Table I. Pictet-Spengler Reactions

compd no.	tryptamine R_1	tryptamine R_2	tryptamine R_3	alkyne R_4	alkyne R_5	tetrahydro-β-carboline	% yield	mp, °C (solvent of cryst)
1	H	H	H	CO_2CH_3	CO_2CH_3	9	83	127 (ether–methanol, 1:1)
2	H	H	C_2H_5	CO_2CH_3	CO_2CH_3	10	89.5	112 (ether–methanol, 1:4)
3	H	CH_3	H	CO_2CH_3	CO_2CH_3	11	74.5	
4	H	CH_3	$CH_2C_6H_5$	CO_2CH_3	CO_2CH_3	12	92	
5	OCH_3	H	H	CO_2CH_3	CO_2CH_3	13	72.5	148
6	H	H	$CH_2CO_2CH_3$	CO_2CH_3	CO_2CH_3	14	91.5	
7	H	H	$CH_2C_6H_5$	CO_2CH_3	CO_2CH_3	15	99.5	148 (ethanol)
7	H	H	$CH_2C_6H_5$	H	CO_2CH_3	16	85	
7	H	H	$CH_2C_6H_5$	H	$COCH_3$	17	76	189 (ether)

10 g, 40 mmol), in 100 mL of $CHCl_3$, one adds in sequence dimethyl acetylenedicarboxylate (5.68 g, 40 mmol, 1 equiv) and trifluoroacetic acid (3.6 mL and then 3.5 mL, 2.4 equiv) at 5-min intervals with continuous stirring at room temperature. After 10 min, the reaction mixture is poured into 100 mL of water and made alkaline by an excess of aqueous 6 N NaOH. The organic layer is separated, washed with water, dried over Na_2SO_4, filtered, and evaporated in vacuo to afford 15.6 g of a white foam, homogeneous on TLC. An analytical sample is obtained by crystallization from ethanol (mp 148 °C): UV λ_{max}^{MeOH} 229 nm, 277, 281, 288; IR ν 3400, 1720, 1205 cm^{-1}; MS, m/e 392 ($M^{+\cdot}$, 1.5), 333 (100), 319 (7), 91 (65); ^1H NMR (401 MHz, $CDCl_3$) δ 9.3 (1 H, s), 4.15 and 3.50 (2 H, AB system, J = 14 Hz), 3.78 and 3.73 (2 × 3 H, s), 3.47 and 3.0 (2 H, AB system, J = 17 Hz). Anal. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.4; H, 6.1; N, 7.1. Found: 70.5; H, 6.1; N, 7.2.

Spectral Data for New Compounds. Data for 9: UV λ_{max}^{MeOH} 226 nm, 275, 282, 291; IR (Nujol) 3360, 1725, 1710, 1700 cm^{-1}; MS, m/e 302 ($M^{+\cdot}$, 12, $C_{16}H_{18}N_2O_4$), 244 (15), 243 (100), 229 (14), 211 (8), 144 (7); ^1H NMR (401 MHz, $CDCl_3$) 8.37 (1 H, s), 3.83 and 3.72 (2 × 3 H, s), 3.35 and 2.94 (2 H, AB system, J = 17 Hz).

Data for 10: UV λ_{max}^{MeOH} 227 nm, 276, 281, 288; IR ν 3400, 1730, 1720 cm^{-1}; MS, m/e 330 ($M^{+\cdot}$, 2), 271 (100), 257 (8); ^1H NMR (401 MHz, $CDCl_3$) δ 9.22 (1 H, s), 3.71 and 3.7 (2 × 3 H, s), 3.32 and 2.85 (2 H, AB system, J = 17 Hz), 1.15 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{18}H_{22}N_2O_4$: C, 65.4; H, 6.7; N, 8.5. Found: C, 65.4; H, 6.7; N, 8.6.

Data for 11: UV λ_{max}^{MeOH} 229 nm, 279, 289, 297; IR ν 3340, 1730, 1200 cm^{-1}; MS, m/e 316 ($M^{+\cdot}$, 11, $C_{17}H_{20}N_2O_4$), 257 (100), 243 (8), 225 (12), 158 (15), 144 (7); ^1H NMR (60 MHz, $CDCl_3$) 3.75 (6 H, s), 3.6 (3 H, s), 3.45 and 2.95 (2 H, AB system, J = 17 Hz).

