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Isocyanurate Formation During Oxazolidinone Synthesis from Epoxides and Isocyanates Catalysed by a Chromium(Salphen) Complex

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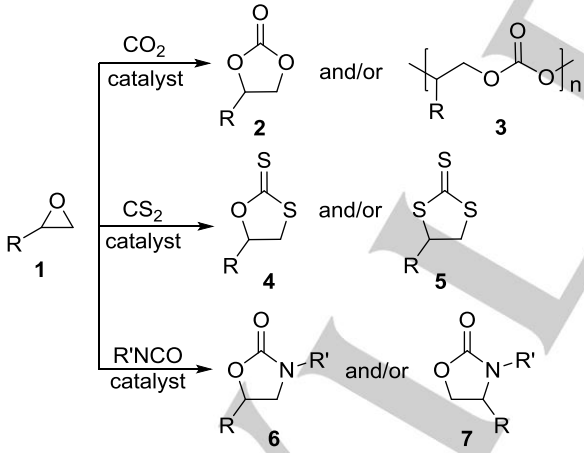
Abstract: Chromium(salphen) complex **10** is found to be a catalyst for the preparation of oxazolidinones from epoxides and isocyanates. Using the optimal reaction conditions (1.5 mol% of chromium(salphen) complex **10** at 80 °C in toluene for 4 hours), six epoxides were reacted with five isocyanates, providing 15 oxazolidinones in up to 90% yield. With electron-deficient isocyanates, cyclotrimerisation of the isocyanate to the corresponding isocyanurates is a competing reaction, showing the importance of matching catalyst activity to that of the substrates.

Introduction

Epoxides **1** are useful building blocks in organic synthesis and a number of five-membered heterocycles can be prepared when they are treated with heterocumulenes. The reaction with carbon dioxide to furnish either cyclic- or poly-carbonates **2** and **3** has been extensively studied.[1,2,3] Other areas of interest include the formation of either cyclic dithiocarbonates **4** or trithiocarbonates **5**,[4] and oxazolidinones **6** and **7**[5] (Scheme 1).



Scheme 1. Synthesis of heterocycles from epoxides and heterocumulenes.

Oxazolidinones are an important class of heterocycles and have been found to be useful compounds in medicinal chemistry,[6] as well as being valuable synthetic intermediates.[7] The reaction of epoxides with isocyanates is one of the most useful and efficient methods for the synthesis of oxazolidinones (Scheme 1). A number of catalyst systems have been reported for this reaction, including ammonium salts,[8] lanthanide salts,[9] lithium halides,[10] magnesium halides,[11] tetraphenylantimony iodide[12] and trialkyltin halides.[13]

Recently, our group has reported a number of highly efficient metal-based catalysts **8–10** for the formation of cyclic carbonates from epoxides and carbon dioxide (Figure 1).[14,15,16] Compounds **8** and **9** also exhibit excellent catalytic activity for the preparation of oxazolidinones.[5a,b] Thus, 5 mol% of bimetallic aluminium(salen) complex **8** in the absence of a co-catalyst was found to be an active catalytic system for the synthesis of a range of mono- and di-substituted oxazolidinones. In the presence of tetrabutylammonium bromide (5 mol%), aluminium heterosorpionate complex **9** (5 mol%) was also shown to be an effective catalyst for the preparation of oxazolidinones. Six epoxides were reacted with six aromatic isocyanates to give 25 oxazolidinones, showing a broad substrate scope.

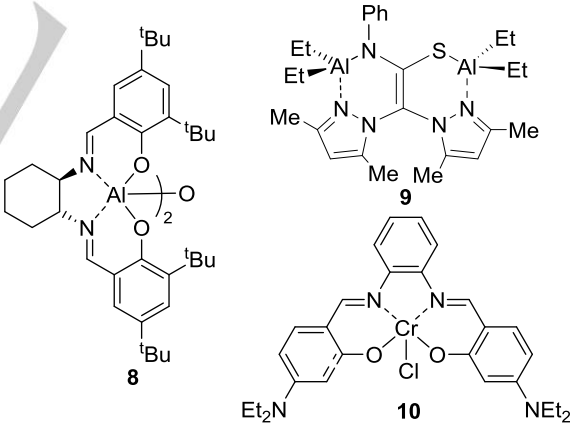


Figure 1. Catalysts for the synthesis of cyclic carbonates and oxazolidinones.

More recently, our group has reported the synthesis of cyclic carbonates from epoxides and carbon dioxide using chromium(salphen) complex **10**.[16] In this case, only 1.5 mol% of complex **10** was necessary to catalyse the synthesis of a range of cyclic carbonates, either from monosubstituted epoxides at room temperature and one bar carbon dioxide pressure, or from disubstituted epoxides at elevated temperature and pressure. In view of the high catalytic activity shown by complex **10**, we decided to investigate its use in the related reaction between epoxides and isocyanates. Herein, we report the use of chromium(salphen) complex **10** as an efficient catalyst for the formation of oxazolidinones from epoxides and isocyanates.

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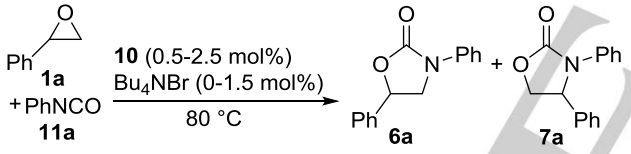
Results and Discussion

Screening studies were carried out using styrene oxide **1a** and phenyl isocyanate **11a** in a 1:1 ratio under various reaction conditions (Scheme 2) and the results are shown in Table 1. Initial experiments were undertaken using 1.5 mol% of both chromium(salphen) complex **10** and tetrabutylammonium bromide (TBAB) as a co-catalyst at 80 °C for 24 hour under solvent-free conditions (Table 1, entry 1). However, the reaction mixture solidified after 30 minutes. This suggested that a solvent was necessary to increase the conversion to the oxazolidinone products. Toluene was selected based on literature precedent[5a,b] and the reaction mixture was heated to 80 °C. After 24 hours, 75% conversion was obtained (Table 1, entry 2). Control experiments proved to be very informative. In the absence of TBAB, chromium(salphen) complex **10** was able to catalyse the reaction itself and a 90% conversion was achieved, whereas in the absence of complex **10**, only 7% conversion was observed (Table 1, entries 3 and 4). Increasing the catalyst loading to 2.5 mol% was not beneficial while lowering the catalyst loading to 0.5 mol% resulted in low conversion (Table 1, entries 5 and 6). To further optimise the reaction conditions, a sample was taken after each hour and it was found that the reaction reached maximum conversion after 4 hours. It was therefore decided that 1.5 mol% of catalyst **10** and heating in toluene at 80 °C for 4 hours were the optimal reaction conditions for the synthesis of oxazolidinones from epoxides and isocyanates.



