ChemPubSoc Europe

DOI: 10.1002/cssc.201601246

CHEMSUSCHEM Full Papers

Carbocation/Polyol Systems as Efficient Organic Catalysts for the Preparation of Cyclic Carbonates

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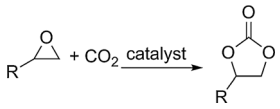
Carbocation/polyol systems are shown to be highly efficient catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide at 50 °C and 5 MPa CO_2 pressure. The best activity was shown by the combination of crystal violet and 1,1′-bi-2-naphthol (BINOL), which could be recycled five times with no loss of activity. The presence of specific interactions between the amino groups of the carbocation and the hydroxyl protons was confirmed by NMR experiments. The Job plots for the crystal violet iodide/BINOL and brilliant green iodide/BINOL systems showed that the catalytic systems consist of one molecule of the carbocation and one molecule of BINOL. Mechanistic studies using a deuterated epoxide indicate that there was some loss of epoxide stereochemistry during the reaction, but predominant retention of stereochemistry is observed. On this basis, a catalytic cycle is proposed.

Introduction

The search for valorization technologies for emitted carbon dioxide (CO_2) is one of the most rapidly growing fields of chemical research.[1] The coupling of CO_2 with epoxides is a highly atom economical process, leading to the production of cyclic carbonates (Scheme 1), which are an important class of industrial intermediates and solvents.[1–4] This methodology is highly sustainable and is already utilized in industry; the volume of cyclic carbonates produced is expected to grow substantially in the near future owing to their use as electrolytes in lithium–ion batteries. The best catalysts for the synthesis of cyclic carbonates are based on a two-component metal complex/nucleophile catalyst combination.[2,3] Recently, purely organic catalysts have become the focus of studies[4] because their use can be more cost-effective, the catalysts are commercially available, usually more sustainable, and less toxic than metal complexes. In particular, quaternary ammonium and phosphonium salts have been widely utilized as catalysts.[4–8] There are also examples of imidazolium salts[9–15] and imidazolium-based ionic liquids[16] used as catalysts for cyclic carbonate synthesis. In addition, two-component systems comprising an alcohol (e.g., phenol) and a quaternary ammonium salt have been successfully tested.[17,18] This system represents a promising class of organic catalysts with the potential for further improvement.[4] Unfortunately, the efficiency of the organic catalysts is no match for metal-based catalysts.[4] This justifies the search for novel classes of organic catalysts.



Scheme 1. Synthesis of cyclic carbonates.

We have previously developed several catalytic systems for the synthesis of cyclic carbonates by coupling of CO_2 and epoxides. These included highly efficient and robust aluminum (salen) complexes,[19,20] and stereochemically inert Co^{III} complexes that function as "Brønsted acids in disguise" with the central metal ion only serving as an activator of the catalytically active Brønsted acidic NH groups.[21]

Herein, we describe the use of well-known, commercially available, and stable carbocations in the form of triarylmethane dyes (Figure 1) as catalysts for the synthesis of cyclic carbonates. We tested the iodide salt form of malachite green (MGI), brilliant green (BGI), and crystal violet (CVI) as bifunctional catalysts, the activities of which were augmented by the addition of Brønsted acids.

Results and Discussion

Although rare, the use of triarylmethylium (trityl) carbocations as catalysts for organic transformations such as Diels–Alder and Michael reactions has been reported.[22] However, to the

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Supporting Information for this article can be found under: http://dx.doi.org/10.1002/cssc.201601246.

This publication is part of a Special Issue around the "1st Carbon Dioxide Conversion Catalysis" (CDCC-1) conference. A link to the issue's Table of Contents will appear here once it is complete.

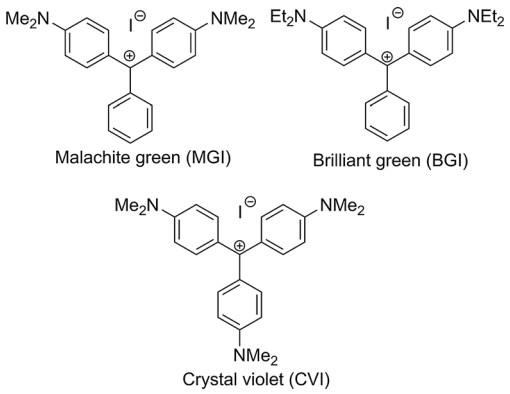


Figure 1. Carbocation dyes used as catalysts for cyclic carbonate synthesis.

best of our knowledge, the use of triarylmethane dyes as organic catalysts has not been previously reported. The reason for this seems to be because the activity of a carbocation is inversely related to its stability.[22–25] However, carbocations exist as halide salts; therefore, they are bifunctional systems that include a Lewis acidic center and a nucleophilic counterion. As such, they are similar to ammonium salts, which are a well-known class of catalysts for the synthesis of cyclic carbonates.[4–8] In addition, the amino substituents of triarylmethane dyes could interact with a Brønsted acid catalyst component. The resulting formation of a hydrogen bond would increase the Lewis acidity of the dyes.

