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One-Pot Alkoxylation of Phenols with Urea and 1,2-Glycols

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A one-pot epoxide-free alkoxylation process has been developed for phenolic compounds. The process involves heating phenols and urea in 1,2-glycols at 170-190 °C using Na_2CO_3/ZnO as co-catalysts under atmospheric conditions. During the course of this new alkoxylation reaction, a five-membered ring cyclic carbonate intermediate, ethylene carbonate (EC) or propylene carbonate (PPC), was produced in-transit as the key intermediate and was subsequently consumed by phenols to form alkoxylated ether alcohols as final products in excellent yields. For instance, phenol, bisphenol A (BPA), hydroquinone and resorcinol were converted into their respective mono-alkoxylated ether alcohols on each of their phenolic groups in 80-95% isolated yields. In propoxylation of phenols, this approach shows great product selectivity favoring production of high secondary alcohols over primary alcohols in isomeric ratios of nearing 95/5. Since ammonia (NH_3) and carbon dioxide (CO_2) evolving from the reaction can be re-combined in theory into urea for re-use, the overall net-alkoxylation by this approach can be regarded as a simple condensation reaction of phenols with 1,2-glycols giving off water as its by-product. This one-pot process is simple, safe and environmentally friendlier than the conventional alkoxylated processes based on ethylene oxide (EO) or propylene oxide (PO). Moreover, this process is particularly well-suited for making short chain-length alkoxyether alcohols of phenols.

Keywords: Alkoxylation; Ethoxylation; Propoxylation; Urea; Green process.

1. INTRODUCTION

Development of an environmentally friendly process for practical industrial chemical transformations is an important consideration nowadays. Society demands it; governments encourage it, and sustainability of the chemical industry hinges upon it. The basic approach in designing green chemical processes is to avoid using hazardous reagents and halogen-derived chemicals in the overall synthetic scheme. In addition, recycling of by-products from the reaction to eliminate wastes and pollutants should also be emphasized.[1,2] Herein, we report an efficient one-pot alkoxylation of phenols with urea and 1,2-glycols that meets these general green chemistry principles.

The most commonly used alkoxylating agents such as ethylene oxide (EO) and propylene oxide (PO) are versatile industrial chemicals. For instance, long-chained polyalkoxyether polyols, major derivatives of alkoxylated products of EO and PO, are widely used in the syntheses of polyurethanes and polyesters.[3,4] Making of hydrophilic polyalkoxyethers especially from polymerization of EO are well known for their utilities in the syntheses of cleaners, detergents, surfactants, and waterborne polymeric intermediates.[5] Typically, the alkoxylation reaction is achieved by introducing EO or PO into an enclosed pressure reactor containing an initiator at about 120-150 °C in the presence of a base catalyst such as NaOH or KOH. Depending upon the amount of epoxides added to the reactor, different chain-lengths of the alkoxylated products can be obtained. However, there is always a possibility of an un-controlled chain-reaction due to rapid exothermic reactions releasing the strained ring energy of the epoxides. Thus, low boiling, volatile EO or PO in pressurized conditions does pose a potential dangerous situation.

Since the use of EO and PO has inherent danger of rapid exothermic reaction, finding alternative raw materials for alkoxylation under atmospheric condition is highly desirable. Ethylene carbonate (EC) and propylene carbonate (PPC) are the potential good candidates for filling this gap. First of all, EC and PPC are high boiling liquids with little ring-strain.[6] Alkoxylation with EC/PPC has been investigated previously.[7] In fact, short-alkoxylated products of phenols have been obtained by using EC or PPC. For in-

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stance, bis-hydroxyethyl ether of bisphenol A (BHE-BPA, **3ba**), a raw material used in polyesters, was prepared simply by heating BPA and EC at about 160 °C in the presence of a base.[7]

