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# PAPER

# Aromatic aldols and 1,5-diketones as optimized fragrance photocages<sup>†</sup>

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Aromatic aldols and 1,5-diketones with abstractable  $\gamma$ -hydrogen atoms are highly photoactive cage molecules for the release of fragrance carbonyl compounds (aldehydes and Michael ketones, respectively). Aldols **3a**–**d** are easily accessible by Mukaiyama addition and are cleaved to form the substrates with high quantum yields under solar radiation. By tuning the properties of the chromophores, a series of  $\delta$ -damascone cages **5** were developed that can be used for selective and fast (**5a**,**e**) or slow (**5b**,**d**) release of fragrances under air and solar irradiation. The intermediates of the Norrish II process were observed by laser transient absorption spectroscopy.

# Introduction

A molecule that is part of a photocage (is "photocaged") is released during UV-vis irradiation. This allows the selective delivery in the presence of bases, acids, metals and thus avoids undesired reaction conditions.<sup>1,2</sup> The electromagnetic radiation serves as a specific trigger for the liberation of the desired molecule. Many biologically active compounds have been the focus of this concept for several decades. Efficient and well-performing photocages were reported for the release of numerous biomolecules and other pharmaceutically relevant compounds.<sup>3–7</sup>

Another version of the photocage concept emphasizes the property that exclusively visible light is the trigger mechanism that releases the active molecule. This concept is advisable for pheromones that are to be cleaved only under daylight conditions.<sup>8</sup> Fragrances for textile applications are another class of compounds because release from textiles is undesired when stored in the dark. Prerequisites for these compounds are thermal stability and on/off controllable photochemical release in the visible part of the solar spectrum. Numerous examples of photocages have been described that are based either on hydrogen atom transfer or on electron transfer initiation.<sup>1,2,9-12</sup> The most convincing photocage approach for the release of fragrances is the photochemical generation of the same kind of species, *i.e.* two carbonyl compounds that can act as fragrances resulting from one single photocage. The corresponding cleavage reaction is the Norrish II photoreaction, one of the most intensively

investigated processes of electronically excited carbonyl compounds.  $^{\rm 13-15}$ 

# **Results and discussion**

In order to realize this concept, the appropriate chromophore is connected to the photocaged molecule in a way that  $\gamma$ -hydrogen transfer and subsequent Norrish II cleavage become efficient. We have tested this approach for aryl alkyl ketones on the basis of acetophenone release. This approach is useful for the liberation of simple terpene hydrocarbons such as  $\beta$ -pinene (1) as was demonstrated for the photocage **2**. This cage was prepared by the *t*-butoxide-mediated metal-free coupling protocol developed by Brown *et al.*<sup>16</sup> This cage exclusively cleaves to the fragrance **1** and acetophenone when irradiated with UV light (Scheme 1).<sup>17</sup> A quantum yield of >90% was determined by valerophenone actinometry.<sup>18</sup>

It was the goal of our further investigation to demonstrate that the benzoyl chromophore is useful also for the release of fragrances from more complex organic substrates.

First, we investigated aromatic aldols as a group of potential photocages. Four photocages were investigated from the



Scheme 1 Synthesis of the  $\beta$ -pinene photocage 2 and photochemical release of the fragrance 1; 9-BBN = 9-borabicyclo[3.3.1]nonane.

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Scheme 2 Synthesis of the aldol photocages **3a–d** by titanium and tin enolate methods.

corresponding aldehydes or ketones and propiophenone: the isobutyraldehyde, *n*-octanal, melonal and the  $\alpha$ -ionone photocages **3a–d**. The aldols **3a–c** were available under Mukaiyama conditions<sup>19</sup> in high yields and in high *syn* diastereoselectivities whereas the ionone derivative **3d** was available *via* tin enolate coupling in moderate yields as a mixture of three diastereoisomers (Scheme 2).<sup>20</sup>

From this series, octanal, melonal and  $\alpha$ -ionone are widely used as fragrances. Aldols have been prepared several times as precursors to functionalized Norrish II precursors<sup>21,22</sup> but to the best of our knowledge the photocleavage of aldols has yet not been investigated. Prior to the photochemical experiments, the thermal stability under the reaction conditions was checked and no thermal contribution to cleavage was detected, only increasing amounts of dehydration after several hours at 60 °C in benzene solution.

