

**2-Octyl Phenyl Ether.** 2-Bromooctane (3.0 g, 0.01554 mol) was added to ethanolic sodium ethoxide (360 mg, 0.01554 mol, of sodium in 100 mL of magnesium-dried ethanol), and the solution was refluxed for 6 h. Ethanol was removed in vacuo, and ether (50 mL) was added. The ether layer was filtered and washed with H<sub>2</sub>O (10 mL), sodium hydroxide solution (5%, 2 × 10 mL), and then H<sub>2</sub>O (2 × 10 mL). The ether layer was dried (MgSO<sub>4</sub>, 2 h), the ether removed in vacuo, and the residue distilled to give 2-octyl phenyl ether: 1.73 g (54%); bp 90–94 °C (0.2 mm) [lit.<sup>24</sup> yield 35–38%; bp 136 °C (10 mm)]; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.1 (q, C<sub>8</sub>), 19.8 (q, C<sub>1</sub>), 22.7 (t, C<sub>7</sub>), 25.6 (t, C<sub>4</sub>), 29.4 (t, C<sub>5</sub>), 31.9 (t, C<sub>6</sub>), 36.6 (t, C<sub>3</sub>), 73.7 (d, C<sub>2</sub>), 115.9 (d, C<sub>o</sub>), 120.4 (d, C<sub>p</sub>), 129.4 (d, C<sub>m</sub>), 158.3 (s, C<sub>i</sub>).

**Rearrangement of 2-Octyl Phenyl Ether.** The title compound (1.0 g, 0.00485 mol) was heated with acridinium trifluoromethanesulfonate 4 (2.4 g, 0.00485 mol) in phenol (5 g, excess) at 160 °C for 48 h. The mixture was triturated with ether (100 mL) and filtered. The ether layer was washed with NaOH solution (10%, 3 × 20 mL) and H<sub>2</sub>O (2 × 15 mL) and dried (MgSO<sub>4</sub>, 2 h). The ether was removed and the residue distilled

at diminished pressure to give a mixture (860 mg, 86%) of *o*-(4-octyl)-, *o*-(3-octyl)-, *o*-(2-octyl)-, *p*-(4-octyl)-, *p*-(3-octyl)-, and *p*-2-octylphenols in the ratio of 15.2:19.9:37.7:5.2:9.2:12.8 as shown by GC/MS (gas chromatographic conditions: 10% DEGS-PS column, 190 °C isothermal, flow rate 30 mL/min; retention times 910, 952, 1144, 1378, 1433, and 1336 s, respectively). The corresponding mass spectra were identical with those from the solvolysis of *N*-*n*-octyl derivative 1a in phenol.

**Acknowledgment.** We thank Dr. G. R. Fenwick (Food Research Institute), England, for discussion of the mass spectra and a sample of BSTFA and Dr. R. W. King and B. Gregory for their help with the experimental GC/MS techniques. We also thank the Kuwait Institute for Scientific Research, Kuwait, for a leave of absence to A.M. E.-M.

**Registry No.** 1a, 73377-30-7; 1b, 73377-34-1; 4, 81898-31-9; phenol, 108-95-2; acetic acid, 64-19-7; benzoic acid, 65-85-0; 2-bromooctane, 557-35-7; 2-octyl phenyl ether, 20012-43-5.

## Reaction of Hemiacetal Esters, Acetals, and Acylals with Alcohols or Acetic Acid

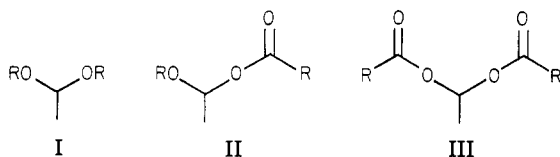
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Hemiacetal esters undergo rapid exchange with alcohols at room temperature to give mixtures of hemiacetal ester and acetal. The equilibration requires acid catalysis, and equilibrium lies far in favor of the acetal (>95%). Acetals undergo exchange with carboxylic acids to give the same equilibrium mixtures as that achieved by using the corresponding hemiacetal ester and alcohol. The use of a large excess of carboxylic acid can convert acetals to hemiacetal esters. Under more vigorous conditions, both acetals and hemiacetal esters react with acetic acid to form acetates. The reaction of hemiacetal esters or acetals with anhydrous hydrogen chloride yields  $\alpha$ -chloro ethers. The thermolysis of hemiacetal esters is also examined. Acylals do not undergo substitution as observed for acetals and hemiacetal esters. The reaction of acylals with alcohols results in ester formation with no exchange. Under acid conditions, hemiacetal esters are more reactive than either acetals or acylals.

