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Catalytic Coupling of Carbon Dioxide with Terpene Scaffolds: Access to Challenging Bio-Based Organic Carbonates

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Abstract: The challenging coupling of highly substituted terpene oxides and carbon dioxide into bio-based cyclic organic carbonates catalyzed by Al(aminotriphenolate) complexes, is reported herein. Both acyclic as well as cyclic terpene oxides were used as coupling partners, showing distinct reactivity/selectivity behavior. Whereas cyclic terpene oxides showed excellent chemo-selectivity towards the organic carbonate product, acyclic substrates exhibited poorer selectivities due to concomitant epoxide rearrangement reactions and the formation of undesired oligo/polyether side products. Considering the challenging nature of these coupling reactions, the isolated yields of the targeted bio-carbonates are reasonable and in most cases in the range 50–60%. The first crystal structures of tri-substituted terpene based cyclic carbonates are reported and their stereo-connectivity suggests that their formation proceeds through a double inversion pathway.

Introduction

The conversion of carbon dioxide (CO₂) into useful organic products is a prominent strategy towards the valorization of this renewable carbon-based feed stock.^[1] Despite the exciting progress in the area of catalytic conversion of CO₂ into various products such as polymers,^[2] synthetic fuels^[3] and fine-chemicals,^[4] a remaining challenge in the area of CO₂ conversion is represented by the limited number of chemical functionalities that can be derived from this C₁ building block. So far, most efforts have been devoted to CO₂ conversion via reductive and non-reductive coupling chemistry. Within the latter category, CO₂ is incorporated into an organic substrate without affecting the oxidation state of the carbon center, and the most prominent among this type of transformations is the formation of organic carbonates using epoxides as reaction partners.^[5]

The catalytic coupling of epoxides and CO₂ is an atom-efficient reaction that has been well-studied and ditto developed over the years, with important contributions to solve key

challenges associated to this process, including enhanced reactivity/selectivity,^[6] improved overall sustainability,^[7] and the development of commercially attractive, recyclable catalysts.^[8] However, there are still important open challenges in this specific area of research, including the limited number of substrates that can be used due to the lack of efficient catalytic strategies for their coupling. Highly substituted epoxides (1,3-dioxolan-2-ones) including those with a 4,5-disubstitution^[9] and 4,4',5-trisubstitution^[10] remain challenging reaction partners despite the presence of such patterns in many naturally occurring plant based organic carbonates (Figure 1).^[11]

Figure 1. Top: naturally occurring organic carbonates based on complex scaffolds. The carbonate unit is marked in blue. Below: some representative terpene scaffolds with similar di- and tri-substituted alkene units highlighted in yellow.

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We have recently become interested in the use of renewable feed stocks such as terpenes as substrates for CO₂ conversion.^[12] Terpenes, including limonene (Figure 1),^[10,13a] have increasingly found applications in polymer science and sustainable materials.^[13b] The formation of cyclic organic carbonates from terpene scaffolds ultimately results in 100% bio-derived compounds with relatively unexplored potential,^[14] and we thus set out to develop an efficient catalytic process for their formation. Here we describe the Al(III) catalysed coupling between CO₂ and

both cyclic and acyclic terpene oxides affording new bio-based carbonates. The first crystal structures of terpene derived carbonates are also presented and the observed stereo-connectivity is linked to a double inversion pathway in the coupling between the oxirane precursors and CO₂.

Results and Discussion

Terpene Carbonates with bicyclic structures. We first devoted our attention to the conversion of 1-methylcyclohexene oxide **1a** to the corresponding cyclic carbonate product **1b** via CO₂ insertion. Up to 70°C we were unable to detect any formation of cyclic carbonate **1b**. This is in line with a previously reported density functional theory analysis of the coupling between limonene oxide (LO, a structurally related trisubstituted oxirane) and CO₂, showing that the kinetic barrier towards cyclic carbonate formation (via backbiting) is comparatively high to the one associated to chain propagation.

Table 1. Screening of reaction conditions in the coupling of methylcyclohexene oxide **1a** and CO₂ to afford cyclic carbonate **1b**.^[a]

Entry	Cat [mol%]	PPNCI [mol%]	T [°C]	t [h]	Yield 1b [%] ^[b]
1	–	3.0	85	24	18
2	–	3.0	85	48	19
3	–	3.0	85	66	31
4	A , 1.0	–	85	24	0
5	A , 1.0	3.0	85	24	26
6	B , 1.0	3.0	85	24	7
7	C , 1.0	3.0	85	24	22
8	D , 1.0	3.0	85	24	17
9	A , 1.0	3.0	85	48	40
10	A , 1.0	3.0	85	66	49 ^[c]
11	A , 1.0	3.0	85	66	1 ^[d]
12	B , 1.0	3.0	85	66	34
13	A , 1.0	1.0	85	66	14

[a] Reaction conditions: 1-methylcyclohexene oxide **1a** (5 mmol), MEK (methyl ethyl ketone, 1.0 mL), $p(\text{CO}_2) = 1.0 \text{ MPa}$ (10 bar). [b] Isolated yield, selectivity for **1b** was >99% in all cases determined by ¹H NMR. [c] Note that

the NMR yield was 75%, in the absence of complex **A** the NMR and isolated yield were both 31% (see entry 3). [d] No MEK used.

