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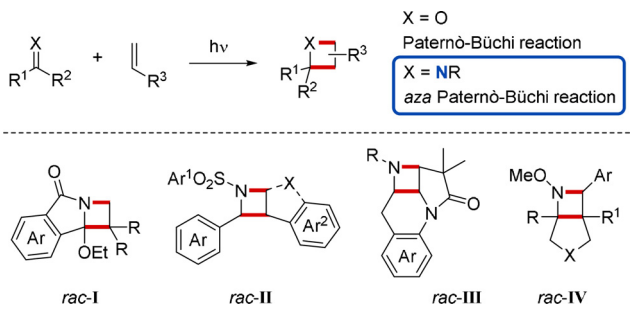
Cycloaddition

Enantioselective, Visible Light Mediated Aza Paternò–Büchi Reactions of Quinoxalinones

*Xinyao Li, Johannes Großkopf, Christian Jandl, and Thorsten Bach**

Abstract: *3-Substituted quinoxalin-2(1H)-ones and various aryl-substituted or tethered olefins underwent an enantioselective, inter- or intramolecular aza Paternò–Büchi reaction upon irradiation at λ = 420 nm in the presence of a chiral sensitizer (10 mol %). For the intermolecular reaction with 1-arylethenes as olefin components, the scope of the reaction was studied (14 examples, 50–99 % yield, 86–98 % ee). The absolute and relative configuration of the products were elucidated by single-crystal X-ray crystallography. The reaction is suggested to occur by triplet energy transfer in a hydrogen-bonded 1:1 complex between the imine substrate and the catalyst. The intramolecular cycloaddition, consecutive reactions of the product azetidines, and an alternative reaction mode of quinoxalinones were investigated in preliminary experiments.*

The creation of strained four-membered rings represents one of the signature transformations of photochemistry. The enone [2+2] photocycloaddition[1,2] as an entry to cyclobutanes and the Paternò–Büchi reaction[3,4] as an entry to oxetanes (Scheme 1) have been established as reliable tools in organic synthesis. Against this background, it is somewhat surprising to note that the synthesis of azetidines by a [2+2] photocycloaddition (aza Paternò–Büchi reaction, Scheme 1) is less well developed.[5] A major challenge in photochemical azetidine formation is posed by the search for suitable chromophores which are readily promoted into reactive excited states from which a defined C–N and C–C bond formation can occur. If the imine itself is meant to serve as the chromophore its substitution pattern should avoid an oxidation in the excited state and a rotation around the C–N bond (*E*/*Z* isomerization). Early work on photochemical azetidine formation was consequently based on the use of cyclic imines many of which carried an electron withdrawing group at the nitrogen atom[6] (e.g. products *rac*-**I**). In more recent work, Maruoka and co-workers showed that *N*-sulfonylated imines represent suitable substrates which undergo an aza Paternò–Büchi reaction with styrenes possibly via a singlet exciplex (products *rac*-**II**).[7] An elegant way to overcome the sometimes problematic photochemistry of imines is to employ the olefin component of an aza Paternò–Büchi reaction as the chromophore. Sivaguru and co-workers selected enamides for this purpose and showed that products with the general structure *rac*-**III** were accessible upon irradiation in the presence of xanthone as a triplet sensitizer at λ = 350 nm.[8] Schindler and co-workers discovered than an iridium catalyst can act as the sensitizer at λ = 427 nm and products of type *rac*-**IV** were obtained from a broad variety of arylalkenes to which oximes (and hydrazones) were linked by a three-atom tether.[9] Also in this case, it was the olefin which is photochemically excited and initial bond formation likely occurs at the C–C bond. In a very recent publication, the Schindler group showed that an intermolecular aza Paternò-Büchi reaction was possible employing 2-isoxazoline-3-carboxylates as imine chromophores and an iridium complex as the sensitizer.[10]



Scheme 1. Top: The Paternò–Büchi reaction as an approach to oxetanes (X = O) and the respective aza variant that leads to azetidines (X = NR). Bottom: Previous work[6–9] on aza Paternò–Büchi reactions resulting in products with the general structures *rac*-**I** to *rac*-**IV**.

