particularly at elevated pressures. Care must be taken to avoid the use of dangerous vapor compositions (maintain $\leq 20\%$ v/v O_2 at total pressures ≤ 200 psia[19]) and to isolate the system from potential ignition sources. The reactor should be grounded to prevent a buildup of static electricity.

The pressurized reaction mixture was irradiated for 1.5 h with a 450-W high-pressure mercury lamp in an externally positioned Pyrex immersion well. The operating pressure was maintained by periodically adding oxygen to replace that which was consumed. The temperature was maintained at 12–19 °C. Upon completion of the irradiation unreacted propylene was slowly vented (3 h), and the reaction mixture was analyzed by quantitative GC. When high concentrations of propylene were used, considerable evaporation of the volatile products occurred, requiring a modification of the sampling procedure. In these reactions a measured volume of the pressurized liquid phase was vented into an ice-cooled coil of stainless steel tubing (0.125 in. o.d.). This sample was then slowly vented into 50 mL of *o*-dichlorobenzene and analyzed by GC.

A solution of *o*-dichlorobenzene (250 mL) containing 1.4 g (9.5 mmol) of 1-phenyl-1,2-propanedione and 0.4 g (4.7 mmol) of biacetyl was placed in the pressure reactor. The reactor was purged with nitrogen and sealed before 45.6 g (1.09 mol) of propylene was charged, bringing the total volume to 339 mL[20] and the pressure to 70 psia. Nitrogen (80 psi) and oxygen (18 psi) were then charged, bringing the total pressure to 168 psia. The mixture was irradiated for 1.5 h at 12–15 °C. Sufficient oxygen was added during the reaction to maintain the pressure at 165–9 psia. The unreacted propylene was slowly vented (3 h) and the solution analyzed by GC. Propylene oxide (11.24 mmol), acetaldehyde (0.86 mmol), and formaldehyde (undetermined) were the only products observed.

Pressurized Photooxidation of 1-Hexene. A solution of 1.0 g (6.7 mmol) of 1-phenyl-1,2-propanedione and 0.28 g (3.3 mmol) of biacetyl in 250 mL of 1-hexene was placed in the pressure reactor. Nitrogen (20 psi) and oxygen (20 psi) were introduced, bringing the pressure to 54 psia. The mixture was irradiated 1.5 h at 19–20 °C and 50–54 psia. After the pressure was released, GC/MS analysis of the reaction mixture showed the formation of *n*-butyloxirane, pentanal, and formaldehyde.

Quantum Efficiency Measurements. The flux of photons from the mercury lamp into the pressurized reactor was measured by potassium ferrioxalate actinometry.[17] The average total flux was determined to be 1.84×10^{-4} einstein min^{-1} ($\pm 3\%$). A second series of measurements was made in which the light was filtered through a solution of 1-phenyl-1,2-propanedione (0.08 M) and biacetyl (0.04 M) in *o*-dichlorobenzene (0.5 cm path length) before entering the reactor. The average value of these measurements (5.92×10^{-5} einstein min^{-1}, $\pm 3\%$) represents the flux of photons outside the absorption band of the sensitizer mixture. Subtraction of this flux from the total photon flux gave the flux of photons capable of being absorbed by the photoepoxidation system (1.25×10^{-4} einstein min^{-1}). This value was used to estimate the quantum efficiencies of propylene oxide formation and propylene conversion.

Acknowledgment. The funding of this work by the Celanese Research Co. is gratefully acknowledged. I thank Mr. Edward Kuczynski and Mr. Vincent Provino for their valuable assistance, Dr. David Kemp for the GC/MS analyses of reaction products, and Dr. Ralph Truitt for the UV–visible spectra of the sensitizers.

Registry No. Propene, 115-07-1; biacetyl, 431-03-8; benzil, 134-81-6; 1-phenyl-1,2-propanedione, 579-07-7.

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(19) Zakaznov, V. F.; Kursheva, L. A.; Fedina, Z. I. *Sov. Chem. Ind. (Engl. Transl.)* **1978**, *10*, 468.

(20) Based on a propylene density of 0.51 g/mL.

Synthesis of Bis(aryloxyethyl) Vinyl Ethers via Phase-Transfer-Catalyzed Nucleophilic Displacement on 2-Chloroethyl Vinyl Ether

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Bis(aryloxyethyl) vinyl ethers can be prepared in high yield by using sodium hydroxide, bis(phenols), and 2-chloroethyl vinyl ether (CEVE) with a tetraalkylammonium salt phase-transfer catalyst. The displacement reaction of the bis(phenol) dianion proceeds in high yield only if both excess CEVE and base are employed. Nucleophilic displacement is considerably faster than elimination reactions involving solvent or catalyst. Small amounts of water have little effect on the reaction. The synthesis has been extended to the preparation of related monoaryloxyethyl vinyl ethers.

