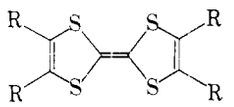
Table I. Polarographic Half-Wave Potentials[a]

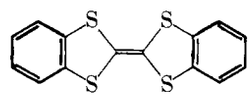
	$E_{1/2}^1$	$E_{1/2}^2$	$\Delta E_{1/2}$
6	+0.936	+1.10	0.164
7	+1.05	+1.21	0.160
8	+1.39	+1.55	0.160
TTF[8]	+0.342	+0.721	0.379

[a] Reversible oxidations in MeCN with added Et_4NClO_4 (0.05 *m*) vs. Ag/Ag^+ (0.1 N in MeCN) with a glassy carbon electrode as the working electrode; the resulting values are given in volts with respect to the saturated calomel electrode.

Reaction of TTF (**1**) with 1 equiv of *m*-chloroperbenzoic acid in a cooled (5–10 °C) two-phase system (CH_2Cl_2/aqueous



1. R = H
3. R = COOMe



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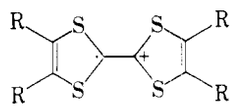

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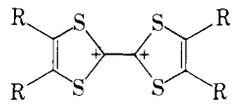

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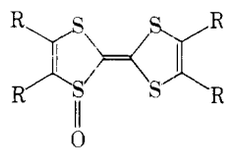
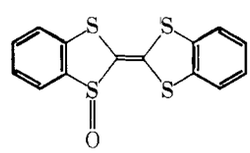


6. R = H
8. R = COOMe



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Na_2HPO_4) gave the pale yellow tetrathiafulvalene *S*-oxide **6**,[6] (68%): mp >90 °C dec; UV λ_{max} (EtOH) 208 (log ϵ 3.92), 265 sh (3.38), 295 (3.50), 350 sh (3.77), 388 nm (3.98). In a similar manner, dibenzotetrathiafulvalene (**2**) was converted (57%) to the lemon yellow *S*-oxide **7**: mp >195 °C dec; UV λ_{max} (EtOH) 208 (log ϵ 3.54), 220 sh (4.36), 296 (3.95), 406 nm (4.19). The highly electron-deficient tetrakis(carbomethoxy)tetrathiafulvalene (**3**) was less easily oxidized, but underwent a similar transformation at room temperature to give orange needles of *S*-oxide **8** (57%): mp >120 °C dec; UV λ_{max} (EtOH) 210 (log ϵ 4.65), 236 (4.52), 303 (4.07), 370 nm (4.17).

All three *S*-oxides (**6, 7,** and **8**) were quantitatively deoxygenated to the corresponding tetrathiafulvalenes (**1, 2,** and **3**) by P_2S_5 in CH_2Cl_2 at room temperature;[7] **8** was reduced most rapidly and **6** was reduced most slowly.

The infrared spectra (KBr) of compounds **6, 7,** and **8** all showed a strong band in the 9.7–9.9-μm region, attesting to the presence of the sulfoxide function. The asymmetry due to the single sulfoxide oxygen was clearly discernible in the NMR spectra of **6** and **8**. The NMR spectrum of **6** (Me_2SO-d_6) showed a clear AB quartet (J = 8 Hz) for R_1 (δ 7.65) and R_2 (δ 6.83); the effect of the sulfoxide oxygen is still noticeable, though barely so, in the second dithiole ring, in which protons R_3 and R_4 appear as apparent close singlets at δ 7.0 and 6.98, respectively. A close examination reveals an AB quartet (J = 8 Hz) for R_3 (δ 6.95) and R_4 (7.08). The NMR spectrum of tetraester **8** ($CDCl_3$) shows a similar influence of the sulfoxide function on the R_1 ester methyl resonance, which is deshielded (δ 3.90) in comparison to the remaining three ester methyls (singlet at δ 3.85).

The first ($E_{1/2}^1$) and second ($E_{1/2}^2$) polarographic half-wave potentials and their difference ($\Delta E_{1/2}$) for the *S*-oxides are given in Table I.

The $E_{1/2}^1$ values show that **6, 7,** and **8** undergo oxidation to their respective monocations less readily relative to the corresponding unoxidized parent donors,[4] while the oxidation sequence due to substituent effects remains the same: **6** > **7** > **8**. Further, a given sulfoxide monocation oxidizes to the dication more easily than the corresponding parent monocation. These systematic differences in oxidation properties of the parent donors and their *S*-oxides are related to the fact that the total free energy (ΔF) for oxidation in solution is a sum of electronic (ΔF_e), solvation (ΔF_s), and intramolecular distortion (ΔF_d) terms, $\Delta F = \Delta F_e + \Delta F_s + \Delta F_d$. The presence of the SO group would then change the molecular contributions to each of the three terms. For example, in addition to overall changes in the molecular electronic states (ΔF_e), the pyramidal bonding around S at each S–O site would markedly distort the TTF ring structure (ΔF_d) and introduce larger dipole moments within each ring (ΔF_s).

