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### **TECHNICAL REPORT NO. 27**

# Enantiomeric Separation of Chiral [α-(1-Naphthyl) Ethyl]Ammonium Perchlorate by Silica Gel-bound Chiral Pyridino-18-Crown-6 Ligands

## by

### P. Huszthy, J.S. Bradshaw, A.V. Bordunov and R.M. Izatt

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Department of Chemistry Brigham Young University Provo, UT 84602-4670

May 11, 1994

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# ENANTIOMERIC SEPARATION OF CHIRAL [ $\alpha$ -(1-NAPHTHYL)ETHYL]AMMONIUM PERCHLORATE BY SILICA GEL-BOUND CHIRAL PYRIDINO-18-CROWN-6 LIGANDS

P. Huszthy, J.S. Bradshaw, A.V. Bordunov and R.M. Izatt

#### Abstract

The separation of  $[\alpha-(1-naphthyl)ethyl]ammonium perchlorate (NapEt) into its (R) and (S) forms using sulica gel-bound dimethylpyridino-18-crown-6 ligand <math>[(S,S)-1]$  with methanol as an eluent is reported. We also report the synthesis of a new silica gel-bound diphenyl-substituted pyridino-18-crown-6 ligand [(R,R)-2] by the following reactions. Dimethyl chelidamate (7) was first alkylated with 11-iodoundec-1-ene (6) on the phenolic oxygen and the resulting ether diester was reduced to form 4-undecenyloxy-2.6-pyridinedimethanol (8). Tosylation of 8 gave ditosylate 9 which was cyclized with (R,R)-diphenyl-substituted tetraethylene glycol [(R,R)-10] to form crown (R,R)-11. Ligand (R,R)-11 was treated with triethoxysilane using a platinum catalyst. The resulting chiral crown-substituted triethoxysilane, (R,R)-12, was reacted with silica gel in toluene at 90° to attach the ligand to silica gel. The results of the separation of (R)- and (S)-NapEt using new silica gel-bound crown (R,R)-2 with methanol as the eluent are also presented.

#### Introduction

In continuation of our studies on enantiomeric recognition of chiral organic ammonium salts by chiral pyridino-18-crown-6 ligands [1-7], we have studied the enantiomeric separation of chiral organic ammonium salts by chiral pyridino-18-crown-6 ligands covalently bonded to silica gel [8]. One and a half decades ago, Cram and coworkers published their pioneering paper [9] on the separation of the enantiomers of several racemic organic ammonium salts using a silica gel-bound chiral bis(binaphthyl)-22-crown-6 ligand. After covalently attaching the chiral ligand to silica gel they treated the adsorbent with an excess of chlorotrimethylsilane to form a less polar material. This treatment reduced tailing and gave better separations on their solid stationary phase. They used a mobile phase consisting of chloroform or dichlomethane solutions of the racemic ammonium salts and 18-crown-6, ethanol, or 2-propanol as carriers [9]. Our preliminary results of the separation of  $[\alpha-(1-naphthyl)ethyl]$ ammonium perchlorate (NapEt) into its (R) and (S) forms using silica gel-bound chiral crown (S,S)-1 (see Figure 1) with acetone/methanol (7/3)(v/v) as the eluent were not completely satisfactory [8].

In this paper, we report a good, almost base-line separation of NapEt into its (R) and (S) forms using silica gel-bound chiral crown (S,S)-1 with methanel as the eluent. We also report the use of (R,R)-2 for the separation of the enantiomers of NapEt. Silica gel-bound chiral crown (R,R)-2 differs from silica gel-bound chiral crown (S,S)-1 in two features: a) (R,R)-2 has a longer connecting arm to silica gel by seven carbon atoms; and b) instead of two methyl substituents, (R,R)-2 contains two phenyl moieties at the chiral centers. These changes were made because silica gel-bound chiral stationary phases eleven carbon atoms removed from the support were very effective for chiral solute separations [10-13], and second, the substitution of two methyl groups in (S,S)-1 by two phenyl groups to form (R,R)-2 should improve chiral recognition and subsequently chiral separation.

#### **Results and Discussion**

•

The separation of (R)- and (S)-NapEt using silica gel-bound (S,S)-1 is shown in Figure 2. This separation study was carried out in a manner similar to that reported [8]. Very concentrated methanol solution of racemic NapEt was placed on a column containing (S,S)-1. The

count was methanel. Methanol was used because it allows for a good separation of enantiomers, reduces greatly the time for a separation, and reduces tailing to a great extent. The amounts of (R)- and (S)-NapEt in each fraction were determined by HPLC using the N-acetyl derivatives of (R)- and (S)-NapEt [8]. Because (S,S)-1 interacts more strongly with (R)-NapEt, (S)-NapEt passes through the column first and (R)-NapEt last as observed in Figure 2.