Based on the accepted mechanism of bifunctional Lewis acid/halide ion catalysis, a potential mechanism of CO_2 addition to epoxides promoted by the dyes is shown in Scheme 2. The Lewis acidic carbocation could activate the epoxide towards nucleophilic attack by the iodide anion. Subsequent addition of CO_2 and the elimination of iodide bring the reaction to completion and regenerate the catalyst.

NMR analysis of mixtures of CVI and propylene oxide (PO) was used to demonstrate the Lewis acidic interaction of the carbocations with epoxides. Both the ^1H and ^{13}C NMR spectra revealed significant shifts of the signals of the dimethylamino groups of CVI and the methyl group of the epoxide to higher fields as the PO concentration increased (see Supporting information). Moreover, the ^{13}C NMR spectra showed a shift of the carbocation's carbon signal (178.02 ppm) to higher field, which correlated with increasing epoxide concentration (Figure 2). Thus, the spectra indicated that the epoxide did coordinate with the carbocation of CVI.

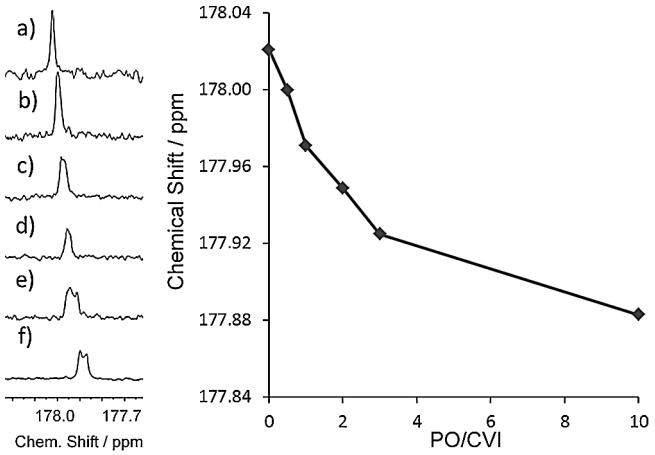
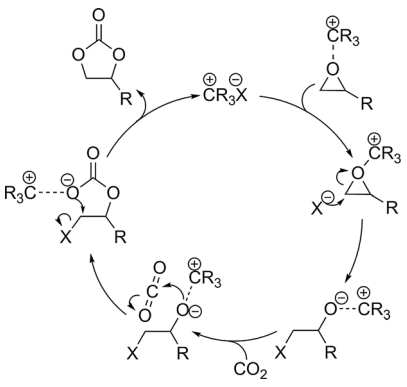


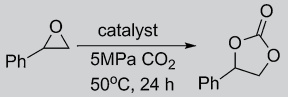
Figure 2. Shifts of the signals of the central carbon atom of CVI upon the addition of increasing concentrations of PO in CD_2Cl_2. a) pure CVI (0.33 M), b) CVI/PO = 2:1, c) CVI/PO = 1:1, d) CVI/PO = 1:2, e) CVI/PO = 1:3, and f) CVI/PO = 1:10. The splitting of the ^{13}C signal in the spectra of e) and f) probably suggests that at low CVI/PO ratios, two PO molecules may interact with each CVI.

The addition of CO_2 to neat styrene oxide (SO) was selected as a benchmark reaction to test the activities of the dyes. As the dyes were commercially available in their chloride form, both MG and CV were tested in their original (Table 1, entries 1,2) and iodide forms (Table 1, entries 3,5). The chloride to iodide exchange was easily achieved in a two-phase CH_2Cl_2/H_2O system using a twentyfold excess of potassium iodide. As expected, the iodide form was much more active; therefore, the iodide form of all the dyes was used for further testing.



Scheme 2. Proposed mechanism of the formation of cyclic carbonates promoted by triarylmethane dyes.

Table 1. Comparison of the catalytic activities of MGI, BGI, CVI, and TBAI.[a]



Entry	Catalyst	Conversion[b] [%]	Selectivity [%]
1[c]	MG	< 1	not determined
2[c]	CV	< 1	not determined
3	MGI	8	> 99
4	BGI	28	> 99
5	CVI	45	> 99
6[d]	CVI	32	> 99
7	TBAI	41	> 99

[a] Reaction conditions: 2 mol% catalyst unless specified otherwise, neat SO. [b] Conversions were determined by ^1H NMR using the catalyst signals as an internal standard. [c] The dyes were used in their chloride forms. [d] The catalyst loading was 1% mol.

CVI was the most active dye. Its catalytic activity was similar to that of tetrabutylammonium iodide (TBAI) (Table 1, entries 5 and 7). The catalytic activity of MGI and BGI was inferior to CVI and TBAI (Table 1, runs 3, 4, 5, and 7). The relative order of activity of the dyes was unexpected. If the Lewis acidity of the cations was the most important factor, the opposite trend would have been expected as the pK_{R^+} values for MGI and CVI are 6.9 and 9.4, respectively.[22] This suggests that a compensating effect influences the catalytic activity of the dye/iodide ion bifunctional catalyst. The observed catalytic activity trend of MGI < BGI < CVI can be explained by stronger association of ion pairs resulting in lower catalytic activity. The dissociation of the ion pairs should lead to a better catalytic performance, which was supported by experiments. Thus, halving the CVI concentration led to a relatively small change in the conversion of SO (Table 1, entries 4 and 6), consistent with greater ion pair dissociation resulting from dilution of the CVI.

