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# tert-BUTYL ESTERS AND ETHERS OF (R,R)-TARTARIC ACID

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Abstract - The unknown tert-butyl esters **2a,b** and -ethers **4a,b** of otherwise nonsubstituted optical pure (R,R)-tartaric acid are synthesized. Esters are made by reaction of 0,0-diacyl protected tartaric acid with isobutene and selective cleavage via transesterification of the protective groups. Ethers are formed by reaction of dibenzyl tartrate with isobutene followed by hydrogenolysis of the benzyl groups. Saponification of the corresponding dimethyl tartrate led to partial racemization forming up to 50% meso product.

## INTRODUCTION

Esters of (R,R)- and (S,S)- tartaric acid are important synthetic starting materials in the field of asymmetric synthesis.[1] Since the invention of their use in the highly enantioselective Sharpless epoxidation process[2] there have been appeared a considerable number of publications using tartrates as a template to induce optical activity.[3-9] Esters of tartaric acid with sterically hindered alcohols can induce a higher enantiomeric excess especially in a Sharpless-type kinetic resolution procedure,[3,9,10] but recently there has also been reported a remarkable higher optical yield using diisopropyl tartrate versus diethyl tartrate in an asymmetric Simmons-Smith reaction[11a] and an asymmetric protonation reaction.[11b]

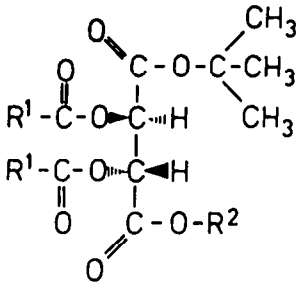
The only well known dialkyl ethers of the free tartaric acid are the 0,0-dimethyl- and the 0,0-diethyl ether.[12] They are usually made by alkaline hydrolysis of the corresponding dialkyl esters, a reaction involving some risk of racemization.[13]

tert-Butyl esters and - ethers of otherwise nonsubstituted[14] optical pure (R,R)- and (S,S)- tartaric acid are not known in the literature. However, a sterically not identified mixture of racemic and/or inactive (R,S)- (=meso) di-tert-butyl ester has been prepared from di-tert-butyl fumarate.[15]

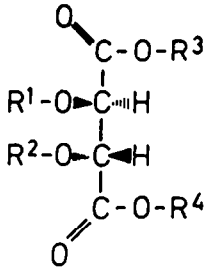
We wish to report a simple synthesis of the optically pure mono- and di-tert-butyl esters as well as the mono- and the di-tert-butyl ethers of the free (R,R)-tartaric acid using isobutene. Although we used in this work the inexpensive (R,R)- acid only, exactly the same procedure starting with the commercially available (S,S)-tartaric acid can be followed to yield the corresponding (S,S)-tert-butyl esters and ethers.

## RESULTS

Figure 1. Esters and Ethers of (R,R)-Tartaric Acid



1 a-e



2 a-4 b

| No | $R^1$ | $R^2$ |
|---|---|---|
| 1a | Me | t-Bu |
| b | Me | H |
| c | Phe | t-Bu |
| d | Phe | H |
| e | Me | Me |

| No | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| 2a | H | H | t-Bu | t-Bu |
| b | H | H | H | t-Bu |
| c | H | H | $(Me)_3Si$ | t-Bu |
| d | H | H | Me | t-Bu |
| 3a | H | t-Bu | Me | Me |
| b | t-Bu | t-Bu | Me | Me |
| c | H | t-Bu | Benzyl | Benzyl |
| d | t-Bu | t-Bu | Benzyl | Benzyl |
| 4a | H | t-Bu | H | H |
| b | t-Bu | t-Bu | H | H |

a)Esters

**2a** could not be made simply by reaction of tartaric acid and isobutene. It gave a mixture of tert-butyl esters and ethers.[15] To overcome the uncontrolled O-alkylation, we used the easily available O,O-diacetyl tartaric acid as O,O-protected starting material. Esterification with isobutene yielded quantitatively the corresponding di-tert-butyl ester **1a**. Selective removal of the acyl protective groups by means of transesterification in methanol yielded the pure crystalline di-tert-butyl ester **2a**. This crucial step required very carefully kept reaction conditions for the following reason: In contrast to the expected enhanced stability of the tert-butyl groups against nucleophiles, **2a** decomposes very easily with aqueous or alcoholic alkali hydroxide. However, this lability could be utilized advantageously to eliminate the catalyst from the reaction mixture as required in the Sharpless epoxidation procedure,[16] because the decomposition products of **2a** are not easily extractable from an aqueous solution with dichloromethane or ether.

