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The Photochemistry of Acyl Azides - IX. Direct and Sensitized Photolytic Generation of Acylnitrenes for Cycloaddition Reactions

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Abstract: Contrary to ethoxycarbonylnitrene, selective reactions - including cyloadditions - can be carried out with benzoylnitrene. This study analyzes the sequence of reactivity of various bond types with respect to benzoylnitrene, which was generated by three different routes: direct photolysis of benzoyl azide, sensitization of azide decomposition via energy transfer, and photoinduced electron transfer. In all cases the same cycloadducts **23**, **24**, and **30** were obtained. Carbonyl activity determines the reactivity of unsaturated ketones and aldehydes with respect to benzoylnitrene.

INTRODUCTION

Benzoylnitrene can be produced only via the photoexcited state of its corresponding precursors.[1,2] The best conditions for efficient production can be found in benzoyl azide (**1**). A significant disadvantage of azide photolysis, however, is the relatively low yield of only approx. 50% of benzoylnitrene. Fifty percent of the energy is lost as a result of photo-Curtius rearrangement, as associated with the production of phenyl isocyanate. Elimination of nitrogen from **1** can, however, also be initiated via photoinduced electron transfer. If this process takes places via a triplet-excited electron donor, it is possible to prevent the production of isocyanate.[3,4] This possibility offers advantages for the synthetic use of aroyl nitrenes.

Ethoxycarbonylnitrene, on the other hand, can also be obtained from the process of thermal nitrogen elimination from the corresponding azide. This possibility is apparently one of the reasons why the reactions of this species have been investigated far more than others. There are difficulties involved, however, in applying the findings from this process to the aroyl nitrenes. These problems arise from the fact that aroyl nitrenes most probably react in the singlet state[5], whereas it is known with respect to ethoxycarbonylnitrene that it occurs in its ground state as a triplet.[6] This aspect is also possibly the reason why the reactions of such nitrenes are relatively unselective.

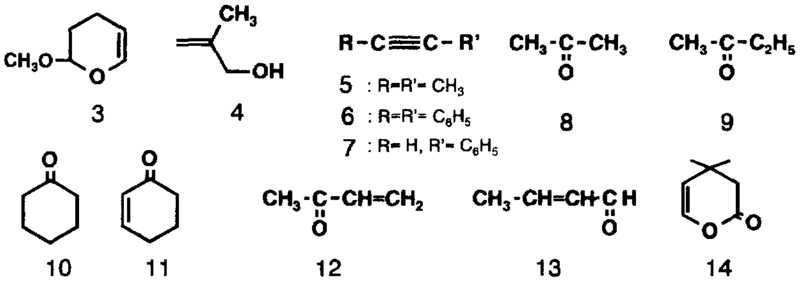
We have concentrated our attention on cycloaddition reactions with acyl nitrenes, and their initiation via photoinduced electron transfer. In a previous study[7], we were able to demonstrate that aroyl nitrenes react with electron-rich olefins to directly produce five-membered-ring heterocycles. We were not able to establish, however, whether this reaction in fact takes place in a concerted manner. Our efforts here were concentrated on the following: extension of cycloaddition reactions to additional double and triple bonds, estimation of the reactivity differences of π systems with respect to each other, and comparison with insertion reactions of nitrene into C-H or O-H bonds. Since the results of reactions which are initiated via photochemical excitation can be extensively influenced by reaction conditions such as excitation wavelength and solvent, a number of reactions of benzoyl nitrenes with ketones which had been conducted in previous studies [8] were repeated under our conditions: i.e., with defined excitation wavelengths and diluted solutions. Reactions were conducted until now with acetylene compounds only with ethoxycarbonyl nitrenes or with acetyl nitrenes. Only extremely small yields of five-membered-ring heterocycles were achieved here.[9,10]

In addition to benzoylnitrene, we have also included for purposes of comparison ethoxycarbonylnitrene. Our intention here was to generate the nitrene by photolytic means. In order to obtain greater details on the sequence of cycloaddition which is initiated by photoinduced electron transfer to aroyl azide, an enol ether was also included in our investigations, in addition to a ketone and an enone.

RESULTS

Benzoylnitrene via photolysis of benzoyl azide 1

The reaction of benzoyl nitrene with the unsaturated alcohol **4**, alkines **5** - **7**, and carbonyl compounds **8** - **14** was initiated by irradiation of **1** in the solvents acetonitrile, dichloromethane, methanol, and cyclohexane in the presence of compounds **4** - **12** (1 ... 10 molar), by light with wavelengths of 254 or 313 nm. A priori, all the compounds **8** - **14** have several attack positions for the nitrene produced in this manner (insertion into CH or OH bonds, addition towards C=O or C=C double bonds), with the result that ordering of the reactivity of the nitrene is possible from the observed products and their yields.

