

Synthesis of 1,3-Dioxan-2-ones by Photo-Aerobic Selenium- π -Acid Multicatalysis

Kilian A. Müller,^[a] Carolin H. Nagel,^[a] and Alexander Breder*^[a]

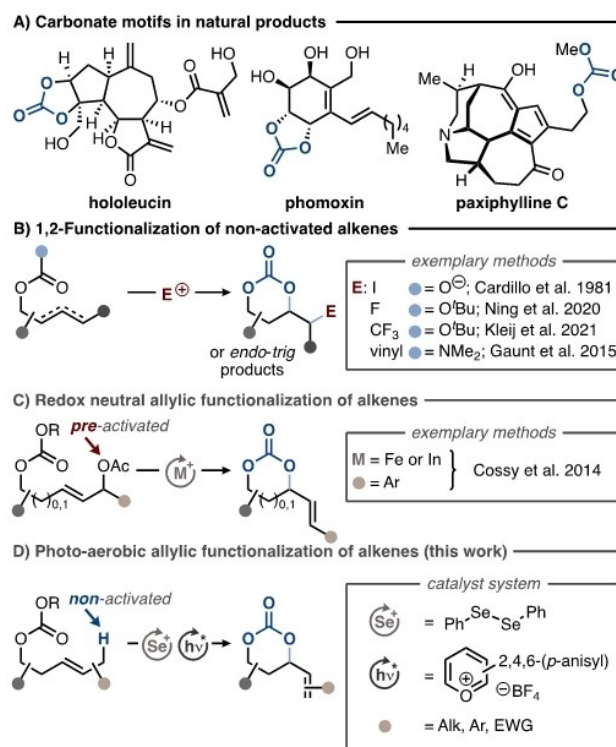
In memory of Professor Klaus Hafner

An expedient method for the synthesis of cyclic carbonates from homoallylic carbonic acid esters by means of photo-aerobic selenium- π -acid multicatalysis is reported. Until now, conceptually related methods commonly relied either on the stoichiometric addition of electrophiles onto the substrate's alkene moiety or the presence of pre-installed leaving groups in allylic position of said alkene to – in part, catalytically – initiate

an intramolecular attack by an adjacent carbonic acid ester group. In sharp contrast, the current study shows that the C–C double bond of homoallylic carbonic acid esters can be directly activated by the catalytic interplay of a pyrylium dye and a diselane using ambient air as the sole oxidant and visible light as an energy source.

Introduction

Carbonic acid esters play a critical role in numerous scientific disciplines such as material sciences (e.g., polycarbonates),^[1] natural product research (Scheme 1A),^[2] and synthetic methodology (Scheme 1B–D).^[3] With regard to the last category, cyclic carbonic acid esters such as 1,3-dioxolan-2-ones and 1,3-dioxan-2-ones have increasingly become a focal point of methodological efforts, since such motifs are frequently shown to serve as lynchpins for the stereoselective synthesis of 1,2-^[4,5] and 1,3-diols.^[6,7] From a synthetic viewpoint, the olefinic double bond has emerged as a tactically privileged functional group for the construction of cyclic carbonic acid esters by – in part, stereocontrolled – intramolecular cyclizations of carbonate nucleophiles onto inherently or catalytically activated C–C π -bonds.^[3,5] Cardillo et al. elegantly harnessed this feature of alkenes by treating allylic and homoallylic alcohols with strong bases in the presence CO₂ and elemental iodine to furnish the corresponding iodocarbonates (Scheme 1B).^[3a] A similar concept has been recently reported by Ning et al., who demonstrated the 6-*endo*-trig fluoro-cyclization of allylic carbonates using *l,l*-difluoro(phenyl)- λ^3 -iodane as the terminal oxidant.^[3b] Gaunt et al. and Kleij et al. expanded this strategy into C–C bond-forming protocols by using vinyl and trifluoromethyl cation synthons, respectively.^[3f,i] As a tactical counter design, Cossy



Scheme 1. Carbonic acid esters in nature and synthetic methodology.

