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Radical Reactions

Radical Reactions Induced by Visible Light in Dichloromethane Solutions of Hünig's Base: Synthetic Applications and Mechanistic Observations

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Abstract: β-(3-Iodopropoxy)-substituted α,β-unsaturated lactams, lactones, and cycloalkenones (eight examples) underwent reductive radical reactions in a dichloromethane solution of *N,N*-diisopropylethylamine (Hünig's base) upon irradiation with visible light ($\lambda = 419$ nm). Apart from plain reduction reactions (hydro-de-iodination), a significant degree of cyclization was observed in three cases. In parallel to the conversion of the substrates, the formation of intensely colored by-products was observed. Based on mass spectrometric evidence and upon comparison with known compounds, the by-products were identified as cyanine dyes. Their formation supports the hypothesis that irradiation of dichloromethane solutions of Hünig's base leads to the formation of radicals, which in turn can either initiate a radical reaction or combine with cyanine precursors. It was shown by deuterium-labelling experiments, that one equivalent of dichloromethane is incorporated into the cyanine dyes and that the reductive quenching of radical intermediates is at least partially due to hydrogen abstraction from the solvent. As a consequence, a reductive cyclization of the starting materials is favored in CD_2Cl_2 solutions as shown for two β-(3-iodopropoxy)-substituted tetronates, which underwent in dichloromethane almost exclusive reduction, but gave predominantly the cyclization products in CD_2Cl_2.

Introduction

It is relatively well-known that tertiary amines can be involved in electron-donor–acceptor (EDA) complexes and in subsequent photoinduced electron transfer (PET) reactions.[1] As early as 1962, Stevenson and Coppinger observed a significant bathochromic shift when comparing the UV/Vis spectra of a triethylamine solution in chloroform with a solution of the same concentration in other solvents such as water, isooctane, or diethyl ether.[2] The effect was even more pronounced for triethylamine solutions in carbon tetrachloride and bromotrichloromethane and was explained by a charge-transfer complex between the two components. Upon exposure of a triethylamine solution in carbon tetrachloride to light, the formation of triethylamine hydrochloride and chloroform was observed, and it was postulated that a photoinduced electron transfer from the amine to carbon tetrachloride occurs, which leads to the formation of a trichloromethyl radical. Similar observations were made by Kochi and co-workers when studying solutions of bicyclic amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO) in carbon tetrabromide or carbon tetrachloride.[3] In the solid state, evidence for a halogen bond between DABCO and carbon tetrabromide was collected, and upon irradiation of a solution of the two components at a wavelength $\lambda > 380$ nm, the DABCO hydrobromide was formed.

In recent years, renewed interest in the existence of EDA complexes of amines and enamines resulted from the observation that radical reactions can be performed upon direct irradiation in the absence of an additional photoredox catalyst.[4] The Melchiorre group successfully employed visible light to trigger enantioselective α-alkylation reactions of aldehydes.[5] Two mechanistic pathways to initiate the radical reaction were found to operate; one including radical generation upon formation of an EDA complex, the other one including direct excitation of an enamine.[5d] In both cases, a single-electron transfer follows to generate a carbon-centered radical that enters the radical-chain process. Zeitler and co-workers reported the formation of iminium ions upon irradiation of tetrahydroisoquinolines in the presence of polyhalomethanes.[6] The discovery was applied to the oxidative α-C–H functionalization of tertiary amines with carbon and heteroatom nucleophiles.

In recent studies aiming to use hydrogen bonding templates or catalysts for enantioselective photoredox reactions,[7] it was accidentally found that even in dichloromethane solution, radicals can be formed from tertiary amines, such as *N,N*-diisopropylethylamine (Hünig's base),[8] upon irradiation with visible light (Scheme 1). Radical reactions were initiated and led to the cyclization or reduction of β-(3-iodopropoxy)-substituted α,β-unsaturated lactams, lactones, and cycloalkenones. In addition, evidence was collected that cyanine dyes form as side products from intermediates **1** and **2**. Detailed results from our synthetic and mechanistic studies are collected in this report.

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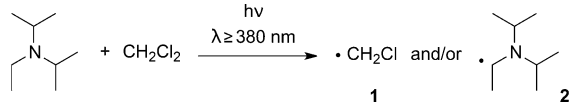
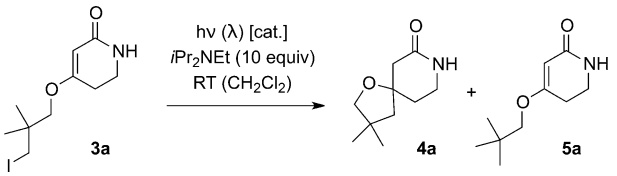


Scheme 1. Putative formation of radicals **1** and **2** upon irradiation of *N*,*N*-diisopropylethylamine (Hünig's base) in dichloromethane solution.

Results and Discussion

The radical cyclization of dihydropyridone **3a** was investigated in the context of enantioselective reactions, which could be potentially performed in the presence of a chiral hydrogen-bonding template. Related visible-light-induced reactions have been previously reported by Kim and Lee to be successful with an iridium-based photoredox catalyst and a relatively large excess of Hünig's base in acetonitrile solution.[9] Considering that the formation of hydrogen bonds is incompatible with a polar solvent, preliminary experiments in our group were conducted in dichloromethane solution employing iridium complexes as catalysts. Cool white lamps ($\lambda = 380$–700 nm) or fluorescent lamps ($\lambda = 419$ nm) were used as light sources (Table 1).[10] It was found that both $[Ir(ppy)_2(dtbbpy)]BF_4$ (ppy = phenylpyridyl; dtbbpy = 4,4′di-*tert*-butyl-2,2′-bipyridine) and $[Ir\{(df)(CF_3)ppy\}_2(bpy)]PF_6$ {(df)(CF_3)ppy = 3,5-difluoro-2-[5′-(trifluoromethyl)-2′-pyridinyl]phenyl, bpy = 2,2′-bipyridine} facilitate a reaction.[11,12] The desired cyclization product **4a** prevailed, but reduction product **5a** was also observed. (Table 1, entries 1, 2). With $[Ir\{(df)(CF_3)ppy\}_2(bpy)]PF_6$, the reaction seemed cleaner but incomplete, which is why the light source was modified (entry 3) and the catalyst loading was increased (entry 4). Expectedly, there was no reaction if the amine was omitted (entry 5). However, much to our surprise, the reaction proceeded almost quantitatively also in the absence of an iridium catalyst (entry 6).

