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Stereocontrolled photo-reaction pathways of *endo*/*exo*-2-benzoyl-substituted bicyclo[2.2.2]oct-5-en-2-ol: Paternò–Büchi reaction *versus* α-cleavage†‡

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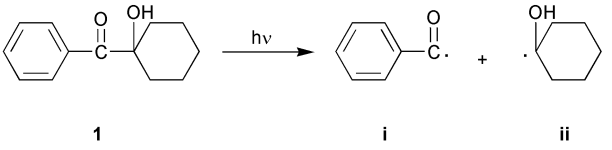
Two stereoisomeric ketones, *endo*- and *exo*-(2-hydroxy-[2.2.2]bicyclo-5-en-1-yl)-phenyl methanone (*endo*-**2** and *exo*-**2**) were synthesized *via* a Lewis acid catalyzed Diels–Alder reaction. Both compounds were tested in terms of their efficiency as photoinitiators for radical polymerization. Whereas the *exo* isomer serves as a good photoinitiator, the curing efficiency is poor in the case of the *endo* derivative. CIDNP investigations and product analysis by NMR and GC-MS together with density functional calculations reveal the distinctly different reaction pathways of the two isomers. On one hand, *exo*-**2** undergoes α-cleavage from the triplet excited state forming a radical pair that is able to induce polymerizations. On the other hand, *endo*-**2** cyclizes in a *Paternò–Büchi* reaction yielding a tetracyclic product **11** and no formation of radicals is observed.

Introduction

α-Hydroxyacetophenone derivatives possessing a quaternary α-carbon atom are among the most efficient photoinitiators that find widespread use in industrial applications.[1–4] One of the most prominent representatives of this class is 1-benzoyl-1-hydroxy-cyclohexane **1**, a commercial photoinitiator that is mostly used in clear coat applications (Scheme 1).

The photochemistry of these compounds is well known and understood.[5,6] Their good performance as photoinitiators is attributed to a very efficient Norrish Type I cleavage producing a benzoyl (**i**) and a α-hydroxyalkyl radical (**ii**). Both radicals have been shown to undergo fast addition to acrylic double bonds, efficiently initiating the polymerization of acrylic components.[7,8]

Despite the high efficiency of the available photoinitiators, their continuous improvement is an ongoing challenge. New substitution patterns can advantageously influence not only the photochemical efficiency, but also properties that are important in technical applications, such as the solubility and the volatility of the compounds. Therefore novel structures are continuously being prepared and evaluated as photoinitiators. This paper reports the photochemistry of a derivative of **1**, 2-benzoyl-bicyclo[2.2.2]oct-5-en-2-ol¶ **2** (Fig. 1), which has been isolated in two isomeric forms, *endo*-**2** and *exo*-**2**‖ exhibiting an interesting dependence of its primary photoreactions upon the configuration.



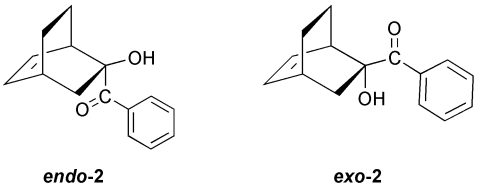
1 **i** **ii**

Scheme 1 Photocleavage of the photoinitiator 1-benzoyl-1-hydroxy-cyclohexane (**1**).

Synthesis and evaluation of new α-hydroxyketone photoinitiators

Since access to novel substitution patterns often requires new synthetic strategies, we have investigated various approaches to aryl cyclohexyl ketones.

An obvious approach to these compounds is based on the Friedel–Crafts acylation of an aromatic compound with a