[a] K. A. Müller, C. H. Nagel, Prof. Dr. A. Breder
Faculty of Chemistry and Pharmacy
University of Regensburg
Universitätsstraße 31, 93053 Regensburg (Germany)
E-mail: alexander.breder@ur.de

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et al. employed allylic and homoallylic carbonates in which the olefinic double bond was pre-activated by the presence of an acetate nucleofuge located at the allylic position opposite to the carbonate unit (Scheme 1C).^[3j] These precursors underwent stereoselective cyclization upon exposure to iron(III) or indium(III) Lewis-acid catalysts. The authors reported that an aryl group at the acetoxyated carbon atom (Scheme 1C, beige sphere) was indispensable for the transient formation of a resonance-stabilized allylic cation intermediate, which was subsequently intercepted by the neighboring carbonate nucle-

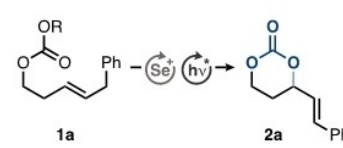
ophile. To showcase the synthetic value of their protocol, this technique was later exploited by the same research group in the total synthesis of diarylheptanoid (3*S*,5*S*)-alpinikatin.^[39] The high utility and versatility reflected by each of these and related methods^[8] emphasize their immense potential in contemporary organic synthesis and thereby foreshadow the continuing need for complementary tactics to expeditiously access cyclic carbonic acid esters.

With regard to step and redox economy as well as carbon efficiency,^[9,10] we considered the direct redox-catalytic activation of an olefinic π -bond to initiate a nucleophilic attack by an adjacent carbonate group as strategically sound (Scheme 1D). This reaction design would obviate the need for any pre-installed leaving groups and the incorporation of unwanted components from the former electrophile into the target structure (e.g., halogen residues), which may entail a laborious removal of these auxiliary groups from the product. On the one hand, such a protocol may allow for the facile installation of the desired 1,3-dioxygenation motif while simultaneously offering an opportunity for further derivatization of the restored alkene moiety. On the other hand, a judicious orchestration of all catalytic parameters may enable the use of nonhazardous, nonpolluting, and even gratuitous terminal oxidants such as ambient air. As a result of these considerations, we disclose herein an unprecedented synthetic entryway toward 1,3-dioxan-2-ones from unbranched homoallylic carbonates by means of photo-aerobic selenium- π -acid multicatalysis.^[11]

Results and Discussion

On the basis of our previous investigations on selenium- π -acid catalyzed redox functionalizations of simple alkenes and alkynes,^[12,13] we became interested in the question whether non-protic nucleophiles such as homoallylic carbonates would undergo an intramolecular oxidative coupling reaction to furnish the corresponding cyclocarbonates. In contrast to protic nucleophiles (e.g., carboxylic acids or alcohols), which can be modulated in terms of their nucleophilicity by suitable bases, the non-protic carbonic acid ester group needs to inherently possess sufficient nucleophilicity from the outset to participate in the envisioned cyclization event. Literature precedence^[3b,f] suggested that Boc-protected (Boc = *tert*-butyloxycarbonyl) homoallylic alcohols might display the aspired reactivity. However, in preliminary experiments these substrates failed to give any of the desired product. Consequently, we replaced the *t*-Bu group for a *p*-methoxybenzyl (PMB) residue with the expectation that it would cleave more easily from the carbonate moiety during the reaction. Thus, when homoallylic carbonate **1a** was exposed to 10 mol% of both (SePh)₂ and 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (TAPT) in MeCN at 465 nm irradiation under ambient air, target dioxanone **2a** was obtained in 27% (Table 1, entry 1). Variation of the catalyst loading (entries 2–5) revealed that 5 mol% of each catalyst resulted in an improved yield of 41% (entry 5). During these experiments we noticed a correlation between the stirring rate and the yields. As a consequence, we performed the title

Table 1. Optimization of catalytic reaction parameters.^[a]