Indeed, when coupling LO and CO₂ at lower temperatures (40–70°C) the only product observed was the poly(limonene)carbonate.^[12a] Hence, higher reaction temperatures were probed in order to direct the chemo-selectivity towards the cyclic carbonate product when using 1-methylcyclohexene oxide **1a**. The substrate 1-methylcyclohexene oxide **1a** was taken as a representative terpene model substrate (Table 1). Al(III) aminotriphenolate complexes **A–D** were used as catalysts together with bis(triphenylphosphine)iminium chloride (PPNCI) as the nucleophilic additive. Although in the presence of the nucleophile only (entries 1–3, Table 1) conversion to **1b** is noted, the addition of a Lewis acid (**A–D**) substantially improves the overall kinetics, most noteworthy when complex **A** is used (entries 5, 9 and 10). As expected, in the absence of PPNCI (entry 4) no conversion was noted. A lower loading of PPNCI (entry 13, 1 mol%) reduced the yield of **1b** to only 14% showing the requirement for a higher loading of the nucleophile. In the absence of solvent (MEK) virtually no conversion was obtained (see entry 11) underlining the crucial role of this solvent to accommodate appropriate mixing of all reactants. The structure of **1b** was confirmed by X-ray analysis and is depicted in Figure 2.

Figure 2. X-ray molecular structure for **1b**. Selected bond lengths (Å) and angles (°) for **1b**: C(1)–O(1) = 1.1988(18), C(1)–O(2) = 1.3442(19), C(1)–O(3) = 1.3487(18); O(2)–C(1)–O(3) = 111.47(12), O(1)–C(1)–O(2) = 124.23(14).

With these optimal conditions in hand we decided to investigate a wider scope of trisubstituted carbonates derived from cyclic epoxides based on terpene scaffolds (see Figure 3). Due to the challenging nature of these coupling reactions, conversion of the respective terpene epoxides proceeds slowly and reaction times of 66 h are typically required (Figure 3). Longer reaction times at 85°C did not improve the conversion levels and neither did higher reaction temperatures.^[15] We first examined limonene oxide (LO) as a substrate using the best conditions probed for the synthesis of **1b**. Whereas pure *trans*-LO was converted into limonene carbonate **2b** in appreciable conversion (73%) and yield (57%), the use of the pure *cis* isomer only led to 4% yield of *cis*-**3b** (by NMR) of its respective carbonate. The extreme sluggish outcome observed for CO₂ coupling with the

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above mentioned *cis*-isomer was confirmed using commercially available LO (a 60:40 *trans/cis* mixture)

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Figure 3. Investigated scope for the formation of trisubstituted bicyclic terpene carbonates. Reaction conditions (unless state otherwise): 1.0 mol% [Al^{tBu}], 3.0 mol% PPNCI, 1.0 mL MEK, 66 h, 85°C, $p(CO_2)^0 = 1.0$ MPa. The diastereo-isomeric ratios (*dr* values, major isomer indicated) and selectivity towards the carbonate products were also determined by ¹H NMR; note that the *dr* relates to the relative position of both substituents on the cyclohexyl ring. ^[a] Conversion relates to total amount of epoxide groups converted to cyclic carbonate ones determined by ¹H NMR (CDCl₃) integration, NMR yield of **6b** was 74%. ^[b] The NMR yield of **7b** was 27% with 24% of **6b** being present along with polyether by-product. ^[c] Reaction performed at 120°C. ^[d] The major stereo-isomer assignment was not possible by 1D/2D NMR due to a combination of complex patterns.

Figure 4. X-ray molecular structures for terpene carbonates *trans*-**2b**, *cis*-**5b**, **6b** and *trans*-**7b** with the adopted numbering scheme. Selected bond lengths (Å) and angles (°) for **2b**: C(2)-O(2) = 1.221(8), C(2)-O(1) = 1.326(8), C(2)-O(3) = 1.344(7); O(2)-C(2)-O(3) = 123.1(7), O(1)-C(2)-O(3) = 112.8(5); Selected data for **5b**: C(1)-O(1) = 1.200(2), C(1)-O(2) = 1.350(2), C(1)-O(3) = 1.338(2); O(2)-C(1)-O(3) = 111.73(14), O(1)-C(1)-O(2) = 123.53(17); Selected data for **6b**: C(1)-O(1) = 1.330(7), C(1)-O(2) = 1.197(7), C(1)-O(3) = 1.333(8), C(6)-O(4) = 1.448(9); O(1)-C(1)-O(3) = 112.6(5), O(1)-C(1)-O(2) = 124.5(7); Selected data for **7b**: C(1)-O(1) = 1.336(7), C(1)-O(2) = 1.474(6), C(1)-O(3) = 1.354(7), C(11)-O(4) = 1.362(7), C(11)-O(5) = 1.182(8), C(11)-O(6) = 1.332(7); O(1)-C(1)-O(3) = 111.3(5), O(1)-C(1)-O(2) = 124.6(5), O(4)-C(11)-O(5) = 110.7(6), O(4)-C(11)-O(6) = 124.0(6).

