Iodine-Catalyzed Synthesis of Spiroorthcarbonates under Neutral Conditions

Mohammad Rahimizadeh,* Mehdi Bakavoli, Ali Shiri, and Hossein Eshghi

Department of Chemistry, School of Sciences, Ferdowsi University of Mashhad, 91775-1436 Mashhad, Iran
**E-mail: rahimizh@yahoo.com*
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Spiroorthocarbonates (SOCs) are one of the most important categories of monomers which polymerize without any shrinkage in volume.[1] They are specially useful in the synthesis of materials such as precision materials, adhesives, and dental composites.[1-3]

There are few methods for the synthesis of SOCs. Sakai *et. al.* reported a novel synthesis of SOCs from the reaction of organotin compounds with carbon disulfide.[4,5] This method is not recommended. Since it involves many steps and highly toxic unstable organotin compounds. Endo and Okawara also reported another synthetic method by treatment of tetraalkylorthocarbonate with various diols in the presence of TsOH as an acidic catalyst.[6] The main disadvantage of this method comes from inevitable formation of symmetrical SOCs during the preparation of unsymmetrical analogs. Synthesis of SOCs is also achieved by using highly toxic thiophosgene which is not advised.[7] The one pot treatment of dichlorodiphenoxymethane and various diols is useful only for the synthesis of symmetrical SOCs.[8] Endo used dichlorodiphenoxymethane in the presence of *p*-toluenesulfonic acid monohydrate for the preparation of asymmetric SOCs.[9] The long reaction times and relatively low yields are the disadvantages of this method. Therefore; an alternative method that can overcome these drawbacks and can be applied to the synthesis of symmetrical and unsymmetrical SOCs is desirable.

Recently, molecular iodine has been the focus of attention in organic transformations as a mild, readily available and neutral Lewis acid.[10] In continuation of our previous research on spiroorthocarbonates,[11,12] in this paper, we wish to report on the use of this catalyst for the synthesis of symmetrical and unsymmetrical SOCs from 2,2-diphenoxy-1,3-dioxane and 1,3-diol under neutral conditions. 2,2-Diphenoxy-1,3-dioxanes (**1a-b**) used in this work were prepared according to literature.[8]

The reaction of 2,2-diphenoxy-1,3-dioxane (**1a**) with 1,3-propanediol as a model reaction was performed in different aprotic solvents in the presence of I_2. On the basis of the reaction times and yields, CH_2Cl_2 was selected as a most suitable solvent for the synthesis of SOCs.

Table 1. Optimization of molar ratio of the catalyst

Entry	Catalyst (% mol)	Reaction Time (min)	Yield (%)
1	0.25	80	78
2	0.5	30	95
3	1	30	97
4	2	30	97

On the other hand, in order to get an insight into the optimum molar ratio of the catalyst, the model experiment was studied in four different molar ratios of the I_2, and the results clearly demonstrate that 0.5% molar ratio of I_2 related to 2,2-diphenoxy-1,3-dioxane is the optimal ratio. (Table 1)

2,2-Diphenoxy-1,3-dioxanes (**1a-b**) were reacted with various diols under neutral conditions in the presence of catalytic amount of molecular iodine (0.5 mol%) in CH_2Cl_2 to yield the corresponding SOCs (**2a-j**). (Scheme 1)

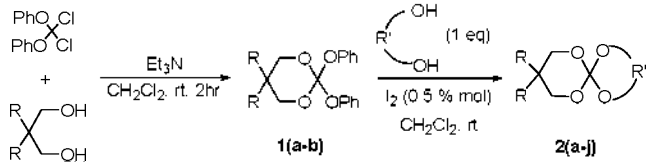
The efficiency and validity of this method for the synthesis of SOCs (**2a-j**) can be deduced from the data in Table 2. Moreover, the prolongation of the reaction has no effect on the product distribution unlike the previous published method which uses protic acid catalyst.[6]

The proposed mechanism of the synthesis of SOCs catalyzed by molecular iodine for a typical synthesis (Entry 1) is presented in Scheme 2.

