yield and in excess of 95% diastereomeric purity as determined by ^{1}H NMR-Eu(fod)$_3$ techniques ($[\alpha]^{25}_D$ -4.2° (*c* 2.00, $CHCl_3$), R_f = 0.48, silica, 50% ether in petroleum ether). This mixture was carried through the following sequence until the coupling with the optically pure tetrahydropyran fragment allowed convenient separation of diastereoisomers. Ozonolysis of hydrazone **13** (CH_2Cl_2, -78 °C, 15 min) proceeded smoothly and in quantitative yield producing the aldehyde **14** from which the synthesis proceeds essentially as we described previously,[7] namely, (**14** → **15**, 60% overall yield) (i) condensation with the lithio salt of methyl-4-(dimethylphosphono)crotonate, (ii) reduction with excess DIBAL, (iii) protection with *tert*-butyldiphenylsilyl chloride, (iv) selective hydrolysis of the *tert*-butyldimethylsilyl ether, (v) oxidation with CrO_3·HCl·pyr, and (vi) condensation with (carbomethoxy)-methylenetriphenylphosphorane; **15** → **16**, 70%: Δ, toluene; **16** → **2**, 100%: *n*-Bu_4NF. Synthetic lactone **2** ($[\alpha]^{25}_D$ +113.00° (c 0.20, $CHCl_3$), R_f 0.40, silica, 50% ether in petroleum ether) obtained by this route exhibited identical spectroscopic and chromatographic properties as the racemic compound previously obtained and fully characterized by spectroscopic and X-ray crystallographic analysis.[7]

With the two important building blocks **1** and **2** at hand, the stage was set for their coupling and the conclusion of the total synthesis of X-14547A. The remaining operations are described in the accompanying communication.[14,15]

(14) Nicolaou, K. C.; Claremon, D. A.; Papahatjis, D. P.; Magolda, R. L. *J. Am. Chem. Soc.*, following paper in this issue.

(15) This work was financially supported by Merck Sharp & Dohme, U.S.A., The A. P. Sloan Foundation, and The Camille and Henry Dreyfus Foundation.

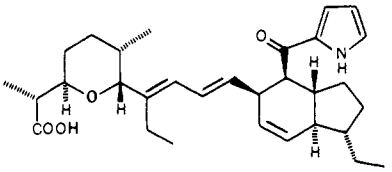
Total Synthesis of Ionophore Antibiotic X-14547A. 2. Coupling of the Tetrahydropyran and Tetrahydroindan Systems and Construction of the Butadienyl and Ketopyrrole Moieties

K. C. Nicolaou,*,† D. A. Claremon, D. P. Papahatjis, and R. L. Magolda

Department of Chemistry, University of Pennsylvania Philadelphia, Pennsylvania 19104

Received June 29, 1981

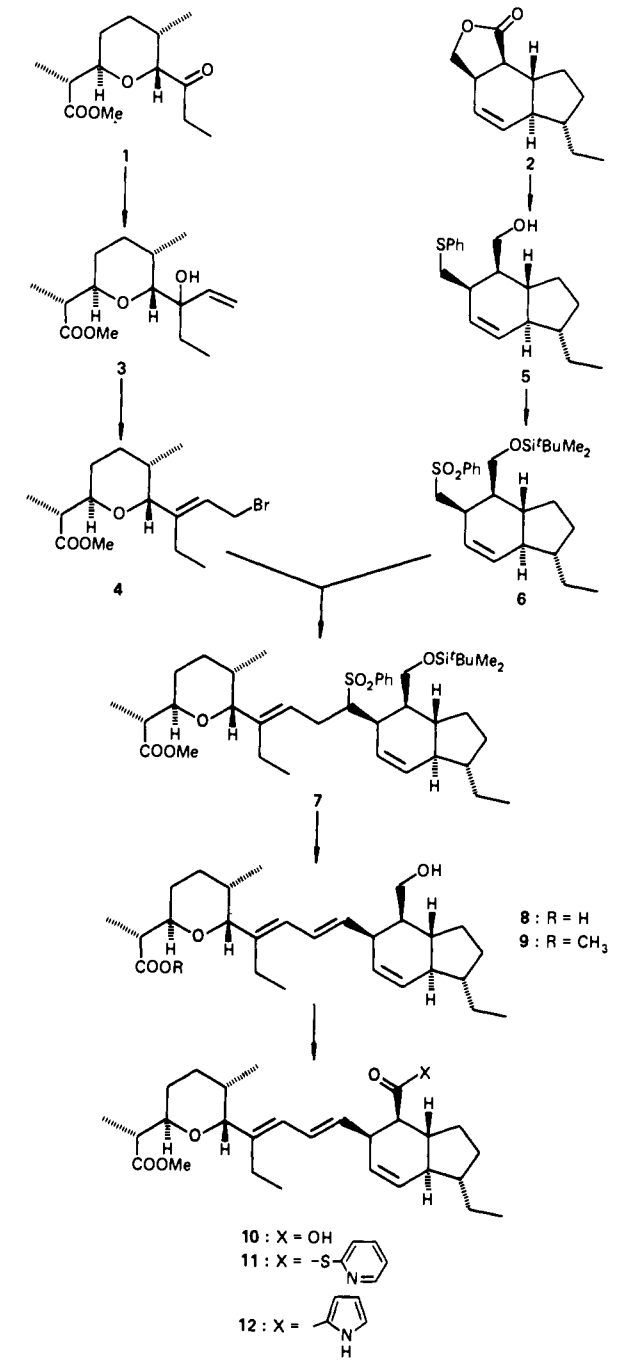
In the preceding paper,[1] we described enantioselective syntheses of the tetrahydropyran and tetrahydroindan building blocks (**1** and **2**, Scheme I) for the total synthesis of the ionophore antibiotic X-14547A. This communication deals with the successful conclusion of the total synthesis of X-14547A, describing a highly efficient coupling of the two fragments **1** and **2** and a two carbon unit and stereoselective constructions of the butadienyl and ketopyrrole systems.



