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Facile Synthesis of Glycerol Carbonate from Glycerol Using Selenium-Catalyzed Carbonylation with Carbon Monoxide

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ABSTRACT: *The commercial production of glycerol has increased considerably for several years, because of its rising inevitable formation as a by-product of biodiesel. For the effective utilization of glycerol, a new synthesis of glycerol carbonate (4-hydroxymethyl-2-oxo-1,3-dioxolane) that is used as solvents and raw material of plastics from glycerol was explored. By combined the selenium-catalyzed carbonylation of slightly excess of glycerol with carbon monoxide and potassium carbonate under 0.1 MPa at 20°C for 4 h in DMF with the oxidation of resulting selenocarbonate salt with molecular oxygen (0.1 MPa, 20 °C) for 2 h, glycerol carbonate was obtained in good yields (83–84%). However, sodium hydride to form sodium alkoxide in situ lowered the yield of glycerol carbonate. Use of triethylamine, 1-methylpyrrolidine, and DBU as bases gave poor results. Furthermore, styrene carbonate was obtained in excellent yield (90%) under similar reaction conditions. The catalytic synthesis of glycerol carbonate was also brought about in the mixed gas atmosphere (carbon monoxide:oxygen = 3:1, 0.1 MPa, 20°C). Glycerol carbonate and styrene carbonate were obtained in reasonable yields (197% and 119%, based on selenium used).* Heteroatom Chem 21:541–545, 2010; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20640

INTRODUCTION

The increase in new renewable oils that have been used for energy applications as automotive fuels has become a new trend in several years. The so-called "biodiesel" is a popular term for the fatty acid methyl esters, formed from transesterification of rapeseed oil with methanol. Biodiesel production in the European Union was estimated to be about 6 Mt in 2006 and is forecasted to increase to about 12 Mt in 2010. Biodiesel has been developed rapidly in United States and in Europe, accompany with the formation of a large quantity of glycerol (**1a**) as a by-product. Obviously, the question arises how this additional **1a** can be used wisely [1].

From a number of glycerol applications, glycerol carbonate (4-hydroxymethyl-2-oxo-1,3-dioxolane, **2a**) and its esters are very interesting derivatives of glycerol (**1a**), because of their usability as solvents for many applications, for instance in colors, varnishes, glues, cosmetics, and pharmaceuticals [1]. Also, glycerol carbonate (**2a**) has a considerable possibility to be an intermediate of polycarbonate production [2] and the use of **2a** was investigated as monomer to synthesize hyperbranched aliphatic polyesters (polyglycerols) [3].

Among the synthetic methods for glycerol carbonate (**2a**) from glycerol (**1a**), the direct synthesis of **2a** by the conversion of **1a** with carbon dioxide has been studied using organic tin compounds (di(*n*-butyl)tin dimethoxide, di(*n*-butyl)tin oxide, and tin dimethoxide) as catalysts. Under the drastic reaction conditions (5.0 MPa of CO_2, 180°C), tin dimethoxide led only to traces of **2a**. However,

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di(n-butyl)tin dimethoxide gave a little conversion of **1a** (maximum 7%) depending on the reaction conditions [4]. Furthermore, the catalytic conversion of **1a** with urea to **2a** has been researched in the presence of heterogeneous zinc catalysts ($Zn(CH_3C_6H_4SO_3)_2$ and $ZnSO_4$). At temperature 140–150°C and a pressure of 4.0 KPa, equimolar amounts of **1a** and urea reacted to afford **2a** in good yields [5]. Also, very recently, synthesis of **2a** from **1a** with dimethyl carbonate in the presence of an uncalcined Mg-Al hydrotalcite catalyst was reported [6].