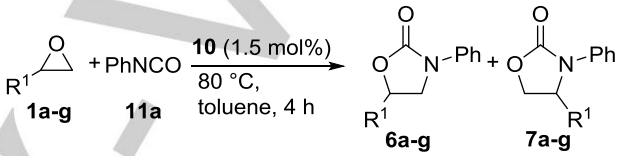
Scheme 2. Reaction of styrene oxide **1a** with phenylisocyanate **11a**.

Table 1. Optimisation of the synthesis of oxazolidinones **6a** and **7a** using complex **10** and TBAB.

Entry	Complex **10** (mol%)	TBAB (mol%)	t (h)	Toluene (mL)	Conversion[a] (%)	**6a**:**7b**[a]
1	1.5	1.5	24	0	70	50:50
2	1.5	1.5	24	0.5	75	66:34
3	1.5	0	24	0.5	90	35:65
4	0	1.5	24	0.5	7	75:25
5	2.5	0	24	0.5	88	50:50
6	0.5	0	24	0.5	28	50:50
7	1.5	0	4	0.5	90	35:65

[a] Conversion of epoxide **1a** into **6a** and **7a** and ratio of **6a:7a** were determined by ^{1}H NMR spectroscopy of the unpurified reaction mixture.

Having determined the optimal reaction conditions for the synthesis of oxazolidinones **6a** and **7a** from styrene oxide **1a** and phenyl isocyanate **11a**, a series of epoxides was used together with phenyl isocyanate **11a** to give oxazolidinones **6b-g** and **7b-g** (Scheme 3). The results of this study are shown in Table 2. Functionalised aliphatic epoxides (3-phenoxypropropylene oxide **1b** and epichlorohydrin **1c**) and unfunctionalised aliphatic epoxide **1d** were all excellent substrates, giving high conversions and excellent regioselectivity to the 3,5-isomers **6b-d** (Table 2, entries 2-4). In contrast, glycidol **1e** was found to be a poor substrate, giving a complex mixture from which no product could be isolated (Table 2, entry 5). When aromatic epoxides **1f** and **1g**, containing a halogen at the *para*-position were used as substrates, good conversions were obtained though with no regioselectivity (Table 2, entries 6 and 7).



1,6,7. a: R^1 = Ph; b: R^1 = CH_2OPh; c: R^1 = CH_2Cl; d: R^1 = C_8H_{17}; e: R^1 = CH_2OH; f: R^1 = 4-ClC_6H_4; g: R^1 = 4-BrC_6H_4

Scheme 3. Reaction of epoxides **1a-g** with phenylisocyanate **11a**.

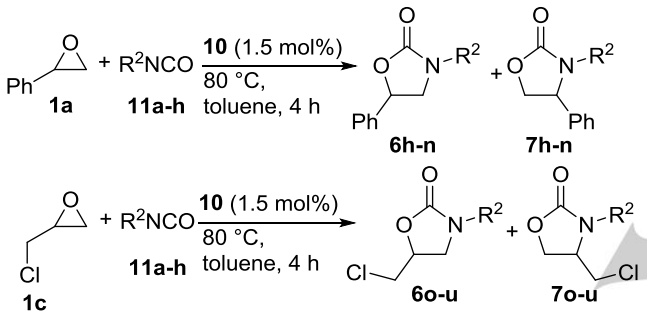
Table 2. Synthesis of oxazolidinone **6a-g** and **7a-g** using epoxide **1a-g**.[a]

Entry	Epoxide	Conversion[b] (%)	Yield[c] (%)
1	**1a** R^1 = Ph	90 (35:65)	**6a**,**7a** (65)
2	**1b** R^1 = CH_2OPh	80 (1:0)	**6b** (62)
3	**1c** R^1 = CH_2Cl	100 (1:0)	**6c** (90)
4	**1d** R^1 = C_8H_{17}	100 (92:8)	**6d** (59)
5	**1e** R^1 = CH_2OH	0	-
6	**1f** R^1 = 4-ClC_6H_4	75 (1:1)	**6f**, **7f** (59)
7	**1g** R^1 = 4-BrC_6H_4	70 (1:1)	**6g**, **7g** (62)

[a] Reactions were carried out using 1.5 mol% chromium(salphen) complex **10** in toluene at 80 °C for 4 hours. [b] Determined by ^{1}H NMR spectroscopy of the unpurified reaction mixture and figure in brackets is the ratio of **6**:**7**. [c] Yield of isolated product after purification by column chromatography.

To further expand the substrate scope, styrene oxide **1a** and epichlorohydrin **1c** were selected as representative aromatic and aliphatic epoxides respectively for the synthesis of oxazolidinones from various isocyanates (Scheme 4). Five substituted aromatic isocyanates **11b-f** and two aliphatic isocyanates **11g** and **11h** were reacted with these epoxides and

the results are summarised in Table 3. It was found that aromatic isocyanates **11b**,**c** gave good to excellent conversions after 4 hours. A 1:1 ratio of 3,4- and 3,5- regioisomers was observed when styrene oxide **1a** was used, while with epichlorohydrin **1c**, complete regioselectivity for the 3,5-isomer was achieved (Table 3, entries 1-5 and 8-12). In comparison, no conversion was obtained when aliphatic isocyanates **11g**,**h** were used (entries 6,7 and 13,14). With aromatic isocyanates that have halogen groups at the *para*-position, chromium(salphen) complex **10** was found to catalyse the formation of both oxazolidinones and isocyanurates (perhydro-1,3,5-triazine-2,4,6-triones) **12** (Figure 2) (Table 3, entries 3-5). Isocyanurates are known to enhance the physical properties of polyurethanes and coating materials,[17] typically by increasing their flame retardation and filming characteristics, and commercial products containing polymeric isocyanurates have increased chemical and thermal resistance.[18]



6,7. h,o: R^2 = 4-$MeOC_6H_4$; i,p: R^2 = 4-MeC_6H_4;
j,q: R^2 = 4-FC_6H_4; k,r: R^2 = 4-ClC_6H_4; l,s: R^2 = 4-BrC_6H_4;
m,t: R^2 = CH_2Ph; n,u: R^2 = Et;

11. a: R^2 = Ph; b: R^2 = 4-$OMeC_6H_4$; c: R^2 = 4-MeC_6H_4;
d: R^2 = 4-FC_6H_4; e: R^2 = 4-ClC_6H_4; f: R^2 = 4-BrC_6H_4;
g: R^2 = CH_2Ph; h: R^2 = Et

Scheme 4. Reaction of epoxides **1a**,**c** with isocyanate **11a-h**.

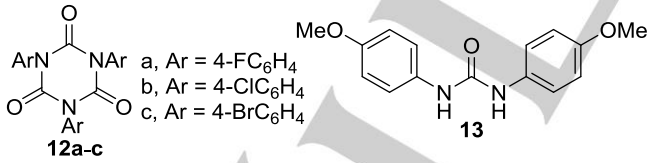


Figure 2. Structure of isocyanurates **12** and urea **13**.