Data for 12: UV λ_{max}^{MeOH} 231 nm, 278 (sh), 287, 295 (sh); IR ν 1725, 1690, 1220, 730 cm^{-1}; MS, m/e 406 ($M^{+\cdot}$, 4, $C_{24}H_{26}N_2O_4$), 347 (100), 333 (11), 271 (16), 157 (13), 91 (83); ^1H NMR (60 MHz, $CDCl_3$) δ 4.05 (1 H, d, J = 14 Hz), 3.8 (3 H, s), 3.65 (3 H, s), 3.35 (3 H, s).

Data for 13: UV λ_{max}^{MeOH} 230 nm, 280, 300 (sh), 310; IR (Nujol) ν 3360, 1725, 1700 cm^{-1}; MS, m/e 332 ($M^{+\cdot}$, 9, $C_{17}H_{20}N_2O_5$), 273 (100), 259 (19), 174 (10); ^1H NMR (60 MHz, $CDCl_3$) δ 9.1 (1 H, s), 3.9 (3 H, s), 1.7 (3 H, s).

Data for 14: UV λ_{max}^{MeOH} 227 nm, 278, 282, 288; IR ν 3400, 1745, 1730, 1715, 1200 cm^{-1}; MS, m/e 374 ($M^{+\cdot}$, 2.5, $C_{19}H_{22}N_2O_6$), 315 (100), 301 (10), 283 (17); ^1H NMR (60 MHz, $CDCl_3$) δ 9.45 (1 H, s), 3.85 (6 H, s), 3.8 (3 H, s), 3.65 (2 H, s).

Data for 16: UV λ_{max}^{MeOH} 232 nm, 273, 282, 290; IR ν 3400, 1730 cm^{-1}; MS, m/e 334 ($M^{+\cdot}$, 18, $C_{21}H_{22}N_2O_2$), 261 (100), 169 (35), 154 (15), 91 (100); ^1H NMR (401 MHz, $CDCl_3$) δ 8.47 (1 H, s), 4.21 (1 H, dd, J = 4.5, 9.5 Hz), 3.82 (2 H, s), 3.73 (3 H, s), 2.98 (1 H, dd, J = 4.5, 16 Hz), 2.86 (1 H, dd, J = 9.5, 16 Hz).

Data for 18: UV_{max}^{MeOH} 228 nm, 281, 289; IR (Nujol) ν 3320, 1690, 1625 cm^{-1}; MS, m/e 318 ($M^{+\cdot}$, 14, $C_{21}H_{22}N_2O$), 261 (100), 199 (22), 169 (15), 156 (22), 91 (88); ^1H NMR (60 MHz, $CDCl_3$) δ 8.9 (1 H, s), 4.85 (1 H, d, J = 8 Hz), 4.2 (2 H, s), 2.15 (3 H, s).

Preparation of Methyl *N*-(2-(3-Indolyl)ethyl)glycinate (6). A solution of methyl glyoxylate (1 g, 11.3 mmol, polymerized form) in 20 mL of benzene is heated at 80 °C for 15 min. Tryptamine (1; 2 g, 12.5 mmol) is then added and stirring is continued for 5 min at 80 °C. In vacuo evaporation leaves a foamy residue (3.1 g) whose NMR properties are consistent with an imine structure (1 H, s at 7.65 ppm; 3 H, s at 3.85 ppm). This residue is dissolved in 25 mL of MeOH, and $NaBH_4$ (1.2 g) is added portionwise over 45 min. Usual workup gives 2.16 g of a thick oil, homogeneous on TLC: ^1H NMR (60 MHz, $CDCl_3$) δ 8.65 (1 H, s), 6.9 (1 H, d, J = 3 Hz), 3.7 (3 H, s), 3.45 (2 H, s), 3.0 (4 H, s), 2.35 (1 H, s).

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Registry No. 1, 61-54-1; 2, 61-53-0; 3, 7518-21-0; 4, 56999-36-1; 5, 608-07-1; 6, 89827-47-4; 7, 15741-79-4; 9, 89827-48-5; 10, 89848-03-3; 11, 89827-49-6; 12, 89827-50-9; 13, 89827-51-0; 14, 89827-52-1; 15, 89827-53-2; 16, 89827-54-3; 17, 89827-55-4; DMAD, 762-42-5; methyl propiolate, 922-67-8; butynone, 1423-60-5; methyl glyoxylate, 922-68-9.