Table 1. Influence of the catalyst on an attempted radical cyclization of dihydropyridone **3a** upon irradiation with visible light.[a]

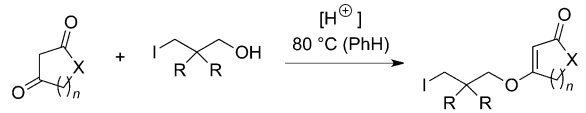


Entry	Catalyst (mol%)	λ [nm]	Conversion [%]	4a [%]	5a [%]
1	$[Ir(ppy)_2(dtbbpy)]BF_4$ (2.5)	380–700	73	54[b]	11[b]
2	$[Ir\{(df)(CF_3)ppy\}_2(bpy)]PF_6$ (2.5)	380–700	49	42	7
3	$[Ir\{(df)(CF_3)ppy\}_2(bpy)]PF_6$ (2.5)	419	72	61	11
4	$[Ir\{(df)(CF_3)ppy\}_2(bpy)]PF_6$ (5.0)	419	100	87	13
5[c]	$[Ir\{(df)(CF_3)ppy\}_2(bpy)]PF_6$ (5.0)	419	–	–	–
6	–	419	89	69	20

[a] The reaction was performed by irradiation at the indicated wavelength for 24 h at a substrate concentration of $c = 20$ mM. The conversion and the relative yields of **4a** and **5a** were determined by ^{1}H NMR spectroscopy. [b] Yield of isolated product. [c] No amine was added to the reaction mixture.

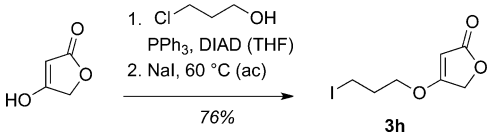
The preliminary result triggered a more extensive study with several β-(3-iodopropoxy)-substituted α,β-unsaturated lactams, lactones, and cycloalkenones of general structure **3** (Table 2). The general procedure to prepare these compounds relied on an acid-catalyzed condensation between the respective β-keto derivatives (which in some cases exist as enols) and either 3-iodopropanol or 2,2-dimethyl-3-iodopropanol.[13,14] Refluxing a benzene solution in a Dean–Stark apparatus gave the respective dihydropyridones **3a** and **3b**, cyclopentenones **3c** and **3d**, cyclohexenones **3e** and **3f**, and tetronate **3g** (entries 1–7, respectively) in yields of 41-96%. For the synthesis of tetronate **3h**, a two-step pathway was taken, which involved an initial Mitsunobu reaction[15] of tetronic acid[16] with 3-chloropropanol followed by a Finkelstein reaction[17] (Scheme 2).

Table 2. Synthesis of β-(3-iodopropoxy)-substituted α,β-unsaturated lactams, lactones, and cycloalkenones **3**.[a]



Entry	X	n	Acid (mol%)	R	Product	Yield[b] [%]
1	NH	2	H_2SO_4 (5.0)	Me	**3a**	65
2	NH	2	H_2SO_4 (5.0)	H	**3b**	96
3	CH_2	1	TsOH (10.0)	Me	**3c**	60
4	CH_2	1	TsOH (10.0)	H	**3d**	88
5	CH_2	2	TsOH (10.0)	Me	**3e**	83
6	CH_2	2	TsOH (10.0)	H	**3f**	70
7	O	1	TsOH (10.0)	Me	**3g**	41

[a] The reaction was performed by refluxing a benzene solution ($c = 0.25$ M) of the substrates (excess alcohol) in a Dean–Stark apparatus. [b] Yield of isolated product.

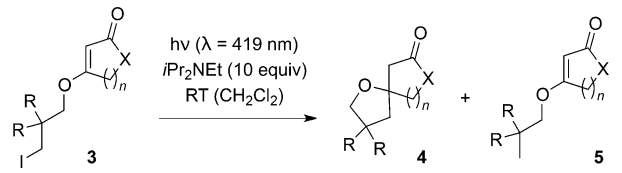


Scheme 2. Synthesis of β-(3-iodopropoxy)-substituted tetronate **3h** by Mitsunobu reaction with 3-chloropropanol and subsequent Finkelstein reaction.

Radical reactions of compounds related to substrates **3** have not been extensively studied. The chloro analogue of iodo compound **3f** was described, and upon heating with tributyltin hydride and azobis(isobutyronitrile) (AIBN) in benzene, gave exclusively the reduction product **5f** (95% yield; see Table 3).[18] A precursor, in which a phenylseleno instead of an iodo group was at the 3-position, was found by Simpkins and co-workers to cyclize to the respective spirocyclic product **4f**, if a solution of Bu_3SnH and AIBN was added to a refluxing solution of the substrate in benzene (64% yield).[19] Reduction product **5f** was obtained in 27% yield. Under our conditions, which require no heat and avoid the use of tin compounds, iodo compound **3f** produced the cyclized product **4f** in 50% and the reduction product **5f** in 29% yield. The reaction time

was kept constant in all experiments and was not adjusted, which is why 14% of starting material was recovered. As expected, the tendency to cyclize is higher for compounds that bear a geminal dimethyl group in the chain (Table 3, entries 1, 3, 5, 7),[20] and satisfactory cyclization yields were also obtained for products **4a** (entry 1) and **4e** (entry 5).

Table 3. Conversion of substrates **3** into cyclization products **4** and reduction products **5** upon irradiation with visible light.[a]



3 4 5

Entry	Substrate	Recovered starting material[b] [%]	Cyclization product	Yield of 4[b] [%]	Reduction product	Yield of 5[b] [%]
1	**3a**	–	**4a**	52	**5a**	12
2	**3b**	–	**4b**	13	**5b**	25
3	**3c**	14	**4c**	12	**5c**	65
4	**3d**	–	**4d**	<10	**5d**	77
5	**3e**	28	**4e**	55	**5e**	15
6	**3f**	14	**4f**	50	**5f**	29
7	**3g**	7	**4g**	25	**5g**	65
8	**3h**	–	**4h**	<10	**5h**	86

[a] The reaction was performed by irradiation at $\lambda = 419$ nm for 24 h at a substrate concentration of $c = 20$ mM. The reaction remained incomplete in several cases. [b] Yield of isolated product.

Although reduction might not be the desired reaction pathway in most synthetic scenarios, it is notable that the yields of reduction products **5c**, **5d**, **5g**, and **5h** (entries 3, 4, 7, 8, respectively) were moderate to high (65–86%). Direct visible-light irradiation of iodides **3** in a dichloromethane solution of *N,N*-diisopropylethylamine thus provides a convenient alternative to a typical tin-mediated reduction or cyclization reaction.