Introduction

The phase-transfer-catalyzed reaction of phenolate anions and alkyl halides has been used to prepare a variety of aryl alkyl ethers.[1,2] In many of these syntheses, relatively large amounts of catalyst are employed. In addition, the bulk of literature investigations has focused on the reactions of monoanions. We report the extension of this method to the preparation of diarylalkyl vinyl ethers with efficient use of the phase-transfer catalyst. The effects of various reaction parameters, especially base concentration and moisture content, have been investigated.

In attempts to identify new materials for cationically initiated polymerization,[3] a variety of bis(aryloxyethyl) vinyl ethers were prepared. Initially, the reaction of selected bis(phenols) with excess chloroethyl vinyl ether (CEVE) and base was run in dimethyl sulfoxide (Me_2SO) solution.[4] It was thought that this reaction could be more easily accomplished by replacing Me_2SO with another solvent and employing a phase-transfer catalyst (PTC). After preliminary evaluation, the reaction of bisphenol A (BPA) with CEVE was chosen as a representative candidate for investigation (eq 1).

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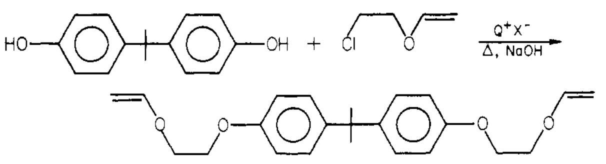
(1) Dehmlow, E. V.; Dehmlow, S. S. "Phase Transfer Catalysis"; Verlag Chemie: Weinhein, West Germany, 1980.

(2) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis Principles and Techniques"; Academic Press: New York, 1978; pp 126–140. Keller, W. E. "Compendium of Phase-Transfer Reactions and Related Synthetic Methods"; Fluka AG: Buchs, Switzerland, 1979; pp 70–74.

(3) Butler, G. B.; Nash, J. L. *J. Am. Chem. Soc.* **1951**, *73*, 2538.

(4) Crivello, J. V.; Conlon, D. A., unpublished results.

0022-3263/83/1948-0342$01.50/0



(1)

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Under the proper conditions BPA diethoxy vinyl ether, BPA-DEVE (1), can be prepared easily and in high yield by using a PTC.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were recorded on either a Varian EM-390 or a CFT-80 spectrometer with deuteriochloroform as solvent. Tetramethylsilane was used as an internal standard. Infrared (IR) spectra were recorded on a Perkin-Elmer 598 grating spectrophotometer in carbon tetrachloride solution unless otherwise indicated. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Gas chromatographic analyses were performed on a Hewlett-Packard 5840A chromatograph with a 6 ft × $^1/_8$ in. 3% OV-17 column.

Liquid chromatographic analyses were performed on a Waters Associates instrument with dual channel UV detectors and gradient elution using a μC_{18} column. Solvents were tetrahydrofuran and a 95:5 water:methanol solution. Elution starts with a 50:50 mixture of solvents and ends with an 80:20 mixture.

Preparation of BPA-DEVE (1). Into a 250-mL round-bottom flask flushed with nitrogen and fitted with paddle stirrer, reflux condenser, addition funnel, and thermometer was placed 45.6 g of *p,p'*-BPA (0.20 mol), 80 mL of distilled 2-chloroethyl vinyl ether, and 100 mL of toluene. The flask contents were stirred for 5 min, and then 20.0 g of NaOH pellets (0.50 mol) was added. This mixture was heated at 80 °C for 0.5 h, and then a solution of 4.56 g tetrabutylammonium bromide (0.014 mol) dissolved in 20 mL of CEVE was added. Total CEVE was 100 mL (0.986 mol). The reaction was heated slowly to 95 °C and allowed to react for 3 h. The mixture was cooled and 200 mL of water added. The layers were separated, and the lower layer (aqueous) was saved for eventual PTC recovery. The organic layer was washed twice with 150-mL portions of deionized water. The organic layer was distilled at 108 °C (760 mmHg) to remove residual water, toluene, and CEVE. Vacuum was applied to remove the last traces of solvent. The yellow oily residue weighed 73.3 g (99.6%). The crude product was recrystallized in heptane (35% solids) to yield 66.8 g (90.8%) of white crystalline BPA-DEVE.