The aldols **3a–d** were irradiated with simulated solar radiation (AM 1.5 solar simulator) under several solvent conditions (benzene, methanol and dipropylene glycol (DPG)). In all cases, the photochemical release of the caged carbonyl compound was observed (Scheme 3).

There is a pronounced solvent dependence of the cleavage/ cyclization ratio for  $\gamma$ -branched substrates **3a,c** that tend to form more cyclobutanol under aprotic conditions. In contrast to that, the substrates **3b,d** preferentially result in cleavage products, *i.e.* serve as efficient photocages for the corresponding fragrance compounds (Table 1). It is remarkable that the elimination products were always formed as the nonconjugated ketones which indicates a predominant photochemical pathway.

In order to examine if this approach works also for nonhydroxylated  $\alpha$ -branched photocages, we examined other substitution and functional group patterns at the caged part of the molecule. The 1,5-diketones **5a** and **5b** were available from  $\delta$ -damascone (**4**) and propiophenone and 4-methoxypropiophenone, respectively, by Ce(III)enolate addition<sup>23</sup> with >95% diastereoselectivity (Scheme 4). The relative *anti* configuration of



Scheme 3 Photolyses of the aldol photocages 3a-d.

 Table 1
 Photochemistry of caged aldols

	Conditions <sup>a</sup>	Norrish II cleavage <sup>c</sup> (%)	% Cyclization/ elimination <sup>c</sup>	${\pmb \Phi_{c}}^d$
3a	Acetonitrile	10	60/30	n.d.
3a	Methanol	90	—/5	0.77
3b	Methanol	100	_	0.78
3b	$DPG^b$	100	_	n.d.
3c	Ethanol	90	—/10	0.80
3d	Methanol	95	<u> </u>	0.47

<sup>*a*</sup> Solar simulator irradiation, AM 1.5, concentrations:  $10^{-3}$  M photocage **3a–d**. <sup>*b*</sup> Dipropylene glycol. <sup>*c*</sup> By <sup>1</sup>H NMR spectroscopy. <sup>*d*</sup> Quantum yields of substrate conversion using the valerophenone actinometry (with  $\Phi_{VP} = 0.7$ ).



Scheme 4 Synthesis of the  $\delta$ -damascone photocages 5a,b.



Fig. 1 UV-vis spectra of photocages 5a and 5b in CH<sub>3</sub>CN.



Scheme 5 Photorelease of  $\delta$ -damascone and propiophenones.

these 1,5-diketones was determined by NOESY measurements. In the visible part of the UV-vis spectra, all compounds have weak absorption shoulders and thus can be excited by solar irradiation (Fig. 1).

Both photocages **5a,b** release the fragrance  $\delta$ -damascone as a mixture of *cis*- and *trans*-isomers when irradiated with simulated solar light (Scheme 5, under AM 1.5 conditions). The total yields of products that are initiated by Norrish II  $\gamma$ -hydrogen transfer is >96% for both photocages (*vide infra*). From **5a**, two

Norrish-Yang products<sup>24</sup> were formed, the cyclobutanols **6** and **7**, respectively, in a total of 30% yield with the trisubstituted cyclobutanol **6** as the major component (>85%). No cyclobutanols were however detected (GC-MS) from the methoxy cage **5b**. Photocage **5b** proved to be an excellent source for the light-induced release of  $\delta$ -damascone. Independently, we detected that the *cis*-*trans*-isomerization of **4** occurs directly also under sunlight conditions<sup>25</sup> and thus the release of these diastereoisomers from **5a,b** does not alter the overall performance of the fragrance.

An astonishing difference in behaviour was observed not only for the product selectivity of photocages **5a** and **5b**, the quantum yields for product formation were also extremely different under aerated conditions. The quantum yields for cleavage are comparable for **5a** under nonpolar and polar protic conditions whereas a 30 times reduction in quantum yield was determined for **5b** under air (Table 2). When the photochemical decomposition of **5a** under air was finished after 1 h ( $10^{-3}$  M in methanol), complete conversion of **5b** needed 48 h under identical conditions.

