Oxetanes from Photocycloaddition of 2-Aminopropenenitriles to Methyl Phenylglyoxylate and Benzils

Christiane van Wolven[a], Dietrich Döpp[a], and Gerald Henkel[b]

[a] Fachbereich Chemie, Universität Duisburg-Essen, D-47048 Duisburg, Germany
[b] Department Chemie und Chemietechnik, Fakultät Naturwissenschaften, Universität Paderborn, D-33098 Paderborn, Germany

Reprint requests to Prof. Dr. D. Döpp. Fax: +49(0)203-379-4192. E-mail: doepp@uni-duisburg.de

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By irradiation of methyl phenylglyoxylate (**1**) in benzene solution in presence of equimolar amounts of 2-aminopropenenitriles $H_2C{=}C(NR_2)CN$ (**3a – e**, NR_2 = morpholino, 1-pyrrolidinyl, 1-piperidinyl, hexamethyleneimino, heptamethyleneimino) the corresponding 2*R**,3*R** head-to-head oxetanes **4a – e** were obtained in moderate yields (11 – 52%) along with 2 – 28% of *rac*-dimethyl 2,3-diphenyltartrate (**2**). In presence of (*S*)-2-(2-methoxymethylpiperidin-1-yl)propenenitrile ((+)-**3g**) **1** is transformed into 26% of **2** and 33% of a mixture of diastereomeric oxetanes **4g**,**4'g** in a ratio of 1.4 : 1 which could be improved to 2.5 : 1 by preparative layer chromatography. The absolute configuration of the major diastereomer **4g** was unambiguously confirmed by a single crystal *X*-ray structure determination to be 2*R*,3*R*,2'*S*. Analogous photoadditions to benzil (**5a**), 4,4'-bis-(trifluoromethyl)benzil (**5b**) and 4,4'-dichlorobenzil (**5c**) with (+)-**3g** and its lower homologue (*S*)-2-(2-methoxymethylpyrrolidin-1-yl)propenenitrile ((-)-**3f**) gave oxetanes only in low yield as detected by ^{1}H NMR. By-products arise from competitive symmetrical α-cleavage of **5**.

Key words: Paternò-Büchi Reaction, Ketene Equivalents, Asymmetric Induction, Diastereoselectivity, *X*-Ray Structure Analysis

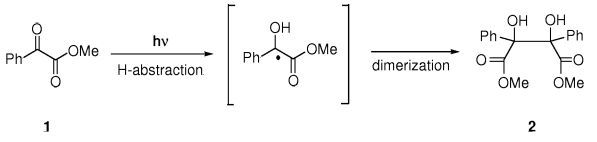
Introduction

The Paternò-Büchi reaction, a well known [2+2]-photocycloaddition, is a standard method to prepare oxetanes [1]. The oxetane ring is a vital component in various biologically active compounds as, for example, fungicidal [2] and antiviral [3] agents or in compounds with bactericidal, insecticidal and other pharmacological properties [4]. Natural product synthesis is another important field of application of oxetanes since the energy rich four-membered ring is a valuable precursor due to its diversified reactivity [5, 6]. Therefore the stereocontrolled formation of oxetanes is of great practical importance.

It has become known from an earlier study [7] that photoexcited symmetrical benzils such as **5a – c** add 2-aminopropenenitriles (*e. g.* **3a – e**) highly regio- and stereoselectively. It was therefore considered worthwhile to investigate also the photocycloaddition of enantiopure 2-aminopropenenitriles (-)-**3f** and (+)-**3g** to **5a – c** and to methyl phenylglyoxylate (**1**) and to search for any chiral inductions. Asymmetric inductions in Paternò-Büchi reactions using either chiral carbonyl compounds and achiral alkenes or achiral carbonyl compounds and chiral alkenes have been reviewed recently [6, 8 – 10].

In their very elegant work on the "isoinversion principle" Scharf *et al.* [11] investigated the oxetanation of enantiopure phenylglyoxylates bearing chiral alkoxy residues and observed temperature dependent diastereoselectivities in the photocycloaddition of achiral 1,3-dioxoles. In contrast, in this study the photoaddition of both achiral and enantiopure 2-aminopropenenitriles to methyl phenylglyoxylate (**1**) is investigated. Thus the alternative approach to that used by Scharf [11] is being tried.

Further, 2-aminopropenenitriles are regarded as so-called captodative (c,d) [12] alkenes because they are substituted with a donor (here an amino group) and an acceptor ("captor", here a cyano group) at the same terminus of the double bond. In a photocycloaddition to *e. g.* a $^3(n,\pi^*)$ excited carbonyl compound this type of alkene will form a c,d-stabilized biradical in which the stabilization is regarded to exceed the sum of the individual stabilizing effects of the donor and the acceptor [12]. This property should on one hand facili-



Scheme 1.

tate the photocycloadditions of such alkenes [13] and on the other hand decrease the thermal stability of the cycloadducts. This study is therefore also aimed at getting more insight into the consequences of c,d-stabilization of biradical intermediates in light induced cycloadditions.

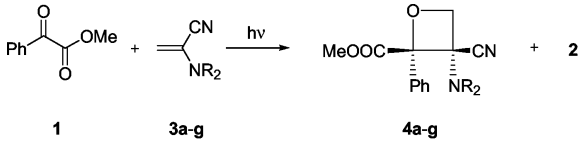
Results and Discussion

*Photoreaction of methyl phenylglyoxylate (***1***) with 2-aminopropenenitriles* **3a – g**

In general, a photoexcited alkyl phenylglyoxylate in solution has several options for chemical deactivation besides decay to the electronic ground state. The excited molecule may react intramolecularly in a Norrish type II mode but only if alkyl is equal to ethyl or larger [14]. Next, due to its $^3(n,\pi)^*$ nature, photoreduction of the keto carbonyl group with a reducing solvent or other suitable reaction partner may ensue. The partitioning between the different options depends also on the concentration of starting material [15]. Therefore, the irradiation ($\lambda \geq 280$ nm) of **1** (0.05 M) in benzene (a not readily reducing solvent) was tested first as a blind experiment. One product, namely the higher melting stereoisomer [16] of dimethyl 2,3-diphenyltartrate (**2**) was isolated in low (8%) yield. This product is probably formed *via* initial intermolecular hydrogen abstraction (not necessarily from the solvent, but perhaps from the methoxy group of a second molecule of **1**) to generate the corresponding ketyl radical which in turn dimerizes (Scheme 1).

When **1** was irradiated in the presence of equimolar amounts of **3a – e**, (-)-**3f** and (+)-**3g** but under otherwise the same conditions as above, two products could be identified (Scheme 2), the main one being the expected oxetane **4a – e**, **g** (**4f** could not be isolated), the minor one being the racemic tartrate **2**, both in moderate yields. In most cases, though, the yield of **2** is larger than in the blind run indicating that alkenes **3** also act as hydrogen donors for **1** as do simple tertiary aliphatic amines with carbonyl compounds [17].