Isocyanurates have previously been prepared by the cyclotrimerisation of isocyanates catalysed by species including organotin[19] and organozinc compounds,[20] copper and nickel halides[21] and palladium,[22] magnesium[23] and iron complexes.[0] The formation of isocyanurates **12a-c** was much less important when the competing reaction was between epichlorohydrin **1c** and isocyanates than when styrene oxide **1a** was used. However, since the separation of oxazolidinones **6q-s** from isocyanurates **12a-c** proved difficult, the isolated yields of these oxazolidinones were less than satisfactory (Table 3, entries 10-12). The formation of isocyanurates as by-products from the reaction between epoxides and isocyanates has not previously been reported. A control experiment using 4-fluorophenyl isocyanate **11d** in the presence of chromium complex **10** under the standard reaction conditions but in the absence of an epoxide also gave isocyanurate **12a**, indicating that chromium complex **10** is a strong Lewis acid and capable of catalysing the cyclotrimerisation of isocyanates. In the absence of chromium complex **10**, only the starting material 4-fluorophenyl isocyanate was recovered. When isocyanates that have an electron-donating substituent at the *para*-position such as **11b** were used, the corresponding urea **13** was isolated rather than the isocyanurate.

Table 3. Synthesis of oxazolidinones **6,7h-u** using complex **10**.[a]

Entry	Epoxide	Isocyanate	Conv.[b] (%)	Yield[c] (%)
1	**1a** R^1 = Ph	**11b** R^2 = 4-$MeOC_6H_4$	60 (1:1)	**6h, 7h** (56)
2	**1a** R^1 = Ph	**11c** R^2 = 4-MeC_6H_4	90 (1:1)	**6i**, **7i** (62)
3	**1a** R^1 = Ph	**11d** R^2 = 4-FC_6H_4	30 (1:1)	**7j** (12)[d]
4	**1a** R^1 = Ph	**11e** R^2 = 4-ClC_6H_4	22 (1:1)	**7k** (10)[e]
5	**1a** R^1 = Ph	**11f** R^2 = 4-BrC_6H_4	23 (1:1)	**7l**(10)[f]
6	**1a** R^1 = Ph	**11g** R^2 = CH_2Ph	0	
7	**1a** R^1 = Ph	**11h** R^2 = Et	0	
8	**1c** R^1 = CH_2Cl	**11b** R^2 = 4-$MeOC_6H_4$	98 (1:0)	**6o** (80)
9	**1c** R^1 = CH_2Cl	**11c** R^2 = 4-MeC_6H_4	96 (1:0)	**6p** (83)
10	**1c** R^1 = CH_2Cl	**11d** R^2 = 4-FC_6H_4	90 (1:0)	**6q** (21)[g]
11	**1c** R^1 = CH_2Cl	**11e** R^2 = 4-ClC_6H_4	85 (1:0)	**6r** (42)
12	**1c** R^1 = CH_2Cl	**11f** R^2 = 4-BrC_6H_4	90 (1:0)	**6s** (36)
13	**1c** R^1 = CH_2Cl	**11g** R^2 = CH_2Ph	0	
14	**1c** R^1 = CH_2Cl	**11h** R^2 = Et	0	

[a] Reactions were carried out using 1.5 mol% of chromium(salphen) complex **10** in toluene at 80 °C for 4 hours. [b] Conversion of epoxides to oxazolidinones **6**,**7** determined by ^{1}H NMR spectroscopy of the unpurified reaction mixture and figure in brackets is the ratio of **6**:**7**. [c] Yield of isolated product after purification by column chromatography. [d] Mixture of oxazolidinone **7j** and isocyanurate **12a** in 40:60 ratio. [e] Mixture of oxazolidinone **7k** and isocyanurate **12b** in 45:55 ratio. [f] Mixture of oxazolidinone **7l** and isocyanurates **12c** in 50:50 ratio. [g] Mixture of oxazolidinone **6q** and isocyanurate **12a** in 95:5 ratio.

The chemo- and regio-selectivities observed when using complex **10** as a catalyst can be explained by the catalytic cycles shown in Scheme 5. Complex **10** can act both as a Lewis

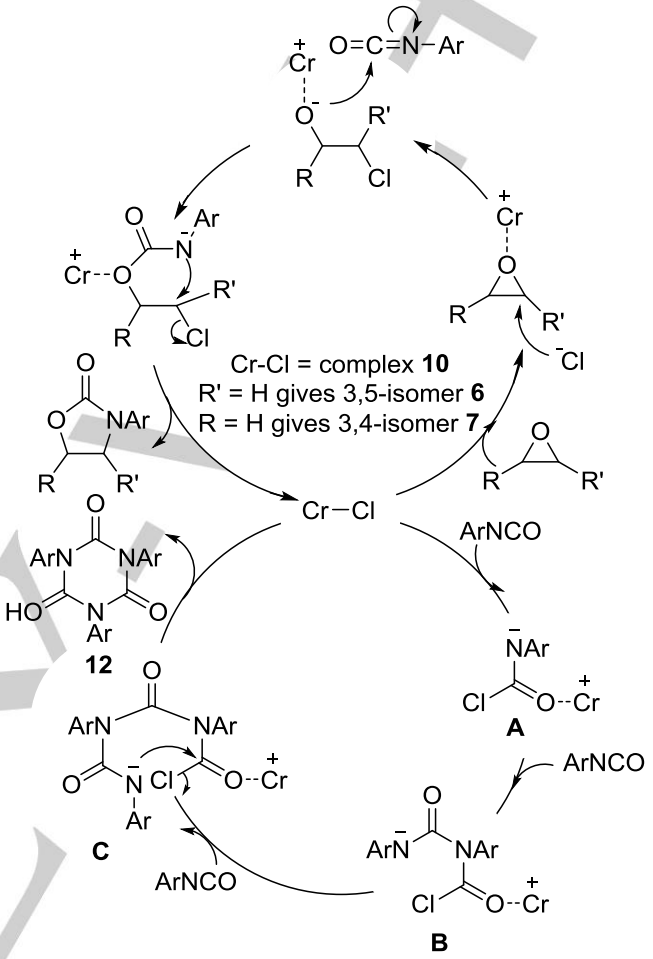
acid and as a source of a good nucleophile (chloride). Substrates **1** and **11** possess three sites which are susceptible to nucleophilic attack: both ends of the epoxide and the central carbon atom of the isocyanate. They also possess two sites for Lewis acid activation: the epoxide oxygen and the isocyanate oxygen. For oxazolidinone formation, the chromium(salphen) species first acts as a Lewis acid, activating the epoxide towards ring-opening by chloride anion. The regioselectivites observed with epoxides **1a-g** are consistent with ring-opening of the activated epoxide normally occurring at the less-hindered, unsubstituted position by an S_N2 type mechanism, eventually giving the 3,5-isomer of the oxazolidinone. However, when R^1 is an aromatic group capable of stabilising a benzylic carbenium ion, then ring-opening of the epoxide at the more-hindered, substituted position ultimately leading to the 3,4-isomer of the oxazolidinone becomes competitive and little or no regioselectivity is observed. The chromium coordinated alkoxide then reacts with the isocyanate to form a carbamate and this ring closes to give oxazolidinone **6** or **7** with regeneration of catalyst **10**. For isocyanurate formation, the isocyanate oxygen atom coordinates competitively to the metal centre, followed by the nucleophilic attack of the chloride anion to give a chromium complexed carbomoyl chloride complex **A**. Following this, the nucleophilic nitrogen can then react further with two molecules of isocyanates before ring-closing with elimination of chloride to form isocyanurates **12** and regenerate catalyst **10**.