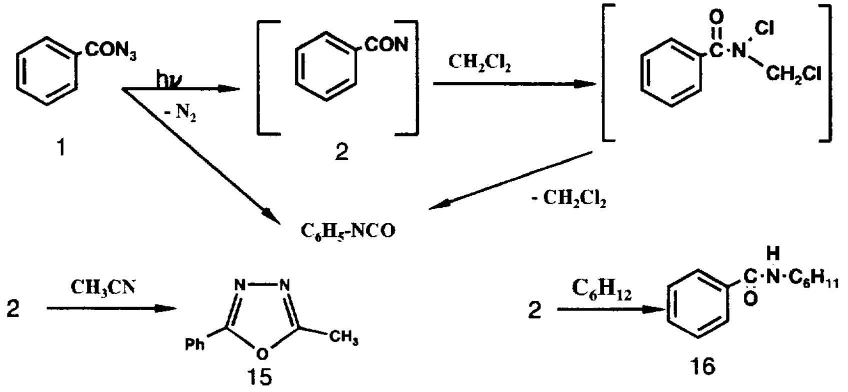


Entirely apart from the reaction conditions, a constant yield of approx. 50% of phenyl isocyanate was detected.

Selection of the solvent took place on the one hand in accordance with the solvent polarity and, on the other, according to the possible competing reactions of the benzoyl nitrene with the solvent. The great reactivity of the acyl nitrenes has had the effect that studies conducted until now were carried out in the environment of the pure reaction partners of the acyl nitrenes, in order to prevent solvent reactions.

In acetonitrile as solvent, cycloaddition to **15** is the competing reaction [11], whereas in cyclohexane, the insertion reaction with **16** competes with the rearrangement process (see Scheme 1). In contrast to findings in [11], we were not able to determine that benzamide was formed under any conditions (HPLC). Use of dichloromethane is associated with special problems, since -- as shown in studies conducted by Sauer et al. [11]

-- significant increase of the isocyanate yield is observed in halogenated solvents.



Scheme 1

We even observed that aroyl azides yield 100% isocyanate as a result of photolysis in dichloromethane (λ_{exc} = 313 nm). We found at the same time, however, that the addition of reaction partners such as electron-rich olefines [7] or fullerene C_{60} [12] resulted in the production of nitrene adducts.

Similiar results were obtained using mixtures of cyclohexane (4.5 M) and acetonitrile (4.5 M) in dichloromethane solution. Nitrene products **15** and **16** were formed. An experiment with a mixture of identical concentrations of both cyclohexane and acetonitrile in dichloromethane has furthermore shown that more insertion product **16** was formed than cycloadduct **15** (Table 1). The reactivity of benzoylnitrene towards the CH bond is therefore more pronounced than towards the acetonitrile triple bond.

Cyclohexanone (**10**) and the enolether **3** are likewise capable of suppressing the formation of isocyanate in dichloromethane, if they are employed in concentrations of 1 mol/l.

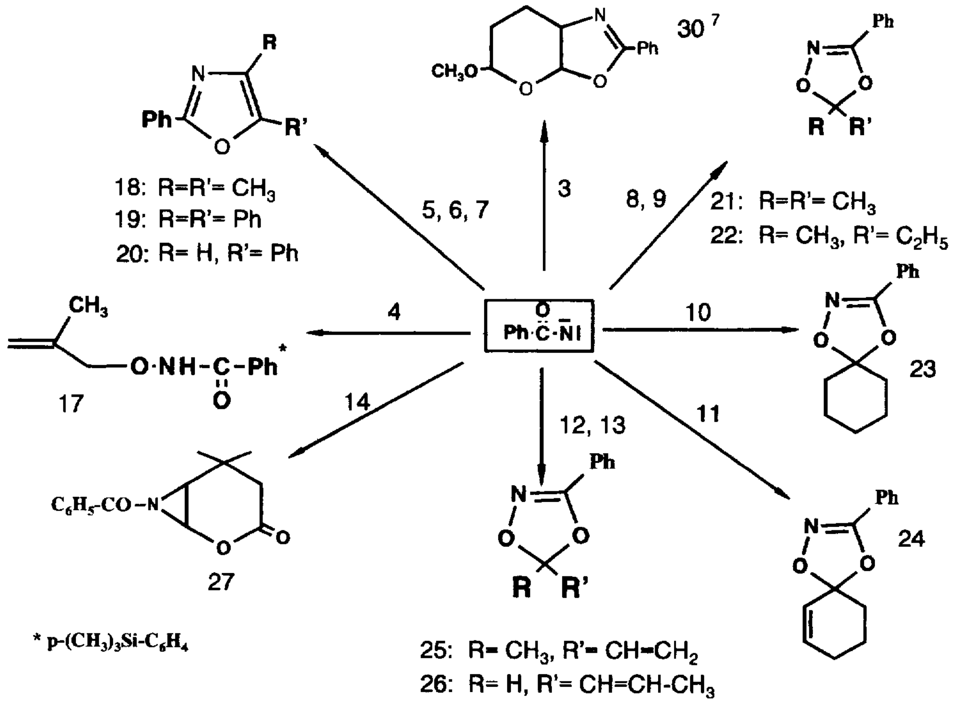
In the two other solvents used as well, the rates of cycloaddition to the added π systems are greater by far than those of the solvent reaction. The insertion reaction of the nitrene **2** into the OH bond of methanol is faster than cycloaddition reactions. No cycloadducts could be detected in this solvent.