The separation of (R)- and (S)-NapEt using silica gel-bound (R,R)-2 is shown in Figure 3. This separation was performed as described above using (S,S-1). Since the parent chiral diphenyl-substituted crown [(R,R)-4] exhibits less recognition for the enantiomers of NapEt as mentioned above, the separation using (R,R-2) was not as good as that using (S,S)-1. As shown in Figure 3, (R)-NapEt elutes first from the column because (R,R)-2 interacts with (S)-NapEt nore strongly. Although a clean separation of enantiomers by (R,R)-2 was not achieved in this one experiment, it is that recognition did take place. Another solvent system could be found

ad a setter separation by Col-2.

#### Experimental

## Separation of R-(+)-and S-(-)-Isomers of NapEt on (S,S)-1 with Methanol as Eluent

This separation was carried out in the same manner using the same column filled with 4.2 g of (S.S)-1 as reported [8] with the following exemptions: a)prior to separation, 50 ml of 1/4 (v/v) triethylamine/methanol and then 100 ml of pure methanol were passed through the column and b)instead of a 3/7 (v/v) methanol/acetone mixture, pure methanol was used as an eluent. The flow rate was 0.048 ml/min. The calculated [8] concentrations of (R)- and (S)-NapEt were plotted versus the ml of eluent as shown in Figure 2.

#### Separation of R-(+)- and S-(-) Isomers of NapEt on (R,R)-2 with Methanol as Eluent

This separation was carried out in the same manner as described above for (S,S)-1 using (R,R)-2 silica gel-bound chiral diphenylpiridino-18-crown-6 with pure methanol as an eluent. The flow rate in this case was 0.017 ml/min. The calculated [8] concentrations of (R)- and (S)- NapEt were plotted versus the ml of eluent as shown in Figure 3.

#### References

- Davidson, R.B., Bradshaw, J.S., Jones, B.A. Dalley, N.K., Christensen, J.J., Izatt, R.M., Morin, F.G., Grant, D.M.: J. Org. Chem., 49, 353 (1984)
- Bradshaw, J.S., Huszthy, P., McDaniel, C.W., Zhu, C.-Y., Dalley, N.K., Izatt, R.M., Lifson, S.: J. Org. Chem., 55, 3129 (1990)
- [3] Huszthy, P., Bradshaw, J.S., Zhu, C.-Y., Izatt, R.M., Lifson, S.: J. Org. Chem., 56, 3330 (1991)
- Bradshaw, J.S., Huszthy, P., McDaniel, C.W., Oue, M., Zhu, C.-Y., Izatt, R.M., Lifson,
  S.: J. Coordination Chem., B 27, 105 (1992)
- [5] Huszthy, P., Oue, M., Bradshaw, J.S., Zhu, C.-Y., Wang, T.-M., Dalley, N.K., Curtis,
  J.C., Izatt, R.M.: J. Org. Chem., 57, 5383 (1992)
- [6] Izatt, R.M., Zhu, C.-Y., Huszthy, P., Bradshaw, J.S.: "Enantiomeric Recognition in Macrocycle-Primary Ammonium Cation Systems," in *Crown Ethers: Toward Future Applications*, ed. by S. R. Cooper, VCH Press, New York, pp. 207-233, 1993
- [7] Chu, I.-H., Dearden, D.V., Bradshaw, J.S., Huszthy, P., Izatt, R.M. J. Am. Chem. Soc., 115, 4318 (1993)
- [8] Bradshaw, J.S., Huszthy, P., Wang, T.-M., Zhu, C.-Y., Nazarenko, A.Y., Izatt, R.M.: Supramolecular Chemistry, 1, 267 (1993)
- [9] Sousa, L.R., Sogah, G.D.Y., Hoffman, D.H., Cram, D.J.: J. Am. Chem. Soc., 100, 4569 (1978)
- [10] Pirkle, W.H., Sowin, T.J.: J. Chromatogr.: 396, 83 (1987)
- [11] Dobashi, A., Dobashi, Y., Kinoshita, K., Hara, S.: Anal. Chem., 60, 1985 (1988)
- [12] Yamashita, J., Satoh, H., Oi, S., Suzuki, T., Miyano, S., Takai, N.: J. Chromatogr., 464, 411 (1989)
- [13] Uray, G., Linder, W.: Chromatographia, 30, 323 (1990)

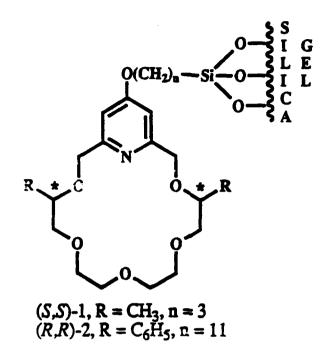


Fig. 1. Silica gel-bound chiral pyridino-18-crown-6 ligands

