through a 5-mm (i.d.) glass tube using a nitrogen stream. (*Caution!* All operations involving nitrous gases must be conducted in a well-ventilated hood due to the toxicity of these gases.) The color of the reaction mixture changed from orange to bright red during the addition. Stirring was continued for 1.5 h as the reaction was allowed to warm to room temperature. The solvent and excess nitrous gases were removed in vacuo to afford 19.7 g (100%) of 1 as a bright red, crystalline solid: mp 173–175 °C, ^{1}H NMR ($CDCl_3$, ppm) 4.22 (s, 6 H, CO_2CH_3); IR (KBr) ν_{max} 2970, 1752, 1445, 1385, 1219, 1175, 1082, 960, 912 cm^{-1}; UV (dioxane) λ_{max} (log ϵ) 520 nm (2.754).

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Registry No. 1, 2166-14-5; 2, 96898-32-7; 3, 3787-09-5; 4, 3787-10-8; ethyl diazoacetate, 623-73-4.

Dimethylboron Bromide Interconversion of Protecting Groups: Preparation of MTM Ethers, *O,S*-Acetals, and Cyanomethyl Ethers

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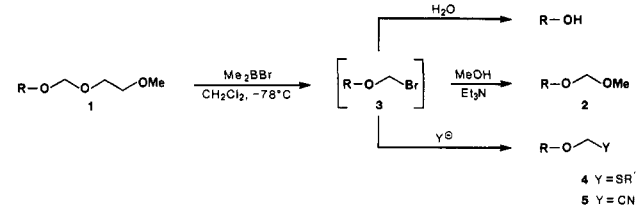
Previously, we have reported on the synthetic utility of dimethylboron bromide for a variety of different chemical transformations such as the mild reduction of sulfoxides to sulfides,[1] the cleavage of ethers (alkyl, aryl, cyclic) to alcohols,[2] and the conversion of acetals and ketals (including MEM, MOM, and THP ethers) to the corresponding aldehydes, ketones, and alcohols.[3] As part of a mechanistic study related to the cleavage of MEM ethers,[3] methanol–MEM ether (1; R = menthyl) was transformed by sequential treatment with dimethylboron bromide and methanol–triethylamine into the corresponding MOM ether 2 (Scheme I). The efficient formation of 2 strongly suggested the presence of the α-bromo ether 3 as the initial product of the cleavage reaction.

This facile route to the α-bromo ether intermediates 3,[4] combined with the general availability of primary, secondary, and tertiary MEM and MOM ethers[5] has prompted us to investigate the reaction of 3 with a variety of other nucleophiles with the intention of developing an approach for the formation of functionalities that are otherwise difficult to obtain. We are reporting herein on the successful utilization of this approach for the general preparation of *O,S*-acetals including MTM [(methylthio)methyl] ethers 4 (R′ = Me) and cyanomethyl ethers 5.

Results and Discussion

MTM ethers are useful functionalities for the protection of alcohols owing to their unique stability characteristics.[6]

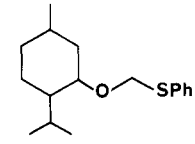
Scheme I



Moreover, they can be selectively removed under very mild conditions (e.g. $HgCl_2$, CH_3CN–H_2O[5], Me_2BBr[3]). However, their utilization in organic synthesis has been somewhat restricted due to problems encountered in their preparation. For example, halomethyl methyl sulfide–sodium hydride has been used for their preparation; however, this method is restricted to primary alcohols[6] and phenols.[7] Acetic anhydride–Me_2SO[8] is useful only for the protection of tertiary alcohols since primary and secondary alcohols are oxidized under these conditions.[9] The use of acetic acid–acetic anhydride–Me_2SO avoids some of these problems; however, prolonged reaction times are required.[10] More recently, modest yields of MTM ethers have been achieved with chloromethyl methyl sulfide–silver nitrate–triethylamine.[11]

