The resultant cloudy solution was stirred for 70 min at −78 °C, triethylamine (27.0 mL, 193.7 mmol) was added, and the milky white solution was stirred for 30 min at that temperature. The reaction was allowed to warm gradually to ambient temperature; after 3 h water (100 mL) was added, and the separated organic layer washed sequentially with aqueous ammonium chloride (25 mL, saturated), aqueous sodium bicarbonate (25 mL, saturated), and brine (50 mL). The organic layer was dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure. Flash chromatography (20% hexanes in ethyl acetate) allowed isolation of 2.36 g (89%) of the dione at a white solid: mp = 65–66 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.53–2.47 (m, 8 H, C(O)CH_2), 2.17–2.10 (m, 4 H, C(O)CH$_2$CH_2); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 213.0, 42.2, 22.1; IR ($CHCl_3$) 1711 (s).

1,5-Bis[(trimethylsilyl)oxy]-1,4-cyclooctadiene (2). To a solution of 1,5-cyclooctanedione (0.3025 g, 2.158 mmol) in 20 mL of THF at ambient temperature under nitrogen was added trimethylsilyl triflate (2.5 mL, 12.94 mmol), followed by triethylamine (3.60 mL, 25.83 mmol), both via syringe. After 2.5 h, most of the solvent was removed from the dark solution under reduced pressure, and the residue was diluted with 20 mL of hexanes and stirred vigorously for several minutes. After stirring was discontinued, the upper hexane layer was transferred into an Erlenmeyer flask, and the hexanes extraction process was repeated two more times on the residual oil. The combined hexane layers were dried over magnesium sulfate and then filtered through a short column of silica gel. Solvents were removed to leave 0.6088 g (99%) of a light yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.88 (t, J = 6.4, 2 H, C(OTMS)=CH), 2.61 (t, J = 6.4, 2 H, C(OTMS)=CHCH_2), 2.32–2.24 (m, 4 H, CH_2C(OTMS)=CH), 1.60–1.49 (m, 2 H, CH_2CH$_2$C(OTMS)=), 0.17 (s, 18 H, Si(CH_3)$_3$).

(1α,5α,7α,9α)-Tricyclo[7.1.0.0^{5,7}]decane-1,5-diol (3). A flask containing the bis(silyl enol) ether **2** (0.6088 g, 2.14 mmol) in 15 mL of ether was fitted with a magnetic stirbar, a reflux condenser, and a calcium chloride drying tube. No nitrogen line was attached. Diethylzinc (14.4 mL, 0.89 M, 12.8 mmol) was added via syringe, followed by methylene iodide (1.7 mL, 21.1 mmol). The mixture was gently refluxed under dry air for 3 h and then allowed to stir at room temperature overnight. The reaction was quenched by addition of saturated aqueous ammonium chloride (10 mL), and then the organic products were extracted with 60 mL of ether. The organic layer was washed with saturated aqueous sodium thiosulfate (5 mL) and brine (5 mL) and then dried over sodium sulfate. Solvent was removed to leave 0.696 g of an oil, which was taken up in 60 mL of THF and treated with n-Bu$_4$NF (7 mL, 1 M in THF, 7 mmol). After 1 h, solvent was removed under reduced pressure, and the residue was diluted with 100 mL of ethyl acetate. The organic layer was washed with saturated aqueous sodium bicarbonate (10 mL), and then the aqueous layer was back extracted with two portions of ethyl acetate (25 mL each). The combined organic layers were dried over sodium sulfate, and the solvent was removed to leave about 1 g of a crude oil. Flash chromatography (ethyl acetate) provided 0.277 g (77%) of the pure product as a white solid. X-ray quality crystals were grown from methylene chloride/ether/petroleum ether: mp 128–130 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.64 (s, 2 H, OH), 2.43 (dd, J = 15.3, 7.2, 2 H, CHHC(OH)(CH$_2$)CH), 2.22 (dt, J = 14.2, 3.3, 1 H, C(OH)(CH$_2$)CHCHH), 2.00 (dt, J = 14.9, 12.1, 1 H, CHHCH$_2$C(OH)(CH$_2$)CH), 1.45 (dt, J = 14.9, 7.2, 1 H, CHHCH$_2$C(OH)(CH$_2$)CH), 1.28–1.17 (m, 2 H, CH$_2$CH$_2$C(OH)(CH$_2$)CHCH$_2$), 1.09 (dd, J = 15.3, 12.1, 2 H, CH$_2$CHHC(OH)(CH$_2$)CH), 0.87 (dd, J = 10.3, 5.2, 2 H, C(OH)(CHH)CH), 0.2 (m, 1 H, C(OH)(CH$_2$)CHCHH), 0.16 (dd, J = 6.7, 5.2, 2 H, C(OH)(CHH)CH); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 58.8, 38.3, 30.5, 27.5, 20.0, 18.6; IR ($CHCl_3$) 3395 (broad, s). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.46; H, 9.62.

