Photooxidation

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Visible-Light Cascade Photooxygenation of Tetrahydrocarbazoles and Cyclohepta[*b*]indoles: Access to *C*,*N*-Diacyliminium Ions

Mario Frahm[+], *Thorsten von Drathen*[+], *Lisa Marie Gronbach*[+], *Alice Voss, Felix Lorenz, Jonas Bresien, Alexander Villinger, Frank Hoffmann, and Malte Brasholz**

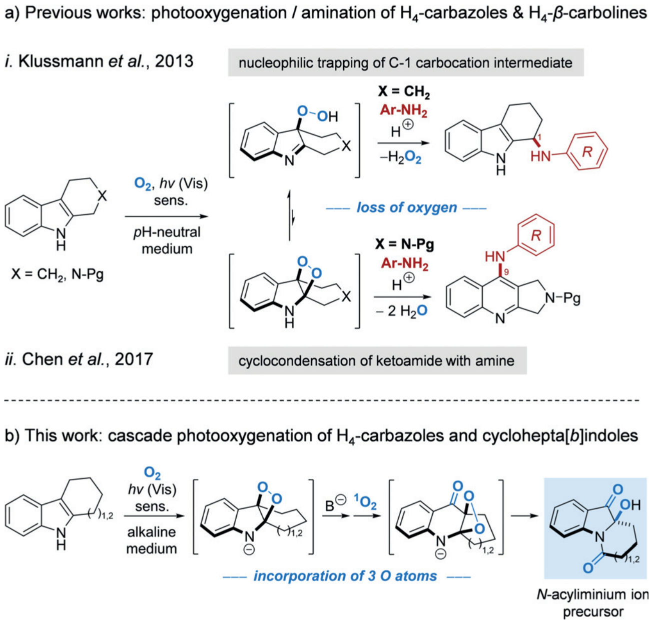
In memory of Rolf Huisgen

Abstract: *Tetrahydrocarbazoles and perhydrocyclohepta-[b]indoles undergo a catalytic cascade singlet oxygenation in alkaline medium, which leads to chiral tricyclic perhydropyrido- and perhydroazepino[1,2-a]indoles in a single operation. These photooxygenation products are new synthetic equivalents of uncommon C,N-diacyliminium ions and can be functionalized with the aid of phosphoric acid organocatalysis.*

The selective oxidation of organic compounds by catalytic aerobic photooxidation has long been a key objective in sustainable synthetic and industrial chemistry.[1] The rapid recent development of chemical photocatalysis with visible light consequently has fueled a growing interest in the development of new photooxygenation reactions with dioxygen, particularly by way of photoelectron transfer-induced and radical C−H oxygenations.[2] Photochemically produced organic peroxides have not only been utilized as key high-energy intermediates in the synthesis of natural products and functional carbo- and heterocyclic target structures,[3] but they have also gained much attention as potential new antiparasitics, especially for combating malaria.[4]

As part of our investigations in the photooxidation of *N*-heterocyclic compounds,[5] we reexamined the dye-sensitized photooxygenation of tetrahydrocarbazoles and tetrahydro-*β*-carbolines, which initially generates the corresponding benzylic hydroperoxides by way of the singlet oxygen ene reaction (Scheme 1 a).[6] In the case of tetrahydrocarbazole, the C-4a hydroperoxide is relatively long-lived in pH-neutral solution, but exposure to Brønsted acids causes the rapid elimination of H_2O_2. The resulting benzylic cation rearranges to a C-1 cation,[7] which can be intercepted with nucleophiles like anilines to give 1-aminotetrahydrocarbazoles, as reported by Klussmann et al.[8] In the case of tetrahydro-*β*-carbolines, however, the benzylic hydroperoxide instantly undergoes C−C bond cleavage via its unstable 1,2-dioxetane congener. Chen and co-workers engaged the so-produced 2-acyl anilides in acid-mediated cyclocondensations with anilines to furnish aminated dihydropyrrolo[3,4-*b*]quinolines.[9]

We report here the cascade photooxygenation of tetrahydrocarbazoles and perhydrocyclohepta[*b*]indoles in alkaline medium, which leads to perhydropyrido- and perhydroazepino[1,2-*a*]indoles in a single operation (Scheme 1 b). Contrary to the previous methods, the initially introduced oxygen is not expelled during a sequence leading back to aromatic products, but three oxygen atoms are permanently integrated into a chiral product structure. This multistep cascade can be regarded as a telescoped photochemical Witkop–Winterfeldt/C−C cleavage reaction, and the perhydropyrido- and perhydroazepino[1,2-*a*]indole products are highly useful synthetic equivalents of new and uncommon *C*,*N*-diacyliminium ions.