Most photochemically generated azetidines have so far been obtained as racemic mixture of enantiomers. The only notable way to access enantioenriched compounds is based on the use of axially chiral enamides which allow for a chirality transfer in the course of the aza Paternò–Büchi reaction.[8] Despite the beauty of atropselective photochemical reactions,[11] they rely on the stoichiometric use of the chiral substrate and do not offer the option of a catalytic enantioselective process. We have now found a way to prepare chiral azetidines in enantiomerically pure form by employing a chiral triplet sensitizer that invites the precoordination of imine substrates by hydrogen bonding and operates with visible light (λ = 420 nm).

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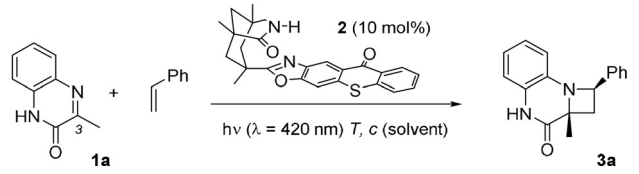
Our study focused on the use of quinoxalin-2(1*H*)-ones (quinoxalinones) as imine components in an aza Paternò–Büchi reaction. Previous work by Nishio[6i,j] had established that they react with olefins upon direct UV irradiation ($\lambda >$ 280 nm) or upon UV irradiation in the presence of a triplet sensitizer (*meta*-methoxyacetophenone) to form azetidines. The synthetically most interesting results had been obtained from the reaction of *N*-substituted quinoxalinones and arylalkenes[12] as olefins which had delivered a single product isomer with defined regio- and simple diastereoselectivity. Our own optimization experiments commenced with 3-methyl-quinoxalinone (**1a**) as the imine component and styrene as the olefin. Phosphorescence spectra (vide infra) indicated that the reactive triplet state of compound **1a** could be accessible by energy transfer from chiral thioxanthone **2**. Compound **2** had been previously employed in enantioselective photochemical reactions[13] and its triplet energy was determined as $E(T_1) = 263\ kJ\,mol^{-1}$ (77 K, $PhCF_3$).[13c] To our delight, we observed in an initial reaction (Table 1, entry 1) with catalytic quantities of **2** (10 mol%) a rapid product formation and could isolate azetidine **3a** as a single product in high yield. Since the enantiomeric excess (*ee*) was not particularly high in acetone (50% *ee*) we screened other solvents (entries 2–4) with the restriction that substrate **1a** was not soluble in non-polar media. 1,2-Dichloroethane (DCE) turned out to be the solvent of choice for the reaction and product **3a** was obtained in almost quantitative yield and with 94% *ee* (entry 4).

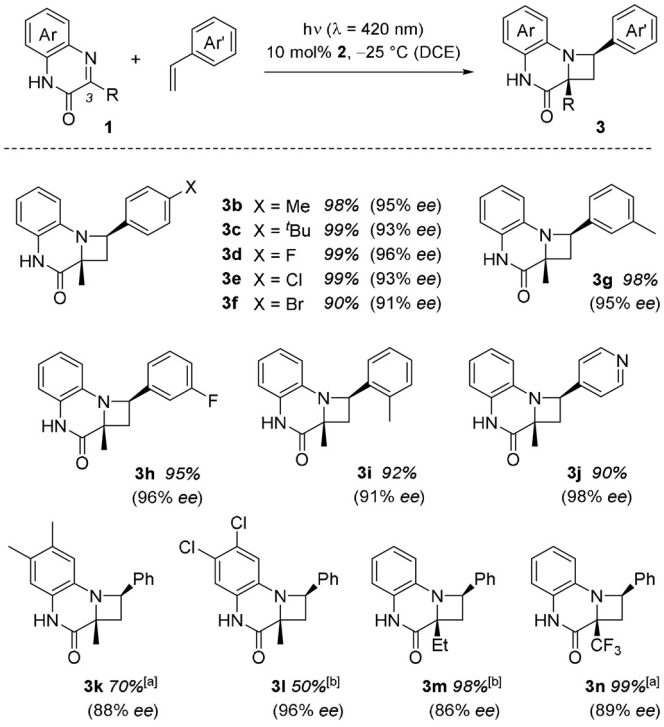
Table 1: Reaction optimization for the catalytic, enantioselective aza Paternò–Büchi reaction of quinoxalinone **1a** and styrene to product **3a**.