The bis(aryloxyethyl) vinyl ethers listed in the Analytical Data section were prepared in a manner similar to that described above. Yields were not optimized. The reactions can be conducted in neat CEVE with results almost identical with those described above. Toluene was added to the reaction to aid in the workup. 1,1-Dichloro-2,2-bis(4-hydroxyphenyl)ethylene was prepared by the method of Campbell and Klopfer.[5]

PTC Recovery. The first aqueous wash was extracted three times with methylene chloride, and the organic layers were combined and evaporated to dryness. The last traces of water were removed by azeotropic distillation with toluene. The solution was evaporated to dryness to give a white solid. The solid was further dried at 40 °C (10 mmHg) to yield 3.67 g of tetrabutylammonium chloride (94.5%). Care must be taken to prevent overheating, which will decompose the catalyst.

Yield of BPA-DEVE vs. Sodium Hydroxide. In a reaction similar to that described for the preparation of BPA-DEVE (20.0 g of BPA, 90 mL of CEVE, 2.0 g of $Bu_4N^+Br^-$, at reflux), the amount of sodium hydroxide added to the reaction was varied between 7.0 and 12.3 g (2.0–3.5 mole ratio of NaOH to BPA). Sodium hydroxide pellets were added to a suspension of BPA in CEVE. After being stirred for 0.5 h, the mixture was heated to reflux and the PTC added. The progress of the reaction was monitored by gas chromatography. *o*-Terphenyl was used as an internal standard. A NaOH/BPA mole ratio of >2.3 is necessary for complete conversion of BPA to product.

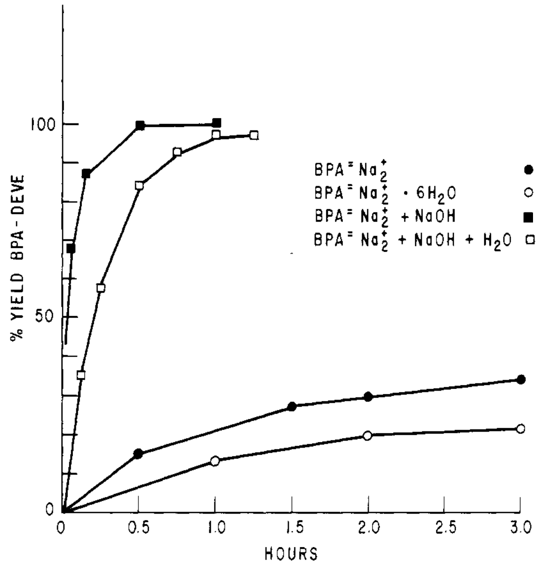

Figure 1. Formation of BPA-DEVE from $BPA^{2-}Na_2^+$.

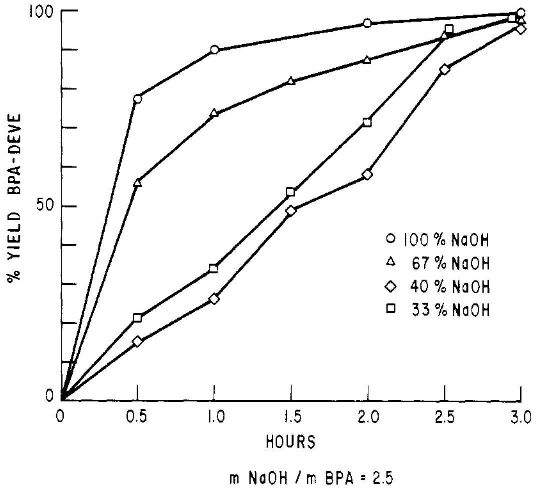

Figure 2. Effect of base strength on yield of BPA-DEVE.

Yield of BPA-DEVE vs. Water. The experiments were similar to those described above. However, the amount of sodium hydroxide added was held constant at 8.8 g (2.5 mole ratio of NaOH to BPA), and the amount of water added to the reaction was varied between 4.4 and 17.6 g. The base was dissolved in the water and poured slowly into the BPA suspension. Results are summarized in Figure 2. It must be kept in mind that even when no water is added, there is 3.2 g of water present due to the formation of BPA dianion.

Preparation of BPA-DEVE Using Preformed BPA-Dianion. Similar conditions were used as those described for the initial preparation of BPA-DEVE; however, instead of reacting BPA and sodium hydroxide in situ, the dry, preformed BPA dianion[6] $BPA^{2-}Na_2^+$ (0.10 mol) was used. In similar experiments, $BPA^{2-}Na_2^+ \cdot 6H_2O$ was substituted for $BPA^{2-}Na_2^+$. In both cases the yield of product was low. When additional sodium hydroxide (0.05 mol) was added to the preformed BPA salt (0.10 mol), product was formed in high yield. When the reaction was repeated with 0.10 mol of $BPA^{2-}Na_2^+$ and 0.05 mol of NaOH with 0.20 mol of H_2O (the amount of water that would be present if the BPA salt were formed in situ), BPA-DEVE was again formed rapidly in high yield. The results of these experiments are summarized in Figure 1.

