The azide radical yields nitrogen. The other intermediate, $Cr(NH_3)_5{}^{2+}$, is very labile and decomposes to give Cr(II) and ammonia.[5]

The fate of Cr(II) is not known because the photolyzed pale green solution has not yet been identified. However, we assume that Cr(II) is oxidized by air to binuclear complexes. Such reactions are typical for the oxidation of Cr(II) by air in acidic solution.[9]

Strong support for the intermediate formation of Cr(II) is given by another experiment. If the redox photolysis of $Cr(NH_3)_5N_3{}^{2+}$ in a slightly acidic medium at 320 m$\mu$ is carried out in the presence of $Co(NH_3)_5$-$H_2O^{3+}$, which is not photosensitive under these conditions, extensive formation of Co(II) does occur. Cr(II) is known to reduce $Co(NH_3)_5H_2O^{3+}$.[10]

The occurrence of a photoredox decomposition of $Cr(NH_3)_5N_3{}^{2+}$ upon irradiation in the CT band may be connected to the observation that $Cr(NH_3)_5Cl^{2+}$ [11] and $Cr(NH_3)_5Br^{2+}$ [12] show a large increase of halide aquation upon irradiation in the CT band. Both observations are consistent with a cage mechanism which was first proposed for the photochemical redox reactions of Co(III) complexes.[13,14] The absence of azide aquation for $Cr(NH_3)_5N_3{}^{2+}$ upon irradiation in the CT region could be explained by the exceptional short lifetime of the azide radical.[15,16] After homolytic splitting of the $Cr^{3+}$–$N_3$ bond, the azide radical may react fast enough to yield nitrogen before a charge recombination $Cr^{2+}\cdots N_3 \nrightarrow Cr^{3+}N_3{}^-$ can take place.

(9) M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3197 (1959).

(10) A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959); J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

(11) H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **62**, 127 (1968).

(12) P. Riccieri and H. L. Schläfer, *Inorg. Chem.*, **9**, 727 (1970).

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(14) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

(15) S. A. Penkett and A. W. Adamson, *J. Amer. Chem. Soc.*, **87**, 2514 (1965).

(16) A. Treinin and E. Hayon, *J. Chem. Phys.*, **50**, 538 (1969).

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## Tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III). A Chiral Shift Reagent for Direct Determination of Enantiomeric Compositions[1]

*Sir:*

We wish to report an nmr method for direct determination of enantiomeric compositions (optical purities) which we have applied successfully to several types of compounds including alcohols, ketones, esters, epoxides, and amines. This method involves use of a new chiral nmr shift reagent, tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) (1). Similar methods based on chemical-shift nonequivalence of enantiomers (in chiral solvents[2] or in the presence of a chiral shift reagent, tris[3-(*tert*-butylhydroxymethylene)-*d*-camphorato]europium(III) (2)[3] have been re-

(1) Supported by the Research Committee of the Graduate School of the University of Wisconsin.

(2) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **91**, 5150 (1969); W. H. Pirkle, R. L. Muntz, and I. C. Paul, *ibid.*, **93**, 2817 (1971).

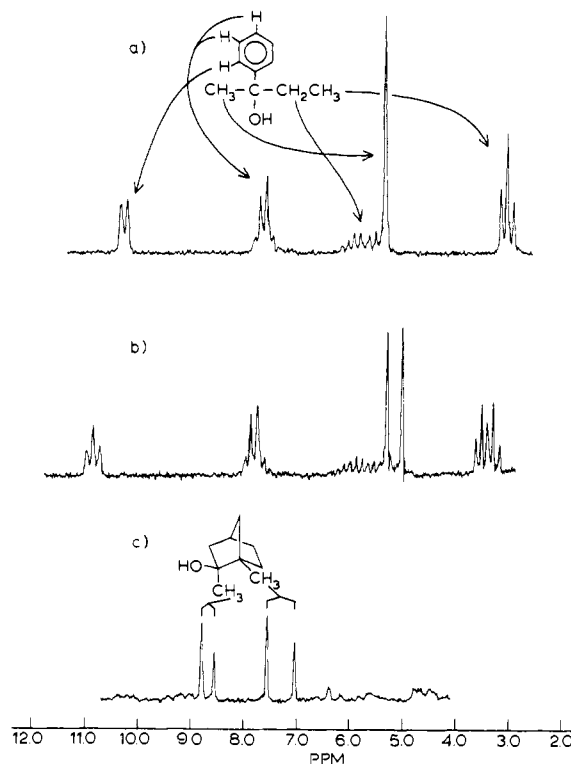(3) G. M. Whitesides and D. W. Lewis, *ibid.*, **92**, 6979 (1970).