Recently, we reported a useful synthetic method for glycerol carbonate (**2a**), which has been developed by the sulfur-assisted carbonylation of glycerol (**1a**) with carbon monoxide under 1.0 MPa at 80°C in DMF, and the oxidation of resulting carbonothioate salts with copper(II) bromide under 0.1 MPa in air at 20°C [7]. However, this synthetic reaction needs slightly severe reaction conditions and metallic oxidants. About 40 years ago, our research group found that selenium-catalyzed carbonylation with carbon monoxide using large excess amount of alkoxides and alcohols under mild reaction conditions (0.1 MPa, 20°C) to give corresponding carbonates in excellent yields [8–10]. Therefore, our objective has been to develop a straightforward synthesis for **2a** by the carbonylation of **1a** with carbon monoxide using selenium-catalyst under milder reaction conditions (0.1 MPa, 20°C) followed by oxidation with molecular oxygen and to establish the catalytic synthesis of **2a** in the mixed gas atmosphere (carbon monoxide and oxygen, 0.1 MPa, 20°C).

RESULTS AND DISCUSSION

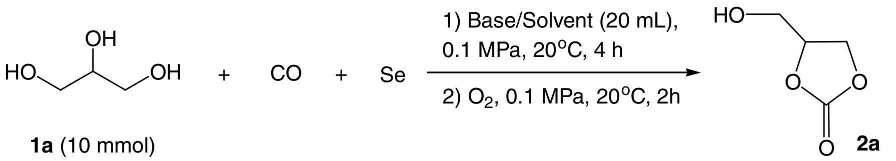
For the stoichiometric synthesis of glycerol carbonate (**2a**), the carbonylation of glycerol (**1a**) with carbon monoxide, selenium, and base and the following oxidation of resulting selenocarbonate salt (**3a**) with molecular oxygen under mild conditions were examined (Scheme 1). At first, reaction of **1a** with carbon monoxide (0.1 MPa) and selenium (1.0 equiv.) in the presence of potassium carbonate (1.0 equiv.) at 20°C for 4 h in DMF solvent was performed. Then, the generated salt **3a** in DMF was oxidized by under an ambient pressure of molecular oxygen at 20°C for 2 h to obtain **2a** in low yield (22%) (Table 1, entry 1). In the previous results of the selenium-catalyzed carbonylation with carbon monoxide, 20–40 equiv. of alkoxides and alcohols was used [8,9]. Then, for the improvement of yields of **2a**, the reactions using excess equivalents of **1a** and potassium carbonate (2–10 equiv.) were tried (entries 2–5). The use of 3–5 equiv. of **1a** and equimolecular amount of potassium carbonate gave excellent results to afford **2a** in 83–84% (entries 3 and 4). Furthermore, the effects on the excess amount of catalyst selenium and potassium carbonate were checked. Yield of **2a** was increased to 58% in the presence of 2.0 equiv. of selenium and 5.0 equiv. of potassium carbonate (entry 8). In this reaction, **2a** was synthesized selectively and the formation of isomeric cyclic carbonate (5-hydroxy-2-oxo-1,3-dioxane) was not observed.

TABLE 1 Influence of Various Conditions on Synthesis of **2a**

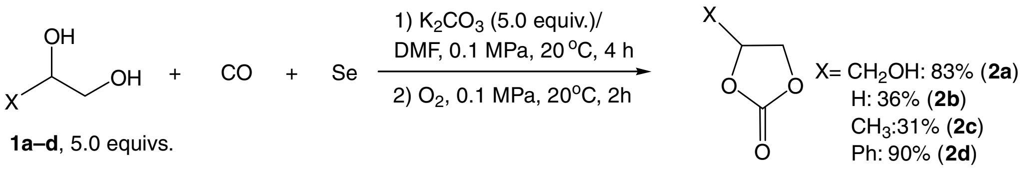
Entry	*Base (mmol)*	*Se (mmol)*	*Solvent*	*Isolated Yield (%)*[a]
1	K_2C0_3, 10	10	DMF	22
2	K_2C0_3, 10	5	DMF	55
3	K_2C0_3, 10	3	DMF	84
4	K_2C0_3, 10	2	DMF	83
5	K_2C0_3, 10	1	DMF	61
6	K_2C0_3, 20	10	DMF	43
7	K_2C0_3, 20	20	DMF	45[b]
8	K_2C0_3, 50	20	DMF	58[b]
9	NaH, 10	3	DMF	40
10	Triethylamine, 10	3	DMF	NR
11	1-Methylpyrrolidine, 10	3	DMF	NR
12	DBU, 10	3	DMF	—[c]
13	K_2C0_3, 10	3	THF	NR

[a] Yields based on selenium.
[b] Yields based on glycerol.
[c] Tar was formed.