The structures of oxetanes **4a – e** have been delineated from their IR, ^{1}H and ^{13}C{^{1}H} NMR spectra. Cyano group stretching frequencies are constantly



3	NR_2	4	(%)	2 (%)
a	Morpholino	**a**	52	2
b	1-Pyrrolidinyl	**b**	11	12
c	1-Piperidinyl	**c**	31	15
d	Hexamethyleneimino	**d**	40	28
e	Heptamethyleneimino	**e**	48	20
f	(*S*)-2-Methoxymethyl-1-pyrrolidinyl	**f**	- *	- *
g	(*S*)-2-Methoxymethyl-1-piperidinyl	**g**	33 **	26

* See text. ** As a 2.5:1 mixture of **4g** and minor diastereomer **4'g** after preparative layer chromatography.

Scheme 2.

found at 2220 – 2226 cm^{-1}, and the methyl ester C=O frequencies range from 1730 – 1747 cm^{-1}. For the sake of better signal resolution, ^{1}H NMR spectra of some oxetanes have also been recorded in C_6D_6. The methylene protons at C-4 give rise to AB systems (in $CDCl_3$: $\delta_A = 4.70 - 4.77$, $\delta_B = 4.67 - 4.74$, $|^2J| = 6.2 - 6.4$ Hz; in C_6D_6 the δ values tend to be upfield by approximately 0.6 ppm) and the ^{13}C resonances for C-4 fall between 72.2 and 73.8 ppm. Molecular ions are best observed in the field desorption (FD) mass spectra, whereas 70 eV EI mass spectra do not show the M^+ ions of **4** but those of the precursor starting materials **1** and **3** due to easy cleavage.

The tendency to undergo degradation under the conditions of reaction or work-up is even more pronounced for the oxetanes obtained from the enantiopure cyanoenamines (-)-**3f** and (+)-**3g**. When **1** was irradiated for 75 min in C_6H_6 in the presence of an equimolar amount of (-)-**3f**, a single oxetane was formed in low amount together with the tartrate **2** as monitored by 300 MHz ^{1}H and ^{13}C{^{1}H} NMR (for 4-H_2: $\delta_A = 5.03$, $\delta_B = 4.72$ ppm, $|^2J| = 6.4$ Hz; C-4: $\delta = 75.4$ ppm). No products, however could be isolated from this experiment. From the homologous alkene (+)-**3g** two diastereomeric oxetanes, **4g** (major) and **4'g** (minor) were obtained after 105 min of irradiation in a ratio of 1.4 : 1 in the original photolysate and in a ratio of 2.5 : 1 after preparative layer chromatography as determined by integration of suitable ^{1}H NMR signals in the different signal sets. A full chromatographic separation of the two diastereomers was not possible, though.

Compounds **4g** and **4'g** showed similar spectral characteristics as **4a – e**. The major isomer **4g**

showed stretching frequencies at 2220 cm^{-1} (CN) and 1729 cm^{-1} (ester C=O) and proton resonances for 4-H_2 in $CDCl_3$ at $\delta_A = 4.75$ and $\delta_B = 4.65$ with $|^2J| = 7.3$ Hz and in C_6D_6 at 4.61 and 4.49 ppm with $|^2J| = 7.1$ Hz, respectively. The resonance of C-4 was found at 70.6 ppm (C_6D_6). The minor isomer **4'g** had its 4-H_2 resonances at 4.93 and 4.85 ppm (in $CDCl_3$) with $|^2J| = 6.9$ Hz and in C_6D_6 at 4.73 and 4.71 ppm with the same $|^2J|$.

It may thus be concluded that all isolated oxetanes **4a – e, g** have the same connectivity and (except **4'g**) relative configuration. The ketoester **1** shows two carbonyl bands in the IR spectrum, that of the ester group at 1740 and that of the benzoyl group at 1689 cm^{-1}. The comparison of the C=O stretching vibrations of educt **1** and products **4** clearly identifies the benzoyl group as the reacting center, as expected. This reactivity is known from other photocycloadditions of phenylglyoxylates [11, 18] and is explainable on the basis of formation of the most stable biradicals in the first bond forming step.

Chemical shifts as well as the values for $|^2J|$ of the C-4 methylene protons demonstrate the CH_2 group being adjacent to oxygen, thus all oxetanes are therefore the head-to-head regioisomers. The relative configuration $(2R^*, 3R^*)$ of the four-membered ring follows from NOE-intensity difference determinations. These are listed for compounds **4a, c, d, e, g** as follows [compound number (solvent): signal saturated / *signals enhanced*] with geminal interactions being omitted:

4a (C_6D_6): Ph-*o*-H / *4-H_B*, *N(CH_{eq})$_2$*; 4-H_A / – ; 4-H_B / *Ph-o-H*, *N(CH_{ax})$_2$*; N(CH_{eq})$_2$ / – ; N(CH_{ax})$_2$ / *4-H_B*.

4c (C_6D_6): Ph-*o*-H / *4-H_B*, *N(CH_{eq})$_2$*; 4-H_A / – ; 4-H_B / *Ph-o-H*, *N(CH_{ax})$_2$*; N(CH_{eq})$_2$ / *Ph-o-H*; N(CH_{ax})$_2$ / *Ph-o-H*, *4-H_B*.

4d ($CDCl_3$) and **4e** (C_6D_6): Ph-*o*-H / *4-H_B*, *N(CH_{eq})$_2$*; 4-H_A / – ; 4-H_B / *Ph-o-H*, *N(CH_{ax})$_2$*; N(CH_{eq})$_2$ / *Ph-o-H*; N(CH_{ax}0)$_2$ / *4-H_B*.

4g ($CDCl_3$): Ph-o-H / *4-H_A*, *6'-H_2*; 4-H_A / *Ph-o-H*, *2'-H*; 4-H_B / – ; 2'-H / *4-H_A*. – (C_6D_6): Ph-o-H / *4-H_B*, *6'-H_{eq}*; 4-H_A / – ; 4-H_B / *Ph-o-H*, *2'-H*; 6'-H_{eq} / *Ph-o-H*. – Since for **4g** the two protons of the 4-H_2 AB system show strong solvent dependencies of their chemical shifts, it should be noted that H_A in $CDCl_3$ becomes H_B in C_6D_6 and *vice versa*.

The absolute configuration of the major isomer **4g** could be identified as 2*R*,3*R*,2'*S* by a single crystal *X*-ray structure determination (Fig. 1 and Table 1). The oxetane ring is strongly twisted very likely due to steric encumbering of the two vicinal six-membered ring substituents.

Table 1. Selected bond lengths, bond angles (standard deviations in brackets) and dihedral angles of compound **4g** in the crystal. The crystallographic numbering does not match the systematic numbering.