Scheme 2 and Table 1 summarize the findings for the corresponding reactions of benzoyl nitrene with quenchers **4** - **12** (p-trimethylsilylbenzoylnitrene was used instead of benzoylnitrene for the reaction with **4**, because purification of the reaction product was possible only in this case).

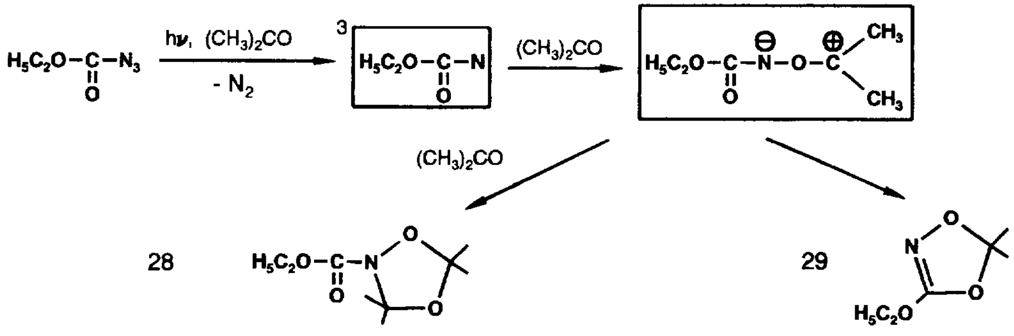
Using photolytically produced ethoxycarbonylnitrene in acetone as solvent, we were able to isolate only two products. These two products can be elucidated by the addition of two (**28**) acetone molecules or one (**29**) acetone molecule to the nitrene (see Scheme 3). The isolated 1:1 adduct **29** exhibits carbonyl absorption in the infrared spectrum, and must accordingly be attributed to an oxazirine - which surprisingly exhibits a low-field shift for the signal of the tertiary ring carbon atom in the ^{13}C-NMR spectrum of 98 ppm.

The ^{13}C NMR spectrum reveals the structure of **28** (two signals for the C atoms in the ring for 94 or 107 ppm; carbonyl absorption of 1892 cm^{-1}).

If, however, a ten-molar solution of acetone in acetonitrile is used for the photolysis of azidoethyl formate, the addition product of the nitrene towards acetonitrile [13] is produced with a yield of 60%.



Scheme 2



Scheme 3

Photoinduced electron transfer

The decomposition of benzoyl azide was investigated in exemplary manner in the presence of the ketones **10** and **11**, as well as enolether **3**. The latter compound offers the advantage that no overlap of ultraviolet absorptions between the reactant and the electron donor takes place. For this reason, tests conducted for solvent dependency of electron transfer are not influenced in this case by dependency of ultraviolet absorption conditions. In addition to **1**, p-cyanobenzoyl azide was investigated for its behavior with respect to

Table 1. Yields of the products obtained upon the photolytic decomposition of **1** in the presence of several quenchers under different reaction conditions

added quencher	λ_{exc}/nm /solvent	adduct yield (%)	yield isocyanate (%)	yield of other products (%)
CH_3CN(4.5 M)/ C_6H_{12} (4.5 M)	254/CH_2Cl_2	**15** (22), **16** (37)	36	-
4 *	254	**17** (29)	40	-
5	254	**18** (24)	50	**15** (8)
6	254	**19** (32)	53	**15** (8)
7	254	**20** (18)	46	**15** (10)
8	254	**21** (30)	40	**15** (10)
8	365, DPA	**21** (10)	45	**15** (12)
8	365, MK	**21** (50)	0	**15** (9)
9	254	**22** (30)	40	**15** (10)
9	365, DPA	**22** (25)	45	**15** (11)
9	365, MK	**22** (45)	0	**15** (20)
10	254	**23** (45)	40	**15** (12)
10	350	**23** (74)	0	**15** (10)
10	350/C_6H_{12}	**23** (46)	0	**16** (5)
10	365/DPA	**23** (39)	21	**15** (8.5)
10	365/DPA/CH_2Cl_2	**23** (48)	34	-
10	350/CH_2Cl_2	**23** (90)	0	-
10	300/CH_2Cl_2	**23** (75)	22	-
10	254/CH_2Cl_2/ C_6H_{12}/CH_3CN	**23** (50)	40	**15** (3); **16** (6)
10	DPA/365	**23** (40)	35	**15** (9)
10	365/DPA/C_6H_{12}	**23** (41)	40	**16** (6)
10	365/MK	**23** (45)	0	**15** (4)
10	365/MK/CH_2Cl_2	**23** (20)	0	-
10	365/MK/C_6H_{12}	**23** (51)	0	**16** (6), **benzamide** (7)
11	254	**24** (25)	51	**15** (13)
11	365, MK	**24** (82)	0	**15** (12)
12	254	**25** (26)	52	**15** (18)
13	254	**26** (41)	46	**15** (8)
14	254	**27** (22)	46	**15** (20)

Solvent acetonitrile, unless otherwise indicated. * instead of **1**: p-trimethylsilylbenzoyl azide; MK = Michler's ketone; DPA = diphenylanthracene sensitization through electron transfer, with the objective of determining the effects from reinforcement of the acceptor characteristics of the aroylnitrene.