A long-lived transient with an absorption maximum at  $\lambda_{\text{max}} = 400 \text{ nm}$  appears upon 308 nm photolysis of **5b** in solution (Fig. 2). The decay follows first-order kinetics with a lifetime  $\tau_{0}$  of 0.2 µs in argon-saturated cyclohexane, 1.5 µs in acetonitrile and 4 µs in trifluoroethanol. The decay is quenched by oxygen with a rate constant of  $k_{0x} = 2-3 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1}$ . The transient lifetime under air is thus markedly shorter,  $\tau_{0} = 0.1$  µs in cyclohexane and 0.2 µs in acetonitrile or methanol. In 2-propanol, the lifetime is not shorter than in acetonitrile, *i.e.* H-atom abstraction from 2-propanol does virtually not take place. Moreover, the

**Table 2** Absorption maxima and quantum yields of Norrish II cleavage of 1,5-diketones **5a,b** in cyclohexane and methanol<sup>*a*</sup>

	Solvent	$\lambda_{\max}$ (nm)	$arPsi_{ m c}$ /argon	$arPsi_{ m c}/{ m air}$
5a	Cyclohexane	242	0.4	0.3
5a	Methanol	245	0.6	0.6
5b	Cyclohexane	266	0.6	0.2
5b	Methanol	273	0.5	0.02

<sup>*a*</sup> In gas-saturated solution,  $\lambda_{irr} = 254$  nm; substrate consumption was followed by UV absorption spectra, conversion of **5a** and **5b** follows an exponential curve and  $\Phi_c$  was determined by the valerophenone actinometry.



Fig. 2 Transient absorption spectra of **5b** in argon-saturated (a) cyclohexane and (b) trifluoroethanol at 20 ns ( $\bigcirc$ ), 1 µs ( $\triangle$ ) and 10 µs ( $\square$ ) after the 308 nm pulse; insets: kinetics at 400 nm as indicated.

above transient properties are very similar upon 248 nm photolysis of 5b (not shown). The lifetime of the transient of 5a upon 248 nm photolysis is much shorter,  $\tau_0 = 40$  ns in argon-saturated cyclohexane, 60 ns in acetonitrile and 120 ns in trifluoroethanol. The absorption spectrum has a maximum at  $\lambda_{max} < 360$  nm and  $k_{\rm ox} = 2-3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The transient of **5a** might be attributed to a 1,4-biradical formed by intramolecular hydrogen transfer. This is consistent with the properties of monoketones, with  $\lambda_{max}$ < 360 nm and a lifetime in the 10–100 ns range, whereas that of the excited triplet carbonyl state as precursor is much shorter.<sup>14,26</sup> This may be in contrast to the diketones, where both lifetimes are rather similar. One literature example refers to 1,5diaryl-1,5-diketones.<sup>27</sup> The transient of **5b** could be attributed to both the excited triplet carbonyl state or the subsequently formed 1,4-biradical. The lifetime increase in polar solvents might be attributed to an increasing  $\pi,\pi^*$  character of the triplet ketone. For comparison, the triplet-triplet absorption spectrum of p-methoxyacetophenone has a maximum at 360 nm, taking that of acetophenone at <300 nm.<sup>28</sup> The lifetime of the triplet ketones at ambient temperature is 5 ns for parent valerophenone and 0.8  $\mu$ s for *p*-methoxyvalerophenone.<sup>29</sup> The important point is that for **5b** in air-saturated methanol  $\Phi_{\rm c}$  is much smaller than under argon (Table 2) since the lifetime is tenfold shorter (Table 3). Oxygen is able to quench both the excited triplet carbonyl state precursor and the 1,4-biradical.<sup>27</sup> Thus, the assignment of the observed transient of 5b is presented as being tentative. In general, the T-T and biradical spectra are not very specific (frequently without observable maximum) and a significant red-shift upon introduction of a p-methoxy group is also expected for the biradical.<sup>14,26,27</sup>

The optimal design for a photocage that selectively releases the desired fragrance by a Norrish II cleavage mechanism with controlled rate and without further side products includes: absorption in the visible range (Fig. 1), low but sufficient triplet energy to direct hydrogen transfer selectively to the energetically preferred  $\gamma$ -position (Scheme 6), slower hydrogen transfer that results in moderate quantum yields especially under air where most triplets are quenched prior to H transfer (Table 2). The two latter properties do also reflect the increasing  $\pi\pi^*$  character of the excited triplet state in the methoxy-substituted cage **5b**.<sup>30</sup> The slow but selective release (see Tables 2 and 4) under air is an important feature for the desired applications.

