JOC Article

Mix-and-Heat Benzylation of Alcohols Using a Bench-Stable Pyridinium Salt

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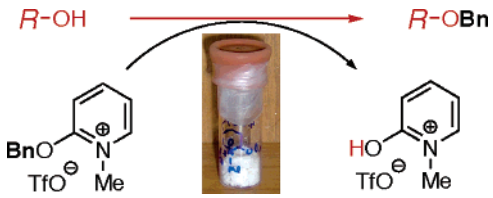

2-Benzyloxy-1-methylpyridinium triflate (**1**) is a stable, neutral organic salt that converts alcohols into benzyl ethers upon warming. The synthesis and reactivity of **1** are described herein. Benzylation of a wide range of alcohols occurs in good to excellent yield.

Introduction

Benzyl ethers are among the most common and important protecting groups in organic synthesis.[1] Like other alkyl ethers, they are advantageous for their stability to a wide range of reaction conditions and for the minimal electronic impact that they impart on the oxygen atom to which they are attached. For example, benzyl ethers are often employed to establish chelation control during addition to chiral aldehydes, which provides selectivity opposite that predicted by the acyclic Felkin−Anh model and observed with bulky silyl ethers.[2] Similarly, benzyl-protected glycosyl donors are "armed" relative to acylated analogues.[3] Among alkyl ethers, benzyl (and modified arylmethyl) ethers are perhaps the most versatile with respect to modes of cleavage, which include hydrogenolysis, oxidation, and acidic decomposition under a range of experimental protocols (Figure 1).[4]

Relatively harsh conditions are typically required for generating benzyl ethers from the corresponding alcohol, with the two most popular protocols being (1) the Williamson ether synthesis, an S_N2-type reaction between alkali metal alkoxides and benzyl bromide, and (2) coupling using benzyl trichloroacetimidate,[5] which is generally promoted by trifluoromethanesulfonic acid (triflic acid, TfOH).[6] Typical benzylation reactions are thus limited to substrates that tolerate either strongly acidic or basic conditions.[7] β-Hydroxy esters, for example, are subject to several acid- or base-catalyzed reactions, including retro-Aldol, elimination, and epimerization of stereogenic centers α- to the carbonyl group. Benzylation of these ubiquitous intermediates in the

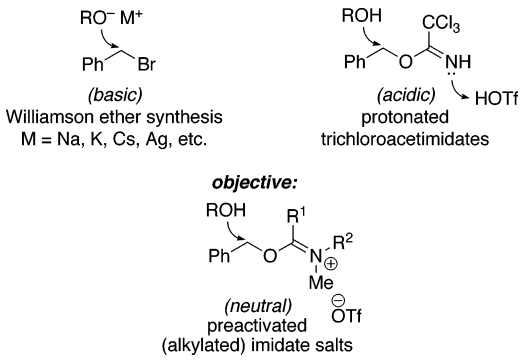

FIGURE 1. Standard benzylation protocols and desired objective.

(1) (a) Greene, T. W., Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley and Sons: New York, 1999. (b) Kocienski, P. J. *Protecting Groups*, 3rd ed.; Thieme: Stuttgart, 2003.

(2) Gawley, R. E.; Aubé, J. In *Principles of Asymmetric Synthesis*; Baldwin, J. E., Magnus, P. D., Eds.; Tetrahedron Organic Chemistry Series 14; Pergamon: Tarrytown, NY, 1996; pp 121−134.

(3) (a) *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker: New York, 1997. (b) Mootoo, D. R.; Konradsson, P.; Udodong, U.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 5583−5584. (c) Paulsen; H.; Richter, A.; Sinnwell, V.; Stenzel, W. *Carbohydr. Res.* **1978**, *64*, 339−362.