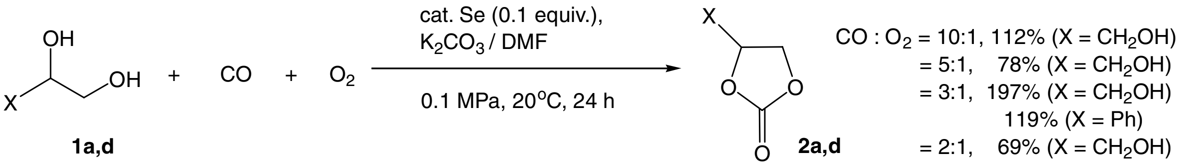
Next, the influence of bases and solvent was examined on the selenium-catalyzed carbonylation of **1a** with carbon monoxide (entries 9–13). In our previous report [8,9], the selenium-catalyzed carbonylation with carbon monoxide was established using alkoxides and alcohols as reactants. Therefore, the use of sodium hydride that leads to in situ formation of sodium alkoxide from **1a** was tried. However, yield of **2a** was lowered (entry 9). Thus, in this



SCHEME 1 Stoichiometric synthesis of **2a**.



SCHEME 2 Some cyclic carbonate synthesis **(2a–d)**.



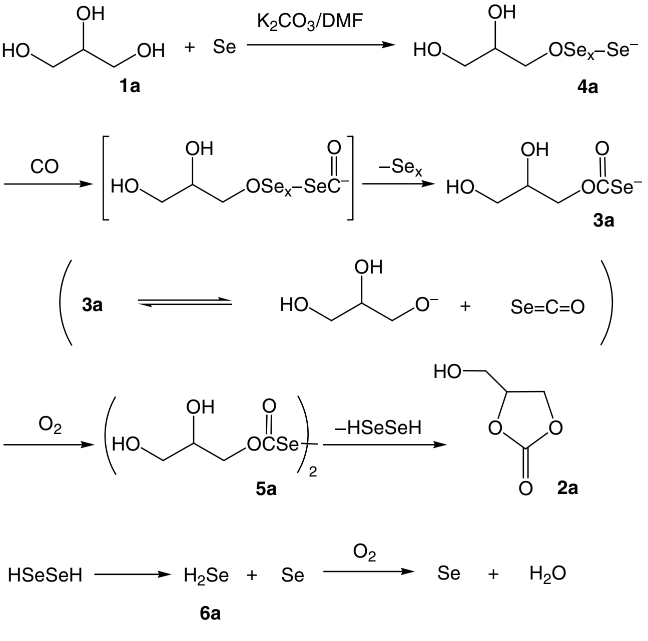
SCHEME 3 Catalytic synthesis of **2a,d**.

reaction system, the troublesome in situ formation of sodium alkoxide was unnecessary. In addition, the carbonylation of 1-pentanol with potassium carbonate as a base was performed under similar selenium-catalyzed reaction conditions and corresponding carbonate was not obtained at all. Using triethylamine and 1-methylpyrrolidine as beses or THF solvent, no reaction was caused (entries 10, 11, and 13). Stronger base (1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)) gave a poor result to afford only tar (entry 12).

Several cyclic carbonates (**2b–d**) from 5.0 equiv. of glycols (**1b–d**) and potassium carbonate were synthesized by the selenium-catalyzed carbonylation with carbon monoxide (0.1 MPa, 20°C) for 4 h and oxidation with molecular oxygen (0.1 MPa, 20°C) for 2 h in similar manner (Scheme 2). The yields of ethylene carbonate (2-oxo-1,3-dioxolane, **2b**) and propylene carbonate (4-methyl-2-oxo-1,3-dioxolane, **2c**) were lowered. However, styrene carbonate (2-oxo-4-phenyl-1,3-dioxolane, **2d**) was obtained in excellent yield.