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[5] Campbell, J. R.; Klopfer, H. J. U.S. Patents 4128731 and 4105857, 1978. Factor, A.; Orlando, C. M. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 579.

[6] White, D. M.; Takekoshi, T.; Williams, F. J.; Relles, H. M.; Donahue, P. E.; Klopfer, H. J.; Loucks, G. R.; Manello, J. S.; Matthews, R. O.; Schulenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1635.

Preparation of BPA-DEVE in *n*-Butyl Alcohol. A 250-mL three-necked flask equipped with a thermometer, overhead stirrer, and reflux condenser was filled with 80 mL of *n*-butyl alcohol, 20.0 g of BPA (0.088 mol), 8.8 g of sodium hydroxide pellets (0.220 mol), 1.0 g of *o*-terphenyl (internal standard), and 18.7 g of distilled CEVE (0.176 mol). The suspension was stirred vigorously under nitrogen with heating at 90 °C; 2.0 g of tetrabutylammonium bromide dissolved in 20 mL of *n*-butyl alcohol was added to the reaction. The reaction was maintained at reflux (106–110 °C). All CEVE was consumed in 4 h. However, unreacted BPA still remained. After 5 h, an additional 18.7 g of CEVE was added to the reaction. The reaction went to completion during the next two hours. Product may be isolated from the reaction by extraction using methylene chloride and water.

A similar reaction without PTC gave results comparable to those observed in the phase-transfer-catalyzed reaction.

BPA-DEVE Stability. In preparations of BPA-DEVE using CEVE as solvent and a large excess of base (3.2:1 NaOH:BPA mole ratio), the yield of product does not diminish if the reaction is allowed to reflux for several hours after the displacement is complete. So that the possibility of an elimination readdition reaction could be examined, 10.0 g of BPA-DEVE was allowed to reflux in 100 mL of *n*-butyl alcohol with 1.8 g of sodium hydroxide pellets and 1.0 g of tetrabutylammonium bromide. After 15 h, no loss of product was observed. The use of 50% aqueous sodium hydroxide did not change the observed stability.

Elimination Reactions of CEVE. The volatile reaction products accompanying the formation of BPA-DEVE with excess base (3.2:1 NaOH:BPA mole ratio) were collected by connecting a dry ice–acetone cooled trap to the reflux condenser. Only a small amount of byproducts (0.2 g) was isolated from a normal run (0.20 mol BPA). The excess base necessary for complete BPA conversion implies that a greater amount of byproducts should have been present. However, volatile products may have been lost since complete sealing of the reaction vessel was not possible while good stirring was maintained.

Judging from the NMR spectra (with comparison to authentic samples), the following products were present: divinyl ether, (DVE, 40%), ethylene oxide (28%), vinyl chloride (24%), and acetaldehyde (8%). The presence of DVE, vinyl chloride, and acetaldehyde was confirmed by GC/MS.

Analytical Data for Bis(aryloxyethyl) Vinyl Ethers. 2,2-Bis(4-(2-(vinyloxy)ethoxy)phenyl)propane (1, BPA-DEVE): yield 90%; mp 54–55 °C (heptane); IR 2960, 2920, 2865, 1635, 1605, 1505, 1245, 1195, 1175 cm^{-1}; ^{1}H NMR δ 7.2–6.7 (m, 8 H, A_2B_2), 6.6–6.3 (2 H dd), 4.3–3.9 (m, 12 H), 1.6 (s, 6 H); ^{13}C NMR 156.4, 151.7, 143.5, 127.7, 114.0, 86.9, 66.4, 66.3, 41.7, 31.0 ppm. Anal. Calcd for $C_{23}H_{28}O_4$: C, 75.0; H, 8.0. Found: C, 74.9; H, 7.9.

4,4′-Bis(2-(vinyloxy)ethoxy)biphenyl: yield 58%; mp 145–148 °C (EtOH); IR (KBr) 2920, 1640, 1600, 1490, 1445, 1320, 1265, 1235, 1195, 1065, 975, 920, 850, 820, 625, 520 cm^{-1}; ^{1}H NMR δ 7.7–7.0 (m, 8 H), 6.9–6.4 (m, 2 H), 4.5–4.0 (m, 12 H); ^{13}C NMR 157.8, 151.7, 133.8, 127.8, 115.0, 87.0, 66.5 66.4 ppm. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.6; H, 6.8. Found: C, 73.6; H, 6.8.