(4) Recent arylmethyl protecting groups that are cleaved under mild conditions: (a) Jobron, L.; Hindsgaul, O. *J. Am. Chem. Soc.* **1999**, *121*, 5835−5836. (b) Plante, O.; Buchwald, S. L.; Seeberger, P. H. *J. Am. Chem. Soc.* **2000**, *122*, 7148−7149. (c) Lam, H.; House, S. E.; Dudley, G. B. *Tetrahedron Lett.* **2005**, *46*, 3283−3285.

(5) (a) Iversen, T.; Bundle, D. R. *J. Chem. Soc., Chem. Commun.* **1981**, 1240−1241. (b) Wessel, H.-P.; Iversen, T.; Bundle, D. R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2247−2250. (c) Eckenberg, P.; Groth, U.; Huhn, T.; Richter, N.; Schmeck, C. *Tetrahedron* **1993**, *49*, 1619−1624.

(6) Boa, A. N.; Jenkins, P. R. Benzyl 2,2,2-Trichloroacetimidate. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley and Sons: New York, 1995; Vol. 1, pp 374−375.

(7) *p*-Methoxybenzyl (PMB) ethers may be formed under mild conditions that do not extend to benzylation (ref 1).

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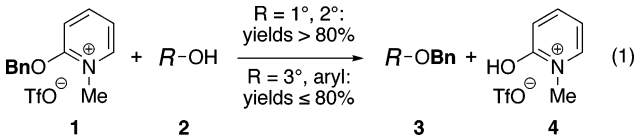
synthesis of polyketides and other important compounds can be problematic. Selective protection of polyol systems (e.g., carbohydrates) can also be complicated by base-catalyzed migration of esters and silyl ethers and by acid-catalyzed cleavage of silyl ethers and acetal linkages.

Benzylation of alcohols under *mild and nearly neutral conditions* would constitute a significant advance in synthetic chemistry. A recent review addresses the myriad options for protecting alcohols using mild, convenient, and environmentally friendly conditions, but no methods for the formation of benzyl ethers are discussed.[8] Silylation and acylation of alcohols can be accomplished under effectively neutral conditions using activated reagents that react with the free alcohol.[1] Imidazole and DMAP are frequently employed to activate silyl and acyl chlorides; conveniently, they are also capable of scavenging any acid that is produced during the course of the reaction. Protonation of benzyl trichloroacetimidate provides an activated reagent that reacts with free alcohols, but this mode of activation precludes neutralization of free acid. In principle, irreversible covalent activation (alkylation) of a trichloroacetimidate surrogate would enable the formation of benzyl ethers in the absence of external base or acid and in the presence of acid scavengers (if desired).

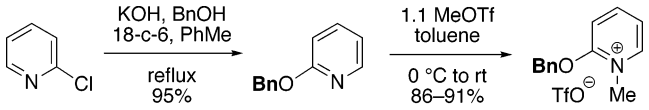
We envisioned that 2-benzyloxypyridine[9] could serve as an imidate surrogate for benzylation of alcohols. Pyridinium salts have been employed in esterification reactions, with Mukaiyama's 2-chloro-1-methylpyridinium iodide being perhaps the most popular.[10] Conversion of alcohols into thioesters and azides using 2-fluoro-1-methylpyridinium tosylate has also been demonstrated.[11] The two pieces of prior knowledge that were most influential in guiding the current work are as follows: (1) certain 2-alkoxypyridinium bromides decompose to bromoalkanes and pyridones;[12] (2) 2-alkoxypyridinium sulfonates do not proceed spontaneously to alkyl sulfonates.[13] We anticipated that decomposition of 2-alkoxypyridinium sulfonates in the presence of alcohols would give rise to alkyl ethers and pyridones, and we reported preliminary data in support of this hypothesis.[14]

Herein we describe in detail our investigation into the synthesis and reactivity of 2-benzyloxy-1-methyl-pyridinium triflate (Bn-OPT, **1**), which indeed provides benzyl ethers simply upon warming in the presence of a free alcohol. The overall balanced equation for the benzylation of alcohols (**2** → **3**) is shown in eq 1. Oxypyridinium triflate **1** may eventually supplant benzyl trichloroacetimidate for the synthesis of benzyl ethers from alcohols.