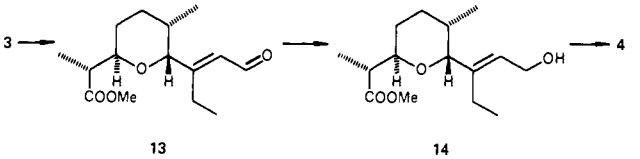
X-14547A

The location of the ketopyrrole unit and the unsaturation in the tetrahydroindan system impose some complications on the coupling of the two fragments and the regioselective formation of the *trans*-butadienyl chromophore due to persistent interference from these systems.[2] It was after considerable experimentation

Scheme I



Scheme II



13 14

that we decided to postpone the construction of the ketopyrrole appendage until the end and to utilize the phenyl sulfone moiety as an auxiliary group for both the coupling reaction and the stereo- and regioselective construction of the *trans*-butadienyl system. The actual synthetic sequence used is outlined in Scheme I.

† Fellow of the A. P. Sloan Foundation, 1979-1983; recipient of a Camille and Henry Dreyfus Teacher-Scholar Award, 1980-1985.

(1) Nicolaou, K. C.; Papahatjis, D. P.; Claremon, D. A.; Dolle, R. E., III, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Wittig-type approaches for the coupling of the two segments of the molecule and construction of the butadienyl system were originally explored but proved unsuccessful, presumably due to the propensity of the carbonyl compounds involved toward rapid enolization.

0002-7863/81/1503-6969$01.25/0

Our plan postulated alkylation of sulfone **6** as its lithium anion with bromide **4** and therefore, the first task was to prepare these intermediates from **2** and **1**, respectively. Addition of vinylmagnesium bromide (1.5 equiv, THF, −78 °C) to the ketone **1** proved completely stereoselective, affording alcohol **3**[3] (stereochemistry not assigned) in 95% yield. This tertiary alcohol was directly brominated by concomitant rearrangement on exposure to phosphorus tribromide (1.5 equiv, Et_2O, −10 °C) leading to the *E*-allylic bromide **4**[4] as the major product (65%) together with its *Z* isomer (25%).[5] A more stereoselective (*E*–*Z* = ca. 6:1) but longer route to **4** involves conversion of the allylic alcohol **3** (Scheme I) to the α,β-unsaturated aldehyde **13** (Scheme II) (CrO_3·HCl·pyr)[6] followed by reduction (1.5 equiv of $NaBH_4$, 1.0 equiv of $CeCl_3 \cdot 6H_2O$, EtOH–H_2O (2:3), −15 °C)[7] to the allylic alcohol **14** and bromination (1.3 equiv of CBr_4, 1.3 equiv of PPh_3, CH_2Cl_2, −40 → 0 °C) in 70% overall yield.