Entry[a]	*c* [mm]	Styrene (equiv)	Solvent	*T* [°C]	Yield[b] [%]	*ee*[c] [%]
1	10	20	acetone	−25	95	50
2	5	20	MeCN	−25	99	61
3	5	20	CH_2Cl_2	−25	99	89
4	5	20	DCE	−25	99	94
5	3.3	20	DCE	−30	99	93
6	5	10	DCE	−25	90	92
7	5	40	DCE	−25	99	94
8[d]	5	20	DCE	−25	92	92
9[e]	5	20	DCE/CH_2Cl_2	−40	85	92
10[f]	5	20	DCE	−25	98	93

[a] Reactions were performed in the respective solvent by irradiation at $\lambda = 420$ nm (fluorescent lamps) at the indicated concentration (*c*) and temperature (*T*) with an excess of styrene and 10 mol% of thioxanthone **2**. The reaction was stopped after full conversion was reached (24–36 h). [b] Yield of isolated product **3a**. Only a single diastereoisomer was formed. [c] The enantiomeric excess was calculated from the enantiomeric ratio (**3a**/*ent*-**3a**) as determined by chiral-phase HPLC analysis. [d] The reaction was performed with 5 mol% of sensitizer **2**. [e] A solvent mixture of DCE and dichloromethane (4/1, v/v) was employed. [f] The reaction was performed on a scale of 1 mmol with re-isolation of the catalyst (90% recovery).

Although the hydrogen bonding interaction which is responsible for the enantioface differentiation should be favored at lower temperature, a decrease in the temperature (entries 5 and 9) had no beneficial influence on the enantioselectivity. Regarding the styrene, the optimization study showed that an excess of 20 equiv was ideal. A decrease led to a lower yield and enantioselectivity (entry 6) while a further increase did not improve the results (entry 7). The reaction can be successfully performed with 5 mol% of the sensitizer (entry 8) but the enantioselectivity suffered slightly under these conditions. Eventually, we ran the reaction on larger scale (1 mmol) and showed that the sensitizer can be almost fully recovered (entry 10). If the reaction was performed with the recovered thioxanthone **2** there was no change in yield and enantioselectivity (see the SI for further details on the optimization experiments). With optimized conditions in hand, a variety of quinoxalinones and arylethenes were employed in the enantioselective aza Paternò–Büchi reaction (Scheme 2). The variation of the *para*-substituents in the aryl ring of the olefin (Ar′) included typical alkyl groups (methyl, *tert*-butyl) and halogen substituents (F, Cl, Br). Products **3b**–**3f** were obtained in excellent yields and in high optical purity (91–96% *ee*). The position of the substituent did not alter the consistently high chemo- and enantioselectivity (products **3g**–**3i**) nor did a 4-pyridyl group instead of a substituted phenyl group (product **3j**). Substrates with different substituents in the benzo ring (Ar) of the quinoxalinone were not as easy to access synthetically as the arylethenes but in the two cases which were studied (products **3k**, **3l**) the enantioselectivity remained high. Eventually, it was probed whether the



Scheme 2. Enantioselective aza Paternò–Büchi reactions of quinoxalinones **1** and various 1-arylethenes. [a] The reaction was performed in CH_2Cl_2 at −70 °C. [b] The irradiation was performed at −35 °C.

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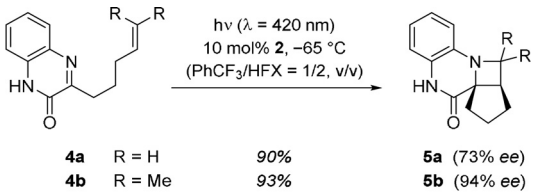
substituent in position C3 could be varied and it was found that products **3m** and **3n** were formed cleanly in 86% and 89% *ee*.

Substitution at the methyl group of compound **1a** is facile after deprotonation[14] and allowed the introduction of alkenyl groups which are tethered to the quinoxalinone ring. The subsequent intramolecular aza Paternò–Büchi reaction of compounds **4** was tested (Scheme 3) and led to the expected tetracyclic products *rac*-**5** when performed with achiral thioxanthen-9-one (TXT) as the sensitizer. Chiral thioxanthone **2** delivered the respective products **5** in equally high yields and with notable enantioselectivity. In this case the solubility of the substrates in nonpolar solvents was higher than in the intermolecular reaction with quinoxalinones **1**. Consequently, the established solvent mixture of trifluorotoluene and hexafluoro-*m*-xylene (HFX)[15] was employed which enables irradiation at temperatures as low as −65 °C. Under these conditions, the enantioselectivity achieved in the aza Paternò–Büchi reaction of trisubstituted olefin **4b** was high (94% *ee*). The less electron rich, terminal olefin **4a** reacted less selectively.