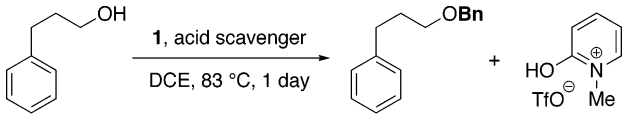
1 **2** **3** **4**

SCHEME 1. Synthesis of 2-Benzyloxy-1-methylpyridinium Triflate (1)



5 **1**

TABLE 1. Initial Optimization



2a **3a** **4**

entry	acid scavenger	equiv of **1**	yield[b,c] (%)
1	2,6-lutidine	1.0	43 (57)
2	Hünig's base	1.0	29 (39)
3	K_2CO_3	1.0	68 (93)
4	MgO	1.0	78 (93)
5	none	1.0	53 (87)
6	MgO	2.0	76 (85)
7	MgO	3.0	87

[a] See the Supporting Information for details. [b] Values in parentheses refer to the calculated yield based on recovered alcohol. [c] Estimated by ^{1}H NMR spectroscopy.

Results and Discussion

1. Synthesis and Isolation of Pyridinium Salt 1. The synthesis of **1** is illustrated in Scheme 1. Benzyl alcohol was coupled with 2-chloropyridine using a modification of a reported procedure[9a] to afford 2-benzyloxypyridine (**5**) in high yield. We then screened a range of alkylating agents and solvents in search of optimal conditions for the irreversible covalent activation of **5**. The current best protocol is to add methyl triflate (bp 94−99 °C) to an ice-cold solution of **5** in toluene and allow the mixture to warm to ambient temperature. A white microcrystalline solid (**1**) forms within minutes. Analytically pure **1** (mp 82−86 °C) can be isolated by filtration or by evaporation of the supernatant under reduced pressure.[15] This salt (**1**) is remarkably stable. We store it under an argon atmosphere either in the refrigerator or on the laboratory benchtop, and the white crystals of **1** are routinely handled open to the air. No differences have been observed between freshly prepared crystals and those that were prepared 3 months prior.

2. Development and Analysis of the Optimal Benzylation Protocol. At room temperature, the title reagent is freely soluble in chlorinated solvents (dichloromethane, chloroform, dichloroethane), partially soluble in ethereal solvents (THF and ether), and insoluble in aromatic hydrocarbons (benzene, toluene). Solutions of **1** and 3-phenylpropanol (**2a**) provided the desired benzyl ether upon heating. Because of its ability to solvate **1** and its convenient boiling point (83 °C), the initial screening of reaction conditions was conducted in dichloroethane (DCE).

The first issue that we endeavored to address was the presumed mild acidity of hydroxypyridinium triflate **4** (Table

(8) Sartori, G.; Ballini, R.; Bigi, F.; Bosica, G.; Maggi, R.; Righi, P. *Chem. Rev.* **2004**, *104*, 199−250.

(9) (a) Serio Duggan, A. J.; Grabowski, E. J. J.; Russ, W. K. *Synthesis* **1980**, 573−575. (b) Cherng, Y.-J. *Tetrahedron* **2002**, *58*, 4931−4935.

(10) (a) Armstrong, A. 2-Chloro-1-methylpyridinium Iodide. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley and Sons: New York, 1995; Vol. 2, pp 1174−1175. (b) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 707−808.

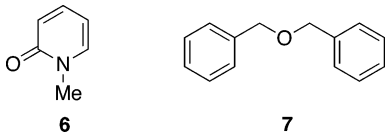
(11) See ref 10b and: (a) Hojo, K.; Yoshino, H.; Mukaiyama, T. *Chem. Lett.* **1977**, 437−440. (b) Hojo, K.; Kobayashi, S.; Soai, K.; Ikeda, S.; Mukaiyama, T. *Chem. Lett*. **1977**, 635−636.

