JOC*Note*

Simple, Rapid Procedure for the Synthesis of Chloromethyl Methyl Ether and Other Chloro Alkyl Ethers[1]

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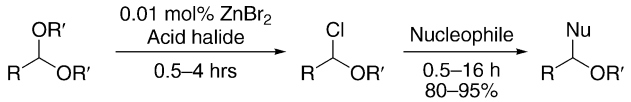
Received June 29, 2005



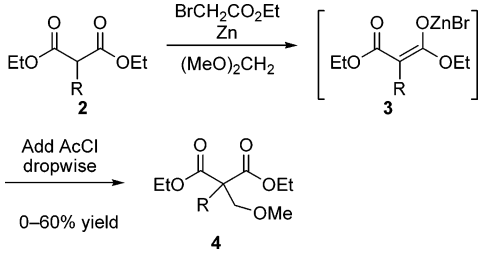
R = H, alkyl, aryl
R′= alkyl
Nu = ROH, RCO_2H, stabilized enolate

Convenient one-pot process

Zinc(II) salts catalyze the reaction between acetals and acid halides to provide haloalkyl ethers in near-quantitative yield. Reactions from millimole to mole scale are typically complete in 1−4 h with 0.01 mol % catalyst. The solutions of haloalkyl ethers thus obtained can be utilized directly in reactions in which the presence of the ester byproduct does not interfere. Excess haloalkyl ether is destroyed on workup, thereby minimizing exposure to this class of carcinogenic compounds.

Chloromethyl methyl ether (MOMCl, **1**) and other haloalkyl ethers are useful reagents for the introduction of acid-sensitive protecting groups for alcohols, phenols, thiols, and carboxylic acids,[2] and they participate in a wide variety of carbon−carbon bond forming reactions as electrophiles and carbene precursors.[3] MOMCl is the most-utilized of this class of reagents, but because its commercial preparation involves the reaction between formaldehyde, methanol, and hydrogen chloride,[4] **1** is typically contaminated with the highly carcinogenic bis-(chloromethyl) ether. As a consequence, a number of procedures have been devised for the synthesis of **1** that do not result in the formation of bis(chloromethyl) ether.[5] It is often only casually acknowledged that MOMCl is hazardous, but current evidence indicates that it is also carcinogenic.[6] In addition, **1** is listed as an extremely hazardous substance by the EPA and European Community, and is subject to extensive regulations governing its distribution, handling, and use. These characteristics have prompted the development of alternative methoxymethylation strategies that circumvent the use of **1** by employing Lewis acid catalyzed exchange reactions between methoxymethyl donors and alcohols,[7] carboxylic acids,[8] and carboxamides.[9] As part of a project to develop a scalable synthesis of methoxymethylated intermediates (**4**) for a medicinal chemistry program,[10] we had occasion to look closely at one of these methods.[8] Our findings, which led to the development of a rapid and convenient protocol for the synthesis of α-halo ethers from symmetric acetals, are described in this note.

SCHEME 1



The methoxymethylation protocol employed by our Discovery colleagues to prepare malonate derivatives **4** was first reported by Gaudemar.[8] This process involves initial deprotonation of the starting malonate ester (**2**) by ethyl 2-bromozinc acetate in dimethoxymethane (DMM) to give an intermediate zinc enolate (**3**), which is then treated with acetyl chloride to furnish the methoxymethylated product (Scheme 1).

It was difficult to obtain consistent results using this procedure, with yields of **4** ranging between 0 and 60%. Our initial efforts to improve this reaction focused on determining the role of zinc in this process, since there is some discrepancy in the literature about the reaction of acetals with acetyl chloride in the presence of Zn(II)

(1) A preliminary version of this work was presented at the 2003 National Organic Symposium, Bloomington, IN.

(2) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis,* 3rd ed.; John Wiley & Sons: New York, 1999. (b) Wuts, P. G. M. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995.