Some of the results that we have obtained for the preparation of MTM ethers are summarized in Table I.[12,13] Under our experimental conditions, primary, secondary, and even tertiary MOM (methoxymethyl) and MEM [(2-methoxyethoxy)methyl] ethers are converted into the corresponding MTM ethers in high yield. Thus, treatment of a CH_2Cl_2 solution of menthol–MOM ether 8 with 2.0 equiv of dimethylboron bromide at −78 °C for 1 h and quenching with diisopropylethylamine and methanethiol gave, after flash chromatography, pure menthol–MTM ether 9 (91% yield) (entry 2). The only detectable side product was a small amount of the parent alcohol. It is noteworthy that benzylic (entry 5) and even tertiary allylic (entry 6) MEM and MOM ethers can be smoothly converted into the desired MTM ethers in good yield. The previously described routes to the latter compounds are generally less efficient.[11]

Other S-substituted thiomethyl ethers are also readily prepared utilizing this methodology. Thus, treatment of menthol-MEM ether 10 with dimethylboron bromide (2.0 equiv, CH_2Cl_2, −78 °C) and quenching with diisopropylethylamine (3.0 equiv) and thiophenol (2.5 equiv) produced the corresponding (phenylthio)methyl ether 21 (84%).



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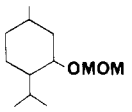
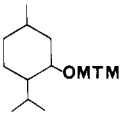
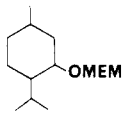
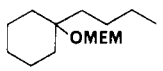
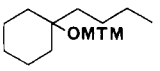
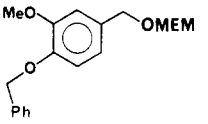
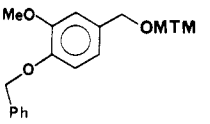
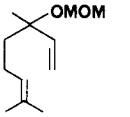
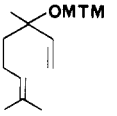
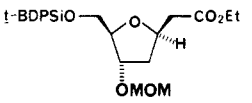
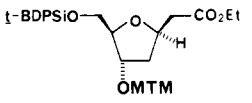
O,S-Acetals also find application as useful carbonyl protecting groups.[5] Cyclic *O,S*-acetals are readily obtain-

(1) Guindon, Y.; Atkinson, J. G.; Morton, H. E. *J. Org. Chem.* **1984**, *49*, 4538.
(2) Guindon, Y.; Yoakim, C.; Morton, H. E. *Tetrahedron Lett.* **1983**, 2969.
(3) (a) Guindon, Y.; Yoakim, C.; Morton, H. E. *J. Org. Chem.* **1984**, *49*, 3912. (b) Guindon, Y.; Morton, H. E.; Yoakim, C. *Tetrahedron Lett.* **1983**, 3969.
(4) To our knowledge, the use of other acetal-cleaving reagents such as Me_3SiBr does not permit the conversion of MEM and MOM ethers into α-bromo ethers 3. Hanessian, S.; Delorme, D.; Dufresne, Y. *Tetrahedron Lett.* **1984**, 2515.
(5) Green, T. W. "Protective Groups in Organic Synthesis"; Wiley-Interscience: New York, 1981 and references cited therein.
(6) Corey, E. J.; Bock, M. G. *Tetrahedron Lett.* **1975**, 3269.
(7) Holton, R. A.; Davis, R. G. *Tetrahedron Lett.* **1977**, 533.
(8) Yamada, K.; Kato, K.; Nagase, H.; Hirata, Y. *Tetrahedron Lett.* **1976**, 65.
(9) Albright, J. D.; Goldman, L. *J. Am. Chem. Soc.* **1967**, *89*, 2416.
(10) Pojer, P. M.; Angyal, S. J. *Aust. J. Chem.* **1978**, *31*, 1031.
(11) Suzuki, K.; Inanaga, J.; Yamaguchi, M. *Chem. Lett.* **1979**, 1277.
(12) Recently the interconversion of MEM ethers to isopropyl thiomethyl ethers using *i*-PrS_2BBr was reported. The utility of MOM ethers was not exemplified. Corey, E. J.; Hua, D. H.; Seitz, S. P. *Tetrahedron Lett.* **1984**, 3.
(13) All new compounds reported herein exhibited spectral properties (IR, ^{1}H NMR, MS) in full accord with their assigned structures and gave satisfactory combustion analyses.