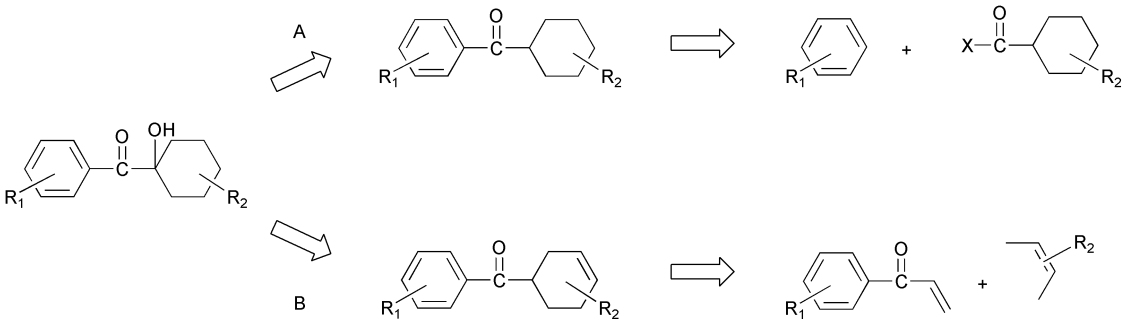


***endo*-2** ***exo*-2**

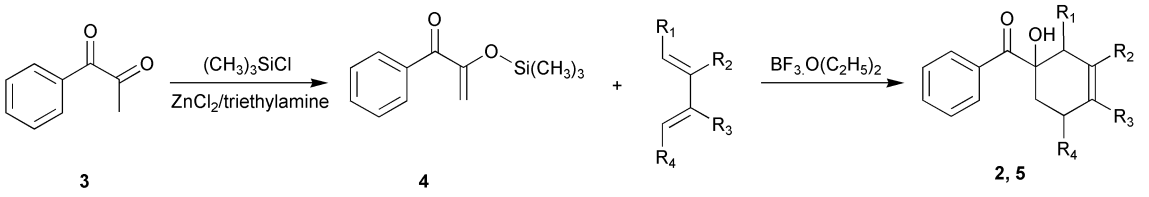
Fig. 1 Structures of *endo*-2-benzoyl-bicyclo[2.2.2]oct-5-en-2-ol (*endo*-**2**) and *exo*-2-benzoyl-bicyclo[2.2.2]oct-5-en-2-ol (*exo*-**2**).

† Dedicated to Professor Dr Z. R. Grabowski and Professor Dr J. Wirz on the occasions of their 75th and 60th birthdays.
‡ Electronic supplementary information (ESI) available: ^{1}H-CIDNP spectra of *exo*-**2**. See http://www.rsc.org/suppdata/cp/b2/b210166a/
§ Former Ciba-Geigy Physics Department.
¶ The name of compound **2** following the IUPAC recommendations is: 2-hydroxy-bicyclo[2.2.2]oct-5-en-2-yl)-phenyl-methanone. For the ease of understanding, we use a nomenclature defining a benzoyl moiety as a substituent throughout this paper.

‖ *Exo* and *endo* as used here refer to the relative position of the benzoyl group. *Exo*-**2** is 1α,2β,4α(2-hydroxy-bicyclo[2.2.2]oct-5-en-2-yl)-phenyl-methanone; *endo*-**2** is 1α,2α,4α(2-hydroxy-bicyclo[2.2.2]-oct-5-en-2-yl)-phenyl-methanone.



Scheme 2 Retrosynthetic approaches to phenyl cyclohexyl ketones.



Scheme 3 Synthesis of 1-benzoyl-1-hydroxy-cyclohex-3-ene derivatives *via* a Lewis acid catalyzed Diels–Alder reaction.

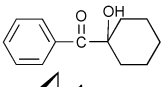
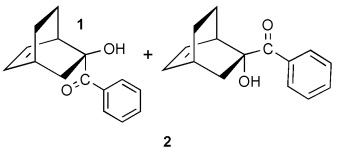
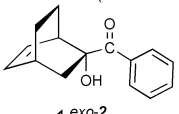
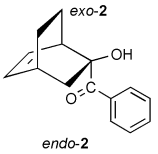
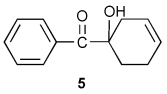
suitable acylation agent (Scheme 2, path A). Retrosynthetic analysis of the target structure suggests another route that uses the Diels–Alder reaction of a diene with a 1-benzoyl substituted alkene (Scheme 2, path B). An attractive feature of this approach is that the six-membered ring is formed in the key reaction step, which provides access to a variety of new substitution patterns, including bicyclic structures.