Figure 1. Spectra of 0.54 *M* 2-phenyl-2-butanol in CCl$_4$ in (a) the presence of 0.13 *M* tris(dipivalomethanato)europium(III) and (b) 0.42 *M* **1**, and (c) spectrum of 0.3 *M* 1,2-dimethyl-*exo*-2-norbornanol in the presence of 0.42 *M* **1**.

ported. However, these appear to be of limited applicability. Magnitudes of nonequivalence in chiral solvents are small ($\leq$0.04 ppm)[2] which limits the usefulness of this technique for determining enantiomeric compositions. Large pseudocontact-shift differences for enantiomeric amines are observed with **2**.[3] However, with neutral compounds magnitudes of nonequivalence are generally too small to be useful. On the other hand, with **1** we have observed pseudocontact shift differences for enantiomeric alcohols of >0.5 ppm. Moreover, there is very little line broadening and in most cases we have achieved complete resolution of signals for enantiotopic[4] protons with a 60-MHz instrument.

Compound **1** was prepared by reaction of 3-trifluoromethylhydroxymethylene-*d*-camphor (3) with europium(III) chloride in the presence of base.[5] The chelate is an amorphous solid that softens at 100° and is very soluble in nonpolar solvents. The nmr spectrum of **1** ranges from +3 to −1 ppm from TMS. Compound **3** was obtained by condensation[6] of *d*-camphor with ethyl trifluoroacetate. *Anal.* Calcd for $C_{12}H_{15}F_3O_2$: C, 58.06; H, 6.09. Found: C, 58.17; H, 6.09.

Parts a and b of Figure 1[7] show spectra of carbon tetrachloride solutions of *dl*-2-phenyl-2-butanol (**4**) in

(4) M. Raban and K. Mislow, *Top. Stereochem.*, **1**, 1 (1967).

(5) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965). The chelate was isolated by precipitation (as a resin) by addition of water and extraction into pentane. After extraction with water the dried pentane solution was concentrated to dryness and the residual **1** was dehydrated under vacuum. This material gave the same results as a sample purified by distillation (0.06 mm). *Anal.* Calcd for $C_{36}H_{42}F_9O_6Eu$: C, 48.38; H, 4.74. Found: C, 48.60; H, 4.72.

(6) K. R. Kopecky, D. Nonhebel, G. Morris, and G. S. Hammond, *J. Org. Chem.*, **27**, 1036 (1962).

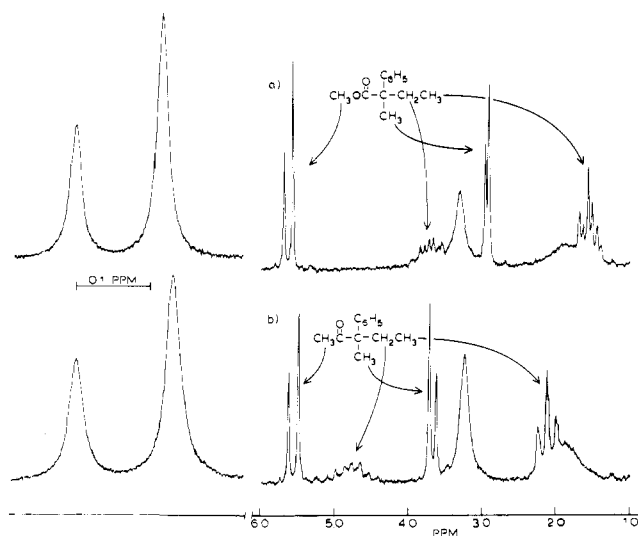(7) Spectra were determined with a Varian A-60 spectrometer.

Figure 2. Spectra of $CCl_4$ solutions of 0.9 $M$ 5 and 0.6 $M$ 6 in the presence of 0.5 $M$ 1. Expanded spectra at left are for the downfield methyl resonances. Unassigned resonances are due to 1.

the presence of tris(dipivalomethanato)europium(III) and in the presence of 1. This comparison shows that similar pseudocontact shifts ($\Delta\delta$) are observed with the two reagents.[8] As illustrated by spectrum b, in the presence of 1 pseudocontact-shift differences for enantiomers are observed. The enantiotopic $\alpha$-methyl singlets are separated 0.29 ppm and the $\beta$-methyl triplets are separated 0.22 ppm which corresponds to $\sim 2J$ and gives rise to a quintuplet. A more dramatic example of nonequivalence is illustrated by the lower spectrum in Figure 1. This spectrum of partly active 1,2-dimethyl-$exo$-2-norbornanol[9] in the presence of 1 shows large shift differences for corresponding methyl groups of the enantiomers. It is interesting to note that nonequivalence is largest ($>0.5$ ppm) for the least shifted methyl group (presumably the 1-methyl).

