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New Synthesis of Glycerol Carbonate from Glycerol Using Sulfur-Assisted Carbonylation with Carbon Monoxide

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ABSTRACT: *The glycerol carbonate synthesis from glycerol, which is an inevitable by-product of biodiesel production, was established. By combined sulfur-assisted carbonylation of glycerol under 1.0 MPa of carbon monoxide at 80°C in DMF with oxidation by copper bromide(II), a facile synthetic method for glycerol carbonate in good yield was developed.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:99–102, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20583

INTRODUCTION

The so-called "biodiesel" is a popular term for the fatty acid methyl esters, formed from transesterification of rapeseed oil with methanol. Biodiesel has been developed rapidly as automotive fuels in United States and in Europe for several years, accompanied with the formation of a large quantity of glycerol (**1a**) as by-product. Obviously, the question arises how this additional **1a** can be used wisely [1].

In 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 the use of **2a** was investigated as monomer to produce hyperbranched aliphatic polyesters (polyglycerols) [2], and glycerol carbonate (**2a**) has a considerable possibility to be an intermediate of polycarbonate production [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 as catalysts. Under the drastic reaction conditions (5.0 MPa of CO_2, 180°C), tin dimethoxide led only to traces of **1a**. However, 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. 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].

About 20 years ago, we found that sulfur-assisted carbonylation with carbon monoxide of alcohols and diols under slightly severe reaction conditions (3.0 MPa, 80°C) to give carbonates in good yields [6]. Recently, we reported the sulfur-assisted carbonylation of diamines with carbon monoxide and oxidation with molecular oxygen ([7] and further references therein). However, milder reaction conditions have been desired for the industrial production.

Therefore, our objective has been to develop a straightforward synthetic method for glycerol carbonate (**2a**) by the carbonylation of glycerol (**1a**) with carbon monoxide and sulfur under milder reaction conditions followed by oxidation.

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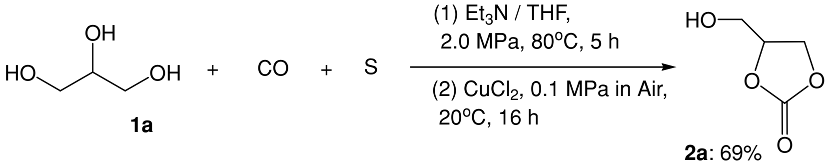


SCHEME 1 Synthesis of glycerol carbonate (**2a**).

RESULTS AND DISCUSSION

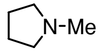
The carbonylation of **1a** with carbon monoxide and sulfur and oxidation with copper chloride(II) to prepare the corresponding **2a** were performed. Glycerol (**1a**) was readily reacted with carbon monoxide (2.0 MPa) and sulfur (3.0 equiv.) in the presence of triethylamine (5.0 equiv.) at 80°C for 5 h in THF solvent. Then, the generated carbonothioate salt **3a** in THF was oxidized by copper chloride(II) under an ambient pressure of air at 20°C for 16 h. Finally, glycerol carbonate (**2a**) was obtained in 69% yield (Scheme 1). In this reaction, **2a** was synthesized selectively and the formation of isomeric cyclic carbonate (5-hydroxy-2-oxo-1,3-dioxane) was not observed.

At first for the improvement of yields of **1a**, the influence of various conditions was examined on the sulfur-assisted carbonylation of **2a** with carbon monoxide (Table 1). Longer reaction time of carbonylation and shorter reaction time of oxidation, and less amount of sulfur and triethylamine caused a lower yield of **1a** (entries 2 and 3). At the reaction temperature between 80 and 100°C, **1a** was obtained in good yields (entries 1 and 4–7). Lower pressure of carbon monoxide led to considerably low yields (entries 8 and 9). Using stronger base (1-methylpyrrolidine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)) gave poor results to afford only tar (entries 10 and 11).

Recently, we found that sulfur-assisted carbonylation of alcohols with carbon monoxide was strongly accelerated by *N*, *N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) [8]. Therefore, glycerol carbonate (**2a**) synthesis by the use of carbonylation of glycerol (**1a**) with carbon monoxide and sulfur in DMF and oxidation with copper chloride(II) was checked (Table 2). Our investigation into the sulfur-assisted carbonylation and oxidation of **1a** employing DMF as a solvent led to the successful synthesis of **2a**. Even, under lower pressure (1.0 MPa) of carbon monoxide, glycerol carbonate (**2a**) was obtained in fairly good yields (entries 1–4).