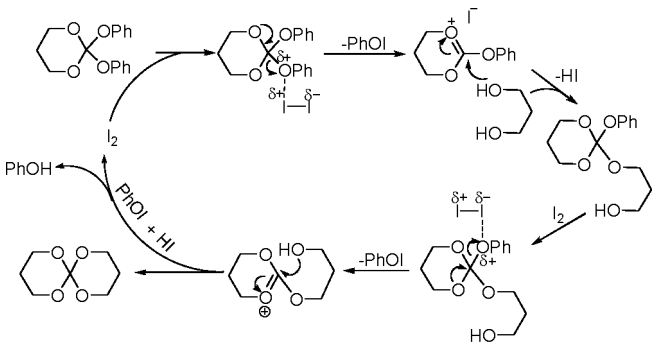
In conclusion, we have developed a new modified, efficient and chemoselective method for the synthesis of symmetrical and unsymmetrical SOCs catalyzed by molecular iodine with good to high yields.

Experimental

The ^{1}H NMR (100 MHz) spectra were recorded on a Bruker

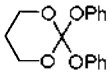
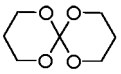
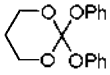
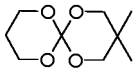
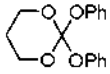
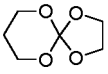
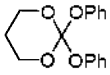
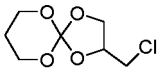
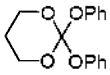
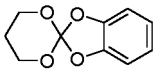
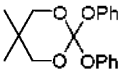
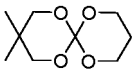
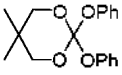
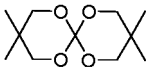
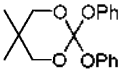
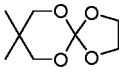
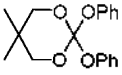
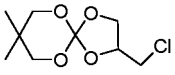
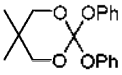
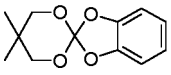


Scheme 1



Scheme 2

Table 2. The results of the reaction of 1,3-dioxane (**1a-b**) with diols in the presence of 0.5% mol molecular iodine

Entry	Substrate	Time (min)	Product	Yield (%)[a]	mp (°C) / bp (mmHg)	
					Found	Reported
1		30		95	130-132	133[5]
2		40		90	113	112-119[8]
3		25		91	76 (2.0)	68 (1.0)[4]
4		40		88	65-66	67-68[7]
5		60		75	131-133	134-136[13]
6		20		88	114	112-119[8]
7		30		93	144-145	143-145[14]
8		20		90	51-53	-
9		35		81	22-24	≈ 20[7]
10		50		83	124	-

[a]Isolated yield.

AC 100 spectrometer. Chemical shifts are reported in ppm downfield from TMS as internal standard. The mass spectra were scanned on a Varian Mat CH-7 at 70 eV. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer.

Synthesis of symmetrical and unsymmetrical SOCs (2a-j). General procedure: To a magnetically stirred solution of synthesized corresponding 2,2-diphenoxy-1,3-dioxane (**1a-b**) (10 mmol) and various diols (10 mmol) in CH_2Cl_2 (50 mL), molecular iodine (0.5 mol%) was added. The progress of the reaction was monitored by TLC using petroleum ether-ethyl acetate (7:3). After the reaction was completed, the solvent was washed with 5% $Na_2S_2O_3$ solution and water, respectively. Then, the organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. For solid products, the precipitate was recrystallized from ethyl acetate. For oily liquid ones, the residue was purified by vacuum distillation. All the products were identified by comparison of their spectral and micro analytical data with those of authentic samples which was prepared according to literature.[9]

8,8-Dimethyl-1,4,6,10-tetraoxaspiro[4.5]decane: (entry 8) ^{1}H NMR (100 MHz, $CDCl_3$): δ 0.98 (s, 6H, CH_3), 3.90 (s, 4H, CH_2), 4.11 (s, 4H, CH_2). IR (ν, cm^{-1}) 2980, 1190; *m/z* 174; Anal. Calcd. For $C_8H_{14}O_4$: C 55.16; H 8.10; Found C 55.03; H 8.02.

Spiro[1,3-benzodioxole-2,2'-(5,5-dimethyl)-1,3-dioxane]: (entry 10) ^{1}H NMR (100 MHz, $CDCl_3$): δ 1.11 (s, 6H, CH_3), 4.07 (s, 4H, CH_2), 6.83 (m, 4H, Ph). IR (ν, cm^{-1}) 3122, 2993, 1205; *m/z* 222; Anal. Calcd. For $C_{12}H_{14}O_4$: C 64.85; H 6.35; Found C 64.76; H 6.29.

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