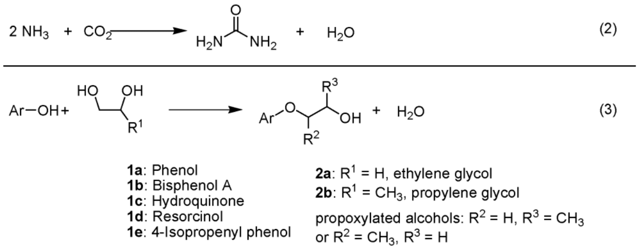
Recent literature[8] indicated that, EC and PPC can be synthesized from urea and 1,2-glycols, but there has not been any report of alkoxylation accomplished by using urea-1,2-glycol mixtures directly. Recently, we reported the first application of this technology in polycarbonate recycling,[9] and it appears to us that this one-pot process has great potential for the general alkoxylation of phenols. Herein, we report the chemistry involved in this convenient one-pot high yield synthesis using urea-glycol mixtures as the raw materials.

2. RESULTS AND DISCUSSION

2.1. General One-Pot Ethoxylation Condition

The one-pot urea-ethylene glycol process for synthesis of ethoxylated ether alcohols was outlined in Scheme I (eq. 1, R^1 = H). Phenols, urea and ethylene glycol were mixed and heated together in solution. In the case of our model study with phenol, we found that mono-ethoxylation product, 2-phenoxyethanol (**3aa**), was isolated in 89% yields at 160 to 180 °C by using urea-ethylene glycol in the presence of catalysts (Na_2CO_3 and ZnO). The reaction was monitored by IR, checking the disappearance of carbonyl absorptions at 1711, 1736, 1774 and 1802 cm^{-1}. The reaction time took approximately 4-6 hours to complete. During the course of the reaction, ammonia evolved from the mixture rapidly, and some urea deposits could be found on the condenser which would account for portion of urea loss. Therefore, an excess of urea in 30% molar excess was typically used to compensate for this apparent loss in the solution. Similarly, in all our studies using bisphenols, high yields of bis-ethoxylated diols were isolated in greater than 80% isolated yield (Table 1).

Scheme I One-pot alkoxylation of phenols using 1,2-glycols-urea catalyzed by Na_2CO_3 and ZnO (eq. 1)



2.2. Mechanism: IR Monitoring, By-product Formations and Optimization

To monitor the reactions involved in this one-pot reaction, the changes of absorption spectra of the reaction mixture in FTIR was followed closely, particularly paying attention to the carbonyl regions. The composition of the product mixture was also examined by ^1H NMR and HPLC to ascertain the product structures and their relative isomeric ratios. As shown in Fig. 1a, the absorption of isocyanic acid, H-N=C=O (2211 cm^{-1}), due to partial decomposition of urea could be detected at a very early stage when the temperature of the mixed solution reached 100 °C. Addition product of isocyanic acid with ethylene glycol, carbamate **7**, was then observed in the solution as indicated by the appearance of a 1711 cm^{-1} carbamate absorption.

Ethylene glycol could also directly react with urea to form carbamate **7** by substitution reaction which is shown

Table 1. Reaction combinations and yields for the alkoxylated products

Entry	Phenolic compound	1,2-Glycol	Product	Isomer ratio[a]	Yield (%)[b]
1	**1a**	**2a**	**3aa**	–	89
2	**1a**	**2b**	**3ab**[c]	– (94/6[e])	92
3	**1b**	**2a**	**3ba**	–	88 (83[f])
4	**1b**	**2b**	**3bb**[d]	92:1:0 (95/5[e])	93
5	**1c**	**2a**	**3ca**	–	91 (85[f])
6	**1c**	**2b**	**3cb**[d]	91:2:0 (92/8[e])	93
7	**1d**	**2a**	**3da**	–	99
8	**1d**	**2b**	**3db**[d]	91:1:0 (91/9[e])	92
9	**1e**	**2a**	**3ea**	–	86 (77[f])

[a] Isomer ratios of 2°-2°, 2°-1° and 1°-1° isomeric propoxylated ether alcohols (by HPLC analyses).

[b] Isolated yields of mono-alkoxylated product(s) for each phenol group.

[c] A mixture of two isomers, 1-phenoxypropan-2-ol and 2-phenoxypropan-1-ol.

[d] Mixtures of 2°-2°, 2°-1° and 1°-1° isomeric alcohols.

[e] Isomeric ratios of (2°/1°) of all mono-propoxylated alcohols (by NMR analyses).