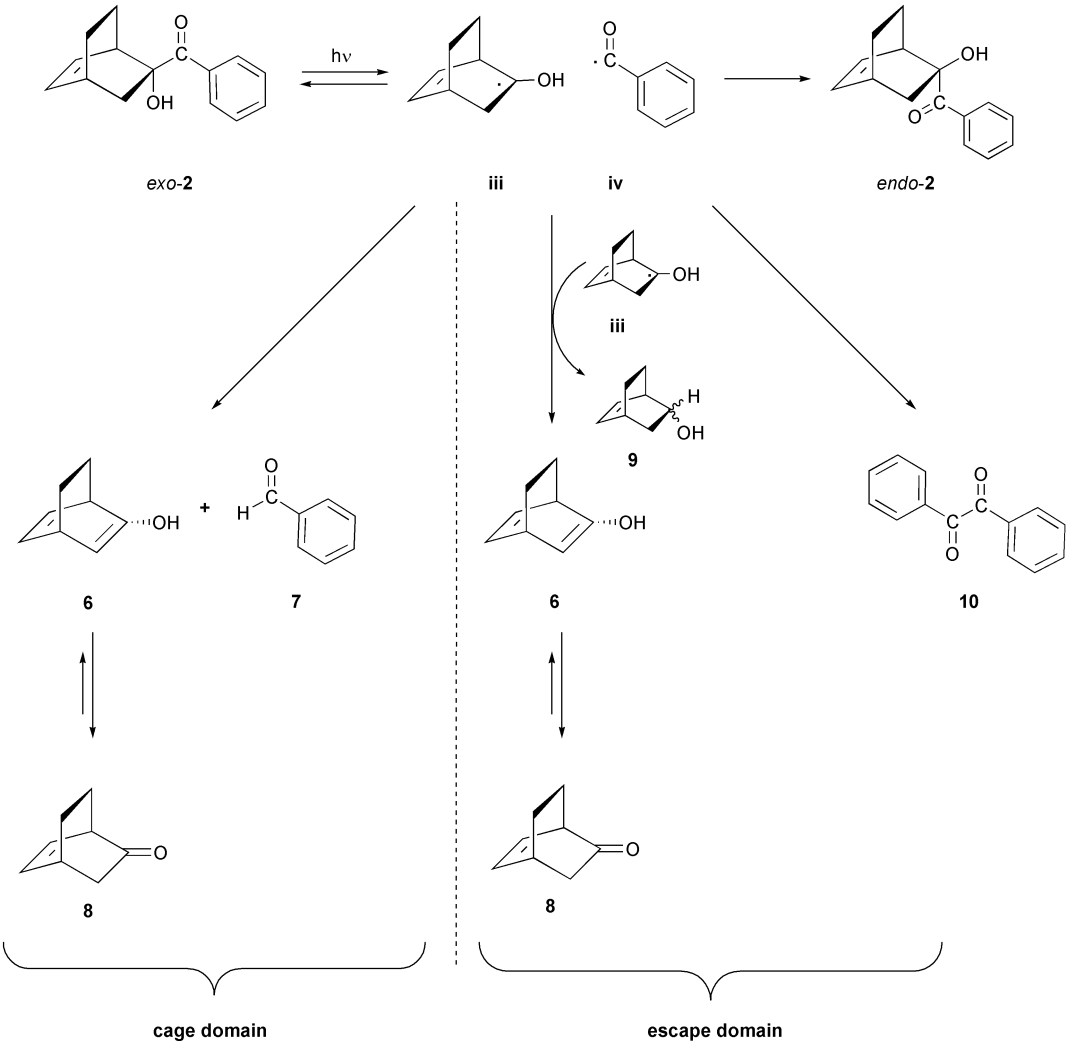
This concept has been realized using the trialkylsilyl enol ether of a 1-phenyl-propane-l,2-dione as the dienophile. Lewis-acid catalyzed Diels–Alder reactions with various dienes give 1-hydroxy-1-benzoyl-cyclohex-3-ene derivatives in a single reaction step, since the silyl ether group in the adduct is cleaved during the acidic work-up to give the corresponding alcohol. By use of this methodology a variety of differently substituted structures are available in a straightforward synthesis (Scheme 3).[9] Catalytic hydrogenation of the double bond allows the synthesis of saturated cyclohexane derivatives, such as **1**, by this reaction pathway.

The reactivity of the compounds prepared by the Diels–Alder route was assessed in a typical clear coat formulation applied in 60 μm thickness on white cardboard. As a measure for the curing efficiency, the number of passes required to get a tack-free coating by passing the sample at a belt speed of 20 m min^{-1} under a mercury high pressure lamp was determined (Table 1).

1-Benzoyl-1-hydroxy-cyclohex-3-ene **5**, obtained by the cycloaddition reaction using butadiene as the diene component, shows an acceptable reactivity that is only slightly lower than that of the state-of-the-art photoinitiator 1-benzoyl-1-hydroxy-cyclohexane **1**. The 2 : 1 mixture of stereoisomers of

Table 1 Performance of various α-hydroxyketones as photoinitiators in the curing of an urethane acrylate clear coat (number of passes required for surface cure, for details see experimental part)

Photoinitiator	Number of passes	Comment
	5	Fully cured
 1 + 2 (*exo*-**2**/*endo*-**2** = 2: 1)	9	Fully cured
 *exo*-**2**	7	Fully cured
 *endo*-**2**	20	Tacky surface, *not fully cured*
 **5**	7	Fully cured



Scheme 4 Photochemical α-cleavage of *exo*-**2**.

2-benzoyl-bicyclo[2.2.2]oct-5-en-2-ol **2**, obtained from the reaction with cyclohexa-1,3-diene, is less efficient. The separation of the two stereoisomers resulted in two α-hydroxy ketone derivatives that had a significantly different efficiency as photoinitiator: While the 2-*exo*-benzoyl-bicyclo[2.2.2]oct-5-en-2-ol (*exo*-**2**) is more efficient than the mixture of the stereoisomers and equals the cyclohexene derivative **5**, 2-*endo*-benzoyl-bicyclo[2.2.2]oct-5-en-2-ol (*endo*-**2**) is a poor photoinitiator that does not give a tack-free coating even after 20 passes in the UV processor.

This surprisingly pronounced effect of the stereochemistry on the photoinitiation efficiency of an α-hydroxy ketone photoinitiator prompted us to investigate the photochemistry of these compounds in more detail in order to elucidate the effects that cause this different behavior.

Photo-reaction pathways

General remarks

Both compounds were investigated by CIDNP experiments. The isomer *exo*-**2** exhibited strong polarizations indicating a radical reaction. In contrast, spin polarizations were absent during the reaction of *endo*-**2**. Therefore, NMR, product analysis, and optical quenching reactions were used for the study of *endo*-**2**. Density functional calculations were performed to get a closer insight into the observed behavior of the two compounds.