(12) Joshi, R. A.; Ravindranathan, T. *Ind. J. Chem. Sect. B* **1984**, *23*, 260−262.

(13) (a) Beattie, D. E.; Crossley, R.; Dickinson, K. H.; Dover: G. M. *Eur. J. Med. Chem.* **1983**, *18*, 277−285. (b) Kornblum, N.; Coffey, G. P. *J. Org. Chem.* **1966**, *31*, 3449−3451.

(14) Poon, K. W. C.; House, S. E.; Dudley, G. B. *Synlett* **2005**, 3142−3144.

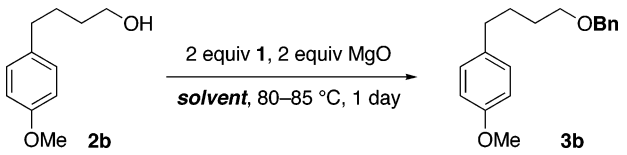
(15) Recrystallization of **1** from THF has no discernible effect on its properties.



6 **7**

FIGURE 2. Observed byproducts.

TABLE 2. Screening for Optimal Solvent



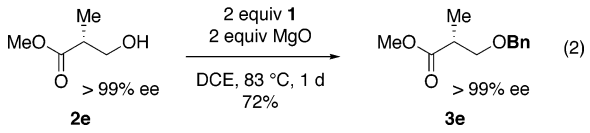
entry	solvent	yield[a] (%)
1	1,2-dichloroethane (DCE)	67
2	nitromethane	low
3	acetonitrile	-
4	*N*-methyl-2-pyrrolidinone (NMP)	-
5	toluene	91
6	benzene	93
7	chlorobenzene	>95
8	benzotrifluoride ($PhCF_3$)	>95

[a] Estimated by ^{1}HNMR spectroscopy.

1). Among the various acid scavengers that we evaluated, heterogeneous inorganic salts were most compatible with the desired benzylation reaction (entries 3−5). Soluble amines seemed to interfere with the coupling reaction (entries 1 and 2), and it was not clear if external amine bases would present any advantage in terms of moderating the potential acidity of pyridinium **4**. Based on these results and a quick cost analysis, magnesium oxide (MgO) emerged as our preferred choice, and so MgO was routinely included in all subsequent experiments.

In addition to the desired benzyl ether, two byproducts were observed in the crude product mixture: 1-methyl-2-pyridone (**6**) and dibenzyl ether (Bn_2O, **7**) (Figure 2). Pyridone **6**, the conjugate base of hydroxypyridinium **4**, is the expected byproduct of the benzylation reactions using **1**. Pyridone **6** is freely water-soluble and easily removed by aqueous extraction. The source of Bn_2O is not clear. It may derive from reaction of **1** with MgO, although small amounts of **7** were also observed during control experiments that did not include MgO. Adventitious moisture may be partly responsible for the formation of **7**. Because dibenzyl ether is unlikely to interfere with most benzylation reactions, we do not consider it to be a serious concern. Nonetheless, it was difficult to separate **7** from many of the alkyl benzyl ethers generated during the course of our investigations.