We employed diphenyl anthracene (DPA) and Michler's ketone (MK) as electron donors. The excitation wavelength was 365 nm: a wavelength at which aroyl azides cannot be excited.

Our findings were as follows: in all cases with **1**, the same products of cycloaddition result as for direct photolytic production of the benzoyl nitrenes. With DPA, in turn, a proportion of 50% of isocyanate is formed. With MK, this competing reaction does not take place. As a result, there is a total increase of yield of the cycloaddition product (see Table 1). With p-cyanobenzoyl azide, on the other hand, we observed no cycloaddition product: instead, the corresponding amide was detected.

DISCUSSION

Direct excitation of the acyl azides

In the addition of acyl nitrenes to π compounds, it is generally expected that formation of a three-membered ring (a cheletropic reaction) will take place. But even with thermally produced ethoxycarbonyl nitrenes, an oxazole has been observed with diphenyl acetylene as reaction partner. [9] Sauer et al. [8] likewise found varying yields -- in accordance with irradiation conditions -- of 1,4,2-dioxazole derivatives, in addition to benzamide and phenylisocyanate, as a result of the reaction of benzoylnitrenes with ketones. Photoinduced addition of the benzoyl azide to the ketone has been discussed as the mechanism involved here.

The general question arising here is whether the five-membered-ring heterocycles are or are not formed in a direct addition reaction without passing through the three-membered-ring stage. This question cannot be answered for addition to acetylenes. We were not able to detect an intermediate product in our monitoring of the photoreaction by means of HPLC: it is well known, however, that 1H-azirines are highly unstable. [14] We cannot therefore preclude the possibility that they occur as intermediate products.

The situation, however, is different for formation of dioxazoles. The corresponding oxaziridines are thermally stable. Following the reaction of benzoyl nitrenes with ketones by HPLC has revealed that they do not originate even during intermediate periods of time. We also verified that the oxaziridines are not photolytically converted to dioxazolidines. This finding of course does not prove the concertedness of the reaction. We were not able to confirm the postulated addition of photoexcited ketone to benzoyl azide. Under the various photolysis conditions which we applied -- i.e., including excitation of the azide with 254 nm, as well as nitrogen separation from the azide initiated by electron transfer -- the same cycloaddition product is produced in every case.

Worthy of note here is the regio-specific reaction as shown in Scheme 2 for all examples of cycloaddition processes. Recently, [7] we posed the question as to whether aroyl nitrenes can to some degree react as 1,3-dipoles. Under consideration of findings obtained from reactions with enones and lactone **14**, it must be concluded that the reactivity of the benzoylnitrene is determined not by the orbital energy, but by the carbonyl activity of the reaction partners. There is otherwise no explanation for the specific reaction at the carbonyl group of the enones and for the absence of addition in ester **14**. In this context, 1,3-dipolar cycloaddition is unlikely for the reaction of the benzoylnitrene to ketones and aldehydes. This cycloaddition leads -- in the case of quasi-isomeric nitril oxide -- to highly preferential addition to the olefinic double bond in enones. [15]

It is furthermore noteworthy that the reactions of the solvent -- present as it is to such predominant degree -- with the benzoyl azide always take place considerably more slowly than the reaction with the added reaction partner. This applies not only to cycloaddition to the heteroanalogous carbonyl group in acetonitrile, but also to CH-insertion reactions. On the other hand, insertion into a polar OH bond is faster than the cheletropic reaction with an olefinic double bond (**17**). On the whole, the great reaction selectivity of the reactive aroylnitrene is definitely clear.

Particularly interesting is also the finding that benzoylnitrene is quite evidently produced in dichloromethane as well, and can be quenched by enolethers and ketones. As a result, the isocyanate yield falls by about 40%, to the level of that also observed in other solvents. Without added quenchers, the nitrene is rearranged into the isocyanate. Since this process occurs exclusively in dichloromethane, we propose as hypothesis that insertion of the nitrene takes place ,as intermediate of the rearrangement, into the CCl bond. If this in fact be true, then the intermediate compound could represent the actual preliminary stage for the rearrangement (Scheme 1). These findings apparently evidence that dichloromethane does not play a special role in the photochemistry of benzoyl azide.