(3) For a review, see: Benneche, T. *Synthesis* **1995**, 1 and references therein.

(4) For a representative lab-scale procedure, see: Marvel, C. S.; Porter, P. K. *Organic Syntheses;* John Wiley & Sons: New York, 1941; Collect. Vol. I, p 377.

(5) The majority of these processes rely on halide exchange between an acid chloride and dimethoxymethane, and typically employ elevated temperature and/or protic acid catalysis to accelerate the reaction. With HCl: (a) Weinstock, L. M.; Karady, S.; Sletzinger, M. U.S. Patent 3,972,947; *Chem. Abstr.* **1976**, *85*, 142633. (b) Amato, J. S.; Karady, S.; Sletzinger, M.; Weinstock, L. M. *Synthesis* **1979**, 970. (c) Linderman, R. J.; Jaber, M.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6499. With H_2SO_4: (d) Chong, J. M.; Shen, L. *Synth. Commun.* **1998**, *28*, 2801. (e) Williams, A. G. WO 02/059070 A1; *Chem. Abstr.* **2002**, *137*, 124930. (f) Reggelin, M.; Doerr, S. *Synlett* **2004**, 1117. By other methods: (g) Stadlwieser, J. *Synthesis* **1984**, 490. (h) Jones, M. *Synth. Commun.* **1984**, *14*, 727.

(6) For a summary of toxicological data and safety recommendations, see: (a) *Sax's Dangerous Properties of Industrial Materials*, 10th ed.; Lewis, R. J., Sr., Ed.; John Wiley & Sons: New York, 2000; Vol. 2, p 854. (b) *Sigma-Aldrich Library of Chemical Safety Data*, 2nd ed.; Lenga, R. E., Ed.; Sigma-Aldrich: Milwaukee, WI, 1988; Vol. 1, p 804. The carcinogenicity of MOMCl has been estimated to be greater than that of vinyl chloride; see Van Duuren, B. L. *Environ. Res.* **1989**, *49*, 143.

(7) From dimethoxymethane using protic and/or Lewis acids: (a) Karimi, B.; Ma'mani, L. *Tetrahedron Lett.* **2003**, *44*, 6051. (b) Patney, H. K. *Synlett* **1992**, 567. (c) Fuji, K.; Nakano, S.; Fujita, E. *Synthesis* **1975**, 276. (d) Olah, G. A.; Husain, A.; Narang, S. C. *Synthesis* **1983**, 896. (e) Gras, J.-L.; Kong Win Chang, Y.-Y.; Guerin, A. *Synthesis* **1985**, 74. (f) Kantam, M. L.; Santhi, P. L. *Synlett* **1993**, 429. (g) Dieter, R. K.; Datar, R. *Org. Prep. Proced. Int.* **1990**, *22*, 63−70. Using other reagents: (h) Marcune, B. F.; Karady, S.; Dolling, U.-H.; Novak, T. J. *J. Org. Chem.* **1999**, *64*, 2446−2449.

(8) Dardoize, F.; Gaudemar, M.; Goasdoue, N. *Synthesis* **1977**, 567.

(9) Ledneczki, I.; Agócs, P. M.; Molnár, A. *Synlett* **2003**, *14*, 2255.

(10) Reiter, L. R.; Freeman-Cook, K. D. WO 03/090752A1; *Chem. Abstr.* **2003**, *139*, 364949.

10.1021/jo051344g CCC: $30.25
Published on Web 10/13/2005

TABLE 1. Survey of Lewis Acids that Catalyze the Reaction between DMM and AcCl[a]

