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(6) In the case of Li^+, $n = 4$ with ligands like acetone, amides, amines, and so on; $m = 6$ if S is H_2O. It is likely that $n = 6$ with Ca^{2+} and Mg^{2+}. Well-defined crystalline 1:4 complexes of amides with Li^+, Na^+, and K^+ and 1:6 complexes with Mg^{2+} have indeed been characterized.[4]

(7) Around 8 *M* Li^+, the molar ratio of Li^+ to H_2O would be around 1:6. In the case of Ca^{2+} and Mg^{2+}, the shifts become appreciable beyond 6 *M* which corresponds to a molar ratio of M^{z+} to H_2O of 1:8.

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(15) To whom all correspondence should be addressed (during 1974–1975): Commonwealth Visiting Professor, St. Catherine's College, Oxford OX1 3UJ, England.

C. N. R. Rao,*[15] K. Gurudath Rao, N. V. R. Reddy

Department of Chemistry, Indian Institute of Technology
Kanpur 208016, India

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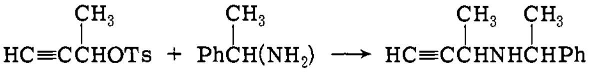
Synthesis of Chiral Allenic Alcohols and Nuclear Magnetic Resonance Determination of Their Enantiomeric Purities Using a Chiral Lanthanide Shift Reagent[1]

Sir:

A remarkable feature of the present knowledge of chiral allenes is the paucity of reliable information concerning their enantiomeric purities.[2] In the present paper we report on a general synthetic method for the preparation of chiral α- and β-allenic alcohols starting with a resolved acetylenic amine of the type **2** and the determination of the enantiomeric composition of these allenic alcohols using ^{1}H NMR spectroscopy in combination with the chiral lanthanide shift reagent tris(3-heptafluorobutyryl-*d*-camphorato)europium(III),[3] $Eu(hfbc)_3$. Prior to our report, chiral β-allenic alcohols have been accessible through Landor's method of asymmetric synthesis in which a 5-alkyl-pent-2-en-4-yn-1-ol is reduced with a chiral lithium aluminum hydride complex.[4] However, no similar method was available for obtaining chiral α-allenic alcohols.

Our synthetic approach rests upon a known procedure for the preparation of racemic α-allenic alcohols[5] and a new preparative method for racemic β-allenic alcohols.[6] A mixture of diastereomeric amines (**1**) was obtained from the separate reactions of (*S*)-(−)- and (*R*)-(+)-α-methylbenzylamine with the *p*-toluenesulfonate of *dl*-3-butyn-2-ol[7] (in MeOH, 3 days at 20°, yield 70%, bp 97–102°, 12 Torr). Two recrystallizations of the hydrochlorides from chloroform gave pure **2a** and **2b** in 75% yield (hydrochloride of **2a**, mp 217–218°, **2b**, mp 217°). The progress of the separations of the diastereomers in these mixtures could be followed from the ^{1}H NMR spectra[8] of the free amines. The propargylic protons gave rise to two quartets at δ 3.12 and 3.55 ppm with fine splitting caused by the acetylenic proton. The major signals (δ 3.55 ppm) were from the enantiomers having the least soluble hydrochlorides, i.e., **2a** and **2b.** The diastereomers were also separated by gas chromatography of the free amines. (OV-25 column, **2a** and **2b** had retention times of 8 min and their diastereomers 6.8 min.)



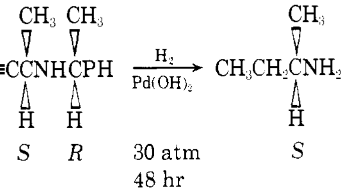
$$HC{\equiv}C\overset{CH_3}{\overset{|}{C}}HOTs + Ph\overset{CH_3}{\overset{|}{C}}H(NH_2) \longrightarrow HC{\equiv}C\overset{CH_3}{\overset{|}{C}}HNH\overset{CH_3}{\overset{|}{C}}HPh$$

1a from (*S*)—$PhCH(NH_2)CH_3$ (*S*)

1b from (*R*)—$PhCH(NH_2)CH_3$

The catalytic reduction of **2b,** made from (*R*)-(+)-α-methylbenzylamine, gave (*S*)-(+)-2-aminobutane as the levo hydrochloride,[9] $[\alpha]^{20}\text{D}$ −3° (*c* 5, EtOH) and the dextro benzamide,[10] $[\alpha]^{22}\text{D}$ +32.9° (*c* 5.19, EtOH). Therefore **2b** must have the *S* configuration at the propargylic carbon atom and **2a** the *R* configuration as shown in Scheme I.