Upon irradiation at $\lambda = 419$ nm, it was noted that the appearance of the reaction mixture changed from colorless to deep yellow. Before searching for means to optimize the ratio of cyclization to reduction product (**4**/**5**), we studied the origin of the prominent color change. Figure 1 substantiates the visual observation using UV/Vis spectra taken from a solution of substrate **3a** in dichloromethane. At the beginning of the reaction, only a strong band below 300 nm was notable, which tails to long wavelengths. After 24 h, there were two new bands with absorption maxima at $\lambda = 320$ and 412 nm. In the absence of light, there was no absorption change.

Considering that it was not clear whether the new bands derive from the iodinated starting material, a solution of *N,N*-diisopropylethylamine in dichloromethane was irradiated at $\lambda = 419$ nm in the absence of any substrate. The concentration of the amine was identical to its concentration in the reaction mixture ($c = 0.2$ M). After two hours, new bands started to evolve, and after six hours, the solution was deeply orange-colored (Figure 2). The absorption band at the shorter wavelength

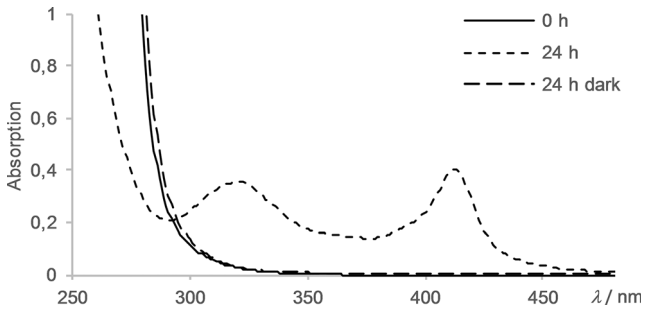


Figure 1. UV/Vis spectra of samples taken from the conversion **3a**→**4a**/**5a** (Table 3, entry 1) in the beginning of the reaction (0 h) and after completion (24 h). For comparison, a UV/Vis spectrum was recorded of a sample that was not irradiated (24 h dark).

could only be detected as a shoulder but the long wavelength absorption occurred, as previously detected (Figure 1), at $\lambda =$ 412 nm. Attempts to isolate the colored material failed as its quantity seemed to be very low. It was possible by time-resolved ^{1}H NMR spectroscopy to detect the formation of iminium ion **6** (Figure 3) in a related reaction mixture (see the Supporting Information for further details). Mass spectrometry revealed the existence of ions with relatively high molecular mass. Electrospray ionization (ESI-MS) in the positive detection mode revealed ions with molecular masses of 225, 265, and 239 Da. HRMS data revealed their atomic composition and made it likely that structures **7**–**9** could be assigned to these ions.

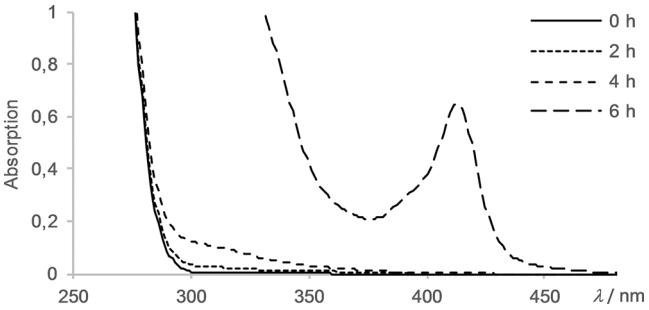
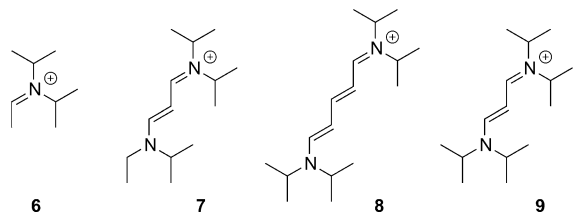


Figure 2. Time-dependent UV/Vis spectra of samples taken from a solution of *N,N*-diisopropylethylamine in CH_2Cl_2 ($c = 0.2$ M) irradiated at $\lambda = 419$ nm.



6 7 8 9

Figure 3. Structure of iminium ions **6**–**9** as detected by ^{1}H NMR spectroscopy and mass spectrometry.

Cations **7**–**9** contain the typical chromophore of cyanine dyes, which in turn are known to exhibit extremely high absorption coefficients ($\varepsilon \geq 50\,000$ M^{-1}cm^{-1}).[21] To substantiate

the hypothesis that the intense color of the solution indeed stems from cyanine dyes, the two known dyes **10** and **11** were synthesized as their perchlorate salts (Figure 4).[22] Compound **10** was almost colorless but showed a strong absorption maximum at $\lambda = 312$ nm ($\varepsilon = 46\,000\ M^{-1}cm^{-1}$). Compound **11** was obtained as a deep orange-colored solid with an absorption maximum at $\lambda = 415$ nm ($\varepsilon = 130\,000\ M^{-1}cm^{-1}$). When comparing the UV/Vis spectra of compounds **10** and **11** with that of the reaction mixture after a reaction time of 24 h (Figure 5), it is apparent that the band at short wavelength correlates well with the UV/Vis spectrum of **10** and the bathochromic absorption with the spectrum of **11**. Even if ions **7**–**9** are formed in minor quantities, their high absorption coefficients can account for intense UV/Vis bands, with ion **8** being mainly responsible for the observed color.

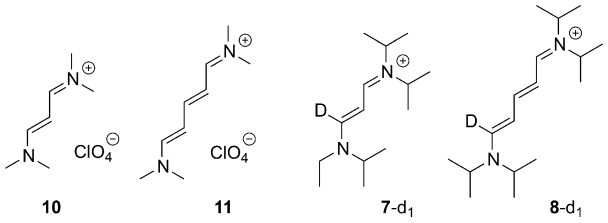


Figure 4. Structure of cyanine dyes **10**, **11** prepared according to known procedures and structure of iminium ions **7**-d_1 and **8**-d_1 detected by mass spectrometry upon irradiation of a solution of iPr$_2$NEt in CD_2Cl_2.