Opening of the lactone **2** with lithium thiophenoxide (5 equiv, from LiH and PhSH, DMF, 110 °C, 3 h) followed by esterification of the resulting acid (CH_2N_2, Et_2O, 0 °C) and reduction with LAH (1.0 equiv, Et_2O, 0 °C) furnished the hydroxyphenyl sulfide **5** in 95% overall yield. Clean oxidation of the sulfur to the sulfone without attack on the double bond was achieved by employing diphenyl diselenide (1.0 equiv) and 30% hydrogen peroxide (5 equiv) in ether–methylene chloride (5:1) solution (0–15 °C, 8 h, 82%).[8] The hydroxy sulfone so obtained was then protected as the *tert*-butyldimethylsilyl ether **6**[4] (1.2 equiv of *t*-$BuMe_2SiCl$, 1.5 equiv of Et_3N, 0.1 equiv of DMAP, CH_2Cl_2)[9] in 95% yield (R_f = 0.57, silica, 25% ether in petroleum ether).

The coupling of the anion of sulfone **6** (1.2 equiv of LDA, THF, −78 °C, 10 min, then 2.0 equiv of HMPA, −78 °C, 5 min) with the bromide **4** (1.5 equiv in THF, −78 °C, 30 min) proved exceptionally efficient (97%) and highly stereoselective. Thus, when racemic **6**[6] was used in the coupling reaction, only two diastereoisomers were obtained in 1:1 ratio (more polar **7**: R_f = 0.28; less polar isomer of **7**: R_f = 0.36, silica, 25% ether in petroleum ether), whereas when the enriched material[1] obtained by the SAMP-hydrazone method of Enders[10] was employed, the ratio of these diastereoisomers was ca. 10:1[11] after separation by flash column chromatography. The major, more polar isomer **7**[4] ($[\alpha]^{25}_D$ −49.5° ($CHCl_3$, *c* 2.10)) was confirmed as the correct diastereoisomer by eventual conversion to the natural product (vide infra). The less polar isomer of **7** ($[\alpha]^{25}_D$ +16.1° ($CHCl_3$, *c* 2.16)) was also taken through the sequence to an isomer of X-14547A methyl ester (vide infra). Although the exact stereochemistry of the generated chiral center during the coupling reaction was not determined, it was interesting to observe that reaction of the dianion derived from the hydroxy sulfone corresponding to **6** and bromide **4** under similar conditions produced a set of different diastereoisomers after silylation. Proceeding with the synthesis, pure **7** was then subjected to elimination to generate the requisite trans double bond in the desired direction under carefully defined conditions (40% triton B in CH_3OH, 45 °C, 24 h) leading to **8** by (a) hydrolysis of the methyl ester, (b) desilylation, and (c) elimination of phenylsulfonic acid. After esterification (CH_2N_2, Et_2O, 0 °C) of the crude reaction mixture and chromatographic purification the methyl ester **9**[4] ($[\alpha]^{25}_D$ −192.4° ($CHCl_3$, *c* 0.58), R_f = 0.18, silica, 40% ether in petroleum ether) was isolated in 80% yield (40% conversion) and the primary alcohol oxidized with excess Jones reagent (acetone, −10 °C, 2 h) to afford the carboxylic acid methyl ester **10** (85%) ($[\alpha]^{25}_D$ −152.4° ($CHCl_3$, *c* = 0.25), R_f = 0.30, silica, 50% ether in petroleum ether).

The final operation remaining for the completion of the synthesis, the incorporation of the pyrrole system, required some delicate chemistry in order to avoid interference from the ester functionality present at the 1-position of compound **10**. For this purpose, it was envisioned that a method involving high activation of the carboxyl group with functionality capable of coordination to a metal in conjunction with an organometallic species carrying the pyrrole moiety might be successful. Indeed, activation of the carboxylic acid **10** as the 2-pyridinethiol ester **11** (1.5 equiv of 2,2′-dipyridyl disulfide, 1.5 equiv of triphenylphosphine, 0.1 M in toluene, 25 °C, 24 h) proved to be an excellent method[12] for the construction of the ketopyrrole unit by reaction with pyrrolemagnesium chloride (5 equiv, freshly prepared from pyrrole and methylmagnesium chloride in toluene–THF at −20 °C)[12] in toluene at −78 °C (0.05 M). The conversion of **10** to **12** was carried out without isolation of the intermediate thiol ester **11** and proceeded in over 90% overall yield under the above conditions. Synthetic **12**[4] ($[\alpha]^{25}_D$ −170.6° ($CHCl_3$, *c* 1.4), R_f = 0.17, silica, 10% ethyl acetate in petroleum ether) exhibited identical properties (NMR, IR, MS, $[\alpha]_D$, TLC) with the naturally derived methyl ester of X-14547A[6] and was smoothly saponified to X-14547A according to the previously described procedure.[6] However, pyrrolemagnesium chloride at higher temperatures smoothly converts either **11** or **12** to the novel diketopyrrole compound **15**[4] ($[\alpha]^{25}_D$ −205.0° ($CHCl_3$, *c* 0.65), R_f = 0.21, silica, 50% ether in petroleum ether) in excellent yield (95%). Following similar