Scheme 1. Photooxygenation/ functionalization of [*b*]-annulated indoles.

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[*] M. Frahm,[+] L. M. Gronbach,[+] A. Voss, F. Lorenz, J. Bresien, A. Villinger, Prof. Dr. M. Brasholz
Institute of Chemistry, University of Rostock
Albert-Einstein-Str. 3A, 18059 Rostock (Germany)
E-mail: malte.brasholz@uni-rostock.de
Homepage: https://www.brasholz.chemie.uni-rostock.de
T. von Drathen,[+] F. Hoffmann
Department of Chemistry, University of Hamburg
Martin-Luther-King-Platz 6, 20146 Hamburg (Germany)

[+] These authors contributed equally to this work.

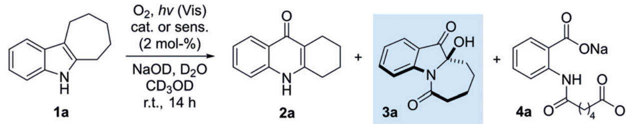
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202007549.

In our initial experiment, we attempted the photooxidation of hexahydrocyclohepta[*b*]indole (**1a**) under basic conditions, and found that alongside the 4-quinolone **2a**, the valuable perhydroazepino[1,2-*a*]indole **3a** was produced in a small amount. Consequently, we aimed to maximize the yield of **3a**. We evaluated various photocatalysts and photosensitizers for the photooxygenation of **1a**, and the reaction mixtures were analyzed by quantitative ^{1}H NMR spectroscopy (Table 1). LED irradiation (460 nm blue) of **1a** alone, in CD_3OD solution in the presence of NaOD and under O_2 atmosphere, led to 15% conversion after 14 h and the generation of only quinolone **2a** in 14% yield. In the presence of 2 mol% of triphenylpyrylium cation (TPP^+), a comparable result was obtained (entries 1 and 2). Using ruthenium(II) tris-bipyrazine and 9-mesityl-10-methylacridinium (Mes^+-Acr) improved conversion of **1a** to 60–77%, to give compound **2a** in 24% and 59% yield, respectively, while the desired hemiaminal **3a** was detected in small quantities of ca. 5%, exclusively as its ring-closed tautomer. However, **3a** was also accompanied by the anthranilic dicarboxylate **4a** in the form of its disodium salt (entries 3 and 4). When the xanthene dyes Eosin Y and Rose Bengal were utilized at 530 nm (entries 5 and 6), full conversion of **1a** was achieved within 14 h. Only in the latter case, also the intermediate quinolone **2a** was fully consumed. However, dicarboxylate **4a** was the major product, formed in 53% yield and in 2.7:1 ratio with respect to hemiaminal **3a** (20% yield). The yellow dye 1,8-dihydroxyanthraquinone (1,8-HOAQ; chrysazine) has an exceptionally high $^1O_2$ sensitizing efficiency among all anthraquinones ($\Phi_\Delta = 0.69$, $S_\Delta = 0.96$ in MeCN),[10,11] and in alkaline medium, it exists as a red dianion ($\lambda_{max} = 505$ nm, Figure S1). Its use (entry 7) led to a slightly improved overall selectivity, with a higher yield of **3a** (35%), but similarly to the reaction with Rose Bengal, undesired compound **4a** still was the major product (52%).

The anthranilic amide **4a** was obviously formed by oxidative C–C cleavage of hemiaminal **3a**,[12] and we hypothesized that hydrogen peroxide generated during the reaction sequence may be the main cause for this undesired degradation reaction. Therefore, we experimented with the addition of various H_2O_2 scavengers and disproportionation catalysts.[13] In the case of Rose Bengal, equimolar amounts of DMTU (1,3-dimethylthiourea)[14] or manganese salts significantly improved the selectivity (entries 8–10), up to 5:1 in favor of **3a** over **4a** when Mn^{IV} oxide was used,[15] and hemiaminal **3a** could be isolated in 54% yield on a preparative scale (entry 10). When 1,8-HOAQ was used as the sensitizer, MnO_2 largely decelerated the photooxidation, resulting in only 44% conversion of **1a** (entry 13). Addition of DMTU or $MnSO_4$ again led to an increased selectivity towards **3a**, with yields of about 40% (entries 11 and 12). Ultimately, when the reaction mixture was diluted to 0.03 M by using toluene as co-solvent and the light source changed to blue CFL lamps, the reaction could be much better controlled even without additives (entry 14). On a preparative scale, hemiaminal **3a** could be isolated reproducibly in 65% yield, yet a total of 6 mol% of 1,8-HOAQ, added in portions, was required to achieve full conversion of the intermediate 4-quinolone **2a.**

