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Synthesis of Chloro Alkoxy and Alkoxy Derivatives of Methyl Oleate

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Abstract Vegetable oil based lubricants typically have improved lubricity and biodegradability over their mineral oil based counterparts. However, vegetable oil lubricants often fail to meet the performance standards of mineral based oils with respect to cold temperature and resistance to oxidation. Olefins are an oxidatively weak point for vegetable based compounds. Removal of the olefin in a vegetable based lubricant through functionalization may increase resistance to oxidation. If the added functionality also causes branching of the alkyl chain, cold temperature properties may be improved. Any chemical modifications considered must be scalable and cost-effective to be useful in a commercial application. In this study, methyl oleate was functionalized into a chloro alkoxy derivative. Sodium hypochlorite (household bleach) and calcium hypochlorite were both used to generate hypochlorous acid in situ. Hypochlorous acid and a series of alcohols (methanol, ethanol, and butanol) were reacted with methyl oleate to make chloro alkoxy compounds in 29.8-77.9 % yields. In

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an effort to make a branched saturated ether we removed the chlorine moiety of the chloro alkoxy compounds. Dehalogenation was achieved under basic conditions over a Pd/C catalyst in 2-propanol. Reaction times increased substantially as the size of the adjacent alkoxy group increased. The reaction rate could be improved by heating the reactions above 100 °C in a pressure reactor. Increased reaction temperature also resulted in an increase in ketone side products from the competing elimination reactions. Saturated ether yields were 4.1-43.2 %.

Keywords Methyl oleate · Oleic acid · Chloro alkoxy · Ether · Hypochlorous acid · Dehalogenation

Introduction

Renewable substitutes for petroleum based products are desirable due to economic, political, and environmental concerns. Vegetable oils and animal fats, as well as their derivatives, find a wide array of uses in many consumable products. Common industrial uses include anti-slip agents for plastic films, plasticizers, non-ionic surfactants, corrosion inhibitors, cosmetics and lubricants [1]. Unmodified vegetable oils used as lubricants often fail to meet low temperature performance standards, such as pour point and cloud point, compared to their mineral oil counterparts [2]. However, low temperature properties can be improved by incorporating functionality to the structure that disrupts molecular packing, such as branching or double bonds. As such, functionalization on the olefin of unsaturated fats can provide chemical handles to introduce various branched moieties. One of the many possible routes is through the use of hypochlorous acid obtained from common household bleach. A difunctional chloro alkoxy material can be made through the reaction of the olefin with hypochlorous acid and alcohol (Fig. 1) [3]. The final product is a mixture of positional isomers (9-chloro-10-alkoxy and 9-alkoxy-10-chloro-) with the chlorine adjacent to the alkoxy substituent. In general, this is an electrophilic halogen addition in the presence of a nucleophilic solvent. A wide variety of halogen sources can be used including elemental halogen, alkyl hypohalites, *N*-halosuccinimides, and in-situ generated hypochlorous acid [4, 5]. Hypochlorous acid generated in situ was used in this study due to its low cost, ease of handling, and potential to scale up. Numerous alcohol nucleophiles will participate in the formation of the chloro alkoxy compounds as well [3, 6].

In the present work, we propose to synthesize chloro alkoxy derivatives of oleic acid and use these intermediate compounds to examine their hydrodehalogenation. Specifically we are interested in replacement of the chlorine moiety with hydrogen to give a completely saturated ether branched structure (Fig. 2). Hydrodehalogenation can be accomplished in several ways including sodium borohydride reduction, organotin hydride reduction, and by catalysis with a noble metal in the presence of a base [7–11]. Hydride reductions would require stoichiometric amounts of reducing agent and be cost prohibitive for large scale use. Very effective systems for hydrodehalogenation [12] have been developed even for chlorohydrins but these mixed metal reductions using aluminum-mercury also require stoichiometric amounts of metal. Therefore we envisioned a catalytic system using a heterogeneous noble metal to be attractive due to the ease of removal and the potential recyclability of the catalyst.

Experimental Procedures

Materials

Oleic acid (90 %), methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, *tert*-butanol, 2-methyl-1-propanol, 2-ethyl-



Fig. 1 Synthesis of chloro alkoxy derivatives of methyl oleate



Fig. 2 Dechlorination of chloro alkoxy compounds to give saturated ethers

1-hexanol, 1-decanol, hydrochloric acid, sulfuric acid, hexane, ethyl acetate, potassium hydroxide, sodium hydroxide, 10 % Pd/C, sodium phosphate monobasic, and metallic sodium were all purchased from the Aldrich Chemical Company (Milwaukee, WI). Bleach was manufactured by the Clorox Professional Products Company (Oakland, CA). Filter paper was manufactured by Whatman (Maidstone, England).