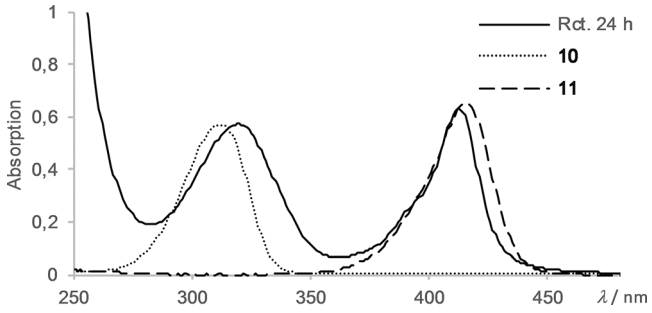
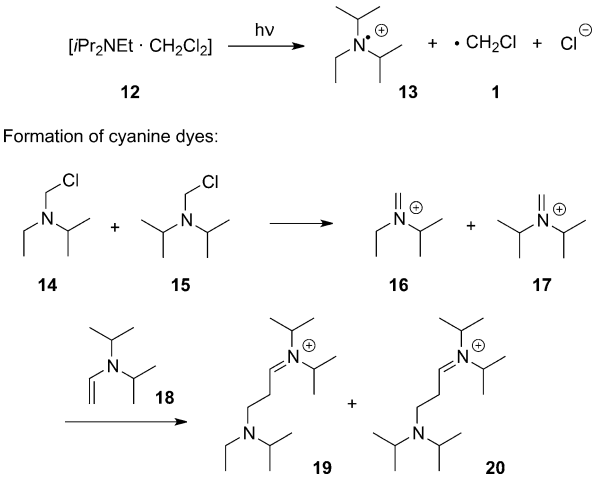


Figure 5. Comparison of the UV/Vis spectra ($c = 0.05$ mM in CH_2Cl_2) of the known cyanine dyes **10** (·····) and **11** (– – –) with the UV/Vis spectrum obtained from the reaction solution (Rct. 24 h = reaction at 24 h; see Figure 1).

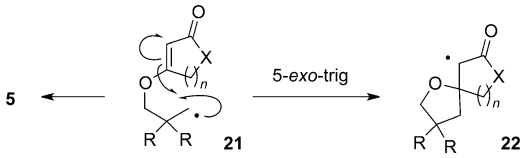
Although it is clear that *N,N*-diisopropylethylamine is a key ingredient in the formation of ions **7**–**9**, the question of whether the solvent was also involved in their formation, remained. To this end, a solution of Hünig's base in CD_2Cl_2 was irradiated in the absence of substrate **5a**. After an irradiation time of 24 h, mass spectrometric analysis (ESI-MS) revealed the existence of two previously unknown ions with molecular masses of 226 and 266 Da. The molecular formula suggested these ions to be the deuterated analogues, **7**-d_1 and **8**-d_1, of the previously detected cyanine dyes **7** and **8** (Figure 3). The only source of deuterium was CD_2Cl_2, and it is thus most likely that a deuterated methyne carbon atom is incorporated in the chain of the chromophore as indicated in Figure 4.

Mechanistically, it is postulated that the weak absorption of the EDA complex **12** of *N,N*-diisopropylethylamine and dichloromethane at long wavelength is sufficient to lead to an electron transfer, over the course of which radical **1** and radical cation **13** are generated (Scheme 3). Whereas radical cation **13** can lose a proton and be further oxidized to iminium ion **6**, an alternative pathway might involve a reaction of radical **1** to form putative intermediates **14** and **15**. Their formation could be explained by reaction of **1** and **13** through a quaternary cation and subsequent dealkylation,[23,24] or by reactions with secondary amines as impurities.[25] Elimination of chloride leads to iminium ions **16** and **17**. Enamine **18,** deriving from iminium ion **6** by deprotonation, can attack either iminium ion to form intermediates **19** and **20**. Their oxidation, either by an EDA complex with dichloromethane or electron transfer to **13**, generates cations **7** and **9**. When cation **9** is attacked by another enamine molecule **18**, diisopropylamine elimination and oxidation lead to cyanine dye **8**.



Scheme 3. Initial photoinduced electron transfer (PET) step upon irradiation of iPr$_2$NEt in CH_2Cl_2 and tentative mechanism for the formation of cyanine dyes **7** and **9**.

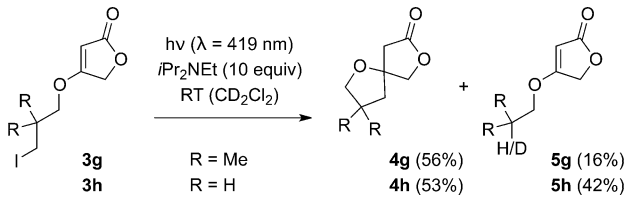
The mechanism depicted in Scheme 3 is at this point tentative but it serves to explain the formation of cyanine dyes **7**–**9**. The initial photochemical step has precedence in related studies on EDA complexes. At this point, it remains open whether the abstraction of the iodine atom from substrates **3** to radical **21** (Scheme 4) occurs by an EDA complex,[26] or whether radical **1** is sufficiently reactive to initiate a radical substitution. According to thermochemical data,[27] the C–I bond in I–CH_2Cl exhibits a dissociation energy of about 220 kJ mol^{-1}. Due to tabulated values for the dissociation energy of a C–I bond in primary alkyl iodides being in the same order of magnitude (220–230 kJ mol^{-1}),[28] the process would be expected to be almost thermoneutral. Irrespective of how radical intermediates **21** are formed, it is obvious that the ratio of **4**:**5** is determined by the relative rates of hydrogen abstraction versus 5-*exo*-trig cyclization. Intermediate **21** can undergo ring closure to radical **22**, which is the immediate precursor of product **4**, or it can undergo competitive hydrogen abstraction to form



Scheme 4. The ratio **4**/**5** of cyclization and reduction product depends on the relative rate of the cyclization **21**→**22** versus hydrogen abstraction from the solvent or from *i*Pr_2NEt: **21**→**5**.

product **5**. If hydrogen abstraction is more rapid, reduction to product **5** prevails.

It was speculated that hydrogen abstraction of intermediate **21** occurs mainly from the solvent and it should thus be feasible to slow down this process in CD_2Cl_2 solution. As a consequence, a significantly improved ratio of **4**:**5** would be expected in favor of cyclization product **4**. To our delight, it was indeed found that substrates **3g** and **3h**, which had shown notoriously low yields in the cyclization process (Table 3), underwent predominantly the respective cyclization reactions in CD_2Cl_2 (Scheme 5). Product **4g** was isolated in 56% and product **4h** in 53% yield.[29] The reduction products **5g** and **5h**, which were isolated as by-products, were found to be mixtures of non-deuterated and mono-deuterated compounds. Product **5g** and **5h** showed a deuterium incorporations of 40 and 22%, respectively. In products **4g** and **4h**, no deuterium incorporation was found.