$(MeO)_2CH_2$ + AcCl → (25 °C, water bath) $MeOCH_2Cl$ + MeOAc (**1**)

entry	catalyst	loading (mol %)	reaction time[b]
1	$ZnBr_2$	10	<1 min[c]
2	$ZnBr_2$	1	<1 min[c]
3	$ZnBr_2$	0.1	<2 min[c]
4	$ZnBr_2$	0.01	15 min
5	$ZnBr_2$	0.001	1 h
6	$Zn(OTf)_2$	0.01	15 min[d]
7	ZnI_2	0.01	15 min[d]
8	$ZnCl_2$	0.01	15 min[d]
9	$Zn(OAc)_2$	0.01	15 min[d]
10	$Sc(OTf)_3$	0.1	30 min
11	LiBr	0.5	48 h
12	$MgBr_2$	0.1	120 h
13	none		[e]

[a] Reactions were conducted neat on a 50 mmol scale using the standard conditions (see Experimental Section). [b] Time for the exchange reaction to proceed to >98% consumption of DMM by ^{1}H NMR analysis of an aliquot of the reaction mixture. [c] Very exothermic reaction. [d] Displayed reactivity similar to that of $ZnBr_2$. [e] Less than 10% reaction after 24 h at 25 °C.

TABLE 2. Solvent Effects on the Rate of Chloride Exchange between DMM and AcCl[a]

$(MeO)_2CH_2$ + AcCl → ($ZnBr_2$ (0.01%), solvent, 25 °C, water bath) $MeOCH_2Cl$ + MeOAc (**1**)

entry	solvent	reaction time[b] (h)
1	neat	0.25
2	CH_2Cl_2	4
3	toluene	4
4	$ClCH_2CH_2Cl$	4
5	EtOAc	4
6	Et_2O	12
7	CH_3CN	48
8	THF	[c]

[a] Reactions were conducted on a 50 mmol scale with 3 volumes of solvent under the standard conditions (see Experimental Section). [b] Time for the exchange reaction to proceed to >98% consumption of DMM by ^{1}H NMR analysis of an aliquot of the reaction mixture. [c] THF reacts slowly to give 4-chlorobutyl acetate (see ref 15).

salts. Gaudemar has noted that $ZnBr_2$ catalyzes the halide exchange reaction between DMM and AcCl to give MOMCl and MeOAc.[8] In a subsequent report by Yue and co-workers, it was observed that these conditions failed for the exchange reaction between AcCl and the arylacetaldehyde-derived acetal 4-$MeOC_6H_4CH_2CH(OMe)_2$, leading to the formation of an aldehyde instead of the expected α-chloro ether.[11] Bailey and co-workers[12] have developed a highly regioselective $ZnCl_2$-catalyzed acetolysis of cyclic formals, which proceeds via an intermediate chloromethyl alkyl ether. Zinc(II) halides have also been reported to be among a range of Lewis acids that catalyze the formation of glycosyl halides from methyl glycopyranosides and acid halides.[13]

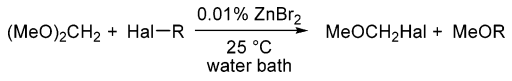
Given these reports, our first experiments were conducted to test Gaudemar's claim of the catalytic activity of $ZnBr_2$ in the exchange reaction between DMM and AcCl. Immediate and strongly exothermic reactions occurred on addition of acetyl chloride to homogeneous solutions of $ZnBr_2$ (10, 1, and 0.1 mol %) in DMM (Table 1, entries 1−3). Within 1−2 min, all heat evolution ceased, and analysis of the reaction mixture by ^{1}H NMR indicated an equimolar mixture of methyl acetate and MOMCl. The use of less $ZnBr_2$ results in a more controllable reaction, and for preparative purposes, we determined that 0.001−0.01 mol % $ZnBr_2$ efficiently catalyzes the exchange reaction between AcCl and DMM within 1 h (entries 4 and 5). A survey of other Lewis acids revealed that several readily available Zn(II) salts catalyze the reaction with an efficiency comparable to that of $ZnBr_2$ (entries 6−9),[14] and all are much more reactive than selected Li, Mg, and Sc salts (entries 10−12). Finally, in a control experiment, the exchange reaction between DMM and AcCl was very slow in the absence of a catalyst, with less than 10% conversion after 24 h at 25 °C (entry 13).