Bis(4-(2-(vinyloxy)ethoxy)phenyl)methane: yield 79%; mp 88–90 °C (EtOH); IR 1635, 1610, 1420, 1355, 1210, 1185, 525 cm^{-1}; ^{1}H NMR δ 7.4–7.0 (m, 8 H), 7.0–6.5 (m, 2 H), 4.6–4.0 (m, 14 H); ^{13}C NMR 157.0, 151.7, 134.1, 129.8, 114.7, 87.0, 66.5, 40.1 ppm. Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.1; H, 7.1. Found: C, 74.1; H, 7.1.

1,3-Bis(2-(vinyloxy)ethoxy)benzene: yield 40%; mp 81–84 °C (EtOH); IR 2930, 1635, 1610, 1590, 1490, 1450, 1320, 1200, 1180, 1155, 680 cm^{-1}; ^{1}H NMR δ 7.2–6.3 (m, 6 H), 4.3–3.9 (m, 12 H); ^{13}C NMR 159.8, 151.6, 129.9, 107.3, 101.9, 87.0, 66.4 ppm. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.2; H, 7.3. Found: C, 67.1; H, 7.4.

1,1-Dichloro-2,2-bis(4-(2-(vinyloxy)ethoxy)phenyl)ethylene: yield 78%; mp 71–73 °C (EtOH); IR 1635, 1615, 1605, 1505, 1250, 1175, 860 cm^{-1}; ^{1}H NMR δ 7.3–6.8 (m, 8 H), 6.6–6.3 (m, 2 H), 4.3–3.9 (m, 12 H); ^{13}C NMR 158.2, 151.6, 139.6, 132.5, 130.9, 117.9, 114.3, 87.1, 66.4 ppm. Anal. Calcd for $C_{22}H_{22}Cl_2O_4$: C, 62.7; H, 5.3; Cl, 16.8. Found: C, 62.9; H, 5.3; Cl, 17.0.

2-(2,6-Dimethylphenoxy)ethyl vinyl ether: yield 73%; bp 90–93 °C (0.70 mm Hg); IR 2920, 1635, 1610, 1475, 1320, 1260, 1190, 975 cm^{-1}; ^{1}H NMR δ 6.9–7.0 (m, 3 H), 6.6–6.3 (m, 1 H), 4.3–4.1 (m, 2 H), 4.0 (s, 4 H), 2.3 (s, 6 H); ^{13}C NMR 155.8, 151.9, 130.8, 129.0, 124.0, 86.9, 70.5, 67.4, 16.1 ppm. Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.0; H, 8.4. Found: C, 75.2; H, 8.6.

2-(2,4,6-Trimethylphenoxy)ethyl vinyl ether: yield 80%; bp 99–101 °C (0.30 mmHg); IR 2920, 1635, 1610, 1485, 1320, 1200, 1150, 970, 855 cm^{-1}; ^{1}H NMR δ 6.8 (s, 2 H), 6.6–6.3 (m, 1 H), 4.3–4.0 (m, 2 H), 3.9 (s, 1 H), 2.2 (s, 9 H); ^{13}C NMR 153.4, 151.8, 133.2, 130.5, 129.4, 86.8, 70.4, 67.3, 20.6, 16.1 ppm. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found: C, 75.9; H, 8.9.

2-Phenoxyethyl vinyl ether: yield 86%; bp 79–81 °C (0.55 mmHg);[9] IR 2920, 1635, 1615, 1595, 1495, 1450, 1320, 1240, 1195, 980, 750, 690 cm^{-1}; ^{1}H NMR δ 7.3–6.8 (m, 5 H, 6.6–6.3 (m, 1 H), 4.3–3.8 (m, 6 H); ^{13}C NMR 158.6, 151.7, 129.5, 121.1, 114.7, 87.0, 66.4, 66.2 ppm.

2-(Thiophenoxy)ethyl vinyl ether: yield 81%; bp 160–163 °C (40 mmHg);[9] IR 1635, 1610, 1480, 1435, 1325, 1200, 1065, 990, 960, 690 cm^{-1}; ^{1}H NMR δ 7.4–7.1 (m, 5 H), 6.5–6.2 (m, 1 H), 4.3–3.8 (m, 4 H), 3.1 (t, 3 H); ^{13}C NMR 151.3, 135.5, 129.8, 129.0, 126.5, 87.1, 66.5, 32.7 ppm.

Results and Discussion

Under the conditions cited in the Experimental Section, the formation of BPA-DEVE was fast. After an initial induction period of 5–30 min, which reflects the formation of the BPA dianion, the reaction was complete in less than half an hour. The product was isolated in high yield. Almost no impurities were detected by gas or liquid chromatographic analysis. No monofunctional product was observed, even at low conversions of BPA. It appeared that the monoalkylated product was much more soluble in the organic layer than the dianion, and hence the second alkylation was much faster than the first. In more polar solvents (Me_2SO, *n*-butyl alcohol, or acetonitrile) both the monofunctional and difunctional vinyl ethers are observed at low BPA conversions. Under these conditions the rate of the first and second displacement reactions of BPA dianion appear comparable.