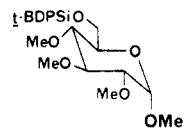
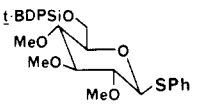
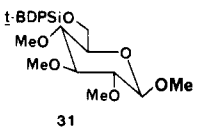
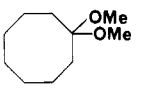
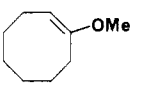
0022-3263/85/1950-5379$01.50/0

Table I. Interconversion of MEM and MOM Ethers to MTM Ethers[a]

ENTRY	SUBSTRATE	PRODUCT	YIELD (%)[b]
1	n-$C_{12}H_{25}$—OMOM (6)	n-$C_{12}H_{25}$—OMTM (7)	87
2	 (8)	 (9)	91
3	 (10)	9	89
4	 (11)	 (12)	90[c]
5	 (13)	 (14)	72[c,d]
6	 (15)	 (16)	79[c,e]
7	t-BDMSiO-(CH$_2$)$_8$OMOM (17)	t-BDMSiO-(CH$_2$)$_8$OMTM (18)	83
8	 (19)	 (20)	82

[a] Unless otherwise stated all reactions were carried out in CH_2Cl_2 using concentrations of 0.1 M in substrate and 2.0 equivalents of Me_2BBr at −78°C for 1h. iPr_2NEt (2.5 equiv.) and MeSH (3.0 equiv.) were then added. [b] Isolated yields of purified products. [c] iPr_2NEt (0.1 equiv.) was included with Me_2BBr as an acid scavenger. [d] 3.0 equiv. of Me_2BBr was used. A small amount (12%) of the corresponding benzyl methyl sulfide was also isolated. [e] The Me_2BBr cleavage reaction was quenched after 10 min at −78°C.

Table II. Interconversion of Acetal Derivatives[a]

ENTRY	SUBSTRATE	THIOL	PRODUCT	YIELD (%)[b]
1	n-C_8H_{17}-CH(OMe)$_2$ (22)	MeSH	n-C_8H_{17}-CH(OMe)SR (23 R = Me)	91
2	22	EtSH	24 R = Et	87
3	22	PhSH	25 R = Ph	93
4	n-C_8H_{17}-CH(OEt)$_2$ (26)	MeSH	n-C_8H_{17}-CH(OEt)SR (27 R = Me)	87
5	26	PhSH	28 R = Ph	89
6	 (29)	PhSH	 (30)	72[c]
7	 (31)	PhSH	30	74[c]
8	n-C_8H_{17}-CH(OMe)SEt (24)	PhSH	n-C_8H_{17}-CH(SPh)SEt (32)	79[d,e]
9	 (33)	MeSH	 (34)	72

[a] Unless otherwise stated all cleavage reactions were conducted in CH_2Cl_2 at 0.1 M in substrate using 2.0 equiv. of Me_2BBr at −78°C for 15 min. iPr_2NEt (2.5 equiv.) and RSH (3.0 equiv.) were then added. [b] Isolated yields of purified products. [c] 1.4 equiv. of Me_2BBr were used at rt for 18 h. This mixture was then treated with iPr_2NEt (2.0 equiv.) and PhSH (2.2 equiv.) at 0°C–rt for 1 h. [d] 3.0 equiv. of Me_2BBr were used at −78°C for 4h. [e] 10% of the diphenylthio acetal was also isolated.

able from the parent aldehydes (e.g. $HOCH_2CH_2SH$, H^+).[14] Acyclic *O,S*-acetals however, are usually prepared from dialkyl acetals by cumbersome acid-catalyzed exchange procedures.[15-17] We have found that our approach allows for the efficient conversion of dialkyl acetals to *O,S*-acetals as illustrated in Table II.