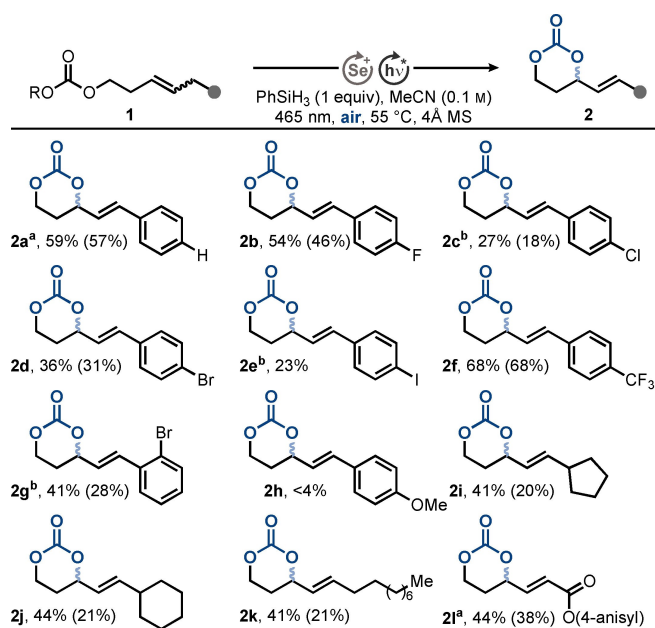
Legend:
SC: (Se)₂ = (ArSe)₂; x mol%
PC: (hv) = photocat.; y mol%

Entry	Solvent	SC/[x]	PC/[y]	Additive	Yield
1	MeCN	SC-1/10	PC-1/10	–	27%
2	MeCN	SC-1/10	PC-1/5	–	27%
3	MeCN	SC-1/10	PC-1/2.5	–	28%
4	MeCN	SC-1/5	PC-1/2.5	–	22%
5	MeCN	SC-1/5	PC-1/5	–	41%
6	acetone	SC-1/5	PC-1/5	–	0%
7	MeNO ₂	SC-1/5	PC-1/5	–	6%
8	(CH ₂ Cl) ₂	SC-1/5	PC-1/5	–	0%
9	THF	SC-1/5	PC-1/5	–	0%
10	HFIP	SC-1/5	PC-1/5	–	0%
11	MeCN	SC-1/5	PC-2/5	–	20%
12	MeCN	SC-1/5	PC-3/5	–	0%
13	MeCN	SC-2/5	PC-2/5	–	15%
14	MeCN	SC-2/5	PC-1/5	–	14%
15	MeCN	SC-3/5	PC-2/5	–	6%
16	MeCN	SC-2/5	PC-4/5	–	5%
17	MeCN	SC-1/5	PC-1/5	PhSiH ₃	53%
18 ^[b]	MeCN	SC-1/5	PC-1/5	PhSiH ₃	40%

[a] Reactions were run on a 0.5 mmol scale in the given solvent (0.1 M) and catalyst loadings. The mixture was irradiated for 16 h at 465 nm under an atmosphere of air (balloon). [b] reaction time = 41 h. Legend: SC = selenium catalyst; SC-1 = (PhSe)₂; SC-2 = (4-MeOC₆H₄Se)₂; SC-3 = (2,6-(MeO)₂C₆H₃Se)₂; PC = photoredox catalyst; PC-1 = TAPT; PC-2 = 10-(3,5-dimethoxyphenyl)-1,3,6,8-tetramethoxy-9-mesitylacridin-10-ium tetrafluoro-borate; PC-3 = 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN); PC-4 = 2,4,6-tris(diphenylamino)-5-chloro-isophthalonitrile.

reaction at a stirring rate between 500 rpm and 750 rpm. Changing to other solvents such as acetone, nitromethane, 1,2-dichloroethane, or THF furnished target **2a** either in low yields or resulted in mere substrate decomposition (entries 6–10). We also screened for other selenium- π -acid precursors and photoredox catalysts with lower redox potentials to avoid the risk of direct alkene oxidation (entries 11–16). However, none of the tested catalysts gave better yields. Since we suspected that the cleavability of the PMB group might be critical for the success of the title reaction, we screened for scavenging additives that were intended to intercept the benzylium ion released from the carbonate moiety (for details, see Supporting Information).^[14] Towards this end, 1 equiv. of PhSiH₃ increased the yield up to 53% at 71% substrate conversion after 16 h (entry 17). Extending the reaction time to full conversion (41 h) gave only 40% of **2a**, indicating that the product suffered some degradation under operative conditions. When the reaction was monitored by ¹H NMR spectroscopy, we found that the product yield reached a maximum of 59% after 24 h and declined after 38 h.