Bond lengths [pm]		Bond angles [°]		Dihedral angles [°]	
C7-C8	160.5(3)	C7-O4-C9	91.65(14)	C7-O4-C9-C8	19.3
C7-O4	144.2(2)	C8-C7-O4	88.92(14)	C9-O4-C7-C8	−18.5
C8-C9	154.2(3)	C7-C8-C9	82.49(14)	O4-C7-C8-C9	17.5
C9-O4	145.1(3)	C8-C9-O4	91.08(15)	C7-C8-C9-O4	−17.4

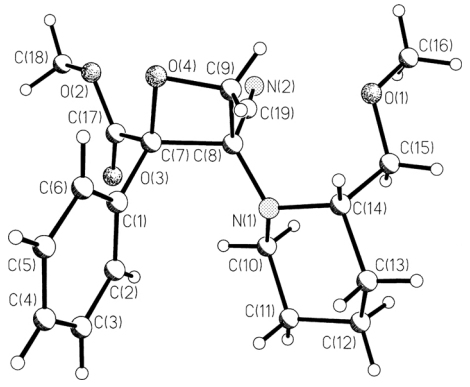
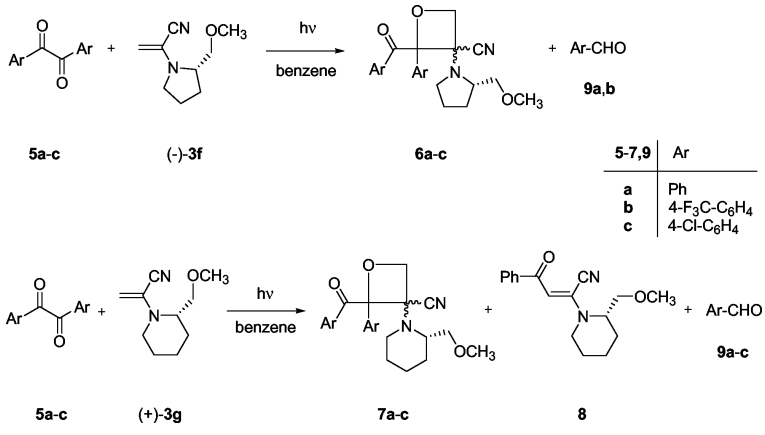


Fig. 1. Structure of compound **4g** in the crystal. The crystallographic numbering does not correspond to the systematic numbering.

The sterically most encumbered and probably labile C7-C8 bond (160 pm) is significantly longer (6 – 16 pm) than the other three bonds of the oxetane ring (see Table 1). The sharp bond angle C7-C8-C9 (82.49°) deviates mostly from the formal angle of 90°. Also, the dihedral angles along the perimeter of the four-membered ring in particular reflect the distortion of the oxetane ring.

In the photoaddition of any of the 2-aminopropenenitriles **3** used two new stereogenic centers (C-2, C-3) are created. From ^{1}H NMR analysis **4g**/**4'g** has to be regarded as a diastereomeric mixture of α-aminonitriles. Thus, the total hydrolysis of the aminonitrile function should give rise to a non-racemic mixture of the enantiomers of the corresponding 3-oxetanone (note that **3g** is in fact a chiral ketene equivalent and the stereocenter C-3 in **4g**/**4'g** is suspended during hydrolysis). Determination of the 3-oxetanone enantiomer ratio should thus shed light on the degree of chiral induction in the photocycloaddition. Therefore a sample of the original **4g**/**4'g** mixture was treated with cupric sulfate and disodium hydrogenphosphate in an acetone/methanol/water mixture following the procedure

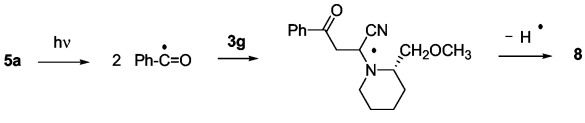


Scheme 3.

by Büchi *et al.* [19]. However, no hydrolysis product at all but a small amount of **1** and 64% of the originally present major diastereomer **4g** could now be separated by silica gel chromatography. This result demonstrates that (i) **4'g** is more easily degraded than **4g** and (ii) retro-[2+2]-addition may successfully compete with hydrolysis of the aminonitrile function under the conditions employed. According to its single crystal *X*-ray structural analysis compound **4g** clearly is the head-to-head homofacial *Re,Re*-adduct. Since the chemical shifts of the minor signal sets in the ^{1}H and ^{13}C NMR spectra of **4g** are very similar to those of the main isomer it is concluded that **4'g** probably is the other homofacial (*Si,Si*-) adduct (2*S*,3*S*,2'*S*).

Reaction of symmetrical benzils with chiral 2-aminopropenenitriles **3f** *and* **3g**

Paternò-Büchi reactions of benzils with several achiral 2-aminopropenenitriles have been reported earlier [7, 20]. Aimed at probing for diastereoselection in the photoaddition of chiral cyanoenamines to diarylethanediones, benzene solutions of benzil (**5a**), 4,4'-bis-(trifluoro-methyl)- (**5b**), and 4,4'-dichlorobenzil (**5c**) containing equimolar amounts of either (-)-**3f** or (+)-**3g** were irradiated in C_6D_6 in an NMR tube. The formation of low yields of oxetanes (**6**,**7**) and of an aldehyde **9** was monitored by ^{1}H NMR spectroscopy in all cases. From benzil (**5a**), oxetanes **6a**, **7a** were formed each as a pair of diastereomers (since two distinct sets of product signals were observed), whereas only one diastereomer of **6b, c** and **7b, c** was observed (but not isolated) from photoexcited **5b, c** (Scheme 3). The latter result does indicate high diastereoselectivity in the addition of **3f, g** to excited **5b, c**, but due to the disappointing preparative efficiency (which in turn is probably due to the instability of the products under the reaction conditions), these cases were not elaborated any further.



Scheme 4.

In the photoaddition of **5a** to **3g** a third addition product could be detected by GC/MS experiments and was later identified as 3-benzoyl-2-(2-methoxymethyl-piperidin-1-yl)-propenenitrile (**8**) by ^{1}H NMR. When cyclohexane was used as solvent instead of benzene, **8** could be isolated in 6% yield in addition to the oxetane **7a**. The *E*-configuration of **8** follows from NOE intensity difference determinations. These are listed in the order: signal saturated / *signals enhanced* (omitting geminal interactions): Benzoyl-*o*-H/ *3-H*; 3-H / *benzoyl-o-H, 2'-H, 6'-H$_{eq}$*; 2'-H / *3-H*; 6'-H$_{eq}$ / *3-H*. Alkene **8** most likely originates from a symmetric α-cleavage of benzil (**5a**) indicating that such cleavage becomes competitive with the Paternò-Büchi reaction. The benzoyl radicals so formed in turn may either pick up a hydrogen atom (forming the aldehyde detected in the reaction mixture) or (typically) react by addition to the captodative [12] alkene **3g** to form an adduct radical which in turn is dehydrogenated to **8** (Scheme 4).

Product quantum yields

To get an idea of the efficiency of the photoaddition of selected cyanoenamines (**3a**,**d**) to **1** and **5a**

quantum yields of oxetane formation were determined with reference to the ferrioxalate actinometer according to Hatchard and Parker [21]. The chemical yield of oxetanes in each run was determined by calibrated ^{1}H NMR signal integration and, in the cycloadditions of alkene **3a**, also by quantitative HPLC. The following values were found:

Addition of **3a** to **1**: $\Phi = 0.125$; $\Phi = 0.11$ (using HPLC); addition of **3d** to **1**: $\Phi = 0.11$; addition of **3a** to **5a**: $\Phi = 0.19$; $\Phi = 0.18$ (using HPLC); addition of **3d** to **5a**: $\Phi = 0.12$.

All product quantum yields fall into the range of 0.1 – 0.2. This is not surprising in the light of the aforementioned options available to the excited states of **1** and **5a**. Still, the quantum yields are sufficient to render, in principle, these oxetanations preparatively useful.