Scheme 5. Preference for a radical cyclization of substrates **3g**,**h** to products **4g**,**h** if the irradiation with visible light was performed in a solution of CD_2Cl_2.

The results support the hypothesis that hydrogen abstraction from the solvent is responsible for the hydro-de-iodination reaction observed in dichloromethane solution. It is likely that the conversion of **22** to **4** also occurs partially by hydrogen abstraction from CH_2Cl_2 and that no deuterium incorporation was detected in the α-position to the carbonyl group due to its acidity. Additional sources for hydrogen atoms are the tertiary and secondary C–H groups in *N*,*N*-diisopropylethylamine.

Conclusion

The serendipitous finding that reductive radical reactions can be induced upon visible-light irradiation of an amine solution in dichloromethane offers a convenient alternative to perform hydro-de-halogenation reactions, which are typically conducted at elevated temperature with tributyltin hydride as the hydrogen source. The reaction conditions are mild and avoid the use of hazardous starting materials. If a subsequent radical cyclization is rapid in comparison with a potential hydrogen abstraction, the method can be employed for the construction of five-membered rings. Mechanistically, we have collected evidence that a chloromethyl radical (**1**) is involved in the photochemical process and that its formation is responsible for the generation of cyanine dyes as by-products. It is suggested that the radical is formed in a PET process upon irradiation of the EDA complex between Hünig's base and dichloromethane. From a synthetic perspective, it would be desirable to avoid the formation of any colored by-products because their absorption reduces the number of available photons, which are required to initiate the formation of radicals. Indeed, the formation of cyanine dyes was found to be more excessive in chloroform solution prohibiting any radical reactions. In this regard, other combinations of amines and halogenated solvents could be more effective to facilitate visible-light-induced radical reactions.

Experimental Section

Materials

Experiments with oxygen or moisture sensitive reagents were performed in flame-dried glassware under an argon atmosphere using Schlenk techniques. Dry THF and CH_2Cl_2 were obtained from an MBraun MB-SPS 800 solvent purification system. The following chemicals and solvents were obtained from commercial sources in the purities as mentioned and used without further purification: benzene (Sigma–Aldrich, puriss., > 99.7%, < 50 ppm H_2O), trifluoroacetic acid (Sigma–Aldrich, ReagentPlus®, 99%), *N*,*N*-diisopropylethylamine (DIPEA, Sigma–Aldrich, biotech. grade, > 99.5%, < 500 ppm H_2O). Technical solvents used for aqueous workup and purification by column chromatography [pentane, diethyl ether (Et_2O), ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2) and methanol (MeOH)] were distilled prior to use. CH_2Cl_2 for irradiation experiments was additionally dried over 4 Å molecular sieves for at least 24 h and degassed by argon purging for 10 min prior to use.

Methods

Thin layer chromatography (TLC) was performed on pre-coated glass-backed Silica gel 60 F_{254} plates (Merck) with visualization effected with ultraviolet irradiation ($\lambda = 254$, 366 nm) and/or staining using a solution of 3 g potassium permanganate, 20 g potassium carbonate, and 5 mL 5% aqueous sodium hydroxide in 300 mL water with subsequent heating. Flash column chromatography with silica gel (230–400 mesh; Merck) was performed according to the method employed by W. C. Still et al.[30] ^{1}H NMR spectra were recorded on Bruker AVHD-300, AV-360, AVHD-400, AVHD-500, or AV-500-Cryo spectrometers at 300 K. Data is reported in the following manner: chemical shift [in parts per million (ppm) relative to residual $CHCl_3$ ($\delta_H = 7.26$ ppm)], multiplicity, coupling constant *J* (measured in Hz to the nearest 0.1 Hz), number of protons and attributed proton. The multiplicity of a signal is indicated as: s-singlet, bs-broad singlet, d-doublet, t-triplet, q-quartet, quint-quintet, sex-sextet, *m*-multiplet, or combinations of these. ^{13}C NMR spectra were recorded on the same Bruker AVHD-300, AV-360, AVHD-400, or AVHD-500 spectrometers at 300 K operating at 75, 91, 101 and 126 MHz respectively with proton decoupling. The chemical shift [in parts per million (ppm)] is reported relative to $CDCl_3$ ($\delta_C =$

77.16 ppm). Structural assignments were made with the aid of COSY, HSQC, and HMBC experiments. Infrared (IR) spectra were recorded on a JASCO IR-4100 (ATR). Only selected characteristic peaks are recorded. High-resolution mass spectra (HRMS) were recorded on a Thermo Fischer Scientific DFS High Resolution MS (HR-EI), or a Thermo Finnigan LTQ FT (HRMS-ESI) with each value obtained within 5 ppm of the calculated mass. Analytic HPLC separation was performed using a YMC ODS-A column (250×4.6) with the solvent ratio acetonitrile/water = 80:20 (+0.1% formic acid) and the flow rate of 1 mL min^{-1}. HPLC-MS measurements were performed on a Dionex Ultimate 300 instrument with a Thermo Scientific LCQ Fleet mass detector. A Waters C-18 HPLC column with a buffer system acetonitrile/water (1% formic acid) was used. Irradiation experiments were performed in a Rayonet RPR-100 photochemical reactor equipped with 16 fluorescence lamps (Rayonet RPR-4190, λ_{max} = 419 nm) using duran phototubes (diameter = 1.0 cm).

Synthetic procedures

General procedure for visible-light-induced radical cyclization: A solution of alkyl iodide (100 μmol, 1.0 equiv) in degassed CH_2Cl_2 (c = 20 mM) was treated with DIPEA (174 μL, 129 mg, 1.00 mmol, 10.0 equiv) and the reaction mixture was irradiated (λ = 419 nm) for 24 h at ambient temperature. The solution was transferred to a separatory funnel, washed with 1 N HCl (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over $MgSO_4$ and filtrated. After removal of the solvent under reduced pressure, the crude product was purified by flash column chromatography (SiO_2) to yield the corresponding products.

3,3-Dimethyl-1-oxa-8-azaspiro[4.5]decan-7-one (4a) and 4-(neopentyloxy)-5,6-dihydropyridin-2(1*H*)-one (5a): Following the general procedure, the reaction of **3a** (31.0 mg, 100 μmol, 1.0 equiv) and DIPEA (174 μL, 129 mg, 1.00 mmol, 10.0 equiv) in CH_2Cl_2 (5 mL) gave, after column chromatography (SiO_2, 2.5 cm×6 cm, EtOAc/MeOH = 98:2×95:5), 9.6 mg (52.4 μmol, 52%) of compound **4a** and 2.3 mg (12.6 μmol, 13%) of compound **5a** as colorless solids.