GC

Both chloro alkoxy synthesis and dechlorination reactions were monitored using GC. A Supelco (Bellefonte, PA) SPB1 30 m \times 0.25 mm \times 0.25 µm film thickness column was used with a helium flow rate of 1.0 ml/min; a head pressure of 142 kPa; 12:1 split ratio; and a 3.0-ml/min septum purge. The temperature program was 225–265 °C at 5 °C/min ramp, followed by a 2 min hold at 265 °C. Some compounds synthesized in this study had a sufficiently high molecular weight to require a hold at 265 °C for up to 20 min. Injector and detector temperatures were set to 250 °C.

GCMS

Products were identified with both electron ionization (EI) and chemical ionization (CI) MS. The GC was equipped with a Supelco SPB1 30 m \times 0.25 mm \times 0.25 µm film thickness column that had a helium flow rate of 0.5 ml/min; a head pressure of 103 kPa; a 1:1 split ratio; and a 2.9-ml/min (CI 2.2 ml/min) septum purge. The temperature program was 150–265 °C at 5 °C/min ramp, followed by a 10–20 min hold at 265 °C. The MS electron multiplier voltage was 1941 V (CI, 1671 V) and the mass range was 50–550 amu. Injector, transfer line and MS source temperatures were set to 250, 280, and 250 °C, respectively. CIMS was configured for positive ionization mode using methane gas.

NMR Spectroscopy

NMR spectra were collected on a Bruker (Karlsruhe, Germany) Avance 500 spectrometer using a 5-mm BBI probe with an absolute frequency of 500.11 MHz for ¹H and 125.76 MHz for ¹³C. Chemical shifts are reported as parts per million from tetramethylsilane with CDCl₃ as solvent. COSY (correlation spectroscopy), HSQC (heteronuclear single quantum correlation), and HMBC (heteronuclear multiple bond correlation) two-dimensional spectra were also collected.

HPLC

Analytical purification was performed with a reversed phase HPLC using a Dynamax Microsorb 60-8 C18 (250 mm \times 4.6 mm) column from Varian (Walnut Creek, CA). All runs were isocratic eluting with acetonitrile and methylene chloride at either an 80/20 or an 85/15 ratio.

General Synthesis of Chloro Alkoxy Positional Isomers Using Bleach Extraction

Methyl oleate (50 g, 169 mmol) was combined with 150 ml of alcohol in a 500-ml round-bottom flask equipped with a magnetic stirrer and thermometer. Dry hypochlorous acid was prepared by adding bleach (0.826 M sodium hypochlorite, 560 ml), ethyl acetate (105 ml), and hexane (45 ml) to a separatory funnel followed by the addition of hydrochloric acid (12 M, 39 ml). Initially a bright green layer formed near the top of the aqueous layer that diffused into the organic layer. After shaking and separation the green color was diminished and present in both layers. The bottom aqueous layer was drawn off and the organic layer was dried over sodium sulfate in a 250-ml Erlenmeyer flask and decanted into the reaction flask containing methyl oleate all at once. After GC analysis had indicated that all the starting material had been consumed, hexane (100 ml) was added. The reaction was placed in a 1-l separatory funnel and washed with saturated sodium chloride (100 ml). The separated bottom aqueous layer was removed and the organic layer was dried over sodium sulfate in a 500-ml Erlenmeyer flask, gravity filtered through a fluted #2 Whatman filter paper, and concentrated in vacuo at 45-50 °C to give the chloro alkoxy product as an oil.

General Synthesis of Chloro alkoxy Positional Isomers Using Calcium Hypochlorite

Methyl oleate (50 g, 169 mmol) was combined with solid calcium hypochlorite (~ 4 g, 110 mmol) and 125 ml of alcohol in a 500-ml round-bottom flask equipped with a