During our initial work on optimizing the exchange reaction, we noted that for experiments on a preparative scale, it was necessary to add the AcCl slowly to prevent a vigorous exotherm and loss of material, even when external cooling was utilized. Additional thermal control is conferred by diluting the catalyst/DMM solution with a non-acetal solvent prior to addition of the acid halide (Table 2). Non-Lewis basic solvents (toluene, dichloromethane, ethyl acetate, and 1,2-dichloroethane) result in the best combination of reaction time and product stability, but ether and acetonitrile can also be used with longer reaction times (>12 h). The use of THF as a dilution solvent during the exchange reaction is not recommended because of the formation of significant amounts of 4-chlorobutyl acetate from acetolysis of the solvent, which is a reaction known to occur under these conditions.[15] Solutions of MOMCl in toluene prepared using this procedure did not degrade after six months of storage at ambient temperature,[16] and were equally effective as freshly prepared MOMCl in alkylation reactions.

The scope of the exchange reaction extends beyond the reaction of dimethoxymethane with acyl chlorides. Other halogenating agents participate in the reaction (Table 3), with relative reactivity in the order $(COCl)_2$ > RCOCl ≈ $SOCl_2$ > RCOBr ≫ $POCl_3$. Reactions between DMM and oxalyl chloride are so vigorous that careful attention to the addition rate is required to prevent uncontrollable exotherms. At the other extreme, complete halogen transfer from phosphorus oxychloride[17] and chlorotrimethylsilane is too sluggish to be of practical use. Acetyl bromide readily participates in the exchange reaction to

(11) Chang, C.; Chu, K. C.; Yue, S. *Synth. Commun*. **1992**, *22*, 1217.
(12) Bailey, W. F.; Carson, M. W.; Zarcone, L. M. *J. Org. Synth.* **1998**, *75*, 177. (b) Bailey, W. F.; Zarcone, L. M. J.; Rivera, A. D. *J. Org. Chem.* **1995**, *60*, 2532. (c) Bailey, W. F.; Rivera, A. D. *J. Org. Chem.* **1984**, *49*, 4958.
(13) Grynkiewicz, G.; Konopka, M. *Pol. J. Chem.* **1987**, *61*, 149.
(14) These sources of Zn(II) are rapidly converted to $ZnCl_2$ in situ by halogen exchange between the Zn(II) salt and MOMCl. For example, when 1 mol % $ZnBr_2$ is employed, 2 mol % MOMBr is present in solution. Under typical reaction conditions with 0.01 mol % or less catalyst, α-halo ethers from the halogenation exchange process cannot be detected.
(15) Synerholm, M. E. *J. Am. Chem. Soc.* **1947**, *69*, 2581.
(16) Purity analysis was conducted by periodically analyzing aliquots by ^{1}H NMR spectroscopy.

TABLE 3. Different Halide Sources in the $ZnBr_2$-Catalyzed Exchange Reaction with DMM[a]



entry	halide source	equiv	reaction time[b] (min)
1	$(COCl)_2$	0.5	<5[c]
2	$SOCl_2$	0.5	30[d]
3	AcCl	1.0	30
4	n-$C_5H_{11}COCl$	1.0	30[d]
5	$POCl_3$	0.33	[e]
6	TMSCl	1.0	[f]
7	AcBr	1.0	45
8	$SOBr_2$	0.5	[g]

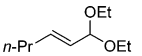
[a] Reactions were conducted neat on a 50 mmol scale using standard conditions (see Experimental Section). [b] Time for the exchange reaction to proceed to >98% consumption of DMM by ^{1}H NMR analysis of an aliquot of the reaction mixture. [c] Very rapid, exothermic reaction. [d] Reactivity is similar to that in AcCl. [e] Reaction stalls at 66% conversion after 16 h. [f] Reaction stalls at 20% conversion after 1 h. [g] Reaction stalls at 50% conversion after 15 min.

