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Intramolecular Photoarylation of Alkenes by Phenyl Cations

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Abstract: Acetone-sensitized irradiation of various *o*-chlorophenyl allyl ethers in polar solvents led to either (dihydro)benzofurans or chromanes. The reaction appeared to involve photoheterolysis of the aryl–Cl bond followed by phenyl cation addition onto the tethered double bond either in 5-*exo* or 6-*endo* modes. The adduct cation gave the end products by deprotonation; addition of chloride anion or of the solvent, depending on the structure; and the conditions used. Preference for the 5-*exo* mode increased in passing from medium polarity (methylene chloride, ethyl acetate) to high polarity solvents (aqueous acetonitrile, methanol, 2,2,2-trifluoroethanol), for which this was often the exclusive path. The same compounds underwent photohomolysis when irradiated in cyclohexane, and radical cyclization was one of the process occurring. Substitution of a methylene group for the ether oxygen atom made 6-*endo* cyclization by far the main path in a related *o*-chlorophenylbutene. Again, the selectivity was higher in polar protic solvents. The results are discussed in terms of in cage ion pair versus free phenyl cation reactions.

Keywords: aryl cations • arylation • C–C coupling • cyclization • photochemistry

Introduction

Aryl cations do not count among the popular intermediates in organic synthesis. These species have remained elusive and their reactivity has been scarcely explored, let alone synthetically exploited. Indeed, although spectroscopically characterized several decades ago in a matrix[1] at low temperature, these cations have been shown to be intermediates in organic reactions in solution only in a few of cases; that is, the solvolysis of some substituted perfluoroalkylsulfonic aryl esters,[2] the solvolytic cyclization of (trifluoromethanesulfonyloxy)dienines,[3] and the decay of the tritiated benzene.[4] A more general case is the thermal or photoinduced dediazoniation of phenyldiazonium salts. The photodecomposition can be more conveniently controlled, but the process occurring is again solvolysis.[5] Due to this indiscriminate reactivity, reaction with a solute, which would be synthetically desirable in particular for the formation of an aryl–C bond, has little significance. However, the lack of selectivity is actually characteristic of the phenyl cation in the singlet state. This can be viewed as a localized carbocation ($\pi^6\sigma^0$) and is the only spin state formed thermally. The triplet state, however, has a $\pi^5\sigma^1$ structure and a carbene character at the divalent carbon (see Scheme 1a). Recently, triplet phenyl cations have been obtained under preparatively useful conditions by photolysis of electron-donating (ED) substituted aryl halides (chlorides or fluorides)[6,7] or esters (mesylates, triflates, or phosphates).[8] As an example, irradiation of haloanilines or methoxyphenyl esters caused the formation of the corresponding triplet phenyl cation (via the triplet state of the reagent) by heterolysis of the Ar–X or Ar–O bond respectively. Under these conditions Ar–C bonds were formed by selective addition of the phenyl cation onto π nucleophiles with no interference by the solvent. Typically, addition onto an olefin gives a phenonium ion and an alkyl aromatic from it (see Scheme 1a).[9] This novel photo-S_N1 reaction has been applied recently to the synthesis of allylaromatics,[9] arylpropionic acids,[10] arylalkenes,[11] alkynes,[12] as well as biaryls.[13] In the cases considered, the ED group (methoxy, hydroxy, amino) was placed in the *para* position with respect to the photolabile nucleofugal group (e.g., Cl, OMs, OTf).

There is only sparse evidence in the literature for the generation of an aryl cation even upon irradiation of aromatic halides or esters bearing an OH(OR) group in the *ortho* rather than in the *para* position. As an example, during the irradiation in aqueous solution of both 2-bromo-[14a] and 2-chlorophenol,[14b] 2-oxocyclohexa-3,5-dienylidene has been detected by laser flash photolysis experiments. This carbene

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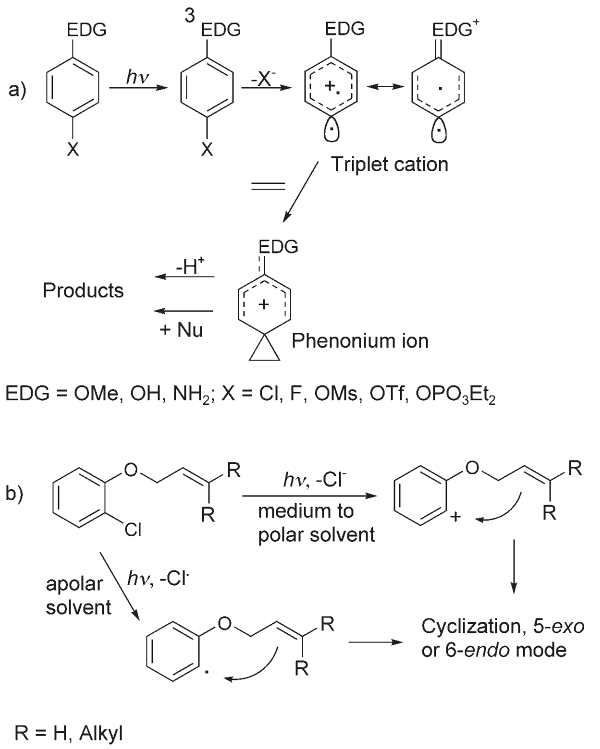


Scheme 1. a) Intermolecular and b) proposed intramolecular chemistry of phenyl cations.

may arise from deprotonation of the corresponding *ortho*-hydroxyphenyl cation, as recently demonstrated for the analogous photodehalogenation of 4-chlorophenol.[15] Interestingly, the photosensitized cleavage of 5-chloro-2-(2,4-dichlorophenoxy)phenol triflate has been found to cause the intramolecular formation of an aryl–aryl bond.[14c]

We surmised that phenyl cations that have a π nucleophile tethered to the *ortho* position might give useful cyclization reactions. An embodiment of this principle is illustrated in Scheme 1b, in which an *O*-allyl group functions both as an activating group for the photoheterolysis step and as a suitable trap for the phenyl cation formed. If verified, this unprecedented intramolecular arylation would be the cationic variation of the well-known cyclization of 2-halophenyl allyl ethers under radicalic or anionic conditions. Furthermore, both we and others observed that 2- and 4-chloroanisole also undergo homolytic photodechlorination in apolar media.[11,16] Thus, the photochemistry of these halides may serve to compare the behavior of a phenyl cation versus that of the corresponding radical, as well as for evaluating the synthetic potential of this novel photocyclization, for example, to obtain (dihydro)benzofurans, an important class of bioactive compounds.[17]

We chose as appropriate models 1-allyloxy-2-chlorobenzene (**1**) and the dimethylated derivative 1-(3-methylbut-2-enyloxy)-2-chlorobenzene (**2**). We wanted to test a butenyl versus an allyloxy group, and so 3-(but-3-enyl)-4-chloroanisole **3** was also used as a model compound. In this case a methoxy group at the 4-position was introduced for activating the dehalogenation. Along with **3**, the corresponding 3-allyloxy derivative (**4**) was considered for the sake of comparison. For the reasons discussed above, the photoreactions were examined in a range of solvents, from cyclohexane to aprotic solvents of increasing polarity (ethyl acetate, acetonitrile or methylene chloride) to protic solvents (MeOH, aqueous MeCN or 2,2,2-trifluoroethanol (TFE)). The presence of a base (triethylamine (TEA), or Cs_2CO_3) has been previously found to improve the product yields, especially in alcoholic solvents, due to the buffering of the acid liberated. Thus all of the experiments were carried out both in the absence and in the presence of a base. The result under the latter conditions is reported only when implying a significant amelioration of the mass balance. The irradiations were carried out by using phosphor-coated lamp (310 nm). Direct irradiation gave different results in the various cases, in part because of the limited absorption of compounds **1** to **4** in this range. Acetone sensitization made the rate of the photoreaction of these compounds more uniform and improved the yields in some cases.

Results

Irradiation of 1-allyloxy-2-chlorobenzene (1): Compound **1** was partially or totally consumed by irradiation (310 nm, ca. 16 h) depending on the solvent used. The reaction was most efficient in cyclohexane, AcOEt, and methanol (from 85% to 96% of consumption) and less so in polar nonprotic solvents (≤30% of conversion). Acetone sensitization, however, made the reaction more efficient and complete conversion was obtained in all of the solvents.[18] Cleavage of the aryl–chlorine bond took place and five- or six-membered cyclic compounds were formed according to the conditions used. Thus, in ethyl acetate, both chlorinated derivatives **5** and **6** were isolated in about the same yield (ca. 20–30%; see Table 1 and Scheme 2). In methylene chloride and in acetonitrile the yield of compound **5** increased significantly (up to 79%), with the concomitant decrement of **6** and the formation of small amount of benzofuran **7**. In water–MeCN 1:3 mixed solvent, alcohol **8** was formed in 21% yield at the expense of derivatives **5**–**7**, and likewise the ether **9** was by far the main product in the reaction in methanol. In the last case, the presence of cesium carbonate increased the overall arylation yield. The presence of TEA was beneficial in TFE, although the solvent incorporating product **10** was formed in a low amount (ca. 10%) along with product **5** (60%) and traces of **7**.