***syn*-2,4-Dimethyl-1,5-cyclooctanedione (4).** To a solution of the bis(cyclopropyl) diol (0.0212 g, 0.126 mmol) in 1 mL of benzene was added amberlyst-15 (0.020 g). The solution was stirred at room temperature under nitrogen overnight and then passed through a plug of $MgSO_4$. Solvent was removed, and the solid residue was purified using flash chromatography (5% ether in methylene chloride, then 20% ether in methylene chloride) to give 0.0167 g (79%) of the diketone as a 3/1 mixture of diastereomers favoring the *syn*-2,4-dimethyl compound. Data reported is for the HPLC purified major product. X-ray quality crystals were grown from ether/petroleum ether: mp 75–76 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.81–2.74 (dqd, J = 12.0, 6.8, 3.3, 2 H, C(O)CHCH$_3$CHH), 2.55–2.49 (ddd, J = 13.0, 13.0, 3.6, 2 H, C(O)CHH), 2.43–2.39 (ddd, J = 13.0, 5.7, 3.5, 2 H, C(O)CHH), 2.37–2.28 (m, 1 H, C(O)CHHCHH), 2.09–2.02 (m, 1 H, C(O)CHHCHH), 1.85–1.77 (dt, J = 14.0, 12.0, 1 H, C(O)CHCH$_3$CHH), 1.67–1.63 (dt, J = 14.0, 3.3, 1 H, C(O)CHCH$_3$CHH), 1.08 (d, J = 6.8, 6 H, C(O)CHCH_3CHH); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 215.5, 45.7, 40.9, 39.7, 22.0, 18.3; IR ($CHCl_3$) 1713 (s).

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Registry No. 1, 1489-74-3; 2, 123540-61-4; 3, 123540-62-5; 3 (bis(trimethylsilyl) ether), 123540-64-7; *syn*-4, 123540-63-6; *anti*-4, 123540-65-8; *cis*-1,5-cyclooctanediol, 23418-82-8.

Supplementary Material Available: Protocols, fractional coordinates, bond distances, torsional angles, and anisotropic temperature factors for the X-ray crystallographic determinations of compounds 3 and 4 (9 pages). Ordering information is given on any current masthead page.

An Improved Procedure for the Conversion of Amines to Alcohols at Low Temperature

Nicholas Nikolaides and Bruce Ganem*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

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One of the best methods for converting aliphatic amines to alcohols involves thermal rearrangement of the corresponding *N*-nitrosoamides (eq 1). This well-studied process[1-3] continues to find new and useful applications.[4-6] The normal experimental procedure for *n*-alkylamines entails isolating and heating the preformed *N*-nitrosoamide **1** for several hours in a nonpolar solvent such as hexane, whereupon transient diazoester **2** is produced. Smooth breakdown of **2** at 70–80 °C to the diazoalkane **3**[7] furnishes ester **4**, which can be saponified to **5**. We now report a milder procedure in which primary *n*-alkylamines are first converted to the corresponding trifluoro- or trichloroacetamides **6** and then nitrosated at 0 °C in acetic acid–acetic anhydride. Accelerated rearrangement to **3** in the presence of excess HOAc leads to acetates **7** (eq 2) without isolation of any intermediates. Besides being simple and