In consideration of comparisons between the reactivity of benzoylnitrenes and ethoxycarbonylnitrenes, it is necessary to consider that the essential difference in such comparisons must be seen in the multiplicity of the ground state. This difference manifests itself in the complete change of reactivity with respect to the carbonyl group. Our reconstruction of the reaction of the photolytically produced ethoxycarbonylnitrene with acetone has verified that an oxaziridine derivative is in fact formed. This reconstruction was necessary, since complete characterization of this addition product was indicated neither in [8] nor in. [16]

When ethoxycarbonylnitrene reacts in the triplet state, a two-stage process must be responsible for leading to the observed addition. For this reason, it was not surprising that we were able to isolate a product (**28**) which indicates the existence of an intermediate. The difference in reactivity is further documented in the reaction with an enone. In their studies of the conversion of thermally or photolytically produced ethoxycarbonylnitrene with mesityl oxide, Hiyama et al. [16] established that only the olefinic double bond is attacked under conditions of formation of an aziridine ring.

The great number of products of reaction with acetone and cyclohexanone observed by Hiyama et al. [17] furthermore definitely confirms that the selectivity of the ethoxycarbonylnitrene is significantly less than that of benzoylnitrenes. We were on the other hand able to show that the reactivity is less than that of benzoylnitrene, when compared with the reaction with acetonitrile and acetone, respectively. These findings reveal that lower selectivity of the ethoxycarbonylnitrene is at the same time associated with lower selectivity.

Photolysis using the irradiation wavelength of 350 nm

Table 1 reveals that the greatest yield of the cycloaddition product toward cyclohexanone is found precisely in dichloromethane. At these excitation wavelengths, isocyanate is also not formed in the solvents cyclohexane and acetonitrile. Although the sources of radiation used (RPR 3500) also emit shorter-wave light, we may preclude direct excitation of **1** on the basis of lack of isocyanate alone. Another mechanism of adduct formation must therefore exist here. We assume that the excited ketone rapidly passes into the triplet state and that energy transfer to the azide then takes place. In the triplet state, however, no rearrangement to isocyanate occurs in conjunction with nitrogen separation. Owing to the typical products **15** and **16** simultaneously produced, it may safely be assumed that nitrene production takes place.

Electron transfer

The absorption conditions of cyclohexanone and DPA (or MK) ensure that light with wavelengths of 350 or 365 nm is predominantly absorbed by the electron donors. Since the photoreaction is faster after addition of electron donors than before such addition, it may be assumed that the reaction mechanism has subsequently changed. The production of isocyanate with DPA, and the appearance of benzamide with use of MK, also support this assumption.

In the presence of photoexcited electron donors, electron transfer to the acyl azide takes place. [4] The differences between the use of DPA and MK as electron donors may be interpreted as follows: in the former case, the primarily produced radical-ion pair is in a singlet state; in the latter case, on the other hand, the triplet state is involved. All resulting differences in the spectrum of products are based on this aspect. A priori, each intermediate stage which is formed after primary electron transfer can serve as starting point for subsequent cycloaddition to the five-membered ring heterocycles, as detailed below:

1. Radical-ion pair from the radical anion of the azide and the radical cation of the electron donor (1)
2. Radical-ion pair from the radical anion of the nitrene and the radical cation (2)
3. Free radical anion of the benzoylnitrene (3)
4. Aroylnitrenes **2**, formed by electron back-transfer within (2).

Since, however, cycloaddition leads via direct azide excitation to the same results, we may assume that acyl nitrene is also finally formed as a result of electron transfer. From this standpoint, photoinduced electron transfer represents a special form of the sensitization of azide photolysis.

The free radical anions of the acyl nitrene may not be considered as reaction partners. From electrochemical tests conducted on benzoyl azide in acetonitrile, [18] it is known that the main reaction of this ion consists of the formation of benzamide. We consequently interpret these results in the sense of competition between the production of acyl nitrene within the ion pair (2), and the escape of the radical anion from the solvent cage. In the triplet state, an isc process must take place prior to electron back-transfer. The probability of the formation of free nitrene radical anions will consequently be greater, and the formation of benzamide will become possible: as is actually observed when MK is employed (see Table 1). Formation of the free radical anion is especially vigorously promoted by an acceptor substituent in the aryl part: as result of which the electron back-transfer becomes thermodynamically less favorable (normal Marcus region of the electron transfer). Since the free radical ions of aroylnitrene are not capable of cycloaddition, explanation is possible of why no product of addition was found with this substituted benzoyl azide via the process of photoinduced electron transfer.

CONCLUSION

Contrary to ethoxycarbonylnitrene, selective reactions -- including cycloaddition processes -- can be conducted with benzoylnitrene. Comparing the obtained product reveals the sequence of reactivity of various bond types with respect to benzoyl nitrene as follows:

$$\mathrm{OH} > \mathrm{C{=}C{-}OR}^{7} > \mathrm{C{=}O} = \mathrm{C{\equiv}C} > \mathrm{CH} > \mathrm{C{\equiv}N}.$$

Solvents such as cyclohexane, dichloromethane, and acetonitrile can be used for reactions of benzoylnitrene with various reaction partners. Photoinduced electron transfer is an effective method for sensitization of azide decomposition. The acceptor strength of the aroyl azide must not be excessive, in order to avoid formation of free radical anions of aroylnitrene which do not react in the desired manner.