With optimized reaction conditions determined, we next set out to evaluate the scope of the title reaction (Scheme 2). A series of unbranched homoallylic carbonates with different functional groups such as halides, ether, and ester moieties was tested. In general, substrates **1b–e** and **1g**, which all embed halogenated aryl residues in the carbon scaffold, were tolerated and predominantly resulted in yields ranging from 8% to 46% (23% to 54% determined by ¹H NMR spectroscopy). Notably,



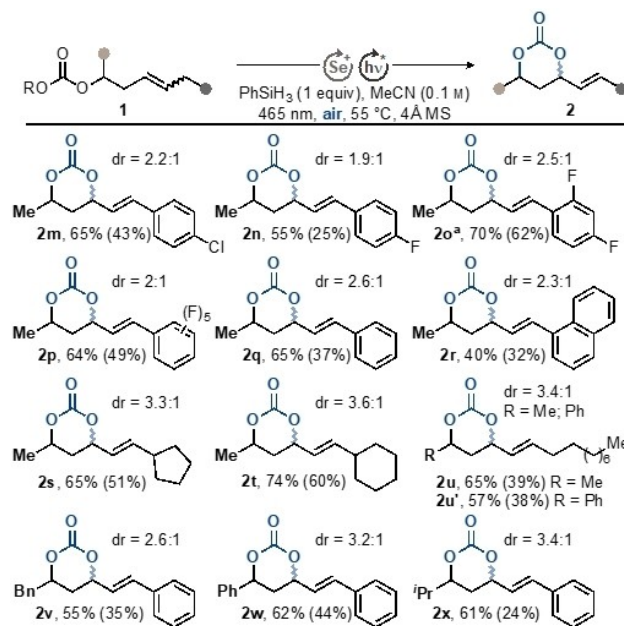
Scheme 2. Conversion of homoallylic, primary carbonates **1** ($n = 1$ mmol). **Se-Cat. 1** = 5 mol%; TAPT = 5 mol%. Reaction time = 24 h to 70 h, yields without brackets were determined by ¹H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Yields with brackets refer to isolated compounds. [a] 1,3-Trimethoxybenzene or 1,3-nitrobenzene used as internal standards. [b] Reaction times longer than 70 h. All products **2** were obtained as *E*-isomers.

changing the position of the halogen substituents from the *para*- (**2d**) to the sterically more demanding *ortho*-position (**2g**) did not significantly affect the product yield. In addition to halogen substituents, we also tested –M and +M-substituents on the arene ring such as 4-trifluoromethyl (**2f**) and 4-methoxy (**2h**) groups, respectively. While product **2f** was isolated in 68% yield, which was significantly higher than dioxanones **2a–e**, product **2h** was observed only in trace amounts (Scheme 2). The latter finding is most likely due to the sensitivity of the newly formed olefinic double bond under the title conditions.

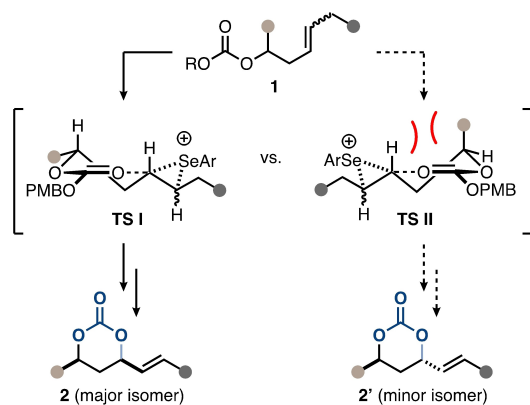
Next, we investigated substrates possessing aliphatic residues and a carboxylic ester group at their termini (**1i–l**). Members of this section of the scope were obtained in isolated yields ranging from 20% to 38% (41% to 44% determined by ¹H NMR spectroscopy). In general, cyclizations of unbranched carbonic acid esters seem to be significantly hampered by side reactions, since full conversion of the starting materials was observed in virtually all cases, while target structures **2b–l** were obtained only in moderate yields. On the one hand, we attribute this observation to the relatively low nucleophilicity of the carbonic ester functionality. On the other hand, we suspect the high rotational flexibility of unbranched starting materials to entropically disfavor the adoption of a suitable conformation leading to efficient cyclization. The combination of these two factors presumably is the reason why oxidative cyclizations of primary homoallylic carbonic acid esters were not reported for other catalytic or stoichiometric systems. Instead, previous procedures predominantly predicated on the use of either