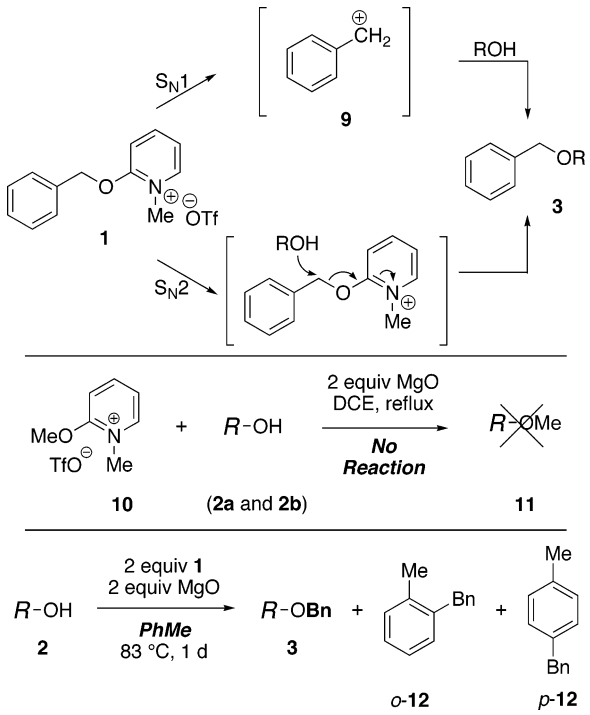
A crucial efficacy test for **1** was the benzylation of chiral β-hydroxy ester **2e** (eq 2). Benzyl ethers derived from such



(2)

chiral alcohols are difficult to obtain under Williamson ether conditions because of the potential both for β-elimination and/or for epimerization of the labile stereogenic center α- to the ester. Attempts at effecting the benzylation of **2e** under Willamson ether conditions were unsuccessful.[16] Benzylation using **1** proceeded efficiently (**2e** → **3e**) with no evidence of epimerization detectable by chiral HPLC analysis.[17] Benzyl ether **3e** was easily separated from Bn_2O by chromatography on silica gel. A series of primary and secondary alcohols were benzylated under similar conditions and with similar efficiencies (70−76% yield), as described in our preliminary report.[14]

SCHEME 2. S_N1 vs S_N2 Mechanistic Observations



Despite limited solubility, mixtures of **1** in many solvents became homogeneous upon warming, especially as the temperatures approached the melting point of **1** (82−86 °C). Toluene emerged as a promising choice in small-scale exploratory experiments. Therefore, we screened a range of aromatic solvents (**2b** → **3b**, Table 2). Yields improved significantly in aromatic hydrocarbon solvents relative to dichloroethane (>90% vs 67%).

Reactions conducted in toluene (and, to a lesser extent, benzene and chlorobenzene) gave rise to trace amounts of benzylated solvent molecules (Scheme 2, vide infra). No such

(16) Widmer, U. *Synthesis* **1987**, 568−570.

(17) In response to a reviewer's suggestion for documentation of the advantage of **1** over benzyl trichloroacetimidate, an additional experiment was conducted using trimethylsilylethanol (**13**) as a test substrate. Note that **13** is subject to Peterson elimination under acidic (or basic) conditions; see: Ager, D. J. *Org. React.* **1990**, *38*, 1. Benzylation of trimethylsilylethanol (**13** → **14**) has not been reported previously. Reaction of **13** with **1** proceeded to complete conversion with no evidence of decomposition, whereas a similar experiment using benzyl trichloroacetimidate yielded no evidence of the desired product (**14**). See the Supporting Information for ^{1}H NMR spectra of the crude product mixtures after aqueous workup.