The type and amount of PTC used was an important variable in this reaction. Initially, potential catalysts were evaluated by reaction with a large excess of base in CEVE solution (~10% catalyst by weight of BPA). In the absence of catalyst, no reaction of BPA was observed even after 24 h at reflux. Tetraalkylammonium salts such as methyltricaprylylammonium chloride (Aliquat 336),[7] methyltrialkyl(C_8–C_{10})ammonium chloride (Adogen® 464),[8] and tetrabutylammonium chloride, bromide, or fluoride were all effective catalysts (>85% yield). However, phosphonium salts ($Bu_4P^+Br^-$, $Ph_4P^+Br^-$) and polyethylene glycols gave much lower yields (~10%) of product under the same reaction conditions. Dibenzo-18-crown-6 gave a 20% yield of product. The tetrabutylammonium salts gave slightly faster conversion than the methyltrialkylammonium salts. Attempts to form a PTC in situ by reacting tributylamine and CEVE[9] in the presence of BPA failed to yield product.

The effect of PTC concentration on yield was investigated by using Aliquat 336 (3.2:1 mole ratio of NaOH to BPA). Reasonable conversion rates require >5% catalyst. Similar results were found with use of tetrabutylammonium halide catalysts. The final choice of catalyst and reaction solvent,[10] was dictated by how easily the catalyst could be removed from product. Adogen 464 and Aliquot 336 are effective catalysts; however, they are not

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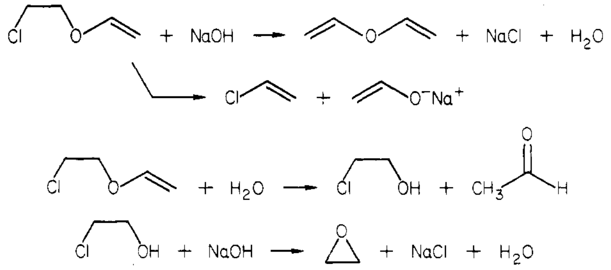
[7] Registered trademark of General Mills Chemicals, Inc.

[8] Registered trademark of Ashland Chemicals Co.; see: Starks, C. S.; Napier, D. R. U.S. Patent 3 992 432, 1976.

[9] Atavin, A. S.; Gusarov, A. V.; Trofinov, B. A. *J. Org. Chem. USSR* **1967**, *3*, 1368.

[10] Use of methylene chloride in this reaction led to the preferential reaction of BPA dianion with solvent forming a BPA polyformal. Hay, A. S.; Williams, F. J.; Loucks, G. M.; Relles, H. M.; Boulette, B. M.; Donahue, P. E.; Johnson, D. S. *Polym. Prepr.* **1982**, *23*, 117.

Scheme I



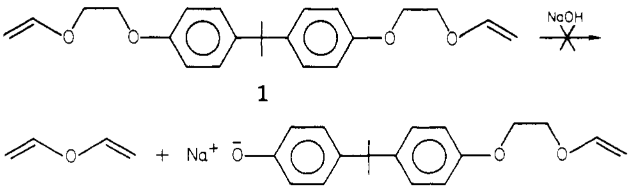
appreciably soluble in water, and separation from the product, which cannot be distilled, is difficult. Similar problems would be encountered by using polyethylene glycols or crown ethers. With the proper choice of solvent tetrabutylammonium halides can be removed from the product by aqueous extraction.[11] Initially, neat CEVE was used as solvent. In order to simplify the separation of the organic and aqueous layers, a 50:50 (v/v) CEVE–toluene solution was employed. Without toluene, CEVE and water are difficult to separate. The introduction of toluene had little effect on the rate and yield of the reaction. The catalyst present at the end of the reaction as tetrabutylammonium chloride was extracted into the aqueous wash. The catalyst can be recovered from the aqueous wash efficiently by extraction with methylene chloride.[11] Both the recovered solvents and catalyst were successfully reused in a BPA-DEVE preparation. The catalyst was recovered in high yield (85–90%); possible deactivation by direct displacement giving aryl *n*-butyl ethers and tributylamine or by elimination giving amine and 1-butene was not observed.[1]

Another major variable in the displacement reaction was the type and amount of base used. With exact stoichiometry, the reaction of BPA, CEVE, and sodium hydroxide gave a 59% yield of BPA-DEVE. High yields were obtained only with excess base present. The variation of yield vs. base was examined. At least 15% excess base is necessary for complete conversion of BPA to product. Usually a 20–50% excess was employed. In these experiments the only water present was generated by the formation of BPA dianion.