magnetic stirrer and thermometer. The flask was cooled in an ice bath and continuously stirred. Sulfuric acid (18 M, 6 ml) and 125 ml of alcohol were combined in a 250-ml Erlenmeyer flask, which was then cooled in the ice bath. The acidic alcohol was added to the round bottom flask containing methyl oleate all at once. Solid calcium salts remained in the bottom of the flask for the duration of the reaction. After GC analysis indicated all starting material had been consumed, hexane (150 ml) was added and the reaction was then placed in a 1-1 separatory funnel and washed with pH 5 buffer solution (150 ml). The separated bottom aqueous layer and insoluble solids were drained off. The organic layer was dried over sodium sulfate in a 500-ml Erlenmeyer flask, gravity filtered through a fluted #2 Whatman filter paper, and concentrated in vacuo at 55-60 °C to give the oil. Often, GC analysis showed the presence of trans-esterified compounds that had to be converted to methyl esters. The material was combined with methanol (150 ml) and sulfuric acid (0.1 M) and placed in a 250-ml round-bottom flask equipped with a cold-water condenser and magnetic stirrer. The reaction was constantly stirred and warmed with a heating mantle to reflux. After 1.5-4 h the reaction was cooled to room temperature and transferred into a 1-l separatory funnel with hexane (150 ml). The reaction was washed twice with pH 5 buffer (250, 100 ml) followed by a wash with a solution of saturated sodium chloride (100 ml). The separated bottom aqueous layer was removed after each wash. The organic layer was dried over sodium sulfate in a 500-ml Erlenmeyer flask, gravity filtered through a fluted #2 Whatman filter paper, and concentrated in vacuo at 55-60 °C. The reaction was heated to 80-110 °C under vacuum (100 mT) on a Kugelrohr distillation apparatus for 1-2 h to remove residual alcohol.

General Dechlorination to Produce Saturated Ethers

In a 500-ml 3-neck round-bottom flask fitted with a cold water condenser, nitrogen inlet, and temperature probe, methyl 9-chloro-10-alkoxy-octadecanoate and methyl 10-chloro-9-alkoxy-octadecanoate (50.0 g, 143.7 mmol) were combined with 250 ml 2-propanol, potassium hydroxide (30.0 g, 534.7 mmol) and 10 % Pd/C (1.0 g, 2 % by weight relative to substrate). The flask was placed under positive nitrogen pressure, magnetically stirred, and heated to 75 °C with a heating mantle. The reaction continued for 65.5-420 h until less than 5 % of the starting material remained as measured by GC. The reaction was then allowed to cool to room temperature. Methanol (300 ml) and concentrated hydrochloric acid (25 ml) were added to the flask until a pH of 1-2 was obtained. The solution was then vacuum filtered with #42 Whatman paper and a layer of silica gel to remove Pd/C and insoluble salts. Hexane (300 ml) was added and the reaction was placed in a 2-1 separatory funnel and washed with pH 5 buffer solution (300 ml). The separated bottom aqueous layer was removed and the organic layer was dried over sodium sulfate in a 500-ml Erlenmeyer flask, gravity filtered through a fluted #2 Whatman filter paper, and concentrated in vacuo at 45-50 °C to give an oil. When GC analysis indicated free fatty acids and soaps present in the oil, the material was taken up in acidic methanol (200 ml, 0.1 M H₂SO₄) and refluxed for 2 h to esterify soaps that had formed during the dechlorination. Hexane (200 ml) was added and the reaction was placed in a 1-l separatory funnel and washed with pH 5 buffer twice. The separated bottom aqueous layer was removed and the organic layer was dried over sodium sulfate in a 500-ml Erlenmeyer flask, gravity filtered through a fluted #2 Whatman filter paper, and concentrated in vacuo at 45-50 °C to give the final product.

General Flash Column Chromatography Procedure

Flash column chromatography was used to purify the crude reaction product eluting with hexane/diethyl ether or hexane/ethyl acetate. The column 2.2 cm \times 36 cm was wet packed with silica gel (60 Å) and 0.5 g of the oil was placed onto the column with 2–3 ml of the elution solvent. Each fraction (20 ml) was spotted on a silica gel (60 Å) thin layer chromatography plate (20 cm \times 20 cm) along with the starting material and developed using the same solvent as the column. The plates were sprayed with 5 % phosphomolybdic acid solution (5 g phosphomolybdic in 100 ml ethanol) and then warmed with a heat gun to develop the stain. Fractions containing product were combined and concentrated in vacuo at 45–50 °C to provide the purified oil.