(3) All new compounds were fully characterized by spectroscopic (^{1}H NMR, IR, MS, $[\alpha]_D$) means and exhibited satisfactory analytical and/or high-resolution data. Yields refer to chromatographically and spectroscopically homogeneous materials.

(4) ^{1}H NMR data of selected key intermediates (250 MHz, $CDCl_3$, Me_4Si): **4**, δ 0.85 (d, J = 7.0 Hz, CH_3), 1.04 (t, J = 7.0 Hz, 3 H, CH_3), 1.08 (d, J = 7.0 Hz, 3 H, CH_3), 1.30–2.30 (m, 7 H, CH_2, CH), 3.08 (m, 1 H, CHO), 3.63 (s, 3 H, $COOCH_3$), 3.95 (m, 1 H, CHCOO), 4.05 (d, J = 9.0 Hz, 2 H, CH_2Br), 4.29 (brs, 1 H, C*H*O), 5.73 (t, J = 9.0 Hz, 1 H, CH=); **6**, δ −0.07 and 0.08 (s, 3 H each, $Si(CH_3)_2$), 0.75 (s, 9 H, $SiC(CH_3)_3$), 0.84 (t, J = 7 Hz, 3 H, C*H*$_3$), 0.98–1.95 (m, 9 H, CH_2, CH), 2.98 (m, 2 H, C*H*$_2SO_2$), 3.40 (dd, J = 9.0, 8.0 Hz, 1 H, C*H*H0), 3.56 (m, 2 H, CH*H*O, C*H*CH_2SO_2), 5.88 (d, J = 10.0 Hz, 1 H, CH=), 5.99 (brd, J = 10.0 Hz, 1 H, C*H*=), 7.54 (m, 3 H, aromatic), 7.88 (m, 2 H, aromatic); **7**, δ 0.01 (s, 6 H, $Si(CH_3)_2$), 0.74 (d, J = 7.0 Hz, 3 H, C*H*$_3$), 0.82 (t, J = 7.0 Hz, 3 H, C*H*$_3$), 0.85 (s, 9 H, $SiC(CH_3)_3$), 0.86 (t, J = 7 Hz, 3 H, C*H*$_3$), 1.02 (d, J = 7.0 Hz, 3 H, CH_3), 1.00–2.00 (m, H, CH_2, CH), 2.55 (t, J = 6.5 Hz, 2 H, =CHC*H*$_2CSO_2$), 2.84 (m, 1 H, C*H*$COOCH_3$), 3.40 (d, J = 10.0 Hz, 2 H, CH_2O), 3.47 (s, 3 H, $COOCH_3$), 3.65 (m, 3 H, CHO, $CHSO_2$, C*H*$CHSO_2$), 4.08 (brs, 1 H, =CCHO), 5.12 (t, J = 7.0 Hz, 1 H, CH=), 5.86 (brd, J = 10.0 Hz, 1 H, CH=), 6.02 (d, J = 10.0 Hz, 1 H, CH=), 7.52 (m, 3 H, aromatic), 7.88 (d, J = 7.0 Hz, 2 H, aromatic); **9**, δ 0.83 (d, J = 7.0 Hz, 3 H, CH_3), 0.90 (t, J = 7.0 Hz, 3 H, C*H*$_3$), 0.96 (t, J = 7.5 Hz, 3 H, CH_3), 1.05 (d, J = 7.5 Hz, 3 H, CH_3), 1.05–2.30 (m, 18 H, CH_2, CH), 3.03 (m, 1 H, C*H*$COOCH_3$), 3.10 (m, 1 H, =CCHC=), 3.42–3.68 (m, 3 H, CH_2O, OH), 3.58 (s, 3 H, $COOCH_3$), 3.89 (m, 1 H, CHO), 4.23 (brs, 1 H, =CC*H*O), 5.44 (dt, J = 10.0, 2.5 Hz, 1 H, CH=), 5.59 (dd, J = 15.0, 10.0 Hz, 1 H, CH=), 5.88 (d, J = 10.0 Hz, 1 H, CH=), 5.94 (d, J = 10.0 Hz, 1 H, CH=), 