Dilute acetonitrile solutions of sulfoxides **6** and **7** give a greenish coloration on treatment with tetracyanoquinodimethane (TCNQ), suggestive of the formation of charge-transfer salts. The preparation of crystalline salts has so far been hampered by the thermal instability of **6** and **7**, as well as their very low solubility in dry nonprotic solvents.

Acknowledgment. This work was supported by grants from the National Science Foundation, CHE 76-83417, the MRL program grant DMR 76-00678, and NATO. We also thank Mr. Paul J. Nigrey for technical assistance.

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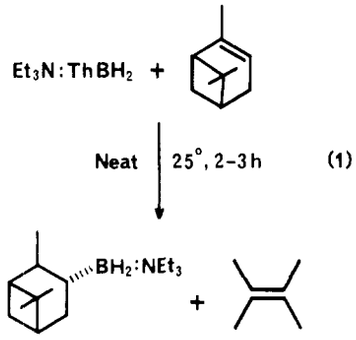
Received August 4, 1978

Simple Synthesis of Monoisopinocampheylborane of High Optical Purity

Summary: *N,N,N′,N′*-Tetramethylethylenediamine (TMED) reacts rapidly at 34 °C with diisopinocampheylborane (IPC_2BH) to displace α-pinene and produce the solid 1:2 adduct of the base and monoisopinocampheylborane (TMED·$2BH_2IPC$). Treatment of this adduct with boron trifluoride etherate precipitates the amine and generates free monoisopinocampheylborane in optical purities approaching 100%, much higher than that of the α-pinene (~94%) utilized in the synthesis of the IPC_2BH.

Sir: Recently the reaction of neat triethylamine–thexylboranes (Et_3N·$ThBH_2$) with neat α-pinene was reported to yield the triethylamine–monoisopinocampheylborane (Et_3N·BH_2IPC) (**1**) adduct (eq 1).[1] Triethylamine could be removed with either THF·BH_3[2] or Et_2O·BF_3[1] to produce the free monoisopinocampheylborane ($IPCBH_2$). Unfortunately, both Et_3N·BH_3 and Et_3N·BF_3 are highly soluble in the usual THF medium and are difficult to separate from the desired product.[1,2] This difficulty can be overcome by isolating the intermediate and placing it in a pentane solution from which



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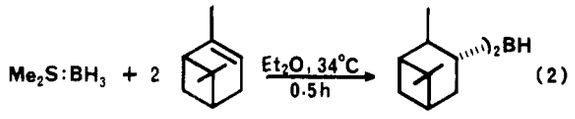
$Et_3N{\cdot}BF_3$ can be crystallized out at −5 °C.[1] A further handicap is the fact that $Et_3N{\cdot}BH_2IPC$ is a liquid which cannot be purified readily. The $IPCBH_2$ reagent, which is highly promising for asymmetric hydroboration[2] and reductions,[3] has been previously synthesized in high optical purity by a relatively long and time-consuming process.[4] It appeared desirable, therefore, to develop a more simple, more direct synthesis of optically pure $IPCBH_2$. The discovery that $IPCBH_2$ forms a crystalline bis adduct with TMED[5] prompted us to explore the reaction between IPC_2BH and TMED as a potential solution to this problem.

The present procedure utilizes borane–methyl sulfide (BMS) in Et_2O for the rapid preparation of IPC_2BH,[6] a fast displacement of α-pinene by TMED, and a convenient removal of TMED from the product with $Et_2O{\cdot}BF_3$. An unexpected development was the discovery that the bis adduct of TMED with $IPCBH_2$ separates in much higher optical purity than the α-pinene used to synthesize IPC_2BH. With this method the synthesis and storing of optically pure $IPCBH_2$ becomes a simple, rapid process. Diisopinocampheylborane (**2**) was prepared in 0.5 h by the reaction of α-pinene with BMS in Et_2O at 34 °C (eq 2). Addition of 0.5 equiv. of TMED at 34



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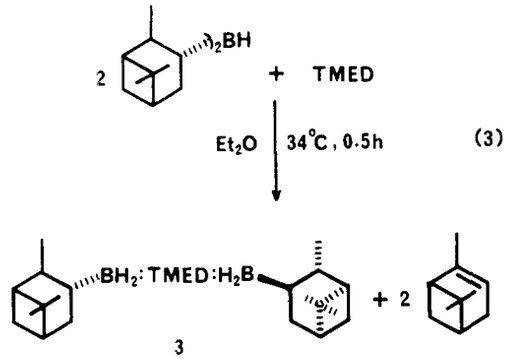
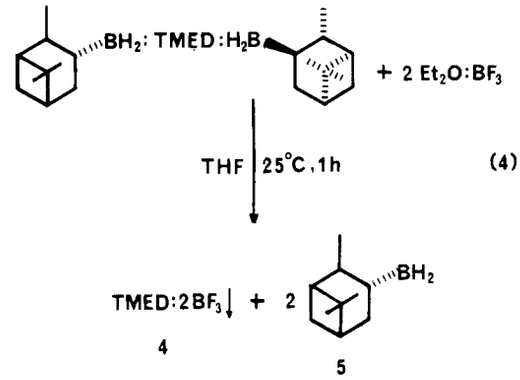
°C results in the displacement of α-pinene and the formation of $TMED{\cdot}2BH_2IPC$ (**3**) (eq 3). The reaction is essentially