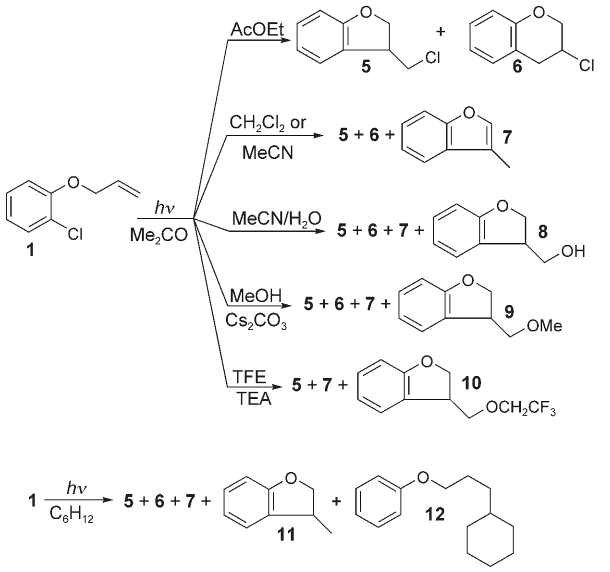
A series of potential traps was tested. Thus, allyltrimethylsilane or benzene (both 1 M) did not cause any significant modification in the product distribution, as determined by GC analysis in the experiments carried out in MeCN or TFE. Likewise, addition of Bu_4NBr (1 M) caused only a slight decrease in the products yield.

In cyclohexane (direct irradiation in this case) the main product formed was 3-methyl-2,3-dihydrobenzofuran **11** (ca.

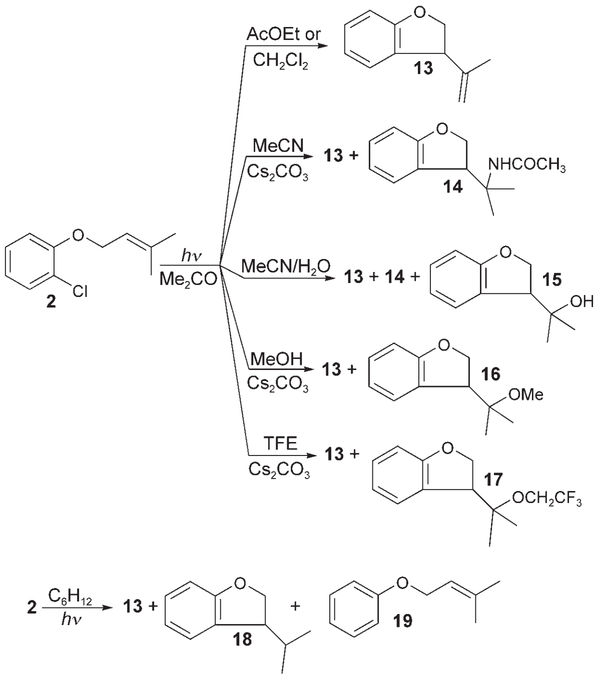
Table 1. Photolysis of **1** and **2** (0.05 M) in various solvents.[a]

Substrate	Solvent	Base	t_{IRR} [h]	Products, yield[b] [%]		
				5-*exo*	6-*endo*	non-cyclized
1	AcOEt	none	16	**5**, 30 (24)	**6**, 20 (20)	
1	CH_2Cl_2	none	16	**5**, 74 (65); **7**, 13 (12)	**6**, 10 (7)	
1	MeCN	none	17	**5**, 79 (69); **7**, 11 (10)	**6**, 5 (tr)	
1	H_2O/MeCN 1:3	none	17	**5**, 44 (39); **7**, 7 (tr.); **8**, 21 (20)	**6**, 1 (tr)	
1	MeOH	Cs_2CO_3	16	**5**, 12 (12); **7**, 2 (tr); **9**, 24 (24)	**6**, 2 (tr)	
1	TFE	TEA	16	**5**, 61 (52); **7**, 4 (tr); **10**, 10 (6)		
1	C_6H_{12}	none	16	**5**, 21 (15); **7**, 6 (tr); **11** 48 (44)	**6**, 7 (tr)	**12** 10 (9)
2	AcOEt	none	17	**13**, 86 (80)		
2	CH_2Cl_2	none	16	**13**, 73 (66)		
2	MeCN	Cs_2CO_3	18	**13**, 48 (39); **14** 10 (10)		
2	H_2O/MeCN 1:3	none	17	**13**, 18 (18); **14**, 30 (22); **15**, 50 (48)		
2	MeOH[c]	Cs_2CO_3	22	**13**, 31 (20); **16**, 65 (50)		
2	TFE	Cs_2CO_3	17	**13**, 10 (9); **17**, 38 (32)		
2	C_6H_{12}[c]	none	16	**13**, 7 (5); **18**, 10 (8)		**19**, 4 (3)

[a] Reactions carried out in the presence of 0.9 M acetone, except where indicated. [b] GC yields. The isolated yields are in parentheses, see Experimental Section. [c] No acetone added.



Scheme 2. Photoreactions of allyl ether **1**.



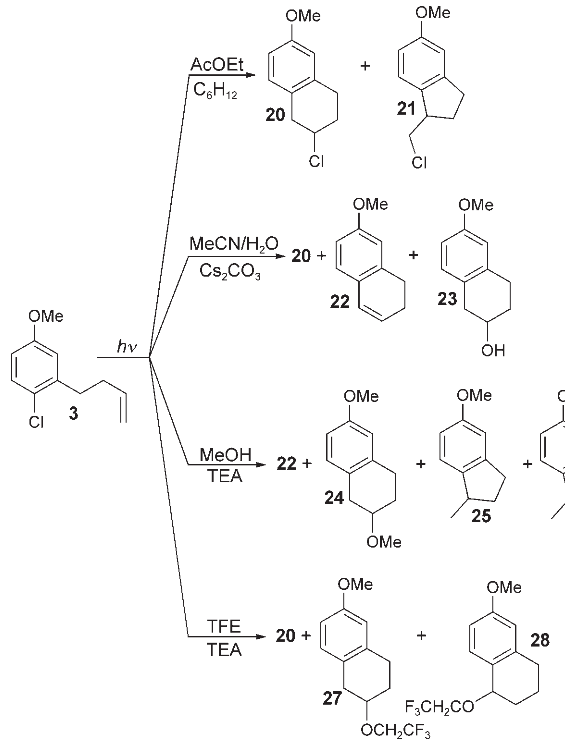
Scheme 3. Photoreactions of allyl ether **2**.

50% yield) accompanied by a number of minor products including compounds **5**–**7** and the cyclohexyl derivative **12**.

Irradiation of 1-(3-methylbut-2-enyloxy)-2-chlorobenzene (2): As in the previous case sensitization by acetone increased the efficiency of the dechlorination process and thus was adopted in all of the irradiation experiments (except that in cyclohexane). Under these conditions, ether **2** was consumed within 22 h of irradiation (see Table 1 and Scheme 3) and the reaction was in general cleaner with respect to **1**. Thus, the unsaturated compound **13** was formed as the only detected product in ethyl acetate (isolated in 80% yield) and was obtained in methylene chloride in 66% yield. In acetonitrile, **13** was in part substituted by acetamide **14** (10% yield). An excellent mass balance (88%) was obtained in water–MeCN 1:3 mixed solvents, in which alkene **13** (18%), amide **14** (22%), and carbinol **15** (48%, main product) were formed. Methyl ether **16** was isolated in a good yield (50%) along with olefin **13** in the irradiation in MeOH in the presence of cesium carbonate. The same base was employed in the reaction in TFE where the yield of compound **13** was the lowest in the series (9%) and trifluoroethyl ether **17** was formed in 32% yield. The presence of benzene (1 M) did not affect the product distribution in the last solvent.

In cyclohexane, compound **2** was completely consumed after 16 h of irradiation and gave an inseparable mixture of compound **13**, the dechlorinated derivative **19** and 3-isopropyl-2,3-dihydrobenzofuran **18**[19] in a ca. 1.5:1:2.5 ratio. In contrast to compound **1**, no 6-*endo* cyclization products were detected in all the experiments with aryl ether **2**.