A Convenient Synthesis of Bis(*N*-methylpiperazinyl)aluminum Hydride: A Reagent for the Reduction of Carboxylic Acids to Aldehydes

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The central nature of the carbonyl group in organic synthesis spurs interest in transformations between various types of carbonyl compounds. One such transformation that remains somewhat problematic is the reduction of carboxylic acids to the corresponding aldehydes. A number of procedures are known for this transformation, including reduction with thexylborane,[1] lithium aluminum hydride reduction to the primary alcohol followed by reoxidation to the aldehyde, and preparation of various acid derivatives (e.g., acid chlorides or esters) followed by reduction.[2-4] These methods suffer various disadvantages; most are two-step procedures, workups may require chromatography, and selectivity is not always high, especially if conjugate reduction is possible.

Some years ago, bis(*N*-methylpiperazinyl)aluminum hydride (BMPA) was first prepared[5] from the reaction of aluminum hydride with *N*-methylpiperazine and shown to reduce aliphatic and aromatic acids to aldehydes in good yields. However, apart from this set of papers by Mu-

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(5) (a) Muraki, M.; Mukaiyama, T. *Chem. Lett.* **1974**, 1447. (b) Muraki, M.; Mukaiyama, T. *Ibid.* **1975**, 215. (c) Muraki, M.; Mukaiyama, T. *Ibid.* **1975**, 875.

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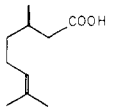
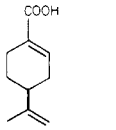
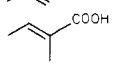
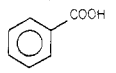
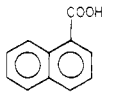
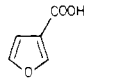
Table I. Reduction of Acids with BMPA

acid	mole ratio BMPA:Acid	time,[a] h	workup procedure	% yield of aldehyde[7]
	2.8:1	6	A	83
n-$C_{15}H_{31}COOH$	2.8:1	8	B	79
	3.9:1	9	B	78
	2.8:1	6	A	72
	2.8:1	12	A	86
	5.9:1	24	B	95
	2.8:1	8	A	62

[a] All reactions were conducted in THF solution, at reflux, under inert atmosphere.

kaiyama, there are no citations describing its use in synthesis. This may be due to the difficulty and expense involved in using aluminum hydride as the starting material.

When our work required the preparation of large quantities of (+)-citronellal from citronellic acid, we became interested in the use of BMPA. We hypothesized that this reagent might be prepared from lithium aluminum hydride, and this is indeed the case. Addition of 1 equiv of *N*-methylpiperazine dihydrochloride to a suspension of 2 equiv of $LiAlH_4$ in THF, followed by addition of 3 equiv of the amine itself, results in the formation of an active aluminum hydride presumed to be BMPA. The reagent can be prepared in situ immediately prior to use, or it can be prepared in larger quantity, titrated to establish active hydride concentration,[6] and stored under inert atmosphere until needed. Solutions prepared in this manner have been shown to retain titer for periods of at least several weeks.

Table I contains a list of representative carboxylic acids that we have reduced with this reagent. In these reactions, a standardized BMPA solution was added to a THF solution of the carboxylic acid or the carboxylic acid was added to a solution of BMPA prepared in situ. After heating at reflux for several hours, quenched aliquots were monitored by gas chromatography, and the reaction continued as necessary until reduction was complete. A 2:1 mole ratio of BMPA to the carboxylic acid is required, but a slight excess was found to be advantageous. A standard workup involved quenching the reaction by careful addition of brine and dilution with ether, followed by extractions of the organic phase with base, acid, and brine (procedure A). Alternatively the excess hydride was quenched with brine, 10% H_2SO_4 was added to dissolve aluminum salts,[8] and after dilution with ether, the same extraction sequence was employed (procedure B).

The reductions of perillic acid and tiglic acid are of special significance. While BMPA has not been used before now for the reduction of conjugated acids, at least in these two cases it works quite well. Following standard reduction and workup, the products were analyzed by GC–MS with special attention to the possibility of conjugate reduction. No trace of the conjugate reduction products was detected, even in the perillic acid reaction where a significant excess of the reducing agent was employed.