Exo-2: CIDNP experiments

Two sets of ^{1}H- and ^{13}C-CIDNP-experiments were carried out: Investigations using a broad band 1 kW mercury high pressure lamp were performed on a 100 MHz spectrometer, whereas a 200 MHz spectrometer was used for the laser experiments (see experimental part). The broad band experiments led to stronger polarizations due to the higher energy and intensity of the irradiation source, resulting in a higher momentary radical concentration.

As mentioned above, photolysis of *exo*-**2** led to clearly visible CIDNP effects. The products of this reaction are summarized in Scheme 4 and can be traced back to a primary radical pair consisting of bicyclo[2.2.2]oct-5-en-1-ol-1-yl radical **iii** and benzoyl radical **iv**.

The strong polarizations are typical for α-cleavage from an excited triplet state and for primary radicals with distinctly different *g* values. Such a reaction is expected for a benzoyl derivative possessing a quarternary α-carbon atom substituted by an electron donating hydroxyl group. In both ^{1}H-CIDNP experiments with *exo*-**2** the signal of the aldehyde proton (9.6 ppm) of benzaldehyde **7** is visible exhibiting enhanced absorption. According to *Kaptein's* rule,[10,11] this polarization pattern is typical for an in-cage β-abstraction of hydrogen after α-cleavage in the triplet state. The overlapping multiplets of ^{1}H-CIDNP spectra are difficult to analyze. Due to the inherently higher resolution and the simpler structure of the resonances, the ^{13}C-CIDNP spectra of the ketone region and the region of the oxygen-substituted quaternary carbons shown

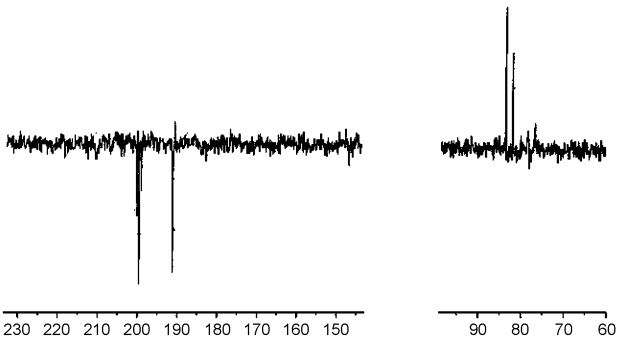


Fig. 2 Two sections (carbonyl and quaternary oxygen-substituted carbons) of the ^{13}C-CIDNP spectrum obtained upon irradiation of *exo*-**2** (ppm *vs.* TMS; solvent: benzene-d_6; 100 MHz spectrometer).

in Fig. 2 are easier to interpret. The following discussion is therefore supported primarily by ^{13}C-experiments.

In the ^{13}C-CIDNP spectra this β-abstraction leads to an emissive resonance of the benzaldehyde carbonyl carbon at 191.3 ppm (compound **7**). α-Cleavage is also substantiated by the formation of benzil (**10**, carbonyl enhanced absorption, 190.7 ppm, escape reaction). In addition, there is one emission type resonance (benzoyl recombination product) near 199 ppm that is not accounted for in Scheme 4 and could be due to the addition of a benzoyl radical to the double bond of the primary alkyl radical with subsequent ring closure.

Abstraction of hydrogen from the β-position of the α-hydroxyalkyl radical **iii** (Scheme 4) gives rise to bicyclo[2.2.2]octa-2,5-dien-2-ol **6**, which undergoes fast tautomerisation to the corresponding bicyclo[2.2.2]octa-5-en-2-one **8**. The vinyl alcohol **6** and the ketone **8** may be formed either in the cage *via* hydrogen abstraction by the benzoyl radical **iv** within the primary radical pair or, after escape of radical **iii**, by a disproportionation reaction with a second α-hydroxyalkyl radical. In addition to the ketone, the latter reaction produces the alcohol **9**.[12] Since the in-cage and the escape reaction pathways lead to opposite polarizations, the two processes tend to diminish the polarization and may result in very weak resonances in the ^{13}C- and ^{1}H-CIDNP spectra.

Since benzaldehyde **7** is clearly visible in both the ^{1}H- and ^{13}C-experiments it seems reasonable to look for polarized NMR-resonances of the recombination to *endo*- and *exo*-**2** and to search also for resonances of the ketone **8**. Note that **8** is not photostable and reacts further upon ultraviolet radiation.[13,14]

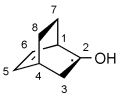
To discuss the expected polarizations, it is helpful to consult the spin density of the primary radical **iii**. Since experimental data for **iii** are not available and it is well established that isotropic hyperfine coupling constants a from density-functional calculations closely match the corresponding experimental values,[15,16] we have calculated these isotropic hyperfine coupling constants a in radical **iii** on the UB3LYP/6-31G* level of theory (see Table 2).