[f] Isolated yields by re-crystallization.

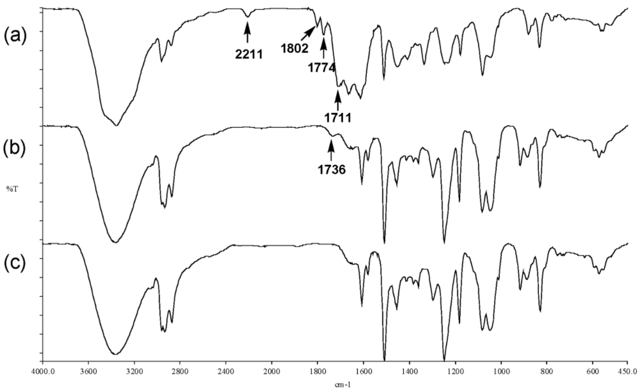
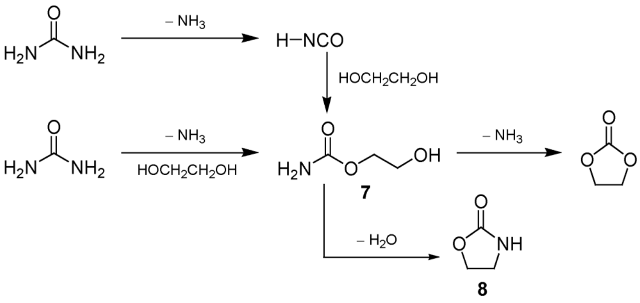


Fig. 1. Ethoxylation of BPA monitored by FTIR: (a) 120 °C, 2 h; (b) 170 °C, 4 h; (c) 180 °C, 6 h.

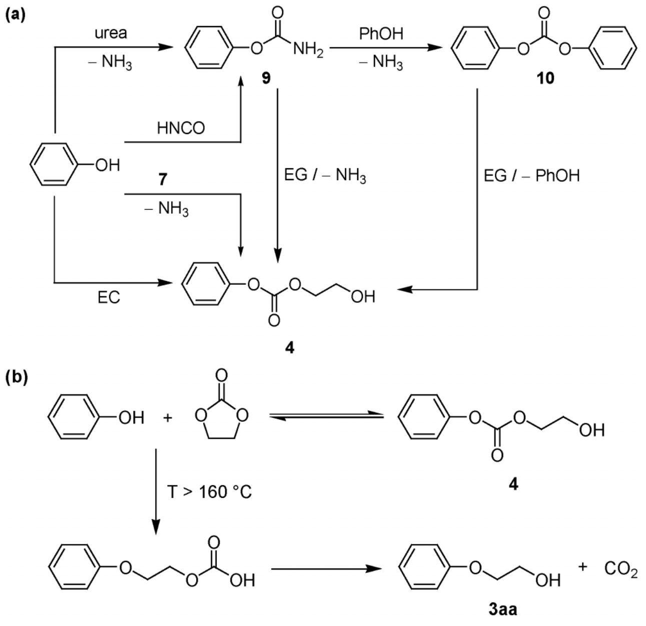
in the Scheme II. Carbamates **7** appeared to undergo an intra-molecular cyclization at a temperature greater than 150 °C in formation of ethylene carbonate (EC). The formation of EC was evidenced by the appearance of absorptions at 1774 and 1802 cm^{-1} in IR analysis. Potential by-product oxazolidone **8**, which may result from intra-molecular dehydration of **7**, was minimized by using ZnO as a co-catalyst as evidenced by showing little absorption at 1732 in the final ethoxylated product.[10,11]

Scheme II Decomposition of urea and formation of cyclic carbonate



Reactions between phenols and the intermediate carbonyl compounds seem complicated because many parallel reactions are proceeding during the reaction. However, logical routes that phenol or its derivatives react with carbonyl intermediates in formation of 2-phenoxyethanol, **3aa**, are compiled in Scheme IIIa-b. In the case of ethoxylation of BPA as the example, the formation of **4**-type carbonate alcohols are observed in IR absorptions at 1736-1740 cm^{-1} as shown in Fig. 1b by the first two hours of heating. Monitoring of the product mixtures at this transition period revealed that two methylene NMR peaks of the **4**-type carbonate alcohols were observed at 4.07 and 4.43 ppm, while two methylene NMR peaks of ethoxylated ethers of **3aa**-like products appeared as two signals at 3.90 and 4.07 ppm (Fig. 2a). After re-heating the product mixtures at about 180 °C for two additional hours, the IR absorptions of carbonate alcohols disappeared completely through evolution of CO_2, and at the same time the ^1H NMR spectrum becomes simplified into Fig. 2b, indicating that ethoxylated ether alcohols became the ultimate prod-