Conclusions

Chromium(salphen) complex **10** was found to catalyse the formation of oxazolidinones from epoxides and isocyanates in the absence of a co-catalyst. Compared to previously reported aluminium(salen) complexes, chromium(salphen) complex **10** appears to be more Lewis acidic. This allows the catalyst loading to be reduced to 1.5 mol% and the reaction time to be reduced to 4 hours. However, the enhanced Lewis acidity of complex **10** causes the reaction to take a different pathway with electron-deficient isocyanates, leading to the formation of isocyanurates **12** by a pathway that involves Lewis acid activation and subsequent trimerisation of the isocyanate rather than Lewis acid activation of the epoxide. These results illustrate that although a strongly Lewis acidic catalyst is desirable to activate the epoxide for the formation of oxazolidinones from epoxides and isocyanates, the optimal catalyst for the process is substrate dependent and requires the electronic properties of both substrates and catalyst to be matched.

Experimental Section

Catalyst **10** was prepared as previously reported.[16] All other compounds were commercially available and used as supplied. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ at 25 °C on a JEOL 400 spectrometer operating at 400 and 100 MHz, respectively. Melting points were determined using a Stuart SMP3 apparatus. Infrared spectra were recorded on a Bruker Vertex 70 instrument.



Scheme 5. Proposed catalytic cycles for the synthesis of oxazolidinones and isocyanurates induced by chromium(salphen) complex **10**.

General procedure for oxazolidinone synthesis

Epoxide **1a**–**g** (0.83 mmol) and isocyanate **11a**–**h** (0.83 mmol) were added to a solution of catalyst 10 (0.013 mmol) in toluene (0.5 mL). The resulting mixture was stirred at 80 °C for 4 hours. After being allowed to cool to room temperature, toluene was removed under pressure to give the crude oxazolidinone products. The conversion of epoxide to oxazolidinone was determined by ^{1}H NMR spectroscopy of the crude mixture. The products were purified by flash chromatography to give compound **6**/**7 a**-**s**.

3,5-Diphenyloxazolidin-2-one (**6a**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (5:1), then hexane–EtOAc (3:1). (85 mg, 43%). M.p. 80–82 °C (lit. 79–82 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* 8.0 Hz, ArH), 7.46–7.37 (7H, m, ArH), 7.15 (1H, t, *J* 8.0 Hz, ArH), 5.65 (1H, d, *J* 8.0, CHO), 4.39 (1H, t, *J* 8.0 Hz, CH_2N), 3.98 (1H, t, *J* 8.0 Hz, CH_2N); ^{13}C (100

MHz, $CDCl_3$) δ 154.7, 138.1, 138.0, 129.1, 129.0, 125.7, 124.2, 118.3, 74.0, 52.7. Mass spec. (ESI): calcd. m/z 240.1019 $[C_{15}H_{14}NO_2]^+$; found: 240.1013. calcd. m/z 262.0838 $[C_{15}H_{13}NO_2+Na]^+$; found: 262.0831. IR (neat, cm^{-1}): 1745.

3,4-Diphenyloxazolidin-2-one (**7a**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (5:1), then hexane–EtOAc (3:1). (44 mg, 22%). M.p. 80–82 °C (lit. 79–82 °C).[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (9H, m, ArH), 7.07 (1H, t, *J* 8.0 Hz, ArH), 7.15 (1H, t, *J* 7.4 Hz, ArH), 5.40 (1H, dd, *J* 8.0, 6.0 Hz, CHN), 4.79 (1H, t, *J* 8.0 Hz, CH_2O), 4.21 (1H, dd, *J* 8.0, 6.0 Hz, CH_2O); ^{13}C (100 MHz, $CDCl_3$) δ 155.9, 138.2, 137.0, 129.4, 128.9, 128.8, 126.2, 120.8, 69.8, 60.7. Mass spec. (ESI): calcd. m/z 240.1019 $[C_{15}H_{14}NO_2]^+$; found: 240.1024. calcd. m/z 262.0838 $[C_{15}H_{13}NO_2+Na]^+$; found: 262.0842. IR (neat, cm^{-1}): 1741.

3-Phenyl-5-phenoxymethyloxazolidin-2-one (**6b**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (3:1), then hexane–EtOAc (2:1) (218 mg, 93%). M.p. 138–141 °C (lit. 139–140 °C).[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (2H, d, *J* 8.0 Hz, ArH), 7.40 (2H, t, *J* 8.0 Hz, ArH), 7.30 (2H, t, *J* 8.0 Hz, ArH), 7.16 (1H, t, *J* 8.0 Hz, ArH), 7.00 (1H, t, *J* 8.0 Hz, ArH), 6.91 (2H, d, *J* 8.0 Hz, ArH), 5.09–4.96 (1H, m, CHO), 4.24–4.19 (3H, m, CH_2O, CH_2N), 4.09 (1H, dd, *J* 8.0, 4.0 Hz, CH_2N); ^{13}C (100 MHz, $CDCl_3$) δ 158.0, 154.4, 138.1, 129.6, 129.1, 124.2, 121.7, 118.3, 114.6, 70.3, 67.8, 47.4. Mass spec. (ESI): calcd. m/z 292.0944 $[C_{16}H_{15}NO_3+Na]^+$; found: 292.0939. IR (neat, cm^{-1}): 1732.

3-Phenyl-5-chloromethyloxazolidin-2-one (**6c**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (2:1) (158 mg, 90%). M.p. 108–110 °C (lit. 101–103 °C).[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, m, ArH), 7.40 (2H, t, *J* 8.0 Hz, ArH), 7.17 (1H, t, *J* 8.0 Hz, ArH), 4.91–4.85 (1H, m, CHO), 4.18 (1H, t, *J* 8.0, Hz, CH_2N), 3.97 (1H, dd, *J* 8.0, 4.0 Hz, CH_2N), 3.81 (1H, dd, J 12.0, 4.0 Hz, CH_2Cl), 3.75 (1H, dd, *J* 12.0, 4.0 Hz, CH_2Cl); ^{13}C (100 MHz, $CDCl_3$) δ 153.9, 137.7, 129.2, 124.4, 118.3, 70.8, 48.2, 44.5. Mass spec. (ESI): calcd. m/z 234.0292 $[C_{10}H_{10}ClNO_2+Na]^+$; found: 234.0296. IR (neat, cm^{-1}): 1728.

