creases K_s for resin–Cs^+, increases K_s for resin–H_3O^+, but has little effect on the other three. Dibenzo[18]crown-6's K_s order of resin–K^+ > –Na^+ > –Cs^+ parallels Frensdorff's[10] stability constant order for dibenzo[18]crown-6's complexation of metal chlorides in methanol. Others noted that substitution of O by S decreases the complexation of alkaline earth metals by crown ethers,[2d,2f] and that [18]crown-6 derivatives complex $K^+ > NH_4^+ > Cs^+$.[10] Binaphthyl crown ether CPK models suggest hole diameters of 2.6–3.1 Å that change with naphthyl–naphthyl dihedral angles (45–135°). "Hinged" cycles adapt somewhat differently to guest-cation size and character.

The maximum cycle adsorption on cationic resin occupies ~4% of the potential sites. Smid,[11] with benzo[18]crown-6 units included in polystyrene polymer, observed 70% maximal crown site utilization by K^+. Resin–crown's steric requirements for complexing K^+ are less than resin–K^+'s requirements for complexing crown.

Chiral crowns **2**–**4**, **6**, and **7** contain C_2 symmetry axes. Chiral alkylammonium salt's complexation to either face of C_2-crowns generates indentical species. Crowns **10** and **13** possess "sidedness," since binding to different faces generates diastereomers. The side chain of **10** is located closer to the C_2 axis of parent cycle **6** than is the side chain of **13**. Thus the two faces that **13** presents to potential chiral guest molecules differ more than the two faces of **10**. This work demonstrates feasibility of synthesizing a variety of chiral crown ethers capable of complexing ammonium, alkylammonium, hydronium, and metal cations.

(10) H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600, 4685 (1971).

(11) S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **4**, 359 (1971).

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Chiral Recognition in Molecular Complexing[1]

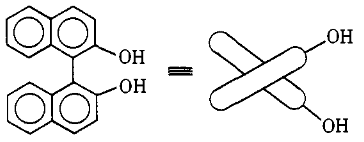
Sir:

Crown ether compounds containing binaphthyls as potential chiral barriers were reported.[2] Chiral recognition properties of optically pure crown ethers complexing (*R*)- and (*S*)-α-phenylethylammonium hexafluorophosphate are described here.

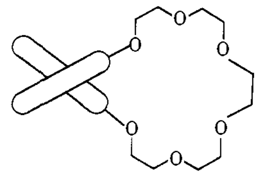
Binaphthol (**1**), resolved to optical purity through its mono-*l*-menthoxyacetic ester, gave $[\alpha]^{25}\mathrm{D}$ −33.6°.[3a] The (superior) reported method[4] gave $[\alpha]^{25}\mathrm{D}$ −33.9°[3a] and $[\alpha]^{25}\mathrm{D}$+ 33.8°.[3a] Although optically stable (100°, 24 hr) in dioxane–water, (−)-**1** racemized 72% with HCl (~1.2 *N*) present and 69% (118°, 23 hr) in butanol–0.667 *M* KOH. Molecular models (CPK) indicate that protonation or hydroxylation of the 1 or 8 positions of (−)-**1** lowers the steric barrier to Ar–Ar rotation. Charge at these positions probably makes bond angles more deformable.

With pentaethylene glycol ditosylate in tetrahydrofuran–potassium *tert*-butoxide (66°, 5 hr), optically pure (−)-**1** gave (−)-**2**[3b] (64%, oil, $[\alpha]^{25}\mathrm{D}$ −70.5°[3a]). In oxygen-free diethylene glycol (sealed tube, 205°), (−)-**2** underwent 0% rotational loss in 6, and 8.6% in 202 hr.

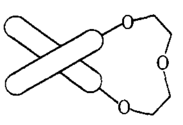
With diethylene glycol ditosylate in tetrahydrofuran–potassium *tert*-butoxide (15 hr, 66°), optically pure (−)-**1** gave (+)-**3**[3b] (5%, mp 230–231°, $[\alpha]^{25}{}_{578}$ +71°[3c]) and (−)-**4**[3b] (31%, $[\alpha]^{25}{}_{578}$ −221°,[3c] mp 123–126°, cyclohexane solvate). Similarly, (+)-**1** gave (+)-**4** ($[\alpha]^{25}{}_{578}$ +221°,[3c] mp 123–126°, solvate). Similarly, (±)-**1** gave (±)-**3**[3b] (8%, mp 227–228°), (±)-**4**[3b] (25%, mp 260–260.5°), and *meso*-**4**[3b] (2%, mp 283–284°). The identity of the pmr spectra of (+)-**4** and (±)-**4** and the substantial difference between these spectra and that of *meso*-**4** established (±)-**4** and *meso*-**4** structures. Whereas (+)-**4** exemplifies the rarely encountered chiral D_2 point group, that of *meso*-**4** is C_s. Since (+)-**1** is *R*,[5] all configurations are assignable.