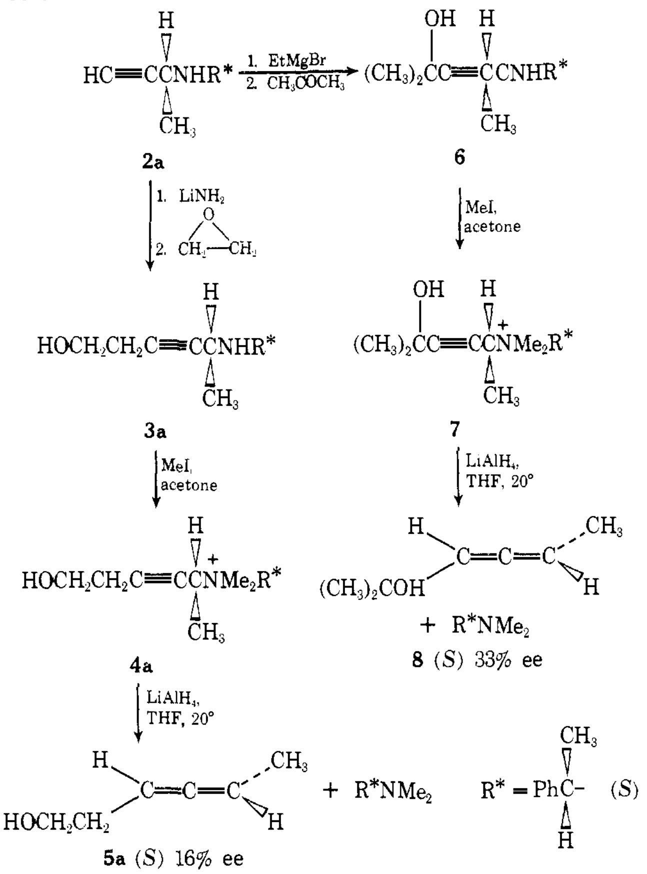
2b



Both enantiomers **2a** and **2b** were converted to their lithium alkynides and added to ethylene oxide (1.5 equiv of $LiNH_2$/2 equiv of ethylene oxide, −40°, 30 hr). The amino alcohols **3a** and **3b** were purified on a silica column (ether; yield 25 and 30% of oily **3a** and **3b,** respectively). The amine **2a** was also added to acetone via its Grignard derivative (2 equiv of EtMgBr was necessary for an acceptable yield) to give the amino alcohol **6** in 50% crude yield. The pure β-acetylenic amino alcohols **3a** and **3b** and the crude α-acetylenic amino alcohol **6** were quaternized with an excess of methyl iodide (acetone, K_2CO_3, 20°, 15 hr). The quaternary salts (**4a, 4b,** and **7**) were allowed to react with lithium aluminum hydride in THF; **4a** gave rise to (*S*)-(+)-3,4-hexadien-1-ol (**5a**),[4a] $[\alpha]^{22}\text{D}$ +12.0° (*c* 2.75, MeOH) approximately 30% yield from **3a; 4b** gave the levorotatory enantiomer **5b,**[4b] $[\alpha]^{22}\text{D}$ −11° (*c* 0.76, MeOH). The absolute configurations of **5a** and **5b** have been assigned by Landor[4] based on the stereospecific Claisen rearrangement of a chiral 1-butyn-3-yl vinyl ether and the Lowe-Brewster rule.[11]

From **7** there was obtained (+)-2-methyl-3,4-hexadien-2-ol (**8**), $[\alpha]^{22}\text{D}$ +32.9° (*c* 9.4, MeOH), in an overall yield of ca. 30% from **6** as determined by GLC. According to the Lowe-Brewster rule,[11] the dextrorotatory α-allenic alcohol **8** should be assigned the (*S*) configuration, which is in accord with the reasonable assumption that the stereochemical course of reactions **4a** → **5a** and **7** → **8** correspond. Assuming these assignments to be correct, since amine **3a** of known *R* configuration at the propargylic carbon gives the

Scheme I



S β-allenic alcohol **4b**, the attack by hydride must be from the same side from which the tertiary amino group departs (i.e., suprafacial). The same is also deduced for the conversion of **7** to **8** based on the known configuration of **6** and the assigned *S* configuration of **8.**

The reverse stereoselectivity was reported by Borden and Corey[12] in allene-forming $LiAlH_4$ reductions of sulfonates of resolved 1,3-di-*tert*-butylpropargyl alcohol; i.e., it was concluded that hydride attacks preferentially trans to the departing sulfonate.[12] Weedon et al. have reported that opening of the epoxy ring of a 4,5-epoxy-2-pentyn-1-ol takes place cis to the hydride attack[13] in accord with our findings.