3-Phenyl-5-octyloxazolidin-2-one (**6d**): Obtained as a white solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (135 mg, 59%). M.p. 71–73 °C (lit. 70– 71 °C).[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (2H, d, *J* 8.0 Hz, ArH), 7.37 (2H, t *J* 8.0 Hz, ArH), 7.13 (1H, t, *J* 8.0 Hz, ArH), 4.66–4.61 (1H, m, CHO), 4.08 (1H, t, *J* 8.0 Hz, CH_2N), 3.66 (1H, dd, *J* 8.0, 7.5 Hz, CH_2N), 1.91–1.68 (2H, m, CH_2), 1.42–1.22 (12H, m, 6×CH_2), 0.90 (3H, t, J 8.0 Hz, CH_3); ^{13}C (100 MHz, $CDCl_3$) δ 155.0, 138.4, 129.0, 123.9, 118.1, 73.1, 50.5, 35.0, 31.8, 29.4, 29.2, 29.1, 24.5, 22.6, 14.1. Mass spec. (ESI): Calcd. m/z 298.1777 $[C_{17}H_{25}NO_2+Na]^+$; found:298.1767. IR (neat, cm^{-1}): 1717.

3-Phenyl-5-(4-chlorophenyl)-oxazolidin-2-one (**6f**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of CH_2Cl_2–hexane (4:1) (68 mg, 30%). M.p. 124–125 °C (lit. 124–126 °C).[5b] ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, d, *J* 8.0 Hz, ArH), 7.43–7.36 (6H, m, ArH), 7.16 (1H, t, *J* 8.0 Hz, ArH), 5.63 (1H, t, *J* 8.0 Hz, CHO), 4.39 (1H, t, *J* 8.0 Hz, CH_2N), 3.93 (1H, dd, *J* 8.0, 7.5 Hz, CH_2N); ^{13}C (100 MHz, $CDCl_3$) δ 154.4, 137.9, 136.6, 135.0, 129.3, 129.1, 127.1, 124.3, 118.3, 73.3, 52.6. Mass spec. (ESI): Calcd. m/z 296.0449 $[C_{15}H_{12}ClNO_2+Na]^+$; found: 296.0449. IR (neat, cm^{-1}): 1733.

3-Phenyl-4-(4-chlorophenyl)-oxazolidin-2-one (**7f**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of CH_2Cl_2–hexane (4:1) (66 mg, 29%). M.p. 140–143 °C (lit. 140–142 °C).[5b] ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (8H, m, ArH), 7.11–7.07 (1H, m, ArH), 5.38 (1H, dd, *J* 12.0, 8.0 Hz, CHN), 4.78 (1H, t, *J* 12.0 Hz, CH_2O), 4.17 (1H, dd, *J* 8.0, 4.0 Hz, CH_2O); ^{13}C (100 MHz, $CDCl_3$) δ 155.7, 139.4, 136.7, 134.9, 129.6, 129.0, 127.6, 124.9, 120.9, 69.6, 60.1. Mass spec. (ESI): calcd. m/z 274.0629 $[C_{15}H_{13}ClNO_2]^+$; found: 274.0633. Calcd. m/z 296.0449 $[C_{15}H_{12}ClNO_2+Na]^+$; found: 296.0448. IR (neat, cm^{-1}): 1733.

3-Phenyl-5-(4-bromophenyl)-oxazolidin-2-one (**6g**): Obtained as a white solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (7:1), then hexane–EtOAc (4:1), then hexane–EtOAc (3:1), (77 mg, 30%). M.p 132–134 °C (lit. 132–134 °C).[5b] ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.53 (4H, m, ArH), 7.41–7.37 (2H,m, ArH), 7.32–7.29 (2H, m, ArH), 7.18–7.14 (1H, m, ArH), 5.61 (1H, t, *J* 8.0 Hz, CHO), 4.39 (1H, t, *J* 8.0 Hz, CH_2N), 3.92 (1H, dd, *J* 8.0, 7.5 Hz, CH_2N); ^{13}C (100 MHz, $CDCl_3$) δ 154.3, 137.8, 137.1, 132.2, 129.2, 127.3, 124.4 123.2, 118.3, 73.3, 52.5. Mass spec. (ESI): calcd. m/z 339.9944 $[C_{15}H_{12}BrNO_2+Na]^+$; found: 339.9940. IR (neat, cm^{-1}): 1726.

3-Phenyl-4-(4-bromophenyl)-oxazolidin-2-one (**7g**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (7:1), then hexane–EtOAc(4:1), then hexane-EtOAc (3:1), (82 mg, 32%). M.p. 157–158 °C (lit. 156–158 °C).[5b] ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, *J* 8.0 Hz, ArH), 7.37–7.25 (4H, m, ArH), 7.19 (2H, d, *J* 8.0, ArH), 7.10 (1H, m, ArH), 5.37 (1H, dd, *J* 8.0, 6.0 Hz, CHN), 4.78 (1H, t, *J* 8.0 Hz, CH_2O), 4.17 (1H, dd, *J* 8.0, 6.0 Hz, CH_2O); ^{13}C (100 MHz, $CDCl_3$) δ 155.7, 137.2, 132.6, 129.2, 129.0, 127.9 125.0, 120.8, 116.5, 69.5, 60.1. Mass spec. (ESI): calcd. m/z 339.9944 $[C_{15}H_{12}BrNO_2+Na]^+$; found: 339.9943. IR (neat, cm^{-1}): 1728.

3-(4-Methoxyphenyl)-5-phenyloxazolidin-2-one (**6h**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane:EtOAc (5:1) (66 mg, 28%). M.p. 100–102 °C (lit. 105–107 °C).[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.38 (7H, m, ArH), 6.93–6.91 (2H, m, ArH), 5.63 (1H, t, *J* 8.0 Hz, CHO), 4.35 (1H, t, *J* 8.0 Hz, CH_2N), 3.94 (1H, dd, *J* 12.0, 8.0 Hz, CH_2N), 3.80 (3H, s, OCH_3); ^{13}C (100 MHz, $CDCl_3$) δ 156.4, 155.0, 138.2, 131.3, 129.0, 128.9, 125.6, 120.3, 114.3, 74.0, 55.5, 53.3. Mass spec. (ESI): calcd. m/z 292.0944 $[C_{16}H_{15}ClNO_2+Na]^+$; found: 292.0933. IR (neat, cm^{-1}): 1732.

3-(4-Methoxyphenyl)-4-phenyloxazolidin-2-one (**7h**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (5:1) (66 mg, 28%). M.p. 134–136 °C (lit. 137–138 °C).[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (7H, m, ArH), 6.78 (2H, d, *J* 8.0 Hz, ArH), 5.31 (1H, dd, *J* 8.0, 6.0 Hz, CHN), 4.77 (1H, t, *J* 8.0 Hz, CH_2O), 4.22 (1H, dd, *J* 8.0, 6.0 Hz, CH_2O), 3.73 (3H, s, OCH_3);

^{13}C (100 MHz, $CDCl_3$) δ 156.8, 156.4, 138.1, 129.8, 129.2, 128.8, 126.5, 123.3, 114.1, 69.7, 61.3, 55.3. Mass spec. (ESI): calcd. m/z 2792.0944 $[C_{16}H_{15}ClNO_2+Na]^+$; found: 292.0934. IR (neat, cm^{-1}): 1739.