The introduction of anion complexing agents should lead to better catalytic performance because of separation of the ion pairs into Lewis acidic and nucleophilic parts, revealing the hidden potential of their activity. For this purpose, several polyalcohols and carboxylic acids (Figure 3) were investigated. These can simultaneously coordinate with iodide, form hydrogen bonds with the amino groups of the dyes, and coordinate an alcoholic oxygen to the cationic center of the dye.

Initially, α,α,α′,α′-tetraaryl-2,2 disubstituted-1,3-dioxolane-4,5-dimethanol (TADDOL) additives were tested with TBAI and BGI to investigate if there were any cooperative interactions between the two catalysts. In these experiments, twice as much TADDOL as bis-TADDOL was used so that the total

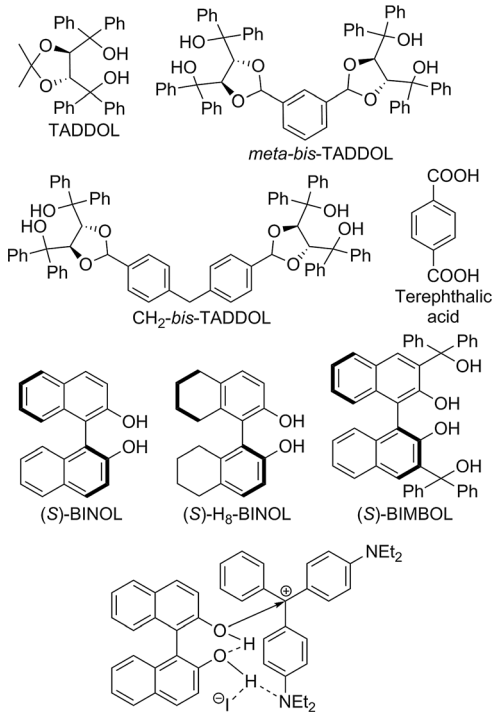


Figure 3. Compounds used as Brønsted acid additives and an example of their postulated mode of action.

Table 2. Activity of polyol additives in the reaction of styrene oxide with CO_2.[a]

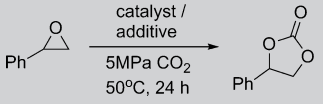
Entry	Polyol	Catalyst	Conversion[b] [%]
1	TADDOL	TBAI	70
2	*meta*-bis-TADDOL	TBAI	71
3	CH_2-bis-TADDOL	TBAI	76
4	TADDOL	BGI	41
5	*meta*-bis-TADDOL	BGI	55
6	CH_2-bis-TADDOL	BGI	64

[a] Reaction conditions: 1.25 mol% of bis-TADDOLs (or 2.5 mol% TADDOL), 2.5 mol% of TBAI (or BGI), neat SO, 50 °C, 5 MPa CO_2, 24 h. [b] Conversions were determined using ^{1}H NMR spectroscopy.

number of available hydroxyl groups is kept constant. The results are shown in Table 2. In the case of TBAI, no significant difference in catalytic activities was detected between the TADDOLs (Table 2, entries 1–3). However, in the case of BGI, the TADDOLs were found to have markedly different activities (Table 2, entries 4–6). The best activator was found to be CH_2-bis-TADDOL, which has the greatest distance between its two pairs of hydroxyl groups (Table 2, entry 6). This observation supports the hypothesis that there are activating interactions between the amino groups of the carbocations and hydroxyl protons of the polyols.

Table 3 summarizes the activities of the dyes relative to TBAI using other types of polyol additives. The polyols themselves were not catalytically active (Table 3, entry 1). The activity of TBAI was increased in the order BIMBOL < TADDOL < H8-BINOL < BINOL, where BIMBOL: 3,3′-bis(hydroxydiphenylmethyl)-[1,1′-binaphthalene]-2,2′-diol, H8BINOL is 5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalene]-2,2′-diol, and

Table 3. Catalytic activity of TBAI, MGI, BGI and CVI in the presence of additives.[a]



Entry	Catalyst (amt. [mol%])	Additive (amt. [mol%])	Conversion[b] [%]	Selectivity [%]
1	–	BINOL, BIMBOL, H8-BINOL, TADDOL (1.0)	< 1	–
2	TBAI (2.5)	BIMBOL (1.25)	53	> 99
3	TBAI (2.5)	H8-BINOL (2.5)	82	> 99
4	TBAI (2.5)	BINOL (2.5)	88	> 99
5	TBAI (1.0)	BINOL (2.5)	69	> 99
6	MGI (1.0)	BINOL (1.0)	12	> 99
7	BGI (2.5)	BIMBOL (1.25)	58	> 99
8	BGI (2.5)	H8-BINOL (2.5)	82	> 99
9	BGI (1.0)	BINOL (1.0)	49	> 99
10	BGI (2.5)	BINOL (2.5)	100	> 99
11	BGI (2.5)	terephthalic acid (2.5)	0	
12	CVI (1.0)	TADDOL (1.0)	48	> 99
13	CVI (1.0)	BIMBOL (0.5)	57	> 99
14	CVI (1.0)	BINOL (1.0)	82	> 99

[a] Reaction conditions: neat SO, 50 °C, 5 MPa CO_2, 24 h. [b] Conversions were determined by ^{1}H NMR using the catalyst signals as an internal standard.