6.12 (dd, J = 15.0, 10 Hz, 1 H, CH=); **12**, δ 0.78 (t, J = 7.5 Hz, 3 H, C*H*$_3$), 0.82 (d, J = 7.0 Hz, 3 H, CH_3), 0.95 (t, J = 7.5 Hz, 3 H, CH_3), 1.10 (d, J = 7.0 Hz, 3 H, CH_3), 1.00–2.10 (m, 13 H, CH_2, CH), 2.80 (m, 1 H, C*H*$COOCH_3$), 3.38 (m, 2 H, CHCO, =CCHC=), 3.68 (s, 3 H, $COOCH_3$), 3.74 (m, 1 H, CHO), 4.12 (d, J = 5.0 Hz, 1 H, =CC*H*O), 5.42 (dd, J = 12.5, 8.0 Hz, 1 H, CH=), 5.50 (dt, J = 10.0, 3.0 Hz, 1 H, CH=), 5.70–5.88 (m, 2 H, CH=), 5.96 (d, J = 10.0 Hz, 1 H, CH=), 6.27 (m, 1 H, pyrrole-CH), 6.87 (m, 1 H, pyrrole-CH), 7.03 (m, 1 H, pyrrole-CH), 9.64 (brs, 1 H, NH); **15**, δ 0.58 (t, J = 7.5 Hz, 3 H, CH_3), 0.83 (d, J = 7.0 Hz, 3 H, CH_3), 0.95 (t, J = 7.5 Hz, 3 H, CH_3), 1.15 (d, J = 7.5 Hz, 3 H, CH_3), 1.10–2.10 (m, 16 H, CH_2, CH), 3.40 (m, 3 H, CHCO, =CCHC=), 4.00 (m, 1 H, CHO), 4.04 (d, J = 5.0 Hz, 1 H, =CC*H*O), 5.36 (dd, J = 13.0, 7.0 Hz, 1 H, CH=), 5.49 (dt, J = 10.0, 3.0 Hz, 1 H, CH=), 5.62–5.84 (m, 2 H, CH=), 5.97 (d, J = 10.0 Hz, 1 H, CH=), 6.25 (m, 2 H, pyrrole-C*H*), 6.89 (m, 1 H, pyrrole-C*H*), 6.94 (m, 1 H, pyrrole-C*H*), 7.05 (m, 2 H, pyrrole-C*H*), 9.67 and 9.93 (br s, 1 H each, NH); **16**, δ 0.76 (t, J = 7.0 Hz, 3 H, CH_3), 0.80 (d, J = 7.0 Hz, 3 H, CH_3), 0.93 (t, J = 7.0 Hz, 3 H, CH_3), 1.04 (d, J = 7.0 Hz, 3 H, CH_3), 0.80–2.05 (m, 16 H, CH_2, CH), 2.90 (m, 1 H, C*H*$COOCH_3$), 3.38 (m, 2 H, CHCO, =CCHC=), 3.58 (s, 3 H, $COOCH_3$), 3.78 (m, 1 H, CHO), 4.15 (d, J = 4.0 Hz, 1 H, =CCHO), 5.40 (dd, J = 13.0, 10.0 Hz, 1 H, CH=), 5.50 (dt, J = 10.0, 3.0 Hz, 1 H, CH=), 5.76–6.00 (m, 2 H, CH=), 6.26 (m, 1 H, pyrrole-CH), 6.88 (m, 1 H, pyrrole), 6.95 (m, 1 H, pyrrole-C*H*), 9.13 (brs, 1 H, NH).

(5) The two isomers were separated by flash column chromatography (silica, 10% ether in petroleum ether, R_f(*E*) = 0.34; R_f(*Z*) = 0.40). It is interesting to note that hydrogen bromide in ether reverses the ratio of the two isomers (*E*–*Z* ca. = 1:2).

(6) Nicolaou, K. C.; Magolda, R. L. *J. Org. Chem.* **1981**, *46*, 1506.

(7) Luche, J.-L.; Gemal, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 5848.