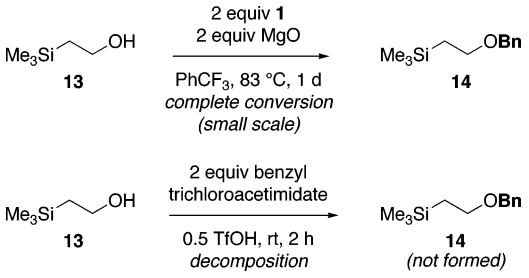
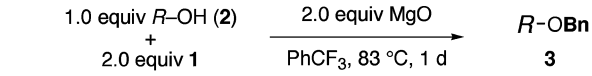
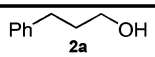
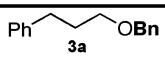
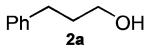
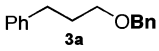
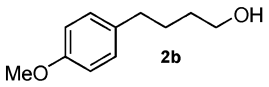
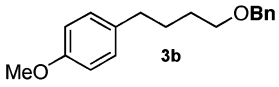
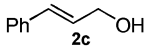
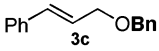
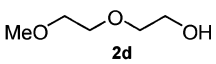
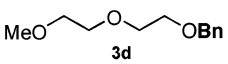
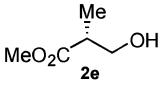
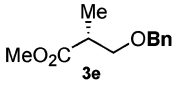
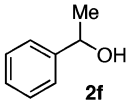
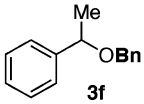
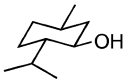
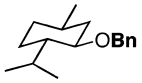
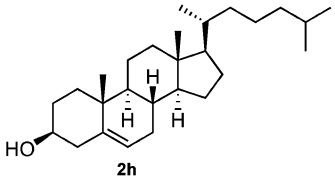
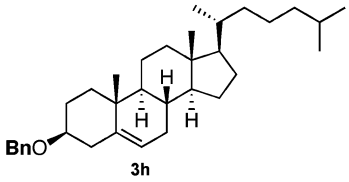
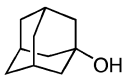
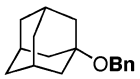
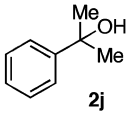
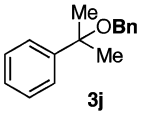
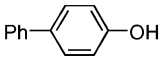
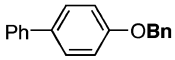


TABLE 3. Scope and Limitations



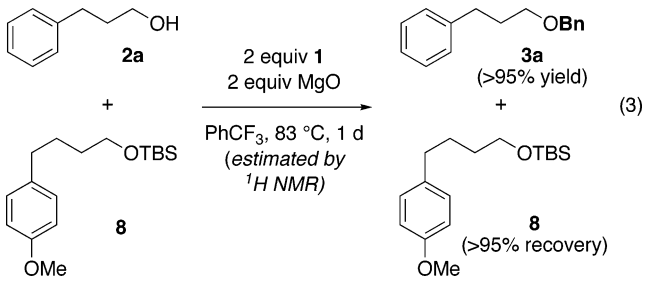
entry	ROH (2)	ROBn (3)	yield[a]
1	 **2a**	 **3a**	>95%
2[b]	 **2a**	 **3a**	>95%
3	 **2b**	 **3b**	>95%
4	 **2c**	 **3c**	n.d.[c]
5	 **2d**	 **3d**	93%[d]
6	 **2e**	 **3e**	85%
7	 **2f**	 **3f**	83%
8	 **2g**	 **3g**	88%
9	 **2h**	 **3h**	n.d.[c]
10	 **2i**	 **3i**	80%
11	 **2j**	 **3j**	44%
12	 **2k**	 **3k**	65%[e]

[a] Yields are estimated by ^{1}H NMR spectroscopy, unless otherwise indicated. [b] Reagent **1** stored for 3 months at room temperature before use. [c] Not determined; see ref 19. [d] Isolated yield of pure product. [e] Unreacted **2k** also observed in the crude product mixture.

products were observed from reactions conducted in benzotrifluoride (α,α,α-trifluorotoluene, $PhCF_3$).

In addition to being an excellent solvent for the present benzylation reactions, benzotrifluoride is low-cost, moderately volatile (bp 100−103 °C), and highly regarded as an environmentally friendly alternative to chlorinated solvents. Benzotrifluoride is our choice of solvent for the benzylation reactions, although Table 2 indicates that other aromatic hydrocarbons are also suitable.