Compound **4a**: R_f = 0.14 (EtOAc/MeOH) = 95/5 [$KMnO_4$]; m.p.: 132–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 5.97 (br s, 1H, NH), 3.58–3.52 (m, 1H, C9-H), 3.55 (d, ^2J = 8.7 Hz, 1H, C2-H), 3.51 (d, ^2J = 8.7 Hz, 1H, C2-H), 3.25 (dddd, ^2J = 11.9 Hz, ^3J = 5.7 Hz, 4.3 Hz, 2.9 Hz, 1H, C9-H), 2.58 (dd, ^2J = 17.4 Hz, ^4J = 2.1 Hz, 1H, C6-H), 2.41 (d, ^2J = 17.4 Hz, 1H, C6-H), 1.94 (virtual dtd, ^2J = 13.5 Hz, ^3J ≅ 4.6 Hz, ^4J = 2.1 Hz, 1H, C10-H), 1.81 (ddd, ^2J = 13.5 Hz, ^3J = 9.8 Hz, 5.7 Hz, 1H, C10-H), 1.71 (d, ^2J = 12.8 Hz, 1H, C4-H), 1.62 (d, ^2J = 12.8 Hz, 1H, C4-H), 1.12 (s, 3H, CH_3), 1.12 ppm (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 171.3 (s, C7), 80.2 (t, C2), 78.9 (s, C5), 51.7 (t, C4), 44.3 (t, C6), 40.4 (s, C3), 38.8 (t, C9), 33.3 (t, C10), 27.4 (q, CH_3), 27.3 ppm (q, CH_3); IR (ATR): $\tilde{\nu}$ = 3189 (br, CON-H), 3062 (w), 2959 (m, C_{sp^3}-H), 2934 (m, C_{sp^3}-H), 2833 (w, C_{sp^3}-H), 1660 (s, C=ONH), 1503 (m), 1051 cm^{-1} (s); MS (ESI): *m/z* (%) = 367 (100, [2*M* < M + > H]$^+$), 184 (70, [*M* < M + > H]$^+$). HRMS (ESI): $C_{10}H_{18}NO_2$ [(M < M + > H)$^+$]; calc.: 184.1332; found: 184.1332.

Compound **5a**: R_f = 0.24 (EtOAc/MeOH) = 95:5 [$KMnO_4$ + UV]; m.p.: 73–75 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 5.34 (br s, 1H, NH), 5.02 (s, 1H, C3-H), 3.46 (s, 2H, CH_2O), 3.42 (td, ^3J = 7.1 Hz, 2.4 Hz, 2H, C6-H), 2.47 (t, ^3J = 7.1 Hz, 2H, C5-H), 0.98 ppm [s, 9H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 170.2 (s, C2/C4), 170.0 (s, C2/C4), 94.0 (d, C3), 78.2 (t, CH_2O), 39.0 (t, C6), 31.6 [s, $C(CH_3)_3$], 28.1 (t, C5), 26.7 ppm [q, $C(CH_3)_3$]; IR (ATR): $\tilde{\nu}$ = 3193 (br, CON-H), 3047 (w, C_{sp^2}-H), 2952 (w, C_{sp^3}-H), 2898 (w, C_{sp^3}-H), 1720 (m), 1647 (s, C=ONH, C_{sp^2}-O), 1341 cm^{-1} (s); MS (ESI): *m/z* (%) = 367 (28, [2*M* < M + > H]$^+$), 184 (100, [*M* < M + > H]$^+$). HRMS (ESI): $C_{10}H_{18}NO_2$ [(*M* < M + > H)$^+$]; calc.: 184.1332; found: 184.1331.

3,3-Dimethyl-1-oxaspiro[4.5]decan-7-one (4e) and 3-(neopentyloxy)cyclohex-2-en-1-one (5e): Following the general procedure, the reaction of **3e** (31.0 mg, 100 μmol, 1.0 equiv) and DIPEA (174 μL, 129 mg, 1.00 mmol, 10.0 equiv) in CH_2Cl_2 (5 mL) gave, after flash column chromatography (SiO_2, 2.5 cm×6 cm, pentane/Et_2O = 2:1 to 1:1), 10.0 mg (54.9 μmol, 55%) of compound **4e** as light yellow oil, as well as 2.7 mg (14.8 μmol, 15%) of compound **5e** as colorless oil and 8.6 mg (27.8 μmol, 28%) recovered starting material.

Compound **4e**: R_f = 0.33 (pentane/Et_2O = 1:1) [$KMnO_4$]; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 3.52 (d, ^2J = 8.7 Hz, 1H, C2-H), 3.48 (d, ^2J = 8.7 Hz, 1H, C2-H), 2.57 (virtual dt, ^2J = 13.7 Hz, ^4J ≅ 1.7 Hz, 1H, C6-H), 2.45 (virtual dt, ^2J = 13.7 Hz, ^4J ≅ 1.2 Hz, 1H, C6-H), 2.39–2.30 (m, 1H, C8-H), 2.24 (dddd, ^2J = 14.3 Hz, ^3J = 9.5 Hz, 5.9 Hz, ^4J = 1.7 Hz, 1H, C8-H), 2.10–1.97 (m, C9-H), 1.97–1.89 (m, 1H, C10-H), 1.83–1.69 (m, 2H, C9-H, C10-H), 1.64 (d, ^2J = 12.8 Hz, 1H, C4-H), 1.58 (d, ^2J = 12.8 Hz, 1H, C4-H), 1.10 ppm [s, 6H, $C(CH_3)_2$]; ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 209.8 (s, C7), 85.7 (s, C5), 78.9 (t, C2), 53.9 (t, C6), 51.9 (t, C4), 40.7 (t, C8), 40.4 (s, C3), 36.8 (t, C10), 27.6 (q, CH_3), 27.4 (q, CH_3), 21.7 ppm (t, C9); IR (ATR): $\tilde{\nu}$ = 2954 (m, C_{sp^3}-H), 2928 (m, C_{sp^3}-H), 2869 (w, C_{sp^3}-H), 1716 (s, C=O), 1224 (m), 1050 cm^{-1} (s); MS (ESI): *m/z* (%) = 183 (100, [*M*+H]$^+$). HRMS (ESI): $C_{11}H_{19}O_2$ [(M + H)$^+$]; calcd: 183.1380; found: 183.1379.