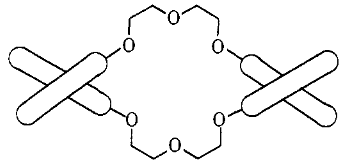
(−)-(*S*)-**1**



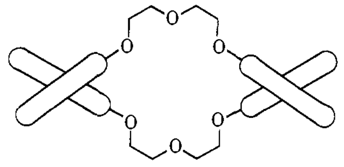
(−)-(*S*)-**2**



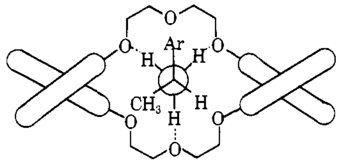
(+)-(*S*)-**3**



(−)-(*SS*)-**4**



meso-**4**



projection looking down C–N of (*R*)-**5** cation complexed with (*SS*)-**4**; Ar = C_6H_5

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(1) This work was supported by U. S. Public Health Service Research Grant No. GM 12640-08 from the Department of Health, Education and Welfare, and by a grant from the National Science Foundation, GP 33533X.

(2) E. P. Kyba, M. G. Siegel, L. R. Sousa, G. D. Y. Sogah, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 2691 (1973).

(3) (a) *c* 0.87–1.0, tetrahydrofuran; (b) carbon and hydrogen analyses were within 0.30 of theory; new compounds gave expected pmr spectra and molecular ions in their mass spectra; (c) *c* 0.81–0.87, CH_2Cl_2.

(4) J. Jacques and C. Fouquay, *Tetrahedron Lett.*, 4617 (1971).

(5) (a) H. Akimoto, T. Shioiri, Y. Iitaka and S. Yamada, *ibid.*, **97** (1968); (b) H. Akimoto and Y. Iitaka, *Acta Crystallogr., Sect. B*, **25**,

Saturation constants[2] of some resin–cations by diastereomeric crown ethers in CH_2Cl_2 are different. For resin-H_3O^+, $-Na^+$, $-K^+$, $-NH_4^+$, and $-Cs^+$, respectively, K_s's of (±)-**4** are 0.19, 0.18, 0.078, 0.043, and 0.011; *meso*-**4** gave 0.087, <0.093, 0.061, 0.042, and 0.014.

Chiral differentiation in complexation of optically pure (+)-(*R*) and (−)-(*S*)-α-phenylethylamine[6] salts ((+)-(*R*)-**5** and (−)-(*S*)-**5**) by optically pure (+)-(*RR*)-**4** was measured (HA-100 nmr, TMS) by partitioning salts between water and chloroform. In run 1, 90 mg of (+)-**4** in 0.7 ml of $CDCl_3$ was shaken 1 min with 150 mg of (−)-**5**·HBr in 0.8 ml of D_2O at ~25°. The spectrum of the $CDCl_3$ layer (dried) showed **5** to be absent. Run 2 duplicated 1, except that 125 mg of $NaPF_6$ was present. The spectrum showed ~0.7 mol of (−)-**5** salt per mole of (+)-**4** in the $CDCl_3$ layer (methyl doublet, J = 7.0 Hz, total methylenes minus methine integrations were compared; CH_3, δ 1.40[7]). The crown ether's spectrum was dramatically different from that of run 1. The methyl doublet was unchanged but the crown spectrum was further averaged by addition of 13.5 mg of (+)-**4**. Dilution by a factor of 2 of the $CDCl_3$ solution produced little chemical shift changes. The aqueous layer contained no crown. Run 3 duplicated 2 except (+)-**5**·HBr was substituted for (−)-**5**·HBr. The spectrum showed ~0.5 mol of (+)-**5** salt per mole of (+)-**4** in the $CDCl_3$ layer (methyl doublet, J = 7.0 Hz, δ 1.11[7]). The spectrum of the crown was changed, but was closer to that of run 2 than to that of run 1. Dilution by a factor of 2 of the $CDCl_3$ layer produced little shift changes. Run 4 duplicated 2 except that (±)-**5**·HBr was substituted for (−)-**5**·HBr. The spectrum showed 0.74 mol of salt per mole of (+)-**4** in the $CDCl_3$ layer and two methyl doublets (59% (−)-**5**, δ 1.40,[7] 41% (+)-**5**, δ 1.14[7]). Run 5 duplicated 2 except that (±)-**4** was substituted for (+)-**4**. The spectrum of the $CDCl_3$ layer showed 0.67 mol of salt per mole of (±)-**4**, and one methyl doublet (δ 1.33[7]). Run 6 duplicated 4 except (−)-**4** was substituted for (+)-**4**, and the partitioning temperature was 0°. The spectrum of the $CDCl_3$ layer showed 0.93 mol of salt per mole of (−)-**4** (62% (+)-**5**, 38% (−)-**5**).