3-(4-Methylphenyl)-5-phenyloxazolidin-2-one (**6i**): Obtained as a white solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (68 mg, 32%). M.p. 96–98 °C (lit. 98–100 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (7H, m, ArH), 7.18 (2H, d, *J* 8.0 Hz, ArH), 5.62 (1H, t, *J* 8.0 Hz, CHO), 4.35 (1H, t, *J* 8.0 Hz, CH_2N), 3.94 (1H, dd, J 8.0, 7.0 Hz, CH_2N), 2.32 (3H, s, CH_3); ^{13}C (100 MHz, $CDCl_3$) δ 153.9, 141.7, 129.5, 129.3, 128.4, 128.3, 126.6, 121.3, 110.0, 74.0, 52.6, 20.8. Mass spec. (ESI): calcd. m/z 276.0995 $[C_{16}H_{15}NO_2+Na]^+$; found: 279.0991. IR (neat, cm^{-1}): 1735.

3-(4-Methylphenyl)-4-phenyloxazolidin-2-one (**7i**): Obtained as a white solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (63 mg, 30%). M.p. 106–108 °C (lit. 105–107 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.20 (7H, m, ArH), 7.03 (2H, d, *J* 8.0 Hz, ArH), 5.35 (1H, dd, *J* 8.0, 6.0 Hz, CHN), 4.76 (1H, t, *J* 8.0 Hz, CH_2O), 4.19 (1H, dd, *J* 8.0, 4.0 Hz, CH_2O), 2.23 (3H, s, CH_3); ^{13}C (100 MHz, $CDCl_3$) δ 156.2, 138.3, 134.5, 134.3, 129.5, 129.3, 128.8, 126.3, 121.1, 69.8, 60.8, 20.8. Mass spec. (ESI): calcd. m/z 276.0995 $[C_{16}H_{15}NO_2+Na]^+$; found: 279.1005. IR (neat, cm^{-1}): 1739.

3-(4-Fluorophenyl)-4-phenyloxazolidin-2-one (**7j**): Obtained as a white solid in a mixture with **12a** after purification by flash chromatography using a solvent system of first hexane–EtOAc (9:1), then hexane– EtOAc (5:1) (28 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4–7.25 (7H, m, ArH), 6.95–6.93 (2H, m, ArH), 5.33 (1H, dd, *J* 12.0, 8.0 Hz, CHN), 4.79 (1H, t, *J* 8.0 Hz, CH_2O), 4.22 (1H, dd, *J* 8.0, 6.0 Hz, CH_2O); ^{13}C (100 MHz, $CDCl_3$) δ 161.5, 156.1, 137.8, 133.0, 129.2, 129.0, 126.4, 123.0 (d, *J* 8 Hz), 115.7 (d, *J* 23 Hz), 69.8, 61.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ 117.1 (s). Mass spec. (ESI): calcd. m/z 280.0744 $[C_{15}H_{12}FNO_2+Na]^+$; found: 280.0716.

3-(4-Chlorophenyl)-4-phenyloxazolidin-2-one (**7k**): Obtained as a pale yellow solid in a mixture with **12b** after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (22 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (7H, m, ArH), 7.21 (2H, d, *J* 8.0 Hz, ArH), 5.36 (1H, dd, *J* 12.0, 8.0 Hz, CHN), 4.79 (1H, t, *J* 8.0 Hz, CH_2O), 4.21 (1H, dd, *J* 8.0, 6.0 Hz, CH_2O); ^{13}C (100 MHz, $CDCl_3$) δ 155.8, 137.7, 135.6, 129.7, 129.6, 128.9, 126.2, 121.9, 69.8, 60.6. Mass spec. (ESI): calcd. m/z 296.0449 $[C_{15}H_{12}ClNO_2+Na]^+$; found: 296.0453.

3-(4-Bromophenyl)-4-phenyloxazolidin-2-one (**7l**): Obtained as a yellow solid in a mixture with **12c** after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (26 mg, 10%). M.p. 132–135 °C (lit. 134–137 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.37 (9H, m, ArH), 5.35 (1H, dd, *J* 8.0, 6.0 Hz, CHN), 4.79 (1H, t, *J* 8.0 Hz, CH_2O), 4.21 (1H, dd, *J* 8.0, 6.0 Hz, CH_2O); ^{13}C (100 MHz, $CDCl_3$) δ 156.2, 132.7, 131.8, 130.0, 129.5, 128.5, 126.0, 123.7, 122.2, 67.2, 61.8. Mass spec. (ESI): calcd. m/z 318.0124 $[C_{15}H_{12}BrNO_2+H]^+$; found: 318.0130.

3-(4-Methoxyphenyl)-5-chloromethyloxazolidin-2-one (**6o**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (3:1) (160 mg, 80%). M.p. 106–108 °C (lit. 105–106 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, d, *J* 8.0 Hz, ArH), 6.92 (2H, d, *J* 8.0 Hz, ArH), 4.89–4.83 (1H, m, CHO), 4.17–4.10 (2H, m, CH_2N), 3.79 (3H, s, OCH_3), 3.78–3.72 (2H, m, CH_2Cl); ^{13}C (100 MHz, $CDCl_3$) δ 156.6, 154.2, 130.9, 120.4, 114.3, 70.8, 55.5, 48.7, 44.6. Mass spec. (ESI): calcd. m/z 264.0398 $[C_{11}H_{12}ClNO_3+Na]^+$; found: 264.0395. IR (neat, cm^{-1}): 1728.

3-(4-Methylphenyl)-5-chloromethyloxazolidin-2-one (**6p**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (3:1) (170 mg, 83%). M.p. 104–106 °C (lit. 104–107 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (2H, d, *J* 8.0 Hz), 7.19 (2H, d, *J* 8.0 Hz), 4.89–4.82 (1H, m, CHO), 4.15 (1H, t, *J* 8.0 Hz, CH_2N), 3.92 (1H, dd, *J* 12.0, 8.0 Hz, CH_2N), 3.89 (1H, dd, *J* 12.0, 4.0 Hz, CH_2Cl), 3.73 (1H, dd, *J* 12.0, 8.0 Hz, CH_2Cl), 2.32 (3H, s, CH_3); ^{13}C (100 MHz, $CDCl_3$) δ 154.0, 135.2, 134.1, 129.6, 118.4, 70.8, 48.3, 44.5, 20.7. Mass spec. (ESI): calcd. m/z 226.0629 $[C_{11}H_{13}ClNO_2+H]^+$; found: 226.0630. IR (neat, cm^{-1}): 1732.