Compound **5e**: R_f = 0.16 (pentane/Et_2O = 1/1) [$KMnO_4$ + UV]; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 5.35 (s, 1H, C2-H), 3.46 (s, 2H, CH_2O), 2.43 (t, ^3J = 6.3 Hz, 2H, C6-H), 2.35 (dd, ^3J = 7.2 Hz, 6.1 Hz, 2H, C4-H), 1.99 (virtual quint, ^3J ≅ 6.4 Hz, 2H, C5-H), 0.98 ppm [s, 9H, $C(CH_3)_3$]; ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 200.0 (s, C1), 178.5 (s, C3), 102.8 (d, C2), 78.2 (t, CH_2O), 36.9 (t, C6), 31.6 [s, $C(CH_3)_3$], 29.1 (t, C4), 26.6 [q, $C(CH_3)_3$], 21.4 ppm (t, C5); IR (ATR): $\tilde{\nu}$ = 2954 (s, C_{sp^3}-H), 2928 (s, C_{sp^3}-H), 2854 (m, C_{sp^3}-H), 1717 (m, C=O), 1653 (s), 1583 (s, C_{sp^2}-O), 1180 cm^{-1} (s). MS (ESI): *m/z* (%) = 365 (100, [2*M* < M + > H]$^+$), 183 (70, [*M* < M + > H]$^+$). HRMS (ESI): $C_{11}H_{19}O_2$ [(*M* < M + > H)$^+$]; calcd: 183.1380; found: 183.1380.

1-Oxaspiro[4.5]decan-7-one (4f) and 3-(propoxy)cyclohex-2-en-1-one (5f): Following the general procedure, the reaction of **3f** (28.0 mg, 100 μmol, 1.0 equiv) and DIPEA (174 μL, 129 mg, 1.00 mmol, 10.0 equiv) in CH_2Cl_2 (5 mL) gave, after flash column chromatography (SiO_2, 2.5 cm×6 cm, pentane/Et_2O = 2:1 to 1:1 to 2:3), 7.7 mg (49.9 μmol, 50%) of compound **4f** as well as 4.5 mg (29.2 μmol, 29%) of compound **5f** as light yellow oils and 3.9 mg (13.9 μmol, 14%) recovered starting material.

Compound **4f**: R_f = 0.19 (pentane/Et_2O = 1:1) [$KMnO_4$]; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 3.90–3.77 (m, 2H, C2-H), 2.48 (virtual dt, ^2J = 13.7 Hz, ^4J ≅ 1.5 Hz, 1H, C6-H), 2.42 (virtual dt, ^2J = 13.7 Hz, ^4J ≅ 1.1 Hz, 1H, C6-H), 2.40–2.31 (m, 1H, C8-H), 2.27 (dddd, ^2J = 15.8 Hz, ^3J = 9.0 Hz, 5.8 Hz, ^4J = 1.2 Hz, 1H, C8-H), 2.08–1.99 (m, 1H, C9-H), 1.94 (virtual tt, ^3J ≅ 8.2 Hz, 6.8 Hz, 2H, C3-H), 1.89–1.83 (m, 1H, C10-H), 1.82–1.69 ppm (m, 4H, 2×C4-H, C9-H, C10-H); ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 209.8 (s, C7), 84.9 (s, C5), 67.4 (t, C2), 53.0 (t, C6), 40.8 (t, C8), 36.7 (t, C4), 35.9 (t, C10), 25.7 (t, C3), 21.8 ppm (t, C9). The spectroscopic data match those reported in the literature.[19b]

Compound **5f**: R_f = 0.11 (pentane/Et_2O = 1:1) [$KMnO_4$ + UV]; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 5.35 (s, 1H, C2-H), 3.78 (t, ^3J = 6.5 Hz, 2H, C1′-H), 2.40 (t, ^3J = 6.3 Hz, 2H, C4-H), 2.34 (dt, ^3J = 7.3 Hz, 6.0 Hz, 2H, C6-H), 1.98 (virtual quint, ^3J ≅ 6.4 Hz, 2H, C5-H), 1.75 (qt, ^3J = 7.4 Hz, 6.5 Hz, 2H, C2′-H), 0.98 ppm (t, ^3J = 7.4 Hz, 3H, C3′-H); ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 200.0 (s, C1), 178.2 (s, C3), 102.9 (d, C2), 70.1 (t, C1′), 36.9 (t, C6), 29.2 (t, C4), 22.1 (t, C2′),

21.4 (t, C5), 10.5 ppm (q, C3′). The spectroscopic data match those reported in the literature.[18]

Deuterium incorporation experiments

3,3-Dimethyl-1,7-dioxaspiro[4.4]nonan-8-one (4g) and 4-(neopentyloxy)furan-2(5*H*)-one (5g): Following the general procedure, the reaction of **3g** (30.0 mg, 100 μmol, 1.0 equiv) and DIPEA (174 μL, 129 mg, 1.00 mmol, 10.0 equiv) in CD_2Cl_2 (5 mL) gave, after flash column chromatography (SiO_2, 2.5 cm×6 cm, pentane/Et_2O = 2:1 to 1:1), 9.6 mg (56.4 μmol, 56%) of compound **4g** as a colorless oil, as well as 2.8 mg (16.5 μmol, 16%) of a mixture of compound **5g** and **5g**-d_1 in a ratio of 60:40.

Compound **4g**: R_f = 0.16 (pentane/Et_2O = 1:1) [$KMnO_4$]; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 4.38 (dd, ^2J = 9.7 Hz, ^4J = 1.0 Hz, 1H, C9-H), 4.14 (d, ^2J = 9.7 Hz, 1H, C9-H), 3.57 (d, ^2J = 8.6 Hz, 1H, C2-H), 3.53 (d, ^2J = 8.6 Hz, 1H, C2-H), 2.76 (dd, ^2J = 17.5 Hz, ^4J = 1.0 Hz, 1H, C6-H), 2.58 (d, ^2J = 17.5 Hz, 1H, C6-H), 1.91 (d, ^2J = 13.2 Hz, 1H, C4-H), 1.82 (d, ^2J = 13.2 Hz, 1H, C4-H), 1.13 (s, 3H, CH_3), 1.11 ppm (s, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 175.5 (s, C7), 85.1 (s, C5), 80.0 (t, C2), 78.3 (t, C9), 48.5 (t, C6), 41.9 (t, C4), 40.0 (s, C3), 26.6 (q, CH_3), 26.3 ppm (q, CH_3); IR (ATR): $\tilde{\nu}$ = 2952 (w, C_{sp^3}-H), 2865 (w, C_{sp^3}-H), 1721 (s, C=O), 1533 (s, C_{sp^2}-O), 1251 (s), 1165 cm^{-1} (s); MS (ESI): *m/z* (%) = 341 (10, $[2M+H]^+$), 171 (100, $[M+H]^+$); HRMS (ESI): $C_{10}H_{15}O_3$ [$(M+H)^+$]; calcd: 171.1016; found: 171.1015.