Conclusions

Achiral 2-aminopropenenitriles **3a – e** bearing cyclic amino groups as donors undergo (as reported earlier [7]) Paternò-Büchi reactions with symmetrical benzils as **5a – c** and with methyl phenylglyoxylate (**1**) with high regio- and variable simple diastereoselectivity in moderate to satisfactory preparative yields. The product oxetanes are of sufficient stability.

In contrast, the enantiopure 2-aminopropenenitriles (-)-**3f** and (+)-**3g**, the donor groups of which are analogous to those of **3b** and **3c**, respectively, show a diversified behaviour. Whereas (-)-**3f** had proven to be a potent enantiopure alkene in the highly regio-, stereo- and diastereoselective photo-Diels-Alder addition to 1-acetonaphthone [27], no stable oxetane could be isolated from irradiations of either **1** or **5a, b** in presence of this alkene. After short irradiation times, two oxetanes from **5a** and one from **5b** could be detected by ^{1}H NMR in the photolysis mixture but were later degraded probably by photosensitized destruction. Likewise, photoexcited **1** did form a single oxetane with (-)-**3f** in small amounts which could, however, not be isolated. The reasons for these findings may be multiple, both steric encumbering by the additional methoxymethyl substituents as well as the high electron donor property of the five-membered ring, which especially may stabilise a captodative radical center in the 1,4-biradicals preceding the oxetanes, may play a role.

In contrast, alkene (+)-**3g** was photoadded with variable induced diastereoselectivity to benzils **5a – c** and with low induced diastereoselectivity to **1**. Trials to separate both diastereomers (**4g**, **4'g**) from the latter reaction failed. An enrichment of the major isomer **4g**, however, was possible due to the high sensitivity of the minor diastereomer **4'g** towards chromatography on silica gel, which caused a faster cleavage to starting materials for **4'g** than for **4g**. Because of the abovementioned complications, temperature dependency studies did not promise to unravel reliable trends and therefore were not undertaken.

Experimental Section

General

Melting points were determined on a Kofler hot stage microscope. A Perkin-Elmer Lambda 40 instrument was used to obtain UV spectra (sh = shoulder). IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Weak (strong) bands are indicated by w (s) after the wave number listing. Bruker WM 300 and DRX 500 instruments were used to obtain 300 MHz ^{1}H (75 MHz ^{13}C{^{1}H}) or 500 MHz ^{1}H (125 MHz ^{13}C{^{1}H}) NMR spectra, respectively, using TMS as an internal standard. ^{13}C Signal assignments (q = quaternary) were made on the basis of DEPT 135/90 spectra. Solutions prepared for NOE experiments were degassed by three successive freeze-pump-thaw cycles. Mass spectra were recorded on an AMD 604 instrument, preferentially at 70 eV EI ionisation. In some cases, field desorption (FD) spectra were recorded in addition. – GC/MS coupling experiments were run with the same instrument in connection with a Hewlett-Packard HP 59/90 II+ gas chromatograph equipped with a 30 m HP5 methylsilicone coated capillary column, which was held at 50 °C for 1 min after injection (at 230 °C) and then gradually warmed up to to 230 °C at 10 °C intervals/min. The flow rate was kept at 1.5 ml He/min. Specific rotations were determined with a Perkin Elmer 241 polarimeter. The concentration is given in [g/100 ml] and the dimension of the specific rotation $[\alpha]_D$ is $[\text{degrees} \cdot \text{ml} \cdot \text{dm}^{-1} \cdot \text{g}^{-1}]$.

Starting materials

Methyl phenylglyoxylate (**1**) and benzil (**5a**) were used as received from Aldrich or Merck, respectively. 4,4'-Bis-(trifluoromethyl)benzil (**5b**) and 4,4'-dichlorobenzil (**5c**) were prepared from the corresponding aldehydes *via* benzoin addition and oxidation of the corresponding benzoins using cupric sulfate/pyridine [22]. 2-Aminopropenenitriles **3a – f** are known from the literature [23 – 26] and have been prepared by adaption of the two principal methods published for **3a** [23] and **3c** [24].

2-Morpholinopropenenitrile (**3a**), m. p. 61 – 63 °C (ref. [23]: 62.5 – 63.5 °C).

2-(1-Pyrrolidinyl)propenenitrile (**3b**) [25] was prepared by adaption of the procedure given in ref. [23], b. p. 31 °C/0.53 mbar. – IR (film): $\tilde{\nu}$ = 2240 (CN), 1610, 1580, 1440, 1370 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 – 1.97 (m, 4H, 3'- and 4'-H_2), 3.15 – 3.22 (m, 4H, 2'- and 5'-H_2), 4.15 (m, 1H, 3-H^1) and 4.46 (m, 1H, 3-H^2). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 25.2 (C-3' and C-4'), 48.7 (C-2'- and C-5'), 93.8 (C-3), 116.4 (CN), 125.8 (C-2).

2-(1-Piperidinyl)propenenitrile (**5c**) [25], b. p. (bulb-to-bulb) 42 °C/0.035 mbar (ref. [24] 100 °C/2.7 mbar). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 – 1.67 (m, 6H, 3'-, 4'- and 5'-H_2), 2.97 – 3.01 (m, 4H, 2'- and 6'-H_2), AB (δ_A = 4.73, δ_B = 4.56, $|^2J|$ = 1.8 Hz, 3-H_2). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 23.7 (C-4'), 24.9 (C-3' and C-5'), 48.9 (C-2' and C-6'), 99.9 (C-3), 116.3 (CN), 130.4 (C-2).

Compounds **3d** [25] and **3e** [25] were prepared by adaption of the method given in ref. [24] and purified by distillation.

2-(Hexamethyleneimino)propenenitrile (**3d**): B. p. 70 °C/ 0.05 mbar. – IR (film): $\tilde{\nu}$ = 2926, 2856 (CH), 2230 (CN), 1601, 1568, 1433 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 – 1.62 (m, 4H, 4'- and 5'-H_2), 1.68 – 1.77 (m, 4H, 3'- and 6'-H_2), 3.26 – 3.31 (m, 4H, 2'- and 7'-H_2), AB (δ_A = 4.40, δ_B = 4.21, $|^2J|$ = 1.7 Hz, 3-H_2). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.3 (C-4' and C-5'), 28.1 (C-3' and C-6'), 50.1 (C-2' and C-7'), 92.8 (C-3), 116.3 (CN), 127.7 (C-2).

2-(Heptamethyleneimino)propenenitrile (**3e**): B. p. 53 °C/ 0.043 mbar. – IR (film): $\tilde{\nu}$ = 2925, 2855, 2230 (CN), 1600, 1564, 1431 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 – 1.75 (m, 10H, 3'-, 4'-, 5'-, 6'-, and 7'-H_2), 3.26 – 3.31 (m, 4H, 2'-H_2 and 8'-H_2), AB (δ_A = 4.42, δ_B = 4.20, $|^2J|$ = 1.7 Hz, 3-H_2). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 26.2, 26.6, 26.7 (C-3', C-4', C-5', C-6' and C-7'), 50.5 (C-2', C-8'), 92.7 (C-3) 116.5 (CN), 127.1 (C-2).