Gas chromatographic studies of the base catalyzed transesterification reaction of **1a** in methanol revealed, that the tert-butyl groups exchange rapidly with the conjugate base of the solvent yielding the corresponding mixed methyl-tert-butyl ester **2d** as the main side product and even small amounts of dimethyl ester. The cleavage of the two protecting acetyl groups via transesterification is just significantly faster than the unwanted side reaction. Consequently, this led us to a time controlled quenching reaction yielding more than 50% of the desired diester **2a**. This product is remarkable stable in acidic solution (acetic acid, diluted hydrochloric acid).

For comparison purposes, **2d** was made from O,O-diacetyl-tartaric acid monomethyl ester following exactly the same procedure via **1e** as the O,O-protected mixed ester. **2d** is somewhat less sensitive against undesired transesterification than **2a**. The side product dimethyl tartrate is more hydrophilic and can be removed with water. An attempt to improve the total yield of diester **2a** by using the dibenzoyl tartaric acid as a starting material failed. The main product of the isobutene reaction was not **1c**, but the tert-butyl monoester **1d**, even in diglyme, which proved to be the best solvent for this catalytic addition reaction.

Because of the free carboxylic function, separation of the monoesters **1b** or **1d** from the bisproducts **1a** or **1c** was easily possible. Selective transesterification of the acyl protective groups of the monoester **1b** was easily achieved in methanolic potassium hydroxide, because insoluble potassium salt of **2b** precipitated immediately. In the case of **1d** potassium benzoate precipitated as well. Problems arose from the very high solubility of the free acid **2b** in water, therefore isolation of **2b** was accomplished by formation of an intermediate, the trimethylsilyl ester,[17] which was hydrolyzed very easily in ether using a small amount of water.

b) Ethers

It is well known, that etherification with isobutene does not work as well as esterification.[18] This was especially true for the etherification of the two hydroxy groups of tartaric acid esters. Diglyme worked best from all solvents examined (toluene, ether, tetrahydrofuran, dioxane). The type of acidic catalyst (sulfuric acid, perchloric acid, methanesulfonic acid) did not play a significant role in terms of reaction rate and yield, however, we could observe a strong influence of the size of the alcohol component of the alkyl tartrate. From the tested ones (methyl, ethyl, tert-butyl, benzyl) the methyl ester reacted best; even there the yield was moderate (30% pure bisether **3b**). However, the monoether **3a** as the only significant by-product could be reused conveniently as starting material for an exhaustive alkylation process. Separation of the diether **3b** could be easily achieved by crystallization from the reaction mixture in petroleum ether, even in the presence of quite large amounts of the monoether.

Hydrolysis of the carboxyl protected tert-butyl ether **3b** to **4b** proved to be troublesome. Due to the size of the tert-butyl groups the reaction with methanolic or ethanolic potassium hydroxide was very slow. This prolonged reaction time (3 days compared with the simple methyl- or ethyl ether which react in a couple of hours [12]) caused a complete racemization of one chiral centre leading to about 50% meso-compound, which could be detected by $^1$H NMR spectroscopy. Crystallographic separation of the meso compound from the desired optically pure **4b**, which should be possible due to diastereomeric relationship, did not work well.

Therefore we decided to use the dibenzyl ester as a starting material for the O-alkylation, which reacted almost as well as the dimethyl ester. Surprisingly, the diether **3d** did not crystallize in contrast to the dimethyl derivative **3b**. Separation of mono-and diether **3c** and **3d** was accomplished by column chromatography on silica gel only (19% yield each).

