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Investigations on photochemistry of *o*-allyloxy-/crotyloxyacetophenones: formation of unexpected intramolecular arene–olefin addition products on n–π* excitation of ketones

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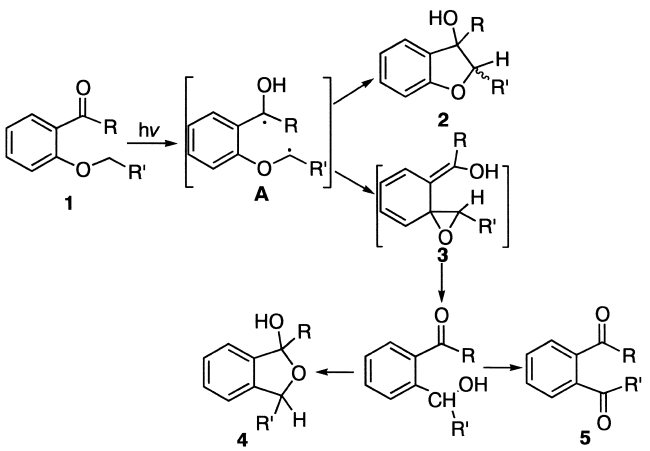
Abstract—Photochemistry of *o*-allyloxy-/crotyloxyacetophenones (**6a**,**b**) has been investigated under different conditions. Irradiation of **6a**,**b** in dry benzene, under N_2 atmosphere (Pyrex filter), led to the isolation of (*syn*)-2-ethenyl/propenyl-3-hydroxy-3-methyl-2,3-dihydrobenzofurans (**7a**,**b**~10%) as the sole product. Irradiation of **6a**,**b** in dry benzene in the presence of 0.1–0.4 mol equiv. of triethylamine resulted in slightly increased formation of **7a**,**b**, besides pinacols (**9** and **10**) and triethylamine addition products (**11** and **12**). However, the formation of **7a**,**b** is suppressed with increasing molar ratios of triethylamine, with increased formation of products (**9**–**13**). On the other hand, irradiation of **6a**,**b** in dry acetonitrile results in the formation of both *syn*-(**7a**,**b**) as well as *anti*-isomers of benzodihydrofuranols (**8a**,**b**), besides some highly unexpected intramolecular arene-olefin addition products (**14**–**16**); formation of these intramolecular arene–olefin addition products is quenched in the presence of 0.1 mol equiv. of triethylamine. With increasing molar ratios of triethylamine, in acetonitrile solvent, the formation of **7**, **8** is also suppressed with increased formation of products (**9**–**13**) derived from photoreduction of carbonyl function through electron transfer from TEA. No product derived from intramolecular interaction of the ketone derived anion radical/ketyl radical with an olefinic moiety has been detected. A plausible mechanistic rationalization of the results obtained is presented. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Photochemical approaches to polycyclic molecules or their precursors have become an important component of organic synthetic methodology.[1] Among the various photochemical transformations utilized, intramolecular hydrogen abstraction, which is one of the primary reactions of a photoexcited carbonyl group, has proven to be quite valuable.[1,2] Normally, 1,4-biradical generation, followed by cyclization leading to cyclobutanols,[1] is favoured over 1,5-biradical generation on account of the enthalpy and entropy of the transition state for the H-abstraction step.[3] However, if the formation of 1,4-biradicals is blocked, i.e. if there are no γ-hydrogens, and reactive δ-hydrogens are present as in *o*-alkoxyaryl ketones (**1**), the 1,5-biradicals can be generated which cyclise, e.g. in case of (**1**), to benzodihydrofuranols (**2**, Scheme 1); the latter reaction has been extensively investigated both mechanistically and for synthetic applications.[4] In general, the yields of benzodihydrofuranols are high in the case of *o*-substituted-benzophenones, *o*-benzyloxyarylglyoxalates, *o*-benzoyl-phenoxyacetates and related systems; however, yields are low, particularly, in the case of aryl alkyl ketones.[4] In the latter case, the reaction is complicated by competing reversible enolization, and formation of spirooxiranes (**3**), the latter leading to dihydroisobenzofurans (**4**) and diketones (**5**).[4] These differences in the behavior of benzophenones and aryl alkyl ketones have been attributed, inter alia, to differences in the life times of the excited states/



Scheme 1.

Keywords: photochemistry; photocycloadditions; photoelectocyclization; hydrogen abstraction; 1,5-biradical; electron-transfer; benzofuranols.

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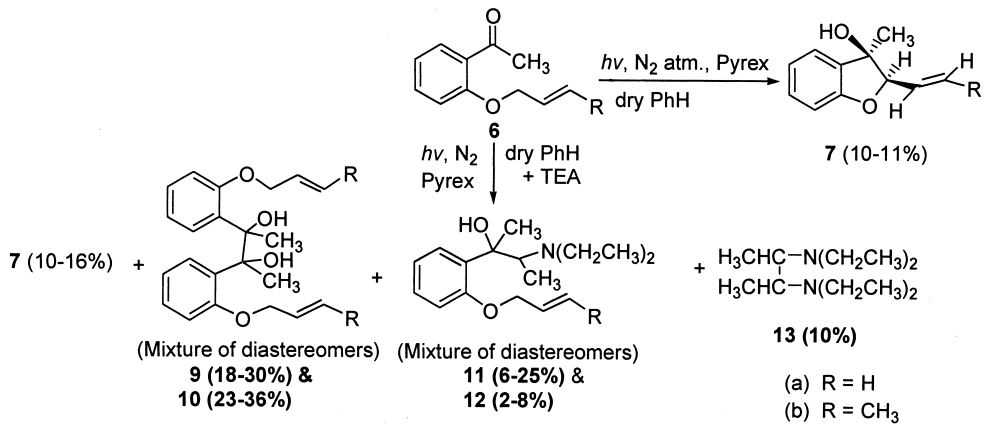


Scheme 2.

rates of intersystem crossing, rotational freedom and conformational preferences of diradicals involved (**A**, Scheme 1).[4] The yield of 1,5-biradicals is also related to conformational preferences as well the nature of the involved excited species (n–π^* or π–π^*).[2,4,5]

Investigations on this reaction both for synthetic applications[4l,6] and for mechanistic understanding continue to attract considerable attention.[7] Recently this reaction has been exploited[4l] to obtain a valuable precursor for aflatoxin–M_2. However, it has been observed that the yields of cyclized products, i.e. benzodihydrofuranols, are very low, under identical irradiation conditions, from 2,6-allyloxyacetophenone.[8] Though not elaborated, it has been attributed to possible role of an electron transfer component in the cyclization process. A similar possible role of electron transfer has also been invoked to explain the concomitant decarboxylation during similar photocyclization of (*o*-acetylphenoxy)acetic acid.[9]

Another mode of the phototransformation in the case of arenes bearing alkenyl substituents is the intramolecular photocycloaddition. The mode, i.e. (2+2), (2+4) or *meta*-addition, of these arene–alkene cycloadditions is reported to depend, inter alia, on the electron-donor/acceptor properties of the arenes and alkenes.[10] However, it has been time and again emphasized that a minimum of three carbon/hetero-atoms tether between the aromatic ring and the olefinic moiety is a must for any intramolecular photocycloaddition.[11]

We have presently investigated the photochemistry of *o*-allyloxy/crotyloxyacetophenones (**6a**,**b**) under varied conditions of irradiation, including solvents such as acetonitrile which is known to favor electron transfer, and in the presence of triethylamine;[†] the latter is well known to quench the photoexcited carbonyl function by charge transfer/electron transfer.[12] A complete characterization of the product profile, including, some unusual intramolecular arene–olefin addition products obtained on n–π^* excitation of the carbonyl function, has been attempted.

[†] The phototransformations in presence of triethylamine were also of interest because it has been reported that radical anions generated from reduction of a photoexcited carbonyl function can be trapped intramolecularly, by an olefinic moiety, in a synthetically useful manner.[1d,13]

2. Results and discussion

Initially, *o*-allyloxy-/crotyloxy-acetophenones (**6a**,**b**) were irradiated in anhydrous benzene with a 125-Watt medium pressure Hg arc employing an immersion well type (Pyrex-glass), water cooled photoreactor, under nitrogen atmosphere for 100 h (50% conversion). Column chromatographic resolution afforded a single identifiable product in both cases (**7a**,**b**, ~10%), besides unreacted **6a**,**b** and some intractable material (Scheme 2); formation of any other reaction product was rigorously excluded by ^{1}H NMR spectral scanning of all the chromatographic fractions. The structures of compounds (**7a**,**b**) are based on spectroscopic data and its comparison with related systems.[‡] The formation of only *syn*-benzodihydrofuranols from irradiation of some *o*-allyloxy/alkoxy-benzophenones under comparable conditions has already been reported in the literature.[4f–h,k]

Subsequently, irradiations of **6a**,**b** were carried out in dry benzene, in the presence of different molar equivalents of TEA and chromatographic resolution of the photolysates afforded various products (**7**–**13**), which have been characterized by rigorous spectroscopic analysis (IR, ^{1}H and ^{13}C NMR and Mass). The results are summarized in Scheme 2 and Table 1.

The diastereomeric mixture of pinacols (**9**, **10**) and triethylamine addition products (**11**, **12**) have been resolved column chromatographically and characterized NMR spectroscopically.[§] An important aspect brought out by these investigations is that at lower molar ratios of triethylamine, there is initially, observed an increase in the formation of **7a**,**b**, however, beyond 0.4 mol equiv. of triethylamine, the formation of **7a**,**b** starts decreasing with the increasing formation of **9**–**13**. The initial increase in production of **7a**,**b** in the presence of triethylamine may be

[‡] The *syn*-stereochemistry in **7a**,**b** was initially based on a comparison of spectroscopic data with the data reported for *syn*-products obtained from the irradiation of related systems[4f,l] and reaffirmed after isolation of the corresponding *anti*-isomers (**8a**,**b**).