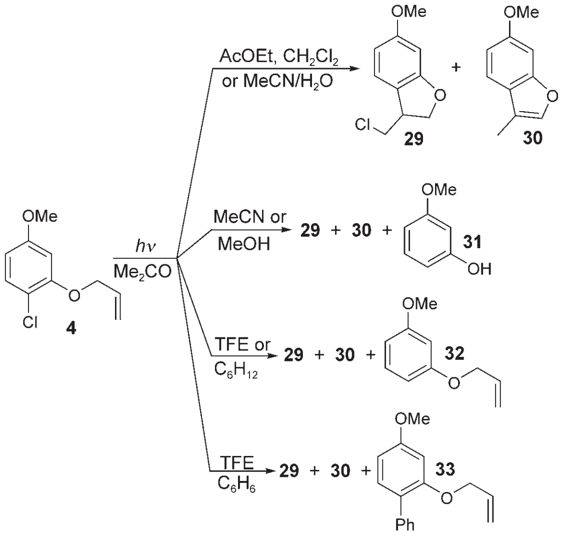
Irradiation of 3-(but-3-enyl)-4-chloroanisole (3): Differently from the case of **1** and **2**, anisole **3** absorbed effectively at 310 nm and reacted in all of the solvents considered with no need of sensitization. (Scheme 4 and Table 2). Thus, irradiation of **3** in neat AcOEt gave an inseparable mixture (ca. 1:1 ratio) of chloride **20** (arising from 6-*endo* cyclization)



Scheme 4. Photoreactions of butenyl anisole **3**.

and **21** (from 5-*exo* cyclization). In aqueous acetonitrile, no five-membered ring derivatives were formed and alkene **22** (13%) and alcohol **23** (18%) were isolated in the reaction along with a comparable amount of chloride **20**. No chlorine-containing products were formed in neat MeOH, in which the main product was the bis-ether **24** (35%), accompanied by 5-methoxy-1-methylindane (**25**) and small amounts of indene **26** and dihydronaphthalene **22**. Photolysis of **3** in TFE yielded chlorinated **20**, and two isomeric trifluoromethyl ethers characterized as **27** (the analogue of **24**) and **28** (20% yield). The presence of benzene (1 M) in TFE again had no effect. The reaction in cyclohexane gave compounds **20** and **21** in about the same yield (ca. 20%) as observed in AcOEt.

Photochemistry of 3-allyloxy-4-chloroanisole (4): The direct photoreaction of aryl ether **4** was less efficient, and conversion was limited to $\leq 15\%$ in 16 h except for the case of cyclohexane, where it reached 95%. Acetone sensitization improved the yields, although in methylene chloride or water/MeCN the conversion remained incomplete even after 30–40 h of irradiation (see Scheme 5 and Table 2). No 6-*endo* analogues of those formed in the irradiation of **3** were identified in the reaction. Benzofurans **29** and **30** were obtained in all cases. The former one predominated in AcOEt (58% yield vs 6%) and less markedly in CH_2Cl_2 and water/acetonitrile. 3-Hydroxyanisole (**31**) was formed in MeCN and was



Scheme 5. Photoreactions of allyl ether **4**.

Table 2. Photolysis of **3** and **4** (0.05 M) in various solvents.[a]

Substrate	Solvent	Base	t_{IRR} [h] (conversion [%])	Products, yield[b] [%] 5-*exo*	6-*endo*	non-cyclized
3	AcOEt	none	20 (100)	**21**, 25 (22)	**20**, 25 (22)	
3	H_2O/MeCN 1:3	Cs_2CO_3	24 (100)		**20**, 18 (15); **22**, 15 (13); **23**, 22 (18)	
3	MeOH	TEA	16 (100)	**25**, 16 (13); **26**, 7 (4)	**22**, tr. (tr.); **24**, 40 (35)	
3	TFE	TEA	16 (100)		**20**, 7 (6); **27**, 18 (17); **28**, 22 (20)	
3	C_6H_{12}	none	16 (100)	**21**, 12	**20**, 20	
4	AcOEt	none	16 (100)	**29**, 58 (50); **30**, 6 (3)		
4	AcOEt[c]	none	16 (100)	**29**, 65 (55); **30**, 10 (5)		
4	CH_2Cl_2	none	32 (77)	**29**, 55 (50); **30**, 22 (19)		
4	MeCN	Cs_2CO_3	22 (100)	**29**, 33 (31); **30**, 5 (tr)		**31**, 23
4	H_2O/MeCN 1:3	none	40 (73)	**29**, 49 (38); **30**, 19 (10)		
4	MeOH	none	9 (100)	**29**, 13 (10); **30**, 4 (tr)		**31**, 78
4	TFE	Cs_2CO_3	34 (90)	**29**, 12 (6); **30**, 3 (tr)		**32**, 7 (tr)
4	TFE[c]	Cs_2CO_3	34 (91)	**29**, 9 (tr); **30**, 2 (tr)		**33**, 32 (27)
4	C_6H_{12}	none	16 (95)	**29**, 76 (71); **30**, 7 (tr)		**32**, 6 (tr)

[a] Reactions carried out in the presence of 0.9 M acetone, except in the case of cyclohexane and compound **3**. [b] GC yields; in parentheses the isolated yields, in both cases based on consumed aryl ether. [c] Reaction carried out in the presence of 1 M benzene.

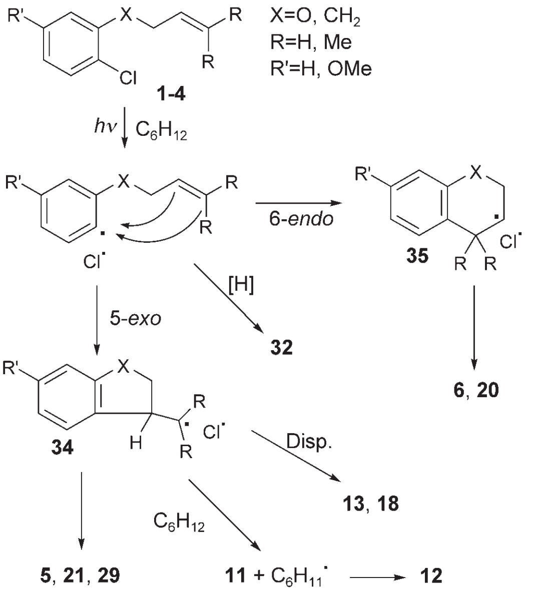
the main product in methanol (78% yield). In TFE the mass balance of isolated products was quite low (ca. 22%) and included dehalogenated **32** (7%). In the presence of benzene (1 M), the biphenyl derivative **33** was the main product (27% isolated yield) in TFE, while the product distribution did not change in AcOEt. As mentioned above the reaction in cyclohexane was quite efficient and compound **29** was obtained in a good yield (76%) along with small amounts of both **30** and **32** (7% each).

Blank experiments were carried out to assess the photostability of **32** in MeCN and MeOH under the irradiation conditions and in both cases deallylation to form **31** took place.

Discussion

Photocyclization paths: The above results show that photoinduced dechlorination of compounds **1** to **4** leads to cyclization as by far the main process in most cases. Indeed, this process occurs both in an apolar solvent, such as cyclohexane, and in polar solvents. It is reasonable that the same pattern as in simple models such as 2- and 4-chloroanisole[11,16] is followed and the process is initiated by either homolysis or heterolysis of the C–Cl bond respectively in apolar and in polar medium.[20,22] The nature of the intermediate is expected to have a major effect on the regioselectivity of the cyclization. As an example, phenyl radicals generated from the corresponding *o*-allyloxyphenyl iodides or bromides by means of triorganogermanium hydrides,[23a] tin dithiocarbonates,[23b] alkylsamarium(III) reagents,[23c] reduction of aryl diazonium salts,[23d] cobalt complexes,[23e] and Pd complexes[23f] showed a marked preference for the 5-*exo*-trig cyclization,[24] just as γ-oxahexenyl radicals do.[25] The same selectivity was observed when the radicals were obtained by photochemical means through an $S_{RN}1$ reaction,[26a] through photoinduced electron transfer with suitable donors,[26b–d] by direct irradiation of an aryl iodide,[27] from phenyl diazonium salts in cyclodextrins (CDs),[26e] or through other photostimulated reactions.[26f,g] Aryl cyclization of *ortho*-butenylphenyl halides was less studied, but also in this case the selectivity is towards 5-*exo*-trig cyclization.[24,28,29a] Interestingly, aryl anions showed the same pattern.[29] There are no comparable examples in the literature on the cyclization of *o*-allyloxy- or butenylphenyl cations, but formally equivalent hexenyl and γ-oxahexenyl cations have been both reported to cyclize with a marked preference towards 6-*endo*-trig rather than the 5-*exo*-trig mode.[30]

In the present case, irradiation in cyclohexane leads to a phenyl radical (see Scheme 6), and this radical cyclizes mainly, as one would expect, in the 5-*exo*-trig fashion to radical **34** rather than to **35** (in a ratio >10:1 for **1** and **4** and evidently 100% from **2**, in which sterical hindering and stability of the tertiary radical force this path; an exception is **3**, with a 3:5 ratio, see below for a comment). In turn, the cyclic radical abstracts hydrogen from the solvent (compound **11** is the main product from **1**, in which the radical mechanism is further supported by the formation of product **12**, incorporating the cyclohexyl radical), disproportionates (see equal amounts of products **13** and **18** from **2** in which a tertiary radical is involved),[31] or adds chlorine. The last process is the main one from the irradiation of **3** and **4**. This suggests that the 4-alkoxyphenyl and the 2,4-dialkoxyphenyl radical/chlorine pairs have some ionic character, which leads both to preferential combination with chlorine and to the slight predominance of the 6-*endo* cyclization over the 5-*exo* mode with the former radical, which lacks the γ-oxa substitution known to favor formation of the five-membered ring.[25]



Scheme 6. Radical pathways after photohomolysis of compounds **1**–**4**.