BINOL is [1,1′-binaphthalene]-2,2′-diol (Table 1, entry 7; Table 2, entries 1–3; and Table 3, entries 2–5). The addition of BINOL also led to an increase in the activities of the carbocation dyes, even for the least reactive MGI (Table 1, entry 3, Table 3, entry 6). The effect was even more pronounced in the case of BGI (Table 1, entry 4, Table 2 entries 4–6, and Table 3, entries 7–10). The order of efficiency of the additives was TADDOL < BIMBOL < H8-BINOL < BINOL. At higher concentrations, the catalyst system of BGI/BINOL became more active than that of TBAI/BINOL (Table 3, entries 4,5 and 9,10). Finally, the most efficient catalyst was CVI/BINOL (Table 1, entries 5,6 and Table 3, entries 12–14). The order of the efficiency was TADDOL < BIMBOL < BINOL. Notably, the inexpensive diol BINOL was more active than the TADDOL derivatives. The greater acidity of BINOL ($pK_a = 13.2$[26] in DMSO) and its lower steric bulk compared to TADDOL ($pK_a = 19.2$[26] in DMSO) could explain this observation. The use of terephthalic acid with BGI (Table 3, run 11) resulted in complete inhibition of the activity of BGI.

^1H and ^{13}C NMR spectra of mixtures of BGI with different concentrations of BINOL were recorded to investigate the nature of the interactions between BINOL and a dye molecule (Figure 4). A significant shift of the peaks attributed to the hydroxyl protons of BINOL to lower fields was the most conspicuous change in the spectra of BINOL (Figure 4, b-e). An upfield shift of the CH_2 protons of the ethylamino groups and the aromatic protons *ortho* to the amino groups were also observed with increasing BINOL concentration (Figure 4, a-d). In addition, a 0.2 ppm upfield shift of the ^{13}C NMR signal of the carbocation was observed in the spectrum with a 1:3 ratio of BGI/BINOL (see Supporting Information). These spectra indicated

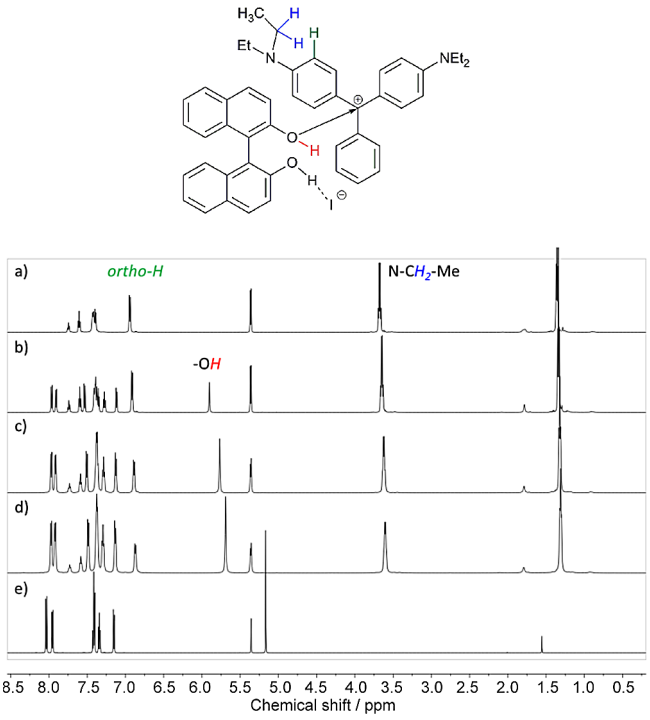


Figure 4. ^1H NMR spectra of different ratios of BGI/BINOL in CD_2Cl_2. a) pure BGI; b) BINOL/BGI = 1:1; c) BINOL/BGI = 2:1; d) BINOL/BGI = 3:1; and e) pure BINOL.

that the Lewis acidic central carbon atom of BGI interacted with BINOL through a lone pair of an OH group in a similar way to its interaction with PO (Figure 2). Such an interaction should lead to higher acidity of the hydroxyl group and a shift of the proton resonance to a lower field.

Job plots of the activity of BGI/BINOL or CVI/BINOL were constructed to determine the optimal ratio between the dyes and BINOL (Figure 5). The total loading of the BINOL–carbocation system was kept constant at 2 mol%. As shown in Figure 5, the highest yields of styrene carbonate were achieved in the BGI/BINOL ratio range of 2:1 to 1:1. A similar dependence was observed for CVI, with the best CVI/BINOL ration of 1:1.