3-(4-Fluorophenyl)-5-chloromethyloxazolidin-2-one (**6q**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (5:1) (125 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, dd, *J* 8.0, 4.0 Hz, ArH), 7.09 (2H, t, *J* 8.0 Hz, ArH), 4.91–4.85 (1H, m, CHO), 4.16 (1H, t, *J* 8.0 Hz, CH_2N), 3.96 (1H, dd, *J* 8.0, 4.0 Hz, CH_2N), 3.81 (1H, dd, *J* 12.0, 4.0 Hz, CH_2Cl), 3.75 (1H, dd, *J* 12.0, 8.0 Hz, CH_2Cl); ^{13}C (100 MHz, $CDCl_3$) δ 159.5 (d, J 244.5 Hz), 154.0, 133.9 (d, J 3.2 Hz), 120.2 (d, J 8.1 Hz), 115.9 (d, J 22.6 Hz), 70.8, 48.4, 44.5. ^{19}F NMR(376 MHz, $CDCl_3$): δ 117.8 (s). Mass spec. (ESI): calcd. m/z 252.0198 $[C_{10}H_9ClFNO_2+Na]^+$; found: 252.0195.

3-(4-Chlorophenyl)-5-chloromethyloxazolidin-2-one (**6r**): Obtained as an orange solid after purification by flash chromatography using a solvent system of hexane–EtOAc (1:1) (100 mg, 42%). M.p. 129–132 °C (lit. 130–133 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, *J* 8.0 Hz, ArH), 7.34 (2H, d, *J* 8.0 Hz, ArH), 4.91–4.85 (1H, m, CHO), 4.14 (1H, t, *J* 8.0 Hz, CH_2N), 3.93 (1H, dd, *J* 8.0, 4.0 Hz, CH_2N), 3.79 (1H, dd, *J* 12.0, 4.0 Hz, CH_2Cl), 3.75 (1H, dd, *J* 12.0, 8.0 Hz, CH_2Cl); ^{13}C (100 MHz, $CDCl_3$) δ 153.7, 136.3, 129.6, 129.1, 119.4, 70.8, 48.0, 44.5. Mass spec. (ESI^+): calcd.m/z 267.9903 $[C_{10}H_9Cl_2NO_2+Na]^+$; found: 267.9905. IR (neat, cm^{-1}): 1741.

3-(4-Bromophenyl)-5-chloromethyloxazolidin-2-one (**6s**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (3:1), then hexane–EtOAc (2:1) (92 mg, 36%). M.p. 126–128 °C (lit. 125–128 °C).[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.44 (4H, m, ArH), 4.92–4.86 (1H, m, CHO), 4.15 (1H, t, *J* 8.0 Hz, CH_2N), 3.94 (1H, dd, *J* 8.0, 4.0 Hz, CH_2N), 3.80 (1H, dd, *J* 12.0, 4.0 Hz, CH_2Cl), 3.75 (1H, dd, *J* 12.0, 8.0 Hz, CH_2Cl); ^{13}C (100 MHz, $CDCl_3$) δ 153.7, 132.7, 132.1, 119.7, 117.3, 70.8, 48.0, 44.4. Mass spec. (ESI+): calcd. m/z 311.9397 $[C_{10}H_9BrClNO_2+Na]^+$; found: 311.9389. IR (neat, cm^{-1}): 1732.

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[1] For recent reviews of cyclic carbonate syntheses see: a) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353; b) A. C. Kathalikkattil, R.

Babu, J. Tharun, R. Roshan, D.-W. Park, *Catal. Surv. Asia* **2015**, *19*, 223; c) B. Yu, L.-N. He, *ChemSusChem* **2015**, *8*, 52; d) M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann, F. E. Kühn, *ChemSusChem* **2015**, *8*, 2436; e) B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang, S.-J. Zhang, *Green Chem.* **2015**, *17*, 108; f) V. D'Elia, J. D. A. Pelletier, J.-M. Basset, *ChemCatChem* **2015**, *7*, 1906.

[2] For recent reviews of polycarbonate syntheses see: a) S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2011**, *255*, 1460; b) M. R. Kember, A. Buchard, C. K. Williams, *Chem. Commun.* **2011**, *47*, 141; c) X.-B. Lu, W.-M. Ren, G.-P. Wu, *Acc. Chem. Res.* **2012**, *45*, 1721; d) D. J. Darensbourg, S. J. Wilson, *Green Chem.* **2012**, *14*, 2665; e) N. Ikpo, J. C. Flogeras, F. M. Kerton, *Dalton Trans.* **2013**, *42*, 8998; f) D. J. Darensbourg, A. D. Yeung, *Polym. Chem.* **2014**, *5*, 3949; g) M. Taherimehr, P. P. Pescarmona, *J. Appl. Polym. Sci.* **2014**, *131*, 41141; h) Y. Qin, X. Sheng, S. Liu, G. Ren, X. Wang, F. J. Wang, J. *CO2 Util.* **2015**, *11*, 3; i) S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini, C. K. Williams, *Chem. Commun.* **2015**, *51*, 6459.

[3] For recent reviews covering cyclic and polycarbonate syntheses see: a) R. Martín, A. W. Kleij, *ChemSusChem* **2011**, *4*, 1259; b) X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462; c) W. N. R. Wan Isahak, Z. A. Che Ramli, M. W. Mohamed Hisham, M. A. Yarmo, *Renew. Sust. Energy Rev.* **2015**, *47*, 93.

[4] a) J. A. Durden, H. A. Stansbury, W. H. Catlette, *J. Am. Chem. Soc.* **1960**, *82*, 3082; b) C. G. Overberger, A. Drucker, *J. Org. Chem.* **1964**, *29*, 360; c) S. Hayashi, M. Fukurawa, Y. Fujino, T. Nakao, K. Nagato, *Chem. Pharm. Bull.* **1971**, *19*, 1594; d) G. E. McCasland, A. B. Zanlungo, L. J. Durham, *J. Org. Chem.* **1974**, *39*, 1462; e) Y. Taguchi, K. Yanagiya, I. Shibuya, Y. Suhara, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 921; f) Y. Taguchi, M. Yasumoto, I. Shibuya, Y Suhara, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 474; j) N. Kihara, Y. Nakawaki, T. Endo, *J. Org. Chem.* **1995**, *60*, 473; h) R. Maggi, C. Malmassari, C. Oro, R. Pela, G. Sartori, L. Soldi, *Synthesis* **2008**, 53; i) I. Yavari, M. Ghazanfarpour-Darjani, Z. Hossaini, M. Sabbaghan, N. Hosseini, *Synlett* **2008**, 889; j) A. Z. Halimehjani, F. Ebrahimi, N. Azizi, M. R. Saidi, *J. Heterocycl. Chem.* **2009**, *46*, 347; k) W. Clegg, R. W. Harrington, M. North, P. Villuendas, *J. Org. Chem.* **2010**, *75*, 6201; l) M. North, P. Villuendas, *Synlett* **2010**, 623; m) J. Cao, M. Yu, H. Li, L. Wang, X. Zhu, G. Wang, Y. Shi, C. Cao, *Res. Chem. Intermed.* **2015**, *41*, 5323; n) C. Beattie, M. North, *ChemCatChem* **2014**, *6*, 1252.