stronger nucleophiles, such as carbonate anions, carbamates, phosphoric, and phosphonic acid esters,^[3a,3h,3l,8a,13,14] or substrates that contain the carbonic ester group in a non-primary homoallylic position.^[3g] Against this background, the scope shown in Scheme 2 underscores the fact that the title procedure leads to reasonable reaction outcomes even with more difficult substrates.

To evaluate whether secondary homoallylic carbonic acid esters would result in a) improved yields in comparison to their primary analogs and b) some degree of stereoselection, we synthesized a representative set of acyclic carbonates **1m–x** and subjected it to our title conditions (Scheme 3). As expected, secondary substrates performed noticeably better, as was first observed in the case of halogenated products **2m–p** (yield range: 25% to 62%). The stereoselection of the methyl substituent at the carbinolic carbon atom ranged from diastereomeric ratios (d.r.) of 1.9:1 to 3.6:1. These d.r. values are similar to those reported by Bartlett et al. (4:1 to 10:1)^[8b] for cognate cyclizations of branched homoallylic carbonic acid esters and Cossy et al. (2.4:1)^[3g] for the intramolecular allylic substitution of acetate nucleofuges by carbonate nucleophiles. It is noteworthy that in our hands the d.r. values of many products increased upon workup and column chromatography while the respective yields decreased, as can be seen from the differences between isolated yields and those determined by ¹H NMR spectroscopy from the crude mixtures. We suspect that in those cases one diastereomer is more prone to hydrolytic decomposition than the other one.



Scheme 3. Conversion of homoallylic, secondary carbonates **1** ($n = 1$ mmol). **Se-Cat. 1** = 5 mol%; TAPT = 5 mol%. Reaction time = 37 h to 41 h, yields without brackets were determined by ¹H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Yields with brackets refer to isolated compounds. Diastereomeric ratios (d.r.) were determined by ¹H NMR spectroscopy of crude products. [a] Reaction times longer than 41 h. All products **2** were obtained as *E*-isomers.



Scheme 4. Mechanistic rationale for the observed *cis*-diastereoselectivity under kinetic conditions.

Branched substrates **1 q–t**, which possess non-halogenated arene and alkyl moieties on the carbonated C-atom, also provided better yields than their unbranched counterparts (Scheme 3). The corresponding products were isolated in 24% to 60% yield and with d.r. values of up to 3.6:1. As was exemplarily analyzed by 2D NMR spectroscopy using product **2 q**, cyclizations occur with *cis*-selectivity (Scheme 4).^[15] To obtain a clearer picture of potential factors governing the diastereomeric outcome of the title reaction, we studied the influence of substituents with differing steric demand at the carbonated terminus of precursors **1**. For this purpose, compounds **1 u–x** were subjected to the title conditions and their d.r. values were compared with that of carbonate **2 q**. As expected, the diastereoselectivity increased with rising steric demand of the respective terminal group, albeit only to a moderate extent. More specifically, while carbonates **2 q** and **2 v**, which possess α -unbranched terminal substituents (i.e., Me and Bn, respectively), each gave a dr of 2.6:1, their α -branched analogs **2 w** and **2 x** exhibited diastereomeric ratios of 3.2:1 and 3.4:1, respectively. These observations correlate well with cognate cyclization reactions reported in the literature,^[39–41] thus indicating that the conversion of **1** into **2** might proceed through similar transition state geometries (Scheme 4). We therefore speculate that the substituent at the carbonated terminus preferably adopts a pseudo-equatorial orientation in the transition state to avoid 1,3-diaxial interactions (TS I vs. TS II). This tendency increases with growing steric demand of this particular group.