In the other solvents, dechlorination is a heterolytic process. Indeed, a cationic path is indicated by the occurrence of deprotonation, nucleophile (solvent) addition, and diagnostic cationic rearrangements under appropriate conditions (see below). The regiochemistry is less easily predicted in this case. As mentioned above, the 6-*endo* cyclization (path b, Scheme 7) is favored for carbocations, but this does not necessarily apply to an open-shell species, such as phenyl cation **36**, particularly if this is formed in the triplet state, in analogy to what found with 4-cloroanisole.

In the experiment, the result depends on structure and conditions. An oxygen atom in the γ-position appears to be determining, since the 5-*exo* mode (via **37**, path a, Scheme 7) predominates in the three allyloxy derivatives **1**, **2**, and **4**. More precisely, this mode is increasingly preferred with increasing solvent polarity with **1** (from 3:2 in ethyl acetate to ≥20:1 in alcohols), while it is exclusive with compounds **2** (in which a tertiary cation is formed) and with **4**. The medium polarity affects not only the mode of cyclization, but also the ensuing chemistry of the cyclized cation by increasing the proportion of the reactions via the free, sol-

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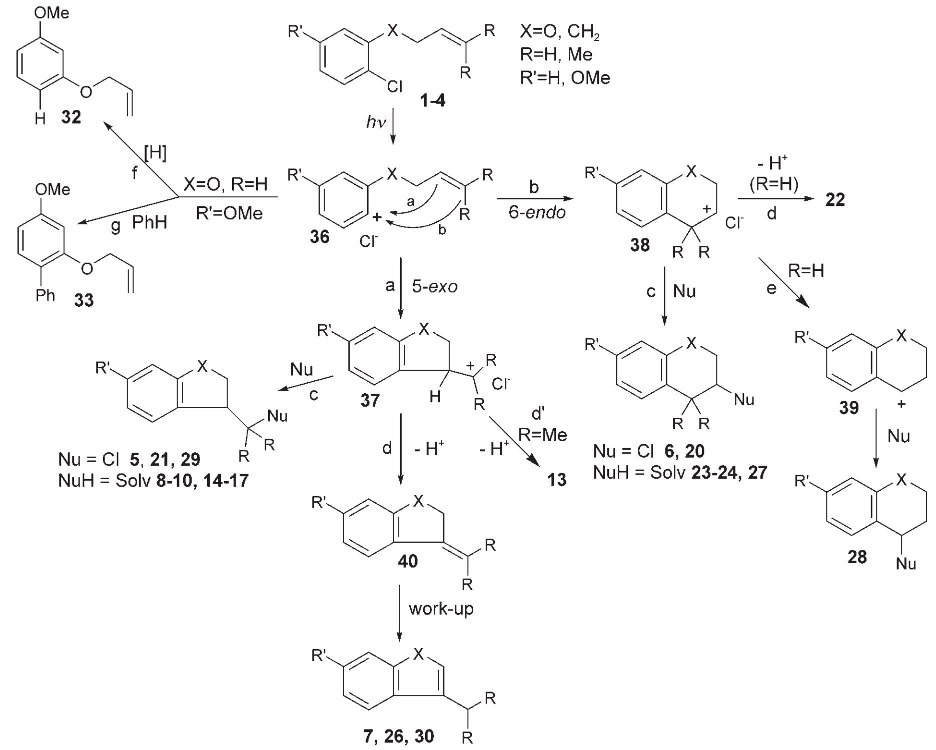
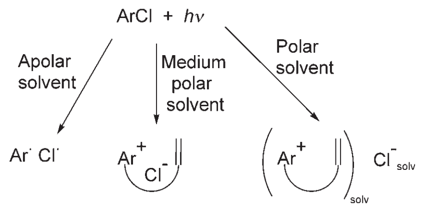


Scheme 7. Pathways in the photoheterolysis of compounds **1**–**4**.

vated cation in comparison to in cage recombination with chloride. Thus, with **1** the product distribution shifts from 100% recombination (path c, Nu = Cl) in ethyl acetate, 88% recombination and 12% deprotonation (path d) in acetonitrile, and 32% recombination, 5% deprotonation, 63% solvent addition (path c, Nu = solvent) in polar, nucleophilic methanol (the yield of the ether is lower in non-nucleophilic TFE). As one may expect, no chloride is formed from **2**, in which **37** is a tertiary cation, and deprotonation (path d′) and solvent addition compete, depending on the nucleophilicity of the latter. With **4**, the pattern is roughly similar to that with **1**. However, in this case, cation **36** is stabilized by a second alkoxy group. This reduces the role of interaction with the tethered alkene. Thus, cyclization is no more the exclusive process from solvated phenyl cation **36** and the diagnostic intermolecular reactions of phenyl cations appear, namely reduction (path f, the main process in hydrogen-donating methanol) and trapping by benzene (path g, the main process with 1 M benzene in TFE). Consistently with this rationalization, the product distribution is not affected by the presence of benzene in AcOEt, in which the reaction occurs in a cage. The product from reduction is evidently **32**, as observed in TFE, but in MeOH this compound undergoes a secondary photocleavage (photo-Claisen) reaction leading to observed **31**, as ascertained by separate irradiation.

With compound **3**, lacking the directing effect of the oxygen atom in the γ-position in the chain, the 6-*endo* mode (path b, via **38**) has its full role. The cationic character of intermediate **36** is apparent when this is solvated in a polar medium, and less marked when paired in a cage with chloride (see Scheme 8).

Thus, products from 6-*endo* cyclization increase with the solvent polarity, from 1:1 in ethyl acetate to 100% in TFE. The ensuing chemistry of cyclized cation **38** changes in a parallel way, with chloride recombination (path c, Nu = Cl) as the only process in ethyl acetate, solvent addition being almost exclusive in nucleophilic methanol (path c, Nu = MeOH) and 84% solvent addition versus 16% deprotonation (path d) in less nucleophilic TFE. The cationic character of intermediate **38** is highlighted by the occurring of the diagnostic hydride shift to form benzylic cation **39** (path e) in TFE.



Scheme 8. Medium dependence of the photochemistry of **1**–**4**.

Some points about the cyclization paths deserve notice. The first one concerns deprotonation of **37**, which reasonably leads to methylenedihydrobenzofuran or methyleneindan derivatives **40** (path d, Scheme 7), in turn evolving to the isolated alkylbenzofuran (or indan) derivatives during workup, by means of a known rearrangement.[23e,32] The last pathway concerns the role of acetonitrile. This weakly nucleophilic solvent apparently forms a reversible adduct with the cyclized cation **37**. This may be both an intermediate en route to elimination (or to addition of some added nucleophile) and a precursor of an acetamide (by moisture addition, Ritter reaction). When **37** is a stabilized tertiary cation, as in the irradiation of **2**, this double role is apparent in the increase of the yield of both alcohol **15** and amide **14** when a high water proportion is present (in the other cases only competitive trapping to form alcohols occurs). Finally, except for the above rationalized case of compound **4**, cyclization must be very fast, as no competitive trapping by an external nucleophile (whether a neutral π nucleophile such as benzene or a Br$^-$ ion) occurs.[6b]

Scope of the reaction: The above data show that photoheterolysis of the C–Cl bond occurs in *ortho*-chlorophenyl allyl ethers both in moderately and in highly polar solvents and leads to cyclization in much better yield than homolysis, which occurs in an apolar solvent such as cyclohexane. Phenyl chlorides are less expensive, more easily available and more stable with respect to the corresponding phenyl bromides or iodides usually employed in other cyclization methods. A large choice of solvents is possible, including chlorinated solvents (not previously tested in arylation reactions that proceed via an aryl cation), and sensitization by acetone dramatically improves the arylation yield in all of those cases in which consumption of the starting chloride by direct irradiation is slow. Importantly, photodechlorination was virtually the only photoprocess and none of the chlorophenyl allyl ethers underwent the photo-Claisen rearrangement, which may have been feared as a competitor, since this occurs in analogous compounds.[33] Cyclization occurred also (with a somewhat lower yield) from a chloride bearing two alkoxy groups, such as **4**, despite the fact that photoformation of the cation had been found to be less efficient with this type of compound,[9] provided that a reducing solvent such as methanol was avoided. As far as can be judged from the photochemistry of **3**, cyclization occurs also with the corresponding butenyl derivatives, with the difference that the 6-*endo* mode is clearly predominating.