These isotropic hyperfine coupling constants are closely related to the magnitude of polarization. The polarization factor (net effect) is proportional to:

$$I_j \sim T_{1j}[|(g-g')\beta B + \tfrac{1}{2}a_j|^{1/2} - |(g-g')\beta B - \tfrac{1}{2}a_j|^{1/2}]$$

Within the diffusion model the polarization produced at the nuclear spin of atom j depends on three kinds of parameters related to magnetism: the hyperfine coupling, a_j, the electron chemical shift values of the two radicals in the primary pair g and g' and the longitudinal relaxation time, T_{1j}.[11,17–19] The value of g refers to the radical on which the carbon or hydrogen was located during the polarization process. The parameter B represents the static magnetic field and β the Bohr magneton. The polarization reaches its optimum, when the

Table 2 Theoretical (UB3LYP/6-31G*) isotropic hyperfine coupling constants (a^{1}_{H}- and a^{13}_{C}/mT) reflecting the spin densities in the primary α-hydroxyalkyl radical **iii** ($g = 2.0023$ was assumed for calculation purposes)



iii

Position	a^{13}_{C}	a^{1}_{H}
1	−0.9	2.3
2	84.1	—
3	3.1	23.2/16.2
4	1.3	0.7
5	0.9	−0.5
6	15.0	3.6
7	8.5	1.6/−0.4
8	0.4	1.0/0.1
Oxygen	−8.2	−3.8

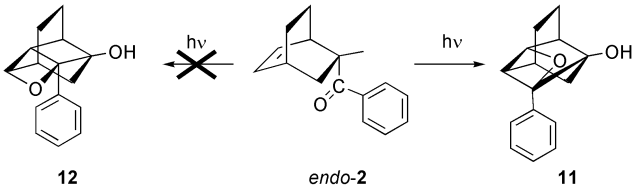
first or the second expression vanishes. At a magnetic field of about 25 T, corresponding to our experiment at 100 MHz ^{1}H-frequency, and a difference between the g values of 2.5×10^{-4}, the optimal hyperfine coupling is 1.35 mT. Therefore, according to the calculated values shown in Table 2, and neglecting the influence of relaxation, ^{13}C and ^{1}H nuclear spins at C(2), C(6), C(7) and the two hydrogens at C(3) (H(3a), H(3b)) are expected to exhibit large polarizations. The resonances of C(6) and C(7) are difficult to assign since they appear in crowded regions of the spectrum.

The ^{13}C-CIDNP experiments performed with *exo*-**2** reveal resonances of *endo*- and *exo*-**2** (see Table 4, experimental part) thus providing evidence for back reaction and isomerisation (Scheme 4). The C(2) atoms of both isomers (82.0 and 83.7 ppm) exhibit pronounced enhanced absorption. The intensities of the two resonances are of the same order of magnitude.

A very weak and broad emission is detected in the ^{13}C-experiment with broad band light irradiation at 210.4 ppm. This resonance has the same chemical shift as the carbonyl carbon of ketone **8**. It is tentatively assigned to this product and the line broadening is attributed to the photo-instability of the ketone. If this assignment is correct, it indicates that the escape route dominates the ketone polarization in the mercury lamp experiment. This interpretation is supported by a strong ^{1}H-CIDNP emission at 1.75 ppm in the 100 MHz experiment, assigned to CH_2(3) of **8** (by comparison with the ^{1}H-NMR of the authentic product). Other ^{1}H-polarizations detected experimentally are an enhanced absorption of H(3) in *exo*-**2**, and, during 200 MHz experiments with acetonitrile as a solvent (low radical concentration), two enhanced resonances at 4.90 and 3.58 ppm, which we tentatively assign to the olefinic hydrogen H(3) of the enol **6** and H(2) of compound **9**, respectively (Figs. S1 and S2, ESI‡).

Endo-2: NMR spectroscopy

Surprisingly, the stereoisomeric structure *endo*-**2** did not show any polarized NMR resonances. Upon irradiation of this isomer, only one product could be detected by NMR with a steadily increasing concentration. After exhaustive irradiation, this product is formed in 98% yield according to GC-MS, and it has the same molecular weight (228 u) as *endo*-**2**. NMR reveals the same number of carbons as the starting material. Notably, the carbonyl C-atom (199.7 ppm) of the starting compound is converted into an sp^3-hybridized carbon substituted by oxygen, with a typical chemical shift of 101.9 ppm. This structural



Scheme 5 Photochemical reaction of *endo*-**2**.

feature strongly points to the product of an intramolecular *Paternò–Büchi*-type [2 + 2] cycloaddition.

The distinctly different photochemical behavior of the two diastereoisomers must be a consequence of the relative spatial arrangement of the carbonyl and the carbon-carbon double bond. In *endo*-**2**, the C=O and C=C double bonds are held in close vicinity by the rigid bicyclic structure, thus allowing cyclization to occur from the excited state.

Two cycloaddition products, **11** and **12**, are feasible, depending on the relative orientation of the C=O and the C=C bond (Scheme 5).

In 1-hydroxy-2-phenyl-3-oxa-tetracyclo[3.3.1.1^{2,4}.0^{8,10}]decane (**12**), the carbonyl oxygen is bound to the more distant C(5) of *endo*-**2** leading to a tetracyclic system containing two four membered rings. On the other hand, when the oxygen adds to C(6) of *endo*-**2**, 2-hydroxy-1-phenyl-9-oxa-tetracyclo[6.1.1.0^{2,7}0^{4,10}]-decane (**11**) emerges, which contains a four membered and a five membered ring next to the two six-membered rings.