EXPERIMENTAL

General remarks and materials

Photochemical reactions in a preparative scale were carried out using a home made merry-go-round photoreactor and a Rayonet Photoreactor RPR 100.

Low pressure mercury lamps (HNU 6, NARVA, Berlin) were used for irradiations with 254 nm light. RPR-3000 and RPR 3500 were used for irradiations with light of 300 and 350 nm wavelength. The reaction solutions were placed in 15 quartz test tubes and irradiated (procedure A). Sensitized photolyses were carried out under nitrogen using 0.01 M diphenylanthracene (DPA) and 0.005 M Michler's ketone (MK) solutions (irradiation wavelength 350 nm, procedure B). Photoreactions in an analytical scale were carried out using quartz cuvettes and high pressure mercury lamps HBO 500 (NARVA, Berlin) combined with metal interference filters (Zeiss, Jena) and filter glasses (Schott, Jena) to select the irradiation wavelength.

HPLC (Shimadzu 6A; RP 18; methanol/ and acetonitrile/water) was used in order to follow the course of reactions. Peak areas were calibrated with solutions of compounds of known concentration. ^{13}C NMR and ^{1}H NMR spectra were recorded in $CDCl_3$ (unless otherwise indicated) on a Bruker WM 300 instrument operating at 300 MHz. Infrared spectra were recorded on a Perkin-Elmer 580 B. Mass spectra were determined using a Hewlett Packard 5995 A.

2-Methyl-allyl 4-trimethylsilylbenzohydroxamate (17)

2-Methyl-2-propen-1-ol **4** (7.2 g, 0.1 mol) und p-trimethylsilylbenzoyl azide (2.2 g, 0.01 mol) were dissolved in acetonitrile (100 ml) and irradiated at 254 nm for 18 hours (99% azide decomposition).The solvent was evaporated under reduced pressure, the residue taken up with methanol and separated by preparative HPLC. Besides 0.9 g (40%) of the corresponding urethane 0.76 g (29%) **17** was isolated as viscous oil.-^{13}C-NMR: δ = -1.2 ($Si(\underline{C}H_3)_3$); 19.24 ($\underline{C}H_3$); 68.19 ($O\underline{C}H_2$); 112.61 (C-2); 118.02 (phenyl); 133, 134, 138 (phenyl); 140 (C-2); 154 ($\underline{C}$=O). - ^{1}H-NMR: δ = 0.25 (s, 9H, $Si(CH_3)_3$); 1.77 (s, 3H, CH_3); 4.59 (s, 2H, OCH_2); 4.93 (d, 1H, C_3H); 5.01 (d,1H, C_3H); 7.44 (4H, phenyl).- MS: (70 eV), m/z (%): 263 (23), M^+. Calc for $C_{14}H_{21}NO_2Si$ (263.4): C 63.84, H 8.05, N 5.32; found.: C 63.56, H 8.30, N 5.33.

4,5-Dimethyl-2-phenyl-oxazole (18)

2-Butyne (5.4 g, 0.1 mol) and **1** (3.7 g, 0.025 mol) were irradiated according to procedure A (20 hours). The reaction mixture was evaporated, taken up with methanol and separated by preparative chromatography (benzene/acetonitrile) affording 1 g (24%) **19** which was identical with an authentic sample.

Triphenyloxazole (19) and 2,5-Diphenyloxazole (20) were obtained according to procedure A using solutions of 0.01 M **1** and 1 M acetylene compounds. The isolated compounds were identical with authentic samples. Yields are displayed in Table 1.

5,5-Dimethyl-3-phenyl-[1,4,2]-dioxazole (21)

1 (1.5 g, 0.01 mol) und 5.8 g acetone (0.1 mol) were dissolved in 100 ml acetonitrile and irradiated at 254 nm (procedure A).

The reaction mixture was evaporated under reduced pressure. The residue was taken up with methanol and separated by preparative chromatography (cyclohexane/ether 3:1).

Besides 0.6 g (40%) phenyl- N-methylcarbamate (from phenylisocyanate) and 0.16 g 5-methyl-2-phenyl-[1,3,4]-oxadiazole **15** (10%) 0.53 g **21** (30%) were obtained as oil. - ^{13}C NMR: δ = 23 ($\underline{C}H_3$); 113 C-5); 122, 127, 129, 131 (phenyl); 159 ($\underline{C}$=N). - ^{1}H NMR: δ = 1.68 (s, 6H, CH_3); 7.4 (m, 3H, phenyl); 7.75 (m, 2H, phenyl). Calc. for $C_{10}H_{11}NO_2$ (177.2): C 67.70, H 7.90, N 6.20; found: C 67.1, H 8.1, N 6.3.

Only 0.18 g **21** (10%) were obtained according to procedure B (DPA). Using procedure B (MK) 0.9 g **21** (50%) could been obtained (see also Table 1).