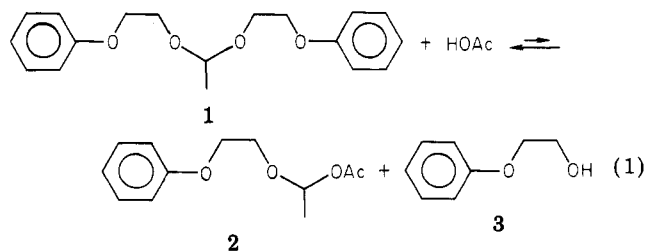
The preparation and reactions of acetals (I) have re-



ceived considerable attention, in part due to the utility of acetals as aldehyde protecting groups.<sup>1</sup> However, aside from the reactions of the cyclic hemiacetal ester derivatives of carbohydrates,<sup>2,3</sup> the chemistry of compounds structurally related to acetals, hemiacetal esters (II),<sup>4,5</sup> and acylals (III)<sup>6</sup> has received less attention. We have examined the relationship between structure and reactivity for acetals, hemiacetal esters, and acylals. Results indicate substantial differences in reactivity caused by the replacement of an alkoxy group by an ester group. This investigation focuses on the acid-catalyzed reactions of acetals, hemiacetal esters, and acylals with alcohols or acetic acid. The mechanism of the thermolysis of hemiacetal esters has also been examined.

## Results and Discussion

**Reactions of Acetals.** The reaction of acetal 1 with acetic acid at room temperature is slow. With equivalent amounts of acetic acid and acetal, only a very small amount of hemiacetal ester 2 is observed (eq 1). The equilibrium



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(2) Coffey, S. "Rodd's Chemistry of Carbon Compounds", 2nd ed.; Elsevier: Amsterdam, 1967; Vol. I, Part F.

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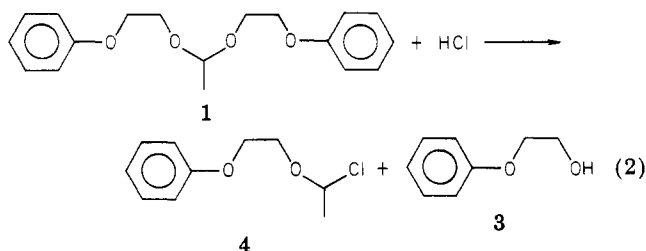
(5) Shostakovskiy, M. F.; Gershtein, N. A. *J. Gen. Chem. USSR (Engl. Transl.)* 1951, 21, 1581, 1757.

(6) Hurd, C. D.; Green, F. O. *J. Am. Chem. Soc.* 1941, 63, 2201.

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may be shifted in favor of hemiacetal ester formation by using larger amounts of acid. Acetic anhydride with strong acid catalysis has been used by others in place of acetic acid to prepare hemiacetal esters from acetals in high yield.<sup>7</sup> With *n*-butanol and 1 in  $\text{CHCl}_3$  solution but with no acetic acid, the slow formation of mixed acetals is observed.

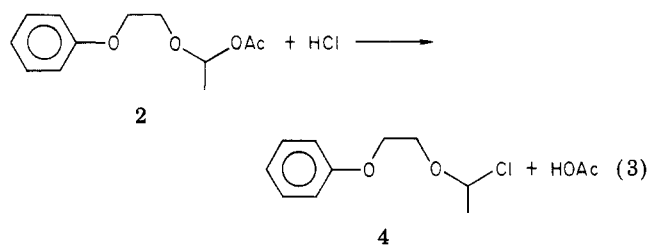
The reaction of acetals with anhydrous hydrogen chloride (HCl) leads to the formation of  $\alpha$ -chloro ethers (eq 2). Chloro ether 4 slowly decomposes under the reaction conditions and was not isolated.



Initially, there was concern over the possibility that the reactions of acetal 1 might be atypical of acetals in general, the result of anchimeric assistance from the phenyl group or the  $\beta$ -oxygen of the phenoxyethoxy substituent. However, the reactions of di-*n*-butyl acetal, where no neighboring group participation is possible, were similar to those of acetal 1.

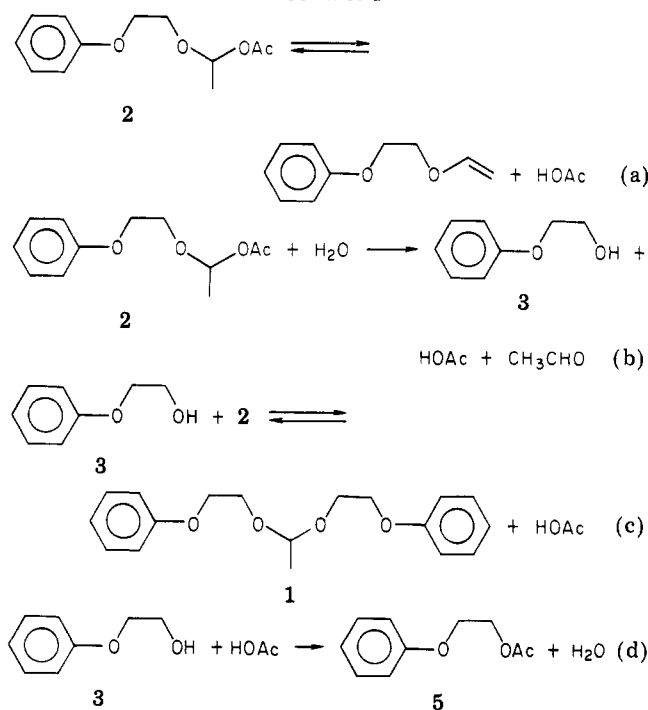
**Reaction of Hemiacetal Esters.** Hemiacetal esters are more reactive toward substitution than acetals.<sup>5</sup> The reaction of hemiacetal esters with alcohols has been used to prepare mixed acetals.<sup>8,9</sup> In chloroform, reaction between equivalent amounts of hemiacetal ester 2 and alcohol 3 rapidly gives a mixture of acetal 1 and hemiacetal ester 2 (>95:5). In chloroform solution at room temperature, the equilibrium mixture is the same as that produced from acetal 1 and acetic acid. Equilibration in carbon tetrachloride is much slower than reaction in chloroform. At room temperature and short reaction times (<24 h), no reaction was observed between acetic acid and 2, even with a trace of trifluoroacetic acid (TFA) added. With stoichiometric amounts of TFA, a new compound, probably the hemiacetal trifluoroacetate, was formed. This material could not be isolated.