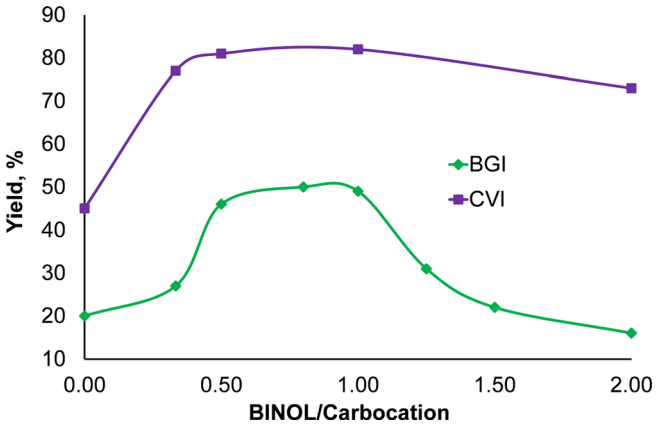
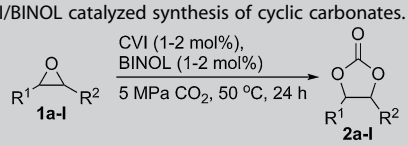


Figure 5. Job plots of the BGI/BINOL and CVI/BINOL systems in the synthesis of styrene carbonate from SO and CO_2. Reaction conditions: neat SO, 2 mol% BINOL + carbocation, 50 °C, 5 MPa CO_2, 24 h.

The 1:1 CVI/BINOL system was used for the synthesis of ten cyclic carbonates **2a–j** from terminal epoxides **1a–j** (Table 4, entries 1–13). Good conversions of the more reactive epoxides **1a**,**d**,**e** were obtained using only 1 mol% of each catalyst component (Table 4, entries 1,6,7). However, other aromatic and aliphatic epoxides **1b**,**c**,**f** gave rather low conversions when 1 mol% of each catalyst component was used; much better results were obtained with 2 mol% of each catalyst (Table 4, entries 2–5,8,9). Therefore, 2 mol% of each catalyst was used with the remaining substrates. Under these conditions, high conversions were obtained with substrates possessing long alkyl chains, ethers, and alcohols in their sidechains (Table 4, entries 7–11). These results show that the CVI/BINOL system has general applicability and tolerates functional groups within the epoxide substrate. Cyclic disubstituted epoxides **1k** and **1l** were also investigated as substrates. Cyclohexene oxide **1k** failed to react when a catalyst loading of 1 mol% of each component was used (Table 4, entry 14). Increasing the catalyst loading to 5 mol% of each component resulted in the formation of *cis*-cyclohexene carbonate in only 10% yield (Table 4, entry 15). No polycarbonate was formed in these reactions. The reaction of cyclopentene oxide **1l** was slightly more successful, giving cyclopentene carbonate **2l** in 31% yield when 5 mol% of each catalyst component was used.

Table 4. CVI/BINOL catalyzed synthesis of cyclic carbonates.



a: R^1 = Ph, R^2 = H; **b:** R^1 = 4-ClC_6H_4, R^2 = H;
c: R^1 = 4-BrC_6H_4, R^2 = H; **d:** R^1 = CH_2Cl, R^2 = H;
e: R^1 = Me, R^2 = H; **f:** R^1 = ^{n}Oct, R^2 = H; **g:** R^1 = ^{n}But, R^2 = H;
h: R^1 = ^{n}Dec, R^2 = H; **i:** R^1 = CH_2OPh, R^2 = H;
j: R^1 = CH_2OH, R^2 = H; **k:** R^1-R^2 = $(CH_2)_4$; **l:** R^1-R^2 = $(CH_2)_3$

Entry	Cyclic carbonate	CVI + BINOL [mol%]	Yield[a] [%]	Conversion[b] [%]	Selectivity [%]
1	**2a**	1+1	72	82	>99
2	**2b**	1+1	48	54	>99
3	**2b**	2+2	54	100	>99
4	**2c**	1+1		76	>99
5	**2c**	2+2	70	100	>99
6	**2d**	1+1	70	100	>99
7	**2e**	1+1	65	100	>99
8	**2f**	1+1		37	>99
9	**2f**	2+2	60	78	>99
10	**2g**	2+2	56	100	>99
11	**2h**	2+2	79	100	>99
12	**2i**	2+2	71	100	>99
13	**2j**	2+2	61	100	>99
14	**2k**	1+1	0		
15	**2k**	5+5	10	20	>99
16	**2l**	5+5	31	70	>99

[a] The cyclic carbonates were isolated by flash chromatography on silica. [b] Conversions were determined by ^{1}H NMR using the catalyst signals as an internal standard.

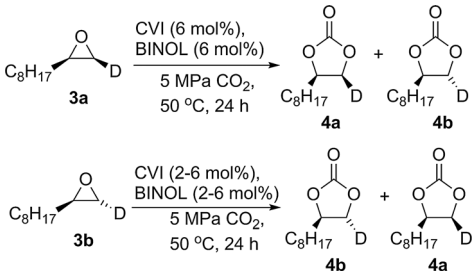
The stability of the CVI/BINOL catalytic system was investigated by reusing the catalysts in the reaction of PO at 50 °C and 5 MPa CO_2 pressure with a reaction time of 24 h. After the first 24 h period, the yield of the cyclic carbonate **2d** was determined by ^{1}H NMR spectroscopy, then another portion of propylene oxide was added to the reaction mixture. The results are shown at Table 5. The system could be recharged five times with no loss of activity.