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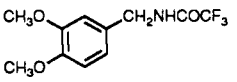
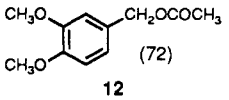
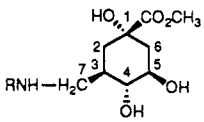
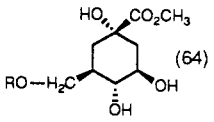
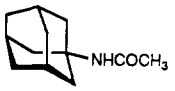
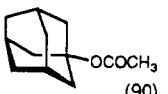
Table I. Preparation of Alcohols from Amines by Rearrangement of *N*-Nitrosoamides to Esters

entry	amide	conditions	product (yield, %)
1	$CH_3(CH_2)_9NHCOCF_3$ **8**	0 °C, 18 h	$CH_3(CH_2)_9OCOCH_3$ (77) **9**
2	$CH_3(CH_2)_9NHCOCCl_3$ **10**	0 °C, 10 h	$CH_3(CH_2)_9OCOCH_3$ (70) **9**
3	 **11**	0 °C, 16 h	 (72) **12**
4	 **13**, R = H **14**, R = $COCF_3$	10 °C, 17 h	 (64) **15**, R = $COCH_3$ **16**, R = H
5	 **17**	rt, 16 h	 (90) **18**

efficient, the technique is compatible with many functional groups. Good results were obtained with five represent-

$$RCH_2NH_2 \xrightarrow[2.\ N_2O_4,\ Na_2CO_3]{1.\ R'COCl} RCH_2N(NO)COR' \xrightarrow{\text{hexane, 70 °C}} [RCH_2N{=}N\text{-}OCOR']$$

$$\underset{\mathbf{3}}{RCH{=}N_2} \rightarrow \underset{\mathbf{4}}{RCH_2OCOR'} \xrightarrow{NaOH} \underset{\mathbf{5}}{RCH_2OH} \quad (1)$$

$$\underset{\mathbf{1}}{RCH_2NH_2} \xrightarrow[CCl_3COCl]{(CF_3CO)_2O\ or} \underset{\mathbf{6}}{RCH_2NHCOCX_3} \xrightarrow{NaNO_2,\ HOAc,\ Ac_2O,\ 0\ °C} \underset{\mathbf{7}}{RCH_2OAc} \rightarrow \mathbf{5} \quad (2)$$

ative structures as summarized in Table I. Nitrosation of the trihaloacetamides **6** was slow in most organic solvents, even in the presence of Na_2CO_3, but proceeded at an acceptable rate in acetic acid–acetic anhydride. From preliminary work with mono- and dihaloacetamides as well as earlier studies on triflamides by White,[4] it was expected that rearrangement of the corresponding *N*-nitrosotrihaloacetamides **1** would be rapid. In fact no transient intermediates were observed at 0 °C. Entries 1 and 2 indicate that the reaction works equally well with trifluoro- and trichloroacetamides. Only ca. 5% of the isomeric 2-decyl acetate was detected as a secondary product. Likewise veratrylamine (entry 3) furnished veratryl acetate **12** in good yield. In entry 4 the relatively complex aminotriol **13** led smoothly as its trifluoroacetamide **14** to **15** whose structure was confirmed by hydrolysis in base to the corresponding tetraol **16**, a key intermediate in the synthesis of a useful shikimate pathway enzyme inhibitor.[8] It should be noted that **15** was formed cleanly as the primary monoacetate without any ring expansion, acyl migration, or concomitant esterification of the free hydroxyl groups.