Addition of anhydrous HCl to hemiacetal ester 2 gives  $\alpha$ -chloro ether 4, the same product formed in the reaction of acetal 1 with HCl. No  $\alpha$ -chloroethyl acetate<sup>10</sup> was observed (eq 3). The reaction of hemiacetal ester 2 with both



HCl and TFA involves formation of a weaker acid (acetic) from a stronger acid. The products of the acid-catalyzed reactions of hemiacetal ester 2 are all consistent with  $\text{S}_{\text{N}}1$

Scheme I



mechanism with acetate as the preferred leaving group (vide infra).

Initially no reaction is observed at room temperature between hemiacetal ester 2 and acetic acid. However, at higher temperature (85–118 °C) or longer reaction times (>48 h), the formation of 2-phenoxyethyl acetate (5) is observed. Similar results are observed on starting from 2-phenoxyethyl vinyl ether, which reacts quickly with acetic acid to give 2 and a small amount of 1 but ultimately yields 5. Acetal 1 also reacts with acetic acid to form 5, but the reaction is slower than that observed for the hemiacetal esters.

The slow reaction of hemiacetal esters with acetic acid produces 2-phenoxyethyl acetate and acetaldehyde. Acetate formation from hemiacetal esters may occur by several routes. A likely pathway is shown in Scheme I.

Hemiacetal ester 2 can be hydrolyzed by adventitious water in the acetic acid to give 2-phenoxyethanol, acetaldehyde, and acetic acid (possibly through a hemiacetal intermediate). The alcohol formed by this hydrolysis can react to give acetal 1 or acetate 5 (steps c or d). With an excess of acetic acid, acetal formation is reversible, and acetal 1 is not observed as a reaction product. 2-Phenoxyethyl acetate (5) is produced by step d as the major product. The acetate formation is driven to completion by the consumption of water via hydrolysis of hemiacetal ester 2. The hydrolysis generates additional alcohol. In this scheme, water acts as a catalyst for the conversion of hemiacetal ester to acetate. Loss of acetaldehyde from the reaction mixture (step b) would make hydrolysis irreversible and ultimately drive the reaction, forming acetate (step d).

If a small amount of water (1%) is intentionally added to an acetic acid solution of hemiacetal ester 2 (or 2-phenoxyethyl vinyl ether) at room temperature, the hemiacetal ester is consumed, yielding acetal 1 and alcohol 3. Acetate formation is not observed at room temperature with short reaction times (<6 h).

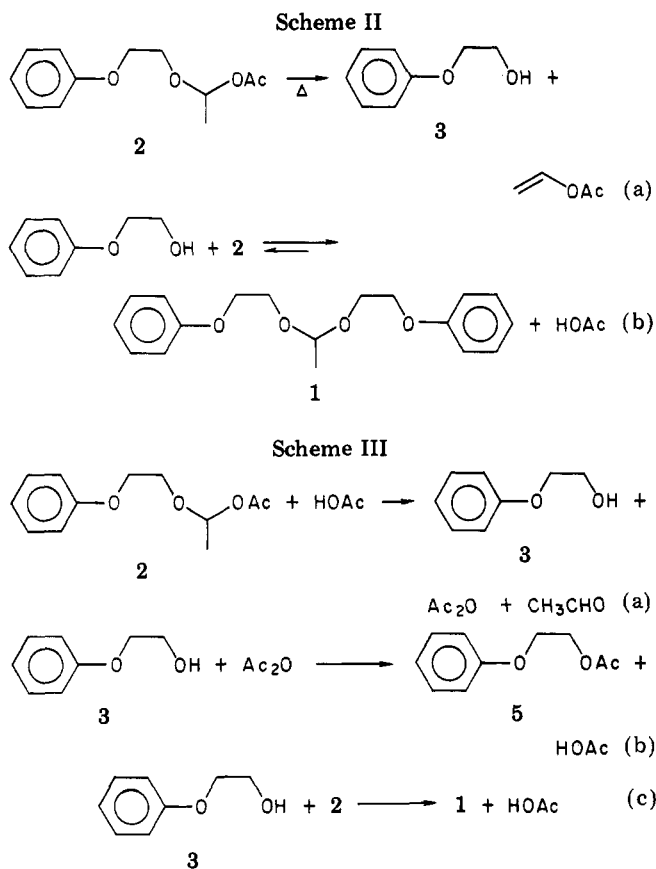
Thermolysis of hemiacetal acetates with efficient removal of acetic acid results in vinyl ether formation in high yield (step a). The thermolysis of hemiacetal acetates under conditions where acetic acid is not removed from

(7) Keith, D. D.; Tortora, J. A.; Yang, R. *J. Org. Chem.* **1978**, *43*, 3711. Hughes, W. B.; Kleene, R. D. *J. Am. Chem. Soc.* **1954**, *76*, 5161.