Next, the effect of oxidizers under 0.1 MPa in air at 20°C was examined. Copper chloride(II) and copper bromide(II) gave excellent results of **2a** synthesis under 1.0 MPa of carbonylation (entries 4 and 5). However, zinc compounds were shown poor results (entries 6 and 7). Unfortunately, no formation of **2a** was observed using hydrogen peroxide (aq. 30%) as an oxidizer (entry 8).

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

Entry	*Temperature of Carbonylation, (°C)*	*Pressure of Carbonylation, (Mpa)*	*Base*	*Isolated Yield (%)*
1	80	2.0	Et_3N	69
2	80	2.0	Et_3N	55[a]
3	80	2.0	Et_3N	34[b]
4	120	2.0	Et_3N	33
5	100	2.0	Et_3N	72
6	60	2.0	Et_3N	48
7	40	2.0	Et_3N	32
8	80	1.0	Et_3N	38
9	100	1.0	Et_3N	64
10	80	2.0	 N-Me	0[c]
11	80	2.0	DBU[d]	0[c]

Reaction conditions: Glycerol (10 mmol), S (30 mmol), base (50 mmol), THF (20 mL), $CuCl_2$ (15 mmol), carbonylation for 5 h, and oxidation for 16 h.

[a] Carbonylation for 22 h and oxidation for 6 h.

[b] S (15 mmol), base (30 mmol).

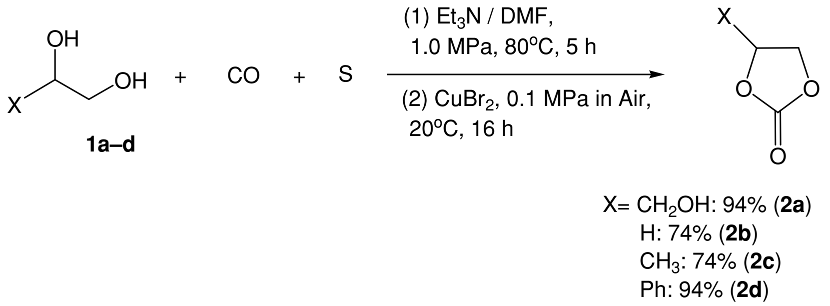
[c] Tar was formed.

[d] 1.8-Diazabicyclo[5.4.0]undec-7-ene.

TABLE 2 Effect of Solvent DMF and Oxidizer

Entry	*Temperature of Carbonylation, (°C)*	*Pressure of Carbonylation, (Mpa)*	*Oxidizer*	*Isolated Yield (%)*
1	100	2.0	$CuCl_2$	79
2	80	2.0	$CuCl_2$	76
3	100	1.0	$CuCl_2$	79
4	80	1.0	$CuCl_2$	87
5	80	1.0	$CuBr_2$	94
6	80	1.0	$ZnBr_2$	0
7	80	1.0	ZnI_2	11
8	80	1.0	H_2O_2	0

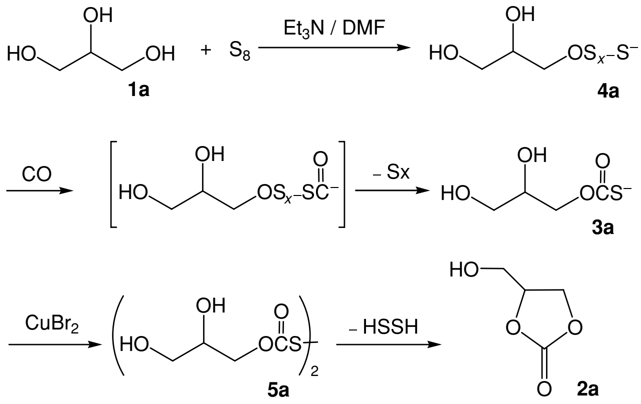
Reaction conditions: Glycerol (10 mmol), S (30 mmol), Et_3N (50 mmol), DMF (20 mL), Oxidizer (15 mmol), carbonylation for 5 h, and oxidation for 16 h.



SCHEME 2 Synthesis of several cyclic carbonates (**2a–d**).

