

Iodine-Catalyzed Synthesis of Spiroorthocarbonates under Neutral Conditions

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Received January 31, 2009, Accepted May 28, 2009

Key Words: Spiroorthocarbonate, Symmetrical, Unsymmetrical, Iodine, Catalyst

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 SOC. Sakai *et al.* reported a novel synthesis of SOC 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 tetraalkyl-orthocarbonate 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 SOC during the preparation of unsymmetrical analogs. Synthesis of SOC 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 SOC.⁸ Endo used dichlorodiphenoxymethane in the presence of *p*-toluenesulfonic acid monohydrate for the preparation of asymmetric SOC.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 SOC 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 SOC 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 I₂. On the basis of the reaction times and yields, CH₂Cl₂ was selected as a most suitable solvent for the synthesis of SOC.

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 I₂, and the results clearly demonstrate that 0.5% molar ratio of I₂ 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 CH₂Cl₂ to yield the corresponding SOC (**2a-j**). (Scheme 1)

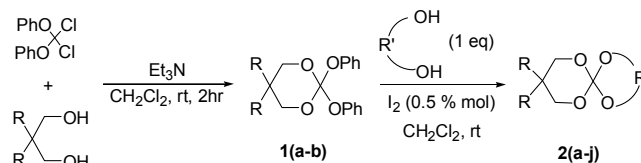
The efficiency and validity of this method for the synthesis of SOC (**2a-j**) can be deduced from the data in Table 2. Moreover, the prolongation of the reaction has no effect on the product distribution unlike the previous published method which uses protic acid catalyst.⁶

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

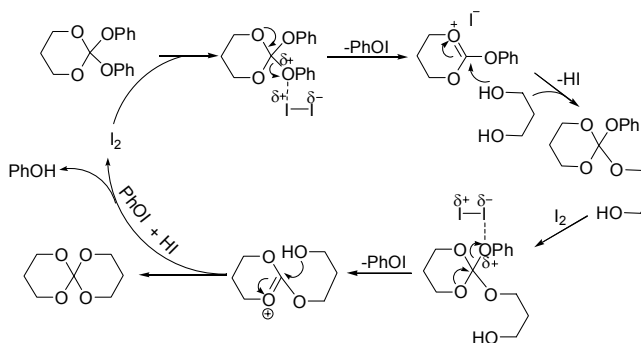
In conclusion, we have developed a new modified, efficient and chemoselective method for the synthesis of symmetrical and unsymmetrical SOC catalyzed by molecular iodine with good to high yields.

Experimental

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



Scheme 1

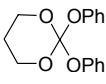
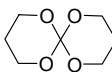
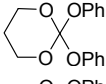
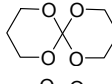
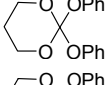
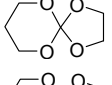
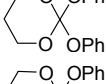
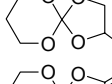
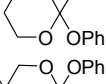
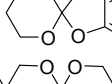
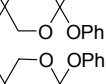
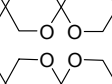
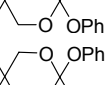
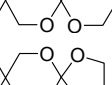
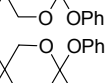
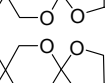
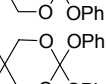
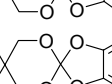
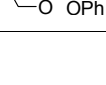
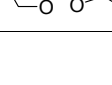


Scheme 2

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

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	-

^aIsolated 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 SOC's (**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 CH₂Cl₂ (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% Na₂S₂O₃ solution and water, respectively. Then, the organic phase was dried over anhydrous Na₂SO₄ 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) ¹H NMR (100 MHz, CDCl₃); δ 0.98 (s, 6H, CH₃), 3.90 (s, 4H, CH₂), 4.11 (s, 4H, CH₂). IR (ν, cm⁻¹) 2980, 1190; *m/z* 174; Anal. Calcd. For C₈H₁₄O₄; 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) ¹H NMR (100 MHz, CDCl₃); δ 1.11 (s, 6H, CH₃),

4.07 (s, 4H, CH₂), 6.83 (m, 4H, Ph). IR (ν, cm⁻¹) 3122, 2993, 1205; *m/z* 222; Anal. Calcd. For C₁₂H₁₄O₄; C 64.85; H 6.35; Found C 64.76; H 6.29.

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