Hydrogenation of the benzyl esters gave enantiomerically pure and crystalline free mono- and ditert-butyl ether of tartaric acid **4a** and **4b** in good yield. In order to check the optical purity of (R,R)-O,O-ditert-butyl tartaric acid **4b**, we made the cyclic anhydride and treated it with an optically pure alkanolamine (1R,2S-ephedrine, o.p. 99%) forming the corresponding diastereomeric monoester according to our described HPLC-procedure.[19] Thus the optical purity (o.p.) of **4b** was analyzed and found to be better than 98%.

## EXPERIMENTAL SECTION

$^1$H NMR spectra were recorded on a Varian A360 (60 MHz) spectrometer. The chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Optical rotations were measured on a Perkin Elmer Polarimeter 441 in a 10cm cell at 22±2 °C. Melting points were taken on a Gallenkamp Apparatus, they are not corrected. Microanalyses were accomplished on a Carlo Erba Analyser. GC-Analyses were performed on a Perkin Elmer (Model 900) using a packed column (SE 30 10%). All chemicals were used as received.

**(R,R)-O,O-Diacetyl-di-tert-butyl tartrate (1a)**
(General method for the reaction of tartaric acid derivatives with isobutene)

In a thick walled round bottomed hydrogenation flask 20 g (85 mmol) (R,R)-O,O-diacetyl tartaric acid was suspended in a mixture of 300 ml dichloromethane and about 2ml of concentrated sulfuric acid. The mixture was cooled to about -15°C and about 60 ml (≈640mmol) isobutene were added. The flask was closed tightly and the mixture was shaken and allowed to warm up to room temperature. After 2-3 hours a clear solution was formed which was allowed to stand for about 3 days. After cooling to about -15°C the flask was opened and the solution was poured into an open beaker (CAUTION: use a well vented hood) containing an ice cold solution of 2 g NaOH, dissolved in 100 ml water. The mixture was vigorously stirred and allowed to reach room temperature, and the pH was adjusted to pH 6-8 using sodium hydrogen carbonate. The organic phase was separated and washed with water, dried ($MgSO_4$) and evaporated very well. Yield 29g (100%) **1a**, an oil or crystals ( $_{mp}$ 65° ). NMR ($CDCl_3$): δ 5.60 (CH) ; 2.16 ($CH_3CO$); 1.41 ($CH_3$) ppm. $[\alpha]^{22}_{546}$ +6.5° (c=1.0, acetone).

**(R,R)-O,O-Diacetyl-mono-tert-butyl tartrate (1b)**
Same reaction conditions as for **1a**, but the reaction time was only 8 h. After identical workup, the yield of diester **1a** as a side product was 5g (17%). The aqueous solution contained the sodium salt of the monoester, which was converted into the free acid with diluted HCl (pH 2). After extraction with ether the organic solution was dried over magnesium sulfate and evaporated. Recrystallization from toluene yielded 13g (52%) colorless ester **1b**. mp 112-13 °C.
- NMR($CDCl_3$): δ 9.20 (s,COOH); 5.72 and 5.60 (d, J=2.8Hz,2CH) ; 2.18 ($CH_3CO$); 1.45 ($CH_3$) ppm; - $[\alpha]^{22}_{546}$ 7.1° (c=1.0, acetone).

**(R,R)-O,O-Dibenzoyl-di-tert-butyl tartrate (1c)**
30g (80 mmol) (R,R)-O,O-Dibenzoyl tartrate was dissolved in 120 ml diglyme and 5 ml perchloric acid (70%) was added. The reaction with isobutene (60ml; 640 mmol) was performed as for **1a**. (1 d; 200ml 1N NaOH). After extraction with 300 ml ether, the organic layer was washed 5 times with water, dried over magnesium-sulfate and the solvent was evaporated. (The combined water fractions contained monoester **1d** as the sodium salt). The residue was crystallized from petroleum ether, the yield was 6.0g (16%); mp 122 °C; NMR δ 8.15 and 7.50 (m, benzoyl), 5.93 (s,CH); 1.39 (s,tert-butyl) ppm; - $[\alpha]^{22}_{546}$ = -90° (c=1.0, acetone).