Several cyclic carbonates (**2a–d**) including glycerol carbonate (**2a**) were synthesized by the sulfur-assisted carbonylation with carbon monoxide (1.0 MPa, 80°C) and oxidation with copper bromide (0.1 MPa in air, 20°C) (Scheme 2). Ethylene carbonate (2-oxo-1,3-dioxolane, **2b**), propylene carbonate (4-methyl -2-oxo-1,3-dioxolane, **2c**), and stylene carbonate (2-oxo-4-phenyl-1,3-dioxolane, **2d**) were obtained in good to excellent yields under milder reaction conditions.

Scheme 3 shows possible paths for the synthesis of glycerol carbonate (**2a**) by the carbonylation of glycerol (**1a**) followed by oxidation of the carbonothioate salt **3a**. First, elemental sulfur undergoes S–S bond fission by the reaction with anion of **1a** to form thiolate anion (**4a**). The reaction of **4a** with carbon monoxide gives carbonothioate salt (**3a**) from carbonylated species. The thus formed carbonothioate salt (**3a**) is oxidized by copper bromide(II) giving **2a** via biscarbonodisulfide (**5a**). Indeed, biscarbonodisulfide formed as intermediate by oxidation of carbonothioate salt was isolated in the carbonate synthesis from alcohols with carbon monoxide and sulfur [9].



SCHEME 3 Proposed path for the synthesis of **2a**.

CONCLUSION

In summary, a useful synthetic method for glycerol carbonate (**2a**) 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 **3a** with copper bromide(II) under 0.1 MPa in air at 20°C. 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. FT-IR 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 and exact mass spectra were measured on a JEOL JMS-600 spectrometer. Glycerol (**1a**), diols **1b–d**, THF, DMF, triethylamine, 1-methylpyrrolidine, DBU, sulfur (99.5%), copper chloride(II), copper bromide(II), zinc bromide(II), zinc iodide(II), hydrogen peroxide (aq. 30%), carbon monoxide (99.9%), and oxygen (99.9%) were used as purchased.

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

In a 100-mL stainless steel autoclave, glycerol (**1a**) (921 mg, 10 mmol), powdered sulfur (962 mg, 30 mmol), triethylamine (6.93 mL, 50 mmol), and DMF (20 mL) were placed with a magnetic stirring bar under an argon atmosphere. The autoclave was then flushed three times with carbon monoxide and finally charged with carbon monoxide at 1.0 MPa at 20°C. The reaction was carried out at

80°C for 5 h with vigorous stirring. After cooling down and evacuation of carbon monoxide, copper bromide (3.350 g, 15 mmol) was added at 20°C under air atmosphere. The reaction mixture was stirred for additional 16 h under ambient pressure of air at 20°C. Then, the resulting mixture was filtered (black copper sulfide was formed), 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 (4-hydroxymethyl-2-oxo-1,3-dioxolane, **2a**). Yield: 1.114 g (94%) yield; oil [10]; IR (neat, cm^{-1}): ν 3444, 2931, 1790 (C=O), 1403, 1179, 1087; ^1H 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, $J = 6$, 8 Hz, 1H, CH_2), 4.48 (t, $J = 8$ Hz, 1H, CH_2), 4.75–4.82 (m, 1H, CH), 5.23 (t, $J = 6$ 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 (2-oxo-1,3-dioxolane, **2b**). Yield: 650 mg (74%) yield; mp 35.6°C (Lit. [6] 36.2°C); IR (KBr, cm^{-1}): ν 2995, 1799 (C=O), 1163, 1068, 773; ^1H 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 (4-methyl-2-oxo-1,3-dioxolane, **2c**). Yield: 752 mg (74%) yield; oil [6]; IR (neat, cm^{-1}): ν 2987, 1791 (C=O), 1389, 1184, 1053; ^1H NMR ($CDCl_3$): δ (ppm) 1.50 (d, $J = 6$ Hz, 3H, CH_3), 4.03 (d,d, $J = 8$, 8 Hz, 1H, CH_2), 4.56 (d,d, $J =$ 8, 8 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).

Stylene carbonate (2-oxo-4-phenyl-1,3-dioxolane, **2d**). Yield: 1.543 (94%) yield; mp 54.0°C (Lit. [6] 56.3°C); IR (KBr, cm^{-1}): ν 1775 (C=O), 1170, 1055, 759, 698; ^1H NMR ($CDCl_3$): δ (ppm) 4.34 (t, $J = 8$ Hz, 1H, CH_2), 4.80 (t, $J = 8$ Hz, 1H, CH_2), 5.67 (t, $J = 8$ 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).

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