(*S*)-2-(2-Methoxymethylpyrrolidin-1-yl)propenenitrile (**3f**) [27, 28] was prepared starting from (*S*)-2-(methoxymethyl)pyrrolidine [29] and 2-chloropropenenitrile analogously to ref. [24] but with isolation of the intermediate adduct 2-chloro-3-(2-methoxymethyl-1-pyrrolidin-yl)propanenitrile and dehydrochlorination of the latter using 1,4-diazabicyclo[2.2.2]octane in toluene at reflux temperature for 4 hr [30]. – B.p. 61 °C/0.08 mbar. – IR (film): $\tilde{\nu}$ = 2978, 2929, 2879, 2832, 2233 (CN), 1604, 1577, 1449, 1346, 1197, 1164, 1115 cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.90 – 2.00 (m, 4H, 3'- and 4'-H_2), 2.99 – 3.05 (m, 1H, 5'-H), 3.22 – 3.26 (m, 1H, 5'-H), 3.36 (s, 3H, OCH_3), ABX (δ_A = 3.42, δ_B = 3.27 [-CH_2O-], δ_X = 3.80 [2'-H], $|^2J|$ = 9.7 Hz, $^3J_{AX}$ = 4.2 Hz, $^3J_{BX}$ = 7.3 Hz), AB (δ_A = 4.51, δ_B = 4.27, $|^2J|$ = 1.2 Hz, 3-H_2). – ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 23.5 (C-4'), 28.5 (C-3'), 49.1 (C-5'), 59.2 (OCH_3), 59.4 (C-2'), 73.85 (CH_2O), 95.0 (C-3), 116.4 (CN), 125.6 (C-2). – $[\alpha]_D^{20}$ = −14.4 (c = 0.7, cyclohexane).

(*S*)-2-(2-Methoxymethylpiperidin-1-yl)propenenitrile (**3g**) was prepared starting from (*S*)-piperidine-2-carboxylic acid (obtained from (*S*)-lysine according to ref. [31]) which was transformed by adaption of the procedure given in ref. [29] into (*S*)-2-methoxymethyl)piperidine which was reacted with 2-chloropropenenitrile to 2-chloro-3-(2'*S*)-2-methoxymethylpiperidin-1-yl)propanenitrile, b. p. 120 °C/0.04 mbar. The latter was kept at reflux with an excess of 1,4-diazabicyclo[2.2.2]octane in toluene and refined, b.p. 56 °C/0.04 mbar. – IR (film): $\tilde{\nu}$ = 2939, 2872, 2233 (CN), 1582, 1447, 1382, 1277, 1266, 1227, 1175, 1135, 1115 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 – 1.85 (m, 6H, 3'-, 4'-, 5'-H_2), 2.75 – 2.85 (m, 1H, 6'-H_{ax}), 3.18 – 3.25 (m, 1H, 6'-H_{eq}), 3.34 (s, 3H, OCH_3), 3.40 – 3.55 (m, 2H, CH_2O), 3.85 – 3.95 (m, 1H, 2'-H), AB (δ_A = 4.63, δ_B = 4.48, $|^2J|$ = 1.8 Hz, 3-H_2). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 18.9 (C-4'), 24.7 and 25.8 (C-3' and C-5'), 43.1 (C-6'), 54.2 (C-2'), 59.0 (OCH_3), 70.0 (OCH_2), 97.9 (C-3), 116.4 (CN), 129.7 (C-2). – $[\alpha]_D^{20}$ = 154 (c = 1.93, cyclohexane).

Preparative scale irradiations

A Philips HPK 125 W high pressure mercury lamp was used in connection with a water-cooled Duran® immersion well ($\lambda \geq$ 280 nm) and a cylindrical vessel (125 ml capacity) with a gas in- and outlet and a magnetic stirrer. Solutions containing 5.0 mmol each of **1** and alkenes **3a – e, g** in 110 ml of benzene (if not stated otherwise) were purged with argon prior to and throughout the irradiation at ambient temperature. Products **2**, **4a – g** were isolated by preparative layer chromatography on plates coated with a 1 mm thick air-dry layer of silica gel Merk PF_{254}, followed by crystallization. Irradiation time, conversions of **1** and yields of isolated products were as follows: With **3a**: 105 min, 94%, 52% of **4a**, 2% of **2**; with **3b**: 75 min, 89%, 11% of **4b**, 12% of **2**; with **3c**: 105 min, 96%, 31% of **4c**, 15% of **2**; with **3d**: 105 min, 81%, 40% of **4d**, 28% of **2**; with **3e**: 120 min, 77%, 48% of **4e**, 20% of **2**; with (+)-**3g**: 105 min, 89%, 33% of a diastereomeric mixture containing 71% of **4g** and 29% of **4'g**, 26% of **2**.

*Dimethyl 2,3-diphenyltartrate (**2**)*: M. p. 163 – 164 °C (ethanol, ref. [16] for racemic mixture: m. p. 159 – 161 °C from methanol/water 10 : 1). – UV (C_6H_{12}): $\lambda_{max}(\log\varepsilon)$ = 252 nm (2.63), 258 nm (2.71), 263 nm (2.66). – IR (KBr): $\tilde{\nu}$ = 3493s (OH), 1708s (C=O), 1263s (C-O) cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.85 (s, 6H, OCH_3), 5.10 (s, 2H, OH), 7.06 – 7.26 (m, 10 H, phenyl-H). – $C_{18}H_{18}O_6$ (330.34): calcd. C 65.45, H 5.49; found C 65.51, H 5.49.

Methyl (2R, 3R*)-3-cyano-3-morpholino-2-phenyloxetane-2-carboxylate (**4a**)*: M. p. 65 – 68 °C. – UV (C_6H_{12}): $\lambda_{max}(\log\varepsilon)$ = 219 nm (3.90, sh), 254 nm (2.52, sh), 260 nm (2.57), 265 nm (2.57), 270 nm (2.41, sh). – IR (KBr): $\tilde{\nu}$ = 2844 (OCH_3), 2226w (CN), 1747s (C=O) cm^{-1}. –

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.30-2.38$ (m, 2H, $N(CH_{ax})_2$), 2.40 – 2.47 (m, 2H, $N(CH_{eq})_2$), 3.31 (m, 2H, $O(CH_{ax})_2$), 3.43 – 3.51 (m, 2H, $O(CH_{eq})_2$), 3.96 (s, 3H, $COOCH_3$), AB ($\delta_A = 4.73$, $\delta_B = 4.71$, $|^2J| = 6.4$ Hz, 4-H_2), 7.38 – 7.45 (m, 3H, phenyl *m*- and *p*-H), 7.61 – 7.68 (m, 2H, phenyl *o*-H). – ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.90$ (broad m, 2H, $N(CH_{ax})_2$), 2.22 – 2.28 (m, 2H, $N(CH_{eq})_2$), 3.00 – 3.14 (m, 4H, $O(CH_2)_2$), 3.39 (s, 3H, $COOCH_3$), AB ($\delta_A = 4.13$, $\delta_B = 4.03$, $|^2J| = 6.4$ Hz), 7.03 – 7.14 (m, 3H, phenyl *m*- and *p*-H), 7.63 – 7.68 (m, 2H, phenyl *o*-H). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 47.7$ ($N(CH_2)_2$), 53.3 ($COOCH_3$), 66.0 ($O(CH_2)_2$), 66.8 (C-3), 72.2 (C-4), 91.4 (C-2), 115.6 (CN), 127.3, 128.2 (phenyl *o*- and *m*-C), 129.7 (phenyl *p*-C), 132.6 (q, phenyl C-1), 168.9 ($COOCH_3$). – MS (EI, 70 eV, 90 °C, decomposition): $m/z = 164$ (3) [M^+ of **3**], 139 (5), 138 (53) [M^+ of **5a**], 137 (4), 136 (7), 122 (3), 109 (4), 107 (7), 106 (12), 105 (100) [$PhCO^+$]. – MS (FD): $m/z = 302$ (27) [M^+], 138 (100) [M^+ of **3a**]. – $C_{16}H_{18}N_2O_4$ (302.33): calcd. C 63.56, H 6.00, N 9.27; found C 63.52, H 6.05, N 9.20.