Conclusion

In summary, we have developed a new protocol for the synthesis of 4-mono- and 4,6-disubstituted 1,3-dioxan-2-ones from unbranched and branched carbonic acid esters, respectively, by photo-aerobic selenium- π -acid multicatalysis. The carbonate products were formed in yields of up to 82% and, in the case of 4,6-disubstituted dioxanones, with a pronounced *cis*-diastereoselectivity. Key advantages of the title protocol are

the applicability of ambient air as the terminal oxidant and visible light as an energy source, which allows to avoid the use of highly reactive or even corrosive – and therefore sensitive – reagents and reactants such as elemental iodine or hypervalent iodanes.

Experimental Section

6-(2,4-Difluorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate **1 o** (377 mg, 1.00 mmol, 1.00 equiv.), 2,4-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (24.8 mg, 51.0 μ mol, 5 mol%), diphenyldiselenide (16.1 mg, 51.6 μ mol, 5 mol%) and phenylsilane (0.12 mL, 1.01 mmol, 1.01 equiv.) were added in a 100 mL flask and dissolved in MeCN (10 mL, 0.1 M). After the addition of 4 Å molar sieves (10 mg, 10 mg/mmol), the mixture was irradiated with blue light (465 nm, 0.35 mA) at a temperature of 55 °C and an atmosphere of air for 62 h. The mixture was concentrated and separated between water (30 mL) and EtOAc (30 mL). After extraction with EtOAc (3 \times 20 mL) and washing with water (2 \times 30 mL) and brine (1 \times 20 mL), the residue was dried over Na₂SO₄ and purified by column chromatography (PE/Et₂O 1:2) to yield 0.157 g (0.618 mmol, 62%) of (*E*)-4-(2,4-difluorostyryl)-6-methyl-1,3-dioxan-2-one **2 o** as a yellowish solid (d.r. = 2.5:1).

TLC: R_f = 0.12 (1:2 PE/Et₂O). IR (ATR): γ [cm⁻¹] = 3440, 2982, 2937, 1737, 1614, 1502, 1431, 1394, 1275, 1238, 1197, 1141, 1092, 969, 850, 813, 768, 731. ¹H NMR (400 MHz, Chloroform-*d*): δ [ppm] = 7.41 (td, J = 8.4, 6.4 Hz, 1H, B/A), 6.94–6.70 (m, 3H), 6.23 (2 \times dd, J = 16.1, 5.9 Hz, 1H, B/A), 5.23 (d, J = 5.4 Hz, 1H, A), 5.07 (ddd, J = 10.6, 6.7, 3.3 Hz, 1H, B), 4.77–4.58 (m, 1H, B/A), 2.31–2.06 (m, 1H, B/A), 1.84 (dt, J = 13.8, 11.6 Hz, 1H, B/A), 1.51–1.41 (m, 3H, B/A). ¹³C NMR (101 MHz, Chloroform-*d*): δ [ppm] = 148.8 (B), 148.7 (A), 128.9 (dd, J = 9.6, 5.0 Hz, C–F, B/A), 127.4 (dd, J = 5.6, 2.2 Hz, C–F, B/A), 125.5 (B/A), 111.8 (dt, J = 21.3, 1.9 Hz, C–F, B/A), 104.3 (t, J = 25.7 Hz, C–F, B/A), 78.9 (B/A), 77.2 (B), 76.3 (A), 75.1 (B), 72.5 (A), 35.3 (B), 33.1 (A), 21.2 (B), 20.9 (A). ¹⁹F{¹H} NMR (376 MHz, Chloroform-*d*): δ [ppm] = –109.6 (d, J = 8.0 Hz, B), –109.7 (d, J = 8.1 Hz, A), –112.8 (d, J = 8.1 Hz, A), –113.3 (d, J = 8.0 Hz, B). HRMS (ESI) calcd. for [C₁₃H₁₂F₂NaO₃]⁺ (M + Na⁺): m/z = 277.0647, found 277.0649.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: alkenes · allylic oxidation · photoredox catalysis · selenium- π -acid catalysis · 1,3-dioxan-2-ones

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