Although mixtures are obtained in most cases, conditions can be chosen under which a single product is obtained in $>50\%$ yield and, for benzofuran derivatives, in $>70\%$ yield. In such cases, the directness and the experimental simplicity of the method suggests that it has some synthetic potential. As an example, compound **13**, here formed in 80% yield, was obtained inefficiently (26% yield, 42% of the starting material recovered) starting from **2** by using a cobalt-based catalyst in the presence of the trimethylsilyl Grignard reagent.[34]

Further studies must address the application of this intramolecular strategy to further substrates bearing different nucleophilic chain (e.g., an alkyne or an aromatic moiety) as well as more substantial mechanistic evidence, for example, with regard to the involvement of an intermediate phenonium ion.

Conclusion

The only photoprocess from *ortho*-chlorophenyl allyl ethers is dechlorination. Apart from the homolytic cleavage in cyclohexane, in the other cases heterolysis occurs and the choice of the medium allows us to test the reactivity of phenyl cation, an open-shell, nonlocalized ion. In particular, *ortho*-substituted phenyl cations were studied here for the first time. Attack to the tethered C–C double bond led to 5-*exo* cyclization and either in-cage chloride recombination or solvent addition from the free ion depending on the nature of the medium (see Scheme 8).

When a methylene group is substituted for an oxygen atom in the side-chain, the 6-*endo* mode predominates. On the other hand, stabilizing the phenyl cation by introducing a further alkoxy group in the *para* position makes intermolecular reaction with π nucleophiles competitive.

Apart from the mechanistic interest, the above results suggest that it is possible to tune the reaction towards the desired cyclization through the choice of reagent and conditions. The mild photochemical method (room temperature and no anhydrous conditions required) avoids the use of potentially toxic or expensive organometallic species, most often required in alternative thermal methods, and allows the use of chlorides rather than bromides and iodides as starting materials. The simplicity of the method is appealing and the cyclized compounds obtained pertain to the classes of some interest, for example, pharmacologically active tetralines.[35]

Experimental Section

NMR spectra were recorded on a 300 MHz spectrometer. Structure attributions were made on the basis of analytical data and of ^{1}H and ^{13}C NMR data accompanied by the appropriate DEPT experiment (chemical shifts are reported in ppm downfield from TMS). The photochemical reactions were performed at 20 °C in quartz tubes by using nitrogen-purged solution and a multilamp reactor fitted with six 15 W phosphor-coated lamps (maximum of emission 310 nm) for the irradiation.

Synthesis of precursors 1–4: Compounds **1** and **2** were prepared from 2-chlorophenol, following the procedure reported by Hattori.[36]

1-Allyloxy-2-chlorobenzene (1): Obtained in 69% yield; colorless oil, lit.[37] b.p. 100–101 °C at 10 mmHg. Spectroscopic data of compound **1** were in accordance with the literature.[36] IR (neat): $\tilde{\nu}=3069$, 2869, 1589, 1485, 1445, 1278, 1248, 1061, 929, 747 cm^{-1}; elemental analysis calcd (%) for C_9H_9ClO: C 64.11, H 5.38; found: C 63.9, H 5.4.

1-(3-Methylbut-2-enyloxy)-2-chlorobenzene (2):[34] Obtained in 79% yield; colorless oil, b.p. 140 °C at 12 mmHg; ^{1}H NMR ($CDCl_3$): $\delta=1.75$ (s, 3H), 1.80 (s, 3H), 4.65 (d, $J=6.6$ Hz, 2H), 5.50–5.60 (m, 1H), 6.90–7.40 ppm (m, 4H); IR (neat): $\tilde{\nu}=2975$, 2932, 1589, 1484, 1445, 1383, 1277, 1242, 1059, 1040, 995, 746 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{13}ClO$: C 67.18, H 6.66; found: C 67.3, H 6.7.

3-(But-3-enyl)-4-chloroanisole (3): Compound **3** was prepared from 2-(bromomethyl)-1-chloro-4-methoxybenzene,[38] following the literature procedure for the allylation of benzyl bromides.[39] Allylmagnesium bromide (~1 M in Et_2O, 1.4 g, 10 mmol) was added dropwise under nitrogen to a solution of 2-(bromomethyl)-1-chloro-4-methoxybenzene (2 g, 8.4 mmol) in anhydrous THF (20 mL). The resulting mixture was stirred at room temperature for 2 h and then refluxed for 3 h. After usual workup, the residue was distilled under reduced pressure to give **3** (colorless oil, 88%). ^{1}H NMR ($CDCl_3$): $\delta=2.35$–2.45 (m, 2H), 2.75–2.85 (m, 2H), 3.80 (s, 3H), 5.00–5.15 (m, 2H), 5.90 (m, 1H), 6.70 (dd, $J=3$, 8.7 Hz, 1H), 6.80 (d, $J=3$ Hz, 1H), 7.25 ppm (d, $J=8.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=33.2$ (CH_2), 33.5 (CH_2), 55.3 (CH_3), 112.5 (CH_2), 115.1 (CH), 115.9 (CH), 125.2, 129.8 (CH), 137.6 (CH), 140.2, 158.1 ppm; IR (neat): $\tilde{\nu}=2935$, 1640, 1597, 1576, 1476, 1280, 1161, 1064, 1028, 913, 801 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{13}ClO$: C 67.18, H 6.66; found: C 67.1, H 6.6.

3-Allyloxy-4-chloroanisole (4): A mixture of 4-chlororesorcinol (4 g, 27.7 mmol), allylbromide (6 mL, 69.2 mmol) and K_2CO_3 (7.65 g, 55.3 mmol) in acetone (100 mL) was refluxed for 3 h. The solvent was then removed in vacuo and the residue was diluted with water and extracted with Et_2O. The organic phase was washed twice with aqueous

NaOH 10 % and the resulting aqueous phases were combined, acidified with HCl (6 N) and again extracted with Et_2O. The last organic extracts were dried and evaporated to give crude 3-allyloxy-4-chlorophenol. This compound (2.2 g, 12 mmol) was dissolved in acetone (50 mL) and then treated with methyl iodide (0.8 mL, 13 mmol) and K_2CO_3 (2.5 g, 18 mmol). The resulting mixture was refluxed for 6 h. After the usual workup, the residue was subjected to chromatography on Al_2O_3 with cyclohexane as the eluant to give **4** (colorless oil, 27 % yield based on starting 4-chlororesorcinol). ^{1}H NMR ($CDCl_3$): $\delta = 3.80$ (s, 3 H), 4.60–4.70 (m, 2 H), 5.30–5.55 (m, 2 H), 6.05–6.15 (m, 1 H), 6.45 (dd, $J = 2.7$, 8.7 Hz, 1 H), 6.55 (d, $J = 2.7$ Hz, 1 H), 7.25 ppm (d, $J = 8.7$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 55.4$ (CH_3), 69.6 (CH_2), 101.4 (CH), 105.5 (CH), 114.7, 117.8 (CH_2), 130.1 (CH), 132.5 (CH), 154.6, 159.2 ppm; IR (neat): $\tilde{\nu} = 2939$, 1599, 1492, 1309, 1204, 1170, 1034, 930, 833 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{11}ClO_2$: C 60.46, H 5.58; found: C 60.5, H 5.5.

Photolysis of compounds 1–4—general procedure: A solution of the precursors **1**–**4** (0.05 M), acetone (0.9 M, see Table 1 and 2 for exceptions) and, when required, an equivalent amount of base (TEA 0.05 M or Cs_2CO_3 0.025 M) in the chosen solvent (30 mL) was irradiated until total consumption of the starting material. The reaction course was followed by thin-layer chromatography (TLC; cyclohexane/ethyl acetate) and gas chromatography (GC). Workup of the photolyzates involved concentration in vacuo and chromatographic separation with silica gel and cyclohexane/ethyl acetate mixtures as eluants. When a water/acetonitrile mixture was used as the photolysis solvent, extraction with diethyl ether of the final solution was performed before column purification.