The results in Table II are quite straightforward, and it is particularly gratifying to note that dimethyl acetals can be transformed into *O*-methyl, *S*-alkyl, and *O*-methyl *S*-phenyl acetals in good yield (entries 1–3).[18] Under identical experimental conditions diethyl acetals work equally well (entries 4 and 5). Also, both α- and β-methyl glycosides are readily converted into the corresponding β-phenylthio glycosides in good yield (entries 6 and 7).[19]

(14) (a) Djerassi, C.; Gorman, M. *J. Am. Chem. Soc.* **1953**, *75*, 3704. (b) Romo, J.; Rosenkranz, G.; Djerassi, C. *Ibid.* **1951**, *73*, 4961.

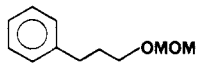
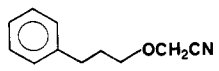
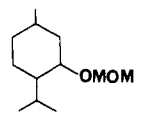
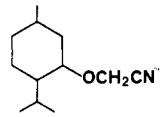
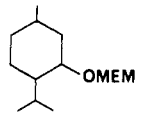
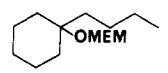
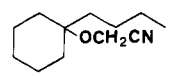
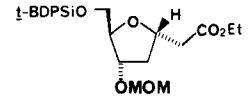
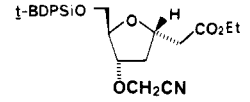
(15) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476.

(16) For interconversions of thioacetals to *O,S*-acetals using methyl fluorosulfonate (Magic Methyl) see: (a) Corey, E. J.; Hase, T. *Tetrahedron Lett.* **1975**, 3267. (b) Hase, T. A.; Kivikari, R. *Synth. Commun.* **1979**, *9*, 107.

(17) For the reactions of α-halo ethers with thio nucleophiles see: (a) Fife, T. H.; Anderson, E. *J. Am. Chem. Soc.* **1970**, *92*, 5464. (b) Hanessian, S.; Bacquet, C.; Lehong, N. *Carbohydr. Res.* **1980**, *80*, C17 and references cited therein.

(18) ^1H NMR analysis of the crude reaction products showed less than 5% of the corresponding *S,S*-acetals to be present.

Table III. Preparation of Cyanomethyl Ethers[a]

ENTRY	SUBSTRATE	PRODUCT	YIELD (%)[b]
1	 35	 36	84
2	n-$C_{12}H_{25}$—OMOM 6	n-$C_{12}H_{25}$—OCH_2CN 37	84
3	 8	 38	89
4	 10	38	79
5	 11	 39	82[c]
6	 40	 41	78
7	n-C_8H_{17}—C(OEt)$_2$ 26	n-C_8H_{17}—C(OEt)(CN) 42	82

[a] All cleavage reactions were carried out in CH_2Cl_2 at 0.2 M in substrate using 2.0 equiv. of Me_2BBr at −78°C for 1h. Excess reagent was then removed (see text) and n-Bu_4NCN (2.0 equiv.) was added at −78°C. [b] Isolated yields of purified product. [c] 0.1 equiv. of iPr_2NEt was included in the cleavage reaction as an acid scavenger.

The latter compounds serve as valuable intermediates in carbohydrate chemistry.[20] Thus, the present methodology represents an attractive alternative for the stereoselective preparation of these compounds.[20] The results in Table II also illustrate that *O,S*-acetals can be smoothly converted into mixed dithioacetals (entry 8). The only dialkyl ketal studied afforded an enol ether derivative under the present reaction conditions (entry 9).