Methyl (2R,3R*)-3-cyano-2-phenyl-3-(1-pyrrolidinyl) oxetane-2-carboxylate (***4b***)*: M. p. 85 – 86 °C. – IR (KBr): $\tilde{\nu} = 2222$w (CN), 1738s (C=O) cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.54-1.67$ (m, 4H, 3'- and 4'-H_2), 2.38 – 2.44 (m, 2H, $N(CH)_2$), 2.55 – 2.62 (m, 2H, $N(CH)_2$), 3.94 (s, 3H, $COOCH_3$), AB ($\delta_A = 4.74$, $\delta_B = 4.70$, $|^2J| = 6.2$ Hz, 4-H_2), 7.38 – 7.42 (m, 3H, phenyl *m*- and *p*-H), 7.68 – 7.72 (m, 2H, phenyl *o*-H). – ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 23.66$ (C-3' and C-4'), 48.39 (C-2' and C-5'), 53.17 ($COOCH_3$), 67.35 (C-3), 73.11 (C-4), 91.54 (C-2), 116.74 (CN), 126.98, 128.15 (phenyl *o*- and *m*-C), 129.36 (phenyl *p*-C), 133.10 (q, phenyl C-1), 169.29 ($COOCH_3$). – MS (FD): $m/z = 286$ (100) [M^+], 122 (26) [M^+ of **3b**]. – $C_{16}H_{18}N_2O_3$ (286.33): calcd C 67.12, H 6.34, N 9.78; found: C 66.91, H 6.42, N 9.70.

(2R,3R*) Methyl 3-cyano-2-phenyl-3-(1-piperidinyl) oxetane-2-carboxylate (***4c***)*: M. p. 85 – 87 °C. – UV (C_6H_{12}): $\lambda_{max}(\log\varepsilon) = 260$ nm (2.53), 267 nm (2.53), 272 nm (2.32, sh). – IR (KBr): $\tilde{\nu} = 2844$ (OCH_3), 2220w (CN), 1739s (C=O) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.09-1.34$ (m, 6H, 3'-, 4'-, and 5'-H_2), 2.18 – 2.24 (m, 2H, $N(CH_{ax})_2$), 2.34 – 2.42 (m, broad, 2H, $N(CH_{eq})_2$), 3.95 (s, 3H, $COOCH_3$), AB ($\delta_A = 4.70$, $\delta_B = 4.67$, $|^2J| = 6.3$ Hz, 4-H_2), 7.37 – 7.45 (m, 3H, phenyl *m*- and *p*-H), 7.60 – 7.68 (m, 2H, phenyl *o*-H). – ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.89-0.99$ (m, 6H, 3'-, 4'-, and 5'-H_2), 1.90 – 1.96 (m, 2H, $N(CH_{ax})_2$), 2.30 (m, broad, 2H, $N(CH_{eq})_2$), 3.39 (s, 3H, $COOCH_3$), AB ($\delta_A = 4.18$, $\delta_B = 4.10$, $|^2J| = 6.2$ Hz, 4-H_2), 7.06 – 7.14 (m, 3H, phenyl *m*- and *p*-H), 7.72 – 7.75 (m, 2H, phenyl *o*-H). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 23.73$, 24.97 (C-3', C-4', and C-5'), 48.47 (C-2' and C-6'), 53.15 ($COOCH_3$), 67.72 (C-3), 72.90 (C-4), 91.71 (C-2), 116.11 (CN), 127.38, 128.09 (phenyl *o*- and *m*-C), 129.39 (phenyl *p*-C), 132.97 (q, phenyl C-1), 168.17 ($COOCH_3$). – MS (EI, 70 eV, 90 °C, decomposition): $m/z = 185$ (3), 137 (5), 136 (53) [M^+ of **3c**], 135 (16), 121 (12), 108 (7), 107 (6), 106 (8), 105 (100) [$PhCO^+$]. – MS (FD): $m/z = 300$ (74) [M^+], 136 (100) [M^+ of **3c**]. – $C_{17}H_{20}N_2O_3$ (300.34): calcd. C 67.98, H 6.71, N 9.33; found C 67.84, H 6.75, N 9.31.

Methyl (2R,3R*)-3-cyano-3-(1-hexamethyleneimino)-2-phenyloxetane-2-carboxylate (***4d***)*: M. p. 94 – 100 °C (with decomposition). – UV (C_6H_{12}): $\lambda_{max}(\log\varepsilon) = 253$ nm (2.67, sh), 260 nm (2.68), 265 nm (2.67), 271 nm (2.52, sh). – IR (KBr): $\tilde{\nu} = 2220$ (CN), 1730s (C=O) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90-1.38$ (several m, 8H, 3'-, 4'-, 5'-, and 6'-H_2), 2.31 – 2.40 (m, 2H, $N(CH_{ax})_2$), 2.45 – 2.53 (m, 2H, $N(CH_{eq})_2$), 3.96 (s, 3H, $COOCH_3$), AB ($\delta_A = 4.74$, $\delta_B = 4.67$, $|^2J| = 6.3$ Hz, 4-H_2), 7.39 – 7.44 (m, 3H, phenyl *m*- and *p*-H), 7.63 – 7.67 (m, 2H, phenyl *o*-H). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 25.96$ and 28.46 (C-3', C-4', C-5', and C-6'), 51.19 (C-2' and C-7'), 53.19 ($COOCH_3$), 68.31 (C-3), 73.81 (C-4), 91.87 (C-2), 117.01 (CN), 127.65 and 128.17 (phenyl *o*- and *m*-C), 129.47 (phenyl *p*-C), 133.18 (q, phenyl C-1), 169.24 ($COOCH_3$). – MS (EI, 70 eV, 110 °C (decomposition): $m/z = 164$ (3) [M^+ of **1**], 151 (4), 150 (33) [M^+ of **3d**], 149 (5), 136 (5), 135 (16), 122 (4), 121 (6), 110 (7), 108 (3), 107 (11), 106 (8), 105 (100) [$PhCO^+$]. – MS (FD): $m/z = 314$ (100) [M^+]. – $C_{18}H_{22}N_2O_3$ (314.38): calcd. C 68.77, H 7.05, N 8.91; found: C 68.79, H 7.07, N 8.84.