Then, the catalytic synthesis of glycerol carbonate (**2a**) was also examined. Under the various ratios of carbon monoxide and oxygen atmosphere (0.1 MPa), the synthesis of glycerol carbonate (**2a**) by the carbonylation of glycerol (**1a**) with potassium carbonate in the presence of catalytic amount of selenium (10 mol%) at 20°C for 24 h was tried (Scheme 3). Yield of **2a** was reached 197% (based on selenium used) using mixed gas (carbon monoxide:oxygen = 3:1). Under similar catalytic reaction conditions (CO:O_2 = 3:1), styrene carbonate (**2d**) was given in 119% (based on selenium used).

Scheme 4 shows possible paths for the synthesis of glycerol carbonate (**2a**) by the carbonylation of glycerol (**1a**) followed by oxidation of the selenocarbonate salt **3a**. First, elemental selenium undergoes Se–Se bond fission by the reaction with anion of **1a** to form selenolate anion (**4a**). The reaction of **4a** with carbon monoxide gives selenocarbonate salt (**3a**) from carbonylated species. Because of equilibrium of **3a** with anion of **1a** and carbonyl selenide, excess amounts of **1a** and potassium carbonate might need to synthesize **2a** in high yields. The formed **3a** is oxidized by molecular oxygen giving **2a** and hydrogen selenide (**6a**) via biscarbonodiselenide (**5a**). Then, **6a** was oxidized to recover elemental selenium. In the carbonate synthesis from alcohols with carbon monoxide and sulfur,



SCHEME 4 Proposed reaction path for the synthesis of **2a**.

biscarbonodisulfide formed as intermediate was isolated by oxidation of carbonothioate salt with copper(II) chloride [11].

CONCLUSION

In summary, a useful synthetic method for glycerol carbonate (**2a**) has been developed by the selenium-catalyzed carbonylation of glycerol (**1a**) with carbon monoxide and potassium carbonate under 0.1 MPa at 20°C in DMF, and the oxidation of resulting selenocarbonate salt (**3a**) with molecular oxygen under 0.1 MPa at 20°C. Slightly excess of **1a** and potassium carbonate gave **2a** in good yields (83–84%). Also, the catalytic reaction of glycerol (**1a**) was performed in the mixed gas atmosphere (carbon monoxide:oxygen = 3:1, 0.1 MPa, 20 °C) to form glycerol carbonate (**2a**) in reasonable yield. From the viewpoint of making good use of **1a**, which is a by-product of biodiesel production, the present method might give an additional field of application on **1a**.

EXPERIMENTAL

Melting points were determined on a Mettler FP 5 instrument and were uncorrected. FTIR spectra were recorded on a JASCO FT/IR-4100 instrument. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 (300 MHz, 75 MHz) instrument. Chemical shifts were reported in ppm relative to tetramethylsilane (δ units). Mass spectra were measured on a JEOL JMS-600 spectrometer. Glycerol (**1a**), diols **1b–d**, DMF, THF, potassium carbonate, sodium hydride, triethylamine, 1-methylpyrrolidine, DBU, selenium (99.9%), carbon monoxide (99.9%), and oxygen (99.9%) were used as purchased.

*Typical Procedure for the Stoichiometric Synthesis of Glycerol Carbonate **2a***

A gray mixture containing glycerol (**1a**) (921 mg, 10 mmol), elemental selenium (237 mg, 3 mmol), and potassium carbonate (1.382 g, 10 mmol) with DMF (20 mL) was vigorously stirred under carbon monoxide (0.1 MPa) at 20°C for 4 h. Into the resulting brown emulsion of selenocarbonate salt (**3a**), molecular oxygen (0.1 MPa) was charged at 20°C. The reaction mixture was stirred for additional 2 h at 20°C. Then, the resulting mixture was filtered and rinsed with *t*-butyl methyl ether (100 mL). After evaporation of solvents and purification by short-column chromatography (silica gel, AcOEt), glycerol carbonate (**2a**) was given.