Trifluoroacetamides of *sec*- and *tert*-alkylamines were not nitrosated under these mildly acidic conditions. Contrary to a literature report, however,[9] the corresponding acetamides did react with $NaNO_2$ in HOAc–Ac_2O at 0 °C and spontaneously rearranged at room temperature. While 2-octylacetamide produced 2-octyl acetate in only 16% yield at room temperature, *N*-1-adamantylacetamide **17** smoothly formed 1-adamantyl acetate **18** in 90% yield (entry 5). Obviously diazoalkanes are not involved in this reaction: direct solvolysis of the corresponding intermediate **2** must form a tertiary carbocation, which undergoes rapid nucleophilic capture by the acetic acid solvent.

In conclusion, a useful rearrangement of nitrosoamides to esters has been improved. When compared to other deamination techniques, including the triazene,[10] triphenylpyridinium,[11] and sulfonimide[12] methods, the very simple modifications described here should prove particularly valuable in the synthesis of alkanols from amines under mild conditions.

Experimental Section

Proton NMR spectra were taken on a Bruker WM-300 (300 MHz) spectrometer. All chemical shifts were reported on the δ scale in parts per million downfield from Me_4Si. Spectra taken in $CDCl_3$ were referenced to residual $CHCl_3$ (7.24 ppm) while spectra in D_2O were referenced to HOD (4.80 ppm). Infrared spectra were obtained on a Perkin-Elmer Model 681 infrared spectrometer and calibrated with polystyrene. Chemical ionization mass spectra (CIMS) were obtained on an AEI MS-902 or Kratos MS-890 instrument using isobutane or methane as reagent gas. Thin-layer chromatography was performed on silica gel 60 F-254 precoated plates (Brinkman). Flash chromatography was performed using silica gel 60 (230–400 mesh, Merck). Acetic acid and acetic anhydride were reagent grade (Aldrich). Sodium nitrite (analytical reagent grade) was obtained from Mallinckrodt. Except for **14**, all trifluoroacetamides were known compounds and prepared by reacting the corresponding amines with trifluoroacetic anhydride in pyridine. In the case of **9**, **12**, and **18**, products were identified by comparison with authentic samples.

Preparation of 3,4-Dimethoxybenzyl Acetate (12): General Procedure for Nitrosation and Rearrangement of Trihaloacetamides. To a solution of **11** (200 mg, 0.76 mmol) in glacial acetic acid (2.5 mL) and acetic anhydride (5 mL) at 0 °C was added $NaNO_2$ (524 mg, 7.6 mmol, 10 equiv). The resulting solution was stirred under Ar at 0 °C for 16 h and then poured over ice and extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (50 mL), 5% Na_2CO_3 (2 × 50 mL), water (50 mL), and saturated NaCl (50 mL) and dried over $MgSO_4$. The dry extracts were filtered and then concentrated in vacuo, and the crude product was purified by flash

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chromatography (3:1 hexane–ethyl acetate) to afford veratryl acetate **12** (114 mg, 72%) as an oil.

Preparation of *n*-Decyl Acetate (9) from *N*-*n*-Decyltrifluoroacetamide (8). From trifluoroacetamide **8** (200 mg, 0.99 mmol) and $NaNO_2$ (683 mg, 10 equiv) in acetic acid (3 mL) and acetic anhydride (6 mL) at 0 °C in 18 h was obtained *n*-decyl acetate **9** (153 mg, 77%).

Preparation of *n*-Decyl Acetate (9) from *N*-*n*-Decyltrichloroacetamide (10). From trichloroacetamide **10** (200 mg, 0.66 mmol) and $NaNO_2$ (528 mg, 6 equiv) in acetic acid (5 mL) and acetic anhydride (10 mL) at 0 °C in 10 h was obtained *n*-decyl acetate **9** (93 mg, 70%).