When a stoichiometric amount of base was used, high yields of BPA-DEVE were not obtained. However, at the end of the reaction all base was consumed. The only compounds present were PTC, NaCl, BPA-DEVE, unreacted CEVE, and BPA. It was apparent that base was consumed in a side reaction with CEVE forming volatile products. The major volatile byproduct was identified as divinyl ether (DVE) with smaller amounts of acetaldehyde, ethylene oxide, and vinyl chloride. The probable reactions leading to the formation of byproducts are summarized in Scheme I.

The formation of DVE, ethylene oxide, and acetaldehyde are not surprising. The former is the product of dehydrohalogenation of the halide, and the latter two are products of CEVE hydrolysis followed by reaction with base. The presence of vinyl chloride is more perplexing. It requires an unusual elimination from CEVE (or possibly chloroethanol).

The possible elimination of DVE from BPA-DEVE under the influence of strong base was investigated (eq 2). In the presence of CEVE, PTC, and excess base at reflux, no decomposition of BPA-DEVE was observed after 6 h.



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Similarly, *n*-butyl alcohol solution with excess NaOH, PTC, but no CEVE, BPA-DEVE was also stable. Addition of a small amount of water to the reaction in *n*-butyl alcohol had no effect on BPA-DEVE stability.

Displacement reactions conducted in refluxing *n*-butyl alcohol with a NaOH to BPA mole ratio of 2.5 and with 2.0 equiv of CEVE showed initial product formation; however, product formation levels off after 4 h. All CEVE was consumed. Addition of a further 2.0 equiv of CEVE to the reaction leads to product formation in high yield. The same reaction is observed with or without PTC in *n*-butyl alcohol.

Attempts to use potassium hydroxide, lithium hydroxide, or sodium carbonate to prepare product were unsuccessful. Potassium hydroxide gave some BPA-DEVE but appeared to react preferentially with CEVE.[12] No reaction was observed in the other cases.

In some instances the amount of water present has an important effect on the outcome of a phase-transfer-catalyzed reaction.[1,2] In order to explore the effects of water on this reaction, we ran the displacement using the preformed disodium salt of BPA.[6] The preformed BPA dianion gives a low yield of product under normal reaction conditions. The presence of a small amount of water has no effect on this result. However, if sodium hydroxide is added to the reaction using preformed BPA dianion, the reaction is complete in less than half an hour, giving BPA-DEVE in high yield. The amount of NaOH added to the reaction made it equivalent to a reaction starting with a NaOH:BPA mole ratio of 2.5 (but without the water formed by reaction with BPA). As shown in Figure 1, addition of enough water to make the reaction equivalent to forming the BPA dianion in situ has little effect on yield.

The effect of greater amounts of water on the reaction, while holding the ratio of mNaOH/mBPA constant at 2.5, is shown in Figure 2. Amounts of water greater than that accompanying the in situ formation of BPA dianion (and the water formed in side reactions with CEVE) slow the rate of product formation. However, after 3 h, the product is obtained in high yield in all cases. In addition to reducing the rate of the reaction, larger amounts of water increase color formation. Attempts to vary the amount of water present while holding the NaOH to BPA mole ratio at 2.0 did not result in yields >60% even at long reaction times. Excess base is crucial to the complete conversion of BPA to product; water has a secondary effect on the reaction.

The highest rate of product formation for the displacement reaction was observed at reflux. Below 65 °C the yield of BPA-DEVE was low, even at long reaction times (~48 h). Between 65 and 95 °C the rate increased by a factor of 8. With CEVE as solvent, the reflux temperature varied from 84 to 109 °C, depending on the amount of water present.

The phase-transfer-catalyzed reaction of BPA and sodium hydroxide with CEVE to prepare BPA-DEVE was extended to the preparation of the vinyl ethers of other bis(phenols) (Analytical Data section). Resorcinol, *p,p′*-

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(11) Sjoberg, K. *Aldrichimica Acta* **1980**, *13*, 55. The solubility of various tetraalkylammonium salts in organic solvents is summarized in the Tridom-Fluka catalog (**1979**, *11*, 674-5).

(12) Ruigh, W. L.; Major, R. T. *J. Am. Chem. Soc.* **1931**, *53*, 2662.

biphenol, bis(4-hydroxyphenyl)methane, and 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene[5] were allowed to react with excess CEVE to give the corresponding bis(vinyl)ethers in modest isolated yield.

Less soluble phenolate dianions fail to yield product. 4,4′-Sulfonyldiphenol, 2,2′,6,6′-tetrabromobisphenol A, and 2,2′,6,6′-tetramethylbisphenol A all failed to yield product after 24 h at reflux.