Table 2. Screening and optimization of reaction conditions in the coupling of acyclic terpene-based epoxides **9a–14a** and CO₂ to afford their cyclic carbonate products **9b–14b**.^[a] Note that the commercial olefinic, terpene precursors are drawn together with their epoxidized derivatives.

Entry	Substrate	Cat [mol%]	PPNCI [mol%]	<i>p</i> (CO ₂) [MPa]	T [°C]	t [h]	Epoxide [%] ^[b]	AA [%] ^[b]	K [%] ^[b]	CC [%] ^[b]	PE [%] ^[b]
1	9a	Al ^{Cl} , 1.0	3.0	1.0	70	66	7	6	9	31	21
2	9a	–	3.0	1.0	70	66	57	2	<1	17	8
3	9a	Al ^{Cl} , 1.0	3.0	1.0	85	66	22	5	3	20	35
4 ^[c]	9a	Al ^{Cl} , 1.0	3.0	1.0	85	66	<1	12	14	52	24
5	9a	–	3.0	1.0	85	66	17	19	7	19	2
6	9a	Al ^{Cl} , 1.0	3.0	3.0	70	66	16	<1	<1	45	22
7	9a	Al ^{Cl} , 1.0	3.0	4.0	70	66	23	<1	<1	36	36
8	9a	–	3.0	4.0	70	66	27	2	<1	15	23
9 ^[c]	9a	Al ^{Cl} , 1.0	3.0	4.0	85	66	3	7	7	56	28
10	14a	Al ^{tBu} , 1.0	3.0	1.0	85	24	23	2	6	51	13
11	14a	Al ^{Cl} , 1.0	3.0	1.0	85	24	40	2	9	31	16
12 ^[c]	10a	Al ^{Cl} , 1.0	3.0	4.0	85	66	8	2	8	47	35
13 ^[c]	11a	Al ^{Cl} , 1.0	3.0	4.0	85	66	5	5	7	61	16
14 ^[c]	12a	Al ^{Cl} , 1.0	3.0	4.0	85	66	3	4	3	71	9
15 ^[d]	13a	Al ^{Cl} , 1.0	3.0	1.0	85	66	<1	15	16	19	30

[a] Reactions conditions: substrates **9a–14a** (2.5 mmol), MEK (methyl ethyl ketone, 0.5 mL), pressure/time/temperature and catalyst/co-catalyst loadings indicated.

[b] NMR yields from ¹H NMR analysis using mesitylene as internal standard; for the use of **9a**: allylic alcohol (AA) peak at δ = 4.93 ppm (septet) and 4.84 ppm (quintet), ketone (K) peak at δ = 2.61 ppm (quintet), epoxide at δ = 2.68 ppm (triplet), cyclic carbonate (CC) peak at δ = 4.20 ppm (multiplet) and oligo/polyether peak in the region δ = 3.3–3.8 ppm. [c] Substrate amount was 5.0 mmol. [d] The ¹H NMR spectrum of the crude mixture showed apart from the CC product **13b** a number of peaks in the region 5.0–5.5 ppm attributed to unknown olefin-containing by-products.

resulting in the almost exclusive formation of *trans*-**4b** from *trans*-LO in 43% isolated yield. The proposed *trans*-connectivity pattern in **2b** was confirmed by NMR analysis and further substantiated by X-ray diffraction (see Figure 4). As far as we know, Figure 4 represents the first structurally characterized terpene based

carbonates. The *trans* nature of carbonate **2b** enforces the idea that these conversions occur with complete retention of configuration as would be expected from a double inversion pathway.^[9b,12c] Interestingly, we previously observed that *cis*-LO reacts faster than its *trans* isomer in copolymerization reactions

resulting in an almost exclusive formation of a *trans* configured copolymer (*i.e.* a formal inversion occurred). Conversely, at higher temperatures (85°C) cyclic carbonate formation starting from the *trans* isomer seems to be the favoured process (*cf.*, formation of *trans-2b* and *trans-4b*, Figure 3). The observed requisite for higher reaction temperatures in the case of cyclic carbonate formation from LO is in agreement with the higher computed kinetic barriers compared with the corresponding copolymerization process.^[12a]

Coupling between CO₂ and other (bi)cyclic terpene oxides (including carvone oxide, limonene diepoxide and menthene oxide) exhibited a similar reactivity giving the respective terpene (mono)carbonates **5b**, **6b** and **8b** in 45–52% yield and high chemo-selectivity.^[16] We also attempted to optimize the synthesis of limonene bis-carbonate **7b** (27%) using more forcing reaction conditions (120°C) but at the cost of the chemo-selectivity. This is likely due to an observed increase of the viscosity of the reaction mixture during the reaction of limonene diepoxide, limiting the diffusion of CO₂ towards the reactive centre; the presence of significant amounts of oligo/polyether product as determined by ¹H NMR is in line with this assumption (see Supporting Information for details). The molecular structures of terpene (bis)carbonates **2b**, **5b**, **6b** and **7b** were determined by X-ray crystallography and confirmed in all cases their proposed formulations. Notably, as far as we know, these X-ray analyses represent the first ones reported for this family of bio-based carbonates, and bis-carbonate **7b** was for the first time isolated and fully characterized.^[10c]