5-Ethyl- 5-methyl-3-phenyl-[1,4,2]-dioxazole (22)

1.5 g **1** (10 mmol) and 7.2 g (100 mmol) ethyl methyl ketone were dissolved in 100 ml acetonitrile and irradiated according to procedure A (254 nm). After 9 hours the solution was evaporated, taken up with methanol and purified by preparative chromatography (cyclohexane/ether 3:1) affording 0.58 g **22** (30%), oil. - ^{13}C NMR: δ = 7.4 ($\underline{C}H_3$); 23.0 (CH_2); 31.0 (CH_3); 117.5 (C-5); 123, 126, 128, 131 (phenyl); 158 ($\underline{C}$=N). - ^{1}H NMR: δ = 1.0 (t, 3H, CH_3); 1.6 (s, 3H, CH_3); 1.95 (q, 2H, CH_2); 7.4 (m, 3H, phenyl); 7.75 (2H, phenyl). Calc. for $C_{11}H_{13}NO_2$ (191.2): C 69.10, H 7.30, N 6.80; found: C 69.5 , H 7.3, N 6.6.

Yields according to procedure B are displayed in Table 1.

Phenyl-1,4-dioxa-2-aza-spiro[4.5]dec-2-ene (23)

Cyclohexanone (9.8 g, 0.1 mol) and 1.47 g **1** (10 mmol) were dissolved in acetonitrile (100 ml) and irradiated according to procedure A (6 hours). After evaporating, taking up with methanol and separating by chromatography (hexane/ethyl acetate 8:2) 0.98 g (45%) **23** were obtained as oil besides 0.19 g (12%) **15** and 0.6 g (40%) phenyl-N-methylcarbamate.

Yields obtained using other solvents, irradiation wavelengths, and procedure B are diplayed in Table 1. - ^{13}C NMR: δ = 23.45, 24.56, 34.34 ($\underline{C}H_2$, cyclohexane); 116.3 (C-5); 123.7, 126.6, 128.6, 131.2 (phenyl); 158.2 ($\underline{C}$=N).- ^{1}H NMR: δ = 1.46, 1.7, 1.89 (m, 10 H, cyclohexane); 7.75(m, 3H, phenyl); 7.78 (m, 2H, phenyl). - MS (70 eV), m/z (%): 217 (26), $M^{\cdot +}$, 119 (34), 55 (100). Calc. for $C_{13}H_{15}NO_2$ (217.3): C 71.85, H 6.95, N 6.44; found: C 71.69, H 7.03, N 6.49.

3-Phenyl-1,4-dioxa-2-aza-spiro[4.5]deca-2,6-diene (24)

2-Cyclohexen-1-one (9.6 g, 0.1 mol) and **1** (1.47 g, 0.01 mol) were dissolved in acetonitrile (100 ml) and irradiated at 254 nm (6 hours). The reaction mixture was evaporated under reduced pressure. The residue was taken up with methanol. Separation from by-products (Table 1) was done by chromatography (hexane/ethyl acetate 8:2). 0.55 g (25%) **24** were obtained as viscous oil. - ^{13}C NMR: δ = 20.0, 24.6, 32.7 ($\underline{C}H_2$, cyclohexene); 112.7 (C-5); 123.6, 126.7, 128.6, 131.3 (phenyl; 124.2 (C-7); 137.2 (C-6); 158.4 (C=N). - ^{1}H NMR: δ = 1.88, 2.11 (m, 6H, cyclohexene); 5.84 (m, 1H, C_7-H); 6.20 (m, 1H, C_6-H); 7.4 (m, 3H, phenyl); 7.8 (m, 2H, phenyl). - MS (70 eV), m/z (%): 137 (12), 105 (100), 77 (65). Calc. for $C_{13}H_{13}NO_2$ (215.2): C 72.56, H 6.05, N 6.51; found: C 72.35, H 6.08 , N 6.48.

5- Methyl- 3- phenyl-5-vinyl-[1,4,2]-dioxazole (25)

Methyl vinyl ketone (7g, 0.1 mol) and **1** (1.47 g, 0.01 mol) in 100 ml acetonitrile were irradiated according to procedure A. Working up of the reaction mixture by chromatography (hexane/ethyl acetate 8:2) afforded 0.5 g (26 %) **25** as oil. - ^{13}C NMR: δ = 23 ($\underline{C}H_3$); 113.6 (C-5); 117.5 ($\underline{C}H_2$, vinyl); 123.4, 126.7, 128.6, 131.4 (phenyl); 135.0 ($\underline{C}$H, vinyl); 158.3 ($\underline{C}$=N). - ^{1}H NMR: δ = 1.77 (s, 3H, CH_3); 5.31; 5.34 (dd, 1H, vinyl); 5.26, 5.62 (dd, 1H, vinyl); 5.95, 6.0 (dd, 1H, vinyl); 7.4 (m, 3H, phenyl); 7.8 (m, 2H, phenyl). - mass spectrum (70 eV), m/z (%): 189 (M^+), Calc. for $C_{11}H_{11}NO_2$ (189.2): C 69.83, H 5.86, N 7.40; found: C 70.15, H 5.67, N 7.86.