The phase-transfer-catalyzed reaction of phenol,[9] 2,6-dimethylphenol, and 2,4,6-trimethylphenol with CEVE and base gave the corresponding ethoxy vinyl ethers in good yield. These results indicate that anion or dianion solubility rather than steric considerations are the key to forming ethoxy vinyl ethers in high yield.

Thiophenol and sodium hydroxide were reacted with CEVE to yield 2-(phenylthio)ethyl vinyl ether. The reaction proceeds in good yield without PTC.[9] None of the above reactions were investigated in detail, nor were yields maximized.

Conclusions

The reaction of BPA dianion with CEVE yields the diaryl ether BPA-DEVE in high yield only if both excess base and a phase-transfer-catalyst are employed. The yield of the reaction varies considerably depending on PTC structure. In this instance tetraalkylammonium salts are substantially more effective than other phase-transfer catalysts. They are also the most easily separated from the product.

It is interesting to note that in this reaction the presence of water is not an important variable (Figures 1 and 2). This observation is surprising when one considers that by changing the amount of water present, the reaction goes from essentially a solid–liquid phase system (BPA dianion–CEVE) to a solid–liquid–liquid system (BPA dianion–H_2O–CEVE). In most reactions CEVE is in contact with an aqueous slurry of BPA dianion and sodium chloride.

The phase-transfer-catalyzed displacement reaction of BPA dianion with CEVE does not result in substantial amounts of monoalkylated product. Even at low conversions, only the difunctionalized vinyl ether is observed. Reaction of the second oxygen of the BPA dianion is much faster than the initial alkylation. In more polar solvents (Me_2SO, *n*-butyl alcohol, or acetonitrile) the reaction behaves more conventionally. The monofunctional and difunctional vinyl ether are observed at low BPA conversions. Under these conditions the rate of the first and second displacement reactions of BPA dianion appear comparable.

One explanation of the failure to observe monofunctional product in the phase-transfer-catalyzed reactions is that the monoether is considerably more soluble in the organic phase than BPA dianion and forms product at a much faster rate. Once in the organic phase, the reaction of the phenolate with CEVE is assumed to be fast. In a better solvent, i.e., Me_2SO, the difference in solubility between the mono- and dianion is not as great, and hence both species yield product at comparable rates. At low conversions the monoether product can be observed in solution.

An alternative explanation of the results of the phase-transfer-catalyzed displacement is that only the bis(tetraalkylammonium) BPA salt is transported into the organic phase, and it reacts rapidly to give the bis(ether) product.[13] This explanation requires transport of the monotetraalkylammonium BPA salt into the organic phase to be slow. The first explanation seems more plausible than the second; however, neither one can be ruled out. The conversion of phenolate groups from the sodium to ammonium form may also be important in determining the reaction products.

The extention of the vinyl ether synthesis to other bis(phenols) indicates that dianion solubility (transport into the organic phase) is a key factor in determining the extent of reaction. This point is illustrated by the reaction of 2,2′,6,6′-tetramethyl BPA with CEVE. In this case no displacement product was formed even after long reaction times with excess base and PTC. Under identical conditions 2,6-dimethylphenol gave the displacement product in quantitative (GC) yield. Both of these reactions were under similar steric constraints; however, the more soluble monoanion gave product while the less soluble dianion did not react.

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Registry No. 1, 52411-04-8; *p,p′*-BPA, 80-05-7; $BPA^{2-}Na_2^+$, 2444-90-8; 2-chloroethyl vinyl ether, 110-75-8; tetrabutylammonium bromide, 1643-19-2; 4,4′-bis[2-(vinyloxy)ethoxy]biphenyl, 84040-76-6; bis[4-[2-(vinyloxy)ethoxy]phenyl]methane, 84040-77-7; 1,3-bis[2-(vinyloxy)ethoxy]benzene, 84040-78-8; 1,1-dichloro-2,2-bis[4-[2-(vinyloxy)ethoxy]phenyl]ethylene, 84049-84-3; 2-(2,6-dimethylphenoxy)ethyl vinyl ether, 84040-79-9; 2-(2,4,6-trimethylphenoxy)ethyl vinyl ether, 84040-80-2; 2-phenoxyethyl vinyl ether, 18370-86-0; 2-(thiophenoxy)ethyl vinyl ether, 6613-39-4; 4,4′-biphenyldiol, 92-88-6; bis(4-hydroxyphenyl)methane, 620-92-8; resorcinol, 108-46-3; 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene, 14868-03-2; 2,6-dimethylphenol, 576-26-1; 2,4,6-trimethylphenol, 527-60-6; phenol, 108-95-2; thiophenol, 108-98-5.

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