**(R,R)-O,O-Dibenzoyl-mono-tert-butyl tartrate (1d)**
The combined aqueous solutions from **1c** were acidified to pH 2 with 2N HCl and **1d** was extracted with ether. After evaporation and extraction with petroleum ether the residue (25g,75%) remained as an amorphous powder. - NMR ($CDCl_3$) δ 8.30-7.30 (Aromat,COOH); 6.08 and 5.88 (d,2.7Hz,CH) 1.38 (s, $CH_3$) ppm; - $[\alpha]^{22}_{546}$ = -100° (c=1.5,acetone).

**(R,R)-O,O-Diacetyl-methyl-tert-butyl tartrate (1e)**
Reaction as described for **1a**, 21.1 g (85 mmol) (R,R)-O,O-diacetyl-monomethyl-tartrate, 20 l day, yield 24 g (93%). mp 60-61 °C (cyclohexane). - NMR($CDCl_3$) δ 5.75 and 5.60 (d,CH); 3.80 (s,$OCH_3$); 2.18 (s, 2 $CH_3CO$); 1.45 (s,tert-butyl) ppm; - $[\alpha]^{22}_{546}$ + 2.0° (c=1.2, methanol).

**(R,R)-Di-tert-butyl tartrate (2a)**
To a stirred and cooled (4°C) solution of 10 g (28.9 mmol) diacetate **1a** in 100 ml methanol a 4°C cold solution of 0.5g KOH in 25 ml methanol was added. After exactly 10 min 500 ml of an aqueous solution of 2 g $NaHCO_3$ was added and the mixture was neutralized with some diluted HCl. Methanol was removed under reduced pressure and the precipitated product was isolated and dried. Recrystallization from hexane yielded 4.1g (54%) pure **2a**, mp 91 °C (racemate and/or meso compound, 84 - 85 °C ). Optical purity of **2a** was not checked particularly. However, $^1$H NMR studies (Varian XL 200) did not show any sign of diastereomeric meso compound, which must be the intermediate of any total racemization.- NMR ($CDCl_3$) δ 4.31 (d,J= 7Hz, CH); 3.13 (d,J= 7 Hz, OH); 1.50 ($CH_3$) ppm; - $[\alpha]^{22}_{546}$ +12.2° (c= 1.0, acetone).

**(R,R)-Mono-tert-butyl tartrate (2b)**
A solution of 0.98 g (17.6 mmol) KOH in 30 ml dry ethanol was added to a solution of 4.6 g (16 mmol) O,O-diacetyl monoester **1d** in 50 ml ethanol. After 3 h the potassium salt of **2b** was isolated and washed with ether. (3.2g, 82%) mp 230 °C,dec.

Preparation of the free acid: To a stirred suspension of the potassium salt in 10 ml dry ether a solution of 2.2 g (20 mmol) trimethyl chlorosilane was added. After 15 min KCl was filtered off and the filtrate was evaporated to remove excess trichloromethane. The residue was characterized by $^1$H NMR ($CDCl_3$) as trimethylsilyl-tert-butyl tartrate **2c**. $\delta$ 5.0 (2 OH); 4.45 (CH); 1.42 ($CH_3$); 0.30 ($CH_3Si$). The oily product was again dissolved in 30 ml ether and shaken intensely with 0.27 g (15 mmol) water for 10 min. The excess water was taken up in 2 g magnesium sulfate and the solution was filtered off and evaporated. As residue 2.2 g (66%) of crystalline monoester **2b** remained, which can be recrystallized at low temperature ( 50°C) from chloroform/benzene, mp 85°C. - NMR ($CDCl_3$) $\delta$ 5.80 (broad, 2OH,COOH) 4.55 (broad, 2 CH); 1.50 (s 3 $CH_3$);- $[\alpha]_{546}^{22}$= +9.88° (c= 1.0, acetone).