Scheme III Reactions occurred between phenols and carbonyl compounds



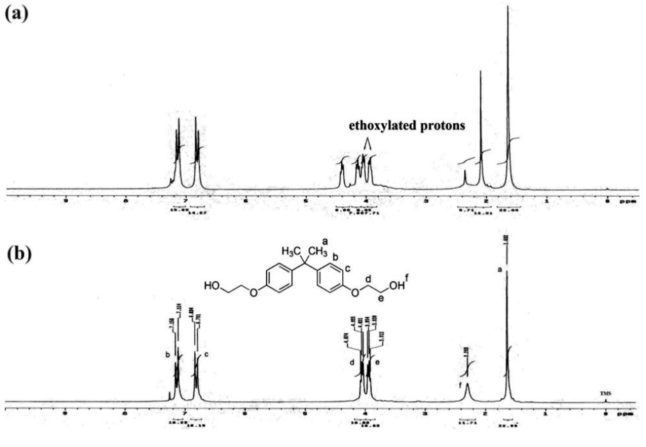


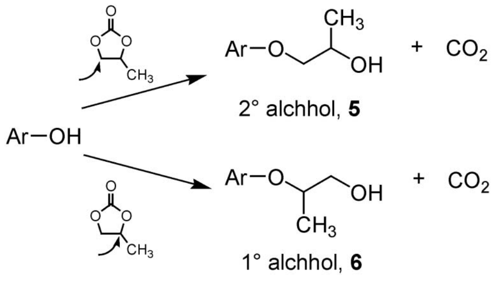
Fig. 2. ^1H NMR spectra. Ethoxylation of BPA: (a) 170 °C, 4 h; (b) 180 °C, 6 h.

uct. Thus, in the one-pot process, EC converted from cyclization of **4**- and **7** plays the key role in alkoxylation.

2.3. Product Selectivity in Propoxylation with Urea and 1,2-Propylene Glycol

One-pot propoxylations of phenols were similarly accomplished at 160-185 °C just by replacing ethylene glycol with 1,2-propylene glycol to react with urea. Although the reaction pathway and mechanism are basically the same in both cases, the products are more complex in propoxylation. This is mainly because propylene carbonate (PPC) is an asymmetrical compound, and two isomeric propoxylated products for each phenol group were expected. Due to the steric hindrance of the methyl group in propylene carbonate, phenol appears to react preferentially at the less-hindered carbon of the PPC to form isomeric 2°-alcohol **5** as the major propoxylated isomer of phenol (Scheme IV). The isomeric molar ratio between secondary (2°) and primary (1°) propoxylated ether alcohols after propoxylation of phenol could be conveniently estimated in the product mixture by checking the relative areas of methyl groups of propoxylated ethers in ^{1}H NMR signals located[12] at ~1.24 and 1.18 ppm corresponding to the secondary and the primary isomers respectively (see Table 1).

Scheme IV Isomeric products in propoxylated ether alcohols



In the case of reactions involving BPA, the selectivity of isomeric 2° diol components in the final products was found to be as high as 95% under sodium carbonate catalyzed reaction at 170-185 °C for 4 hours. As indicated in Fig. 3a, the methyl peaks of all 2° diols at ~1.25 ppm are dominant as compared with those of 1° diols at 1.18 ppm. This high selectivity of propoxylated ether products has never been observed previously in either PO (85%) or PPC (90%) propoxylation.[13,14] This selectivity has also been confirmed by HPLC analysis in showing 2°-2° bis-propoxylated diol being predominant component (92%) with 2°-1° (1%) and 1°-1° (< 1%) diols as the minor products. In short, one-pot urea-propylene glycol propoxylation offered a very unique route to high secondary ether alcohols of phenols especially with sodium carbonate as the base-catalyst.