The distinction between **11** and **12** is made in three steps:

1. The ^{13}C chemical shifts are assigned to individual carbons by the established linear shift rules and by theoretical calculations.

2. HETCORE experiments connect ^{1}H- and ^{13}C-chemical shifts, thereby assigning protons to the corresponding carbons.

3. ^{1}H–^{1}H coupling constants are then compared with the two hypothetical structures described above. The proton network is tested through double resonance and COSY experiments. In addition, gs-HMBC experiments were performed to confirm the chemical structure.

These three steps led to the conclusion that compound **11** with only a single four membered ring is the only product formed in the *Paternò–Büchi* reaction. Moreover, B3LYP/6-31G* calculations predict a lower energy for this structure, the difference from isomer **12** being 4.8 kcal mol^{-1}. These results are in good agreement with the previous work of Schaffner and Jeger who observed the formation of similar products.[20,21]

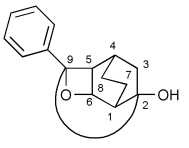
The crucial point in this chain of arguments is the correct assignment of the ^{13}C-chemical shift values; these assignments are given in Table 3. The chemical shift values assigned to C(9) and C(6) of **11** are typical for oxetane derivatives (see for instance[22]). Five and six membered cyclic ethers would exhibit smaller chemical shift values.

In addition, arguments why the hypothetical structure **12** (Fig. 3) is not formed can be presented.

Double resonance experiments revealed that H(4) exhibits a coupling with H(5) and no coupling with a hydrogen on an oxygen-substituted tertiary carbon atom, which, in structure **12**, would correspond to a coupling between H(5) and H(4) in the oxetane moiety.

According to calculations, the tetrahedral angle between H(5) and H(4) in **12** is −42.6°. This angle should manifest itself in a coupling of a few cycles. The experimentally observed coupling between H(4) and H(5) attributed to **11** would convert to a long range coupling between H(6) and H(4) in **12**. However, a long-range W-coupling between these two protons is extremely unlikely, since the C–C–H(4) and C–C–H(6) planes in **12** define an angle of approximately 50°.

Table 3 Experimental ^{1}H and ^{13}C and calculated (GIAO/B3LYP/6-311+G(2d,p)//B3LYP/6-31G*) ^{13}C chemical shift values (ppm *vs.* TMS; benzene-d$_6$) for the Paternò–Büchi product **11**. The numbering of the positions is adjusted to the numbering of the parent bicyclic system **2** and radical **iii**



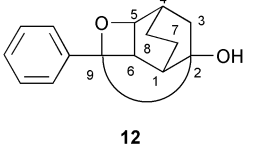
11

Position	^{13}C calc.	^{13}C exp.	^{1}H exp.
1	58.0	48.7 (d)	2.4 (m)
2	91.7	84.3 (s)	–
3	41.0	37.0 (t)	2.0/1.5 (m)
4	33.0	26.5 (d)	1.6 (m)
5	68.8	56.9 (d)	3.1 (m)
6	84.1	81.5 (d)	4.3 (dxd)
7	21.8	17.5 (t)	1.8/1.5 (m)
8	27.9	23.6 (t)	1.3/0.7 (m)
9	101.9	97.2 (s)	–

The proton bound to the oxygen substituted carbon (C(6) in **11** and C(5) in **12**) exhibits two couplings to the two vicinal protons. One of these couplings is to the tertiary proton H–C(1) vicinal to the HO-substituted C(2). This again excludes the structure **12**. The proposed structure is also in agreement with HMBC experiments: The tertiary hydrogen of the oxygen-substituted carbon exhibits a coupling with the spin of C(2). This is in agreement with structure **11** and excludes **12**.

Reactivity considerations

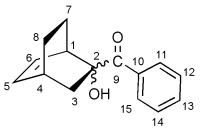
The above described results show that the two stereoisomers, *endo*- and *exo*-**2**, embark on distinctly different reaction pathways upon irradiation. Whereas it is evident that the *exo* isomer cannot undergo an intramolecular *Paternò–Büchi* reaction due to the unfavorable arrangement of the C=O group and the bicyclic C=C double bond, it is astonishing that the intramolecular cycloaddition of *endo*-**2** is found to be the dominating reaction. The preference for the *Paternò–Büchi* product can be traced back to the following factors. The double bond in the bicyclic system can be regarded as electron rich, leading to a preference for the cycloaddition.[20] Since no products pointing to a cleavage of *endo*-**2** could be found by NMR and GC-MS, the cyclization must proceed much faster and, presumably, in a different domain of molecular reactivity. According to the CIDNP spectra of *exo*-**2** and several additional examples[6,23–25] α-cleavage generally proceeds *via* the triplet excited state of the ketone. However, *Paternò–Büchi* reactions are more likely to proceed *via* the excited singlet state.[26–28] In order to probe this, we have added an excess of naphthalene as a triplet quencher to the reaction solution. Irradiation was performed at 342 nm to avoid excitation of naphthalene. Independent of the irradiation time, NMR



12

Fig. 3 Structure of the hypothetical Paternò–Büchi product **12**. The numbering of the positions is adjusted to the numbering of the parent bicyclic system **2** and radical **iii**.