[§] The diastereomeric pinacols have been resolved chromatographically into *syn*-(**10**) and *anti*-(**9**) isomers, and the NMR characterization has been further authenticated by molecular modelling and finally by X-ray crystallographic characterization of *anti*-diastereomer (**10**) (to be published elsewhere).

Table 1. Reaction conditions and percentage yields of products obtained from irradiation of *o*-allyloxy/crotyloxyacetophenones (**6a**,**b**) in benzene

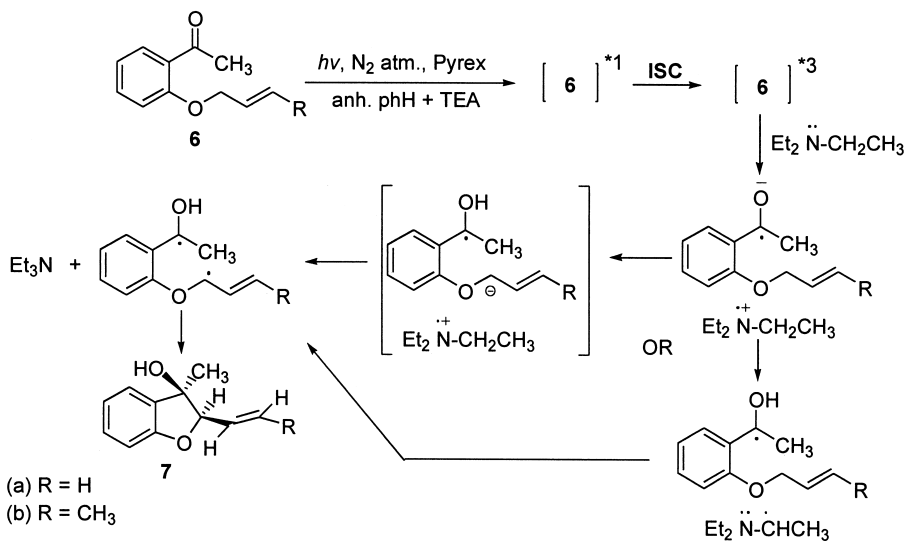
Entry	TEA (mol equiv.)	R	Irradiation time (h)	Conversion (%)	% Yield of products					
					7	**9**	**10**	**11**	**12**	**13**
1	Nil	H	100	51	11					
		CH_3	100	49	10					
2	0.1	H	24	70	15	18	23			
		CH_3	24	68	14	20	26			
3	0.4	H	24	80	16	20	27	6		
		CH_3	24	80	15	21	28	5	2	
4	0.5	H	22	90	10	25	32	8		
		CH_3	22	90	10	23	30	7	2	
5	1.0	H	20	100		30	36	18		
		CH_3	20	100		29	35	13	4	
6	2.5	H	15	100		26	30	25		10
		CH_3	15	100		25	30	18	8	10

due to the known biradical life-time enhancing effect of Lewis bases through H-bonding, thereby preventing the quenching of biradicals by reverse-H transfer.[14] Such hydrogen bonding by Lewis bases is also reported to diminish the stereoselectivity leading to benzodihydrofuranols, having an *anti*-arrangement around the C2–C3 bond;[14] however, no such *anti*-product has been detected in the present case. At present, there is no evidence available to confirm the involvement of a reversible photoelectron transfer catalysis[15] as delineated in Scheme 3, though, amines are reported to sensitize the benzophenone promoted photoaddition of acetonitrile to olefins.[16]

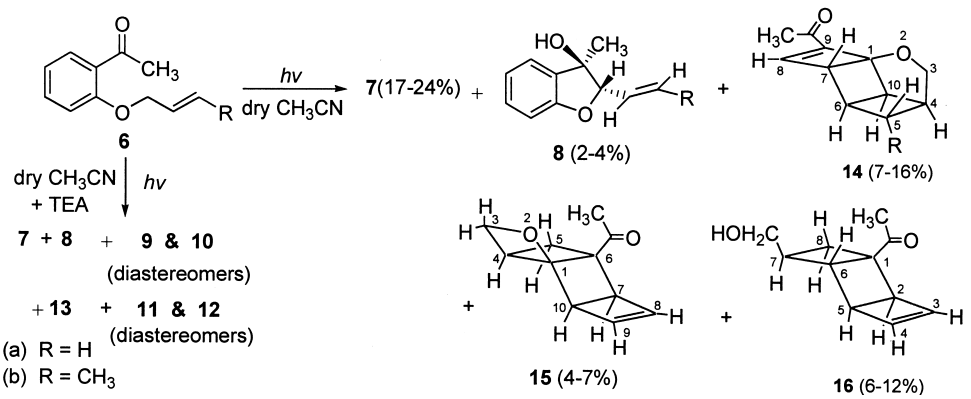
Subsequently, irradiations of **6a**,**b** were carried out in dry acetonitrile and in the presence of varying (increasing) amounts of triethylamine. The products were resolved by column and preparative layer chromatography, and characterized spectroscopically. The results are summarized in Scheme 4 and Table 2.

Compound (**8a**) was obtained only as a mixture with **7a**. The characteristic feature of its ^{1}H NMR spectrum were a doublet at δ 4.86 (J=6.99 Hz, C2–H), which is shifted downfield as compared to the C2–H resonance in **7a** (δ 4.61, J=6.54 Hz,); such a variation in chemical shifts is anticipated[41,17] because in **7a** C2–H is *cis* to the C3-methyl and in **8a** it is *cis* to the C3-hydroxyl. As anticipated[41,17] the C3–Me resonance, which appeared at δ 1.65 in **7a**, was shifted upfield (δ 1.45) in **8a**. The ^{13}C NMR assignments are also in accordance with the assigned structures. In **7a**, the resonance for C2 appeared at δ 101.41 and in **8a** at δ 100.60. C3 appeared at δ 92.10 in **7a**, which is shifted downfield as compared to C3 in **8a** (δ 94.21). The C3–Me appeared at δ 24.63 in **7a** and was shifted upfield in **8a** (δ 23.21). Similarly, compound (**8b**) was obtained only as a mixture with **7b** and its structure has been assigned on the basis of detailed NMR spectral analysis of the mixture.

Two similar compounds isolated from irradiation of **6a**,**b** have been characterized, respectively, as polycyclic unsaturated ketones (**14a**) and (**14b**). Though derived from **6a**,**b**, the ^{1}H NMR spectra of these molecules did not reveal any resonance in the aromatic region. Instead, the ^{1}H NMR spectra of these molecules revealed an olefinic-H resonance (broad singlet) at δ 5.88 in **14a** and δ 5.74 in **14b**. The presence of unsaturated carbonyl moieties in **14a**,**b** was indicated by the IR spectra and corroborated by ^{13}C NMR spectra through a resonance at δ 200.5 in the case of **14a**, and δ 199.61 in the case of **14b**. The presence of an intact acetyl moiety was confirmed through the methyl resonance at δ 2.24 in **14a** and δ 2.15 in **14b**. As the above-mentioned IR and NMR spectral features suggested the presence of a



Scheme 3.



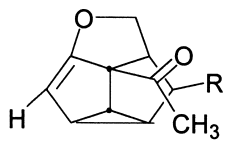
Scheme 4.

Table 2. Reaction conditions and percentage yields of products obtained from irradiation of *o*-allyloxy-/crotyloxyacetophenone in acetonitrile

Entry	TEA (mol equiv.)	R	Irradiation time (h)	Conversion (%)	Product yield (%)									
					7	**7+8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
1	Nil	H	100	60	17	6						7	4	6
		CH_3	100	59	17	5						8		
2	0.1	H	24	80	20	7	15	22	10					
		CH_3	24	80	18	6	16	23	8	3				
3	0.4	H	23	90	18	6	22	30	14					
		CH_3	23	88	21	5	22	29	11	4				
4	0.5	H	22	100	14	4	25	32	15					
		CH_3	22	100	13	4	24	31	13	6				
5	1.0	H	19	100			28	36	20		10			
		CH_3	19	100			27	34	14	7	10			
6	2.5	H	15	100			20	26	25		20			
		CH_3	15	100			20	27	18	7	20			
7[a]	Nil	H	30	90	24	7						15	7	12
		CH_3	30	90	23	7						16		

[a] Irradiation carried out by 400 W lamp; all other irradiations were carried out by 125 W lamp.

1-acetylcyclobutene moiety (cf. Ref. 1m) and only one olefinic-H resonance was present in each case, it was inferred that the transformation leading to the products (**14a**,**b**) involved the addition of the side chain olefinic moiety to the aromatic ring, through an intramolecular (2+2) cycloaddition, which is followed by 4π-electrocyclization. Such 4π-photocyclizations are precedented in cyclohexadiene intermediates.[18] The structures are also supported by the presence of two resonances for oxygen linked carbons in both compounds, i.e. δ 69.41 (C1 in **14a**), δ 78.8 (quat., C3 in **14a**), δ 69.06 (C1 in **14b**), and δ 78.40 (quat., C3 in **14b**). The assigned structures, stereochemistry as well as ^{1}H connectivities have been established by ^{1}H decoupling experiments and supported by comparison of the NMR data with reported data for related systems.[1h,18] An important aspect of the ^{1}H NMR spectra which needs mention here is that the C3–Hs showed up as two distinct resonances, i.e. as a doublet (1H, J_{gem}=13.3 Hz) at δ 4.52 and a double doublet at δ 4.11 (1H, J_{gem}=13.3 Hz and J_{vic}=5.43 Hz) in **14a**, and in case of **14b** as a doublet δ 4.35 (1H, J=13.35 Hz), and a double doublet at δ 4.01 (1H, J_{gem}=13.35 Hz and J_{vic}=5.43 Hz). That only one of the C3–Hs is coupled with C4–H is supported by molecular modeling (DTMM, version 2.0) which indicated that one of the C3–H has a dihedral angle of ~93° with C4–H. The mass spectra also corroborated the assigned structures. It may be mentioned here that an alternative structure (**17**) for these compounds derived from a *meta*-addition, was ruled out because the hydrogens of the cyclopropane moiety in **17** were anticipated to have low chemical shifts values[11d,e,19] and no such upfield shifted resonances were present in the ^{1}H NMR spectra of **14a**,**b**.