3-Phenyl-5-propenyl-[1,4,2]-dioxazole (26)

Crotonaldehyde (7 g, 0.1 mol) and **1** (1.47 g, 0.01 mol) were irradiated with light of 254 nm (procedure A). After separation of the products by chromatography (hexane/ethyl acetate 8:2) 0.77 g **26** (41%) were obtained as oil. - ^{13}C NMR: δ = 17.74 ($\underline{C}H_3$); 109.2 (C-5); 123, 126.8, 128.7, 131.5 (phenyl); 124.6 ($\underline{C}$H); 136.2 ($\underline{C}$H); 159.3 ($\underline{C}$=N). - ^{1}H NMR: δ = 1.80, 1.83 (m, 3H, CH_3); 5.7 (m, 1H, propenyl); 6.2 (m, 1H, propenyl); 6.3 (d, 1H, C_5-H); 7.4 (m, 3H, phenyl); 7.8 (m, 2H, phenyl). - MS (70 eV), m/z (%): 189 (4), $M^{\cdot +}$, 119 (42), 105 (100), 77 (47), Calc. for $C_{11}H_{11}NO_2$ (189.2): C 69.83, H 5.86, N 7.40; found: C 69.44, H 5.93, N 7.34.

7-Benzoyl-5,5-dimethyl-2-oxa-7-aza-bicyclo[4.1.0]heptan-3-one (27)

3,4-Dihydro-4,4-dimethyl-2H-pyran-2-one (12.6 g, 0.1 mol) and **1** (1.47 g, 0.01 mol) were irradiated according to procedure A. After purification as described for **26** 0.55 g (22%) **27** were obtained. mp: 200°C (subl.). - ^{13}C NMR: (acetone-d_6): δ = 25.15 ($\underline{C}H_3$); 27.11 ($\underline{C}H_3$); 42.46 (C-4); 44.30 (C-6); 67.17 (C-1); 129.6, 129.9, 133.0, 134.2 (phenyl); 167.8 (C-3); 176.0 (benzoyl). - ^{1}H NMR (acetone-d_6): δ = 1.20 (s, 3H, CH_3); 1.27 (s, 3H, CH_3); 2.04, 2.3 (m, 2H); 3.02 (d, 1H, C_6-H); 5.21 (d (5Hz), 1H, C_1-H); 7.5 (m, 3H, phenyl); 8.1 (m, 2H, phenyl). - MS (70 eV), m/z (%): 203 (11), 105 (100), 77 (29). Calc. for $C_{14}H_{15}NO_3$ (245.3): C 73.45, H 6.17, N 5.71; found: C 73.13, H 6.20, N 5.73.

Photolysis of azido ethylformate in acetone solution

2.15 g (0.022 mol) azide in 100 ml acetone (pyrex tubes) were irradiated with light of 300 nm (RPR 3000, Rayonet). After 10 hours (50% azide decomposition) the solution was evaporated under reduced pressure. The residue was separated by chromatography (hexane/ether 5:1). 1.Fraction: **1-(3,3,5,5-Tetramethyl-[1,2,4]dioxazolidin-2-yl)propanon-1-one (28)**, oil, yield 0.7g, (16%). - ^{13}C NMR: δ = 14.49 ($\underline{C}H_3$); 25.31; 25.64 (2x$\underline{C}H_3$); 62.28 (O-CH_2); 93.93 (C-3); 107.44 (C-5); 154 ($\underline{C}$=O). - ^{1}H NMR: δ = 1.31 (t, 3H, CH_3); 1.48 (s, 6H, 2xCH_3); 1.55, (s,6H, 2xCH_3); 4.26 (q, 2H, CH_2). IR (cm^{-1}): 1958 (CO). Calc. for: $C_9H_{17}NO_4$ (203.3): C 53.20, H 8.37, N 6.90; found: C 53.13, H 8.20, N 6.43. 2.Fraction (n-hexane/ether 5:2):

1-(3,3-Dimethyl-oxaziridin-2-yl)-propan-1-one (29),
oil, yield 0.6 g, (20%). - ^{13}C NMR: δ = 14.43 ($\underline{C}H_3$); 21.96; 29.69 (2x$\underline{C}H_3$); 61.97 (O-$\underline{C}H_2$); 98.93 (C-3); 154 ($\underline{C}$=O). - ^{1}H NMR: δ = 1.28 (t, 3H, CH_3); 1.66 (s, 6H, 2xCH_3); 4.18 (q, 2H, CH_2). IR (cm^{-1}): 1792 (CO). Calc. for $C_9H_{17}NO_3$ (145.3): C 49.66, H 7.59, N 9.66; found: C 49.13, H 7.20, N 9.43.

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REFERENCES AND NOTES

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