Preparation of Trifluoroacetamide 14 and Rearrangement to Monoacetate 15. To a solution of aminotriol **13** (25 mg, 0.10 mmol) in dry pyridine (1 mL) containing (*N*,*N*-dimethylamino)pyridine (2 mg) was added trifluoroacetic anhydride (63 mg, 3 equiv) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. Pyridine was removed in vacuo, and the residue was dissolved in water (5 mL). After extracting with $CHCl_3$ (3 × 5 mL) to remove impurities, the aqueous phase was freeze-dried to afford the crude trifluoroacetamide. Flash chromatography (10:1 CH_2Cl_2–CH_3OH) afforded pure **14** (30 mg, 95%): mp 156–158 °C; ^1H NMR (D_2O) δ 3.81 (3 H, s, OCH_3), 3.80 (1 H, m, H-5), 3.65 (1 H, dd, J = 13.8, 4.2 Hz, H-7), 3.46 (1 H, dd, J = 13.6, 7.3 Hz, H-7′), 3.32 (1 H, dd, J = 10.2, 9.8 Hz, H-4), 2.21–2.02 (2 H, m, H-2_{eq}, H-3), 1.89 (2 H, m, H-2_{ax}, H-6_{eq}), 1.74 (1 H, dd, J = 13.4, 11.4 Hz, H-6_{ax}); IR (KBr) 3428, 1704–1734, 1262, 1139, 804 cm^{-1}; CIMS (m/e) 316 (5.6, M + 1).

To a solution of **14** (20 mg, 0.06 mmol) in acetic acid (250 μL) and acetic anhydride (500 μL) at 0 °C was added $NaNO_2$ (42 mg, 10 equiv). The reaction mixture was stirred for 17 h at 10 °C, poured over ice, and extracted with CH_2Cl_2 (3 × 10 mL) to remove impurities. The residual aqueous layer was freze-dried to afford crude monoacetate. Flash chromatography (10:1 CH_2Cl_2–CH_3OH) afforded pure **15** as a clear oil (10 mg, 65%): ^1H NMR ($CDCl_3$) δ 4.29 (2 H, br s, H-7, H-7′), 3.84 (3 H, s, OCH_3), 3.83 (1 H, m, H-5), 3.44 (1 H, dd, J = 10.3, 9.9 Hz), 2.17 (3 H, s, $OCOCH_3$), 2.31–1.91 (5 H, br m, H-6_{ax}, H-6_{eq}, H-2_{ax}, H-2_{eq}, H-3); IR (KBr) 3400, 1740–1700 (broad), 1280, 1215, 1145, 1060 cm^{-1}; CIMS m/e (relative intensity) 263 (M + 1, 21), 245 (M + 1 - H_2O, 13), 227 (M + 1 - $2H_2O$, 20%).

To a solution of monoacetate **15** (10 mg, 0.04 mmol) in anhydrous CH_3OH (0.4 mL) was added 1% KOH in CH_3OH (2 equiv). The solution was stirred at room temperature for 2 h and then concentrated in vacuo, and the residue was chromatographed (4:1 CH_2Cl_2–CH_3OH) to afford pure tetrol **16** (8 mg, 91%) as a colorless oil, identical in every respect with a previously prepared sample:[7] $[\alpha]_D$ +5.3° (c = 1.5, H_2O); ^1H NMr (D_2O) δ 3.82 (3 H, s, OCH_3) 3.77 (2 H, br s, H-7, H-7′), 3.38 (1 H, dd, J = 9.7, 9.6 Hz, H-4), 2.16 (1 H, ddd, J = 13.5, 4.6, 2.9 Hz, H-6_{eq}), 1.98–1.87 (4 H, br m, H-6_{ax}, H-2_{ax}, H-2_{eq}, H-3); IR (film) 3350, 1735, 1240, 1060 cm^{-1}; CIMS m/e 221 (5, M + 1).