This work has shown that BMPA can be prepared, easily and inexpensively, from lithium aluminum hydride. Because yields are generally high and standardized solutions can be stored until needed, this is a convenient reagent for the direct reduction of carboxylic acids to aldehydes. Furthermore, in contrast to many other commonly used procedures, purification of the product aldehyde is straightforward. The major impurity is the unreacted carboxylic acid, which can be removed by simple extractions. These advantages should combine to make BMPA a popular reagent for this transformation.

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. Tetrahydrofuran was redistilled from sodium/benzophenone immediately prior to use. Gas chromatographic analyses were conducted on a Varian 3700 gas chromatograph using a 6 ft by 2 mm i.d. column packed with 3% OV-17 on Gas Chrom Q. The ^1H NMR spectra were recorded on a JEOL FX-90Q or a Brucker WM 360 spectrometer, using deuteriochloroform as the solvent. Low-resolution mass spectra were recorded with a Hewlett-Packard 5985B instrument; electron-impact (EI) spectra were obtained at 70 eV.

***N*-Methylpiperazine Dihydrochloride.** Anhydrous HCl was bubbled through a solution of *N*-methylpiperazine (20 g, 0.2 mol) in diethyl ether (400 mL) carefully maintained at 0 °C. A white precipitate formed, which was isolated by filtration, washed several times with ether, and then dried in vacuo: yield 33 g (95%); mp 224 °C (lit.[9] mp 225–230 °C).

Bis(*N*-methylpiperazinyl)aluminum Hydride. To a briskly stirred suspension of lithium aluminum hydride (6.94 g, 0.183 mol) in anhydrous THF (400 mL) at 0 °C was added solid *N*-methylpiperazine dihydrochloride (15.77 g, 0.091 mol) over a period of 15 min. As soon as the addition was complete, *N*-methylpiperazine (26.56 g, 0.265 mol) was added. The resulting mixture was allowed to warm to room temperature and then stirred for 2 h. At the end of this period the suspended particles were allowed to settle from solution. The clear supernatant was then transferred to a dry 1-L bottle sealed with a septum. The active hydride concentration of this solution was determined to be 0.28 M by hydrolysis.[6] Repeated analysis of this solution over a period of several weeks showed no loss of activity.

Procedure A: Citronellic Acid. To a stirred solution of citronellic acid (690 mg, 4.0 mmol) in THF (30 mL) under argon at 0 °C was added 2.8 equiv of BMPA (60 mL, 0.19 M, 11 mmol) over a period of 5 min. After removal of the ice bath, the reaction mixture was allowed to warm to room temperature and then heated to reflux. The reaction was monitored periodically by GC and found to be complete after 6 h. After diluting the THF solution with diethyl ether (100 mL), excess hydride was quenched by careful addition of saturated aqueous NaCl (30 mL), and the phases were separated. The aqueous layer was washed with additional ether (2 × 100 mL), and the combined organic extracts were then washed with 2 N NaOH (2 × 15 mL), 2 N HCl (2 × 25 mL), and saturated aqueous NaCl (25 mL). After the ether solution was dried (Na_2SO_4), concentration in vacuo gave 520 mg of citronellal (83%; purity >99% by GC and GC–MS).

Procedure B: Perillic Acid. To a stirred solution of *l*-perillic acid (500 mg, 3.0 mmol) in THF (30 mL) under argon at 0 °C was added 2.8 equiv of BMPA (30 mL, 0.29 M, 8.7 mmol). The

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reaction mixture was allowed to warm to room temperature and then heated at reflux. When the reduction was found to be incomplete by GC analysis after 6 h, an additional 10 mL (2.9 mmol) of the BMPA solution was added. The reaction mixture was then heated an additional 3 h and the reduction then was found to be complete. After addition of diethyl ether (100 mL) and careful quenching with saturated aqueous NaCl (20 mL) and 10% H_2SO_4 (30 mL), the phases were separated. The aqueous layer was washed with ether (2 × 100 mL), and the combined organic extracts were then washed with 2 N NaOH (2 × 15 mL), 2 N HCl (2 × 25 mL), and saturated aqueous NaCl (25 mL). After drying over Na_2SO_4, evaporation of the ether in vacuo gave 350 mg of *l*-perillaldehyde (78%; purity >99% by GC and GC–MS).