Glycerol carbonate **2a.** Yield: 299 mg (84%) yield; oil [7]; IR (neat, cm^{-1}): ν : 3444, 2931, 1790 (C=O), 1403, 1179, 1087; ^{1}H NMR (d_6-DMSO) δ (ppm): 3.46–3.53 (m, 1H, CH_2), 3.62–3.69 (m, 1H, CH_2), 4.27 (d,d, $J = 5.9, 8.4$ Hz, 1H, CH_2), 4.48 (t, $J = 8.4$ Hz, 1H, CH_2), 4.75–4.82 (m, 1H, CH), 5.23 (t, $J = 5.7$ Hz, 1H, OH); ^{13}C NMR (d_6-DMSO) δ (ppm): 60.6, 65.8, 77.0, 155.1; MS (CI, reagent gas: methane) *m/z* (%): 119 ($M + H^+$, 100), 63 (4), 57 (37).

Ethylene carbonate **2b.** Yield: 63 mg (36%) yield; mp 35.6°C, (Lit. [12] 36.2°C); IR (KBr, cm^{-1}) ν : 2995, 1799 (C=O), 1163, 1068, 773; ^{1}H NMR ($CDCl_3$) δ (ppm): 4.53 (s, 4H, CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm): 64.5, 155.4; MS *m/z* (%): 88 (M^+, 100), 73 (4), 58 (13).

Propylene carbonate **2c.** Yield: 63 mg (31%) yield; oil [12]; IR (neat, cm^{-1}) ν: 2987, 1791 (C=O), 1389, 1184, 1053; ^{1}H NMR ($CDCl_3$) δ (ppm): 1.50 (d, $J = 6.2$ Hz, 3H, CH_3), 4.03 (d,d, $J = 8.4, 8.4$ Hz, 1H, CH_2), 4.56 (d,d, $J = 8.4, 8.4$ Hz, 1H, CH_2), 4.81–4.92 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) δ (ppm): 19.2, 70.5, 73.5, 154.9; MS *m/z* (%): 102 (M^+, 5), 100 (11), 87 (14), 57 (100).

Styrene carbonate **2d.** Yield: 296 mg (90%) yield; mp 54.0°C, (Lit. [12] 56.3°C). IR (KBr, cm^{-1}) ν: 1775 (C=O), 1170, 1055, 759, 698; ^{1}H NMR ($CDCl_3$) δ (ppm): 4.34 (t, $J = 8.2$ Hz, 1H, CH_2), 4.80 (t, $J = 8.2$ Hz, 1H, CH_2), 5.67 (t, $J = 8.2$ Hz, 1H, CH), 7.34–7.48 (m, 5H, CH); ^{13}C NMR ($CDCl_3$) δ (ppm): 71.1, 77.9, 125.8, 129.2, 129.7, 135.8, 154.8; MS *m/z* (%): 164 (M^+, 100), 91 (61), 90 (91), 78 (57).

*General Procedure for the Catalytic Synthesis of Glycerol Carbonate **2a***

A mixture of glycerol (**1a**) (921 mg, 10 mmol), elemental selenium (79 mg, 1 mmol), and potassium carbonate (1.382 g, 10 mmol) with DMF (20 mL) was very vigorously stirred under the mixed gas (carbon monoxide:oxygen = 3:1, 0.1 MPa). The mixed gas was circulated at 20°C for 24 h. The resulting pale yellow emulsion was filtered and rinsed with *t*-butyl methyl ether (100 mL). After evaporation of solvents and purification by short-column chromatography (silica gel, AcOEt), glycerol carbonate (**2a**) was afforded in 197% yield (based on selenium used) (232 mg).

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