(8) Nicolaou, K. C.; Magolda, R. L.; Sipio, W. J.; Barnette, W. E.; Lysenko, Z.; Joullié, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 3784. Reich, H. J.; Chow, F.; Peake, S. L. *Synthesis* **1978**, 299.

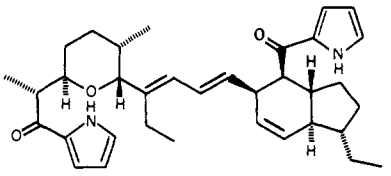
(9) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 99.

(10) Enders, D.; Eichenauer, H. *Chem. Ber.* **1979**, *112*, 2933. Enders, D.; Eichenauer, H. *Tetrahedron Lett.* **1977**, 191.

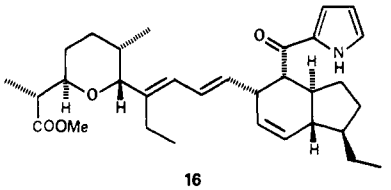
(11) This ratio is somewhat less than expected from the observed enrichment of the SAMP-hydrazone **13**.[1] This is probably due to partial racemization of the aldehyde **14**[1] during its handling.

(12) For a systematic study of this method, see: Nicolaou, K. C.; Claremon, D. A.; Papahatjis, D. P. *Tetrahedron Lett.*, in press.

methodology the diastereoisomer **16**[4] ($[\alpha]^{25}_D$ +141.8° ($CHCl_3$, *c* 0.11), R_f = 0.15, silica, 10% ethyl acetate in petroleum ether) of X-14547A methyl ester was also synthesized from the less polar isomer of **7** and exhibited similar spectral properties to **12**.



15



16

The described methodology not only produces the ionophore X-14547A in its natural enantiomeric form but also allows for ready access to a variety of interesting analogues of this natural product for property evaluation. Further synthetic and biological investigations in this area are continuing.

Acknowledgment. We express our many thanks to Dr. J. W. Westley of Hoffmann LaRoche, Nutley, NJ, for samples of X-14547A and helpful discussions. Our thanks are also due to Drs. George T. Furst and T. Terwilliger of the Department of Chemistry, University of Pennsylvania, for their spectroscopic assistance in this project. This work was financially supported by Merck Sharp and Dohme, U.S.A., The A. P. Sloan Foundation, and the Camille and Henry Dreyfus Foundation.

Novel Packing Material for Optical Resolution: (+)-Poly(triphenylmethyl methacrylate) Coated on Macroporous Silica Gel[1]

Yoshio Okamoto,* Shiro Honda, Ichiro Okamoto, and Heimei Yuki*

Department of Chemistry, Faculty of Engineering Science Osaka University, Toyonaka, Osaka 560, Japan

Shizuaki Murata and Ryoji Noyori

Department of Chemistry, Nagoya University Chikusa, Nagoya 464, Japan

Hidemasa Takaya

Chemical Materials Center Institute for Molecular Science Okazaki 444, Japan

Received June 16, 1981

Optically active poly(triphenylmethyl methacrylate) (PTrMA) is an efficient chiral packing material for liquid chromatographic resolution.[2-4] The polymer has chirality due to its helicity and is insoluble in organic solvents when the degree of polymerization exceeds about 60.[5] Various racemic compounds, particularly those having aromatic groups, were resolved by high-performance liquid chromatography (HPLC) with the finely ground insoluble polymer.[4]

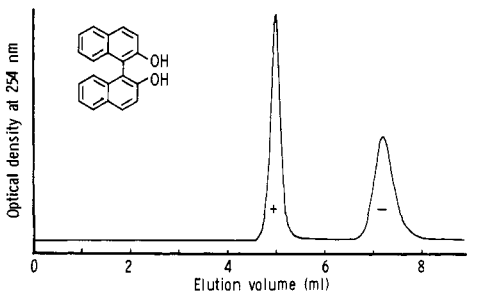


Figure 1. Resolution of 2,2′-dihydroxy-1,1′-binaphthyl (**1**). Column, 25 × 0.46 cm (i.d.); eluant, methanol; flow rate, 0.50 mL/min; temperature, 20 °C.