A variety of functionalized cyclohepta[*b*]indoles **1a**–**1l** were subjected to the optimized reaction conditions and the scope of the cascade photooxygenation is depicted in Figure 1. Substrates **1b**–**e**, **1i**, and **1l** were readily prepared by Fischer indolization of cycloheptanone with the corresponding aryl hydrazines. Cycloheptaindoles with bromine substitution at C2 and C3 of the aromatic ring were further derivatized by Suzuki coupling reactions to give the C2- and C3-alkylated and arylated derivatives **1f**–**h** and **1j**,**k** (see SI for details). All photooxygenation reactions were performed using 1,8-HOAQ (conditions a) as well Rose Bengal/MnO_2 (conditions b). 1,8-HOAQ appeared to be the superior sensitizer in most cases (best results are shown in Figure 1). The cascade reaction was found to be sensitive with regard to the aromatic substituent. Compared to the reaction of **1a**, both the halide-substituted perhydroazepino[1,2-*a*]indoles **3b**–**d** and the donor-substituted derivative **3e** were isolated with yields of 30–40%.[16] The alkylated compounds **3f**–**i** were again accessible in good yields between 50–61%, including the sensitive cyclopropane derivative **3h**. The C2-arylated compound **3j** was isolated in 48% yield while its C3-regioisomer **3k** was obtained in 40% yield, interestingly accompanied by product **3a** (12% yield), apparently as the result of an unexpected C3-dearylation. In all examples **3**, the intermediate 4-quinolones **2** were generally fully consumed when Rose Bengal was utilized; when 1,8-HOAQ was used, intermediates **2** were present in up to 15% yield after the reaction in several cases. Reacting the highly electron-deficient

Table 1: Cascade photooxygenation of cyclohepta[*b*]indole **1a**.



Entry	Cat./Sens.	λ_{ex} [nm]	Conv. of **1a** [%][a]	Yield [%][b] **2a**:**3a**:**4a**
1	none	460	15	14:0:0
2	$TPP{\cdot}BF_4$	460	12	11:0:0
3	$Ru(bpz)_3(PF_6)_2$	460	60	24:5:2
4	Mes^+-Acr·ClO_4	460	77	59:6:2
5	Eosin Y	530	100	13:31:21
6	Rose Bengal	530	100	0:20:53
7	1,8-HOAQ	460	100	0:35:52
8	Rose Bengal, DMTU	530	100	0:45:10
9	Rose Bengal, $MnSO_4$	530	100	0:35:7
10	Rose Bengal, MnO_2	530	100	0:55(54)[c]:11
11	1,8-HOAQ, DMTU	460	100	0:40:12
12	1,8-HOAQ, $MnSO_4$	460	100	0:38:10
13	1,8-HOAQ, MnO_2	460	44	29:2:2
14	1,8-HOAQ, $PhCH_3$	400–450	98	7:66(65)[c,d]:10

All reactions performed at 0.05 M concentration and irradiated with 10 W LED. [a] Determined by ^{1}H-NMR. [b] ^{1}H NMR yield against 1,3,5-trimethoxybenzene standard. [c] Yield of isolated product from preparative run on 0.25 mmol scale and using KOH aq./MeOH. [d] $PhCH_3$ cosolvent, *c* (**1a**) = 0.03 M, 2 mol% catalyst addition at 0, 5, 10 h, total duration 15 h, 36 W blue CFL lamps.

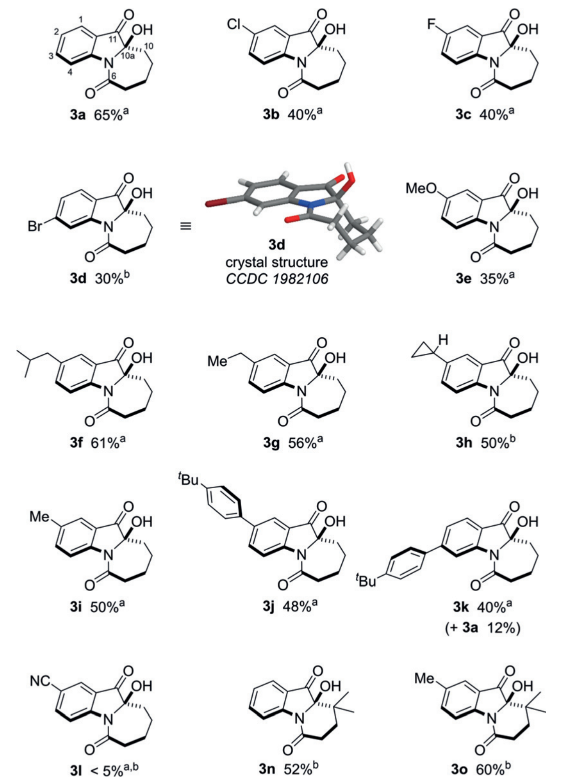
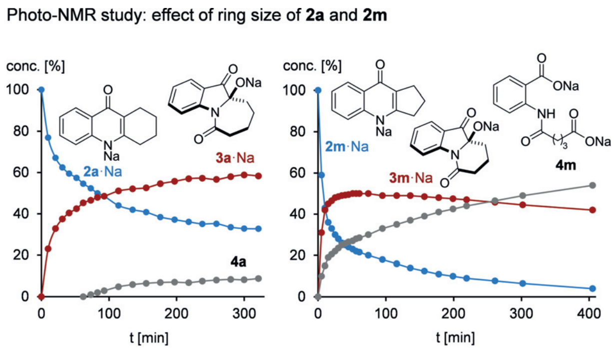


