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Working with Hazardous Chemicals

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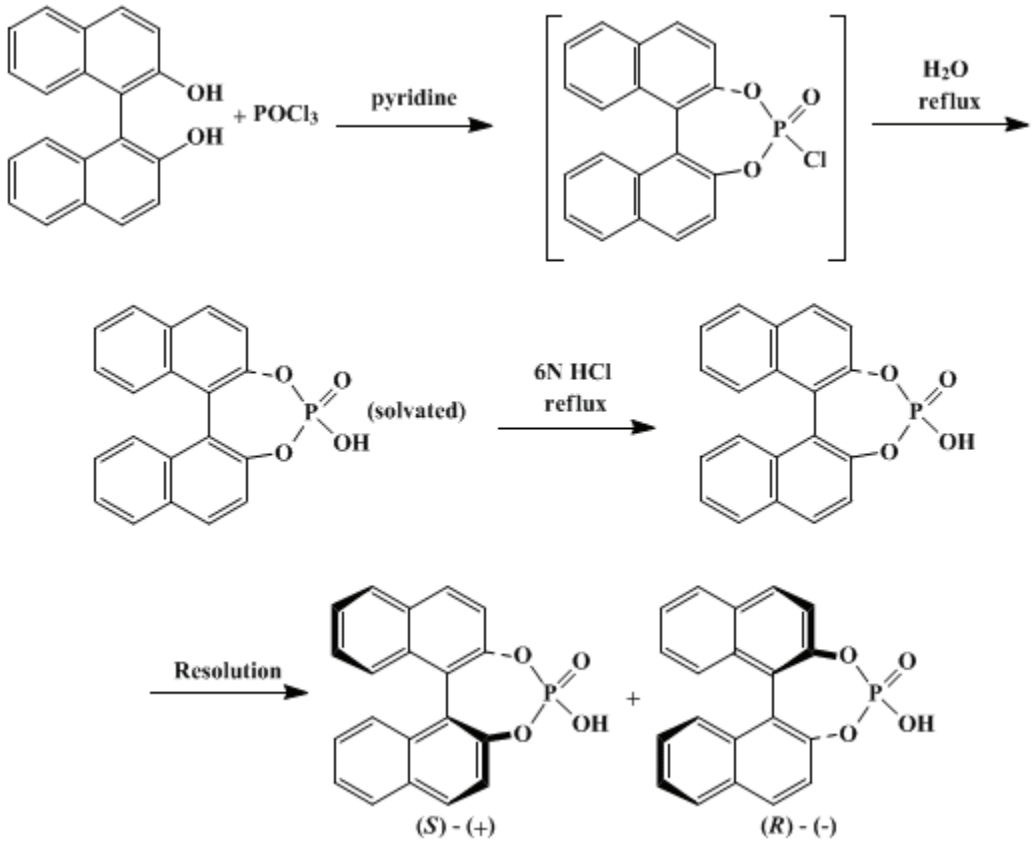
ENANTIOMERIC (*S*)-(+)- AND (*R*)-(−)-1,1'-BINAPHTHYL-2,2'-DIYL HYDROGEN PHOSPHATE

[Dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin, 4-hydroxy-, 4-oxide]



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Checked by P. R. Carlier and K. Barry Sharpless.

1. Procedure

Caution! Part A of this procedure should be carried out in an efficient hood to avoid exposure to noxious vapors (pyridine, phosphorus oxychloride).

A. *(±)-Binaphthylphosphoric (BNP) acid*. A 1-L, three-necked flask, fitted with a magnetic stirring bar, a pressure-equalizing dropping funnel, a reflux condenser topped by a calcium chloride drying tube, and a thermometer, is charged with 450 mL of pyridine and, while stirring, with 100 g (0.35 mol) of (±)-1,1'-bi-2-naphthol (Note 1).

To this stirred suspension, 73.6 g (0.48 mol) of freshly distilled phosphorus oxychloride is added dropwise, whereupon the temperature rises to about 80°C, most of the binaphthol dissolves, and pyridine hydrochloride crystals form. Complete dissolution is achieved by heating to 90°C. The stirred solution is allowed to cool to 50–60°C. (Crystallization occurs at about 85°C.) To the stirred suspension, 40 mL of water is added dropwise *(Caution! Exothermic reaction!)*, which raises the temperature to the boiling point (ca. 118°C). The resulting solution, cooled to about 60°C, is transferred to a l-L dropping funnel and the flask is rinsed with pyridine (2 × 20 mL). The solution and rinse are combined and added dropwise with vigorous stirring to 900 mL of 6 *N* hydrochloric acid (Note 2), which gives a precipitate