To investigate the mechanism of the reaction, deuterated epoxides **3a**,**b**[26] were used to study the stereochemistry of

Table 5. Reusability of the CVI-BINOL catalytic system.[a]

Entry	Cycle	Catalyst system concentration [mol%]	Conversion[b] [%]
1	1	2	100
2	2	1	100
3	3	0.67	95
4	4	0.5	74
5[c]	5	2	100

[a] Reaction conditions: 1 mol% BINOL, 1 mol% CVI, neat PO (50 mg, 0.06 mL, 0.86 mmol), 50 °C, 5 MPa CO_2, 24 h. The second and subsequent cycles included the addition of a fresh 50 mg portion of epoxide **1d** to the reaction mixture after each 24 h reaction period. [b] Conversions were determined using ^{1}H NMR spectroscopy. [c] Reaction conditions: 1 mol% BINOL, 1 mol% CVI, both recovered from the experiment of entry 4 following distillation of **2d**, neat PO (50 mg, 0.06 mL, 0.86 mmol), 50 °C, 5 MPa CO_2, 24 h.



Scheme 3. Use of deuterated epoxides **3a**,**b** to study the stereochemistry of the cyclic carbonates.

the reaction (Scheme 3). In both cases, deuterated cyclic carbonates **4a**,**b** were formed with predominant retention of the epoxide stereochemistry. However, some epimerization was observed, which depended on the amount of catalyst used, as shown in Table 6. A control experiment in which epoxide **3b** was heated to 50 °C under nitrogen in the presence of 2 mol% of both CVI and BINOL showed that it did not epimerize under these conditions.

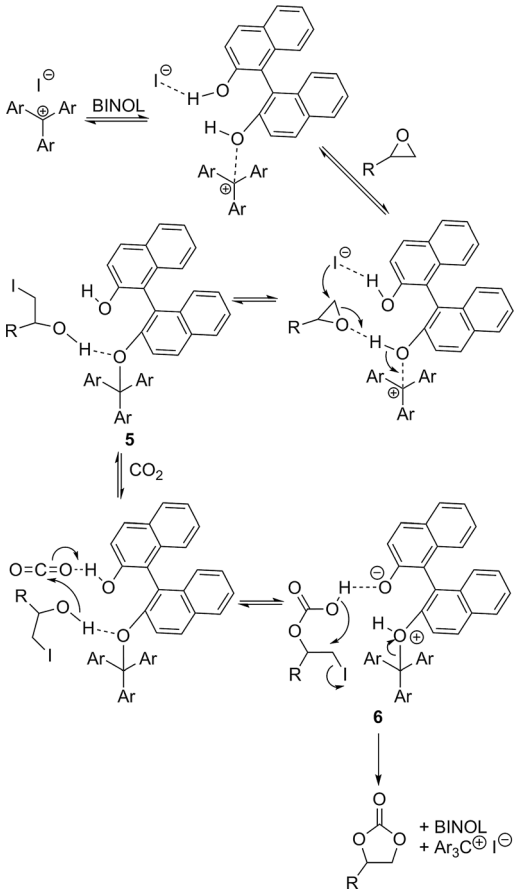
Table 6. Synthesis of deuterated cyclic carbonates **4a**,**b**.[a]

Entry	Epoxide	Catalyst system concentration [mol%]	Ratio of **4a**/**4b**
1	**3b**	2	11:89
2	**3b**	6	22:78
3	**3a**	6	73:27

[a] Reaction conditions: 2–6 mol% BINOL, 2–6 mol% CVI, neat epoxide **3a** or **3b**, 50 °C, 5 MPa CO_2, 24 h.

On the basis of the spectroscopic and stereochemical studies, a possible mechanism for the reaction is proposed in Scheme 4. The carbocation acts as a Lewis acid, activating the BINOL to become a stronger Brønsted acid. The increase in the acidity of the BINOL OH group allows it to form a stronger hydrogen bond with the epoxide and triggers the epoxide ring opening by the iodide ion to give intermediate **5**. The iodide ion itself may be positioned in space by the second OH group of BINOL. The remaining OH group in intermediate **5** could coordinate to CO_2, both activating and organizing it towards intramolecular carbonate formation to give intermediate **6**, which can then cyclize to form the cyclic carbonate product and regenerate the catalyst components.

Intermediates **5** and **6** could also undergo a non-productive S_N2 reaction of the alkyl iodide with external iodide. This reaction would only be visible (as a loss of stereochemical purity) in deuterated epoxides such as **3a**,**b**, and the relative rate of reaction with iodide to intramolecular cyclization of the carbonate is expected to increase as the concentration of iodide in the reaction increases, i.e., with increased catalyst loading, which accounts for the results presented in Table 6.



Scheme 4. A possible mechanism rationalizing the synergistic effect of BIMBOL on the activity of the dyes in the synthesis of cyclic carbonates.

Experimental Section

Materials

Commercial reagents were used as received unless stated otherwise. Column chromatography was performed using Silica Gel Kieselgel 60 (Merck).

Instrumentation

^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300, Bruker Avance III-400, and Bruker Avance 600 spectrometers. Melting points were determined in open capillary tubes and are uncorrected. Elemental analysis was performed at the elemental analysis laboratory of the Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS). All solvents were purified according to standard procedures.