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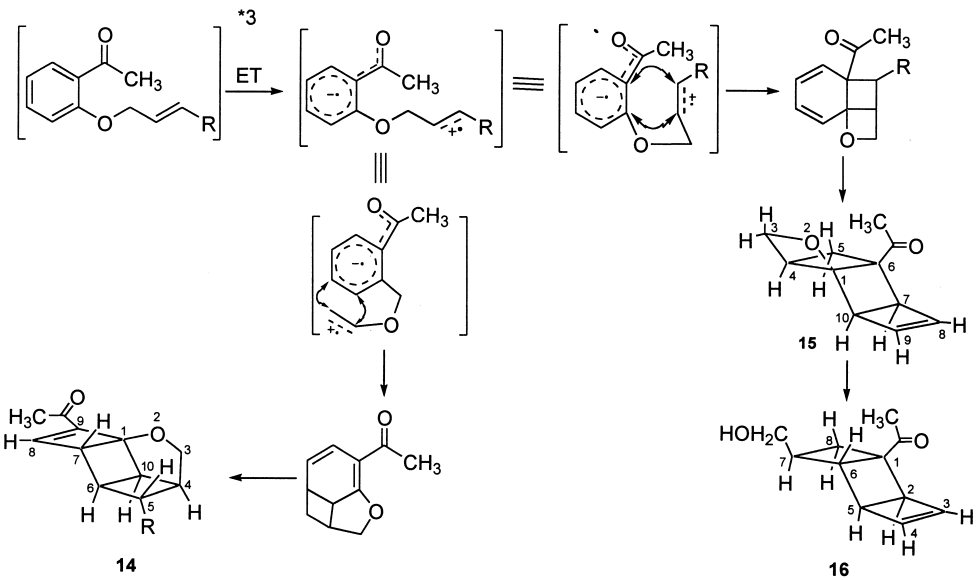
Another product isolated in small amount (7%) from the photolysis of *o*-allyloxyacetophenone, has been characterized as intramolecular cycloadduct (**15a**). The assigned structure is again based on rigorous spectroscopic analysis. Its ^{1}H NMR spectrum did not reveal any resonance in the aromatic region. However, it revealed two resonances in the olefinic region i.e., a doublet at δ 6.06 (1H, J=2.84 Hz) coupled to another broad doublet at δ 5.88 (1H, J=2.84 Hz). The C3–Hs were located as a 1H double doublet at δ 4.29 (J=8.76, 4.73 Hz), and a 1H doublet at δ 4.07 (J=8.76 Hz). A 1H broad doublet at δ 3.88 (J=3.06 Hz) has been assigned to C7–H and a 2H multiplet at δ 3.40 comprised the C4–H and C10–H resonances. The upfield part of the spectrum had a double doublet (1H) at δ 2.08 (J_{gem}=13.52 Hz and



Scheme 5.

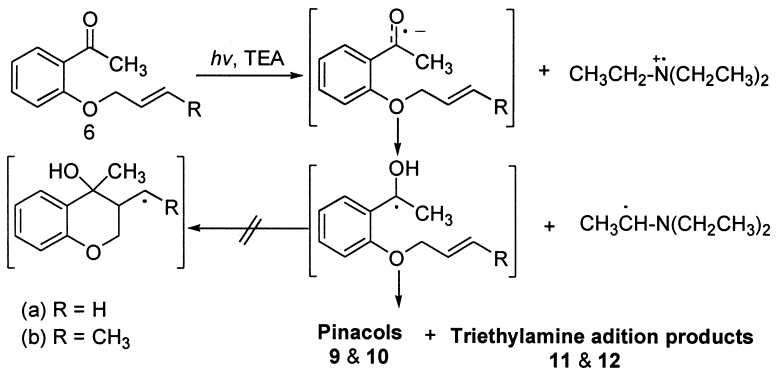
J_{vic}=7.17 Hz, C5–H) and the other C5–H was located as a multiplet at δ 1.51. All these assignments were aided by rigorous decoupling experiments to establish ^{1}H connectivities. The ^{13}C NMR spectrum revealed a carbonyl carbon resonance at δ 206.6. The oxygen-linked carbons appeared at δ 82.32 (C1) and δ 71.24 (C3), and a quaternary carbon resonance at δ 56.42 (C6); other ^{13}C NMR spectral assignments, which supported the assigned structure, include resonances at δ 54.24 (C7), δ 48.72 (C10), δ 40.80 (C5), δ 30.72 (C4) and δ 26.04 ($CO\mathit{C}H_3$). The mass and IR spectral data also supported the assigned structure.

Yet, another compound which was isolated in 12% yield from the photolysis of *o*-allyloxyacetophenone has been characterized as the intramolecular photoaddition product (**16a**). It revealed an M^+ ion at 178 indicating the addition of two mass units during phototransformation. The presence of an intact CH_3CO-moiety was inferred from the IR spectrum (band at 1715 cm^{-1}) and confirmed by ^{1}H NMR (3H, singlet at δ 2.19), and ^{13}C NMR (carbonyl carbon resonance at δ 204.0). Its ^{1}H NMR spectrum further revealed an –OH resonance at δ 8.02. The ^{1}H NMR showed complete absence of any resonance in the aromatic region of the spectrum, and instead revealed two doublets in the olefinic region at δ 6.00 and 5.79 (J=2.70 Hz); as mentioned in the case of compound (**15a**), this pattern was characteristic of a cyclobutene moiety.[1k,m] ^{1}H NMR also revealed a 2H multiplet at δ 4.20, which is assigned to a $-OCH_2-$ moiety. The upfield part of the spectrum revealed two double doublets at δ 3.53 and 3.31 for C2–H and C5–H and two multiplets at δ 2.85 and 2.52 for C7–H and C6–H, respectively. Further, a critical assignment made in its ^{1}H NMR spectrum was that of the C8–Hs, which appeared as two distinct resonances, i.e. a double doublet at δ 1.75 (J=6.11, 12.93 Hz) and a multiplet at δ 1.35, and implied that only one of the C8–Hs is coupled with C7–H. That the compound **16a** has a free $-CH_2OH$ group is also corroborated by the ^{13}C NMR spectrum which revealed a single resonance for an oxygen linked carbon at δ 65.21, which was also shifted upfield as compared to the $-OCH_2-$ resonance in compound **14a** (δ 69.41) and **15a** (δ 71.24);[20] overall ^{13}C NMR assignments were in agreement with the assigned structure. The assigned stereochemical dispositions are based on J values and ^{1}H connectivities worked out by rigorous decoupling experiments.

It may be mentioned here that some mixed fractions were also obtained, which showed the presence of many other related products as indicted by their ^{1}H NMR spectra, however, these could not be resolved sufficiently for any structural assignments to be made. ^{1}H NMR of one of the fractions revealed resonances (multiplets) in the upfield part of the spectrum, which were characteristic of a possible *meta*-addition product;[11d,e,19] the total amount of these intramolecular addition products, including the unassigned fractions, accounted for ~50% of the photoproducts.

Subsequently, irradiations of **6a**,**b** were carried out in dry acetonitrile in the presence of different molar equivalents of triethylamine and chromatographic resolution of the photolysates afforded various products (Scheme 4, Table 2). Overall, the trend is similar to the one observed for irradiation of **6a**,**b** in dry benzene in the presence of triethylamine. Initially, at lower molar ratios of triethylamine, there was obtained an increase in the formation of **7a**,**b** and with increase in the relative molar ratio of triethylamine the formation of **7a**,**b** decreased with the concomitant increased formation of **9**–**13**.

Mechanistically, the formation of intramolecular photoaddition products is highly unexpected. As mentioned earlier a minimum of a three-carbon/heteroatom tether has been reported to be essential for any intramolecular arene-alkene photocycloaddition.[11] Accordingly, it has been reported that no intramolecular photocycloaddition product could be detected from benzyl vinyl ether and only β-phenylpropanaldehyde was isolated. Similarly, allyl phenyl ether is reported to afford only Claisen rearrangement products on irradiation.[21] The formation of various intramolecular photoaddition products, therefore, is a consequence of very special circumstances where the aryl ring is bearing an electron withdrawing substituent and the



Scheme 6.

olefinic moiety can be considered as an electron donor. The reaction is initiated by n–π* excitation (Pyrex filter) and involves intramolecular electron transfer as supported by the observed solvent dependence of formation of these products (**14**–**16**), i.e. they are formed in acetonitrile and not in benzene, and their formation is inhibited by addition of even 0.1 mol equiv. of triethylamine. The sequence of events possibly leading to **14**–**16** is outlined in Scheme 5.