*Methyl (2R*3R*)-3-cyano-(1-heptamethyleneimino)-2-phenyloxetane-2-carboxylate (***4e***)*: M. p. 91 – 93 °C – UV (C_6H_{12}): $\lambda_{max}(\log\varepsilon) = 259$ (2.74), 265 (2.70), 272 nm (2.52, sh). – IR (KBr): $\tilde{\nu} = 2223$ (CN), 1730s (C=O) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96-1.47$ (several m, 10H, 3'- to 7'-H_2), 2.30 – 2.48 (m, 2H, $N(CH_{ax})_2$), 2.49 – 2.57 (m, 2H, $N(CH_{eq})_2$), 3.94 (s, 3H, $COOCH_3$), AB ($\delta_A = 4.77$, $\delta_B = 4.75$, $|^2J| = 6.3$ Hz, 4-H_2), 7.37 – 7.47 (m, 3H, phenyl *m*- and *p*-H), 7.66 – 7.72 (m, 2H, phenyl *o*-H). – ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 24.14$ and 26.72, (C-3' to C-7'); 50.60 (C-2' and C-8'), 53.16 ($COOCH_3$), 69.07 (C-3), 73.49 (C-4), 92.33 (C-2), 117.43 (CN), 127.40 and 128.38 (phenyl *o*- and *m*-C), 129.56 (phenyl *p*-C), 133.14 (q, phenyl C-1), 169.20 ($COOCH_3$). – MS (EI, 70 eV, 90 °C, decomposition): $m/z = 301$ (< 1) [M^+-HCN], 297 (< 1), 164 (22) [M^+ of **1** and **3e**], 149 (10), 136 (6), 135 (5), 124 (6), 122 (3), 121 (10), 110 (5), 108 (3), 107 (7), 106 (8), 105 (100) [$PhCO^+$]. – MS (FD): $m/z = 328$ (100) [M^+], 164 (21) [M^+ of **1** and **3e**]. – $C_{19}H_{24}N_2O_3$ (328.40): calcd C 69.49, H 7.37, N 8.53; found: C 69.52, H 7.32, N 8.51.

Methyl (2R,3R)-3-cyano-3-[(2'S)-methoxymethyl-1-piper-idinyl]-2-phenyloxetane-2-carboxylate (pure major diastereomer **4g***)*: M. p. 108 – 112 °C. – UV (C_6H_{12}): $\lambda_{max}(\log\varepsilon) = 259$ nm (2.71, sh), 265 nm (2.64, sh). –

IR (KBr): $\tilde{\nu} = 2220$ (CN), 1729s (C=O) cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.77-1.47$ (m, 6H, 3'-, 4'-, and 5'-H_2), 2.68 – 2.76 (m, 2H, 6'-H_2), 2.92 – 2.96 (m, 1H, 2'-H), 3.02 – 3.05 (m, 1H, CH^1OCH$_3$), 3.29 (s, 3H, OCH$_3$), 3.68 – 3.73 (m, 1H, CH^2OCH$_3$), 3.91 (s, 3H, COOCH$_3$), AB ($\delta_A = 4.75$, $\delta_B = 4.65$, $|^2J| = 7.3$ Hz, 4-H_2), 7.35 – 7.47 (m, 3H, phenyl *m*- and *p*-H), 7.62 – 7.68 (m, 2H, phenyl *o*-H). – ^1H NMR (300 MHz, C_6D_6): $\delta = 0.69-1.18$ (m, 6H, 3'-, 4'-, and 5'-H_2), 2.50 – 2.54 (m, 1H, CH^1OCH$_3$), 2.54 – 2.62 (m, broad, 1H, 2'-H), 2.62 – 2.72 (m, 1H, 6'-H_{ax}), 2.93 – 3.02 (m, 1H, 6'-H_{eq}), 3.08 (s, 3H, -CH_2OCH_3), 3.37 – 3.44 (m, 1H, CH^2OCH$_3$), 3.40 (s, 3H, COOCH$_3$), AB ($\delta_A = 4.61$, $\delta_B = 4.49$, $|^2J| = 7.1$ Hz, 4-H_2), 7.10 – 7.22 (m, 3H, phenyl *m*- and *p*-H), 7.79 – 7.84 (m, 2H, phenyl *o*-H). – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 19.73$ C-4'), 25.03 and 28.33 (C-3' and C-5'), 43.08 (C-6'), 53.05 (COO*C*H$_3$), 53.60 (C-2'), 58.16 (CH$_2$O*C*H$_3$), 67.90 (C-3), 69.49 (*C*H$_2$OCH$_3$), 70.54 (C-4), 93.36 (C-2), 118.37 (CN), 126.82 and 128.05 (phenyl *o*- and *m*-C), 128.86 (phenyl *p*-C), 133.32 (q, phenyl C-1), 169.61 (*C*OOCH$_3$), – $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): $\delta =$ 19.96 (C-4'), 25.38 and 28.54 (C-3' and C-5'); 43.43 (C-6'), 52.37 (COO*C*H$_3$), 53.80 (C-2'), 57.97 (CH$_2$O*C*H$_3$), 68.42 (C-3), 69.49 (*C*H$_2$OCH$_3$), 70.64 (C-4), 93.76 (C-2), 118.93 (CN), 127.48 and 128.23 (phenyl *o*- and *m*-C), 128.85 (phenyl *p*-C), 134.73 (q, phenyl C-1), 170.16 (*C*OOCH$_3$). – MS (EI, 70 eV, 95 °C, decomposition): $m/z = 222$ (5), 194 (3), 180 (6), 165 (3), 136 (10), 135 (100), 108 (14), 107 (10), 106 (9), 105 (93) [PhCO$^+$]. – MS (FD): $m/z = 344$ (16) [M$^+$], 300 (10), 299 (5), 181 (16), 180 (100) [M$^+$ of **3g**], 172 (14), 135 (15). – $C_{19}H_{24}N_2O_4$ (344.41): calcd. C 66.26, H 7.02, N 8.13; found: C 66.34, H 7.07, N 8.13. – $[\alpha]_D^{20} = +27$ ($c = 0.1$, C_6H_{12}).

The following data could be extracted for the minor isomer **4'g** from the NMR spectra of the **4g**/**4'g** mixture: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.18-3.12$ (m, 1H, CH^1OCH$_3$), 3.28 (s, 3H, OCH$_3$) 3.96 (s, 3H, COOCH$_3$), AB ($\delta_A = 4.93$, $\delta_B = 4.85$, $|^2J| = 6.9$ Hz, 4-H_2). – (500 MHz, C_6D_6): $\delta = 2.83$ (s, 3H, OCH$_3$), 3.51 (s, 3H, COOCH$_3$), AB ($\delta_A = 4.73$, $\delta_B = 4.71$, $|^2J| = 6.9$ Hz, 4-H_2). – $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 52.49$ (COO*C*H$_3$), 58.28 (CH$_2$-O-*C*H$_3$), 68.26 (C-3), 75.38 (C-4), 93.29 (C-2), 118.00 (CN), 135.53 (phenyl C-1), 169.83 (C=O).

Analytical scale irradiations

As specified below, degassed sample solutions (0.5 ml, C_6D_6) in 5 mm diameter NMR tubes were mounted on the outer wall of the immersion well as used above and externally cooled with water during the irradiation. The progress of the reaction was monitored periodically and at the specified irradiation times by 300 MHz ^1H NMR spectroscopy. Oxetanes were detected in the reaction mixtures by their typical AB systems for 4-H_2, for aldehydes the formyl ^1H signal was diagnostic.