Cyanomethyl ethers **5** are excellent acyl anion equivalents in intermolecular alkylation reactions.[21] To date, the preparation of these derivatives from simple aliphatic alcohols has been a difficult process.[22] Recently, the conversion of MEM ethers to cyanomethyl ethers under somewhat vigorous conditions using diethylaluminum cyanide (toluene, reflux) has been described.[12]

We have found that both MEM and MOM ethers can be directly converted into cyanomethyl ethers by sequential treatment with dimethylboron bromide and tetra-*n*-butylammonium cyanide[23] as illustrated in Table III. Under our experimental conditions[24] the reaction is equally applicable to the preparation of primary, secondary, and tertiary cyanomethyl ethers. The absence of nitrile or elimination byproducts in the conversion of the tertiary MEM ether **11** underscores the utility of this method (entry 5). It should also be noted that this methodology can be used for the formation of protected aldehyde cyanohydrins as shown by the efficient formation of **42**.

Previously,[1-3] we have shown that acetates, benzoates, and isolated olefins are essentially inert to dimethylboron bromide. In the present study we have found that MTM ethers, cyanomethyl ethers, and related derivatives can be prepared in the presence of other common protecting groups such as *tert*-butyldiphenylsilyl (*t*-BDPSi) and *tert*-butyldimethylsilyl (*t*-BDMSi) ethers, methyl ethers, benzyl ethers, and ethyl esters. This again demonstrates the value of the chemoselectivity of dimethylboron bromide.

Conclusion

In summary, dimethylboron bromide can be used efficiently, under mild conditions, for the interconversion of both MEM and MOM ethers into the corresponding MTM ethers in excellent yield. Under similar reaction conditions dialkyl acetals afford *O,S*-acetals. The utility of this methodology for the preparation of cyanomethyl ethers has also been exemplified.

Experimental Section

General Procedures. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 681 spectrophotometer. Proton nuclear magnetic resonance spectra (^1H NMR) were obtained on a Bruker AM 250 (250 MHz) spectrometer. Either tetramethylsilane or chloroform (δ 7.26) was used as the reference. Mass spectrometric (MS, 70 eV) measurements were performed by Morgan Schaffer (Montreal, Quebec, Canada) using a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Elemental analysis was performed by Guelph Chemical Laboratories Ltd. (Guelph, Ontario, Canada) or Galbraith Laboratories Inc. (Knoxville, TN).

Crude products were purified by flash chromatography using 230–400 mesh silica gel (E. Merck). The purity of known compounds was ascertained by TLC using commercial silica gel plates (Analtech, Uniplate-Silica Gel GF) and by spectral means (IR, ^1H NMR).

Glassware and syringes were dried in an oven (120 °C) prior to use. Methylene chloride, acetonitrile, and diisopropylethylamine were distilled from CaH_2 and stored over 4-Å molecular sieves.

Dimethylboron bromide was purchased from the Alfa Division of the Ventron Corp., or it was prepared as outlined previously.[3a] Care should be taken when manipulating neat dimethylboron bromide as it is *pyrophoric* when exposed to moist air. Solutions (1.8–1.5 M) of this reagent (CH_2Cl_2) have been stored at −5 °C

(19) In the ^1H NMR ($CDCl_3$, 250 MHz) the C_1 proton of **30** appeared as a doublet (J = 9.9 Hz) at δ 4.52, thus fully corroborating the assigned stereochemistry. Ogawa, T.; Matsui, M. *Carbohydr. Res.* **1977**, *54*, C17.

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(24) For best results, excess reagent and the dimethylborate byproduct were removed under vacuum (0.2–0.25 torr, −78 °C to room temperature) prior to the addition of cyanide. Addition of solvent and *n*-Bu_4NCN (−78 °C to room temperature) then afforded the desired products. The use of NaCN or KCN failed to provide useful yields of the cyanomethyl ethers.

for several months without noticeable decomposition or handling problems.

Tetra-*n*-butylammonium cyanide was purchased from Fluka and dried [60 °C (0.2 torr)] for 24 h prior to use. Solutions of this reagent were prepared in dry CH_3CN.