Table 4 ^{13}C chemical shift values of *endo*- and *exo*-**2** (ppm *vs.* TMS; solvent: benzene-d_6)



endo/exo-**2**

Position	*endo*-2	*exo*-2
C=O	199.7 (s)	199.9 (s)
C(10)	135.5 (s)	136.6 (s)
C(5)	133.6 (d)[a]	137.5 (d)
C(6)	133.2 (d)[a]	130.6 (d)
C(13)	132.1 (d)	132.3 (d)
C(11), C(15)	130.5 (d)	130.9 (d)
C(12), C(14)	128.2 (d)	128.4 (d)
C(2)	82.0 (s)	83.7 (s)
C(3)	41.2 (t)	42.0 (t)
C(1)	39.0 (d)	40.2 (d)
C(4)	30.8 (d)	31.0 (d)
C(8)	24.9 (t)	23.4 (t)
C(7)	19.1 (t)	20.4 (t)

[a] Assignment uncertain.

spectra showed that, even in the presence of naphthalene, product **11** is exclusively formed. Thus we conclude that the cyclization reaction proceeds *via* the singlet excited state.

Conclusions

The above photochemical and photophysical studies clearly demonstrate distinct differences between the photoreactivity of *endo*-**2** and *exo*-**2**. The carbonyl and the alkene double bonds are well separated in *exo*-**2**. This arrangement precludes any addition reaction between these moieties and leaves the way to the expected α-cleavage. This translates into *exo*-**2** being a good photoinitiator. On the other hand, *endo*-**2** is a very poor photoinitiator. This can be traced back to the highly efficient (*ca.* 98%) conversion to the tetracyclic product **11** *via* an intramolecular *Paternò–Büchi* reaction. Such a photochemical reaction has been used previously for the synthesis of different cyclic ethers.[20,21,29]

Notably, no α-cleavage could be established for *endo*-**2**. Our results show that the cyclization proceeds *via* the excited singlet state. Thus this very fast reaction overrules the α-cleavage which requires intersystem crossing into the triplet state.

Experimental part

Synthesis

Materials and equipment for the synthesis. Reagents and solvents were obtained from commercial suppliers and used as received unless otherwise noted. Solvents were used without purification if they were either spectrometric or HPLC grade. Column chromatography was performed using standard grade silica gel (32–63 μm, 60 Å). Elemental analyses were performed at Ciba Specialty Chemicals analytical department. Nuclear magnetic resonance (NMR) spectra were recorded on a 200 MHz spectrometer using $CDCl_3$ as solvent. Chemical shifts relative to TMS at 0.0 ppm are reported in parts per million (ppm) for ^{1}H-NMR on the δ scale.

A. 1-Phenyl-2-[(trimethylsilyl)oxy]-prop-2-en-1-one (4)[30]. Anhydrous zinc chloride (0.46 g, 3.4 mmol) was added to 146 ml dry trimethylamine and stirred until a suspension was formed. After addition of 1-phenyl-propane-1,2-dione (19.85 g, 134 mmol) in 50 ml dichloromethane, the solution was cooled in an ice bath and trimethylchlorosilane (15.89 g, 145 mol) was slowly added. The reaction mixture was stirred at room temperature overnight, diluted with 200 ml dry diethylether and the precipitated salt removed by filtration over hyflo. Evaporation of the solvent *in vacuo* gave 1-phenyl-2-trimethylsilyloxy-prop-2-en-1-one **4** as yellowish oil that was used for the next reaction step without further purification.

B. (2-Hydroxy-bicyclo[2.2.2]oct-5-en-2-yl)-phenyl-methanone (2). 10 ml (100 mmol) freshly distilled cyclohexa-1,3-diene were added to a solution of 1-phenyl-2-trimethylsilyloxy-prop-2-en-1-one (8 g, 36 mmol) in 40 ml dry dichloromethane. After cooling to 0 °C, boron trifluoride ethyl etherate (4.6 ml, 36 mmol) was added and the solution stirred for 4 h. The solvent and excess cyclohexa-1,3-diene were removed *in vacuo* and the residue dissolved in 250 ml of methanol. After addition of 25 ml 1N HCl, the mixture was stirred during 30 minutes before being neutralized with 100 ml saturated $NaHCO_3$. The aqueous phase was extracted with ether, the organic extracts dried over magnesium sulfate and evaporated. The residual oil was purified by chromatography on silica gel (hexane/ethyl acetate 9 : 1) and the main fraction subjected to a bulb-to-bulb distillation (150 °C/0.07 Torr) to yield 65% of a colorless oil, which according to ^{1}H-NMR analysis consisted of a mixture of approximately 76% **2** and 24% 2-hydroxy-2-phenyl-bicyclo[3.2.1]non-6-en-3-one. The latter compound is formed by an acid-catalyzed rearrangement of **2**. Repeated chromatography on silica gel allowed the separation of the stereoisomeric mixture of **2** and finally the separation of *endo*-**2** and *exo*-**2**.