Photochemical reactions of 1-allyloxy-2-chlorobenzene (1)

In ethyl acetate: After 16 h of irradiation, purification (C_6H_{12} as the eluant) of the raw photolyzate afforded 3-chloromethyl-2,3-dihydrobenzofuran (**5**; 60 mg, 24 % yield) as a colorless oil and 4-chlorochromane (**6**; 52 mg, 20 % yield) also as a colorless oil. Data for **5**: The spectroscopic data of compound **5** were in accordance with the literature.[40] MS: *m*/*z* (%): 168 (50) [M^+], 131 (10), 119 (100) [M^+-CH_2Cl], 103 (15), 91 (95), 77 (25), 65 (30), 51 (40), 48 (20); elemental analysis calcd (%) for C_9H_9ClO: C 64.11, H 5.38; found: C 64.2, H 5.3. Data for **6**: ^{1}H NMR[41] ($CDCl_3$): $\delta = 3.10$ (dd, 1 H, $J = 7.7$ and 17 Hz), 3.35 (dd, $J = 4.7$, 17 Hz, 1 H), 4.05–4.15 (m, 1 H), 4.35–4.50 (m, 2 H), 6.85–7.20 ppm (m, 4 H); ^{13}C NMR ($CDCl_3$): $\delta = 35.1$ (CH_2), 50.8 (CH), 69.5 (CH_2), 116.6 (CH), 118.9, 121.1 (CH), 127.9 (CH), 129.6 (CH), 153.1 ppm; IR (neat): $\tilde{\nu} =$ 2878, 1584, 1490, 1458, 1231, 1040, 754 cm^{-1}; elemental analysis calcd (%) for C_9H_9ClO: C 64.11, H 5.38; found: C 64.2, H 5.4.

In methylene chloride: After 16 h of irradiation, purification of the raw photolyzate afforded **5** (164 mg, 65 % yield), **6** (18 mg, 7 % yield) and 3-methylbenzofuran (**7**; 24 mg, 12 % yield) as colorless oils. The spectroscopic data of compound **7** were in accordance with the literature.[42] MS: *m*/*z* (%): 131 (55) [M^+-1], 103 (20), 77 (15), 63 (5), 51 (15); elemental analysis calcd (%) for C_9H_8O: C 81.79, H 6.10; found: C 81.7, H 5.9.

In acetonitrile: After 17 h of irradiation, purification of the raw photolyzate afforded **5** (174 mg, 69 % yield) and **7** (20 mg, 10 % yield).

In water/acetonitrile 1:3: After 16 h of irradiation, purification (from cyclohexane/ethyl acetate 99:1 to 7:3 as the eluant) of the raw photolyzate afforded **5** (99 mg, 39 % yield) and 2,3-dihydrobenzofuran-3-yl-methanol (**8**; 45 mg, 20 % yield) as colorless oils. The spectroscopic data of compound **8** were in accordance with the literature.[43] Elemental analysis calcd (%) for $C_9H_{10}O_2$: C 71.98, H 6.71; found: C 71.8, H 6.8.

In methanol: The reaction was carried out in the presence of Cs_2CO_3. After 16 h of irradiation, purification of the raw photolyzate afforded **5** (28 mg, 12 % yield) and 2,3-dihydro-3-(methoxymethyl)benzofuran (**9**; 54 mg, 24 % yield) mixed with part of compound **5**. Data for **9**: ^{1}H NMR ($CDCl_3$, from the mixture): $\delta = 3.40$ (s, 3 H), 3.65 (dd, $J = 5.5$, 8.7 Hz, 1 H), 3.70–3.80 (m, 2 H), 4.45 (dd, $J = 5.6$, 9 Hz, 1 H), 4.65 (t, $J = 9$ Hz, 1 H), 6.80–7.30 ppm (m, 4 H); ^{13}C NMR ($CDCl_3$, from the mixture): $\delta =$ 29.6 (CH_2), 42.4 (CH), 58.9 (CH_3), 75.2 (CH_2), 109.5 (CH), 120.2 (CH), 124.6 (CH), 128.6 (CH), 130.5, 160.1 ppm; MS: *m*/*z* (%): 164 (25) [M^+], 119 (70), 91 (100), 77 (10), 65 (20), 51 (10), 45 (30); IR (neat, for the mixture): $\tilde{\nu} = 2928$, 1597, 1484, 1458, 1230, 1153, 1100, 1015, 977, 752 cm^{-1}.

In TFE: The reaction was carried out in the presence of TEA. After 16 h of irradiation, purification of the raw photolyzate afforded **5** (132 mg, 52 % yield) and 2,3-dihydro-3-[(2,2,2-trifluoroethoxy)methyl]benzofuran (**10**; 20 mg, 6 % yield) mixed with part of compound **5**. Data for **10**: ^{1}H NMR ($CDCl_3$, from the mixture): $\delta = 3.55$–3.85 (m, 3 H), 3.80 (m, 2 H), 4.40–4.70 (m, 2 H), 6.80–6.95 (m, 2 H), 7.15–7.30 ppm (m, 2 H); ^{13}C NMR ($CDCl_3$, from the mixture): $\delta = 42.4$ (CH), 68.5 (q, $J = 34$ Hz), 74.0 (CH_2), 74.9 (CH_2), 109.7 (CH), 120.4 (CH), 124.6 (q, $J = 175$ Hz, CF_3), 124.7 (CH), 126.8, 128.9 (CH), 160.1 ppm; MS: *m*/*z* (%): 232 (20) [M^+], 133 (5) [$M^+-OCH_2CF_3$], 119 (85) [$M^+-CH_2OCH_2CF_3$], 105 (5), 91 (100), 77 (10), 65 (20), 51 (10), 40 (25); IR (neat, for the mixture): $\tilde{\nu} =$ 3045, 2930, 1595, 1481, 1458, 1230, 1152, 1013, 975, 751 cm^{-1}.

In cyclohexane: After 16 h of irradiation, purification of the raw photolyzate afforded **5** (37 mg, 15 % yield), 3-methyl-2,3-dihydrobenzofuran (**11**; 89 mg, 44 % yield) and 3-phenoxypropylcyclohexane (**12**; 29 mg, 9 % yield). Data for **11**: The spectroscopic data of compound **11** were in accordance with literature data.[26a] elemental analysis calcd (%) for $C_9H_{10}O$: C 80.56, H 7.51; found: C 80.6, H 7.3. Data for **12**: ^{1}H NMR ($CDCl_3$): $\delta = 0.85$–1.00 (m, 2 H), 1.15–1.45 (m, 6 H), 1.65–1.90 (m, 7 H), 3.90 (t, $J = 6.7$ Hz, 2 H), 6.90–7.00 (m, 3 H), 7.25–7.35 ppm (m, 2 H); ^{13}C NMR ($CDCl_3$): $\delta = 26.2$ (CH_2), 27.0 (CH_2), 33.2 (CH_2), 33.6 (CH_2), 37.4 (CH), 68.2 (CH_2), 114.4 (CH), 120.3 (CH), 129.2 (2 CH), 159.0 ppm; MS: *m*/*z* (%): 218 (100) [M^+], 135 (5), 124 (10), 107 (10), 94 (70), 81 (40), 69 (50), 55 (65), 41 (65); IR (neat): $\tilde{\nu} = 2923$, 2850, 1600, 1497, 1244, 1171, 1035, 751, 690 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{22}O$: C 82.52, H 10.16; found: C 82.7, H 10.3.

Photochemical reactions of 1-(3-methylbut-2-enyloxy)-2-chlorobenzene (2)

In ethyl acetate: After 17 h of irradiation, purification (cyclohexane/ethyl acetate 98:2 as the eluant) of the raw photolyzate afforded 3-isopropenyl-2,3-dihydrobenzofuran (**13**; 192 mg, 80 % yield) as a colorless oil. The spectroscopic data of compound **13** were in accordance with the literature.[44] MS: *m*/*z* (%): 160 (100) [M^+], 145 (72), 131 (48), 117 (26), 91 (62); elemental analysis calcd (%) for $C_{11}H_{12}O$: C 82.46, H 7.55; found: C 82.4, H 7.6.

In methylene chloride: After 16 h of irradiation, purification of the raw photolyzate afforded **13** (159 mg, 66 % yield) with the sample obtained as above.