of pyridine-solvated binaphthylphosphoric (BNP) acid (Note 3). This crude product is collected by suction filtration. The wet cake is transferred to a 2-L, large-necked flask and stirred with 300 mL of 6 *N* hydrochloric acid. The suspension is heated to boiling (possible foaming!) and immediately cooled. The solid is thoroughly filtered by suction, washed twice with 20 mL of water (Note 4), and air-dried to afford 114–119 g (94–99%) of (±)-binaphthylphosphoric acid. This compound, which decomposes without melting at about 300°C (Note 5), is pure enough to be resolved. Analytical crystalline samples can be obtained from ethanol.

B. *(S)-(+)- and (R)-(−)-BNP acid*. In a 2-L flask 95.2 g (0.27 mol) of racemic binaphthylphosphoric (BNP) acid and 80.4 g (0.27 mol) of (+)-cinchonine (Note 6) are dissolved in 985 mL of hot methanol (Note 7). To the hot (65°C) solution is added 420 mL of hot water via a dropping funnel over the course of 20 min. During the addition the solution is vigorously stirred and maintained at 65–70°C. At the end of the addition, the flask is transferred to another (cool) stirring plate. Crystallization starts at approximately 60°C, and stirring is maintained until the solution has reached room temperature (Note 8). The crystals are collected, washed with a 2 : 1 methanol–water mixture (3 × 45 mL), and air-dried to afford 76.6 g of salt consisting of 91% p salt [(+)-acid, (+)-base] and 9% n salt [(−)-acid, (+)-base], $[\alpha]_{546}^{25}$ + 424° (methanol, c 0.99) (Note 9) and (Note 10).

(*S*)-(+)-BNP ACID. A 2-L, three-necked flask, equipped with addition funnel, reflux condenser, magnetic stirring bar, and thermometer, is charged with 76.6 g of the above-mentioned salt and 500 mL of ethanol. The salt is dissolved by heating to reflux, and 570 mL of 6 *N* hydrochloric acid is added with vigorous stirring over the course of 30 min. The temperature is maintained at 75–80°C during the addition, and the acid begins to precipitate. Once the addition is complete, the solution is allowed to cool without stirring to room temperature. The solid is collected, washed with water (5 × 90 mL), and air-dried to afford 26.7 g of (*S*)-(+)-BNP acid, $[\alpha]_{546}^{25}$ + 712° (methanol, c 0.98) (Note 11). The yield based on enantiomer present in the racemate is 56%. The product is free from contamination by cinchonine, as shown by ^{1}H NMR (Me_2SO, 250 MHz), and elemental analysis. HPLC analysis of the methyl ester derivative employing a chiral stationary phase (Note 12) shows the acid to be greater than 99.4% ee. Partially resolved samples, recovered by adding water to the filtrates, may be purified by crystallization from ethanol or by digestion in hot methanol (Note 13).

(*R*)-(−)-BNP ACID. The filtrate from the initial crystallization of the cinchonine salt is evaporated nearly to dryness to give 107 g of crude salt, $[\alpha]_{546}^{25}$ −113° (methanol, c 0.95), consisting of approximately 81% n salt and 19% p salt (Note 14) and (Note 10). A 2-L, three-necked flask equipped with addition funnel, reflux condenser, magnetic stirring bar, and thermometer is charged with 107 g of the crude salt and 700 mL of ethanol. The salt is dissolved by heating to reflux, and 790 mL of 6 *N* hydrochloric acid is added with vigorous stirring over the course of 30 min. The temperature is maintained at 75–80°C during the addition, and the acid begins to precipitate. Once the addition is complete, the solution is allowed to cool without stirring to room temperature. The solid is collected, washed with water (5 × 100 mL), and air-dried to afford 23.3 g of (−)-BNP acid, $[\alpha]_{546}^{25}$ −717° (methanol, c 1.00) (Note 11). The yield based on enantiomer present in the racemate is 49%. The product is free from contamination by cinchonine, as shown by ^{1}H NMR (Me_2SO, 250 MHz) and elemental analysis. HPLC analysis of the methyl ester derivative employing a chiral stationary phase (Note 12) shows the acid to be 100.0% ee.