Results and Discussion

Initial work to synthesize a chloro alkoxy compound from methyl oleate utilized a bleach and acetic acid extraction procedure reported by Mund and Isbell [3]. Using the Mund and Isbell conditions, methanol and methyl oleate produced the two desired methyl 9-chloro-10-methoxyoctadecanoate and methyl 10-chloro-9-methoxy-octadecanoate positional isomers (chloro methoxy), as well as chlorohydrin, dichloro, and chloro acetate products. Substituting hydrochloric acid for acetic acid reduced side product formation. Hydrochloric acid has limited solubility in the organic extraction solvents and therefore does not participate directly or catalyze further side reactions such as decomposition of hypochlorous acid. Preliminary experiments showed that a large excess of bleach and hydrochloric acid (2.75 equivalents each) would be needed, since hypochlorous acid has limited stability and the extraction is an equilibrium process. A complete consumption of the starting material was achieved when the extraction solvent mixture was changed from 50/50 hexane/ethyl acetate to 30/70 hexane/ethyl acetate, which was due to an increased amount of hypochlorous acid being extracted.

To further minimize side products and increase chloro alkoxy yields, we explored using calcium hypochlorite and sulfuric acid to generate hypochlorous acid, while excluding water. Only a slight excess (1.3 equivalents) of calcium hypochlorite and sulfuric acid is needed for complete conversion. This synthesis of the chloro methoxy compound resulted in similar yields as compared to the bleach extraction methodology described above, but with less chlorohydrin side product. Concentrated acetic acid, hydrochloric acid, and phosphoric acid were also examined as proton sources with inferior results compared to the sulfuric acid.

For short chain primary alcohols, bleach extracted hypochlorous acid worked well. Longer chain and secondary alcohols that exhibit decreased nucleophilicity failed to produce appreciable chloro ether yields. As the nucleophilicity of the alcohol decreased from methanol to propanol, reaction times increased. As a result, more chlorohydrin was generated. Bleach extracted hypochlorous acid failed to completely react when 1-butanol was the nucleophilic alcohol. For this reason 1-butyl, 2-propyl, 3-methyl-1-propyl, tert-butyl, 2-ethyl-hexyl, and decyl chloro alkoxy derivatives were synthesized using calcium hypochlorite and sulfuric acid. Calcium hypochlorite/sulfuric acid reactions required longer reaction times, which required increased amounts of reactants and allowed acid catalyzed transesterification of the methyl ester to occur. After workup to remove excess alcohol, the methyl ester was regenerated by refluxing the crude products in acidic methanol. Product distribution for all chloro alkoxy derivatives is summarized in Table 1. Under these conditions the order of reactivity observed for alcohols was $1^{\circ} > 2^{\circ} \gg 3^{\circ}$. *tert*-Butanol required 12 days to finish even when heated to 50 °C and produced a significantly lower yield of chloro alkoxy products.

Dechlorination can be a difficult chemical transformation and chlorine is the most difficult of the halogens within the series of Cl, Br, and I to reduce from an organic molecule. However, the formation of the chlorinated compounds offers some advantages since these compounds can be made with less expense compared to the bromo and iodo derivatives and offer a greater degree of stability for storage. However, deactivating groups adjacent to the halogenbearing carbon such as in the case of the alkoxy substituent in this study increases the difficulty for removal of

Table 1 Chloro alkoxy products from methyl oleate

Alcohol	% Chloro alkoxy ^a	% Chlorohydrin ^a	% Dichloro ^a	Reaction time (h)
Methanol	77.9	6.0	3.9	1
Ethanol	56.3	14.1	8.4	2
1-Propanol	59.3	17.7	4.4	3
1-Butanol	67.4	2.6	10.1	24
2-Propanol	57.8	6.3	15.3	168
3-Methyl-1- propanol	61.4	6.7	11.3	168
tert-Butanol	29.8	19.9	29.8	288
2-Ethyl-hexanol	55.7	9.2	13.5	46
1-Decanol	58.0	4.4	8.8	42

^a Yield from GC

chlorine. Strong hydride-type reducing agents like the metal hydrides would be typical choices for removal of organo chlorine compounds but would require stoichiometric quantities of an expensive hydride as well as the possibility of the unwanted reduction of the carboxyl functionality. We envisioned a catalytic process for the reduction of the chloro alkoxy derivates that would leave the carboxyl functionality intact. Reduction of the chloro methoxy was first achieved in this study using Pd/C and sodium hydroxide in 2-propanol [9]. Base-catalyzed elimination of hydrogen chloride competes with the chlorine reduction. This elimination gives rise to a variety of side products originating from both the chloro alkoxy compound, as well as, the chlorohydrin and dichloro compounds. Side products include enol ethers, enols, and vinyl halides. Both the enol ethers and enols are susceptible to acidic hydrolysis to give ketones as a final product.