The enantiomeric purities of **5** and **8** were determined with the aid of the chiral lanthanide shift reagent,[3a] $Eu(hfbc)_3$.[3] Use of the C-1 proton signals in **5a** and **5b** for the determination of the per cent enantiomeric excess (% ee), is complicated by the fact that these two protons on each enantiomer are internally diastereotopic. In the presence of $Eu(hfbc)_3$, the signals for the diastereotopic C-1 protons of **5a** are shifted differently yielding the AB part of an ABX_2 pattern appearing on either side of the central triplet in Figure 1A. The C-1 proton signals of **5b** are each shifted by the same amount yielding a simple triplet appearing in the center of Figure 1A. These patterns are simplified considerably by decoupling the protons on C-2 (Figure 1B and 1C). The % ee obtained from the integrations of these signals in Figure 1B and 1C are as follows: **5a** ($[\alpha]^{22}D$ +12.0°) % ee = 16 ± 1.3% and **5b** ($[\alpha]^{22}D$ −11°) % ee = 13 ± 1.4%. These error limits represent one standard deviation of a series of integrals. Table I contains the gradients of each of the signals of **5a** and **5b.**

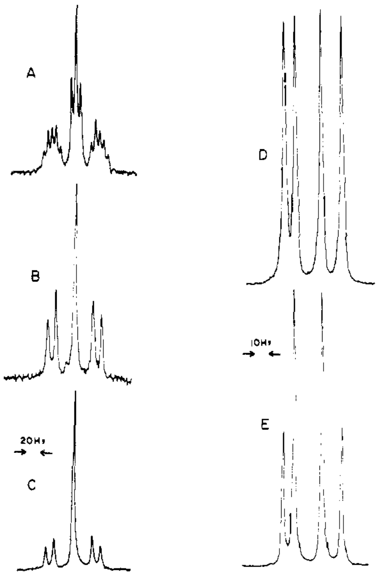
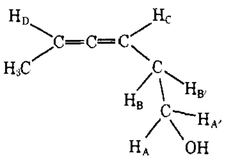
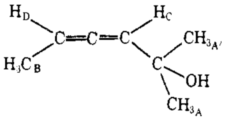


Figure 1. (A–C) NMR spectra of C-1 protons of **5** at a molar ratio of lanthanide shift reagent $Eu(hfbc)_3$ to **5** (LSR/substrate) of 1.1: (A) *dl* mixture with no decoupling; (B) **5a** (16% ee) with C-2 protons decoupled; (C) **5b** (13% ee) with C-2 protons decoupled. (D–E) NMR spectra of the geminal methyls of **8** at a molar ratio of 1.2: (D) *dl* mixture; (E) **8** (33% ee).

Table I. Gradients[a] for the Signals of 5 and 8 in the Presence of $Eu(hfbc)_3$

Compound	Signal	Gradient[a]	
		R[b]	S[b]
 5	H_A	23.3	22.8
	$H_{A'}$	23.3	23.9
	H_B, $H_{B'}$	13.4	13.4
	H_C	8.52	8.52
	H_D	3.77	3.77
	CH_3	2.54	2.54
 8	H_C	9.96	9.96
	H_D	1.94	1.94
	CH_{3A}	9.03	9.12
	$CH_{3A'}$	9.37	9.28
	CH_{3B}	1.12	1.12

[a] The gradient used here is the slope of the initial (low molar ratio) linear portion of a plot of chem shift (δ) vs. molar ratio (LSR/substrate). Gradients were determined by incremental dilution method (similar to that of Shapiro[14]) keeping the substrate concentrate at 0.32 *M* in $CDCl_3$. The spectra were run on a Varian XL-100 operating at 35°. [b] Assuming configurations as discussed in text.

The ^1H NMR spectrum of **8** in the presence of $Eu(hfbc)_3$ shows that the signals for the protons on C-5 and the geminal methyl groups are shifted differently for the enantiomers. These geminal methyl signals were used for determination of % ee. Again, since the two methyls on each enantiomer are internally diastereotopic, their signals can be shifted differently, yielding four singlets for the *dl* mixture (Figure 1D). Integration of these signals in the spectrum of the partially active material (Figure 1E) gives for **8** ($[\alpha]^{22}D$ +32.9°) % ee = 33 ± 1.9%. Table I contains the gradients for **8** and its enantiomer.

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for the Varian XL-100 NMR spectrometer used in these studies.