Figure 1. Scope of photooxygenation products. Reactions performed on 0.25 mmol scale, yields after chromatography. a) 1,8-HOAQ (3×2 mol%), O_2, $h\nu$ 400–450 nm CFL (36 W), KOH aq., MeOH/ $PhCH_3$, r.t., 14–20 h. b) Rose Bengal (2 mol-%), O_2, $h\nu$ 530 nm LED, MnO_2 (1 equiv), NaOH aq., MeOH, r.t., 14–20 h.

2-cyanocyclohepta[*b*]indole **1l** gave only low conversion and generated a mixture of products where compound **3l** could be detected in trace amounts only.

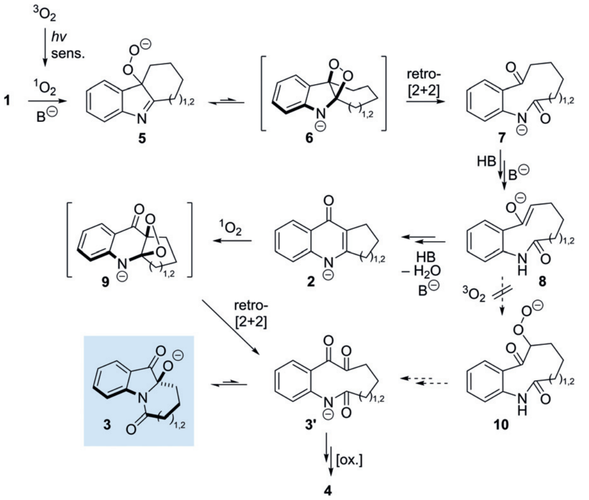
Under the conditions established for cyclohepta[*b*]indoles, 1,2,3,4-tetrahydrocarbazole (**1m**) reacted much faster and the corresponding anthranilic amide **4m** was formed quantitatively after 14 h reaction time, regardless of which sensitizer was used. To gain insight into the effect of ring size, we investigated the photooxygenation of the intermediate quinolones **2a** and **2m** by in situ ^{1}H NMR spectroscopy, in oxygen-saturated CD_3OD/ NaOD solution with 445 nm blue laser photoexcitation and using 2 mol% 1,8-HOAQ (Scheme 2).

Under these model conditions, conversion of the cyclohexane-fused quinolone **2a** was comparably slow (65% after 5 h), the seven-membered hemiaminal **3a** being the main product, accompanied by only ca. 10% of dicarboxylate **4a**. Consistently, a reaction time of 42 h was needed in a preparative run aimed at converting quinolone **2a** quantitatively into **4a** (see SI). Photooxygenation of the five-membered-ring quinolone **2m**, derived from tetrahydrocarbazol **1m**, proceeded much faster, and the six-membered-ring hemiaminal **3m** formed rapidly, but it was further converted into dicarboxylate **4m** almost instantaneously. As a consequence, compound **3m** could be isolated only in small amounts in preparative experiments. However, introduction of a *gem*-dimethyl group in the C3-position of tetrahydrocarbazole allowed for the isolation of the corresponding perhydropyrido[1,2-*a*]indoles with good yields, as exemplified by products **3n** (52%) and **3o** (60%) in Figure 1. Hence, in these examples, the *gem*-dimethyl group could stabilize the hemiaminals **3n** and **3o** against oxidative degradation.



Scheme 2. Photo-NMR study of the photooxygenation of quinolones **2a** and **2m**.