When further increasing this effect by donor substitution like in the 3,4-dioxolane **5c**, we did no longer observe any Norrish II photochemistry (Table 4). The analogous 3,4-dimethoxy derivative **5d** showed comparable reactivity as **5b**, however, cyclobutanol formation was again observed and the 4-methyl derivative **5e** behaved like the unsubstituted cage **5a**. Overall, we have

**Table 3** Lifetimes ( $\mu$ s) of the transients from **5b** in solution<sup>*a*</sup>

Solvent	$\tau_0$ /argon	τ/air
Cyclohexane	0.17	0.10
Acetonitrile	1.5	0.2
Methanol	2	0.2
Trifluoroethanol	4	0.25

<sup>*a*</sup> Upon photolysis at 308 nm,  $\lambda_{obs} = 400$  nm.



Scheme 6 Norrish type II hydrogen transfer from 5a-5e and subsequent processes.

Table 4 Photolyses of the  $\delta$ -damascone cages 5a–5e

	Full conv. $(h)^a$	Cleavage	Cyclization
5a	1.5	+	+
5b	48	+	_
5c		-	_
5d	48	+	+
5e	1.5	+	+

 $^a\,10^{-3}$  M in methanol, >98% conversion, solar simulation, GC-MS detection of product formation.

developed superior photochemical cage compounds for volatile aldehydes and the important fragrance  $\delta$ -damascone.

# Conclusion

In summary, the selective and controlled release of several families of fragrances was achieved by Norrish II cleavage of acetophenone and propiophenone derivatives: terpene alkenes, aliphatic aldehydes and ketones ( $\alpha$ -ionone) or  $\alpha$ , $\beta$ -unsaturated ketones ( $\delta$ -damascone).

# **Experimental**

### Materials and methods

All reactions were carried out under nitrogen atmosphere in oven-dried and/or flame-dried glassware with magnetic stirring. Unless otherwise mentioned, all reagents were purchased from commercial sources and were used without further purification. All solvents employed in the reactions were distilled over appropriate drying agents prior to use.

Reactions were monitored by thin-layer chromatography on silica-gel precoated sheets. Chromatograms were visualized by fluorescence quenching ( $\lambda = 254$  nm) or by staining using anisal-dehyde stains. Flash column chromatography was performed using silica gel 60 (particle size 0.040–0.063 mm) purchased from Acros. Chemical yields refer to pure isolated substances. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker DPX-300, DRX-500, or AV-600 spectrometers. Mass spectra and accurate mass determinations were obtained with a Finnigan MAT 900S by electrospray ionization. Infrared spectra were recorded with a

Perkin-Elmer FT-IR-S 1600 FT spectrometer. For the GCMSanalysis of the crude product mixtures as well as for quantum yield determination of the solar simulation experiments, a GC (Agilent 6890)–MS (Agilent 5975) system was used with a 30 m (250  $\mu$ m diameter) HP-5MS column (Macherey-Nagel, 5% phenylmethyl siloxane). Hydrogen was used as the mobile phase and the 50–300 M method was used for all measurements: column preheated to 50 °C, temp. program 25 °C min<sup>-1</sup> to 300 °C.

For the laser flash measurements, an excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns and energy <50 mJ) was used for excitation at 308 nm, another (EMG 201 MSC) for 248 nm. The absorption signals were measured with a digitizer (Tektronix 7912AD) and an Archimedes 440 computer for data handling.

#### Synthesis of caged aldols 3a-d: general procedure for 3b and 3d

To a stirred solution of 1.34 g (10 mmol) of propiophenone in 20 ml of dichloromethane were successively added 12 ml (12 mmol) of TiCl<sub>4</sub> (1 M in CH<sub>2</sub>Cl<sub>2</sub>) and 1.85 g (14 mmol) of tributylamine at -78 °C under argon atmosphere (method A). After 30 min, 1.53 g (12 mmol) of octanal was added to the mixture and stirred at -78 °C for 2 h. The reaction mixture was quenched with water and extracted twice with ether. The organic phase was washed with water and subsequently with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The obtained crude oil was purified by SiO<sub>2</sub>-column chromatography (cyclohexane : ethyl acetate = 9 : 1) to give (2*RS*,3*SR*)-3-hydroxy-2-methyl-1-phenyl-decan-1-one (**3b**; 2.1 g, 80%).

The photocage **3d** was prepared following a corresponding tin enolate route (method B): To a stirred solution of 1.34 g (10 mmol) of propiophenone in 20 ml of dichloromethane were successively added 4.50 g (11 mmol) of tin(II)triflate, 1.35 g (12 mmol) of N-ethylpiperidine, and after 15 min 2.50 g (13 mmol) of  $\alpha$ -ionone in 20 ml of dichloromethane of at 0 °C under argon atmosphere. Standard workup resulted in 970 mg (30%) of **3d**.