2.4. Catalysts Used in Urea-Glycol Alkoxylation

During the course of our yield optimization study, bases other than sodium carbonate, such as cesium carbonate and potassium carbonate, were examined as possible catalyst alternatives. Under the identical conditions described earlier, IR monitoring reveals that the major products obtained from cesium and potassium carbonates are still mono-alkoxylated ether alcohols. However, two notable differences have been observed. First, the yields of mono-ethoxylated products for each phenol groups in potassium or cesium carbonate mediated reactions were found to be lower than those run with sodium carbonate. In other words, higher ethoxylated products were found in the products in greater proportions, which could be readily quantified from the areas of extra NMR absorptions corresponding to the second extended ether ethylene protons located at 3.5 ppm and 3.8 ppm. For instance, 11% of higher ethoxylated products were present in a reaction in K_2CO_3 catalyzed reaction of phenol. Second, in the case of propoxylation, selectivity of secondary alcohols in propoxylation mixtures became substantially reduced when potassium or cesium carbonate was used. As an example, the selectivity

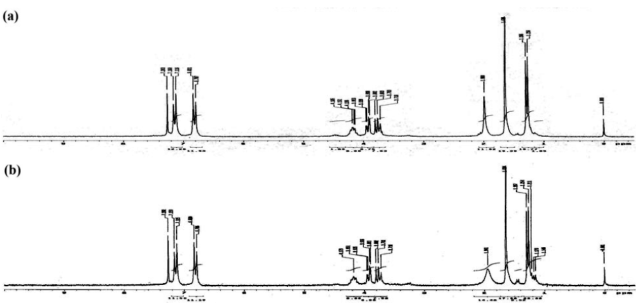


Fig. 3. Propoxylated ether diols of BPA prepared under different conditions by one-pot propoxylation. Propoxylation conditions: (a) initially at 100 °C and then slowly raised to 185 °C in 4 hours, 2°/1° = 95/5; (b) initially at 160 °C and then quickly raised to 185 °C in 3 hours, 2°/1° = 89/11.

of isomeric products with 2° alcohols of BPA was down to about 70% in Cs_2CO_3 (Fig. 4a and 4b, 1.15-1.30 ppm). In the case of potassium carbonate catalyzed propoxylation, formation of primary isomeric alcohols also were found to increase to about 44%. Thus, the yield and the isomer selectivity of mono-alkoxylated product for each phenol group become reduced when strong bases were applied.

2.5. Higher Alkoxylation of Phenols with EG/PG-Urea Alkoxylation

In traditional EO/PO alkoxylation, long-chained alkoxylated ether alcohols in molecular weights of several thousands could readily be achieved by prolonged reaction with excess EO/PO addition. However, a similar type of oligomerization seems more difficult to accomplish in a urea-glycol one-pot approach. The major hindrance is due to the complication when excess of solid urea is used in the reaction solution. For instance, while using three-molar excess of urea per phenol group and K_2CO_3 as catalyst in ethoxylation, the resulting products had an average extension of only 2.3 repeating units of ethoxyether for each phenol (calculated from ^1H NMR, 3.5-4.1 ppm) (Fig. 5). In the most elaborated conditions, the repeating units could be extended to about 3.0 ethylene oxide units per phenol group with a 4-fold molar excess of urea to phenol in one-pot urea-ethylene glycol approach. In the case of propoxylation with urea-propylene glycol catalyzed with K_2CO_3, the extension of propylene oxide units was even less efficient. Highest propoxylation extension was found to be about 2 units under 4 mole excess of urea. Therefore, it is reasonable to conclude that the present one-pot process is more suited for short alkoxylation extensions of phenols.