**(R,R)-tert-Butyl-methyl tartrate (2d)**
To a solution of 12.2 g (40 mmol) **1e** in 100 ml methanol a solution of 0.56 g (10 mmol) potassium hydroxide in 100 ml methanol was added. After 1 hour at room temperature 1 ml 6N HCl was added. The organic solvent was evaporated at low temperature, the residue taken up in 100 ml dichloromethane, washed with three portions of 5 ml water and dried over magnesium sulfate. After removal of the solvent 7 g (79%) **2d** remained as an oil. Kugelrohr distillation (oven temperature 160°C, 0.3 mbar) yielded the analytical pure sample. - NMR ($CDCl_3$) $\delta$ 4.47 and 4.38 (d,J=2Hz,CH); 3.80 (s,$OCH_3$); 3.20 (broad,2OH); 1.50 (s, $CH_3$) ppm. $[\alpha]_{546}$ = +8.8° (c=1.0, acetone).

**(R,R)-O-tert-Butyl-dimethyl tartrate (3a)**
**(R,R)-O,O-Di-tert-butyl-dimethyl tartrate (3b)**
A solution of 30 g (0.17 mol) (R,R)-dimethyl tartrate in 120ml diglyme and 12 ml concentrated sulfuric acid was treated with 60ml (0.64 mol) liquid isobutene as described for **1a** . (2 days, 14g NaOH in 200ml water). The aqueous phase was extracted with 200ml ether, the organic phases were combined, washed very carefully 4 times with water and dried over magnesium sulfate. Yield 30 g oil, containing about 15% monoether. Crystallization from 100 ml petroleum ether yielded 14.7g (30%) very well grown crystals of **3b**, mp 66°C. Recrystallization from cyclohexane yielded an analytical pure sample, mp 68°C. Purification of the residual mother liquid on a silica gel column (petroleum ether: ethyl acetate 3:1) yielded additionally 4.5g (9%) **3b** as well as 9g (22.6%) of the monoether **3a** as an oil (by changing the eluent to ethyl acetate).
**3a**: NMR ($CDCl_3$) 4.45 (m,3H; $D_2O$: CH 4.50 and 4.40 d, J=2Hz); 3.78 ($OCH_3$); 3.20 (OH); 1.15 $CH_3$) ppm;- $[\alpha]_{546}^{22}$ = +33° (c=1.0, dichloromethane).
**3b**: $^1$H NMR ($CDCl_3$) $\delta$ 4.28 (s,CH); 3.70 (s,$OCH_3$); 1.18 ($CH_3$) ppm. $[\alpha]_{546}^{22}$ = +55.9° (c=1.0, dichloromethane).

**(R,R)-O-tert-Butyl-dibenzyl tartrate (3c)**
**(R,R)-O,O-Di-tert-butyl-dibenzyl tartrate (3d)**
A solution of 10 g (30 mmol) (R,R)-dibenzyl tartrate[20] in 80 ml diglyme containing 5ml concentrated sulfuric acid was treated with 30 ml (0.32 mol) isobutene as described for **1a**.(3 d, 7g NaOH in 200 ml water). After extraction with 300 ml ether, the organic layer was washed with 5 portions of 100 ml water, dried over magnesium sulfate and evaporated, yielding 9g of a mixture of **3c** and **3d** as an oil. DC-control (silica, hexane:ethyl acetate 3:1) showed two spots of about equal size for the monoether **3c** ($R_f$ 0.6) and di-ether **3d** ($R_f$ 0.4) and some benzylalcohol ($R_f$ 0.95). Separation of the mixture on a silica column (500g; 35-70 ; ethyl acetate/ petroleum ether 5:1 ; 2 bar) yielded 2.5 g (19%) chromatographically pure bisether **3d** as an oil and 2.2 g (19%) crystalline monoether **3c** (mp 74°C). **3c**: NMR ($CDCl_3$) 7.32 (sharp m,10H, benzyl); 5.18 (s, $CH_2$) 5.32 and 5.02 (1H,d,12 Hz,$CH_2$); 4.58 and 4.42 (1H,d,2.4Hz, CH); 3.0 (1H,broad,OH); 1.08 (s,9H, $CH_3$) ppm; $[\alpha]_{546}$ = +22.5° (c=1.0, acetone). **3d**: NMR ($CDCl_3$) $\delta$ 7.30 (sharp m, benzyl); 5.15 and 4.90 (d, J=12Hz, $CH_2$); 4.32 (s,CH); 1.13 (s, $CH_3$) ppm; - $[\alpha]_{546}^{22}$= +28.5° (c=1.0, acetone).