Preparation of MTM Ethers. A typical procedure follows: To a cold (−78 °C), stirred solution of menthol–MOM ether **8** (1 mmol) in 8.8 mL of dry CH_2Cl_2, under argon, was added a CH_2Cl_2 solution of dimethylboron bromide (1.73 M, 1.16 mL). The reaction mixture was stirred at −78 °C for 1 h and then treated with diisopropylethylamine (2.5 mmol) and a solution of methanethiol in CH_2Cl_2 (10 M, 0.3 mL). After 1 h at −78 °C the mixture was cannulated into a stirred mixture of THF (5 mL) and saturated aqueous $NaHCO_3$ (5 mL). Ether (50 mL) was then added. The organic layer was separated, washed with saturated aqueous $NaHCO_3$, water, and brine, and dried over $MgSO_4$. Removal of solvent and purification by flash chromatography gave pure menthol–MTM ether **9** (91%): IR (neat) 2955, 2920, 1061, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76–1.12 (m, 3 H), 0.79 (d, J = 6.8 Hz, 3 H), 0.88 (d, J = 8.2 Hz, 3 H), 0.90 (d, J = 6.5 Hz, 3 H), 1.23 (m, 1 H), 1.35 (br m, 1 H), 1.57–1.71 (m, 2 H), 2.02–2.30 (overlapping m, 2 H), 2.14 (s, 3 H), 3.38 (ddd, J = 10.5, 10.5, 4.1 Hz, 1 H), 4.62 (d, A part of AB, J = 11.8 Hz, 1 H), 4.68 (d, B part of AB, J = 11.8 Hz, 1 H); MS m/e (relative intensity) 216 (2), 169 (26), 139 (38), 83 (100), 61 (10). Anal. Calcd for $C_{12}H_{24}OS$: C, 66.61; H, 16.78. Found: C, 66.47; H, 16.81.

Preparation of *O,S*-Acetals. In a typical procedure these compounds were prepared essentially as outlined above. After the addition of diisopropylethylamine and the appropriate thiol the reaction mixtures were stirred at −78 °C for only 15 min. Workup using 10% aqueous K_2CO_3 in place of saturated aqueous $NaHCO_3$ (vide supra) and purification yielded the desired *O,S*-acetals.

Preparation of Cyanomethyl Ethers. A typical procedure follows: To a cold (−78 °C), stirred solution of dodecanol–MOM ether **6** (0.5 mmol) in 1.9 mL of dry CH_2Cl_2, under argon, was added a solution of dimethylboron bromide (1.56 M, 0.64 mL) in CH_2Cl_2. After 1 h at −78 °C, solvent and excess reagent were removed under vacuum (0.25 torr, −78 °C to room temperature). The resultant material was dissolved in 2.5 mL of CH_2Cl_2, cooled to −78 °C, and then treated with a solution of *n*-Bu_4NCN (1.0 M, 1.5 mL) in CH_3CN. Stirring was continued at −78 °C for 1 h and room temperature for 1 h. Saturated aqueous $NaHCO_3$ (5 mL) and ether (50 mL) were then added. The organic layer was washed with saturated aqueous $NaHCO_3$, water, and brine and dried over $MgSO_4$. Concentration and purification by flash chromatography gave pure cyanomethyl ether **37** (84%): IR (neat) 2923, 2855, 1111 cm^{-1} (the CN absorption was not observed, see ref 22); ^1H NMR ($CDCl_3$) δ 0.88 (br t, 3 H), 1.22–1.40 (m, 18 H), 1.56–1.66 (m, 2 H), 3.58 (t, J = 6.0 Hz, 2 H), 4.24 (s, 2 H). Anal. Calcd for $C_{14}H_{27}ON$: C, 74.61; H, 12.08. Found: C, 74.80; H, 12.25.