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the reaction mixture does not result in vinyl ether formation (apparently readdition of acid to form hemiacetal ester is fast). At high temperature, hemiacetal acetate 2 is slowly converted to acetal 1. Acetaldehyde is detected as a byproduct in this reaction.

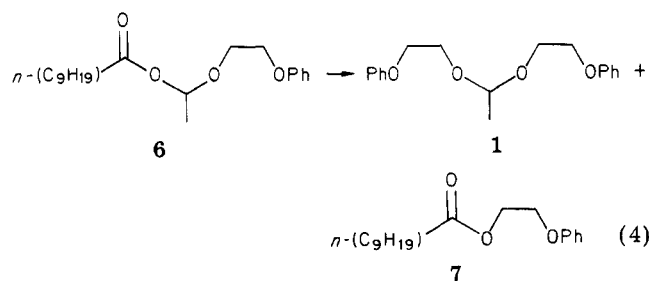
The thermolysis reaction mechanism is similar to that shown in Scheme I. Without excess acetic acid, acetal formation (step c) is not reversible, and 1 is the major reaction product. Acetate formation (step d) is not a major pathway without excess acetic acid to drive the reaction. In this reaction, the nature of the reaction generating alcohol (step b) is unclear. The presence of adventitious water in the reactants, a reasonable postulate in the acetate-forming reaction with excess acetic acid, is ruled out by infrared spectra of the starting material.<sup>11</sup> If a small amount of water (~1%) is intentionally introduced into this reaction, the formation of acetal is enhanced.

There are at least two other plausible routes for the generation of 2-phenoxyethanol from hemiacetal ester 2 under thermolysis. A reaction involving alcohol elimination to yield vinyl acetate is a reasonable possibility. The alcohol generated in this step is captured by 2-phenoxyethyl vinyl ether or hemiacetal ester 2 to yield acetal 1 (Scheme II). However, several aspects of the observed reaction indicate that Scheme II may not be the mechanism of alcohol formation under thermolysis conditions. The elimination of alcohol from 2 is expected to be difficult, and acetal 1, which could undergo a similar elimination, is stable under the reaction conditions. In addition, neither the expected byproduct, vinyl acetate, nor possible products derived from it, 2-phenoxyethyl acetate (5) or

1,1-diacetoxy ethane, are detected in the reaction mixture. Scheme II also does not easily account for the formation of acetaldehyde in the reaction. Control experiments showed no reaction of 1,1-diacetoxyethane, vinyl acetate, or 2-phenoxyethyl acetate under the thermolysis conditions.

Another possible route to alcohol formation under the thermolysis conditions where acetic acid is retained is shown in Scheme III. However, again neither the byproduct, acetic anhydride, nor its possible reaction product, 2-phenoxyethyl acetate, is observed.

The thermolysis of hemiacetal ester 2 with retained acetic acid is conducted at ~200 °C. The acetic acid refluxes vigorously and is only present to a limited vinyl in the hemiacetal ester solution. To investigate the effect of keeping the acid generated in better contact with the hemiacetal ester, the thermolysis of hemiacetal ester 6 was examined (eq 4). Thermolysis of 6 was much faster than



thermolysis of 2 at 200 °C. The sample darkened rapidly, behavior which was not observed with 2 (possibly due to reaction of acetaldehyde). As in the thermolysis of 2, hemiacetal ester 6 initially gave acetal 1 and acetaldehyde. At longer reaction times (1 h), ester 7 was observed as the major product; all hemiacetal ester was consumed. Thermolysis of 2, where a more volatile acid was generated, did not result in ester formation.

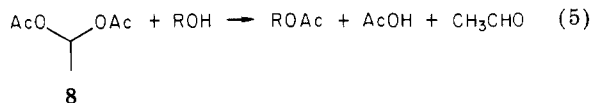
The reactions of 2 and 6 under thermolysis conditions support the mechanism proposed in Scheme I. When acetic acid is generated, it is retained efficiently enough to prevent vinyl ether formation. However, acetic acid is not present in sufficient concentration to convert acetal 1 to acetate 5. In the case where decanoic acid is generated (eq 4), the less volatile acid is present in sufficient concentration to reverse step c. Ester formation, step d, predominates under these conditions (as it does when a large excess of acetic acid is used).