Formation of Acyclic Terpene Carbonates. We next turned our focus on the formation of terpene carbonates based on acyclic scaffolds. Our investigation started with the epoxide derived from citronellyl acetate **9a** (Table 2) using the optimal conditions developed for the synthesis of most of the bicyclic terpene carbonates (*i.e.*, 85°C, 1.0 MPa, 66 h; 3.0 mol% PPNCI) but using AlCl₃ (1 mol%) as the Lewis acid.^[17] Whereas the conversion of **9a** already proceeds at 70°C (entry 1) with a 31% NMR yield for the corresponding cyclic carbonate **9b**, at 85°C (entry 3) we unexpectedly observed a poorer outcome in terms of chemo-selectivity. Increasing the scale of the reaction (entry 4) did result in further improvement, but a combination of the latter with a higher applied CO₂ pressure (entries 6, 7 and 9; 3.0–4.0 MPa) gave slightly more satisfactory results observing formation of the corresponding cyclic carbonate in 56% NMR yield (51% isolated, Figure 5) while further suppressing by-product formation. Notably, the reaction performed with only the nucleophilic additive (PPNCI) proceeded with significantly lower efficiency (*cf.*, entries 2 and 8).

It should be noted that the overall chemo-selectivity towards the carbonate **9b** was much poorer than the ones observed starting from the aforementioned bicyclic terpene oxides.^[18] Beside the formation of substantial amount of oligo/polyether (Table 2, entry 9, 28%; **9e**),^[19] the formation of two other side-products was noted. These side-products were isolated and fully characterized for the citronellyl acetate case (see Experimental Section and Supporting Information for details), and were unambiguously identified as an allylic alcohol (**9c**) and a ketone (**9d**), both arising from the rearrangement of the starting epoxide **9a** (see Figure 6). The allylic alcohol **9c** may arise from a

phenolate-assisted rearrangement of the epoxide **9a**; such conversions have precedence though are typically carried out with strong bases.^[20] Additionally, Lewis acid induced Meinwald type rearrangement of epoxides to ketones has been well-established.^[21]

Figure 5. Schematic structures of the terpene derived carbonates **9b–14b**, their isolated yields after chromatographic purification and diastereo-isomeric ratios (*dr*) for **9b** and **11b**. For terpene carbonates **10b** and **12b** the amount of (*E*) and (*Z*) isomers, respectively, was >98%.

Figure 6. ¹H NMR trace (CDCl₃, region 2.0–5.1 ppm) for the crude product obtained in the conversion of terpene oxide **9a** and the assigned peaks, MEK stands for methylethyl ketone. Note that the R group in the schematic figures represents a –CH₂CH₂CH(Me)CH₂CH₂OAc side chain. For a full NMR trace see the Supporting Information.

In order to rule out the possibility that the terpene scaffold itself induces the aforementioned side-product formation, we carried out the synthesis of the non-functionalized, tri-substituted cyclic carbonate **14b** derived from trimethyloxirane **14a**: in essence the same product distribution was observed (Table 2, entries 10 and 11, Figure 5) confirming that side-product formation does not depend on the nature of the terpene scaffold. Furthermore, the less polar and more volatile nature of **14a** seem

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to influence the course of the coupling reaction as for this substrate the use of the Al^{tBu} complex gave better results (Table 2, entries 10 and 11).

Having determined the optimized conditions for the preparation of acyclic terpene carbonates (Table 2, entry 9) we then extended the scope of these transformations to terpene oxides **10a–13a** which were converted into the respective cyclic carbonate products **10b–13b** (entries 12–15). In general, apart from the desired carbonate products, similar distributions of side-products (allylic alcohol, ketone and oligo/polyether) were observed, together with small amounts of the starting material. The desired cyclic carbonate products were conveniently isolated by column purification of the crude mixtures in yields of up to 61% (for **11b** and **12b**; Figure 5). Notably, using a myrcene based scaffold (**13b**) led to the formation of a complex reaction mixture as other side reactions involving the conjugated double bonds occurred. Indeed, we were not able to isolate a pure sample of **13b** using chromatographic separation as further degradation occurred during the purification step. It is well-known that isoprenes show good polymerization potential in the presence of Lewis acids^[22] and this subunit is also present in **13b** (highlighted in green). Thus, it seems reasonable to assume that further impurities to the ones reported in Table 2 (entry 15) may also be ascribed to oligo-myrcene species (see Supporting Information for details) resulting from diene activation catalysed by complex **B**.

