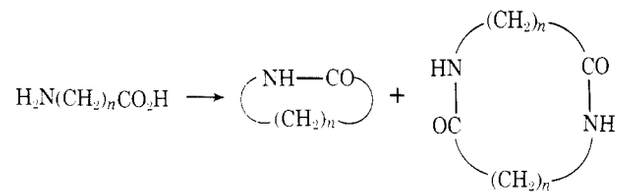
Table II. Formation of Lactams from ω-Amino Acids Using Catecholborane



ω-amino acid: n =	lactam: size (% yield)	dimer: size (% yield)[a]	dimer properties
3	5 (>95)		
5	7 (85)		
6	8 (6)	16 (18)	mp 246–249 °C,[b] *m/e* 255 (M^+), 128 (base)
7		18 (10)	mp 273–275 °C,[b] *m/e* 282 (M^+), 142 (base)
11	13 (6)	26 (25)	mp 203–206 °C, *m/e* 394 (M^+, base)
12	14 (9)	28 (22)	mp 152–154 °C, *m/e* 422 (M^+, base)
14	16 (13)	32 (17)	mp 168–171 °C, *m/e* 478 (M^+, base)

[a] All monomers were identified by comparison with authentic samples. Dimers were fully characterized by IR, NMR, and mass spectrometry. [b] This melting point was identical with that of a known sample of dimer (ref 12).

purity.[8] Both 3-methoxy- and 4-nitrocatechol also form the derived boranes in standard fashion and a preliminary survey of their reactivity suggests that the former comprises a somewhat superior coupling reagent.

Our interest in closing rings at the site of an amide bond requires a reagent that is capable of carboxyl activation without interference by a basic amino group. The direct addition of catecholborane to a homogeneous 1:1 mixture of nonanoic acid and benzylamine in THF simulates lactamization conditions and produces the desired nonanoic acid *N*-benzylamide in 85% yield. These "in situ" couplings are general and small amounts of pyridine (2–3 equiv) accelerate them, possibly by transforming the acyloxyborane to a more reactive acylpyridinium salt.

Most parent ω-amino acids are but sparingly soluble in nonaqueous solvents, nevertheless we can prepare their lactams by the acyloxyborane technique under heterogeneous conditions. For example, when 6-aminocaproic acid (1.85 mmol) is suspended in pyridine (30 mL) at 80 °C and treated with catecholborane (2.78 mmol), the solid slowly dissolves and caprolactam is formed in 85% yield. γ-Aminobutyric acid similarly affords 2-pyrrolidinone (>95%). Table II summarizes our experience with a series of homologous substrates. Substantial proportions of medium-ring monomers are not formed, although the cyclization becomes more favorable in the case of 14- and 16-membered lactams. In each of these experiments, controls clearly establish that no ring closure whatsoever occurs if the borane is omitted.[9]

Our results contrast with similar studies on the formation of macrocyclic lactones[10] and may reflect more stringent geometric demands imposed on the ring and on the ring-forming process by the planar amide bond. However the heterogeneous conditions we describe are of unknown (but probably high) dilution and make an accurate assessment of rate data impossible. Recently we have discovered the combination of soluble ω-amino acid tetra-*n*-butylammonium salts with *B*-chlorocatecholborane in pyridine also produces lactams and that under such homogeneous circumstances, dimer formation does not occur at up to 0.05 M concentrations. Thus, for example, the 6-, 12-, and 15-carbon ω-amino acid salts furnish only the corresponding monomeric lactams in yields of 65, 15, and 17%, respectively. This result suggests either that two independent cyclization mechanisms are operating or that the observed dimers arise from complex surface effects. In future work we hope to explore these possibilities.

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(9) No more than 2% of 2-pyrrolidinone is spontaneously formed when γ-aminobutyric acid is heated 16 h in pyridine.
(10) E. J. Corey and K. C. Nicolaou, *J. Am. Chem. Soc.*, **96**, 5614 (1974).
(11) The following is a typical experimental procedure. To a flame-dried 50-mL pear-shaped flask fitted with magnetic stirrer, serum cap, and N_2 inlet was added catecholborane (1.0 M in THF, 6.0 mL), then nonanoic acid (0.87 mL, 5.0 mmol) in THF (4 mL). The clear solution was stirred 1 h at room temperature, then taken up in a 10-mL syringe and added dropwise (motor-driven syringe pump, 0.2 mL/min) to a rapidly stirred solution of benzylamine (1.09 mL, 10.0 mmol) in THF (4 mL) at −78 °C. Upon completion of addition the reaction mixture was warmed slowly to room temperature and stirred overnight. The bulk of THF was removed using a rotary evaporator to produce a white solid which was immediately dissolved in 5% NaOH (15 mL) and ether (15 mL). The aqueous phase was extracted three more times with ether and the combined organic layers were washed with water (5 mL), 5% NaOH (20 mL), 5% HCl (30 ml), and brine (30 mL). Drying and concentration afforded 1.12 g (92%) of white powder, mp 66–67 °C, identical with an authentic sample of *N*-benzylnonanoic amide and pure by NMR, IR, and TLC.
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(13) Fellow of the Alfred P. Sloan Foundation, 1978–1980.

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S-Oxides of Tetrathiafulvalenes

Summary: The first tetrathiafulvalene *S*-oxides have been synthesized. These include the mono *S*-oxides of tetrathiafulvalene, dibenzotetrathiafulvalene, and tetrakis(carbomethoxy)tetrathiafulvalene. The polarographic properties of these novel sulfoxides are described.

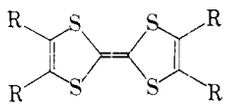
Sir: Tetrathiafulvalene (**1**, TTF) and its derivatives have been the subject of intensive chemical and physical study in recent years, due to the fact that many compounds of this group can form crystalline, electrically conducting charge-transfer salts.[1,2] This property is dependent upon the relative ease with which the TTF system can be oxidized by a variety of means to give the radical cation (**4**) or the dictation (**5**).[3,4] This type of one-electron or two-electron oxidation is, indeed, the only known transformation of the basic TTF system with the exception of the recently described[5] lithium–hydrogen interchange reaction of TTF. We now report the first synthesis of a new type of TTF oxidation product, namely a tetrathiafulvalene *S*-oxide.

Table I. Polarographic Half-Wave Potentials[a]

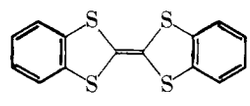
	$E_{1/2}^1$	$E_{1/2}^2$	$\Delta E_{1/2}$
6	+0.936	+1.10	0.164
7	+1.05	+1.21	0.160
8	+1.39	+1.55	0.160
TTF[8]	+0.342	+0.721	0.379

[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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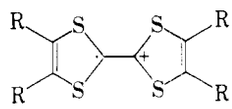

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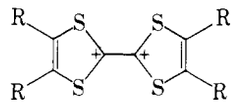

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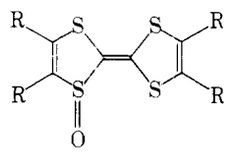
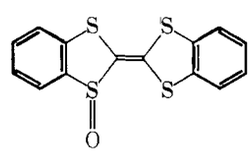


6. R = H
8. R = COOMe



7

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.

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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