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Registry No. **6**, 34458-41-8; **7**, 87770-95-4; **8**, 91898-14-5; **9**, 99054-41-8; **10**, 91898-15-6; **11**, 87770-94-3; **12**, 99054-42-9; **13**, 99054-38-3; **14**, 99054-43-0; **15**, 99054-39-4; **16**, 59304-70-0; **17**, 91898-33-8; **18**, 99054-44-1; **19**, 99054-40-7; **20**, 99096-76-1; **21**, 99054-58-7; **22**, 18824-63-0; **23**, 99054-46-3; **24**, 99054-45-2; **25**, 99054-47-4; **26**, 54815-13-3; **27**, 99054-48-5; **28**, 99054-49-6; **29**, 91898-23-6; **30**, 99054-50-9; **31**, 91928-35-7; **32**, 99054-51-0; **33**, 25632-03-5; **34**, 50438-51-2; **35**, 91898-11-2; **36**, 99054-52-1; **37**, 70282-70-1; **38**, 99054-53-2; **39**, 99054-54-3; **40**, 99054-55-4; **41**, 99054-56-5; **42**, 99054-57-6; Me_2BBr, 5158-50-9; *i*-Pr_2NEt, 7087-68-5; MeSH, 74-93-1; Br_4NCN, 10442-39-4; EtSH, 75-08-1; PhSH, 108-98-5; 4-(benzyloxy)-3-methoxybenzyl methyl sulfide, 99054-59-8.

Supplementary Material Available: Full characterization data (IR, ^1H NMR, mass spectral, chemical analysis) for all new compounds (5 pages). Ordering information is given on any current masthead page.

Applications of Di-*tert*-butyliminoxyl Radical to Organic Synthesis. Oxidation of Amines to Imines[1]

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Most iminoxyl radicals can be observed only in the form of transients by EPR spectroscopy. However, the highly hindered di-*tert*-butyliminoxyl radical (**1**) is sufficiently long-lived for it to be isolated as a volatile, blue liquid.[2,3] In inert solvents it decays with bimolecular kinetics to yield an O–C coupled dimer.[2]

$$\underset{\mathbf{1}}{t\text{-}Bu_2C{=}NO\cdot} \qquad \underset{\mathbf{2}}{t\text{-}Bu_2C{=}NOH}$$

In preliminary studies[2,4] it was shown that **1** abstracts hydrogen from a variety of organic compounds. We have previously studied the di-*tert*-butyliminoxyl-mediated oxidation of a variety of phenols at room temperature and found the radical to be an efficient reagent for the synthesis of quinones and related oxidation–addition compounds.[5] The reduction of the radical regenerates the parent oxime **2**, which can be separated from the reaction medium and reconverted into **1**.

Both in the former and present study it was advantageous to have an inexpensive and efficient synthesis of **1**. In the original study,[2,4] oxime **2** was oxidized to **1** with silver oxide in benzene. We now report a very straightforward approach that makes use of ceric ammonium nitrate to perform the oxidation of **2** in methanol in a few minutes at room temperature. The radical **1**, which gives a blue solution, can be used directly in methanol, extracted into pentane or hexane, or recovered neat after evaporation of the solvent. We have consistently obtained yields around 80% of **1** with this method, as long as an exact 1:1 molar ratio of starting reagents is present, since ceric ion also destroys the radical. The blue color of the radical is due to a weak absorption extending from about 530 to beyond 800 nm and can be used for spectrometric quantitation.

We have explored the feasibility of a direct, room-temperature dehydrogenation of primary and secondary amines with **1** to give the corresponding imines. In general, the literature procedures[6] for dehydrogenation of amines to imines do not have a wide scope and usually require strong conditions.

We report here the direct conversion of primary and secondary amines to imines with **1** in pentane or hexane under mild conditions. Due to the high inherent reactivity of most imines, in the initial attempts it was chosen to transform the imines in situ to the 2,4-dinitrophenylhydrazine derivatives of the corresponding carbonyl compounds.[7] *N*-Benzylmethylamine (**3**) was then chosen to carry out a detailed HPLC study of the reaction since the derived imine, *N*-benzylidenemethylamine (**4**) is commercially available and suitable as a reference compound in product analysis. The results are summarized in Table I.

For the cases when the 2,4-dinitrophenylhydrazine derivative isolation was used, the reported reaction time

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