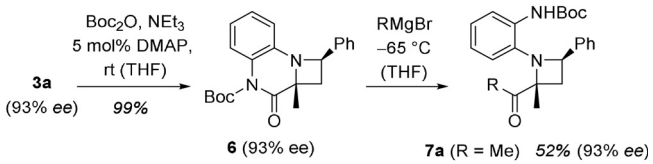
In a brief study we investigated whether compounds like **3a** could be converted into monocyclic N-protected azetidines without compromising their optical purity (Scheme 4). To this end, lactam **3a** was acylated to its *tert*-butoxycarbonyl (Boc) derivative **6** which in turn was subjected to nucleophilic attack by Grignard reagents. Lactam ring opening proceeded smoothly[16] and gave—under non-optimized conditions—the desired azetidines **7** in 52% and 71% yield. The *ee* was determined at each stage of the sequence and remained constant (93% *ee*).

As alluded to in the introductory section the relative configuration of aryl-substituted azetidines **3** had not been previously established. We succeeded in receiving suitable crystals of compound **3f** which were studied by single-crystal X-ray crystallography (Scheme 5).[17] The aryl ring and the methyl substituent within the azetidine were shown to be *cis*



4a R = H *90%* **5a** (73% *ee*)
4b R = Me *93%* **5b** (94% *ee*)

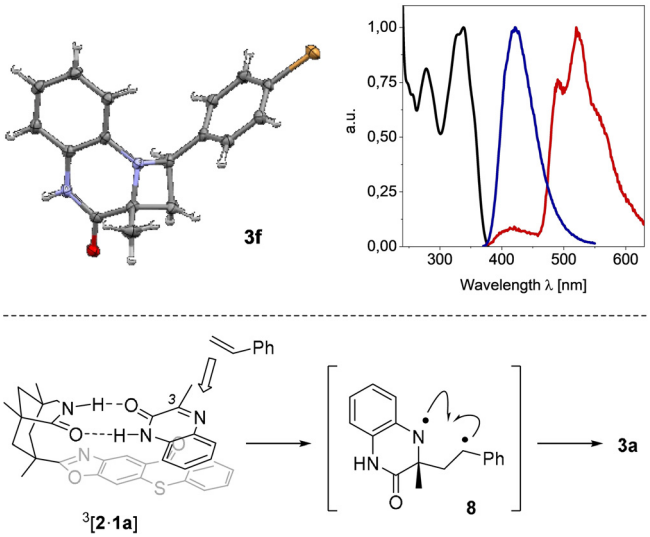
Scheme 3. Enantioselective intramolecular aza Paternò–Büchi reaction of quinoxalinones **4** upon irradiation with visible light (HFX = hexafluoro-*m*-xylene).



6 (93% ee)

7a (R = Me) *52%* (93% *ee*)
7b (R = Bn) *71%* (93% *ee*)

Scheme 4. Ring opening reactions of the six-membered lactam **6** to generate N-protected chiral azetidines **7** with retention of configuration.



Scheme 5. Constitution and absolute configuration of product **3f** (top left), absorption (rt, EtOH), fluorescence (rt, EtOH), and phosphorescence (77 K, EtOH) spectra of quinoxalinone **1a** (top right), and mechanistic picture of the enantioselective aza Paternò–Büchi reaction to product **3a**.

positioned to each other. The structure revealed a significant pyramidalization of the nitrogen atom which is potentially induced by the aryl group that rests in a pseudoequatorial position within the puckered ring system. Anomalous diffraction data allowed us to assess the absolute configuration of the product and the configuration of all other azetidines was based on analogy. The C–C bond at position C3 of the quinoxalinone is formed at its *Re* face.

The photophysical properties of quinoxalinone **1a** were studied by luminescence measurements (see the SI for details). Fluorescence spectra were recorded in EtOH solution at ambient temperature and the energy of the 0-0 transition was determined as $E(S_1) = 318\ kJ\,mol^{-1}$. The triplet energy was estimated from the phosphorescence spectrum which was recorded in an EtOH matrix at 77 K. With an $E(T_1) = 250\ kJ\,mol^{-1}$ the compound can undergo an exothermic energy transfer from thioxanthone **2**. In line with previous studies on catalyst **2**[13] we suggest that hydrogen bonding to substrate **1a** occurs readily and facilitates not only the energy transfer but also in a subsequent step the C–C bond formation within complex ^{3}[**2**·**1a**]. As shown in Scheme 5, the *Si* face of **1a** is shielded by the thioxanthone entity which leaves for the styrene to attack only the *Re* face. The intermediate 1,4-diradical **8** collapses after intersystem crossing (ISC) diastereoselectively into the azetidine product. The crystal structure of **3f** indicates that the *cis* configuration of the aryl and the methyl group is clearly preferable as a *trans* configuration would induce a massive steric repulsion of the two arene rings. Although energy transfer from the triplet state of **2** to styrene is energetically feasible[18] this pathway is less likely. If operational, it would be difficult to explain why the enantioselectivity is so high with a catalyst loading of only 10 mol%. In addition, the intramolecular energy transfer in complexes of **2** with the quinoxalinone should be preferred.[13c,g,19] An