Having identified our preferred solvent, acid scavenger, and time and temperature, we were ready to probe the scope and limitations of what we consider to be mild and effectively neutral benzylation conditions. The tolerance of this protocol for sensitive functionality will be determined in due course, but for an initial data point we tested our benzylation reaction in the presence of a primary silyl ether (eq 3).[18] The desired benzyl ether (**3a**) was obtained in excellent yield, and silyl ether **8** was recovered unchanged.[17]



3. Mix-and-Heat Benzylation of Alcohols: Scope and Limitations. Table 3 illustrates the benzylation reactions of representative alcohols under our preferred conditions. Primary (entries 1−6) and secondary (entries 7−9) alcohols all provided the desired benzyl ethers (**3a**−**h**) in good to excellent yield. Among these substrates are an allylic alcohol (entry 4), a homoallylic alcohol (entry 9), and a β-hydroxy ester (entry 6). We saw no difference between freshly prepared reagent and a sample of **1** that had been aged for three months (cf. entries 1 and 2).

Tertiary alcohols and phenols provided variable results (entries 10−12). 1-Adamantanol (**2i**), which is not prone to elimination, afforded benzyl ether **3i** in good yield. Tertiary benzylic alcohol **2j**, which is highly prone to elimination, provided only a moderate yield of ether **3j**. These two substrates may approximate the upper and lower limits of benzylation efficiency for tertiary alcohol substrates using **1**. Phenols (e.g., **2k**, entry 12) reacted sluggishly in our study, possibly due to a decrease in nucleophilicity relative to aliphatic alcohols. Because benzylation of phenols can be accomplished using Mitsunobu conditions,[20] this class of substrates was not investigated further.

4. Insights into the Potential Reaction Mechanism. The mechanistic course of benzylation reactions using **1** undoubtedly falls along the continuum between S_N1 and S_N2 pathways (Scheme 2). Although we have not performed detailed kinetic studies, two key observations are more consistent with an S_N1-type mechanism. Benzylation reactions conducted in toluene afforded trace amounts of *o*-**12** and *p*-**12**. We assume that these compounds derive from Friedel−Crafts alkylation of toluene, which suggests the presence of a highly electrophilic benzylating species (e.g., benzyl cation **9**) in the reaction mixture and argues in favor of a more S_N1-like pathway. Methoxypyridinium salt **10**[21] was completely inert under similar conditions, which argues against an S_N2-type pathway. We therefore surmise that the actual benzylation event using **1** is better approximated by the S_N1 mechanism. This conclusion is consistent with behavior observed in trichloroacetimidate reactions.[22]

Conclusion

We report the synthesis and reactivity of 2-benzyloxy-1-methylpyridinium triflate (**1**), a novel benzylation reagent for alcohols. Salt **1** is easy to prepare, bench-stable, and preactivated. No acidic or basic promoters are needed for benzyl transfer, which occurs simply upon warming in the presence of the alcohol substrate. Work on this and related reagents is in progress.

Experimental Section

2-Benzyloxypyridine (5). The following is a modification of a reported procedure.[9a] A mixture of benzyl alcohol (2.00 g, 18.5 mmol), 2-chloropyridine (3.46 g, 30.5 mmol), KOH (3.42 g, 61.0 mmol, ground with a mortar and pestle), toluene (37 mL), and 18-crown-6 (24.4 mg, 0.925 mmol) was heated at reflux for 1 h with azeotropic removal of water (Dean−Stark trap). The reaction mixture was then cooled to room temperature and partitioned between ethyl acetate (20 mL) and water (10 mL). The organics were washed (brine), dried (Na_2SO_4), filtered, concentrated under vacuum, and purified on silica gel (elution with 100:1 hexane/EtOAc) to provide 3.28 g of **5** (96% yield) as a yellow liquid.