**(R,R)-O-tert-butyl tartaric acid (4a)**
A solution of 1.17 g (3 mmol) monoether **3c** in 30 ml ethylacetate was hydrogenated with 50mg Pd on carbon at normal pressure for 2 hours. The solution was filtrated and the residual carbon was extracted with ethanol. After evaporation of the combined solvents the residue was purified with ether. The yield was 0.58 g (94%) crystalline free acid **4a**. An analytical pure sample was obtained by treatment with ice cold, dry acetone, mp 67°C. - NMR ($CDCl_3$/DMSO-$d_6$ 6:1) $\delta$ 8.80 (broad s, COOH); 4.40 and 4.30 (broad d, J=2Hz, CH);1.13 (s,$CH_3$) ppm.-$[\alpha]_{546}^{22}$= +46° (c=1.0,acetone).

**(R,R)-O,O-Di-tert-butyl tartaric acid (4b)**
1) A solution of 2.00 g (4.5 mmol) di-ether **3d** in 30ml ethyl acetate was hydrogenated with 50mg Pd on carbon (10%) at normal pressure for 2 hours. After filtration of the catalyst, the solvent was evaporated and the residue was washed with ether. The yield was 1.1g (93%) **4b**. An analytical pure sample was obtained by reprecipitation with sodium hydrogen carbonate/hydrogen chloride , pH 1.5.
mp 134°C.- NMR ($CDCl_3$) $\delta$ 8.80 (s,COOH); 4.43 (s,CH); 1.22 (s,$CH_3$) ppm. $[\alpha]_{546}^{22}$ = +54.7° (c=1.0, acetone).

2) Ester hydrolysis with racemisation: A solution of 1.45g (5mmol) bisether **3b** in 15 ml methanol containing 0.84 g (15 mmol) KOH was heated under reflux for 80 h. After neutralization with HCl the solvent was evaporated, the residue was dissolved in water and acidified to pH 1. The crystalline precipitate was isolated and washed with water and ether. $^1$H NMR analysis revealed, that the product was a 1 : 1 mixture of two diastereomeric di-tert-butyl esters of tartaric acid with two just separated singulets for CH and $CH_3$ assigned to the R,R and the optically inactive R,S form. The specific $\alpha$ value was $+20^0$ (c = 1.0, acetone), somewhat less than 50% of the optical pure R,R- compound **4b**.

**Table 1.** Elemental Analyses

| Compounds | Formulae | | Calcd % | | Found % | |
|---|---|---|---|---|---|---|
| | | | C | H | C | H |
| **1a** | $C_{16}H_{26}O_8$ | 346.37 | 55.48 | 7.57 | 55.60 | 7.49 |
| **1b** | $C_{12}H_{18}O_8$ | 290.27 | 49.65 | 6.26 | 49.86 | 6.35 |
| **1c** | $C_{26}H_{30}O_8$ | 470.53 | 66.37 | 6.43 | 66.48 | 6.60 |
| **1d** | $C_{22}H_{22}O_6$ | 414.42 | 69.10 | 5.80 | 69.35 | 5.95 |
| **1e** | $C_{13}H_{20}O_8$ | 304.33 | 51.30 | 6.64 | 51.20 | 6.71 |
| **2a** | $C_{12}H_{22}O_6$ | 262.30 | 54.95 | 8.50 | 55.15 | 8.63 |
| **2b** | $C_8H_{14}O_6$ | 206.22 | 46.59 | 6.86 | 46.09 | 6.68 |
| **2d** | $C_9H_{16}O_6$ | 220.25 | 49.08 | 7.34 | 49.19 | 7.48 |
| **3a** | $C_{10}H_{18}O_6$ | 234.25 | 51.27 | 7.74 | 51.34 | 7.59 |
| **3b** | $C_{14}H_{26}O_6$ | 290.35 | 57.91 | 9.02 | 57.86 | 9.07 |
| **3c** | $C_{22}H_{26}O_6$ | 386.44 | 68.38 | 6.78 | 68.19 | 6.64 |
| **3d** | $C_{26}H_{34}O_6$ | 442.55 | 70.56 | 7.74 | 70.32 | 7.83 |
| **4a** | $C_8H_{14}O_6$ | 206.19 | 46.60 | 6.84 | 46.80 | 6.70 |
| **4b** | $C_{12}H_{22}O_6$ | 262.30 | 54.95 | 8.45 | 54.76 | 8.44 |