It may be mentioned here that intramolecular (2+2) photoadditions followed by further rearrangement of the photoadducts are precedented in the case of certain *p*-subsituted acetophenones[1k,l] and 2-subsituted-1-acetylnaphthalenes,[11,10b] and among these, the former are postulated to involve donor–acceptor interactions. In general, the donor–acceptor interactions are known to be involved in *ortho*-photoaddition, which is particularly favored if the addends differ substantially in their ionization potentials.[10a,22] However, all the reported examples conform to the criterion of a minimum three methylenes/heteroatom separation between arene and olefin. Therefore, the reported addition, to the best of our knowledge, is the first case wherein the above-mentioned limiting condition for arene–olefin intramolecular photo-cycloaddition has been surpassed. Exciplexes, which are generally believed to be involved in such reactions between donor–acceptor systems, have not been investigated in the present case. The conversion of (**15**) to oxetane ring opened product (**16**) may also be a photochemical transformation. The facile 4π-photochemical electrocyclization is well known in a number of cases.[18]

In the case of a non-polar solvent, i.e. benzene, the preferred formation of *syn*-adducts in which bulky groups are placed in *trans*-arrangement has been attributed[4f,g] to the relative sizes of the substitutents and their influence on the mode of rotation of bonds during ring closure of 1,5-biradicals. However, in polar solvents, hydrogen bonding of the –OH group with the solvent molecule increases its bulkiness leading to formation of the *anti*-adducts, *albeit* as minor products.[4f,g,23]

The conformational preferences play an overwhelming role in controlling the product profile. Beyond 0.5 mol equiv. of TEA, the whole of carbonyl moiety is reduced to anion radicals and is partitioned into pinacols (**9** and **10**) and triethylamine addition products (**11** and **12**), and no intramolecular reactions of anion radicals or ketyl radicals, as reported in certain cases,[13] occurs (Scheme 6).

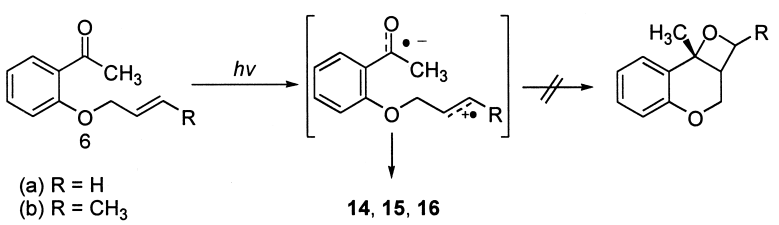
The role of conformational preference is also evident in not obtaining any oxetane (Scheme 7) and intervention of rather cumbersome transition states leading to photocycloadducts (**14**–**16**).

The above results have clearly established that the generally accepted limiting condition of a three-atom tether between an aryl ring and an alkene moiety for intramolecular photocycloaddition is easily overcome by polar interactions. Intramolecular H-abstraction by photo-excited carbonyl followed by cyclization of 1,5-biradical is an inefficient process in the case of *o*-alkenylmethoxyacetophenones, which is slightly favored in presence of lower molar equivalents of triethylamine and is quenched at higher concentrations. A substantial amount of further investigations will be necessary to completely unravel the mechanistic details of these phototransformations, particularly, the role of conformational preferences in determining the overall photo-product profile from these molecules.

3. Experimental

3.1. General

A Bruker AC-200FT (200 MHz) NMR spectrometer was



Scheme 7.

used to record ^1H and ^{13}C NMR spectra. Chemical shifts are reported in ppm as downfield displacements from tetramethylsilane used as internal standard and *J* values as Hertz. IR spectra were recorded on Shimadzu DR 2001 FT-IR spectrophotometer either as thin layer with few drops of $CHCl_3$ or as KBr pellets. Mass spectra were recorded (EI method) on Shimadzu GCMS-QP-2000A spectrometer. Microanalytical data were collected on Perkin–Elmer 240C elemental analyzer and reported in percent atomic abundance. All melting points and boiling points are uncorrected; melting points are measured in open glass-capillaries. Chromatographic separations have been carried out by either column chromatography over silica gel (60–120 mesh) or preparative layer chromatography over silica gel—G coated plates (2.0 mm thick layer).

3.1.1. *o*-Allyloxy/crotyloxy acetophenones (6a,b). These were prepared by reacting *o*-hydroxyacetophenone (10 mL, 8.3 mmol), respectively, with allyl bromide (10 mL, ~1.4 mol equiv.) and crotyl bromide (12 mL, ~1.4 mol equiv.) by stirring under reflux in dry alcohol free acetone (100 mL), in presence of anhydrous K_2CO_3 (12.0 g). The reactions were monitored by TLC and after completion of reactions (12 h), the K_2CO_3 was filtered of, washed with little acetone and the solvent from the filtrates was distilled off. Pure products (**6a**,**b**) were isolated by vacuum distillation of the residual viscous oils and characterized spectroscopically.

3.1.2. *o*-Allyloxyacetophenone (6a). A colorless oil (yield 12 g), bp 82–84 °C/10 mm; λ_{max} (MeOH): 247, 305 nm; ν_{max} ($CHCl_3$): 1680 (s), 1610 (s), 1595 (s), 1480 (s), 1450 (s), 1420 (s), 1360 (s), 1290 (s), 1280 (s), 1160 (s), 1130 (s)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.72 (dd, 1H, *J*=8.4, 1.83 Hz, C6–H), 7.42 (m, 1H, arom.-H), 6.91 (m, 2H, arom.-Hs), 6.17–5.96 (m, 1H, C2′–H), 5.42 (dd, 1H, *J*=14.0, 1.5 Hz, C3′–H), 5.31 (br d, 1H, *J*=7.6 Hz, C3′–H), 4.62 (d, 2H, *J*=5.1 Hz, C1′–Hs), 2.63 (s, 3H); δ_C ($CDCl_3$, 50 MHz): 199.28 (C=O), 157.67 (C2), 133.27 (CH), 132.39 (CH), 130.04 (CH), 128.36 (C1), 120.3 (CH), 117.81 (CH_2=), 112.60 (CH), 69.16 (–O*C*H_2), 31.73 (CO*C*H_3); Mass: *m*/*z* (%): 176 (M^+, 18); (Found: C, 74.79, H, 6.99. $C_{11}H_{12}O_2$ requires C, 74.98, H, 6.86%).

3.1.3. *o*-Crotyloxyacetophenone (6b). A colorless oil (yield 11.9 g), bp 86–88°C/10 mm; λ_{max} (MeOH): 245, 305 nm; ν_{max} ($CHCl_3$): 1680 (s), 1600 (s), 1500 (s), 1460 (s), 1380 (s), 1370 (s), 1300 (s), 1180 (s), 1160 (s), 1080 (s)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.72 (dd, 1H, *J*=7.10, 1.5 Hz, C6–H), 7.38 (dt, 1H, *J*=8.24, 1.5 Hz, C4–H), 6.97 (m, 2H, arom.-Hs), 5.85–5.74 (m, 2H, C2′–H and C3′–H), 4.56 (br d, 2H, *J*=5.52 Hz, C1′–H), 2.63 (s, 3H), 1.76 (d, 3H, *J*=4.6 Hz, C4′–Hs); δ_C ($CDCl_3$, 50 MHz): 200.01 (C=O), 158.01 (C2), 133.47 (CH), 130.74 (CH), 130.36 (CH), 129.07 (C1), 125.56 (CH), 120.60 (CH), 112.91 (CH), 69.35 (–O*C*H_2), 35.31 (CO*C*H_3), 17.81 (=CH*C*H_3); *m*/*z* (%): 190 (M^+, 27); (Found: C, 75.62, H, 7.61. $C_{12}H_{14}O_2$ requires C, 75.76, H, 7.42 %).

3.2. General procedure for irradiation of *o*-allyloxy-/crotyloxyacetophenones (6a,b) in dry benzene

o-Allyloxy-/crotyloxyacetophenones (**6a**,**b**, 500 mg) were dissolved in thiophene-free dry benzene (250 mL) and taken in an immersion well type Pyrex-glass, water cooled, photoreactor. Solutions were purged with dry oxygen free N_2 for at least 15 min prior to irradiation. The irradiations were carried out with a 125-Watt medium pressure Hg arc placed coaxially inside the reactor and N_2 was continuously bubbled through the solutions during irradiation. At the end of reaction (Tlc), solvent from the photolysates was distilled-off under reduced pressure using a rotary evaporator and products were separated by column chromatography over silica (60–120 mesh) using hexane–chloroform (gradient) as eluent.

3.2.1. Irradiation of *o*-allyloxyacetophenone (6a) in dry benzene. Irradiation of a solution of *o*-allyloxyacetophenone (**6a**, 500 mg) in thiophene-free dry benzene (250 mL) for 100 h, afforded: unreacted **6a** (245 mg). (*syn*)-2-Ethenyl-3-hydroxy-3-methyl-2,3-dihydrobenzofuran (**7a**) as colorless viscous oil (55 mg), λ_{max} (MeOH): 211, 237, 269, 272, 292 nm; ν_{max} ($CHCl_3$): 3488 (b), 1620 (w), 1600 (s), 1476 (s), 1465 (w), 1375 (m), 1280 (m), 1240 (m), 1215 (m), 1094 (s)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.33–7.20 (m, 2H, arom.-Hs), 6.97–6.85 (m, 2H, arom.-Hs), 6.18–6.01 (m, 1H, C1′–H), 5.61 (dd, 1H, *J*=15.9, 1.47 Hz, C2′–H), 5.44 (dd, 1H, *J*=11.6, 1.3 Hz, C2′–H), 4.63 (bd, 1H, *J*=6.54 Hz, C2–H), 1.65 (s, 3H, C3–Me); δ_C ($CDCl_3$, 50 MHz): 161.41 (C7a), 132.91 (C3a), 131.52 (CH), 130.27 (CH), 123.31 (CH), 121.11 (CH), 118.41 (H_2C=), 110.64 (CH), 92.03 (C2), 77.80 (C3), 24.63 (C3–Me); *m*/*z*(%): 176 (40, M^+), 116 (100); (Found: C, 74.74, H, 6.67. $C_{11}H_{12}O_2$ requires C, 74.98, H, 6.86%).

