the reaction mixture contains diazoketone **69** isomers, *i.e.*, the corresponding diazirines.

Using diazoketone **69a** as an example, we determined the isomerization conditions for the starting diazo compounds into diazirines and isolated the corresponding diazirine.[101] This was done on the basis of analysis of the energy level diagram of diazoketone **69a**, which allowed us to select monochromatic light sources for the excitation of the initial diazoketone **69a** at 266 nm and 405 nm. We found that in both cases, the same transformation products are formed. However, the short-wavelength photolysis ($\lambda$ = 266 nm) resulted in decomposition of diazirine, which accumulated in the reaction mixture during irradiation at 405 nm and was isolated from the mixture as colourless crystals.

Thus, on long-wavelength irradiation, the Wolff rearrangement involves exclusively the excited diazoketone molecules, because diazirine itself does not absorb light at $\lambda$ = 405 nm. On exposure to light at $\lambda$ = 266 nm, diazirine isomerizes to diazoketone **69a**, but 15 – 20 min later, intense decomposition of diazoketone starts, giving the Wolff rearrangement product (**107**), and substituted hydrazone **108a** forms as the adduct of diazoketone **69a** with the THF molecule starts to be accumulated. Hence, under these conditions, the rearrangement and the formation of substituted hydrazone **108a** occur for diazoketone **69a**, arising from diazirine *via* photoisomerization.

The carbon atom at the diazo group is known to occur in the sp$^2$-hybridized state, while the diazo group nitrogen atoms are sp-hybridized; the overlap of the atomic orbitals gives rise to the three-centre ($\pi_x$) and two-centre ($\pi_y$) molecular orbitals (Fig. 1).

Presumably, upon light excitation, one electron of the pair located in the $p_y$ orbital passes to the antibonding $\pi_x^*$-orbital of the neighbouring nitrogen atom (Scheme 42). The remaining unpaired $p_y$-electron is located outside the common $\pi_x$ plane and, hence, it should have enhanced reactivity. Theoretically, there are two pathways for stabilization of this biradical intermediate: reactions with partners, hydrogen donors and intramolecular recombination.

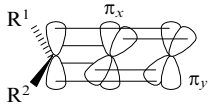
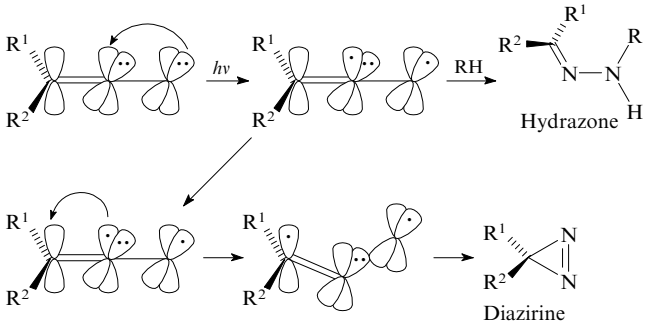



**Figure 1.** Molecular orbitals of the diazo group.

**Scheme 42**




The former pathway is implemented in the 'insertion' of the terminal nitrogen atom into the α-C – H bond of the tetrahydrofuran ring to give the corresponding hydrazone **108**. This reaction is likely to proceed *via* the triplet ES because the lifetime of the singlet ES is too short for the observed intermolecular interaction to take place. This assumption is confirmed by sensitized photolysis experiments.

The latter pathway implies intramolecular stabilization – recombination yielding a diazirine ring. According to published data,[136] the closure of the linear moiety into a ring occurs *via* the biradical species with unpaired electrons on the carbon atom and the terminal nitrogen atom.

## VI. Conclusion

Analysis of the published data demonstrates that most of the studies dealing with the photochemistry of diazocarbonyl compounds consider transformations involving elimination of a nitrogen molecule. Most interest is attracted by 1,2-nucleophilic rearrangements, first of all, the Wolff rearrangement.

This is quite understandable, because this reaction is widely used in laboratory practice. Furthermore, whereas previously this reaction was known as a step of the synthesis of carboxylic acid homologues and as a convenient ring contraction method, in recent years, the emphasis in the synthetic chemistry has been put on the synthesis of various heterocycles by this reaction. First of all, this concerns the cycloaddition of ketenes formed as the intermediates of the Wolff rearrangement. The photochemical Wolff rearrangement is the key step in the preparation of many biologically important pharmaceutical agents, including antibiotics. Moreover, it can be used on an industrial scale for the search for new components of light-sensitive materials replacing silver.

The Nikolaev and Rodina's discovery of a new photochemical reaction of diazo compounds with hydrogen

donors proceeding with retention of nitrogen atoms is of interest as a potential test for the presence of excited triplet molecules. The diazirine synthesis by the photochemical route is often the only approach to the preparation of strained heterocycles with two heteroatoms, the recent interest in which is related to their use in the molecular biology and biochemistry as photoaffinity labels to study protein – protein interactions and to isolate and identify unknown proteins.[153 – 155] Thus, this line of research in the photochemistry of diazo compounds also appears highly promising.

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