The mechanism of alcohol formation from hemiacetal ester thermolysis, with retained acid, is unclear.<sup>11</sup> The reactions discussed may play a role in alcohol formation, or other unanticipated reactions may come into play. The unidentified route(s) of alcohol formation in the thermolysis with retained carboxylic acid may also operate in the reaction conducted in acetic acid solution. Whatever the exact route of alcohol formation under thermolysis conditions, the essentials of Scheme I remain intact.

Scheme I reconciles the formation of two dissimilar products from very similar reactions of the same starting material. As in the case of the acetal reactions, the substitution of *n*-butanol for 2-phenoxyethanol or a *n*-butoxy group for a 2-phenoxyethoxy group made no substantial change in the reaction of hemiacetal esters.

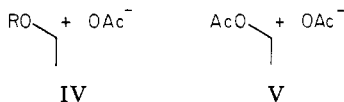
**Reaction of Acylals.** The reaction of 1,1-diacetoxyethane (8) with 2-phenoxyethanol or *n*-butanol took a different path than the reaction of acetals and hemiacetal esters with alcohols. Under conditions of acid catalysis, only attack on the acetate group is observed, resulting in formation of an acetate, acetaldehyde, and acetic acid (eq 5). No hemiacetal ester is observed. No reaction of 1,1-

(11) Since water can act as a catalyst in the decomposition of hemiacetal esters under thermolysis conditions, only a small amount of water is needed to give the observed reactions. A referee points out that water adsorbed on the surface of the glassware could lead to the observed results. Glassware was dried under ambient laboratory conditions, but no special attempts were made to further eliminate adsorbed water.



diacetoxyethane (to possibly form acetic anhydride and acetaldehyde) is observed at room temperature with an equivalent amount of acetic acid with or without a trace of TFA added. Reaction of 1,1-diacetoxyethane with anhydrous HCl gave 1-chloroethyl acetate<sup>10</sup> as well as other unidentified products.

As noted for hemiacetal formates,<sup>5</sup> hemiacetal acetates are more reactive than either the corresponding acetals or acylals. Upon reflection, these results are not surprising. When compared to an acetal, hemiacetal esters possess a better leaving group (acetate) and are more reactive. In the case of acylals, the leaving group of both species is the same; however, the hemiacetal forms a much more stable carbonium ion (IV vs. V). (Alternatively, the developing



positive charge in the transition state is better accommodated in the case of the hemiacetal ester than in the acylal.) The acylal intermediate, V, is disfavored to the extent that a different mode of reactivity is observed vs. the hemiacetal ester.

### Experimental Section

**General Methods.** All nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM 390 or CFT 80 spectrometer with deuteriochloroform (CDCl<sub>3</sub>) as the solvent (unless otherwise indicated) and tetramethylsilane as an internal standard. Infrared (IR) spectra were recorded on a Perkin-Elmer 598 infrared spectrophotometer by using CCl<sub>4</sub> as the solvent. Mass spectra were recorded on a Varian MAT 311A system (resolution 10 000). Unless otherwise indicated, materials were used as received from commercial sources without purification.

**Preparation of 1-(2-Phenoxyethoxy)ethyl Acetate (2).**<sup>5,12</sup> 1-(2-Phenoxyethoxy)ethyl acetate (2) was prepared by the TFA-catalyzed (0.01 g) additional of glacial acetic acid (0.60 g) to an equivalent amount of distilled 2-phenoxyethyl vinyl ether<sup>13</sup> (1.64 g). The reaction was complete in 1 h at room temperature. Similar reactions without TFA went to completion in 12 h, judging by the NMR spectra.

The product was isolated in >90% yield by evaporation of solvent and catalyst under vacuum. The product may be carefully distilled under vacuum (95–97 °C, 0.15 mm); however, at higher temperatures, elimination of acetic acid to give starting material occurs.

1-(2-Phenoxyethoxy)ethyl acetate (2): bp 95–97 °C (0.15 mm); IR 1635, 1595, 1495, 1370, 1240, 1170, 1145, 690 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.1 (m, 5 H), 5.9 (q, 1 H), 4.0 (m, 4 H), 2.0 (s, 3 H), 1.4 (d, 3 H); <sup>13</sup>C NMR, 170.6, 158.8, 129.5, 121.0, 114.7, 96.6, 67.7, 67.0, 21.1, 20.7 ppm; mass spectrum, *m/e* (relative intensity) 224 (8), 164 (42), 138 (5), 120 (60), 107 (12), 94 (63), 77 (80), 43 (100); precise mass calcd 224.10484, found 224.10471. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>: C, 64.27; H, 7.19. Found: C, 64.46; H, 7.30.

2-Phenoxyethyl vinyl ether:<sup>13</sup> bp 79–81 °C (0.55 mm); IR 2920, 2870, 1635, 1610, 1595, 1490, 1320, 1240, 1200, 690 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.1 (m, 5 H), 6.4 (m, 1 H), 4.1 (m, 6 H); <sup>13</sup>C NMR 158.6, 151.7, 129.5, 121.1, 114.7, 87.0, 66.4, 66.3 ppm; mass spectrum, *m/e* (relative intensity) 164 (70), 120 (60), 107 (17), 94 (58), 77 (100).