3.2.2. Irradiation of *o*-crotyloxyacetophenone (6b) in dry benzene. Irradiation of a solution of (**6b**, 500 mg) in thiophene-free dry benzene (250 mL) for 100 h afforded: unreacted **6b** (255 mg). (*syn*)-2-(1-Propenyl)-3-hydroxy-3-methyl-benzodihydrofuran (**7b**) as colorless gummy material (50 mg), λ_{max} (MeOH): 218, 248, 278, 286 nm; ν_{max} ($CHCl_3$): 3480 (s), 1612 (m), 1599 (s), 1475 (m), 1455 (m), 1410 (w), 1381 (m), 1340 (m), 1315 (m), 1290 (w), 1275 (w), 1260 (w), 1240 (m), 1202 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.24–7.11 (m, 2H, arom.-Hs), 6.88–6.74 (m, 2H, arom.-Hs), 5.98–5.84 (m, 1H, C1′–H), 5.74–5.62 (m, 1H, C2′–H), 4.47 (bd, 1H, *J*=7.56 Hz, C2–H), 1.79 (bd, 3H, *J*=6.30 Hz, C2′–Me), 1.53 (s, 3H, C3–Me); δ_C ($CDCl_3$, 50 MHz): 159.13 (C7a), 133.35 (C3a), 132.49 (CH), 130.24 (CH), 124.57 (CH), 123.39 (CH), 121.04 (CH), 110.70 (CH), 92.30 (C2), 77.92 (C3), 24.06 (C3–Me), 18.23 (C2′–Me); *m*/*z* (%): 190 (M^+, 8), 173 (55), 172 (31), 159 (20), 147 (20), 145 (23), 137 (48), 131 (35), 121 (44), 119 (25), 107 (23), 105 (26), 91 (44), 77 (31), 56 (100); (Found: C, 75.65, H, 7.50. $C_{12}H_{14}O_2$ requires C, 75.76, H, 7.42%).

3.3. General procedure for irradiation of *o*-allyloxy-/crotyloxyacetophenone (6a,b) in benzene in presence of TEA

Irradiations of *o*-allyloxy-/crotyloxyacetophenones (**6a**,**b**, 500 mg) were carried out in thiophene-free dry benzene with varying amounts of triethylamine (0.1–2.5 mol equiv.) in an immersion well type Pyrex glass, water cooled photoreactor with a 125-Watt medium pressure Hg arc.

Solutions were purged with dry oxygen free N_2 for at least 15 min prior to irradiation and N_2 was continuously bubbled during irradiation. The progress of the reaction was monitored by Tlc. At the end of the reaction, solvent was distilled off from photolysates under reduced pressure and the products were separated by column chromatography over silica (60–120 mesh, column packed in hexane) using hexane–chloroform (gradient) followed by chloroform, and chloroform–acetone (gradient) as eluents.

3.3.1. Irradiation of *o*-allyloxyacetophenone in benzene in presence of TEA. Irradiation of a solution of *o*-allyloxyacetophenone **6a** (500 mg) in dry benzene (250 mL) and triethylamine (39.5 μL, 0.1 mol equiv.) for 24 h afforded: unreacted **6a** (150 mg). (*syn*)-2-Ethenyl-3-hydroxy-3-methyl-2,3-dihydrobenzofuran (**7a**, 75 mg). Pinacol (**9a**) as colorless crystals (90 mg), mp 83–84°C (hexane–benzene 1:2), λ_{max} (MeOH): 211, 237, 239 nm; ν_{max} (KBr): 3500 (s), 3000 (m), 1600 (s), 1575 (m), 1493 (m), 1450 (m), 1425 (m), 1410 (w), 1400 (w), 1355 (m), 1300 (m), 1233 (s), 1120 (w), 1065 (m), 1015 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.39 (bd, 2H, *J*=7.7, 1.43 Hz, arom.-Hs), 7.08 (dt, 2H, *J*=7.46, 1.35 Hz, arom.-Hs), 6.90 (t, 2H, *J*=7.46 Hz, arom.-Hs), 6.60 (bd, 2H, *J*=8.17 Hz, arom.-Hs), 5.76–5.67 (m, 2H, 2×C*H*═), 5.43 (b s, 2H, exchanges with D_2O, 2×OH), 5.32 (dd, 2H, *J*=17.84, 1.44 Hz, 2×*trans* olefinic-H), 5.25 (dd, 2H, *J*=10.94, 1.31 Hz, 2×*cis*-olefinic-H), 4.15 (dd, 2H, J_{gem}=11.88 Hz, J_{vic}=5.97 Hz, $-OCH_2$), 4.05–3.88 (bm, 2H, $-OCH_2$), 1.66 (s, 6H, 2×CH_3); δ_C ($CDCl_3$, 50 MHz): 156.26 (quat.), 133.07 (quat.), 132.62 (CH), 130.42 (CH), 127.96 (CH), 120.89 (CH), 118.52 (CH), 112.03 (CH), 81.74 (quat.), 69.49 ($-OCH_2$), 24.74 (Me); *m/z* (%): 318 [M^+-36 (2×H_2O), 20], 303 (18), 295 (37), 294 (23), 293 (62), 278 (19), 277 (30), 263 (24), 237 (26), 236 (23), 235 (41), 223 (45), 221 (49), 211 (26), 203 (22), 177 (100); (Found: C, 75.56, H, 7.49. $C_{22}H_{26}O_4$ requires C, 74.65, H, 7.39%). Pinacol (**10a**) as colorless crystals (115 mg), mp 103–104°C (hexane–benzene 1:2); λ_{max} (MeOH): 211, 237, 240 nm; ν_{max}: 3480 (s), 2995 (m), 1599 (s), 1470 (m), 1491 (m), 1449 (m), 1426 (m), 1368 (s), 1287 (m), 1227 (s), 1180 (w), 1150 (w), 1120 (m), 1105 (w), 1085 (m), 1070 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.15–7.06 (dt, 2H, *J*=7.68, 1.75 Hz, arom.-Hs), 6.99 (bd, 2H, *J*=7.24 Hz, arom.-Hs), 6.83–6.68 (m, 4H, arom.-Hs), 5.97–5.80 (m, 2H, 2×C*H*═CH_2), 5.46 (s, 2H, exchanges with D_2O, 2×OH), 5.28–5.19 (m, 4H, 2×H_2C═), 4.34–4.12 (doublet of AB quartet, 4H, *J*=15.61, 5.2 Hz, 2×–OCH_2), 1.62 (s, 6H, 2×CH_3); δ_C ($CDCl_3$, 50 MHz): 156.64 (quat.), 132.97 (CH), 132.52 (quat.), 130.15 (CH), 128.06 (CH), 120.53 (CH), 118.13 (CH), 112.83 (CH), 82.37 (quat.), 69.67 ($-OCH_2$), 24.61 (Me); *m/z* (%): 318 [M^+-36 (2×H_2O), 73], 303 (45), 295 (33), 293 (66), 278 (32), 277 (53), 263 (39), 238 (33), 237 (38), 236 (37), 235 (66), 223 (61), 221 (68), 219 (31), 211 (38), 207 (51), 205 (21), 203 (26), 202 (25), 177 (99), 133 (26), 121 (100), 119 (96); (Found: C, 75.44, H, 7.57. $C_{22}H_{26}O_4$ requires C, 74.65, H, 7.39%).

Irradiation of a solution of (**6a**, 500 mg) in dry benzene (250 mL) in presence of TEA (158.0 μL, 0.4 mol equiv.) for 24 h afforded: unreacted **6a** (100 mg). **7a** (80 mg). Pinacol (**9a**, 100 mg). Pinacol (**10a**, 135 mg). Triethylamine addition product (**11a**, slightly contaminated with a minor diastereomer) as pale yellow gummy material (30 mg), λ_{max} (MeOH): 220, 271, 280 nm; ν_{max} ($CDCl_3$): 3420 (b), 3017 (s), 2928 (s), 2857 (m), 1620 (m), 1598 (m), 1580 (m), 1560 (m), 1487 (m), 1458 (m), 1445 (m), 1355 (m), 1238 (m), 1227 (m), 1165 (m), 1040 (m), 1010 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.63 (dd, 1H, *J*=7.0, 1.5 Hz, arom.-H), 7.16 (dt, 1H, *J*=7.69, 1.5 Hz, arom.-H), 6.92 (t, 1H, *J*=7.41 Hz, arom.-H), 6.80 (bd, 1H, *J*=8.05 Hz, arom-H), 6.15–5.98 (m, 1H, C*H*═), 5.44 (bs, 1H, OH), 5.36–5.27 (m, 2H, CH_2═), 4.53 (bd, 2H, *J*=5.20 Hz, $-OCH_2$), 3.36 (q, 1H, *J*=6.85 Hz, N–C*H*–Me), 2.76–2.39 (m, (overlapping quartets) 4H, 2×NCH_2Me), 1.75 (s, 3H, $-CH_3$), 1.11 (t, 6H, *J*=7.02 Hz, 2×CH_3), 0.92 (d, 3H, *J*=7.06 Hz, $-CHCH_3$); δ_C ($CDCl_3$, 50 MHz): 156.14 (quat.), 133.14 (quat.), 128.27 (CH), 127.96 (CH), 121.04 (CH), 118.19 (CH), 112.07 (CH), 109.0 (CH), 75.56 (quat.), 69.24 (OCH_2), 64.09 (N–CH–CH_3), 46.24 (NCH_2CH_3), 26.96 (═$CHCH_3$), 12.22 (NCH_2CH_3), 10.11 (N–CH–CH_3); *m/z* (%): 278 (M^++1, 9), 277 (M^+, 19), 261 (30), 260 (29), 252 (18), 250 (20), 232 (27), 230 (22), 220 (20), 219 (21), 218 (28), 207 (27), 205 (16), 204 (27), 203 (22), 202 (27), 100 (100); (Found: C, 73.39, H, 9.60, N, 5.29. $C_{17}H_{27}NO_2$ requires C, 73.61, H, 9.81, N, 5.05%).