#### Spectroscopic data for the aldol photocages 3a-d

**3a**: yield: 90%; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.93–7.99 (2H, m), 7.57–7.63 (1H, m), 7.46–7.52 (2H, m), 3.68 (1H, dd, J = 2.7, 6.9 Hz), 3.64 (*syn*; 1H, dd, J = 2.7, 8.1 Hz), 1.78 (1H, dqq, J = 8.1, 6.6, 6.9 Hz), 1.25 (3H, d, J = 6.9 Hz), 1.04 (3H, d, J = 6.6 Hz), 0.96 (3H, d, J = 6.9 Hz); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 205.9 (C<sub>q</sub>), 135.8 (C<sub>q</sub>), 133.4 (CH), 128.8 (CH), 128.4 (CH), 76.6 (CH), 41.8 (CH), 30.7 (CH), 19.1 (CH<sub>3</sub>), 19.0 (CH<sub>3</sub>), 10.7 (CH<sub>3</sub>); IR [cm<sup>-1</sup>]: 3503, 2963, 1678, 1451, 1215, 972, 710; HRMS (EI 70 eV, C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>): *m/z* 163.08 ([M]<sup>+</sup>, –C<sub>3</sub>H<sub>7</sub>), calcd.: 163.0759, found:163.007, error: <5 ppm.

**3b**: yield: 80%; b.p = 175–180 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.93–7.97 (2H, m), 7.53–7.62 (1H, m), 7.46–7.52 (2H, m), 4.03 (1H, m), 3.47 (1H, dq, J = 2.8, 7.2 Hz), 3.07 (s, 1H, O–H), 1.25–1.58 (13H, m), 0.88 (3H, t, J = 6.9 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 205.9 (C<sub>q</sub>), 135.9 (C<sub>q</sub>), 133.4 (CH), 128.8 (CH), 128.5 (CH), 71.3 (CH), 44.5 (CH), 34.3 (CH<sub>2</sub>), 31.8

(CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>), 11.0 (CH<sub>3</sub>); IR [cm<sup>-1</sup>]: 3469, 2921, 1672, 1446, 1213,966, 705; HRMS: (EI 70 eV,  $C_{17}H_{26}O_2$ ): *m/z* 244.18 ([M]<sup>+</sup>, -H<sub>2</sub>O), calcd.: 244.1827, found: 244.183, error: <5 ppm.

**3c**: yield: 75%; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.94 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 5.08 (t, J = 7.2 Hz, 1H), 3.73–3.64 (m, 2H), 3.08 (s, 1H), 2.14–2.03 (m, 1H), 1.97–1.73 (m, 4H), 1.64 (s, 3H), 1.58 (s, 3H), 1.24 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 205.7 (C<sub>q</sub>), 135.8 (C<sub>q</sub>), 133.4 (CH), 131.1 (C<sub>q</sub>), 128.8 (CH), 128.4 (CH), 124.7 (CH), 75.3 (CH<sub>2</sub>), 17.7 (CH<sub>3</sub>), 15.7 (CH<sub>3</sub>), 10.7 (CH<sub>3</sub>); IR [cm<sup>-1</sup>]: 3442, 3148, 2970, 1676, 1486, 1375, 1215, 1118, 968, 709; HRMS: (EI 70 eV, C<sub>17</sub>H<sub>26</sub>O<sub>2</sub>): m/z 256.18 ([M]<sup>+</sup>, -H<sub>2</sub>O), calcd.: 274.192, found: 274.191, error: <5 ppm.

**3d**: yield: 30%; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.92 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.7 Hz, 2H), 5.47 (m, 2H), 5.28 (s, 1H), 4.22 (d, 1H), 3.62 (quin, J = 7.1 Hz, 1 H), 1.9 (m, 2H), 1.58 (m, 1 H), 1.33 (m, 9H), 1.1 (m, 1H), 0.9 (m, 2 H), 076–0.58 (m 5 H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 206.8 (Cq), 138.4 (Cq), 137.9 (CH), 133.9 (CH), 133.4 (Cq), 129.1 (CH), 128.5 (CH), 128.3 (CH), 120.6 (CH), 73.8 (Cq), 53.6 (CH), 46.4 (CH), 31.8 (CH<sub>2</sub>), 31.3 (CH<sub>3</sub>), 27.2 (CH<sub>2</sub>), 26.8 (CH<sub>3</sub>), 25.9 (CH<sub>3</sub>), 22.8 (CH<sub>3</sub>), 22.5 (CH<sub>3</sub>), 12.6 (CH<sub>3</sub>); IR [cm<sup>-1</sup>]: 3473, 2962, 1673, 1448, 1222, 970, 708; HRMS: (EI 70 eV, C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>): *m/z* 308.21 ([M]<sup>+</sup>, -H<sub>2</sub>O), calcd.: 308.21, found: 308.214, error: <5 ppm.