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Registry No. $LiAlH_4$, 16853-85-3; BMPA, 54709-78-3; citronellic acid, 502-47-6; perillic acid, 7694-45-3; tiglic acid, 80-59-1; hexadecanoic acid, 57-10-3; benzoic acid, 65-85-0; 1-naphthalenecarboxylic acid, 86-55-5; 3-furancarboxylic acid, 488-93-7; (+)-citronellal, 2385-77-5; hexadecanal, 629-80-1; perillal, 2111-75-3; tiglal, 497-03-0; benzaldehyde, 100-52-7; 1-naphthalenecarboxaldehyde, 66-77-3; 3-furancarboxaldehyde, 498-60-2.

A Novel, Useful, and Inexpensive Preparation of *S*-Methyl Methanesulfonothioate

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As part of a more general program for devising new synthetic procedures that are selective, efficient, mild, easy to run, and inexpensive, we report preparation of the title compound $CH_3SSO_2CH_3$. This sulfonate, which is available commercially, has may uses. Among these, introduction of SCH_3 groups in aromatic rings,[1,2] thiomethylation of exposed activated C–H and S–H bonds in organic molecules and in proteins,[3–5] and substitution by the SCH_3 group into the four- or the six-membered ring of cephalosporin antibiotics and into the four-membered ring of penicillin derivatives have been especially frequent in recent years.[6–11]

Our preparation of this useful reagent improves upon previous methods[11–14] by requiring only inexpensive starting materials, by its easy implementation, and by its very good overall yield (80–85% isolated yield).

We have no indications yet on the mechanism of this intriguing reaction; optimization of the reaction conditions (heating temperature and duration, reactant ratios) is consistent with the following empirical equation

$$4(CH_3)_2SO + 4(CH_3)_3SiCl \longrightarrow [X] \xrightarrow[HOCH_2-CH_2OH]{3\ equiv} 2H_3CS\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_3 \quad (1)$$

which corresponds to an 80% isolated yield, and we plan to make the appropriate experiments for studying it. We discovered it in serendipitous manner when preparing formaldehyde acetals from alcohols and chlorotrimethylsilane in the presence of Me_2SO.[16] Subsequently, we found that using Me_2SO also as the solvent led to a much improved yield.

Experimental Section

In a 500-mL two-necked flask fitted with a magnetic stirrer, an addition funnel, and reflux condenser, both fitted with $CaCl_2$ drying tubes, 250 mL of Me_2SO was introduced with ice bath cooling during ca. 10 min. Chlorotrimethylsilane (0.64 mol) was then added as a rapid drip through the addition funnel. The reaction was slightly exothermic, and a white solid appeared. The mixture was stirred for 20 min while the temperature was maintained close to 0 °C, and 0.48 mol of ethylene glycol was added as a rapid drip through the addition funnel. The reaction mixture was allowed to warm to room temperature over a period of about 2 h. This mixture was heated at 60 °C (the solid redissolved) for 18 h, followed by 42 h at 110 °C. After the solution cooled to room temperature, it was poured into a mixture of 200 mL of water and 200 mL of methylene chloride. The organic layer was then extracted three times with water, dried over anhydrous $MgSO_4$, filtered, and concentrated. Distillation gave *S*-methyl-methanesulfonothioate as a colorless oil: 32 g (80% isolated yield); bp 67–70 °C (0.4 mmHg) [lit.[14] bp 122 °C (16 mm)]; ^1H NMR (CCl_4) δ 3.3 (s), 2.7 (s) (lit.[15] δ 3.28, 2.69); IR (neat) 1305 (s, SO_2), 1130 (s, SO_2), 960 (s), 745 (s) cm^{-1} (lit.[14] 1310, 1130 cm^{-1}); MS, *m/e* 126 (M^+, 100), 111 (M^+ – Me, 7), 79 (M^+ – SMe, 84). Anal. Calcd C, 19.04; H, 4.79. Found: C, 19.15; H, 4.98.

Acknowledgment is made to Programmation de la Politique Scientifique, Brussels, for support of this research (Action Concertée 82/87-34) and to Fonds National de la Recherche Scientifique, Brussels, for help in purchasing the IR spectrometer used in this work. We thank also Stéphane Chalais for his technical assistance.

Registry No. $Me_2S{=}O$, 67-68-5; Me_3SiCl, 75-77-4; $HO(CH_2)_2OH$, 107-21-1; $CH_3SSO_2CH_3$, 2949-92-0.

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