Preparation of 1-Adamantyl Acetate (18) from *N*-1-Adamantylacetamide (17). To a solution of **17** (Aldrich; 500 mg, 2.6 mmol) in glacial acetic acid (9 mL) and acetic anhydride (17 mL) at 0 °C was added $NaNO_2$ (1.80 g, 26 mmol, 10 equiv). The resulting solution was stirred at 0 °C for 15 min, slowly warmed to room temperature, and stirred for 16 h. The reaction mixture was then poured into ice and extracted with ether (3 × 50 mL). The combined organic extracts were washed with water (50 mL), 5% Na_2CO_3 (2 × 50 mL), water (50 mL), and saturated NaCl (50 mL). After drying ($MgSO_4$) and filtration, the extracts were concentrated in vacuo to a white solid. Flash column chromatography (9:1 hexane–ethyl acetate) afforded pure 1-adamantyl acetate **18** (455 mg, 90%), which was identical in every respect with an authentic sample prepared by acetylation of 1-adamantanol.

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Registry No. **8**, 10574-25-1; **9**, 112-17-4; **10**, 123488-80-2; **11**, 122365-02-0; **12**, 53751-40-9; **13**, 123488-81-3; **14**, 123488-82-4; **15**, 123488-83-5; **16**, 123488-84-6; **17**, 880-52-4; **18**, 22635-62-7.

[[2-(Methylthio)phenyl]thio]methyl (MTPM): A New Protecting Group of Hydroxyl Groups Capable of Conversion to a Methyl Group

Mitsuo Sekine*,[1] and Takeshi Nakanishi

Department of Life Chemistry, Tokyo Institute of Technology, Nagatsuta, Midoriku, Yokohama 227, Japan

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In the synthesis of natural products having complex structures such as macrolides, carbohydrates, and nucleosides, selective protection of a certain functionality is of great importance to realize stepwise construction of target molecules. In particular, the hydroxyl group has been masked with a wide variety of protecting groups during chemical conversions of other functional groups.[2-4] In this paper, we describe [[2-(methylthio)phenyl]thio]-methyl (MPTM) as a new type of protecting group of primary and secondary alcoholic functions, which can also serve as a precursor of the methyl group.

In a previous paper,[5] we reported that the 1,3-benzodithiol-2-yl (BDT) group could be converted to the methyl group via reductive C–S bond cleavage by Raney nickel. When this Raney nickel reduction was applied to the synthesis of 5′-*O*-methylthymidine (**2**) via 5′-*O*-(1,3-benzodithiol-2-yl)thymidine (**1**),[6] the yield (15–51%) of **2** varied depending on the freshness and the strong adsorptive property of the Ni surface.[7] In the hope of finding a more effective method for this conversion, reaction of **1** with 2.5 equiv of tributyltin hydride (TBTH)[8,9] was carried out in benzene in the presence of azobis(isobutyronitrile) (AIBN) under reflux for 1.5 h (Scheme I). However, this reaction did not give the desired product **2** but afforded instead quantitatively ring-opened product **3** on the basis of TLC analysis.[10] Isolation of this product by silica gel column chromatography caused considerable decomposition. Nevertheless, **3** was isolated in 36% yield and characterized.[11] The C–SAr bond of **3** was not reduced by TBTH upon prolonged heating. Since this result was rationalized in terms of the presence of the sterically hindered *o*-(tributylstannyl)thio group, the in situ S-methylation of **3** to form less hindered synthetic intermediate **4** was attempted. It was found that the methylation of **3** with 10 equiv of MeI was dependent upon the solvents employed. Benzene, dichloromethane, acetone, acetonitrile, and 2-propanol were ineffective. In contrast, it was found that treatment of **3** with MeI in dimethylformamide at room temperature for 2.5 h gave **4** in an optimized yield of 85%. In tetrahydrofuran (THF), the reaction proceeded rather slowly to give the desired *S*-methyl product **4** in ca. 60% yield after 2 days. Interestingly, the S-methylation was accelerated by addition

(1) The present address is Department of Environment Chemistry and Engineering, Tokyo Institute of Technology, Nagatsuta, Midoriku, Yokohama 227.

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(11) Gutierrez[10] also described that considerable decomposition of *S*-tributylstannane derivatives occurred during silica gel chromatography.

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