Irradiation of a solution of **6a** (500 mg) in dry benzene (250 mL) in presence of triethylamine (197.6 μL, 0.5 mol equiv.) for 22 h, afforded: unreacted **6a** (50 mg). **7a** (50 mg). Pinacol (**9a**, 125 mg). Pinacol (**10a**, 160 mg). Triethylamine addition product (**11a**, 40 mg).

Irradiation of a solution of **6a** (500 mg) in dry benzene (250 mL) in presence of triethylamine (395.2 μL, 1.0 mol equiv.) for 20 h afforded: pinacol (**9a**, 150 mg), pinacol (**10a**, 180 mg), triethylamine addition product (**11a**, 90 mg).

Irradiation of a solution of **6a** (500 mg) in dry benzene (250 mL) in presence of triethylamine (987.9 μL, 2.5 mol equiv.) for 15 h afforded: pinacol (**9a**, 130 mg), pinacol (**10a**, 150 mg), triethylamine addition product (**11a**, 125 mg), triethylamine dimer (**13**) as a pale viscous oil (50 mg), ν_{max} ($CHCl_3$): 2966, 1600, 1455, 1396, 1242, 1170, 1160, 1060, 960, 908, 661) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): δ 3.19–2.94 (m, 10H(q at δ 3.14, *J*=7.32 Hz, partially overlapping another distorted q centered at δ 3.08)), 1.50–1.27 (m, 18H); *m/z*: 101 (15), 100 (100, M^+/2).

3.3.2. Irradiation of *o*-crotyloxyacetophenone (6b) in dry benzene in presence of TEA. Irradiations of *o*-crotyloxyacetophenone (**6b**, 500 mg) in dry benzene (250 mL) in presence of triethylamine (36.6 μL, 0.1 mol eq.) under the above conditions for 24 h afforded: unreacted **6b** (160 mg). **7b** (70 mg). Pinacol **9b** as colorless crystals (100 mg), mp 95–96°C (hexane–benzene 1:2); ν_{max} (KBr): 3482 (s), 3010 (s), 1599 (s), 1580 (m-s), 1490 (s), 1449 (s), 1400 (s), 1375 (m), 1282 (s), 1240 (s), 1200 (m), 1001 (m-s)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.40 (d, 2H, *J*=6.77 Hz, arom.-Hs), 7.06 (bt, 2H, *J*=7.67 Hz, arom.-Hs), 6.87 (t, 2H, *J*=7.37 Hz, arom.-Hs), 6.58 (d, 2H, *J*=8.14 Hz, arom.-Hs), 5.76–5.64 (m, 2H, 2×C*H*═), 5.52–5.41 (m, 4H, CH_3CH═×2 and 2×OH), 4.16–4.07 (m, 2H, $-OCH_2$), 4.00–3.90 (m, 2H, $-OCH_2$), 1.75 (d, 6H, *J*=6.26 Hz, 2×CH_3), 1.66 (s, 6H, 2×CH_3); δ_C ($CDCl_3$, 50 MHz): 157.03 (quat.), 132.60

(quat.), 130.64 (CH), 130.12 (CH), 128.03 (CH), 125.87 (CH), 120.33 (CH), 112.72 (CH), 81.87 (quat.), 69.46 ($-OCH_2$), 24.86 (Me), 17.99 ($=CHCH_3$); *m/z* (%): 346 [M^+-36 ($2\times H_2O$), 48), 331 (34), 309 (27), 292 (25), 291 (28), 277 (34), 201 (29), 192 (43), 191 (95), 175 (80), 173 (46), 159 (35), 137 (72), 121 (40), 56 (100); (Found: C, 75.18, H, 8.08. $C_{24}H_{30}O_4$ requires C, 75.36, H, 7.91%). Pinacol (**10b**) as colorless crystals (130 mg), mp 117–118°C (hexane–benzene 1:2); ν_{max} (KBr): 3400 (b s), 3000 (w-m), 1600 (s), 1578 (s), 1488 (m), 1448 (m), 1375 (m), 1280 (m), 1225 (s), 1180 (w), 1120 (w-m), 1082 (w-m), 1057 (m), 1000 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.15–6.97 (dt, 2H, *J*=7.68, 1.74 Hz, arom.-Hs), 6.97 (d, 2H, *J*=7.04 Hz, arom.-Hs), 6.81–6.68 (m, 4H, arom.-Hs), 5.82–5.68 (m, 2H, $2\times CH=$), 5.64–5.53 (m, 4H, 2×OH and $2\times=CHCH_3$), 4.21–4.05 (doublet of AB quartet, 4H, *J*=11.28, 6.32 Hz, $2\times-OCH_2$), 1.76 (dd, 6H, *J*=6.05, 1.02 Hz, $2\times-CH_3$), 1.60 (s, 6H, $2\times CH_3$); δ_C ($CDCl_3$, 50 MHz): 157.16 (quat.), 132.38 (quat.), 130.60 (CH), 130.00 (CH), 127.99 (CH), 125.74 (CH), 120.23 (CH), 112.60 (CH), 82.41 (quat.), 69.35 ($-OCH_2$), 24.76 (Me), 17.95 ($=CHCH_3$); *m/z* (%): 346 [M^+-36 ($2\times H_2O$), 44], 331 (36), 309 (26), 292 (27), 291 (26), 277 (30), 201 (30), 192 (45), 191 (97), 175 (82), 173 (42), 159 (36), 137 (73), 121 (43), 56 (100); (Found: C, 75.19, H, 8.02. $C_{24}H_{30}O_4$ requires C, 75.36, H, 7.91%).

Irradiation of a solution of (**6b**, 500 mg) in dry benzene (250 mL) in the presence of triethylamine (146.4 μL, 0.4 mol equiv.) for 24 h afforded: unreacted **6b** (105 mg). **7b** (75 mg). Pinacol (**9b**, 105 mg). Pinacol (**10b**, 140 mg). Triethylamine addition product **11b** as pale viscous oil (25 mg), λ_{max} (MeOH): 215.8, 273, 279, 306 nm; ν_{max} ($CHCl_3$): 3425 (b), 3000 (s), 2980 (w), 1597 (s), 1581 (m), 1485 (s), 1448 (s), 1379 (s), 1290 (m), 1240 (s), 1165 (w), 1074 (s), 1003 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.50 (dd, 1H, *J*=7.72, 1.75 Hz, arom-H), 7.07 (dt, 1H, *J*=7.77, 1.70 Hz, arom.-H), 6.87–6.72 (m, 2H, arom.-Hs), 5.74–5.65 (m, 2H, $CH=$ and $=CHCH_3$), 4.39 (d, 2H, *J*=4.64 Hz, OCH_2), 4.20 (br s, OH), 3.05 (q, 1H, *J*=7.12 Hz, $N-CH-CH_3$), 2.56–2.29 (m, 4H, $2\times NCH_2CH_3$), 1.70 (d, 3H, *J*=5.25 Hz, $=CHCH_3$), 1.47 (s, 3H, $-CH_3$), 0.95 (t, 6H, *J*=7.22 Hz, $2\times NCH_2CH_3$), 0.89 (d, 3H, *J*=6.97 Hz, $-CHCH_3$); δ_C ($CDCl_3$, 50 MHz): 155.99 (quat.), 136.52 (quat.), 129.85 (CH), 128.05 (CH), 127.79 (CH), 126.53 (CH), 120.77 (CH), 112.65 (CH), 75.02 (quat.), 69.17 (OCH_2), 63.50 ($N-CH-CH_3$), 44.98 (NCH_2CH_3), 24.37 ($=CHCH_3$), 17.97 ($-CH_3$), 13.48 (NCH_2CH_3), 10.28 ($N-CH-CH_3$); *m/z* (%): 292 (M^++1, 7), 291 (M^+, 16), 274 (21), 200 (53), 199 (21), 191 (21), 190 (55), 175 (35), 173 (27), 161 (20), 160 (20), 121 (37), 101 (20), 100 (100); (Found: C, 74.03, H, 10.31, N, 4.66. $C_{18}H_{29}NO_2$ requires C, 74.18, H, 10.03, N, 4.81%). Triethylamine addition product **12b**, as a pale viscous oil (10 mg), λ_{max} (MeOH): 215.4, 272, 279, 306 nm; ν_{max} ($CHCl_3$): 3420 (b), 3010 (m), 2980 (w), 2800 (m), 1597 (m), 1580 (w-m), 1485 (m), 1445 (s), 1380 (m), 1244 (m), 1074 (m), 1060 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.55 (dd, 1H, *J*=7.73, 1.39 Hz, arom.-H), 7.07 (bt, 1H, *J*=7.70, 1.52 Hz, arom.-H), 6.83 (t, 1H, *J*=7.46 Hz, arom.-H), 6.71 (d, 1H, *J*=8.04 Hz, arom.-H), 5.75–5.66 (m, 2H, $CH=$ and $=CHCH_3$), 4.37 (d, 2H, *J*=4.76 Hz, OCH_2), 3.17 (q, 1H, *J*=7.0 Hz, $N-CH-CH_3$), 2.54–2.09 (m, 4H, *J*=7.34 Hz, $2\times NCH_2CH_3$), 1.70 (d, 3H, *J*=5.70 Hz, $=CHCH_3$), 1.60 (s, 3H, CH_3), 0.97 (t, 6H, *J*=7.05 Hz, $2\times NCH_2CH_3$), 0.81 (d, 3H, *J*=7.06 Hz, $-CHCH_3$); δ_C ($CDCl_3$, 50 MHz): 155.62 (quat,), 135.98 (quat.), 129.82 (CH), 128.11 (CH), 127.73 (CH), 126.40 (CH), 120.70 (CH), 112.19 (CH), 77.23 (quat.), 68.80 (OCH_2), 63.78 ($N-CH-CH_3$), 45.13 (NCH_2CH_3), 24.32 ($=CHCH_3$), 18.97 ($-CH_3$), 14.29 (NCH_2CH_3), 9.88 ($N-CH-CH_3$); *m/z* (%): 292 (M^++1, 9), 291 (M^+, 23), 274 (29), 200 (48), 199 (35), 191 (27), 190 (59), 175 (45), 173 (36), 161 (29), 160 (20), 101 (19), 100 (100); (Found: C, 74.37, H, 10.19, N, 4.53. $C_{18}H_{29}NO_2$ requires C, 74.18, H, 10.03, N, 4.81%).