Effects of 1 on the nmr spectra of some other types of compounds are summarized in Table I. This table shows pseudocontact-shift differences ($\Delta\Delta\delta$) for the

Table I. Pseudocontact-Shift Differences for Enantiomers ($\Delta\Delta\delta$) in the Presence of 1[a]

| Compound | Proton | $\Delta\Delta\delta$, ppm |
|---|---|---|
| 2-Octanol | $\alpha$-$CH_3$ | 0.11 |
| 1,2-Dimethyl-$endo$-2-norbornanol | { 1-$CH_3$ | 0.37 |
|  | { 2-$CH_3$ | 0.33 |
| 1-Phenylethanol | $\alpha$-H | 0.30 |
| 1-Phenylethyl acetate | -$CO_2\overset{\mid}{\underset{\mid}{C}}CH_3$ | 0.18 |
| 1-Methyl-2-norbornanone | 1-$CH_3$ | 0.17 |
| 3,3-Dimethyl-2-aminobutane | $\alpha$-$CH_3$ | 0.28 |
| $cis$-$\beta$-Methylstyrene oxide | $\beta$-$CH_3$ | 0.27 |

[a] Concentration of 1, $\sim 0.4$ $M$ (200 mg/0.6 ml of $CCl_4$). Molar ratio of 1/substrate, $>0.6$.

(8) For information regarding pseudocontact shifts and nmr shift reagents see (a) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971); (b) R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1522 (1971); and (c) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *Chem. Commun.*, 749 (1970), and references in these papers.

(9) H. L. Goering, C. Brown, S. Chang, and J. V. Clevenger, *J. Org. Chem.*, **34**, 624 (1969).

indicated enantiotopic protons. Nonequivalence was not observed with ethers. Magnitudes of pseudocontact shifts ($\Delta\delta$) and of $\Delta\Delta\delta$ depend on the ratio of 1 to substrate. Conditions have been optimized only for 4. In this case $\Delta\delta$ and $\Delta\Delta\delta$ (for both methyl groups) increase with the 1/4 ratio until the latter reaches $\sim 0.7$ after which there is no change. This suggests[8b] that at ratios $>0.7$ (optimum conditions) essentially all of the substrate is coordinated. In this connection it is significant that nonequivalence was not observed for protons that are enantiotopic by internal comparison,[4] $e.g.$, 2-propanol and dimethyl sulfoxide.

Nonequivalence of enantiomers is also observed with the praseodymium analog of 1 and shift differences are at least as large as with 1; however, resolution is generally poorer. In this case induced shifts are in the upfield direction.[8c,9a]

The use of 1 for direct determination of enantiomeric compositions is illustrated by Figure 2 which shows spectra of optically active methyl 2-methyl-2-phenyl-butanoate (5) and 3-methyl-3-phenyl-2-pentanone (6) in the presence of 1. Both compounds were prepared from the same sample of partially resolved 2-methyl-2-phenylbutanoic acid (excess $S$ isomer)[10] and have the same optical purities. For 5, nonequivalence is observed for the $O$-methyl ($R$, 5.68 ppm; $S$, 5.56 ppm) and 2-methyl protons ($R$, 2.98 ppm; $S$, 2.93 ppm). Similarly, for 6, nonequivalence is observed for the acyl-methyl ($R$, 5.62 ppm; $S$, 5.49 ppm) and 3-methyl protons ($S$, 3.72 ppm; $R$, 3.62 ppm). Expanded sweep widths of the downfield methyl resonances are shown to the left of the corresponding spectrum.[7] Peak areas of the expanded signals correspond to optical purities of 27.7% for 5 and 27.3% for 6 as compared to 25.8% for 5 and 25.4% for 6 determined from rotations.[10] It is noteworthy that in the spectrum of 6 the sense[2] of nonequivalence is reversed for the acyl-methyl and 3-methyl singlets. This indicates that nonequivalence results from intrinsicly different magnetic environments for coordinated enantiomers. Differences in stability constants for complexes of enantiomers may also contribute to nonequivalence.

(9a) NOTE ADDED IN PROOF. We have also investigated the europium and praseodymium chelates derived from 3-heptafluoropropylhydroxy-methylene-$d$-camphor. These chiral chelates have nmr shift properties similar to the chelates derived from 3. Nonequivalences for enantiomers are of about the same magnitude and resolution is similar for corresponding chelates.

(10) D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, **76**, 4516 (1954); D. J. Cram, A. Langemann, J. Allinger, and K. P. Kopecky, *ibid.*, **81**, 5740 (1959).

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### The Determination of Enantiomeric Purity Using Chiral Lanthanide Shift Reagents[1]

*Sir:*

Tris[$tert$-butylhydroxymethylene-$d$-camphorato]europium(III) (1) induces contact and/or pesudocontact shifts of different magnitudes in corresponding protons