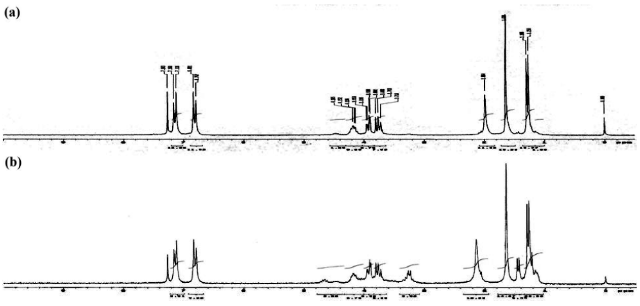


Fig. 4. Propoxylated ether diols of BPA: catalyzed by (a) Na_2CO_3; (b) Cs_2CO_3.

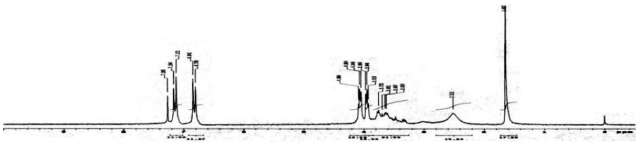


Fig. 5. Higher ethoxylation of BPA: BPA/urea/EG = 1/8/10, catalyzed by K_2CO_3.

2.6. Competitive Reaction between in EG/PG-Urea Alkoxylation

A competitive reaction between EC vs. PPC was run to alkoxylate phenol simultaneously from equal moles of excess EG/PG solution mixture. The relative mole ratios among the key reactants in the competitive alkoxylation are set at 3.0/3.0/1.5/1.0 for EG/PG/urea/phenol respectively in the comparative reaction. This controlled reaction catalyzed by Na_2CO_3-ZnO at 175 °C was designed to differentiate the rate of ethoxylation/propoxylation under the one-pot condition. From the IR monitoring of reaction mixture, it appears that the formation of EC (1802, 1774 cm^{-1}) and PPC (1791 cm^{-1}) were both observed during the course reaction. The ^1H NMR analysis of the isolated alkoxylated products by the area ratios of propoxylated regions at 1.28 (methyl group) and 6.90-7.33 ppm of the aromatic region concluded a calculated 70/30 (R = 2.33/1) ratio in favor of ethoxylation. This ratio indicates that EG has a significant rate advantage over PG in performing the alkoxylation if run simultaneously in the mixture. It implies that steric-hindrance of methyl group in PG and PPC does have a retarding rate impact on both the cyclization (ring closure to PPC) and the alkoxylation (ring opening) rates as compared to those of EG.

2.7. Green Chemistry Implication

If NH_3 and CO_2 released from the process were recaptured and recycled back to urea[15,16] as indicated in Scheme I, eq. 2, the overall alkoxylation of one-pot urea-glycol process can be regarded as a simple condensation reaction of phenol with 1,2-glycols yielding alkoxylated alcohol giving off water as the only by-product (Scheme I, eq. 3). This overall ethoxylation in theory has a calculated atom-utilization efficiency of 88.5% for phenol and 89.8% for BPA respectively.[17] Thus, urea can be regarded as a recyclable carrier while the 1,2-glycols become the only consumed reagents in the whole process. In the case of propoxylation, the atom-utilization efficiencies for phenol and BPA are calculated to be 89.4% and 90.5% respectively.

3. CONCLUSION

In summary, we have developed a one-pot process for alkoxylation of phenols using an urea-1,2-glycol mixture as the reagent. This process is ideal for extending short alkoxylated alcohols of 1-3 units to each phenol group. It was found that glycols are not only the idea solvents for dissolution of urea, but also provide a media with high enough boiling points for carrying out the alkoxylation in atmospheric condition. In a propoxylation reaction with urea-propylene glycol, formation of mono-extended units with isomeric secondary alcohols were found to be as high as 95% selectivity, which is the highest among all possible propoxylation methods. Because the reagents used are safe and inexpensive, and chemical efficiency is high, this convenient one-pot process could have a practical value in synthesis of ether alcohols from phenols in replacing EC and PPC.