A series of dechlorination experiments was performed to maximize yields, minimize reaction time, and optimize reactants. Two reactions without Pd/C or sodium hydroxide failed to produce a chlorine reduction. As depicted in Table 2, several alcohols were then explored to compare product distribution and reaction times (entries 1-8). Methanol, tert-butanol, 2-heptanol, and isobutanol all produced low yields of the desired alkoxy compounds. Sodium hydroxide should be more soluble in methanol in comparison to isopropanol, but the lower reflux temperature of methanol limited the amount of products. tert-Butanol was used to compare a tertiary alcohol to the secondary isopropanol. 1-butanol, 2-heptanol, and glycerin were considered to see if higher reaction temperatures would result in shorter reaction times. Glycerin had to be heated to 110 °C before reaction occurred and the only product observed was ketone. Table 2 entry 9 was heated in 10 °C increments to determine the lowest temperature at which the reaction would proceed (70 °C). 2-methyl-1propanol was also reacted at 70 °C due to its structural similarity to isopropanol. Reactions (entries 2 and 3) with ethanol and isopropanol had the highest yields with modest amounts of ketone side product. These two reactions required somewhat lengthy reaction times to consume the starting material, but ultimately both solvents were successful because their boiling points are sufficiently high enough for the reaction to occur. Additionally, ethanol and isopropanol are small enough so that steric interactions on the surface of the Pd catalyst are not hindered. Table 2 entries 10 and 11 showed that potassium hydroxide and Pt/C in ethanol were less reactive in comparison to entry 2. Metallic sodium was reacted with ethanol and isopropanol to form the stronger alkoxide bases for dechlorinations. Alkoxide bases (Table 2 entries 12 and 13) reacted slightly faster than the equivalent reactions with sodium hydroxide, but the small increase (5.9 %) in dechlorinated product did not merit the use of metallic sodium over the much easier to handle sodium hydroxide. Sodium acetate, sodium bicarbonate, and sodium carbonate were reacted to determine if a weaker base than sodium hydroxide would catalyze the dechlorination, but all three failed to react.

Base optimization of the dechlorination was studied in a series of 20 reactions as shown in Table 3. Reaction time was limited to 24 h, which is a common requirement for industrial scale up. Ethanol required a larger excess of base to cause dechlorination, and at two equivalents (entries 1 and 6) neither sodium hydroxide nor potassium hydroxide produced products. Eight equivalents of sodium hydroxide in ethanol (entry 4) were necessary to achieve a similar amount of products as four equivalents of potassium hydroxide in isopropanol (entry 17). Isopropanol with four equivalents of potassium hydroxide (entry 17) produced the highest amount of ether (57.3 %) and the highest ratio of product to ketone (12:1) and as such was used for all subsequent dechlorination reactions. Additional reactions were then completed with increasing amounts of Pd/C. Chloro methoxy was reacted with 4, 6, 8, 10, and 20 % Pd/C (by weight) and four equivalents of potassium hydroxide in isopropanol. Increased Pd/C resulted in similar yields (55.4-63 %) and product ratios (10:1-14:1) to the reaction that contained 2 % Pd/C (by weight).

Chloro ethoxy, chloro 1-propoxy, and chloro 1-butoxy were then reacted under these optimized conditions of four equivalents of potassium hydroxide and 2 % Pd/C (by weight). Longer chain chloro ethers required a much longer reaction time, over 400 h for the chloro 1-butoxy compound. For the dechlorination to be synthetically useful on an industrial scale, these extended reaction times needed to be overcome. In order to reduce the time needed to dechlorinate longer chain chloro alkoxy compounds, initial dechlorination was performed at 75 °C on the benchtop for 1–2 days. An observed reaction rate at 75 °C was plotted

Entry	Base	Solvent	Temp (°C)	Time (h)	% Alkoxy ^b	% Ketone ^b	% Starting Material ^{b,c}
1	NaOH	Methanol	65	22	1.2	6.3	71.4
2	NaOH	Ethanol	78	159	75.5	10.5	5.4
3	NaOH	Isopropanol	83	72	63.3	14.5	0.0
4	NaOH	Isobutanol	70	119	7.0	4.7	58.4
5	NaOH ^d	1-Butanol	118	13	16.5	13.8	10.8
6	NaOH ^d	tert-Butanol	82	23	6.2	2.0	74.4
7	NaOH ^d	2-Heptanol	100	24	1.4	14.6	32.5
8	NaOH	Glycerin	70-110	95	0.0	20.5	67.0
9	NaOH ^d	Isopropanol	50-70	164	50.9	8.1	8.9
10	КОН	Ethanol	75	146	32.0	8.3	20.5
11 ^e	КОН	Ethanol	75	128	10.4	20.9	44.5
12	Na	Ethanol	75	97	59.0	17.1	7.9
13	Na	Isopropanol	75	68	69.2	6.9	0.0