provide MOMBr, but thionyl bromide is less effective as a brominating agent (entries 7 and 8). For applications requiring purified α-halo ethers, the products from the exchange reaction can be conveniently separated by distillation when a higher molecular weight acyl halide is employed (entry 4).[5c,d,f]

Other acetals can be used in this reaction, and a representative set of chloroalkyl ethers prepared via this method is listed in Table 4. The best substrates for this reaction are acyclic symmetric aliphatic and benzylic acetals (entries 1−7), which are efficiently converted to α-halo ethers in high yield. These solutions of α-haloalkyl ethers can be utilized directly in reactions with alcohols, acids, phenols, and stabilized enolates to give the expected products in high yields (Table 5). Upon completion of the reaction, unreacted α-halo ether is decomposed during aqueous workup by vigorously mixing the initial biphasic mixture for 5−15 min before separating the phases.[18] The last four entries in Table 4 illustrate current limitations of this method. Allylic acetals react to form a complex mixture of products (entry 8). The acyclic mixed acetal t-$BuOCH_2OMe$[19] halogenates to provide a mixture of products favoring **1** (ratio 85:15, entry 9). Reaction of a simple cyclic mixed acetal (2-methoxytetrahydropyran, entry 10) proceeds regioselectively, but the resulting α-halo ether slowly decomposes under the reaction conditions. More-substituted acetals such as methyl 2,3,4,6-tetraacetyl glucopyranoside (entry 11) are unreactive, even at elevated temperatures using higher catalyst loadings.

In conclusion, we have described a useful method for the rapid preparation of α-halo alkyl ethers by the Zn(II)-catalyzed exchange reaction between acyclic acetals and acid halides. The solutions of haloalkyl ethers thus obtained can be utilized without isolation in base-mediated reactions in which the presence of the ester byproduct does not interfere, including alkylations of acids, alcohols, phenols, and stabilized enolates. The present procedure offers a significant operational advance over existing methods for preparing α-haloethers because of its greater generality and rapidity. Because the preparation and use of these reagents is conducted in one vessel and excess reagent is decomposed on workup, exposure issues arising from the handling of these potential carcinogens can be minimized. Finally, the results of this study suggest that methoxymethylation reactions conducted under Gaudemar conditions proceed via a stepwise process, consisting of rapid formation of MOMCl in solution followed by reaction with the in situ nucleophile.

TABLE 4. Zn(II)-Catalyzed Synthesis of α-Halo Ethers

entry	acetal	α- halo ether	conditions[a] (time)[b]	yield (%)[c]
1	$(EtO)_2CH_2$	$EtOCH_2Cl$ **5**	A,B (6 h)	98
2			A,T (8 h)	98
3		 **6**	A,B (1 h)	92
4			O,T (1 h)	98
5		 **7**	A,B (1 h)	92[d]
6		 **8**	A,T (0.5 h)	93
7		 **9**	A,T (0.5 h)	>95[d]
8		—	A,T (0.5 h)	[e]
9	t-$BuOCH_2OMe$	t-$BuOCH_2Cl$ + MOMCl	A,B (0.5 h)	[f]
10			A,B (1 h)	[g]
11			A,B	No Rxn

[a] Conditions: A, AcCl; O, oxalyl chloride; B, $ZnBr_2$; T, $Zn(OTf)_2$. Equimolar amounts of acetal and halogen source were employed with 0.01−0.025% catalyst. [b] Time for the exchange reaction to proceed to no further conversion by ^{1}H NMR analysis of an aliquot of the reaction mixture. [c] Percent α-haloether in the reaction mixture; remainder is unreacted acetal, as determined by ^{1}H NMR analysis of the reaction mixture. [d] Product is extremely susceptible to hydrolysis, resulting in the formation of substantial amounts of aldehyde when dissolved in the NMR solvent. [e] The acetal decomposes under the reaction conditions. [f] Selectivity is 85:15 MOMCl:t-$BuOCH_2Cl$. [g] The exchange reaction is initially regioselective (after 1 h, 94:6 ratio of cyclic chloroether to acyclic chloroether at 66% conversion), but the products are unstable and decompose under the reaction conditions.