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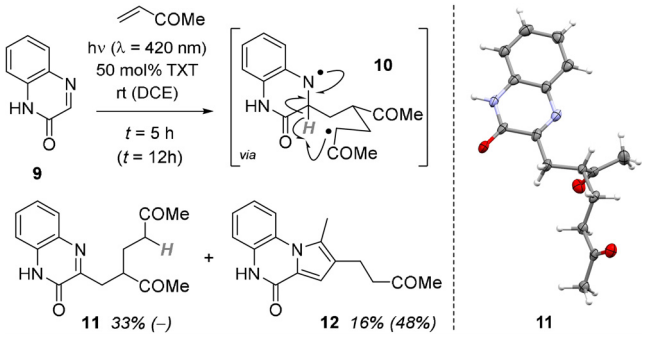
alternative reaction pathway via single electron transfer from quinoxalinone is thermodynamically disfavored. Although the triplet state of quinoxalinones can be quenched by reductants,[20] a reduction by styrenes is not feasible. The ground state reduction potential of compound **1a** was determined as E_{red} (**1a**/**1a**$^{\bullet-}$) = −1.78 V vs. SCE which indicates that the triplet state is only a weak oxidant with a caluclated[21] E_{red} (^{3}**1a**/**1a**$^{\bullet-}$) = +0.81 V.

A notable observation was made when studying possible photocycloaddition reactions of quinoxalinone **9** which is unsubstituted at position C3. Unlike the 3-alkylated substrates **1** and **4** the compound did not produce an azetidine when reacted under sensitized conditions. Instead, a C3-substitution product was formed with styrene in low yield (see the SI for details). With methyl vinyl ketone the outcome of the reaction was even more surprising (Scheme 6). Sensitized irradiation with TXT as achiral sensitizer produced a mixture of two products one of which turned out to be diketone **11**. The product was isolated in 33% yield after five hours of irradiation and its constitution was elucidated by single crystal X-ray crystallography.[22] The other product, which was isolated as the only product after prolonged irradiation, was tentatively identified as pyrrole **12**. It appears to be formed as consecutive product of diketone **11** in a Paal-Knorr type condensation reaction.[23] The formation of product **11** indicates that the 1,4-diradical related to **8** does in this instance not close to an azetidine ring but undergoes addition at the C-terminus to a second molecule of methyl vinyl ketone. The resulting 1,6-diradical **10** appears to react by γ-hydrogen abstraction at the C3 carbon atom where the indicated hydrogen atom (*H*) likely stems from. Unfortunately, the limited stability of **11** compromised any attempts to study the enantioselectivity of the process.



Scheme 6. Photochemical twofold addition of methyl vinyl ketone to quinoxalinone **9** delivering diketone **11** and pyrrole **12** via 1,6-diradical intermediate **10** (left), crystal structure of product **11** (right). Yields within parentheses refer to the prolonged reaction time (12 h).

In summary, we have shown that 3-substituted quinoxalinones can be successfully employed as imine components in enantioselective aza Paternò–Büchi reactions mediated by sensitizer **2**. The lactam part of the quinoxalinones enables a directed two-point hydrogen-bond interaction with the catalyst which is responsible for a facile exothermic triplet energy transfer and for an efficient enantioface differentiation. Arylalkenes serve as olefinic substrates which not only guarantee a rapid formation of the first stereogenic center but also deliver the stereogenic center to which the aryl group is attached with high simple diastereoselectivity. The reactivity pattern of quinoxalinone heavily depends on the 3-substituent and the two-fold olefin addition to substrate **9** is an unprecedented photochemical reaction which deserves further studies.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloaddition · heterocycles · hydrogen bonds · photochemistry · sensitizers

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