For most protons large chemical shift differences are visible in the spectra between complexed and noncomplexed components and between diastereomeric complexes. The $ArOCH_2$ and CH_3 peaks differ most obviously. Complexed and noncomplexed crowns' spectral differences probably reflect mainly Ar–Ar and Ar–O–CH_2 dihedral angle differences between relatively flexible crowns and rigid complexes. Asymmetrically disposed binaphthyls magnetically differentiate in complexes between the methyls of uncomplexed enantiomerically related amines. Averaging between complexed and noncomplexed crown signals and between methyls of (+)-**4**·(−)-**5** and (−)-**4**·(−)-**5** demonstrates that the complexes and their components equilibrate rapidly on the pmr time scale.

Pure (−)-**4** (3.00 g), (±)-**5**·HCl (3.9 g), and $NaPF_6$ (4.2 g) were distributed between 25 ml of chloroform and 30 ml of water at 0°. Extraction procedures separated the chloroform layer's cyclic ether and amine. Distilled **5** (0.333 g, 65%) was 62% (+)-**5** and 38% (−)-**5**, $[\alpha]^{25}_{578}$ +9.41° (c 7.56, $CHCl_3$). These results were predicted from those of runs 1–6.

By chiral recognition in complexation equilibria, (*SS*)-**4** selects (*R*)-**5** over (*S*)-**5** salt, and (*SS*)-**4**·(*R*)-**5** is ~266 cal/mol more stable (0°) than (*SS*)-**4**·(*S*)-**5** complex. Molecular models (CPK) of these diastereomeric complexes differ visibly, and the more stable complex looks more stable in its model. Optically active host cycles with C_2 axes (*e.g.*, (−)-**4**) present identical faces to potential chiral guest amines, and "sidedness" problems are avoided. Multiplate partitioning by liquid–liquid or solid–liquid processes should allow complete resolution of racemic primary amines by optically active cyclic ethers, or of racemic cycles by optically active amines. These and future generation chiral cyclic ethers will find use in optical resolution by partitioning and in determining configuration and optical purity.

1491 (1969); (c) I. Hanazaki and H. Akimoto, *J. Amer. Chem. Soc.*, **94**, 4102 (1972); (d) H. Akimoto and S. Yamada, *Tetrahedron*, **27**, 5999 (1971).

(6) (a) W. Theilacker and H. G. Winkler, *Chem. Ber.*, **87**, 690 (1954); (b) W. Leithe, *ibid.*, **64**, 2827 (1931).

(7) Downfield peak.

(8) (a) National Research Council of Canada Postdoctoral Fellow, 1971–1972; (b) Public Health Service International Postdoctoral Research Fellowship, 1971–1972; (c) National Institutes of Health Postdoctoral Fellow, 1971–1972.

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A New Synthesis of Aldehydes Using 1-Vinylthioallyllithium. A Facile Route to Propylure

Sir:

The present paper describes a general two-step sequence which permits the highly stereoselective conversion of a halide (RX) to the trans γ,δ-unsaturated aldehyde ($RCH{=}CHCH_2CH_2CHO$). This involves the alkylation of 1-vinylthioallyllithium (**1**) and the subsequent thio-Claisen rearrangement.[1,2] The method is applicable to a variety of R groups and is certainly an addition to the host of recently developed aldehyde syntheses.[3]

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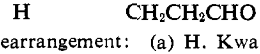
(1) For recent practical modifications of the Claisen rearrangement of allyl vinyl ethers, see (a) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Justus Liebigs Ann. Chem.*, **641**, 1 (1961); D. Felix, K. Gschwend-Steen, A. E. Wick, and A. Eschenmoser, *Helv. Chim. Acta*, **52**, 1030 (1969); (b) W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. T. Li, D. J. Faulkner, and M. R. Petersen, *J. Amer. Chem. Soc.*, **92**, 741 (1970). Both of these methods allow the easy, high-yield addition of an *acetic acid* unit to the γ carbon of an allylic alcohol. The present method, in contrast, could introduce a *five carbon* unit at one time, and 1-vinylthioallyllithium has been shown to serve effectively as the equivalent of the unknown vinylic anion as shown below.



$$\overset{Li}{\underset{H}{}}{>}C{=}C{<}\overset{H}{\underset{CH_2CH_2CHO}{}}$$

(2) Thio-Claisen rearrangement: (a) H. Kwart and T. J. George, *Chem. Commun.*, 433 (1970), and references cited therein; (b) E. J. Corey and J. I. Shulman, *J. Amer. Chem. Soc.*, **92**, 5522 (1970); (c) K. Kondo and I. Ojima, *J. Chem. Soc., Chem. Commun.*, 62 (1972).

(3) (a) 1,3-Dithiane method: E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965); (b) dihydro-1,3-oxazine method: A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer, *J. Amer. Chem. Soc.*, **91**, 763 (1969); (c) 1,3-bis(methylthio)allyllithium method: E. J. Corey, B. W. Erickson, and R. Noyori, *ibid.*, **93**, 1724 (1971).