Irradiation of a solution of **6b** (500 mg) in dry benzene (250 mL) in the presence of triethylamine (183.0 μL, 0.5 mol equiv.) for 22 h afforded: unreacted **6b** (50 mg), **7b** (50 mg), pinacol (**9b**, 115 mg), pinacol (**10b**, 150 mg), triethylamine addition product (**11b**, 35 mg), triethylamine addition product (**12b**, 10 mg).

Irradiation of a solution of **6b** (500 mg) in dry benzene (250 mL) in presence of triethylamine (366.1 μL, 1.0 mol equiv.) for 20 h afforded: pinacol (**9b**, 145 mg), pinacol (**10b**, 175 mg), triethylamine addition product (**11b**, 65 mg), triethylamine addition product (**12b**, 20 mg).

Irradiation of a solution of **6b** (500 mg) in dry benzene (250 mL) in presence of triethylamine (915.3 μL 2.5 mol equiv.) for 15 h afforded: pinacol (**9b**, 125 mg), pinacol (**10b**, 150 mg), triethylamine addition product (**11b**, 90 mg), triethylamine addition product (**12b**, 40 mg), triethylamine dimer (**13**, 50 mg).

3.4. General procedure for irradiation of *o*-allyloxy-/crotyloxyacetophenone in dry acetonitrile

o-Allyloxy-/crotyloxyacetophenones (**6a**,**b**, 500 mg) were dissolved in dry acetonitrile (250 mL) and taken in an immersion well type Pyrex-glass, water cooled photoreactor. Solutions were purged with dry oxygen free N_2 for at least 15 min prior to irradiation. The irradiations were carried out with a 125/400-Watt medium pressure Hg arc placed coaxially inside the reactor and N_2 was continuously bubbled during irradiation. At the end of reaction, solvent was removed from the photolysate under reduced pressure using a rotary evaporator and products were separated by column chromatography over silica gel (60–120 mesh) using hexane-chloroform (gradient) as eluent. Some of the column fractions were pooled and further resolved by preparative layer chromatography over silica gel—G coated plates (run in $CHCl_3$–benzene 1:1 and compounds extracted with chloroform).

Irradiation of a solution of **6a** (500 mg) in dry acetonitrile (250 mL) for 50 h, with a 125-Watt medium pressure Hg arc afforded: unreacted **6a** (200 mg). **7a** (85 mg). Mixture of **7a** and **8a** as colorless viscous oil (1:1, 30 mg), ν_{max} ($CHCl_3$): 3488 (b), 1622 (m), 1601 (s), 1476 (s), 1468 (w-m), 1371 (m), 1282 (m), 1240 (m), 1219 (m), 1094 (s)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.33–7.20 (m, arom.-Hs), 6.97–6.82 (m, arom.-Hs), 6.18–6.00 (m, C1′–H in **7a**), 5.92–5.75 (m, 1H, C1′–H in **8a**), 5.61 (dd, 1H, *J*=15.9, 1.47 Hz, C2′–H in **7a**), 5.44–5.29 (m, C2′–H in **7a** and C2′–Hs in **8a**), 4.86

(bd, J=6.99 Hz, C2–H in **8a**), 4.63 (bd, J=6.53 Hz, C2–H in **7a**), 1.65 (s, C3–Me in **7a**), 1.45 (s, C3–Me in **8a**); δ_C ($CDCl_3$, 50 MHz): 161.41 (C7a), 133.72 (C3a in **8a**), 132.91 (C3a in **7a**), 131.52 (CH), 131.48 (CH), 130.28 (CH), 130.24 (CH), 123.41 (CH), 123.31 (CH), 121.11 (CH), 121.09 (CH), 118.67 (H_2C=), 118.43 (H_2C=), 110.64 (CH), 110.60 (CH), 92.81 (C2 in **8a**), 92.03 (C2 in **7a**), 77.80 (C3 in **7a**), 77.30 (C3 in **8a**), 24.62 (C3–Me in **7a**), 23.21 (C3–Me in **8a**); m/z (%): 176 (53, M^+), 161 (41), 160 (20), 133 (32), 119 (65), 116 (100), 77 (21), 56 (45); (Found: C, 74.71, H, 7.05. $C_{11}H_{12}O_2$ requires C, 74.98, H, 6.86%). Photocycloadduct (**14a**) as pale viscous oil (35 mg); ν_{max} ($CHCl_3$): 3011 (s), 2928 (s), 2338 (s), 1700 (s), 1603 (s), 1560 (m), 1540 (m), 1510 (w), 1410 (w), 1367 (s), 1238 (m), 1226 (m), 1215 (m), 1192 (m), 908 (s)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 5.88 (bs, 1H, C8–H), 4.52 (d, 1H, J=13.3 Hz, C3–H), 4.11 (dd, 1H, J=13.3, 5.43 Hz, C3–H), 2.98–2.93 (m, 1H, C7–H), 2.86–2.76 (m, 2H, C6–H and C10–H), 2.70–2.56 (m, 1H, C5–H), 2.45–2.31 (m, 2H, C4–H and C5–H), 2.24 (s, 3H, $-COCH_3$); δ_c ($CDCl_3$, 50 MHz): 200.5 (C=O), 157.21, 147.50, 78.80 (C1), 69.41 (C3), 53.01 (C7), 36.30 (C10), 32.02 (C5), 30.99 (C4), 29.33 (C6), 28.88 (Me); m/z (%): 177 (M^++1, 10), 176 (M^+, 25), 159 (24), 158 (70), 147 (46), 121 (38), 105 (42), 91 (62), 84 (41), 83 (35), 81 (35), 79 (45), 78 (47), 71 (32), 69 (49), 67 (35), 65 (38), 58 (56), 56 (100); (Found: C, 74.75, H, 7.12. $C_{11}H_{12}O_2$ requires C, 74.98, H, 6.86%). Photocycloadduct (**15a**) as pale viscous oil (20 mg); ν_{max} ($CHCl_3$): 3023 (s), 2929 (s), 1718 (s), 1608 (s), 1520 (m), 1465 (m), 1362 (s), 1219 (m), 1226 (m), 1218 (w-m), 1192 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 6.06 (d, 1H, J=2.84 Hz, C8–H), 5.88 (d, 1H, J=2.84 Hz, C9–H), 4.29 (dd, 1H, J=8.76, 4.73 Hz, C3–H), 4.07 (d, 1H, J=8.76 Hz, C3–H), 3.88 (d, 1H, J=3.06 Hz, C7–H), 3.46–3.39 (m, 2H, C4–H and C10–H), 2.08 (dd, 1H, J=13.52, 7.17 Hz, C5–H), 1.52–1.49 (m, 1H, C5–H), 1.31 (s, 3H, CH_3); δ_C ($CDCl_3$, 50 MHz): 206.6 (C=O), 131.69, 130.24, 82.32 (C1), 71.24 (C3), 56.42 (C6), 54.24 (C7), 48.72 (C10), 40.80 (C5), 30.72 (C4), 26.04. m/z (%): 177 (M^++1, 9), 176 (M^+, 18), 158 (54), 147 (42), 121 (39), 105 (43), 91 (57), 84 (45), 83 (35), 81 (33), 79 (39), 78 (41), 71 (28), 56 (100); (Found: C, 74.69, H, 6.58. $C_{11}H_{12}O_2$ requires C, 74.98, H, 6.86%). Photocycloadduct (**16a**) as pale viscous oil (30 mg); ν_{max} ($CDCl_3$): 3345 (m), 2918 (s), 2854 (s), 1715 (C=O), 1611 (s), 1512 (m), 1462 (m), 1214 (m), 1201 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 8.02 (s, 1H, –OH), 6.00 (d, 1H, J=2.70 Hz, C3–H), 5.79 (d, 1H, J=2.70 Hz, C4–H), 4.22–4.18 (m, 2H, $-CH_2-OH$), 3.53 (dd, 1H, J=7.4, 2.15 Hz, C2–H), 3.31 (dd, 1H, J=7.4, 3.21 Hz, C5–H), 2.90–2.79 (m, 1H, C7–H), 2.58–2.49 (m, 1H, C6–H), 2.19 (s, 3H, $-COCH_3$), 1.75 (dd, 1H, J=12.93, 6.11 Hz, C8–H), 1.35 (m, 1H, C8–H); δ_C ($CDCl_3$, 50 MHz): 204 (C=O), 139.49 (CH), 134.86 (CH), 65.21 (CH_2-O-), 55.85 (C1), 54.65 (C2), 49.89 (C5), 47.00 (C6), 37.13 (C8), 29.78 (C7), 28.86 (CH_3); m/z (%): 178 (M^+, 4), 177 (M^+-1, 9), 112 (20), 84 (17), 83 (31), 71 (55), 70 (49), 69 (35), 58 (100), 57 (34), 56 (79); (Found: C, 74.05, H, 8.11. $C_{11}H_{14}O_2$ requires C, 74.13, H, 7.92%).