Experimental Section

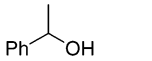
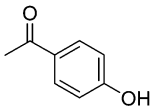
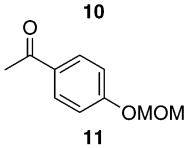
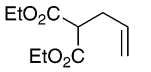
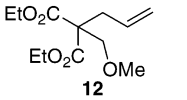
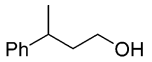
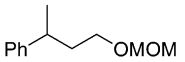
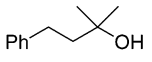
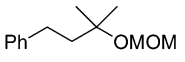
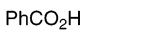
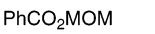
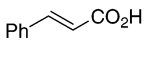
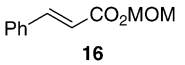
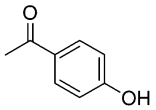
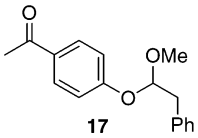
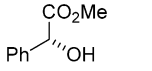
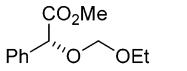
Catalyst Considerations. For small- and medium-scale reactions with DMM, such small amounts of catalyst are required that we found it easiest to dispense the correct amount

(17) The reaction with $POCl_3$ proceeds rapidly (less than 1 h) to 33% conversion, and then slows substantially, with 66% conversion after 16 h at 45 °C. In this instance, reaction endpoint monitoring is inaccurate because of the evaporative losses of the DMM and MOMCl during the extended reflux.

(18) The initial aqueous quench is mildly exothermic, and typically >98% of residual α-halo ether is decomposed when heat evolution has ceased, which is 5 min or less for preparative scale experiments (100 mmol scale). See Supporting Information for additional details.

(19) Goff, D. A.; Harris, R. N., III; Bottaro, J. C.; Bedford, C. D. *J. Org. Chem.* **1986**, *51*, 4711.

TABLE 5. Alkoxyalkylation with In-Situ Generated α-Halo Alkyl Ethers[a]

entry	starting material	α-halo ether (equiv)	product	yield[b] (%)
1		**1** (2.0)	 **10**	92
2		**1** (2.0)	 **11**	86
3[c]		**1** (2.0)	 **12**	80
4		**1** (2.0)	 **13**	92
5		**1** (2.0)	 **14**	92
6		**1** (1.2)	 **15**	92
7		**1** (1.2)	 **16**	96
8		**8** (1.33)	 **17**	93
9		**5** (1.5)	 **18**	85

[a] Reactions were typically conducted at ambient temperature with 1.2−1.5 equiv of *i*-Pr_2NEt in toluene. Products were isolated using a standard aqueous workup; see Supporting Information. [b] Isolated yield of purified products. [c] Reaction was conducted in THF using NaH as base.

of catalyst from standard solutions of $ZnBr_2$ in DMM (10−20 mg/mL). These standard solutions retain all catalytic activity for at least one month if well-sealed. The solubility of zinc halides is poor in more-substituted acetals, so $Zn(OTf)_2$, which has improved solubility, has proven easiest to utilize in these cases. For large-scale reactions, $Zn(OAc)_2$ is an excellent catalyst because it is easy to manipulate and not hygroscopic.