Table 2 Dechlorination reactions of chloro methoxy^a

^a All the reactions were catalyzed with Pd/C (2 % by weight) and excess base (3-5 equivalents) except where noted

^b Yield from GC

^c Starting material chloro methoxy

^d 12-18 equivalents of base used

e Pt/C catalyst

Table 3 Effect of base concentration on dechlorinations in ethanol and isopropanol^a

Entry	Solvent	Base	Equivs of base	% Alkoxy ^b	% Ketone ^b	% Starting material ^{b,c}	Alkoxy/ketone ratio
1	EtOH	NaOH	2.0	0.0	2.9	83.2	0.0
2	EtOH	NaOH	4.0	7.2	7.8	67.6	0.9
3	EtOH	NaOH	6.0	40.6	11.7	20.6	3.5
4	EtOH	NaOH	8.1	47.6	20.9	19.9	2.3
5	EtOH	NaOH	10.0	23.9	22.2	25.8	1.1
6	EtOH	KOH	2.2	0.0	2.3	83.8	0.0
7	EtOH	KOH	4.4	10.1	12.8	52.1	0.8
8	EtOH	KOH	5.9	6.2	16.1	59.5	0.4
9	EtOH	KOH	7.9	33.9	27.2	9.5	1.2
10	EtOH	KOH	9.7	39.2	21.2	7.4	1.8
11	IPA	NaOH	2.4	13.5	3.0	72.2	4.5
12	IPA	NaOH	4.1	10.9	6.4	62.7	1.7
13	IPA	NaOH	5.8	6.3	4.5	70.4	1.4
14	IPA	NaOH	8.1	3.1	6.5	77.6	0.5
15	IPA	NaOH	9.6	5.1	5.6	75.2	0.9
16	IPA	KOH	2.4	36.6	3.8	30.2	9.6
17	IPA	KOH	4.0	57.3	4.7	1.0	12.2
18	IPA	KOH	6.0	30	12.1	29.5	2.5
19	IPA	KOH	7.8	18.4	20.9	32.1	0.9
20	IPA	KOH	10.0	19.1	31.9	21.1	0.6

^a 24 h at 75 °C, Pd/C (2 % by weight), 1 g of chloro methoxy and 10 ml alcohol

^b GC Yields

^c Methyl oleate

on a 1st order rate plot and then extrapolated to estimate a time for the reaction to consume the starting material. Using the approximation that a 10 $^{\circ}$ C increase in reaction

temperature would double the reaction rate, a higher reaction temperature was chosen that would complete the reaction in approximately 24 h. The reactions were then

Table 4 Dechlorination of chloro alkoxy compounds^a

ID	Temp (°C)	Time (h)	% Alkoxy ^b	% Ketone ^b	% Starting material ^b
Methoxy	75	65	43.2	9.9	2.6
Ethoxy	75	160	37.0	7.4	7.8
Propoxy	75	328	42.3	9.3	2.2
Propoxy	105	24	25.7	17.3	0.8
Butoxy	75	424	38.7	8.8	4.3
Isopropoxy ^c	115, 125	24, 24	19.3	13.4	6.9
Isobutoxy ^d	125	24	19.3	19.3	5.9
2-EH ether ^e	125	24	4.1	16.3	27.6
Decoxy ^f	125	24	21.7	18.2	7.3

 a ~50 g of chloro alkoxy in 250 ml IPA with Pd/C (2 % by weight) and KOH (4 equivalents)

^b Yield from GC

^c No reaction at 75 °C, 18 % starting material unreacted at 115 °C

^d 8.8 % product after 24 h at 75 °C

^e 2-ethyl-hexyl, no reaction at 75 °C

 $^{\rm f}$ 2.9 % product after 24 h at 75 $^{\circ}{\rm C}$

transferred to a pressurized bomb and carried out at this elevated temperature. This strategy produced modest yields of ethers while simultaneously increasing ketone products as shown in Table 4 for most of the chloro alkoxy compounds.

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