2. Notes

1. Commercial dry pyridine, stored over Linde 4A molecular sieves, was used without further purification. The 1,1'-bi-2-naphthol is commercially available from Aldrich Chemical Company, Inc. The submitters prepared it by oxidizing a hot aqueous suspension of commercial 98% pure 2-naphthol (Merck-Schuchardt) with ferric chloride[2] to obtain crude colored binaphthol (80–90% yield). Unless this material is purified and decolorized by successive crystallization and digestion in hot toluene, the color will be retained in the binaphthylphosphoric acid (60–65% overall yield).
2. The reverse addition of 6 *N* hydrochloric acid to the pyridine solution results in the formation of a thick and syrupy precipitate, which prevents stirring.
3. Regardless of the conditions of precipitation or crystallization, a polymorphic solvate is obtained that consists of 2 BNP acid : 1 pyridine : 1 H_2O, according to elemental analyses. Pyridine peaks are

apparent in the ^{1}H NMR spectrum (δ 8.71 and 8.78 in d_6-DMSO). Desolvation occurs at 210–230°C on the Kofler bench or by heating to reflux in 6 *N* hydrochloric acid.
4. The solubility of BNP acid in water is about 2 g/L at 20°C.
5. The BNP acid is polymorphic. A metastable form, identical with the enantiomers and therefore a conglomerate,[3] was sometimes obtained when working above 40°C; the usual stable form is a racemic compound.[3] The IR spectrum (Nujol, cm^{-1}) of the racemate is as follows: 950 (strong), 1025 (strong, broad), 1185 (medium), 1200 (strong), 1220 (strong); of conglomerate: 1050 (strong, broad), 1200 (medium), 1230 (strong), 1255 (medium).
6. Commercial (+)-cinchonine (Aldrich Chemical Company, Inc.), $[\alpha]_D^{25}$ +288° (ethanol, c 0.5), was used without further purification.
7. The checkers observed coloration of this solution and stirred it with 10 g of Norit activated carbon, followed by filtration through a Celite pad. The pad was washed with hot methanol (2 × 50 mL). The submitters did not report any coloration.
8. In order to achieve an efficient resolution it is imperative that the addition of water be even and slow; otherwise premature precipitation or oiling of the cinchonine salt may occur. Likewise, stirring must be maintained during the cooling period to achieve high yields and to avoid the formation of oils. The salt is collected as soon as the mixture cools to room temperature, because the more soluble salt deposits as an oil on standing. The submitters suggest that the yield may be improved by carrying out the crystallization in a cold bath until the solution reaches room temperature. It should be noted that the checkers did not observe crystallization until a packet of seed crystals was opened in their laboratory.
9. The submitters obtained 78.5 g of salt composed of 97% p and 3% n salts, $[\alpha]_{546}^{25}$ +471° (methanol, c 0.9).
10. The p and n salts, prepared from the pure (+)- or (−)-acids and cinchonine and crystallized from methanol–ethyl acetate and methanol–acetone–ethyl acetate, respectively, exhibit the following rotations (±3%) in methanol:

	$[\alpha]_\lambda^{25}$				
Salt	589 nm	578 nm	546 nm	436 nm	
p	+409°	+428	+492	+890	(c 0.7)
n	−211	−222	−256	−474	(c 0.8)

11. Two crystallizations from ethanol did not change the optical rotations of (+)- and (−)-BNP acid, which are as follows:

	$[\alpha]_\lambda^{25}$				
	589 nm	578 nm	546 nm	436 nm	365 nm
Methanol	595° ± 7	624 ± 7	720 ± 8	1328 ± 15	2050 ± 25
Ethanol	574 ± 16	602 ± 17	694 ± 20	1267 ± 25	1828 ± 40

Both enantiomers decompose without melting above 300°C. The solid-state IR spectra of the enantiomers and the racemate (conglomerate) are identical. The checkers obtained a rotation of −705° at 546 nm.
12. The methyl ester derivatives were prepared by treating BNP acid with diazomethane in methanol–ether. A Regis Pirkle Type 1-A preparative column (25 cm × 10 mm i.d.) was used and the conditions were as follows: 10% 2-propanol/hexanes, 8.0 mL/min, detector at 284 nm. The (*R*)-(−) enantiomer is eluted first and the peaks are well separated (α = 1.24).[4]
13. BNP acid, racemate and enantiomers are sparingly soluble in water and organic solvents, except alcohols. Their solubilities at 25 ± 0.5°C in methanol and 95% ethanol, expressed in g/100 mL of solvent and g/100 mL of solution (in brackets) are as follows:

	Racemate	Enantiomer
Ethanol	10.3 ± 0.5 (11.5)	5.7 ± 0.2 (6.7)