Synthesis of carbocations

Malachite green iodide. Malachite green chloride (1.0 g, 2.7 mmol) dissolved in CH_2Cl_2 (10 mL) was added to a solution of KI (7.0 g, 42 mmol) in water (10 mL). The resulting suspension was stirred at room temperature for 4 h, then the organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to give malachite green iodide (0.95 g, 94%) as green crystals. M.p. 100–102 °C; IR (KBr): $\tilde{\nu}$ = 2920, 2851, 1583, 1363, 1167 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.73–7.68 (m, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.8 Hz, 4H), 7.34 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.9 Hz, 4H), 3.40 ppm (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.68, 156.98, 141.00, 139.50, 134.73, 133.13, 128.61, 127.38, 113.98, 41.43 ppm. X-ray fluorescence data: no Cl was detected.

Brilliant green iodide. Brilliant green mono-oxalate (1.0 g, 2.0 mmol) dissolved in CH_2Cl_2 (10 mL) was added to a solution of KI (7.0 g, 42 mmol) in water (10 mL). The resulting suspension was stirred at room temperature for 4 h, then was neutralized by the addition of aqueous NaOH. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to give brilliant green iodide (0.92 g, 90%) as green crystals. M.p. 186–189 °C; IR (KBr) $\tilde{\nu}$ = 3060, 2972, 2928, 1580, 1341, 1186 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.73–7.68 (m, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.8 Hz, 4H), 7.34 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.9 Hz, 4H), 3.40 ppm (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.68, 156.98, 141.00, 139.50, 134.73, 133.13, 128.61, 127.38, 113.98, 41.43 ppm. X-ray fluorescence data: no Cl was detected.

Crystal violet iodide. Crystal violet chloride (1.0 g, 2.4 mmol) dissolved in CH_2Cl_2 (10 mL) was added to a solution of KI (7.0 g, 42 mmol) in water (10 mL). The resulting suspension was stirred at room temperature for 4 h, then the organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to give crystal violet iodide (0.94 g, 92%) as green crystals. M.p. 192–194 °C; IR (KBr) $\tilde{\nu}$ = 3087, 2913, 2852, 2808, 1581, 1358, 1171 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.03 (d, J = 9.0 Hz, 6H), 6.60 (d, J = 9.0 Hz, 6H), 3.03 ppm (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.57, 155.32, 139.44, 126.25, 112.32, 40.76 ppm. X-ray fluorescence data: no Cl was detected. Calculated for $C_{25}H_{30}IN_3.H_2O$: C, 58.03; H, 6.23; N, 8.12. Found: C, 57.95; H, 6.19; N, 7.99.

Synthesis of cyclic carbonates

All cyclic carbonate syntheses were performed in autoclaves with 5 MPa carbon dioxide starting pressure. The reactions were heated to 50 °C and magnetically stirred. After completion of the reaction, the autoclave was cooled to room temperature before the pressure was released. The reaction mixture was analyzed by ^1H NMR spectroscopy and passed through a pad of silica to separate the catalyst. Column chromatography (SiO_2, EtOAc/hexane, 1:3) was then used to purify the cyclic carbonates.

Styrene carbonate **2a**: M.p. 50–52 °C; IR (ATR): $\tilde{\nu}$ = 3037, 2921, 1782, 1160, 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44–7.32 (m, 5H), 5.66 (t, J = 8.0 Hz, 1H), 4.82–4.73 (m, 1H), 4.37–4.26 ppm (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.00, 135.88, 129.80, 129.31, 126.00, 78.11, 71.28 ppm.

4-Chlorostyrene carbonate **2b:** M.p. 67–70 °C; IR (ATR) $\tilde{\nu}$ = 3087, 2964, 2912, 1789, 1162, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.48–7.25 (m, 4H), 5.65 (t, J = 8.0 Hz, 1H), 4.79 (t, J = 8.2 Hz, 1H), 4.29 ppm (dd, J = 8.6, 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.65, 135.85, 134.35, 129.59, 127.37, 77.34, 71.10 ppm.

4-Bromostyrene carbonate **2c:** M.p. 70–72 °C; IR (ATR) $\tilde{\nu}$ = 2951, 2522, 2161, 2017, 1981, 1801, 1771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.64 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 8.0 Hz, 1H), 4.30 ppm (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.5, 134.8, 132.5, 127.4, 123.9, 77.2, 70.9 ppm.

3-Chloropropylene carbonate **2d**: IR (ATR) $\tilde{\nu}$ = 2967, 1779, 1159, 1055 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.02–4.93 (m, 1H), 4.60–

4.53 (m, 1H), 4.37 (dd, J=8.9, 5.7 Hz, 1H), 3.82–3.67 ppm (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ=154.49, 74.48, 67.06, 44.03 ppm.

Propylene carbonate **2e**: IR (ATR) $\tilde{\nu}$=2988, 2924, 1781, 1174, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.92–4.67 (m, 1H), 4.64–4.38 (m, 1H), 4.07–3.89 (m, 1H), 1.43 ppm (d, J=6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ=155.22, 73.74, 70.78, 19.45 ppm.