## General procedure for $\delta$ -damascone photocages

1-(4-Methoxyphenyl)-2,3-dimethyl-5-(2,6,6-trimethylcyclohex-3-envl)pentane-1,5-dione (5b): The lithium enolate from 4-methoxypropiophenone was produced from the reaction of 12 mmol of LDA from 1.7 ml (12 mmol) of diisopropylamine and 9.1 ml (14.5 mmol) of a 1.6 M solution of n-BuLi in n-hexane) in 30 ml of THF at -78 °C with a solution of 1.97 g (12 mmol) of 4-methoxypropiophenone in 30 ml of THF, which was added by a syringe. The reaction mixture was stirring for 1 h. This solution was subsequently treated with a solution of 0.52 g (1.4 mmol) of cerium(III) chloride (pre-dried under vacuum conditions for 2 h) in 30 ml of THF and stirred for 30 min at -78 °C. To this solution, a solution of 2.3 g (12 mmol) of  $\delta$ -damascone was added dropwise over 10 min and stirred for 3 h. After warming to r.t., 40 ml of a saturated aqueous NH<sub>4</sub>Cl solution was added and extracted 2× with 50 ml of diethyl ether. The combined organic phases were washed with a water, brine and dried over MgSO<sub>4</sub>. After filtration and solvent evaporation, the crude material was washed twice with 20 ml of cold pentane resulting in 3.25 g of a colorless solid (76%), m.p. = 80 °C.

GC/MS (50–300 M), m/z: 55, 69, 77, 94, 107, 123, 135, 164, 233, 356; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) ( $\delta$ , ppm): 7.93 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 6.93 Hz, 2 H), 5.46 (m, 2H), 3.87 (s, 3H), 3.52 (quin, J = 6.6 Hz, 1H), 2.74–2.15 (m, 5H), 1.93 (d, J = 17.7 Hz, 1H), 1.65 (d, J = 17.4 Hz, 1H), 1.13–1.10 (m, 3H), 1.09–1.02 (m, 3H), 0.95–0.84 (m, 8H), 0.76 (d, J = 6.9 Hz, 1H);

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) (δ, ppm): 213.7 (C<sub>q</sub>), 202.6 (C<sub>q</sub>), 163.4 (C<sub>q</sub>), 131.9 (CH), 130.5 (CH), 129.8 (CH), 124.0 (CH), 113.8 (CH), 62.5 (CH), 55.5 (C<sub>q</sub>), 50.1 (CH<sub>2</sub>), 44.3 (CH), 41.7 (CH<sub>2</sub>), 33.1 (C<sub>q</sub>), 31.4 (CH), 30.7 (CH), 29.8 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 19.8 (CH<sub>3</sub>), 18.8 (CH<sub>3</sub>), 12.7 (CH<sub>3</sub>).