Exo-**2**: mp. 47–50 °C. ^{1}H-NMR (benzene-d_6): 8.5 (m, H–C(11) and H–C(15)); 7.20 (H–C(12), H–C(13) and H–C(14)); 6.30–6.10 (m, H–C(5) and H–C(6)); 3.15 (m, H–C(1)); 2.50 (m, H–C(4)); 2.90 (dxd, H–C(3)); 1.7–0.9 (m, H_{ab}–C(7), H_{ab}–C(8) (m), H_{ab}–C(3)). (Found: C, 78.93; H, 7.01. Calc. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07.)

Endo-**2** mp. 69 °C. ^{1}H-NMR (benzene-d_6): 8.35 (m, H–C(11) and H–C(15)); 7.20 (H–C(12), H–C(13) and H–C(14)); 6.45–6.05 (m, H–C(5) and H–C(6)); 3.00 (m, H–C(1)); 2.40 (m, H–C(4)); 2.4–1.1 (m, H_{ab}–C(7), H_{ab}–C(8), H_{ab}–C(3)). (Found: C, 78.75; H, 7.00. Calc. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07)

The ^{13}C-NMR shifts of both stereoisomers are collected in Table 4.

C. 2-Benzoyl-2-hydroxy-cyclohex-3-ene (5). Following the procedure described for **2**, compound **5** was prepared using 1,3-butadiene instead of cyclohexa-1,3-diene. Yield; 55%, colorless oil with a boiling temperature of 140–145 °C/0.06 Torr (bulb-to-bulb distillation). ^{1}H-NMR: 8.1–7.7 (m, 2 aromatic H); 7.35–7.0 (m, 3 aromatic H), 5.55 (m with AB character, 2-C(3) and H–C(4)); 3.8 (OH); 2.85–1.85 (6H C(2, 5) and C(6). (Found: C, 78.26; H, 7.98. Calc. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88.)

D. Bicyclo[2.2.2]oct-5-en-2-one (8). This compound was synthesized following a literature procedure.[31] 1-Cyano-bicyclo[2.2.2]oct-5-ene was obtained by the cycloaddition of acrylonitrile to cyclohexa-1,3-diene. This compound was chlorinated α to the nitrile group with phosphorous pentachloride, followed by hydrolysis with potassium hydroxide in dimethylsulfoxide to give bicyclo[2.2.2]oct-5-en-2-one **8**.

Application studies

For the application studies, an unpigmented urethane acrylate formulation consisting of the following components was used (parts by weight of the components):

50 parts Actylan AJ 20 (urethane acrylate, UCB).

15 parts TMPTA (trimethylolpropane triacrylate).

15 parts diluent QM 672 (dicyclopentenyloxyethyl acrylate, Rohm and Haas).

10 parts HDODA (hexanedioldiacrylate).

10 parts *N*-vinylpyrrolidone.

2% by weight of the photoinitiators **1**, **2**, *exo*-**2**, *endo*-**2** or **5** were dissolved in the formulation. For the measurement of the reactivity, the formulation was applied as a film of 60 μm thickness onto white cardboard. These samples were passed under a PPG UV processor unit using two mercury medium-pressure lamps of 80 W cm^{-1} output with a belt speed of 20 m min^{-1}. The irradiation was repeated until a fully cured surface, measured by drilling a soft tissue on the surface, was obtained. If no fully cured surface was obtained after 20 passes, the experiment was stopped. The results are collected in Table 1.

CIDNP

CIDNP-experiments were performed on two different NMR-spectrometers: An earlier set of ^{1}H- and ^{13}C-experiments were carried out on a Varian XL-100 Fourier spectrometer. The UV-source was a 1 kW SP-1000 Philips mercury high pressure lamp (continuous light irradiation). The light was filtered by an aqueous solution of $NiSO_4$ and $CuSO_4$ to eliminate most of the infrared and visible light. Two quartz lenses focused the light onto the polished end of a Suprasil quartz rod that served as a light guide.

NMR and a second set of CIDNP experiments were carried out on a Bruker AVANCE DPX 200 spectrometer with a wide bore magnet. In these experiments, the light source was a Questek excimer laser in combination with a Lambda Physik dye laser (342.5 nm). The duration of the laser pulse was *ca.* 10 ns and the radiofrequency 30° pulse 1.5 μs. The CIDNP experiments were carried out in benzene-d_6, cyclohexane-d_{12} and acetonitrile-d_3.

Selective decoupling, DEPT, HETCOR,[32] INAPT[33,34] and gs-HMBC[35] experiments were performed using multinuclear broad band probe head with *z*-gradient.

Quantum mechanical calculations

The Gaussian 98 A.7[36] software package was used for all QM calculations. Both structure optimizations and single point energy calculations were performed by the B3LYP/6-31G* method.[37,38] For the GIAO[39] calculations of ^{13}C chemical shifts the 6-311+G(2d,p) basis set was employed.

GC-MS

A HP Series II 5980 instrument equipped with a 25 m 5% phenyl-methyl-silicone (OV-3, SE-52) column was used for the GC-MS measurements.

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