The significant by-product formation generally observed for the synthesis of acyclic terpene carbonates **9b–14b** as opposed to the chemo-selective formation of bicyclic carbonate structures **1b–5b** and **8b** can be explained taking into account the different transformations involving the metal-alkoxide intermediate formed after nucleophilic ring-opening of the epoxide group.^[23] In particular, it should be noted that polyether formation remains a competitive process even for CO_2 coupling reactions with acyclic substrates carried out at higher pressure (4.0 MPa, cf. entry 4 and 9, Table 2). This observation suggests that, after initial coordination of the epoxide to the Lewis acid catalyst and subsequent nucleophile-assisted ring opening, acyclic substrates favour the insertion of an additional epoxide molecule rather than CO_2 insertion. This behaviour can be ascribed to the nature of the Lewis acid catalyst employed: in particular, a chloride-substituted Al(aminotriphenolate) complex (*i.e.*, Al^{Cl}) was used with acyclic substrates **9a–14a**. Previous studies have shown that this Al^{Cl} complex combined with NBu_4I is a highly active binary catalyst for terminal epoxide/ CO_2 conversion into cyclic carbonates. Detailed computational and kinetic studies supported the view that CO_2 insertion into the initially formed Al-alkoxide bond is the rate-limiting step.^[6d] Thus, the higher Lewis acidity of Al^{Cl} , when compared to Al^{tBu} , results in a relatively more stable Al-alkoxide intermediate with a lower nucleophilic character, thus making the CO_2 insertion step slower. This former observation seems to corroborate with the modest chemo-selectivities attained in the synthesis of acyclic terpene carbonates **9b** and **11b–14b**. As a result substantial oligo/polyether formation is noted.

In order to qualitatively assess the influence of the structure of the Al-complex on the overall selectivity, we decided to prepare terpene carbonate **9b** (based on citronellyl acetate) using the

Al^{tBu} complex under the same conditions as reported in entry 9 (Table 2). Whereas the use of Al^{Cl} gives rise to virtually full conversion of the starting epoxide **9a** (97%), significant formation of oligo/polyether **9e** (28%) is also noted with a calculated chemo-selectivity towards the carbonate **9b** of 57% (56% NMR yield). Notably, the presence of Al^{tBu} results in lower conversion of epoxide **9a** (71%) alongside with formation of a much lower amount of oligo/polyether (8%) with an overall chemo-selectivity of 67% for carbonate **9b** (46% NMR yield).

In contrast, the use of Al^{tBu} with bicyclic terpene oxides led to the chemo-selective formation of the respective terpene carbonates (Figure 3). This is in agreement with our former notion that this Lewis acidic complex is primarily involved at the initial stage of the coupling between the epoxide and CO_2 , as previously proposed for oxetane/ CO_2 coupling reactions promoted by Al^{tBu} .^[24] Upon formation of a metal hemi-carbonate intermediate, the metal-mediated formation of the cyclic carbonate is sterically disfavoured. This causes to release the hemi-carbonate from the coordination sphere of the metal following fast outer-sphere cyclization. The combined observed differences in chemo-selectivity underline the importance of matching the reactivity and product selectivity features in the formation of terpene based cyclic carbonates.

Conclusions

In summary, we have developed the first general and effective route towards bio-based, cyclic carbonates derived from various terpene scaffolds. A binary catalyst comprising a Lewis acidic Al(III) complex and a nucleophilic additive (PPNCI) is able to mediate these challenging conversions with different degrees of chemo-selectivity: bicyclic terpene oxides were converted with high selectivity whereas the acyclic substrates showed inferior chemo-selectivity under comparable temperature/pressure conditions. The highly challenging nature of these conversions limit to some extent the isolated yields of the terpene carbonates (typically between 50–60%), though the results shown herein offer a reference point for catalyst development to further optimize the reactivity/selectivity features of such processes. Our future activities therefore aim at improving these aspects by carefully designing suitable (aminophenolate) ligand scaffolds and selection of appropriate Lewis acid metals favouring CO_2 insertion into the metal-alkoxide bond after nucleophilic activation of the epoxide substrate.

Experimental Section

General Information

^1H , $^{13}\text{C}\{^1\text{H}\}$ and the 2D NMR spectra were recorded on a Bruker AV-300, AV-400 or AV-500 spectrometer using the residual solvent peak for calibration. Mass spectrometric analyses and X-ray diffraction studies were performed by the Research Support Group at the ICIQ (Tarragona). FT-IR measurements were carried out on a Bruker Optics FTIR Alpha spectrometer. Carbon dioxide was purchased from PRAXAIR and used without further purification. Solvents used in the synthesis of the

complexes were dried using an Innovative Technology PURE SOLV solvent purification system.

General Procedure for the Bicyclic Terpene Carbonates

All reactions were performed in a 30 mL stainless steel reactor. As a typical experiment, 560.8 mg (5.0 mmol) of 1-methylcyclohexene oxide (**1a**) were introduced in the inner Teflon vessel of a 30 mL autoclave alongside with 34.7 mg (0.05 mmol) of Al^{IBu} , 86.1 mg (0.15 mmol) of PPNCI and 1.0 mL of methyl ethyl ketone (MEK). Three cycles of pressurization and depressurization of the reactor ($p\text{CO}_2 = 0.5$ MPa) were performed, and the pressure was finally stabilized at 1.0 MPa. The reactor was heated to the required temperature ($T = 85$ °C), and the mixture was then stirred for another 66 h. Hereafter, the reaction was stopped and the autoclave was allowed to cool down by immersion in an ice bath for 1 h before venting. The reaction mixture was diluted in 2.0 mL of CDCl_3 and a weighed quantity of mesitylene (typically around 10 % mol with respect to the epoxide substrate) was added. A quantitative ^1H NMR determination was carried out on samples consisting of 100 μL of this solution diluted with 0.5 mL of CDCl_3 . After concentration of the crude reaction mixture *in vacuo*, the cyclic carbonate product **1b** (3a-methylhexahydrobenzo[d][1,3]dioxol-2-one) was isolated upon purification through a short silica path using CH_2Cl_2 as eluent.