In acetonitrile: The reaction was carried out in the presence of Cs_2CO_3. After 18 h of irradiation, purification of the raw photolyzate afforded **13** (94 mg, 39 % yield) and *N*-[2-(2,3-dihydrobenzofuran-3-yl]propan-2-yl) acetamide (**14**; 33 mg, 10 % yield, colorless oil). Data for **14**: ^{1}H NMR ($CDCl_3$): $\delta = 1.25$ (s, 3 H), 1.30 (s, 3 H), 2.00 (s, 3 H), 4.35 (dd, $J = 4$, 8 Hz, X part of an ABX system, 1 H; CH), 4.45–4.55 (m, AB part of an ABX system, 2 H), 5.35 (br s, 1 H), 6.80 (d, $J = 8$ Hz, 1 H), 6.85–6.90 (m, 1 H; ArH), 7.10–7.20 ppm (m, 2 H; ArH); ^{13}C NMR ($CDCl_3$): $\delta = 23.9$ (CH_3), 24.2 (CH_3), 24.5 (CH_3), 47.7 (CH), 55.9, 73.5 (CH_2), 109.5 (CH), 120.1 (CH), 125.8 (CH), 127.2, 128.6 (CH), 160.7, 169.6 ppm (C=O); IR (neat): $\tilde{\nu} = 3273$, 1642, 1551, 1240, 957, 761 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{17}NO_2$: C 71.21, H 7.81; found: C 71.1, H 7.9.

In water/acetonitrile 1:3: After 17 h of irradiation, purification (from cyclohexane/ethyl acetate 99:1 to 1:1 as the eluant) of the raw photolyzate afforded **13** (43 mg, 18 % yield), **14** (72 mg, 22 % yield), and 2-[2,3-dihydrobenzofuran-3-yl]-2-propan-2-ol (**15**; 68 mg, 48 % yield, colorless oil). The spectroscopic data of compound **15** were in accordance with the literature.[45] elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.13, H 7.92; found: C 74.0, H 8.0.

In methanol: The reaction was carried out in the presence of Cs_2CO_3. After 22 h of irradiation, purification of the raw photolyzate afforded **13** (48 mg 20 % yield) and 2,3-dihydro-3-(2-methoxypropan-2-yl)benzofuran **16** (144 mg, 50 % yield, colorless oil). Data for **16**: ^{1}H NMR ($CDCl_3$): $\delta =$ 1.10 (s, 3 H), 1.25 (s, 3 H), 3.30 (s, 3 H), 3.60 (dd, $J = 4.8$, 9.2 Hz, 1 H), 4.50 (t, $J = 9.2$ Hz, 1 H), 4.60 (dd, $J = 4.8$, 9.2 Hz, 1 H), 6.75–6.90 (m, 2 H), 7.10–7.20 (m, 1 H), 7.25 ppm (d, $J = 7.5$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta =$ 21.0 (CH_3), 21.7 (CH_3), 49.1 (CH_3), 50.5 (CH), 73.0 (CH_2), 76.7, 109.4 (CH), 119.9 (CH), 125.9 (CH), 127.4, 128.4 (CH), 160.8 ppm; IR (neat): $\tilde{\nu} = 2975$, 2936, 1610, 1593, 1484, 1460, 1365, 1235, 1149, 1077, 964, 747 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.97, H 8.39; found: C 75.0, H 8.4.

In TFE: The reaction was carried out in the presence of Cs_2CO_3. After 17 h of irradiation, purification of the raw photolyzate afforded **13** (22 mg, 9 % yield) and 2,3-dihydro-3-[2-(2,2,2-trifluoroethoxy]propan-2-yl)benzofuran (**17**; 124 mg 32 % yield, colorless oil). Data for **17**: ^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (s, 3 H), 1.25 (s, 3 H), 3.60 (dd, $J = 4.7$, 9 Hz, 1 H), 3.75–3.90 (m, 2 H), 4.50–4.65 (m, 2 H), 6.80–6.95 (m, 2 H), 7.15–7.25 (m, 1 H), 7.35 ppm (d, $J = 7.4$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 21.1$ (CH_3), 21.5 (CH_3), 51.3 (CH), 60.2 (q, $J = 34$ Hz), 72.8 (CH_2), 78.8, 109.5 (CH), 120.1 (CH), 124.1 (q, $J = 276$ Hz, CF_3), 126.1 (CH), 126.7, 128.7 (CH), 160.7 ppm; IR (neat): $\tilde{\nu} = 3425$, 2114, 1651, 1485, 1460, 1387, 1371, 1280, 1234, 1160, 1110, 1017, 969, 750 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{18}F_3O_2$: C 61.08, H 6.59; found: C 61.0, H 6.6.

In cyclohexane: After 16 h of irradiation, purification of the raw photolyzate afforded a complex mixture (14 mg) containing **13** (5 %), 3-isopropyl-2,3-dihydrobenzofuran (**18**;[46] 8 %) and (3-methyl-but-2-enyl)phenyl ether (**19**;[47] 3 %) in an approximate 1.5:2.5:1 ratio as evidenced by ^{1}H and ^{13}C NMR spectroscopy and GC/MS analysis, which are in accordance with the literature.[46–47] Data for **18**: MS: m/z (%): 162 (33) [M^+], 119 (56), 91 (100), 65 (13); data for **19**: MS: m/z (%): 162 (11) [M^+], 94 (100), 66 (26).

Photochemical reactions of 3-(but-3-enyl)-4-chloroanisole (3)

In ethyl acetate: After 20 h of irradiation, purification (C_6H_{12} as the eluant) of the raw photolyzate afforded a mixture (124 mg) containing 2-chloro-1,2,3,4-tetrahydro-6-methoxynaphthalene (**20**; 62 mg 22 % yield, see below) and 1-chloromethyl-5-methoxyindane (**21**;[48] 62 mg 22 % yield). Data for **21**: ^{1}H NMR ($CDCl_3$, from the mixture): $\delta = 1.95$–2.20 (m, 1 H), 2.25–2.45 (m, 1 H), 2.80–3.10 (m, 2 H), 3.45–3.60 (m, 2 H), 3.75–3.90 (m, 4 H), 6.70–6.80 (m, 2 H; ArH), 7.20 ppm (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, from the mixture): $\delta = 30.4$ (CH_2), 31.0 (CH_2), 46.6 (CH), 48.5 (CH_2), 55.3 (CH_3), 110.0 (CH), 112.2 (CH), 124.5 (CH), 135.4, 146.0, 159.4 ppm; IR (neat, for the mixture): $\tilde{\nu} = 2948$, 1609, 1504, 1260, 1236, 1036 cm^{-1}.

In water/acetonitrile 1:3: The reaction was carried out in the presence of Cs_2CO_3. After 24 h of irradiation, purification (from cyclohexane/ethyl acetate 99:1 to 7:3 as the eluant) of the raw photolyzate afforded **20** (44 mg, 15 % yield, colorless oil), 7-methoxy-1,2-dihydro-naphthalene (**22**; 31 mg, 13 % yield, colorless oil), and 6-methoxy-1,2,3,4-tetrahydro-2-naphthol (**23**; 48 mg 18 % yield, colorless oil). Data for **20**: ^{1}H NMR ($CDCl_3$): $\delta = 2.05$–2.20 (m, 1 H), 2.25–2.40 (m, 1 H), 2.80–3.10 (m, 3 H), 3.30 (dd, $J = 4.8$, 15 Hz, 1 H), 3.80 (s, 3 H), 4.40–4.50 (m, 1 H), 6.65 (d, $J = 2.5$ Hz, 1 H), 6.70–6.75 (m, 1 H), 7.10 ppm (d, $J = 8.4$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 28.8$ (CH_2), 33.7 (CH_2), 39.9 (CH_2), 56.5 (CH_3), 58.1 (CH), 113.8 (CH), 114.6 (CH), 127.0, 131.2 (CH), 137.1, 159.3 ppm; IR (neat): $\tilde{\nu} = 2931$, 1611, 1507, 1458, 1263, 1154, 1128, 1040, 876 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{13}ClO$: C 67.18, H 6.66; found: C 67.0, H 6.6. The spectroscopic data of compounds **22**[49] (elemental analysis calcd (%) for $C_{11}H_{12}O$: C 82.46, H 7.55; found: C 82.3, H 7.6.) and **23**[50] (elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.13, H 7.92; found: C 74.2, H 8.0.) were in accordance with the literature.