Compound **5g**: R_f = 0.23 (pentane/Et_2O = 1:1) [$KMnO_4$]; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 5.06 (t, ^4J = 1.2 Hz, 1H, C3-H), 4.65 (d, ^4J = 1.2 Hz, 2H, C5-H), 3.67 (s, 2H, CH_2O), 1.00 ppm [s, $C(CH_3)_3$]; ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 179.8 (s, C2/C4), 173.8 (s, C2/C4), 88.9 (d, C3), 82.5 (t, CH_2O), 68.0 (t, C5), 31.9 [s, $C(CH_3)_3$], 26.4 ppm [s, $C(CH_3)_3$]. The spectroscopic data match those reported in the literature.[13b]

Compound **5g–d_1**: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 5.06 (t, ^4J = 1.2 Hz, 1H, C3-H), 4.66 (d, ^4J = 1.2 Hz, 2H, C5-H), 3.67 (s, 2H, CH_2O), 1.01 [s, 6H, $C(CH_3)_2(CH_2D)$], 0.99 ppm [t, $^1J_{HD}$ = 1.6 Hz, 2H, $C(CH_3)_2(CH_2D)$; ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 179.8 (s, C2/C4), 173.8 (s, C2/C4), 88.9 (d, C3), 82.5 (t, CH_2O), 68.0 (t, C5), 31.8 [s, $C(CH_3)_2(CH_2D)$], 26.4 [q, $C(CH_3)_2(CH_2D)$], 26.4 ppm [tt, $^1J_{CD}$ = 19.3 Hz, $C(CH_3)_2(CH_2D)$]; MS (ESI): *m/z* (%) = 381 (20, $[2M+K]^+$), 343 (5, $[2M+H]^+$), 172 (50, $[M+H]^+$); HRMS (ESI): $C_9H_{14}DO_3$ [$(M+H)^+$]; calcd: 172.1078; found: 172.1078.

1,7-Dioxaspiro[4.4]nonan-8-one (4h) and 4-(propoxy)furan-2(5*H*)-one (5h): Following the general procedure, the reaction of **3h** (27.0 mg, 100 μmol, 1.0 equiv) and DIPEA (174 μL, 129 mg, 1.00 mmol, 10.0 equiv) in CD_2Cl_2 (5 mL) gave, after flash column chromatography (SiO_2, 2.5 cm×6 cm, pentane/Et_2O = 1:1 to 1:2 to 1:4), 12.1 mg (52.7 μmol, 53%) of compound **4h** as a colourless oil as well as 6.0 mg (42.2 μmol, 42%) of a mixture of compound **5h** and **5h–d_1** in a ratio of 78:22.

Compound **4h**: R_f = 0.08 (pentane/Et_2O = 1/1) [$KMnO_4$]; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 4.30 (dd, ^2J = 9.6 Hz, ^4J = 0.8 Hz, 1H, C9-H), 4.16 (d, ^2J = 9.6 Hz, 1H, C9-H), 3.93–3.85 (m, 2H, C2-H), 2.71 (dd, ^2J = 17.5 Hz, ^4J = 0.8 Hz, 1H, C6-H), 2.54 (d, ^2J = 17.5 Hz, 1H, C6-H), 2.06–1.94 ppm (m, 4H, C3-H, C4-H); ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 175.3 (s, C7), 84.7 (s, C5), 77.4 (t, C9), 68.0 (t, C2), 40.7 (t, C6), 34.1 (t, C4), 25.8 ppm (t, C3). The spectroscopic data match those reported in the literature.[28]

Compound **5h**: R_f = 0.14 (pentane/Et_2O = 1:1) [$KMnO_4$]; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 5.06 (t, ^4J = 1.2 Hz, 1H, C3-H), 4.62 (d, ^4J = 1.2 Hz, 2H, C5-H), 3.99 (t, ^3J = 6.5 Hz, 2H, C1′-H), 1.80 (qt, ^3J = 7.4 Hz, 6.5 Hz, 2H, C2′-H), 1.01 ppm (t, ^3J = 7.4 Hz, 3H, C3′-H); ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 179.6 (s, C2/C4), 173.8 (s, C2/C4), 88.9 (d, C3), 74.5 (t, C1′), 68.0 (t, C5), 22.0 (t, C2′), 10.3 ppm (q, C3′). The spectroscopic data match those reported in the literature.[13b]

Compound **5h–d_1**: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 5.07 (t, ^4J = 1.1 Hz, 1H, C3-H), 4.64 (d, ^4J = 1.1 Hz, 2H, C5-H), 4.00 (t, ^3J = 6.5 Hz, 2H, C1′-H), 1.87–1.76 (m, 2H, C2′-H), 1.00 ppm (tt, $^1J_{HD}$ = 1.9 Hz, ^3J = 7.5 Hz, 2H, C3′-H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 179.7 (s, C2/C4), 173.8 (s, C2/C4), 88.9 (d, C3), 74.5 (t, C1′), 68.0 (t, C5), 21.9 (t, C2′), 10.1 ppm (tt, $^1J_{CD}$ = 19.6 Hz, C3′); MS (ESI): *m/z* (%) = 287 (5, $[2M+H]^+$), 144 (20, $[M+H]^+$); HRMS (ESI): $C_7H_{10}DO_3$ [$(M+H)^+$]; calcd: 144.0765; found: 144.0765.

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Keywords: cyanines · cyclization · photochemistry · radical reactions · reduction

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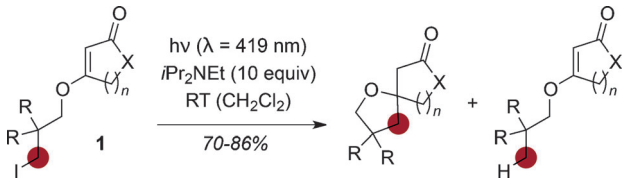

Colored footprint: The visible-light-mediated radical reaction of substrates **1** (X = O, CH_2, NH; n = 1,2) is triggered by photochemical excitation of an electron-donor–acceptor complex between Hünig's base and CH_2Cl_2. Strongly absorbing by-products were observed after irradiation and were identified as cyanine dyes.

Radical Reactions

*A. Böhm, T. Bach**

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Radical Reactions Induced by Visible Light in Dichloromethane Solutions of Hünig's Base: Synthetic Applications and Mechanistic Observations