**5a**: yield: 65% ( $M = 326.47 \text{ g mol}^{-1}$ ); GC/MS (50–300 M), m/z: 326, 293, 203, 161, 123, 105, 69, 41;  $t_{\rm R}$  (50–300 M) = 10.507 min; IR [film, cm<sup>-1</sup>]: 2960, 1705, 1678, 478, 472; <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): 7.94 (d, J = 7.2 Hz, 2 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.48 (t, J = 7.7 Hz, 2 H), 7.55–7.52 (m, 1H), 5.43 (d, J = 10.2 Hz, 1 H), 3.56 (quin, J = 7.6 Hz, 1 H), 2.57–2.53 (m, 1H), 2.48–2.41 (m, 2H), 2.48 (d, J = 2.4 Hz, 1 H), 2.44 (d, J = 9.0 Hz, 1H), 2.18 (d, J = 10.0 Hz, 1 H), 1.97 (d, J = 18.0 Hz, 1 H), 1.69 (dd, J = 5.2 Hz, 18.0 Hz, 1 H), 1.58 (s, 1 H), 1.17 (d, J = 6.8 Hz, 3 H), 1.07 (d, J = 6.7 Hz, 3 H), 0.97 (s, 3 H), 0.94 (s, 3 H), 0.78 (d, J = 6.9 Hz, 3 H); <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): 213.2(C<sub>q</sub>), 204.1 (C<sub>q</sub>), 136.9 (C<sub>q</sub>), 132.9 (CH), 131.9 (CH), 128.7 (CH), 128.3 (CH), 124.0 (CH), 62.6 (CH), 50.1 (CH<sub>2</sub>), 44.7 (CH), 41.7 (CH<sub>2</sub>), 33.1 (C<sub>a</sub>), 31.8 (CH), 30.7 (CH), 29.8 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 19.8 (CH<sub>3</sub>), 18.8 (CH<sub>3</sub>), 12.6 (CH<sub>3</sub>); HRMS: (EI 70 eV, C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>): *m/z* 308.21 ([M]<sup>+</sup>, -H<sub>2</sub>O), calcd.: 308.21, found: 308.214, error: <5 ppm.

#### Photolyses of photocaged compounds 3a-d, 5a-5e

(a) Quantum yield determination: 5 ml Pyrex vessels of  $10^{-3}$  M solutions of the photocage compound in spectrograde solvents were irradiated in a multilamp photoreactor (Luzchem® LZC-4) in a carousel with 4 samples (2 photocage samples and 2 actinometer samples) with phosphor-coated low-pressure mercury lamps with a maximum emission at 300 nm. The solutions were purged with argon or with synthetic air, respectively, before irradiation. Samples were analyzed after constant irradiation times by a Agilent 6890 GCMS system until 20% conversion was reached for the fastest process. Alternatively, samples were irradiated at 308 nm in cuvettes under argon or with synthetic air by an excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns and energy <50 mJ) and analyzed by HPLC.

(b) Preparative photolyses: 50 ml of 0.1 M solutions of the photocage in spectrograde solvents were irradiated in Pyrex vessels in Rayonet® photoreactors with phosphor-coated low-pressure mercury lamps with a maximum emission at 300 and 350 nm, respectively.

(c) Irradiation with a solar light simulator. 2 ml  $10^{-2}$  M solutions of the photocages were irradiated by a Solar Light® XPS200 equipped with a 150 W Xe arc lamp and a AM1.5 filter setup as well with a IR filter using polystyrene 4 × 4 multiwell plates with 4 ml probe volume. The solutions were irradiated under air in all cases and samples were analyzed after constant irradiation times by a Agilent GCMS system (*vide supra*).

Cyclobutanol **6**: M = 326.47 g mol<sup>-1</sup>; GC/MS (50–300 M), m/z: 326, 309, 203, 143, 123, 105, 77, 55;  $t_R(50-300 M) =$ 10.85 min; IR [cm<sup>-1</sup>]: 3441, 2950, 1697, 1365, 701, 483; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.40–7.36 (m, 4H), 7.28 (m, 1H), 5.56 (m, 1H), 5.49 (d, J = 6 Hz, 1H), 2.67 (m, 2H), 2.55–2.46 (m, 2H), 3.36–2.31 (quin, J = 6 Hz, 1H), 2.27 (d, J = 12 Hz, 1 H), 2.10–1.97 (m, 2H), 1.73–1,70 (dd, J = 18 Hz, 1 H), 1.23–1.21 (m, 3 H), 0.98 (t, 6 H), 0.90 (t, 5H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 214.2 (C<sub>q</sub>), 146.9 (C<sub>q</sub>), 132.1 (CH), 130.3 (CH), 128.5 (CH), 127.3 (CH), 124.9 (CH), 124.3(CH), 77.3 (C<sub>q</sub>), 62.7 (CH), 53.7 (CH<sub>2</sub>), 46.7 (CH), 41.8 (CH<sub>2</sub>), 40.2 (CH<sub>2</sub>), 33.2 (CH<sub>3</sub>), 32.4 (CH), 31.7 (C<sub>q</sub>), 30.0 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 20.1 (CH<sub>3</sub>), 12.7 (CH<sub>3</sub>); HRMS: (EI 70 eV,  $C_{22}H_{30}O_2$ ): *m/z* 326.22 [M]<sup>+</sup>, calcd.: 326.2245, found: 326.224, error: <5 ppm.

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