3

complete in 0.5 h. The reaction mixture is then transferred to a centrifuge tube. Upon cooling, the bis adduct **3** is thrown out as a crystalline solid. α-Pinene and methyl sulfide are removed by centrifugation, followed by decantation of the supernatant liquid. After washing with pentane, **3** is isolated in ~80% yield. Spectral (^1H NMR and ^{11}B NMR) data revealed that the derivative **3** is very pure. Methanolysis provided pure $IPCB(OMe)_2$ by ^1H NMR. The isopinocampheol obtained after oxidation of **3** showed $[\alpha]^{25}_D$ −35.79° (c 0.9, C_6H_6), a value equal to the highest optical rotation previously achieved.[4] At this stage it is appropriate to point out that the α-pinene used in the preparation of **2** possessed only ~94% optical purity, and the intermediate **2** was not purified prior to the synthesis of **3**.[4] Hence, an important outcome of this method is the fact that from an optically impure substrate the adduct **3** can be prepared in exceptionally high optical purity, approaching 100%.

Amine–boranes react sluggishly with olefins at 25 °C.[2] Thus, the removal of TMED from the adduct **3** is necessary to facilitate the hydroboration reaction. Fortunately, TMED can be very effectively removed from the adduct **3** with $Et_2O{\cdot}BF_3$.[5] Thus, when $Et_2O{\cdot}BF_3$ is added to a THF solution of **3** at 25 °C, $TMED{\cdot}2BF_3$ (**4**) precipitates out within 1 h, leaving $IPCBH_2$ (**5**) in solution for ready hydroboration of olefins (eq 4).[2] The $IPCBH_2$ solution can be separated by decantation in nearly quantitative yield. Since the compound **4** is very inert, its removal is not crucial for further hydroboration.



4 5

The following procedure for the preparation of $IPCBH_2$ is typical. With the usual experimental setup, all operations were carried out under nitrogen in a 100-mL flask.[7] The flask was charged with borane–methyl sulfide (2.0 mL, 20.0 mmol) and anhydrous diethyl ether (11.3 mL). The reaction mixture was heated under reflux. Addition of (+)-α-pinene (7.36 mL, 46 mmol)[8] led to the quantitative formation of IPC_2BH (~20 mmol) in 0.5 h. TMED (1.51 mL, 10 mmol) was added to the refluxing solution and the refluxing was continued for another 0.5 h. The reaction mixture was then transferred to a centrifuge tube. On cooling the adduct **3** crystallized out. Methyl sulfide and α-pinene were removed by centrifugation, followed by decantation.[7] Solids were washed with pentane (3 × 5 mL) and dried under vacuum (12 mm) to provide 3.32 g (~80%) of $TMED{\cdot}2BH_2IPC$: mp 140–141 °C (recrystallized from Et_2O); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00 (d, 6 H, J = 7 Hz), 1.1 (s, 6 H), 1.16 (s, 6 H), 2.63 (s, 12 H), 3.20 (s, 4 H); ^{11}B NMR (THF, relative to $Et_2O{\cdot}BF_3$) δ +1.80 (br s). Oxidation of **3** with alkaline hydrogen peroxide afforded isopinocampheol, $[\alpha]^{27}_D$ −35.79° (c 0.9, C_6H_6). To liberate the free monoalkylborane **5**, the adduct **3** (3.32 g, 8.0 mmol) was dissolved in THF (16 mL) and $Et_2O{\cdot}BF_3$ (1.97 mL, 16 mmol) was added with constant stirring. After 1 h the solid $TMED{\cdot}2BF_3$ was centrifuged and the supernatant liquid was analyzed for free monoalkylborane **5**. Hydrolysis of an aliquot (1 mL) evolved hydrogen (~1.6 mmol, 100%). Another aliquot (10 mL) after oxidation with alkaline hydrogen peroxide provided isopinocampheol (8 mmol) by GLC analysis.

This new procedure thus describes a direct, rapid synthesis of IPC_2BH, optically pure $TMED{\cdot}2BH_2IPC$, and $IPCBH_2$. The air stable solid adduct $TMED{\cdot}2BH_2IPC$ alleviates handling and storing problems. Finally, the $Et_2O{\cdot}BF_3$ procedure is generally useful for removal of TMED from the $TMED{\cdot}RBH_2$ adducts, now readily available.

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(9) Postdoctoral Research Associate on Grant No. GM 10937 from the National Institutes of Health.

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