Data for 3a-methylhexahydrobenzo[d][1,3]dioxol-2-one (**1b**): ^1H NMR (500 MHz, 298 K, CDCl_3): $\delta = 4.35$ (t, $^3J = 4.1$ Hz, 1H), 2.09–2.03 (m, 1H), 1.85–1.80 (m, 2H), 1.76–1.65 (m, 2H), 1.56–1.49 (m, 2H), 1.48 (s, 3H), 1.38–1.27 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, CDCl_3): $\delta = 154.95$, 82.92, 81.19, 33.80, 26.01, 23.42, 20.52, 18.80; FT-IR (neat): 1771 cm^{-1} (C=O); HRMS (ESI+, CH_3OH): m/z calcd. ($\text{C}_8\text{H}_{12}\text{O}_3$): 179.0679 (M+Na) $^+$; found: 179.0678.

General Procedure for the Acyclic Terpene Carbonates

All reactions were performed in a 30 mL stainless-steel reactor. In a typical experiment, 1.07 g (5.0 mmol) of 5-(3,3-dimethyloxiran-2-yl)-3-methylpentyl acetate (**9a**) were introduced in the inner Teflon vessel of a 30 mL autoclave alongside with 34.8 mg (0.05 mmol) of Al^{Cl} , 86.1 mg (0.15 mmol) of PPNCI and 1.0 mL of methyl ethyl ketone (MEK). Three cycles of pressurization and depressurization of the reactor ($p\text{CO}_2 = 0.5$ MPa) were performed, after which the CO_2 pressure was finally stabilized at 4.0 MPa. The reactor was heated to the required temperature ($T = 85$ °C), and the mixture was stirred for a further 66 h. Hereafter the reaction was stopped and the autoclave was allowed to cool down completely by immersion in an ice bath for 1 h before venting. The reaction mixture was diluted with 2.0 mL of CDCl_3 and a weighed quantity of mesitylene (typically around 10 % mol with respect to the epoxide substrate) was added. A quantitative ^1H NMR determination was carried out on samples consisting of 100 μL of this solution diluted with 0.50 mL of CDCl_3 . The cyclic carbonate product, 5-(5,5-dimethyl-2-oxo-1,3-dioxolan-4-yl)-3-methylpentyl acetate **9b**, was isolated in 51% yield by purification using column chromatography (support: SiO_2 , eluent: hexane/diethyl ether 1:1 v/v, $R_f = 0.16$). The by-products 6-hydroxy-3,7-dimethyloct-7-en-1-yl acetate **9c** ($R_f = 0.26$) and 3,7-dimethyl-6-oxooctyl acetate **9d** ($R_f = 0.18$) were also isolated and fully characterized; the yields were 1 and 5 %, respectively.

Data for 5-(5,5-dimethyl-2-oxo-1,3-dioxolan-4-yl)-3-methylpentyl acetate (**9b**), mixture of diastereo-isomers with a *dr* of 51:49: ^1H NMR (300 MHz, 298 K, CDCl_3): $\delta = 4.28$ – 4.17 (m, 1H), 4.17– 4.00 (m, 2H), 2.04 (s, 3H), 1.81– 1.48 (m, 7H), 1.49 (3H), 1.48– 1.38 (m, 1H), 1.37 (s, 3H), 1.32– 1.06 (m, 1H), 0.94 (d, $^3J = 6.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, CDCl_3): $\delta = 171.26$, 154.19, 85.95, 85.78, 84.10, 62.67, 35.39, 33.30, 33.18, 29.81,

29.79, 26.83, 26.22, 21.34, 21.13, 19.30; FT-IR (neat): 1786 and 1733 cm^{-1} (C=O); HRMS (ESI+, CH_3OH): m/z calcd. ($\text{C}_{13}\text{H}_{22}\text{O}_5$) 281.1359 (M+Na) $^+$; found: 281.1362.

Data for 6-hydroxy-3,7-dimethyloct-7-en-1-yl acetate (**9c**), mixture of diastereo-isomers with a *dr* of 1:1: ^1H NMR (500 MHz, 298 K, CDCl_3): $\delta = 4.93$ – 4.87 (m, 1H), 4.81 (s, 1H), 4.13– 4.02 (m, 2H), 4.00 (t, $^3J = 6.5$ Hz, 1H), 2.02 (m, 3H), 1.82 (s, 1H), 1.69 (s, 3H), 1.68– 1.18 (m, 6H), 1.13– 1.01 (m, 1H), 0.94– 0.84 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, CDCl_3): $\delta = 171.33$, 171.32, 147.66, 147.56, 111.29, 111.09, 76.28, 76.12, 63.03, 63.01, 35.55, 35.53, 32.69, 32.65, 32.26, 32.21, 29.90, 29.89, 21.11, 19.53, 17.60, 17.44; FT-IR (neat): 1737 cm^{-1} (C=O); HRMS (ESI+, CH_3OH): m/z calcd. ($\text{C}_{12}\text{H}_{22}\text{O}_3$) 237.1461 (M+Na) $^+$; found: 237.1457.