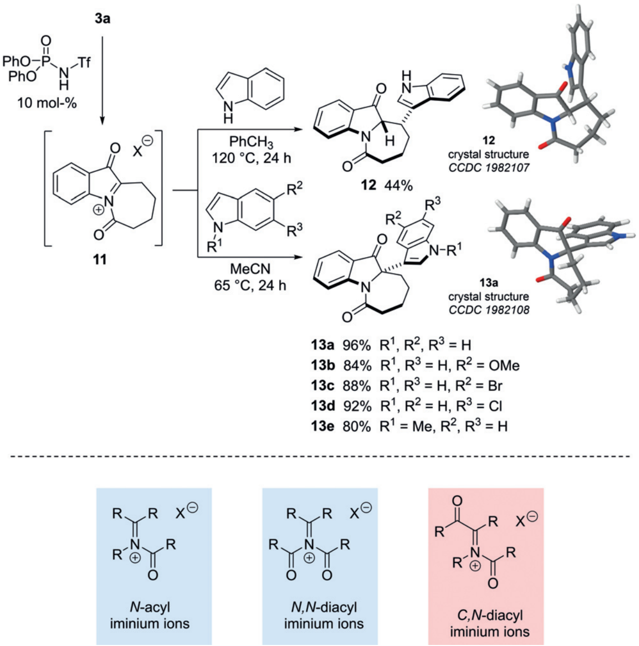
The proposed mechanism of the cascade photooxygenation, in strongly alkaline medium, is depicted in Scheme 3. When either sensitizer is used, Rose Bengal or 1,8-HOAQ, singlet oxygen is the dominant reactive oxygen species (ROS) in the reaction sequence. This was verified by studying the influence of various ROS scavengers on the reactions **1a** → **3a** + **4a** and **2a** → **3a** + **4a** (Tables S1 and S2), and the $^1O_2$-quencher sodium azide (NaN_3) showed the most pronounced effect on the overall reaction rate and product distribution. The ene reaction of substrate **1** with $^1O_2$ intially gives hydroperoxide **5**, which under basic conditions undergoes rapid C–C cleavage to keto amide **7** via the unstable 1,2-dioxetane **6**. The enolate **8** cyclizes by aldol condensation ("Camps" cyclization[17]) to give 4-quinolone **2** as product of a photochemical Witkop–Winterfeldt[18]-type reaction. The singlet oxygenation of **2** followed by ring cleavage of a second dioxetane **9**, via a charge-transfer-induced decomposition,[19] generates product **3**. The oxidation of quinolones **2** is fast for



Scheme 3. Proposed mechanism.

strained cyclopentane derivatives ($n = 1$), while for cyclohexane derivatives ($n = 2$), it becomes the rate-determining step. A conceivable second product-forming pathway involving addition of O_2 to the enolate **8**, to give the hydroperoxide **10** as a precursor to **3**, can be ruled out as neither **10** nor related intermediates could be observed.[20] The C−C cleavage of hemiaminal **3** to dicarboxylate **4** commences from the ring-opened 1,2-diketone tautomer **3′** and can occur by photooxidation as well as by the attack of in situ generated hydrogen peroxide (see SI).

The perhydroazepino- and pyrido[1,2-*a*]indoles **3** are new precursors to *N*-acyl iminium ions,[21] and we attempted their activation by phosphoric acid organocatalysis.[22] Our preliminary results, shown in Scheme 4, indicated that strong Brønsted acids like *N*-triflyl phosphoramides[23] are required to effectively convert model compound **3a** into the iminium ion **11**. Moreover, a strong effect of solvent was observed in the arylation reaction with 1*H*-indole. In toluene solution, a reaction temperature of 120 °C was necessary to achieve full conversion of hemiaminal **3a** within 24 h; however, elimination to the corresponding enone was predominant, and the 1,4-addition product **12** was isolated as the major product in 44 % yield. When acetonitrile was used, the temperature could be lowered to 65 °C, and pleasingly, the Friedel–Crafts product **13a** could be isolated in 96 % yield. Various substituted indoles including *N*-methylindole could be employed as nucleophiles, leading to products **13b**–**13e**, whose *N*-acyl-2-(indol-3-yl)-3-oxoindoline core structure is encountered in several natural products, and thus this class of compounds may be of value in drug discovery research.[24] Iminium ion **11** is one of the rare examples from the class of *C*,*N*-diacyliminium ions,[25] and a systematic study of this chemotype's reactivity has not been undertaken so far. Further investigations are currently underway in our laboratory and more results will be reported in due course.



Scheme 4. Brønsted acid catalyzed functionalization of **3a** via *C*,*N*-diacyliminium ion **11**.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cascade reactions · indoles · *N*-acyliminium ions · photooxidation · singlet oxygen

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