**Preparation of 1-(2-Phenoxyethoxy)ethyl Decanoate (6).** The reaction was similar to that run above and used 1.64 g of 2-phenoxyethyl vinyl ether and 1.72 g of decanoic acid dissolved

in 10 mL of methylene chloride with 0.01 g of TFA. The reaction was complete in 1 h at room temperature. At longer reaction times (~24 h), the product could be prepared without adding the TFA catalyst.

The product could not be distilled without decomposition.

1-Butoxyethyl acetate<sup>6</sup> was prepared in a manner similar to that for compound 6 by using *n*-butyl vinyl ether and acetic acid.

1-(2-Phenoxyethoxy)ethyl decanoate (6): IR 2920, 2840, 1730, 1595, 1495, 1240, 1130, 685 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.4–6.8 (m, 5 H), 6.0 (q, 1 H), 4.3–3.8 (m, 4 H), 2.3 (t, 2 H), 1.8–1.1 (m, 17 H), 1.0–0.8 (m, 3 H); <sup>13</sup>C NMR 173.5, 158.8, 129.5, 121.0, 114.8, 96.5, 67.7, 67.0, 34.6, 32.0, 29.5, 29.4, 25.0, 22.8, 20.8, 14.1 ppm; mass spectrum, *m/e* (relative intensity) 199 (7), 164 (42), 138 (10), 129 (30), 120 (42), 94 (62), 77 (97), 72 (90); precise mass calcd 336.2300, found 336.2304. Anal. Calcd for C<sub>20</sub>H<sub>32</sub>O<sub>4</sub>: C, 71.39; H, 9.59. Found: C, 71.35; H, 9.57.

1-Butoxyethyl acetate:<sup>6</sup> IR 2950, 1630, 1365, 1235, 1165, 1140, 925 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 5.9 (q, 1 H), 3.6 (m, 2 H), 2.0 (s, 3 H), 1.4 (m, 7 H), 0.9 (t, 3 H); <sup>13</sup>C NMR 170.4, 96.4, 68.9, 31.9, 21.1, 20.8, 19.4, 13.8 ppm; mass spectrum, *m/e* (relative intensity) 101 (50), 87 (78), 85 (40), 57 (100).

**Preparation of 2-Phenoxyethyl 1-Chloroethyl Ether (4).** Gaseous HCl was slowly bubbled into a solution of 1.0 g of 2-phenoxyethyl vinyl ether in 10 mL of CCl<sub>4</sub>. The temperature was kept below 30 °C. The reaction was monitored by NMR spectroscopy. Addition of HCl was stopped when all the vinyl ether was consumed. Excess HCl was bubbled off with N<sub>2</sub>. The product was characterized in solution. Attempts to isolate the product resulted in secondary reactions.

2-Phenoxyethyl 1-chloroethyl ether (4): IR 2930, 1595, 1490, 1240, 1140, 1060, 950, 685, 605 cm<sup>-1</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 7.3–6.7 (m, 5 H), 5.7 (q, 1 H), 4.3–3.7 (m, 4 H), 1.7 (d, 3 H); <sup>13</sup>C NMR (CCl<sub>4</sub>/CD<sub>2</sub>Cl<sub>2</sub>) 159.6, 130.4, 122.1, 115.5, 97.2, 69.7, 67.3 ppm.

**Preparation of 1-(2-Phenoxyethoxy)ethyl Trifluoroacetate.** 2-Phenoxyethyl vinyl ether (1.64 g) was dissolved in 15 mL of CCl<sub>4</sub>, and dry, distilled TFA (1.14 g) was added dropwise with stirring. The temperature was kept below 40 °C. The reaction was complete within 15 min of the end of the acid addition. The product was characterized in solution. Attempts to isolate the product resulted in secondary reactions.

1-(2-Phenoxyethoxy)ethyl Trifluoroacetate: IR 2920, 1770, 1690, 1485, 1210, 1155, 1120, 1025, 950, 680 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 7.3–6.7 (m, 5 H), 6.1 (q, 1 H), 4.0 (m, 4 H), 1.5 (d, 3 H); <sup>13</sup>C NMR (CCl<sub>4</sub>/CD<sub>2</sub>Cl<sub>2</sub>) 158.5, 157.0 (q, *J*<sub>CF</sub> = 1.9 Hz), 129.5, 121.3, 114.5, 114.5 (q, *J*<sub>CF</sub> = 14.5 Hz), 101.9, 68.7, 66.8, 20.4 ppm.

**Preparation of 1,2-Bis(2-phenoxyethoxy)ethane (1).** 2-Phenoxyethanol (1.38 g) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> with 1.64 g of 2-phenoxyethyl vinyl ether. TFA (0.05 g) was added, and the reaction mixture was stirred for 6 h at room temperature. The solvent was removed and the product distilled under vacuum; 2.1 g (70% yield).