We report here preparation of a novel packing material for HPLC consisting of the soluble lower molecular weight (+)-PTrMA and the complete resolution of some racemic aromatic compounds on a column packed with packing prepared by coating macroporous silica gel with the soluble polymer. Interestingly, the new packing shows chiral recognition to a different degree than that displayed by the insoluble (+)-PTrMA packing; the former was successfully employed for completely resolving racemic compounds which are not separated with the latter. The new packing also made it possible to perform expeditious chromatography without lowering the degree of resolution.

Soluble (+)-PTrMA was prepared by the polymerization of the monomer with (+)-6-benzylsparteine–butyllithium complex. The reaction gave a soluble polymer of high optical rotation in a better yield[6] than the reaction with (−)-sparteine–butyllithium catalyst.[2,4,5] Macroporous spherical silica gel particles, LiChrospher SI 1000 (Merck),[7] were silanized with a large excess of dichlorodiphenylsilane and triethylamine at refluxing temperature in toluene.[8] The silanized gel (2.50 g) was coated with (+)-PTrMA (0.55 g) by using THF (10 mL) as solvent. The (+)-PTrMA-coated silica gel (ca. 2.5 g) thus obtained was slurry packed in a stainless steel tube [25 × 0.46 cm (i.d.)].[9]

2,2′-Dihydroxy-1,1′-binaphthyl, an interesting atropisomeric compound,[10,11] was completely resolved by this column, as shown in Figure 1, using methanol as eluant. Various 2,2′-disubstituted 1,1′-binaphthyls were also resolved efficiently as summarized in Table I, where the resolution data by the ground insoluble (+)-PTrMA column are also listed.[12] The separation factor, α, depends greatly on the substituents in the racemic compounds, and the two columns give different values. The (+)-PTrMA-coated silica gel column resolves **4** and **5** almost completely, although the ground (+)-PTrMA column does not work effectively

(1) Chromatographic Resolution. 4. For part 3, see: Okamoto, Y.; Okamoto, I.; Yuki, H. *J. Polym. Sci., Polym. Lett. Ed.*, in press.

(2) Yuki, H.; Okamoto, Y.; Okamoto, I. *J. Am. Chem. Soc.* **1980**, *102*, 6356.

(3) Nakazaki, M.; Yamamoto, K.; Maeda, M. *J. Org. Chem.* **1981**, *46*, 1985.

(4) Okamoto, Y.; Okamoto, I.; Yuki, H. *Chem. Lett.* **1981**, 835.

(5) (a) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763. (b) Okamoto, Y.; Suzuki, K.; Yuki, H. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3043.

(6) (+)-6-Benzylsparteine was prepared from (−)-sparteine; $[\alpha]^{25}_D$ +30.4° (*c* 1, EtOH) (Leonard, N. J.; Thomas, P. D.; Gash, V. W. *J. Am. Chem. Soc.* **1955**, *77*, 1552). The polymerization was carried out by adding 5 mol % of the catalyst to the monomer in toluene at −78 °C. Polymer soluble in THF and insoluble in methanol was obtained almost quantitatively. This was reprecipitated from a THF solution into a mixture of hexane–benzene (2:1) to remove oligomers; yield 87%, $[\alpha]^{25}_D$ +343° (*c* 0.5, THF).

(7) Mean particle size, 10 μm; mean pore diameter, 100 nm; specific surface area, 20 m^2/g.

(8) The carbon content of the silanized gel was found to be 1.9% by elementary analysis which corresponds to 0.13 mmol of diphenylsilyl group/gram of support.

(9) Theoretical plate numbers of the column for acetone and benzene were 6800 and 4700, respectively, at a flow rate of 0.50 mL/min. The void volume was estimated to be 3.33 mL with water. HPLC was accomplished on a JASCO TRI ROTAR-II equipped with a JASCO UV-100-III detector and by using methanol as eluant at 20 °C. Racemates used are either well-known compounds or their derivatives.

(10) Newcomb, M.; Toner, J. L.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 4949 and references cited therein.

(11) (a) Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129. (b) Noyori, R.; Tomino, I.; Nishizawa, M. *Ibid.* **1979**, *101*, 5843. (c) Nishizawa, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 2821. (d) Nishizawa, M.; Yamada, M.; Noyori, R. *Ibid.* **1981**, *22*, 247.

(12) Insoluble (+)-PTrMA (1.3 g) in the size range 20–44 μm was packed in a stainless-steel tubing [25 × 0.46 cm (i.d.)]. Flow rate of methanol was 0.72 mL/min and the void volume was 3.4 mL. The theoretical plates of the column for acetone was 2200.

0002-7863/81/1503-6971$01.25/0