1,2-Decylene carbonate **2f**: IR (ATR) $\tilde{\nu}$=2931, 2835, 1796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.71–4.68 (m, 1H), 4.52 (t, J=8.0 Hz, 1H), 4.06 (t, J=8.0 Hz, 1H), 1.83–1.63 (m, 2H), 1.47–1.26 (m, 12H), 0.87 ppm (t, J=8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.1, 77.0, 69.4, 33.9, 31.8, 29.3, 29.1, 29.0, 24.3, 22.6, 14.1 ppm.

1,2-Hexylene carbonate **2g**: IR (ATR) $\tilde{\nu}$=2941, 2922, 2899, 1796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.73–4.66 (m, 1H, OCH), 4.52 (t, J=8.0 Hz, 1H), 4.06 (t, J=8.0 Hz, 1H), 1.86–1.65 (m, 2H), 1.49–1.35 (m, 4H), 0.92 ppm (t, J=8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.1, 76.8, 69.4, 33.5, 26.4, 22.2, 13.8 ppm.

1,2-Dodecylene carbonate **2h**: IR (ATR) $\tilde{\nu}$=2931, 2832, 1798 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.73–4.66 (m, 1H), 4.52 (t, J=8.0 Hz, 1H), 4.06 (t, J=8.0 Hz, 1H), 1.84–1.70 (m, 2H), 1.63–1.26 (m, 16H), 0.88 ppm (t, J=8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.1, 77.1, 69.4, 33.9, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 24.3, 22.6, 14.1 ppm.

3-Phenoxypropylene carbonate **2i**: M.p. 94–96 °C; IR (ATR) $\tilde{\nu}$= 3429, 3061, 2989, 2924, 2328, 1791 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.30 (t, J=8.0 Hz, 2H), 7.02 (t, J=8.0 Hz, 1H), 6.91 (d, J=8.0 Hz, 2H), 5.06–5.01 (m, 1H), 4.62–4.55 (m, 2H), 4.24 (dd, J=11.0, 4.0 Hz, 1H), 4.16 ppm (dd, J=11.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=157.7, 154.6, 129.7, 122.0, 114.6, 74.0, 66.8, 66.2 ppm.

Glycerol carbonate **2j**: IR (ATR) $\tilde{\nu}$=3382, 2901, 1799 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.84–4.78 (m, 1H), 4.52 (t, J=8.0 Hz, 1H), 4.44 (dd, J=8.0, 4.0 Hz, 1H), 3.96 (d, J=16.0, 4.0 Hz, 1H), 3.68 ppm (d, J=16.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.4, 76.6, 65.8, 61.6 ppm.

cis-Cyclohexene carbonate **2k**: M.p. 35–37 °C; IR (ATR) $\tilde{\nu}$=2933, 2861, 1784 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.70–4.65 (m, 2H), 1.91–1.87 (m, 4H), 1.66–1.57 (m, 2H), 1.46–1.36 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.4, 75.7, 26.8, 19.2 ppm.

Cyclopentene carbonate **2l:** M.p. 30–33 °C; IR (ATR) $\tilde{\nu}$=2967, 2871, 1789 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=5.11–5.10 (m, 2H), 2.19–2.14 (m, 2H), 1.83–1.63 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.4, 81.8, 33.1, 21.5 ppm.

Conclusions

Catalytic systems consisting of commercially available carbocations and polyols were found to be active as catalysts for the synthesis of cyclic carbonates. Carbocations in these systems act as activators of polyol hydroxyl groups, increasing their Brønsted acidity. Malachite green, brilliant green, and crystal violet have been used as antiseptic, antibacterial and fungicidal agents to treat both humans and animals.[27] As such, they can be considered as greener and safer catalysts than those based on complexes of toxic metals such as cobalt, chromium, and aluminum. The catalytic activity of the dye based catalysts is comparable to those often reported for metal-based catalysts,[2,3] although not as good as the activity of the very best metal based systems,[20] which have been extensively developed over more than a decade.

Acknowledgements

The authors gratefully acknowledge the financial support from a RFBR research grant No. 15-03-05648, a Russian Science Foundation grant No. 16-14-00112 and a RAS Presidium grant of basic research No. P-8 and from the European Union Seventh Framework Programme FP7-NMP-2012 under grant agreement number 309497.

Keywords: carbocations · carbon dioxide · catalysts · cyclic carbonates · phenols

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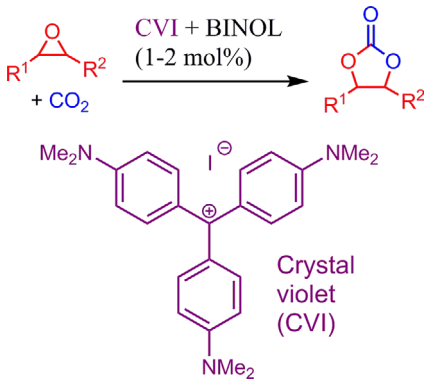
Received: September 7, 2016
Published online on ■■ ■■, 0000

Double team! Triarylmethane dyes and 1,1′-bi-2-naphthol are combined to form an organocatalytic system for the synthesis of cyclic carbonates from epoxides and carbon dioxide. A catalytic cycle is proposed based on mechanistic studies using a deuterated epoxide as a substrate.



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Carbocation/Polyol Systems as Efficient Organic Catalysts for the Preparation of Cyclic Carbonates

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