General Procedure for Exchange Reactions. Catalyst (0.001−0.01 mol %) and acetal (1 equiv) are mixed in a flask fitted with a reflux condenser and an internal thermocouple thermometer. For temperature control, the flask is immersed in an ambient-temperature water bath. An inert cosolvent (3 mL of solvent/mL of acetal) is added at this time if desired. A halide source (1 equiv) is introduced to the flask portionwise so that the reaction temperature remains below 45 °C, and the reaction mixture is then allowed to cool to ambient temperature. Reaction progress is monitored by removing aliquots from the reaction mixture and analyzing them by NMR. These exchange reactions can be very exothermic, so slow addition of the halide source and dilution of the reaction mixture with an unreactive cosolvent are recommended to prevent a runaway reaction and unnecessary exposure. **CAUTION:** Due to the known carcinogenicity of **1** and potential carcinogenicity of other α-halo ethers described in this note, we recommend that exposure be minimized by limiting the handling of solutions of α-halo ethers once they have been formed.

Chloromethyl Methyl Ether (1) as a Solution in Toluene. A three-neck 500 mL flask fitted with a thermocouple thermometer, reflux condenser, and addition funnel was charged with dimethoxymethane (44.25 mL, 0.50 mol, 1 equiv), toluene (133 mL, 3 volumes), and $Zn(OAc)_2$ (9.2 mg, 0.01%). Acetyl chloride (35.5 mL, 0.50 mol, 1 equiv) was placed in the addition funnel, and was then introduced into the reaction mixture at a constant rate over 5 min. The $Zn(OAc)_2$ dissolved shortly after addition of the AcCl was started. During the next 15 min, the reaction mixture warmed slowly to 45 °C, and then cooled to ambient temperature over 3 h, at which time analysis of an aliquot of the reaction mixture by NMR indicated complete consumption of DMM. Solutions of MOMCl in toluene prepared using this stoichiometry have a density of 0.91 g/mL, are approximately 2.1 M (18% w/w), and are stable for months if adequately sealed. ^1H NMR ($CDCl_3$): δ 5.44 (s, 2H, MOMCl), 3.64 (s, 3H, MeOAc), 3.49 (s, 3H, MOMCl), 2.03 (s, 3H, MeOAc).

Methoxymethylation of an Alcohol: 1-Methoxymethyl-1-phenylethane (10). α-Phenethyl alcohol (5 mL, 41.5 mmol, 1 equiv) and diisopropylethylamine (9.0 mL, 1.25 equiv) were added sequentially to a toluene solution of MOMCl (2.1 M, 40 mL, 83 mmol, 2 equiv), prepared following the general procedure. The reaction mixture was maintained at ambient temperature for 16 h, at which time HPLC analysis indicated that the starting material had been consumed (starting material t_R = 4.46 min, product t_R = 7.25 min). The light yellow solution was partitioned between EtOAc and a saturated aqueous NH_4Cl solution, and the biphasic mixture was stirred vigorously for a minimum of 5 min to ensure all residual **1** had been decomposed. The resulting clear, colorless organic layer was removed, washed with a saturated aqueous $NaHCO_3$ solution and then with brine, dried with $MgSO_4$, and concentrated under reduced pressure. Purification by distillation (Kugelrohr, OT 106 °C, 5 mmHg) provided the title compound as a clear, colorless oil (6.32 g, 38.0 mmol, 92% yield). R_f = 0.5 (5:1 hexanes:EtOAc). ^1H NMR ($CDCl_3$): δ 7.31 (m, 4H), 7.27 (m, 1H), 4.75 (q, J = 6.5 Hz, 1H), 4.57 (d, A of AB, J = 6.8 Hz, 1H), 4.54 (d, B of AB, J = 6.8 Hz, 1H), 3.37 (s, 3H), 1.47 (d, J = 6.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 143.2, 128.4, 127.5, 126.3, 94.0, 73.9, 55.3, 23.6. IR (neat, cm^{-1}): 2976, 2931, 2887, 1451, 1153, 1098, 1026, 917, 758, 699, 544. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.52; H, 8.73.

Acknowledgment. We thank Mark Mitton-Fry and Russ Linderman for proofreading the manuscript.

Supporting Information Available: Experimental procedures and characterization data for α-halo ethers in Table 4 and alkoxylalkylated products in Table 5. This material is available free of charge via the Internet at http://pubs.acs.org.

JO051344G