2-Benzyloxy-1-methylpyridinium Triflate (1). To a cold (0 °C) solution of 2-benzyloxypyridine (**5**) (100 mg, 0.54 mmol) in toluene (0.540 mL) was added methyl trifluoromethanesulfonate (64 μL, 0.57 mmol). The mixture was allowed to warm to room temperature, which resulted in the formation of a white crystalline precipitate. After 40 min, the volatiles were removed in vacuo, providing 0.172 g (91% yield) of **1** as a white microcrystalline solid, mp 82−86 °C. A similar large-scale experiment afforded 6.52 g (86% yield) of **1** as a white solid, which was collected by filtration of the crude reaction mixture through a fritted glass funnel, followed by drying under vacuum: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, J = 7.8 Hz, 1H), 8.34 (apparent t, J = 8.3 Hz, 1H), 7.59 (d, J = 9.0 Hz, 1H), 7.53−7.42 (m, 6H), 5.58 (s, 2H), 4.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 148.0, 143.8, 132.5, 129.6, 129.1, 128.5, 119.0, 112.1, 74.5, 42.0; HRMS (ESI^+) found 200.1070 ($M - OTf)^+$ (calcd for $C_{13}H_{14}NO^+$ 200.1075).

Standard Procedure for Benzylation of Alcohols (2 → 3). A mixture of pyridinium triflate **1** (100 mg, 0.29 mmol), benzotrifluoride ($PhCF_3$, 0.29 mL), MgO (11.5 mg, 0.29 mmol, vacuum-dried), and alcohol **2** (0.14 mmol) was heated at 83 °C for 1 day. The reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was concentrated under vacuum and purified on silica gel to yield benzyl ether **3** (see Table 3), admixed with varying amounts of Bn_2O.

Benzylation of Diethylene Glycol Monomethyl Ether (Monoglyme, 2d). A mixture of pyridinium triflate **1** (581 mg, 1.67 mmol), benzotrifluoride ($PhCF_3$, 1.7 mL), MgO (67 mg, 1.7 mmol), and **2d** (100 mg, 0.83 mmol) was subjected to the standard procedure to afford 0.163 g (93%) of diethylene glycol benzyl methyl ether (**3d**) as a pale yellow liquid, which exhibited spectroscopic properties consistent with the reported data.[23]

Benzylation of 1-Adamantanol (2i). A mixture of pyridinium triflate **1** (100 mg, 0.29 mmol), benzotrifluoride ($PhCF_3$, 0.29 mL), MgO (11.5 mg, 0.29 mmol), and **2i** (21.8 mg, 0.14 mmol) was subjected to the standard procedure to afford 0.0363 g of a yellow oil, which was determined by ^{1}H NMR analysis to consist of 8.7 mg of Bn_2O and 0.0276 g (80%) of 1-benzyloxyadamantane (**3i**). Spectroscopic analysis was consistent with the data reported previously for **3i**.[24]

Acknowledgment. We thank the FSU Department of Chemistry and Biochemistry for support of this work, the NMR Facility for spectroscopic support, the Krafft laboratory for the use of their IR spectrometer and melting point apparatus, and Dr. Umesh Goli for assistance with mass spectrometry.

Supporting Information Available: Characterization data and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Silyl ether **8** was prepared in quantitative yield by treating a solution of 4-(4-methoxyphenyl)butan-1-ol in CH_2Cl_2 with DMAP (0.10 equiv), Et_3N (2.0 equiv), and TBSCl (1.1 equiv). See the Supporting Information for characterization data.

(19) The mass balance exceeded the theoretical yield of **3**, and dibenzyl ether (**7**) was observed by TLC and/or ^{1}H NMR analysis. The amount of **7** could not be estimated with any precision based on the ^{1}H NMR spectra because the diagnostic benzylic singlets were coincident.

(20) Hughes, D. L. *Org. React.* **1992**, *42*, 335−656.

(21) Methoxypyridinium triflate **10** was prepared in 85% yield (unoptimized) by a procedure similar to that used for the preparation of **1**. See the Supporting Information for characterization data.

(22) Cramer, F.; Hennrich, N. *Chem. Ber.* **1961**, *94*, 976−989.

(23) Grobelny, Z.; Stolarzewicz, A.; Maercker, A.; Krompiec, S.; Kasperczyk, J.; Rzepa, J. *J. Organomet. Chem.* **2004**, *689*, 1580−1585.

(24) Hartz, N.; Prakash, G. K. S.; Olah, G. A. *Synlett* **1992**, 569−572.