Irradiation of a solution of **6a** (500 mg) in dry acetonitrile (250 mL) for 30 h, with a 400-Watt medium pressure Hg arc afforded: unreacted **6a** (50 mg), **7a** (125 mg), mixture of **7a** and **8a** (35 mg), photocycloadduct (**14a**, 75 mg), photocycloadduct (**15a**, 35 mg), photocycloadduct (**16a**, 60 mg).

3.4.1. Irradiation of *o*-crotyloxyacetophenone 6b in dry acetonitrile. Irradiation of a solution of **6b** (500 mg) in dry acetonitrile (250 mL) for 50 h, with a 125-Watt medium pressure Hg arc afforded: unreacted **6b** (205 mg). **7b** (85 mg). Mixture of **7b** and **8b** (~1:1, 25 mg), ν_{max} ($CHCl_3$): 3480 (s), 1610 (m), 1596 (s), 1473 (m), 1450 (m-s), 1410 (m), 1381 (m), 1340 (m), 1315 (m), 1290 (w), 1278 (w-m), 1257 (m), 1240 (m), 1207 (m-s)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 7.27–7.12 (m, Ar-Hs), 6.90–6.74 (m, Ar-Hs), 6.06–5.88 (m, 1H, C1′–H in **7b** and **8b**), 5.83–5.65 (m, C2′–H in **7b** and **8b**), 4.77 (bd, J=7.60 Hz, C2–H in **8b**), 4.49 (bd, J=7.39 Hz, C2–H in **7b**), 1.79 (bd, 3H, J=6.30 Hz, C2′–Me in **7b**), 1.72 (d, 3H, J=6.19 Hz, C2′–Me in **8b**), 1.53 (s, 3H, C3–Me in **7b**), 1.38 (s, 3H, C3–Me in **8b**); δ_C ($CDCl_3$, 50 MHz): 159.13 (C7a), 133.35 (C3a in **7b**), 132.61 (C3a in **8b**), 132.49 (CH), 130.61 (CH), 130.24 (CH), 125.77 (CH), 124.57 (CH), 123.39 (CH), 121.04 (CH), 120.89 (CH), 112.18 (CH), 110.70 (CH), 93.42 (C2 in **8b**), 92.30 (C2 in **7b**), 77.92 (C3 in **7b**), 77.25 (C3 in **8b**), 24.06 (C3–Me in **7b**), 23.34 (C3–Me in **8b**), 18.23 (C2′–Me in **7b**), 17.8 2 (C2′–Me in **8b**); m/z (%): 190 (M^+, 17), 173 (63), 172 (45), 147 (27), 145 (20), 137 (67), 131 (43), 121 (29), 119 (32), 107 (21), 91 (58), 77 (41), 56 (100); (Found: C, 75.59, H, 7.57. $C_{12}H_{14}O_2$ requires C, 75.76, H, 7.42%). Photocycloadduct (**14b**) as pale viscous oil (40 mg): ν_{max} ($CHCl_3$): 3004 (s), 2919 (s), 2369 (s), 1699 (s), 1607 (m), 1461 (m), 1405 (m), 1367 (s), 1295 (m), 1252 (m), 1218 (m), 1166 (m), 1055 (m)) cm^{-1}; δ_H ($CDCl_3$, 200 MHz): 5.74 (bs, 1H, C8–H), 4.35 (d, 1H, J=13.35 Hz, C3–H), 4.01 (dd, 1H, J=13.35, 5.43 Hz, C3–H), 2.84 (m, 1H, C7–H), 2.76–2.63 (m, 2H, C6–H and C10–H), 2.56–2.45 (m, 1H, C5–H), 2.21 (m, 1H, C4–H), 2.15 (s, 3H, $-COCH_3$), 1.07 (d, 3H, J=7.2 Hz, C5–CH3); δ_C ($CDCl_3$, 50 MHz): 199.61 (C=O), 157.34, 146.50, 78.40 (C1), 69.06 (C3), 49.51 (C7), 38.09 (C10), 36.32 (C5), 32.99 (C4), 29.74 (C6), 29.44 ($COCH_3$), 21.17 (CH_3); m/z (%): 191 (M^++1, 5), 190 (M^+, 37), 147 (8), 121 (24), 91 (35), 83 (32), 79 (23), 77 (25), 71 (47), 70 (41), 69 (45), 58 (87), 56 (100); (Found: C, 75.54, H, 7.60. $C_{12}H_{14}O_2$ requires C, 75.76, H, 7.42%).

A solution of **6b** (500 mg) in dry acetonitrile (250 mL) for 30 h with a 400-Watt medium pressure Hg arc afforded: unreacted **6b** (50 mg), **7b** (115 mg), mixture of **7b** and **8b** (35 mg), photocycloadduct (**14b**, 80 mg).

3.5. General procedure for irradiation of *o*-allyloxy-/crotyloxyacetophenones (6a,b) in acetonitrile in the presence of TEA

Irradiations of *o*-allyloxy-/crotyloxyacetophenone (**6a**,**b**, 500 mg) were carried out in presence of varying amounts of triethylamine (0.1–2.5 mol equiv.) in an immersion well type Pyrex-glass, water cooled photoreactor, with a 125-Watt medium pressure Hg arc. Solutions were purged with dry oxygen free N_2 for at least 15 min prior to irradiation and N_2 was continuously bubbled during irradiation. Progress of the reaction was monitored by Tlc. At the end of the reaction, solvent was removed from the photolysate under reduced pressure using a rotary evaporator and

products were separated by column chromatography over silica (60–120 mesh, column packed in hexane) using hexane–chloroform (gradient) followed by chloroform, and chloroform–acetone (gradient) as eluents.

3.5.1. Irradiation of *o*-allyloxyacetophenone in acetonitrile in the presence of TEA. Irradiation of a solution of *o*-allyloxyacetophenone **6a** in dry acetonitrile (250 mL) in presence of triethylamine (39.5 μL, 0.1 mol equiv.) for 24 h afforded: unreacted **6a** (100 mg), **7a** (100 mg), mixture of **7a** and **8a** (35 mg), pinacol (**9a**, 75 mg), pinacol (**10a**, 110 mg), triethylamine addition product (**11a**, 50 mg).

Irradiation of a solution of **6a** (500 mg) in dry acetonitrile (250 mL) and triethylamine (158.0 μL, 0.4 mol equiv.) for 23 h afforded: unreacted **6a** (50 mg), **7a** (90 mg), mixture of **7a** and **8a** (30 mg), pinacol (**9a**, 110 mg), pinacol (**10a**, 150 mg), triethylamine addition product (**11a**, 70 mg).

Irradiation of a solution of **6a** (500 mg) in dry acetonitrile (250 mL) in presence of triethylamine (197.6 μL, 0.5 mol equiv.) for 22 h afforded: **7a** (70 mg, mixture of **7a** and **8a** (20 mg), pinacol (**9a**, 125 mg), pinacol (**10a**, 160 mg), triethylamine addition product (**11a**, 75 mg).

Irradiation of a solution of **6a** (500 mg) in dry acetonitrile (250 mL) in presence of triethylamine (395.2 μL, 1.0 mol equiv.) for 19 h afforded: pinacol (**9a**, 140 mg), pinacol (**10a**, 180 mg), triethylamine addition product (**11a**, 100 mg), triethylamine dimer (**13**, 50 mg).

Irradiation of a solution of **6a** (500 mg) in dry acetonitrile (250 mL) in presence of triethylamine (987.9 μL, 2.5 mol equiv.) for 15 h afforded: pinacol (**9a**, 100 mg), pinacol (**10a**, 130 mg), triethylamine addition product (**11a**, 125 mg), triethylamine dimer (**13**, 100 mg).

3.5.2. Irradiation of *o*-crotyloxyacetophenone in dry acetonitrile in the presence of TEA. Irradiation of a solution of *o*-crotyloxyacetophenone **6b** (500 mg) and triethylamine (36.6 μL, 0.1 mol equiv.) in dry acetonitrile (250 mL) for 24 h afforded: unreacted **6b** (100 mg), **7b** (100 mg), mixture of **7b** and **8b** (30 mg), pinacol (**9b**, 80 mg), pinacol (**10b**, 115 mg), triethylamine addition product (**11b**, 40 mg), triethylamine addition product (**12b**, 15 mg).

Irradiation of a solution of **6b** (500 mg) and triethylamine (146.4 μL, 0.4 mol equiv.) in dry acetonitrile (250 mL) for 23 h afforded: unreacted **6b** (60 mg), **7b** (90 mg), mixture of **7b** and **8b** (25 mg), pinacol (**9b**, 110 mg), pinacol (**10b**, 145 mg), triethylamine addition product (**11b**, 55 mg), triethylamine addition product (**12b**, 20 mg).

Irradiation of a solution of **6b** (500 mg) and triethylamine (183.0 μL, 0.5 mol equiv.) in dry acetonitrile (250 mL) for 22 h afforded: **7b** (65 mg), mixture of **7b** and **8b** (20 mg), pinacol (**9b**, 120 mg), pinacol (**10b**, 155 mg), triethylamine addition product (**11b**, 65 mg), triethylamine addition product (**12b**, 30 mg).

Irradiation of a solution of **6b** (500 mg) and triethylamine (366.1 μL, 1.0 mol equiv.) in dry acetonitrile (250 mL) for 19 h afforded: pinacol (**9b**, 135 mg), pinacol (**10b**, 170 mg), triethylamine addition product (**11b**, 70 mg), triethylamine addition product (**12b**, 35 mg), triethylamine dimer (**13**, 50 mg).

Irradiation of a solution of **6b** (500 mg) and triethylamine (915.3 μL, 2.5 mol equiv.) in dry acetonitrile (250 mL) for 15 h afforded: pinacol (**9b**, 100 mg), pinacol (**10b**, 135 mg), triethylamine addition product (**11b**, 90 mg), triethylamine addition product (**12b**, 35 mg), triethylamine dimer (**13**, 100 mg).

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