Data for 3,7-dimethyl-6-oxooctyl acetate (**9d**): ^1H NMR (300 MHz, 298 K, CDCl_3): $\delta = 4.09$ (m, 2H), 2.61 (m, 1H), 2.46 (m, 2H), 2.04 (s, 3H), 1.74– 1.33 (m, 5H), 1.09 (d, $^3J = 6.9$ Hz, 6H), 0.91 (d, $^3J = 6.2$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, CDCl_3): $\delta = 215.2$, 171.6, 63.2, 41.3, 38.2, 35.8, 31.0, 30.0, 21.5, 19.7, 18.8, 18.7; FT-IR (neat): 1737, 1710 cm^{-1} (C=O); HRMS (ESI+, CH_3OH): m/z calcd. ($\text{C}_{12}\text{H}_{22}\text{O}_3$) 237.1461 (M+Na) $^+$; found: 237.1459.

Crystallographic Studies

The measured crystals were stable under atmospheric conditions; nevertheless they were treated under inert conditions immersed in perfluoro-polyether as protecting oil for manipulation. Data Collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX II 4K CCD area detector, a FR591 rotating anode with Mo $\text{K}\alpha$ radiation, Montel mirrors and a Kryoflex low temperature device ($T = -173$ °C). Full-sphere data collection was used with ω and ϕ scans. Programs used: Data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction SAINT+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008–1 (2008). Structure Solution: SHELXTL Version 6.10 (Sheldrick, 2000) was used.^[25] Structure Refinement: SHELXTL-97-UNIX VERSION.

Crystallographic Data for 1b

$\text{C}_8\text{H}_{12}\text{O}_3$, $M_r = 156.18$, monoclinic, $P2(1)$, $a = 7.6622(8)$ Å, $b = 6.4129(6)$ Å, $c = 7.7635(8)$ Å, $\alpha = 90^\circ$, $\beta = 98.300(3)^\circ$, $\gamma = 90^\circ$, $V = 377.48(8)$ Å 3 , $Z = 2$, $\rho = 1.374$ $\text{mg}\cdot\text{M}^{-3}$, $\mu = 0.104$ mm^{-1} , $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 168$, crystal size = $0.40 \times 0.20 \times 0.20$ mm^3 , $\theta(\text{min}) = 2.651^\circ$, $\theta(\text{max}) = 32.20^\circ$, 3344 reflections collected, 2037 reflections unique ($R_{\text{int}} = 0.0282$), $\text{GoF} = 1.063$, $R_1 = 0.0345$ and $wR_2 = 0.0868$ [$I > 2\sigma(I)$], $R_1 = 0.0358$ and $wR_2 = 0.0880$ (all indices), min/max residual density = $-0.319/0.379$ [$\text{e}\cdot\text{Å}^{-3}$]. Completeness to $\theta(32.20^\circ) = 90.4\%$. CCDC 1451773.

Crystallographic Data for 2b

$\text{C}_{11}\text{H}_{16}\text{O}_3$, $M_r = 196.24$, monoclinic, $P2(1)$, $a = 6.048(4)$ Å, $b = 15.614(9)$ Å, $c = 6.338(5)$ Å, $\alpha = 90^\circ$, $\beta = 117.776(16)^\circ$, $\gamma = 90^\circ$, $V = 529.5(6)$ Å 3 , $Z = 2$, $\rho = 1.231$ $\text{mg}\cdot\text{M}^{-3}$, $\mu = 0.088$ mm^{-1} , $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 212$, crystal size = $0.20 \times 0.20 \times 0.20$ mm^3 , $\theta(\text{min}) = 2.61^\circ$, $\theta(\text{max}) = 25.89^\circ$, 3756 reflections collected, 1719 reflections unique ($R_{\text{int}} = 0.1029$), $\text{GoF} = 1.014$, $R_1 = 0.0873$ and $wR_2 = 0.2090$ [$I > 2\sigma(I)$], $R_1 = 0.1027$ and $wR_2 = 0.2162$ (all indices), min/max residual density = $-0.379/0.540$ [$\text{e}\cdot\text{Å}^{-3}$], flack parameter $x = 0.7(10)$. Completeness to $\theta(25.89^\circ) = 98.8\%$. CCDC 1451771.

Crystallographic Data for 5b

$C_{11}H_{14}O_4$, $M_r = 210.22$, orthorhombic, $P2(1)2(1)2(1)$, $a = 6.8787(9)$ Å, $b = 7.5688(9)$ Å, $c = 20.495(3)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1067.1(2)$ Å³, $Z = 4$, $\rho = 1.309$ mg·M⁻³, $\mu = 0.099$ mm⁻¹, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 448$, crystal size = $0.40 \times 0.20 \times 0.20$ mm³, $\theta(\min) = 1.99^\circ$, $\theta(\max) = 30.60^\circ$, 11222 reflections collected, 3225 reflections unique ($R_{\text{int}} = 0.0271$), $\text{GoF} = 1.078$, $R_1 = 0.0370$ and $wR_2 = 0.0928$ [$I > 2\sigma(I)$], $R_1 = 0.0418$ and $wR_2 = 0.1018$ (all indices), min/max residual density = $-0.204/0.314$ [e·Å⁻³], flack parameter $x = -0.1(4)$. Completeness to $\theta(30.60^\circ) = 98.7\%$. CCDC 1451774.