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Alf Claesson,* Lars-Inge Olsson
Department of Organic Chemistry
Faculty of Pharmacy, University of Uppsala
S-751 23 Uppsala, Sweden

Glenn R. Sullivan, Harry S. Mosher*
Department of Chemistry, Stanford University
Stanford, California 94305

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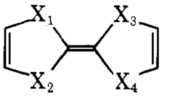
Ionization Potentials and Donor Properties of Selenium Analogs of Tetrathiafulvalene

Sir:

The substitution[1] of selenium for sulfur in tetrathiafulvalene (TTF, **1**) extends the metallic state of its charge transfer salt with tetracyano-*p*-quinodimethane (TCNQ)[2,3] to lower temperature. Furthermore, this modification still maintains the original TTF-TCNQ crystal structure,[1] a factor which may facilitate attempts to correlate molecular properties of the constituent molecules with the resultant solid state properties of the charge transfer salt. In order to characterize the changes in donor properties that occur in going to the selenium analogs of TTF, we have carried out measurements of some of the relevant molecular properties of TTF, tetraselenafulvalene (TSeF, **2**), and *cis*- and *trans*-diselenadithiafulvalene[4] (DSeDTF, **3** and **4**).



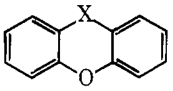
1, $X_{1-4} = S$
2, $X_{1-4} = Se$
3, $X_{1,3} = S$; $X_{2,4} = Se$
4, $X_{1,4} = S$; $X_{2,3} = Se$

Table I. Electrochemical, Spectroscopic, and Mass Spectroscopic Data on TTF, DSeDTF, and TSeF[a]

	Electrochemical[b]			Spectroscopic		Mass spectrometry
Donor	ϵ_1 peak	ϵ_2 peak	IP[c]	E_{CT}[d]	IP[e]	IP
TTF	0.33[f]	0.70[f]	7.03	3.77	7.00	6.95[h,i]
DSeDTF	0.40	0.72	7.10	3.83[g]	7.06	
TSeF	0.48	0.76	7.18	3.91	7.14	7.21

[a] Energy in eV. [b] Cyclic voltammograms were run in CH_3CN at a platinum working electrode (5×10^{-5} *M*, 0.1 *M* tetraethylammonium perchlorate, 0.20 V/sec sweep rate, volts vs. SCE). [c] Calculated using the equation: IP = ϵ_1 peak + 6.70 from V. D. Parker, *J. Am. Chem. Soc.*, 96, 5656 (1974). [d] Energy of lowest charge transfer band (CCl_4 as acceptor), determined by difference spectroscopy in hexane solvent. [e] Calculated from $E_{CT} = IP^D - E_A^{CCl_4} + C$: E_A = 0.65 eV from G. Briegleb, Angew Chem., *Int. Ed. Engl.*, 3, 617 (1964). *C* = 2.58 eV from calibration with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine in CCl_4. [f] Similar values reported by D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garret, and N. D. Canfield, *J. Am. Chem. Soc.*, 93, 2258 (1971). [g] Average of two charge transfer bands observed. [h] Data from ref 12. [i] IP from photoelectron spectroscopy, 6.86 eV: R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferraris, *J. Electron Spectrosc. Relat. Phenom.*, 2, 207 (1973).

Cyclic voltammograms of TTF, DSeDTF, and TSeF in CH_3CN at a platinum working electrode exhibit two reversible one-electron couples which correspond to the formation of the radical cation and the dication of these donors, respectively. The oxidation peak potentials, summarized in Table I, reveal an unexpected result. DSeDTF and TSeF were more difficult to oxidize, that is, they are *weaker donors*, than TTF.[5] This finding contrasts with the typical lowering of the ionization energy encountered when replacing sulfur with selenium in heteroaromatic systems. For example, in going from X = S to X = Se in compounds **5** and **6**, the ionization energy was found to decrease by 0.07[6] and 0.11 eV,[7] respectively. Interestingly, the difference between the first and second oxidation potentials decreases in going from TTF to DSeDTF to TSeF (Table I). Small values for the ionization energy and for $\epsilon_2 - \epsilon_1$ have been suggested[8] as being desirable for electronic conduction in these charge-transfer salts.



5

6

The energy of charge transfer absorption upon complex formation with an acceptor provides an alternate method for judging donor strength.[9] The high energy (0.14 eV) shift in this absorption band for CCl_4 as acceptor[10] in going from TTF to TSeF (Table I) is consistent with the electrochemical finding that TSeF is a weaker donor. Furthermore, the calculated association constants[11] indicate that TTF (*K* = 0.13) is more effective than TSeF (*K* = 0.05) in forming the donor-CCl_4 complex, a result that depends on a number of donor properties including ionization potential, polarizability, and charge density.

Measurement of the gas phase ionization potential of TSeF, by a mass spectrometric method described previously for TTF,[12] eliminates the possibility that solvation effects or other artifacts connected with the spectroscopic and electrochemical methods may be responsible for the observed ordering of donor strengths. The results of these measurements are summarized in Table I. The agreement of the ionization potentials derived from the three methods is remarkable, perhaps fortuitous, considering the diversity of the measurements.[13]