In methanol: The reaction was carried out in the presence of TEA. After 16 h of irradiation, purification of the raw photolyzate afforded 1,2,3,4-tetrahydro-2,6-dimethoxynaphthalene (**24**; 102 mg, 35 % yield, colorless oil), and a mixture of 5-methoxy-1-methylindane (**25**; 32 mg, 13 % yield) and 5-methoxy-1-methyl-1-indene (**26**; 10 mg, 4 % yield). Data for **24**: ^{1}H NMR ($CDCl_3$): $\delta = 1.75$–1.90 (m, 1 H), 2.00–2.15 (m, 1 H), 2.75–3.10 (m, 4 H), 3.45 (s, 3 H), 3.60–3.70 (m, 1 H), 3.80 (s, 3 H), 6.65 (d, $J = 2.7$ Hz, 1 H), 6.70 (dd, $J = 2.7$, 8.3 Hz, 1 H), 7.00 ppm (d, $J = 8.3$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 27.2$ (CH_2), 27.6 (CH_2), 34.2 (CH_2), 55.1 (CH_3), 55.7 (CH_3), 75.9 (CH), 112.1 (CH), 113.1 (CH), 126.4, 130.2 (CH), 137.0, 157.6 ppm; MS: m/z (%): 192 (100) [M^+], 160 (75), 145 (20), 134 (80), 104 (15), 91 (20), 77 (10), 65 (10), 51 (10); IR (neat): $\tilde{\nu} = 2938$, 1610, 1514, 1467, 1278, 1236, 1155, 1136, 1040, 967 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{16}O_2$: C 74.97, H 8.39; found: C 74.9, H 8.3. Data for **26**: ^{1}H NMR ($CDCl_3$, from the mixture): $\delta = 2.15$ (d, $J = 1.6$ Hz, 3 H), 3.35 (brs, 2 H), 3.90 (s, 3 H), 6.10 (d, $J = 1.6$ Hz, 1 H), 6.60–6.95 (m, 2 H), 7.25 ppm (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, from the mixture): $\delta = 13.0$ (CH_3), 37.5 (CH_2), 55.5 (CH_3), 110.1 (CH), 111.4 (CH), 119.0 (CH), 125.8, 126.4 (CH), 139.4, 146.0, 157.7 ppm; MS: m/z (%): 160 (100) [M^+], 145 (50), 129 (25), 115 (65), 102 (10), 91 (20), 77 (5), 63 (15), 51 (15), 40 (10); IR (neat, for the mixture): $\tilde{\nu} = 2948$, 1611, 1487, 1257, 1164, 1037, 975 cm^{-1}. The spectroscopic data of compound **25** were in accordance with the literature.[51]

In TFE: The reaction was carried out in the presence of TEA. After 16 h of irradiation, purification of the raw photolyzate afforded a mixture of **20** (18 mg, 6 % yield), 2-(2,2,2-trifluoroethoxy)-1,2,3,4-tetrahydro-6-methoxynaphthalene (**27**; 70 mg 17 % yield), and 1-(2,2,2-trifluoroethoxy)-1,2,3,4-tetrahydro-6-methoxynaphthalene (**28**; 78 mg, 20 % yield). Further purification of the fractions containing product **27** afforded a pure sample of such compound. Data for **27**: ^{1}H NMR ($CDCl_3$): $\delta = 1.80$–1.95 (m, 1 H), 2.05–2.15 (m, 1 H), 2.75–2.85 (m, 2 H), 2.95 (m, 1 H), 3.15 (dd, $J = 5$, 16 Hz, 1 H), 3.80 (s, 3 H), 3.85–4.00 (m, 3 H), 6.65 (d, $J = 2.7$ Hz, 1 H), 6.75 (dd, $J = 2.7$, 8.4 Hz, 1 H), 7.00 ppm (d, $J = 8.4$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 27.1$ (CH_2), 27.9 (CH_2), 34.3 (CH_2), 55.1 (CH_3), 65.8 (q, $J = 34$ Hz), 77.3 (CH), 112.2 (CH), 113.1 (CH), 124.6 (q, $J = 274$ Hz, CF_3), 125.9, 130.1 (CH), 136.6, 157.8 ppm; IR (neat): $\tilde{\nu} = 2933$, 1610, 1505, 1465, 1277, 1236, 1158, 1125, 1039, 968 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{18}F_3O_2$: C 61.08, H 6.59; found: C 61.2, H 6.4. Data for **28**: ^{1}H NMR ($CDCl_3$, from the mixture): $\delta = 1.80$–1.95 (m, 1 H), 2.00–2.15 (m, 1 H), 2.60–3.10 (m, 4 H), 3.80 (s, 3 H), 3.85–4.00 (m, 2 H), 4.60 (t, $J = 4.4$ Hz, 1 H), 6.65 (m, 1 H), 6.80 (dd, $J = 2.7$, 8.4 Hz, 1 H), 7.30 ppm (d, $J = 8$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, from the mixture): $\delta = 18.2$ (CH_2), 27.9 (CH_2), 29.2 (CH_2), 55.1 (CH_3), 66.0 (q, $J = 34$ Hz), 76.9 (CH), 112.1 (CH), 113.4 (CH), 124.6 (q, $J = 175$ Hz, CF_3), 125,9, 130.1 (CH), 136.6, 159.2 ppm; IR (neat, for the mixture): $\tilde{\nu} = 2933$, 1610, 1501, 1465, 1277, 1252, 1157, 1123, 1038, 968 cm^{-1}.

In cyclohexane: After 16 h of irradiation, purification (C_6H_{12} as the eluant) of the raw photolyzate afforded of a mixture (124 mg) containing **20** (56 mg, 22 % yield) and **21** (34 mg, 22 % yield).

Photochemical reactions of 3-allyloxy-4-chloroanisole (4)

In ethyl acetate: After 16 h of irradiation, purification (C_6H_{12} as the eluant) of the raw photolyzate afforded 3-chloromethyl-2,3-dihydro-6-methoxybenzofuran (**29**; 149 mg, 50 % yield, colorless oil) and 6-methoxy-3-methylbenzofuran (**30**; 7 mg, 3 % yield, see below). Data for **29**: ^{1}H NMR ($CDCl_3$): $\delta = 3.50$–3.60 (m, 1 H), 3.65–3.80 (m, 2 H), 3.80 (s, 3 H), 4.50–4.60 (m, 1 H), 4.65–4.75 (m, 1 H), 6.40–6.50 (m, 2 H), 7.10 ppm (d, $J = 8.1$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 43.9$ (CH), 46.3 (CH_2), 55.0 (CH_3), 75.3 (CH_2), 96.0 (CH), 106.0 (CH), 118.5, 124.3 (CH), 160.9, 161.2 ppm; IR (neat): $\tilde{\nu} = 2957$, 1621, 1598, 1498, 1283, 1198, 1147 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{11}ClO_2$: C 60.46, H 5.58; found: C 60.4, H 5.5.

In methylene chloride: After 32 h of irradiation (77 % of consumption of **4**), purification of the raw photolyzate yielded **29** (115 mg, 50 % yield) and **30** (36 mg, 19 % yield, colorless oil). Both yields were calculated on consumed **4**. The spectroscopic data of compound **30** were in accordance with the literature.[52] elemental analysis calcd (%) for $C_{10}H_{10}O_2$: C 74.06, H 6.21; found: C 74.1, H 6.3.

In acetonitrile: The reaction was carried out in the presence of Cs_2CO_3. After 22 h of irradiation purification of the raw photolyzate yielded **29** (92 mg 31 % yield) and 4-methoxyphenol (**31**; 23 % yield) which was determined by GC analysis.

In water/acetonitrile 1:3: After 40 h of irradiation (73 % of consumption of **4**), purification of the raw photolyzate yielded **29** (83 mg, 38 % yield) and **30** (17 mg, 10 % yield, colorless oil). Both yields were calculated on consumed **4**.

In methanol: After 9 h of irradiation purification of the raw photolyzate yielded **29** (30 mg, 10 % yield) and **31** (78 % yield), which was determined by GC analysis.

In TFE: The reaction was carried out in the presence of Cs_2CO_3. After 42 h of irradiation purification of the raw photolyzate yielded **29** (18 mg, 6 % yield) as the only isolated product.

In TFE in the presence of benzene: The reaction was carried out in the presence of Cs_2CO_3. After 42 h of irradiation in the presence of benzene (1 M), purification of the raw photolyzate yielded 2-allyloxy-4-methoxybi-

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phenyl (**33**; 97 mg, 27% yield) as the only isolated product. ^{1}H NMR ($CDCl_3$): $\delta = 3.80$ (brs, 3H, OCH_3), 4.50–4.60 (m, 2H, CH_2), 5.20–5.40 (m, 2H, CH_2), 5.90–6.15 (m, 1H), 6.55–6.75 (m, 1H), 7.10–7.55 ppm (m, 7H); ^{13}C NMR ($CDCl_3$): $\delta = 54.9$ (CH_3), 68.7 (CH_2), 100.0 (CH), 104.6 (CH), 113.9 (CH), 114.4, 116.5 (CH_2), 126.0 (CH), 127.4 (CH), 128.7 (CH), 129.0 (CH), 130.8 (CH), 132.7 (CH), 137.9, 155.9, 159.6 ppm; IR (neat): $\tilde{\nu} = 2941$, 1590, 1492, 1312, 1201, 1167, 1033 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{16}O_2$: C 79.97, H 6.71; found: C 80.0, H 6.8.

In cyclohexane: After 16 h of irradiation, purification of the raw photolyzate yielded **29** (211 mg, 71% yield) as the only isolated product.

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