Crystallographic Data for 6b

$C_{11}H_{16}O_4$, $M_r = 212.24$, triclinic, $P-1$, $a = 6.4255(11)$ Å, $b = 9.2997(16)$ Å, $c = 9.3869(15)$ Å, $\alpha = 103.713(5)^\circ$, $\beta = 94.235(5)^\circ$, $\gamma = 103.972(5)^\circ$, $V = 523.67(15)$ Å³, $Z = 2$, $\rho = 1.346$ mg·M⁻³, $\mu = 0.102$ mm⁻¹, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 228$, crystal size = $0.06 \times 0.04 \times 0.005$ mm³, $\theta(\min) = 2.26^\circ$, $\theta(\max) = 25.44^\circ$, 11714 reflections collected, 1810 reflections unique ($R_{\text{int}} = 0.0813$), $\text{GoF} = 2.226$, $R_1 = 0.1174$ and $wR_2 = 0.3344$ [$I > 2\sigma(I)$], $R_1 = 0.1607$ and $wR_2 = 0.3434$ (all indices), min/max residual density = $-0.475/0.421$ [e·Å⁻³]. Completeness to $\theta(25.44^\circ) = 94.5\%$. CCDC 1451772. Note that the very small size of the crystal resulted in poor quality crystal data; despite this, the atom connectivity patterns as proposed in Figure 4 could be confirmed.

Crystallographic Data for 7b

$C_{12}H_{16}O_6$, $M_r = 256.25$, orthorhombic, $P2(1)2(1)2(1)$, $a = 8.3285(17)$ Å, $b = 11.495(2)$ Å, $c = 12.522(3)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1198.8(4)$ Å³, $Z = 4$, $\rho = 1.420$ mg·M⁻³, $\mu = 0.114$ mm⁻¹, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 544$, crystal size = $0.30 \times 0.10 \times 0.10$ mm³, $\theta(\min) = 2.41^\circ$, $\theta(\max) = 24.70^\circ$, 4780 reflections collected, 2006 reflections unique ($R_{\text{int}} = 0.0751$), $\text{GoF} = 1.030$, $R_1 = 0.0625$ and $wR_2 = 0.1430$ [$I > 2\sigma(I)$], $R_1 = 0.0922$ and $wR_2 = 0.1624$ (all indices), min/max residual density = $-0.245/0.316$ [e·Å⁻³]. Completeness to $\theta(24.70^\circ) = 99.2\%$. CCDC 1451775.

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Keywords: aluminium • biocarbonates • carbon dioxide • homogeneous catalysis • terpenes

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- [16] A larger scale reaction using 10 g (65.8 mmol) of *cis/trans* limonene oxide and CO₂ (1.0 MPa) in a 45 mL stainless steel autoclave at 85°C for 66 h was also probed. Somewhat lower conversion (35%) and isolated yield (3.7 g, 29%) was obtained compared to formation of **4b** in Figure 3 (43% isolated yield). We ascribe this to a lower CO₂-to-substrate ratio inside the reactor; however, the result suggests that larger-scale synthesis of **4b** is potentially feasible. See Supporting Information for more details.
- [17] For the acyclic terpene oxide substrates we found that the use of the Al^{Cl} complex provided the best combination of conversion and selectivity and therefore proceeded with this complex. Note that again MEK was used as solvent since the acyclic terpene oxides are viscous oils and a relatively high loading of Al^{Cl} and the nucleophilic additive are required. The neat reaction between methyl cyclohexene oxide and CO₂ (Table 1, entry 11; only 1% conversion) is further reason for considering the use of a solvent in these reactions.
- [18] In some of the reactions we noted an imperfect mass balance by combining the molar amounts of cyclic carbonate, starting epoxide and by-products as reported in Table 2. We observed that upon cooling the reaction mixture that under certain conditions up to 10-15% of epoxide remained in other sections of the reactor, *i.e.* not in the Teflon insert containing the reaction mixture. In a separate experiment we determined this amount by washing these sections following ¹H NMR analysis: this showed unambiguously the presence of the epoxide substrate.
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Entry for the Table of Contents:

FULL PAPER

Bioconversions: A general catalytic method for the challenging coupling between terpene oxides and CO₂ has been developed furnishing bicyclic and acyclic bio-carbonates in appreciable yields. The chemoselectivity features of both types of carbonate syntheses was studied in detail, and the first crystallographic analyses of such terpene carbonate scaffolds are presented. The results pave the way for the use of terpenes as synthons towards new materials and fine chemicals.

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Catalytic Coupling of Carbon Dioxide with Terpene Scaffolds: Access to Challenging Bio-based Organic Carbonates