Table 2. Crystal data and structure refinement for compound **4g**.

Chemical formula	C_{19} H_{24} N_2 O_4
Formula weight	344.40
Temperature [K]	150
Crystal system, space group	monoclinic, $P2_1$
Crystal size [mm]	$0.64 \times 0.28 \times 0.24$
Unit cell dimensions	
[Å]	$a = 8.652$ (2)
	$b = 12.451$ (3)
	$c = 8.744$ (2)
[°]	$\beta = 112.42$ (2)
Volume [Å^3]	870.8(4)
Z, calculated density [g/cm^3]	2, 1.314
Absorptions coefficient [mm^{-1}]	0.092
F (000)	368
Theta range [°]	2.52 to 27.00
Limiting indices	$0 < h > 11$,
	$0 < k > 15$,
	$-11 < l > 10$
Reflections collected / unique	2105 / 1990 [R(int) = 0.0109]
Completeness to $\theta = 27.00°$	100%
Absorptions correction	ψ-scan
Transmission range	0.973 – 0.964
Refinement method	Full-matrix least-squares (F^2)
Data / parameters	1990 / 228
Goodness-of-fit (F^2)	1.061
Final R Indices [$I > 2\sigma(I)$]	$R_1 = 0.0319$, $wR_2 = 0.0805$
R indices (all data)	$R_1 = 0.0357$, $wR_2 = 0.0830$
Extinction coefficient	0.008 (4)
Largest diff. peak and hole [e Å^{-3}]	0.309 and −0.143

The following runs were made:

1) Benzil (**5a**, 50 mg, 0.24 mmol) and **3f** (42 mg, 0.25 mmol). After 40 min two oxetanes were detected: $\delta_{A1} = 4.71$, $\delta_{B1} = 4.60$ ppm, $|^2J| = 6.9$ Hz; $\delta_{A2} = 4.95$, $\delta_{B2} = 4.38$, $|^2J| = 6.3$ Hz. – $\delta = 9.70$ (s): benzaldehyde (**9a**).

2) Benzil (**5a**, 25 mg, 0.12 mmol) and **3g** (25 mg, 0.14 mmol). Two oxetanes were detected after 30 min: $\delta_{A1} = 4.63$, $\delta_{B1} = 4.53$ ppm, $|^2J| = 6.2$ Hz; $\delta_{A2} = 4.83$, $\delta_{B2} = 4.53$ ppm, $|^2J| = 6.2$ Hz. After 300 min, oxetane 1 had completely disappeared, only oxetane 2 was still present. – GC/MS (70 eV): 3.76 min: benzaldehyde (**9a**), 9.82 min: **3g**; 14.23 min: **5a**; $m/z = 210$ (3%); 23.31 min: compound **8a**. This compound will be spectrally characterized below.

3) 4,4'-Bis(trifluoromethyl)benzil (**5b**, 25 mg, 0.072 mmol) and **3f** (17 mg, 0.10 mmol). After 10 min only one oxetane ($\delta_A = 4.93$, $\delta_B = 4.29$ ppm, $|^2J| = 6.4$ Hz) was detected but was completely degraded again after 120 min of irradiation. $\delta = 9.44$ ppm (s): 4-trifluormethylbenzaldehyde (**9b**).

4) 4,4'-Bis(trifluoromethyl)benzil (**5b**, 25 mg, 0.072 mmol) and **3g** (20 mg, 0.11 mmol). After 10 min of irradiation one oxetane ($\delta_A = 4.71$, $\delta_B = 4.47$ ppm, $|^2J| = 6.6$ Hz) had formed. After 220 min this oxetane had been completely degraded whereas the signals of **3g** and **9b** ($\delta =$

9.43, s) had remained. – GC/MS (70 eV): t = 3.64 min: **9b**, m/z (%) = 174 (76) [M^+]; 9.82 min: **3g**; 12.67 min: **5b**, m/z = 346 (1) [M^+].

5) 4,4'-Dichlorobenzil (**5c**, 4 mg, 0.014 mmol) and **3g** (3.1 mg, 0.017 mmol). After 15 min one oxetane only was observed (δ_A = 4.66, δ_B = 4.46 ppm, $|^2J|$ = 6.5 Hz) together with the singlet of 4-chlorobenzaldehyde (**9c**, δ = 9.42 ppm). – GC/MS (70 eV): t = 5.86 min: **9c**, m/z (%) = 142 (21) [M^+]; 9.82 min: **3g**; 17.50 min: **5c**, m/z (%) = 278 (1) [M^+].

*E-3-Benzoyl-2-(2-methoxymethylpiperidinyl)propenenitrile (**8**)*: IR (film): $\tilde{\nu}$ = 2230 (CN), 1638 (C=C) cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55 – 1.88 (m, 6H, 3'-, 4'- and 5'-H_2), 3.12 – 3.18 (m, 1H, 6'-H_{ax}), 3.38 (s, 3H, OCH_3), 3.48 – 3.52 (m, 1H, CH^1OCH_3), 3.65 – 3.70 (m, 1H, CH^2OCH_3), 3.79 – 3.82 (m, 1H, 6'-H_{eq}), 4.39 – 4.44 (m, 1H, 2'-H), 6.40 (s, 1H, 3-H), 7.41 – 7.50 (m, 2H, phenyl *m*-H), 7.51 – 7.53 (m, 1H, phenyl *p*-H), 7.89 – 7.93 (m, 2H, phenyl *o*-H). – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 18.97 (C-4'), 25.06 and 26.08 (C-3' and C-5'), 44.73 (C-6'), 55.64 (C-2'), 59.43 (OCH_3), 71.13 (CH_2OCH_3), 102.68 (C-3), 113.66 (CN), 127.88 and 128.56 (phenyl *o*- and *m*-C), 132.20 (phenyl *p*-C), 133.69 (q, phenyl C-1), 139.33 (C-2), 186.40 (C=O). – MS (EI, 70 eV, 125 °C, decomposition): m/z (%) = 284 (4) [M^+], 263 (5), 262 (29), 240 (6), 239 (34), 216 (3), 186 (5), 156 (3), 151 (4), 147 (5), 137 (4), 135 (9), 128 (5), 123 (5), 122 (3), 116 (4), 109 (8), 107 (8), 106 (11), 105 (100) [$PhCO^+$].

Crystal structure determination of compound **4g**

Data collection was performed using a Siemens P4 four-circle diffractometer with rotating anode generator, graphite monochromator and scintillation counter, λ = 0.71073 Å (Mo-K_α). The structure was solved with direct methods using SHELXS-97. Structure refinements were performed against F^2 using SHELXL-97. Empirical absorption corrections were applied. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealizied geometry and refined with isotropic displacement parameters (see Table 2). The programs by G. M. Sheldrick, University of Göttingen, Germany, were used. – *X*-ray data have been deposited at the Cambridge Crystallographic Data Centre (CCDC 238272). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CD2 1EZ, U.K. [Fax +44-1223/336033; e-mail: deposite@ccdc.cam.ac.uk].

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