1,1-Bis(2-phenoxyethoxy)ethane (1): bp 157–159 °C (0.15 mm); IR 1595, 1495, 1240, 1135, 690 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.1 (m, 10 H), 4.9 (q, 1 H), 4.0 (m, 8 H), 1.3 (d, 3 H); <sup>13</sup>C NMR 158.9, 129.5, 120.9, 114.7, 100.0, 67.4, 63.4, 19.5 ppm; mass spectrum, *m/e* (relative intensity) 209 (6), 165 (23), 167 (10), 138 (22), 121 (90), 120 (23), 94 (100); precise mass calcd 302.15179, found 302.15216. Anal. Calcd for C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>: C, 71.50; H, 7.33. Found: C, 71.53; H, 7.36.

1,1-Dibutoxyethane was prepared from *n*-butyl vinyl ether and *n*-butanol in a manner similar to that used to prepare 1.

1,1-Dibutoxyethane: IR 2950, 2860, 1375, 1130, 1070 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 4.7 (q, 1 H), 3.5 (m, 4 H), 1.4 (m, 8 H); <sup>13</sup>C NMR 99.8, 65.0, 32.2, 19.9, 19.6, 14.0 ppm; mass spectrum, *m/e* (relative intensity) 159 (18), 101 (100), 83 (17).

**Reaction of Hemiacetal Ester 2 with 2-Phenoxyethanol (3).** Distilled hemiacetal ester 2 (0.22 g) was allowed to react with an equivalent amount of 3 (0.14 g) in CDCl<sub>3</sub> solution (3 mL). The progress of the reaction was monitored by the disappearance of starting material and the appearance of product in the NMR. The spectra of the products were compared to those of authentic samples.

The reaction of 2 with 3 to give a >95:5 mixture of acetal to hemiacetal ester is fast (~0.5 h). No reaction was observed in the absence of alcohol.

**Reaction of Acetal 1 with Acetic Acid.** The distilled acetal 1 (0.30 g) was dissolved in CDCl<sub>3</sub> (3 mL) and allowed to react with

(12) Voronkov, M. G. *J. Gen. Chem. USSR (Engl. Transl.)* 1949, 19, 255.

(13) Atavin, A. S.; Gusarov, A. V.; Trofimov, B. A. *J. Org. Chem. USSR (Engl. Transl.)* 1967, 3, 1368.

an equivalent amount of glacial acetic acid (0.06 g). The reaction was monitored by NMR spectroscopy. At equilibrium (~1 h), a small amount of hemiacetal ester was formed; the equilibrium mixture was very similar to that obtained by reacting hemiacetal ester 2 with 3.

A similar reaction was observed between glacial acetic acid (0.12 g) and 1,1-dibutoxyethane (0.35 g) in  $\text{CDCl}_3$  (3 mL).

The reaction of di-*n*-butyl acetal with equal amounts of 2-propanol or *tert*-butyl alcohol with TFA catalysis (~1%) leads to the formation of mixed acetals. Product mixtures were not separated.

Reaction of a  $\text{CDCl}_3$  solution of 1 with anhydrous HCl resulted in initial formation of  $\alpha$ -chloro ether 4 followed by the formation of secondary products after several hours at room temperature.

**Reaction of Hemiacetal Ester 2 with Acetic Acid.** The reaction of hemiacetal ester 2 (1.0 g) with acetic acid (10 mL) was conducted under nitrogen at reflux. The progress of the reaction was monitored by NMR spectroscopy. The reaction is slow, but after ~48 h the hemiacetal ester was completely converted to acetate 5. At room temperature (<24 h) no reaction is observed between hemiacetal ester 2 and acetic acid. However, at long reaction times (>48 h) some acetate formation is observed in the NMR spectrum.

Thermolysis reactions where acetic acid was retained in the mixture were conducted by heating a neat sample of the hemiacetal ester in a flask equipped with a condenser and thermometer under nitrogen. The hemiacetal esters were only partially reacted (~25-50%) after ~24 h at 200 °C. Under conditions where acetic acid is removed from the reaction mixture (attempted distillation), hemiacetal ester 2 is decomposed to give 2-phenoxyethyl vinyl ether.

Analysis of the reaction mixtures by gas chromatography was not possible due to partial decomposition of the hemiacetal ester under the analysis conditions.

**Thermolysis of Hemiacetal Ester 6.** A neat sample of 6, prepared without TFA catalysis, was heated at 200 °C in a flask fitted with condenser and thermometer. Thermolysis under  $\text{N}_2$  resulted in initial formation of acetal 1 followed by formation of 2-phenoxyethyl decanoate (7). The reaction was monitored by NMR spectroscopy. Reaction spectra were compared to those of authentic samples. After 2 h, ester 7 was the major reaction product (~85%).

**Preparation of Phenoxyethyl Carboxylates 5 and 7.** An authentic sample of 5 was prepared by refluxing 2-phenoxyethanol (13.8 g) with 10 mL of acetic anhydride in 50 mL acetic acid. The reaction was heated under  $\text{N}_2$  for 6 h. The product was isolated by vacuum distillation; 10.7 g (59% yield).