4. EXPERIMENTAL

4.1. Representative Procedure for the One-Pot Alkoxylation: Preparation of BHE-BPA (3ba)

A 250-mL, three-necked, round-bottomed flask equipped with magnetic stirring bar, nitrogen inlet and reflux condenser was charged with 22.8 g (0.1 mol) of bisphenol A, 24.8 g (0.4 mol) of ethylene glycol and 0.2 g (1.89 mmol) of sodium carbonate. The mixture was then heated to 100-120 °C until BPA dissolved entirely to give a homogeneous solution. To this solution was added 0.2 g (2.46 mmol) of zinc oxide and 18.0 g (0.3 mol) of urea. After that, the reaction mixture was heated to 170-190 °C and maintained for 4-6 hours until no carbonyl absorption can be detected by FTIR for the reaction mixture. The solution was then cooled to about 50 °C, diluted with 100 mL of ethyl acetate and stirred for 10-15 min. After the catalyst was filtered off, the solution was concentrated on a rotary evaporator. The excess unreacted ethylene glycol was removed by vacuum distillation. The resulting viscous oil (29.2 g) was recrystallized from 50% aqueous ethanol solution to give 27.8 g (83%) of an off-white solid (mp 110-111 °C, lit. mp 112 °C).[18] ^{1}H NMR analysis confirms that the chemical structure of the solid is in fact the targeted molecule 2,2′-(4,4′-(propane-2,2-diyl)bis(4,1-phenylene)) bis(oxy)diethanol, **3ba**.

4.2. Characterization of Alkoxylated Products

2-Phenoxyethanol (3aa): ^{1}H NMR (200 MHz, $CDCl_3$)[12] δ 6.8-7.4 (m, 5H), 4.07 (t, 2H), 3.95 (t, 2H), 2.0 (s, 1H, -OH).

1-Phenoxypropan-2-ol: ^{1}H NMR (200 MHz, $CDCl_3$)[12] δ 6.8–7.4 (m, 5H), 3.9-4.4 (m, 3H), 2.1 (s, 1H, -OH), 1.2 (d, 3H).

2,2′-(4,4′-(Propane-2,2-diyl)bis(4,1-phenylene))-bis(oxy)diethanol (3ba): ^{1}H NMR (200 MHz, $CDCl_3$)[7] δ 7.16 (d, J = 8.8 Hz, 4H), 6.83 (d, J = 8.6 Hz, 4H), 4.07 (t, 4H), 3.95 (t, 4H), 2.29 (s, 2H, -OH), 1.63 (s, 6H); mp 110-111 °C (lit. 112 °C).[18]

1,1′-(4,4′-(Propane-2,2-diyl)bis(4,1-phenylene))-bis(oxy)dipropan-2-ol: ^{1}H NMR (200 MHz, $CDCl_3$)[9] δ 7.16 (d, J = 8.8 Hz, 4H), 6.83 (d, J = 8.8 Hz, 4H), 3.71-4.25 (m, 6H), 1.98 (s, 2H, -OH), 1.63 (s, 6H), 1.28 (d, J = 6.4 Hz, 6H).

2,2′-(1,4-Phenylenebis(oxy))diethanol (3ca): ^{1}H NMR (200 MHz, Acetone-d_6)[19] δ 6.84 (s, 4H), 4.00 (t, 4H), 3.83 (t, 4H), 2.04 (s, 2H, -OH); mp 102-106 °C (lit. 106-107 °C).[20]

1,1′-(1,4-Phenylenebis(oxy))dipropan-2-ol: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.84 (s, 4H), 3.69-4.41 (m, 6H), 2.55 (s, 2H, -OH), 1.28 (d, 6H).

2,2′-(1,3-Phenylenebis(oxy))diethanol (3da): ^{1}H NMR (200 MHz, $CDCl_3$)[19] δ 6.4-7.1 (m, 4H), 4.0 (t, 4H), 3.8 (t, 4H), 2.1 (s, 2H, -OH); mp 81-85 °C (lit. 86 °C).[21]

1,1′-(1,3-Phenylenebis(oxy))dipropan-2-ol: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.4-7.1 (m, 4H), 3.8-4.1 (m, 6H), 2.1 (s, 2H, -OH), 1.28 (d, 6H).

2-(4-(Prop-1-en-2-yl)phenoxy)ethanol (3ea): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.29 (s, 1H), 5.00 (s, 1H), 4.11 (t, 2H), 3.98 (t, 2H), 2.12 (s, 3H), 1.86 (s, 1H, -OH); mp 84-85 °C.

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