## REFERENCES


1 Seebach, D.; Hungerbühler, E. Modern Synthetic Methods **1980** (Scheffold R., Ed.), Vol 2, pp 91-171. Salle and Sauerländer, Aarau, Switzerland.
2 Katsuki, T.; Sharpless, K.B. J.Am.Chem.Soc. **1980**, 102, 5974.
3 Pfenninger, A. Synthesis **1986**, 89.
4 Castaldi, G.; Cavicchioli, S.; Giordano, C.; Uggeri, F. Angew.Chem. **1986**,98, 273; Angew.Chem,Int.Ed.Engl.**1986**, 25, 259.
5 Roush, W.R.; Haltermann, R.L. J.Am.Chem.Soc. **1986**, 108, 294.
6 Rossiter B.E. Asymmetric Synthesis **1985**, 5, 193-246 (Ed. Morrison, J.D., Academic Press).
7 Pitchen, P.; Dunach, E.; Deshmukh, M.N.;Kagan, H.B. J.Am.Chem.Soc. **1984**, 106,8188.
8 Boldrini, G.P.; Lodi, L.; Tagliavini, E.; Tarasco, C.; Trombini, C.; Umani-Ronchi,A. J.Org.Chem. **1987**, 522, 5447.
9 Martin, V.S.; Woodard, S.S.; Katsuki, T.;Yamada, Y.;Ikeda, M.; Sharpless, K.B. J.Am.Chem.Soc. **1981**, 103, 6237.
10 Miyano, S; Lu, L.D.-L; Viti, S.M.; Sharpless, K.B. J.Org.Chem. **1985**, 50, 4350.
11 (a) Arai, I.; Mori, A.; Yamamoto, H. J.Am.Chem.Soc. **1985**,107, 8254.
(b) Gerlach, U; Hünig, S. Angew.Chem. **1987**, 99, 1323; Angew.Chem,Int.Ed.Engl. **1987**, 26, 1283.
12 (a) Purdie, T.; Pitkeatly, W. J.Chem.Soc. **1899**, 75, 153
(b) Young, Ch.R. J.Chem.Soc. **1914**, 105, 1228.
13 Wilka, E.-M.; Thesis **1980**,p 27; ETH Zürich No 6592.
14 Kolasa, T.; Miller, M.J. Tetrahedron Lett. **1987**, 28, 1861.
15 Blake, J.; Tretter, J.R.;Juhasz, G.J.;Bonthrone, W.; Rapoport,H. J.Am.Chem.Soc. **1966**, 88, 4061.
16 Rossiter, B.E.; Katsuki, T.; Sharpless, K.B., J.Am.Chem.Soc. **1981**, 103, 464.
17 Bestmann, J; Moenius, Th. Angew.Chem. **1986**, 98, 1007. Angew.Chem,Int.Ed.Engl. **1986**, 25, 994.
18 Fieser; L.F.; Fieser, M. Reagents for Organic Synthesis **1967**, 522, (J.Wiley and Sons, New York).
19 Lindner, W; Leitner C.; Uray G.; J.Chromatogr. **1984**, **316**, **605**.
20 Patterson, T.S. J.Chem.Soc. **1913**, 103, 176.