2-Phenoxyethyl acetate (5): bp 84-85 °C (0.12 mm); IR 1740, 1595, 1495, 1220, 1060, 690  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.4-6.8 (m, 5 H),

4.5-4.1 (m, 4 H), 2.0 (s, 3 H);  $^{13}\text{C}$  NMR 170.7, 158.8, 129.7, 121.2, 114.8, 65.9, 62.9, 20.5 ppm; mass spectrum, *m/e* (relative intensity) 180 (7), 120 (5), 107 (3), 94 (18), 87 (93), 77 (16); precise mass calcd 180.0786, found 180.0781. Anal. Calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_3$ : C, 66.65; H, 6.71. Found: C, 66.57; H, 6.83.

An authentic sample of 7 was prepared by adding a chloroform solution of decanoyl chloride (3.82 g) to a pyridine solution of 2-phenoxyethanol (2.76 g). The reaction mixture was stirred at reflux under  $\text{N}_2$  overnight. The product was isolated by repeated aqueous extraction and purified by vacuum distillation; 5.3 g (90% yield).

2-Phenoxyethyl decanoate (7): bp 157-160 °C (0.15 mm); IR 2920, 2850, 1735, 1595, 1495, 1455, 1240, 1170, 690  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.3-6.8 (m, 5H), 4.4-4.1 (m, 4 H), 2.3 (t, 2 H), 1.8-1.1 (m, 14 H), 1.0-0.8 (m, 3 H);  $^{13}\text{C}$  NMR 173.7, 158.6, 129.5, 121.2, 114.7, 66.0, 62.6, 34.2, 31.9, 29.2, 25.0, 22.7, 14.1 ppm; precise mass calcd 292.2038, found 292.1999. Anal. Calcd for  $\text{C}_{18}\text{H}_{28}\text{O}_3$ : C, 73.93; H, 9.65. Found: C, 73.96; H, 9.80.

**Reaction of Hemiacetal Ester 2 with TFA or HCl.** A  $\text{CDCl}_3$  solution (5 mL) of 2 (0.10 g) was allowed to react with an equivalent amount of dry TFA (0.51 g). The NMR spectra showed complete conversion of 2 to 1-(2-phenoxyethoxy)ethyl trifluoroacetate and acetic acid.

In a similar experiment anhydrous HCl was bubbled into a  $\text{CDCl}_3$  solution of 2 to give chloro ether 4.

**Reaction of 1,1-Diacetoxyethane (8) with Alcohols.** Distilled 1,1-diacetoxyethane 8 (1.46 g) was allowed to react with either *n*-butanol (0.74 g) or 2-phenoxyethanol (1.38 g) in chloroform solution with a variety of catalysts (~1%; TFA, HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{BF}_3\cdot\text{OEt}_2$ , or tetraisopropyl titanate). In each case, conversion of alcohol to acetate was observed, with formation of acetaldehyde and acetic acid. At long reaction times (~24 h) high levels of conversion (>85%) were achieved. Often, trace amounts of acetal were observed, probably arising by reaction of alcohol with acetaldehyde.

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**Registry No.** 1, 82337-98-2; 2, 82337-99-3; 3, 122-99-6; 4, 82338-00-9; 5, 6192-44-5; 6, 82338-01-0; 7, 23495-14-9; 8, 542-10-9; TFA, 76-05-1; acetic acid, 64-19-7; 2-phenoxyethyl vinyl ether, 18370-86-0; decanoic acid, 334-48-5; 1-butoxyethyl acetate, 33931-54-3; *n*-butyl vinyl ether, 111-34-2; 1-(2-phenoxyethoxy)ethyl trifluoroacetate, 82338-02-1; 1,1-dibutoxyethane, 871-22-7; *n*-butanol, 71-36-3; 2-propanol, 67-63-0; *tert*-butyl alcohol, 75-65-0; decanoyl chloride, 112-13-0.

## Configuration Determination of (*R*)-(-)-1,1,2-Triphenyl-3,3-dimethylbutane and the Stereochemistry of the Reaction of Benzhydryllithium with (*R*)-(+)- $\alpha$ -Phenylneopentyl Chloride

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A three-step synthesis of optically pure (*R*)-(-)-1,1,2-triphenyl-3,3-dimethylbutane from (*R*)-(-)- $\alpha$ -*tert*-butylphenylacetic acid has been accomplished. The synthesis of  $\alpha$ -phenylneopentyl chloroformate from optically pure (*R*)-(+)-1-phenyl-2,2-dimethyl-1-propanol was followed by decomposition at 95 °C to give samples of (*R*)-(+)-1-chloro-1-phenyl-2,2-dimethylpropane having much higher optical purities ( $[\alpha]_D^{25} +72^\circ$ ,  $+67^\circ$ ) than samples obtained with thionyl chloride ( $[\alpha]_D^{25} +41^\circ$ ,  $+47^\circ$ ).

Previously, we reported kinetic results on the coupling reactions of triphenylmethylithium and diphenylmethylithium with neopentyl iodide, neopentyl bromide, and benzyl fluoride to produce hydrocarbon coupling products as shown in eq 1a-c.<sup>1</sup> For study of the stereo-

chemistry of the coupling process,  $\alpha$ -phenylneopentyl chloride (6) seemed to offer an ideal system for theoretical,

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