[5] a) T. Baronsky, C. Beattie, R. W. Harrington, R. Irfan, M. North, J. G. Osende, C. Young, *ACS Catal.* **2013**, *3*, 790; b) J. A. Castro-Osma, A. Earlam, A. Lara-Sánchez, A. Otero, M. North, *ChemCatChem* **2016**, *8*, 2100; c) C. Beattie, M. North, *RSC Adv.* **2014**, *4*, 31345.

[6] a) G. S. K. K. Reddy, A. Ali, M. N. L. Nalam, S. G. Anjum, H. Cao, R. S. Nathans, C. A. Schiffer, T. M. Rana, *J. Med. Chem.* **2007**, *50*, 4316; b) N. Fresno, M. Macías-González, A. Torres-Zaguirre, M. Romero-Cuevas, P. Sanz-Camacho, J. Elguero, F. J. Pavón, F. Rodríguez de Fonseca, P. Goya, R. Pérez-Fernández, *J. Med. Chem.* **2015**, *58*, 6639.

[7] a) W. R. Roush, R. A. James, *Aust. J. Chem.* **2002**, *55*, 141; b) J. A. Birrell, E. N. Jacobsen, *Org. Lett.* **2013**, *15*, 2895; c) V.Laserna, W. Guo, A. W. Kleij, *Adv. Synth. Catal.* **2015**, *357*, 2849.

[8] G. P. Speranza and W. J. Peppel, *J. Org. Chem.* **1958**, *23*, 1922.

[9] a) C. Qian, D. Zhu, *Synlett* **1994**, 129; b) H.-Y. Wu, J. -C. Ding, Y.-K. Liu, *J. Indian Chem. Soc.* **2003**, *80*, 36; c) M. T. Barros, A. M. F. Phillips, *Tetrahedron: Asymmetry* **2010**, *21*, 2746.

[10] a) L. Aroua, A. Baklouti, *Synth. Commun.* **2007**, *37*, 1935; b) J. E. Herweh, W. J. Kauffman, *Tetrahedron Lett.* **1971**, *12*, 809; c) J. E. Herweh, *J. Heterocycl. Chem.* **1968**, *5*, 687; d) J. E. Herweh, T. A. Foglia, D. Swern, *J. Org. Chem.* **1968**, *33*, 4029; e) H. Siegel, H. Wittmann, *Monatsh. Chem.* **1982**, *113*, 1005.

[11] X. Zhang, W. Chen, C. Zhao, C. Li, X. Wu, W. Z. Chen, *Synth. Commun.* **2010**, *40*, 3654.

[12] a) A. Baba, M. Fujiwara, H. Matsuda, *Tetrahedron Lett.* **1986**, *27*, 77; b) M. Fujiwara, A. Baba, H. Matsuda, *J. Heterocycl. Chem.* **1988**, *25*, 1351; c) M. Fujiwara, A. Baba, H. Matsuda, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1069.

[13] a) I. Shibata, A. Baba, H. Iwasaki, H. Matsuda, *J. Org. Chem.* **1986**, *51*, 2177; b) M. Fujiwara, A. Baba, Y. Tomohisa, H. Matsuda, *Chem. Lett.* **1986**, 1963; c) A. Baba, K. Seki, H. Matsuda, *J. Heterocycl. Chem.* **1990,** *27*, 1925; d) K. Yano, N. Amishiro, A. Baba, H. Matsuda, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2661.

[14] For a review of compound **8** see: M. North, *ARKIVOC* **2012**, (part (i)), 610.

[15] A. Otero, A. Lara-Sánchez, J. Fernández-Baeza, C. Alonso-Moreno, J. Tejeda, J. A. Castro-Osma, I. Márquez-Segovia, L. F. Sánchez-Barba, A. M. Rodríguez, M. V. Gómez, *Chem. Eur. J.* **2010**, *16*, 8615.

[16] J. A. Castro-Osma, M. North, X. Wu, *Chem. Eur. J.* **2016**, *22*, 2100.

[17] H. A. Duong, M. J. Cross, J. Louie, *Org. Lett.* **2004**, *6*, 4679.

[18] a) Z. Wirpsza in *Polyurethanes: Chemistry, Technology and Application*, Ellis Horwood, London, UK, **1993**; b) A. K. Zitinkina, N. A. Sibanova, O. G. Tarakanov, *Russ. Chem. Rev.* **1985**, *54*, 1866; c) T. Nawata, J. E. Kresta, , K. C. J. Frisch, *Cell. Plast.* **1975**, 267; d) L. Nicholas, G. R. J. Gmitter, *Cell. Plast.* **1965**, 85.

[19] a) A. J. Bloodworth, A. G. Davies, *J. Chem. Soc.* **1965**, 6858; b) S. R. Foley, G. P. A. Yap, D. S. Richesom, *Organometallics* **1999**, *18*, 4700.

[20] Z. Guo, X. Wei, H. Tong, D. Liu, *J. Organomet. Chem.* **2015**, *776*, 136.

[21] J. F. Villa, H. B. Powell, *Synth. React. Inorg. Met.-Org. Chem.* **1976**, *6*, 59.

[22] a) S. G. Lee, K. Y. Choi, Y. J. Kim, S. Park, S. W. Lee, *Dalton Trans.*, **2015**, *44*, 6537; b) F. Paul, S. Moulin, O. Piechaczyk, P. Le Floch, J. A. Osborn, *J. Am. Chem. Soc.* **2007**, *129*, 7294.

[23] H. R. Sharpe, A. M. Geer, H. E. L. Williams, T. J. Blundell, W. Lewis, A. J. Blake, D. L. Kays, *Chem Commun.* **2017**, *53*, 937.

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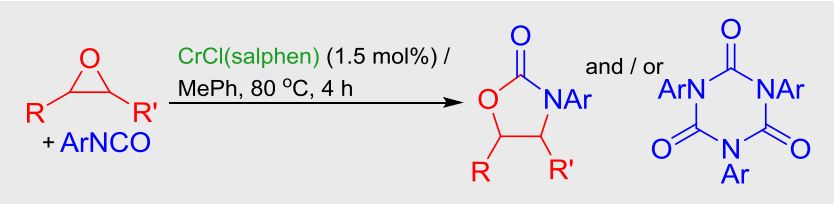

A tale of two reactions. A chromimium(salphen) complex catalyses the formation of oxazolidinones from epoxides and isocyanates. However, with particularly electron-deficient isocyanates, the complex catalyses cyclotrimerisation of the isocyanate to an isocyanurate instead.

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Isocyanurate Formation During Oxazolidinone Synthesis from Epoxides and Isocyanates Catalysed by a Chromium(Salphen) Complex