Methanol	2.5 ± 0.1 (3.1)	2.1 ± 0.1 (2.6)

As shown by these data, the racemate is approximately twice as soluble as the enantiomers in ethanol, whereas in methanol, the solubilities are nearly the same. This is because the racemate forms a crystalline compound (solvate) with methanol as shown by IR and NMR (Me_2SO) spectra, and by elemental analysis. The racemate dissolves more rapidly in refluxing methanol than do the enantiomers. Accordingly, partially resolved samples having an enantiomeric excess of 80–90% can be conveniently purified by merely digesting them for 10–15 min in refluxing methanol. In general, partially resolved BNP acid can be purified by crystallization from ethanol. In this case, the dissolution rate is particularly slow and the desired solution is obtained by using solvent in excess, then concentrating the solution.
14. The submitters obtained 103 g of material consisting of about 85% n and 15% p salts, $[\alpha]_{546}^{25}$ −150° (methanol, c 0.8).

3. Discussion

Marschalk[5] first prepared BNP acid by the action of phosphorous oxychloride on binaphthol without any solvent, followed by hydrolysis of the isolated acid chloride. The procedure herein described was only briefly mentioned, without any experimental details, in a paper describing the resolution of BNP acid and its use as a resolving agent.[6]

The BNP acid has also been prepared by Cram and co-workers[7] from binaphthol and phosphorus oxychloride, although under quite different conditions, which involved isolation of the intermediate acid chloride and its hydrolysis by aqueous tetrahydrofuran, and extraction of BNP acid with ethyl acetate. In our hands, this extraction could not be carried out without using larger volumes of solvent and water than those reported. More recently, it has also been prepared by Japanese authors who used a slightly modified method.[8]

The resolution of BNP acid by crystallizing the (+)-acid–cinchonine salt, then the (−)-acid–cinchonidine salt, was first mentioned in a short paper and subsequently described in a patent.[6]

A modification of this procedure was used by Cram et al.,[7] who likewise obtained the (+)-BNP acid via its cinchonine salt, but they isolated the (−)-enantiomer directly from the more soluble salt, without using cinchonidine, in 59% and 46% respective yields. Both enantiomers, precipitated by 6 *N* hydrochloric acid from their cinchonine salt solutions, had to be purified by successive digestions with hot 6 *N* hydrochloric acid and water in order to decompose any remaining cinchonine salt. These purifications are avoided by using the procedure described herein.

BNP acid has also been resolved via some other salts: with strychnine,[9] 2-amino-1,2-diphenylethanol,[10] 2-aminobutanol,[11] 2-amino-1-(4-nitrophenyl)-1,3-propanediol in the presence of acetone, which forms an oxazolidine with the chiral base.[12] A chromatographic resolution of BNP acid was unsuccessfully attempted with natural polymers.[13]

Some physical properties of BNP acid have been studied (triplet-state circular dichroism,[14] luminescence, photoracemization.[15]).

Derivatives have been prepared: methyl esters (enantiomers and racemate)[6,9,10,11,12,13] and D-glucopyransoyl ester.[16]

Enantiomeric (*S*)-(+)- and (*R*)-(−)-BNP acids are useful resolving agents, which give well-crystallized, easily separated salts with a variety of amines. They have been used in the preparation of the enantiomers of biologically and therapeutically active compounds, such as α-difluoromethyl-α-aminovaleric acid,[17] cephalosporin,[18] dibenzothiepin,[19] benzodiazepine derivatives[20] and 3-hydroxyphenyl-*N*-propylpiperidine,[21] 7-phenylquinolizidine,[22] barbituric acid derivative,[23] and thiazepinones,[24] among others. BNP acid also has been used for the direct resolution of underivatized *o*-tyrosine.[25]

(+)-BNP acid, linked to silica gel, has been used in HPLC resolution of helicenes.[26]

BNP acid was tried as an auxiliary for asymmetric synthesis of carboxylic acids.[27] It was used as a NMR chiral complexing agent for amine purity determination.[28]

Chiral recognition of *R*- and *S*-BNP acids by permethylated β-cyclodextrins was described,[29] and chirality of secondary carbinols was determined by CD (circular dichroic) measurements of their *R*- or *S*-BNP esters.[30]

Reduction of (*S*)-(+)-and (*R*)-(−)-BNP methyl esters[6] or acids[7] by lithium aluminum hydride, or by Red-Al (this volume, p. 46) yields respectively the known (*S*)-(−)- and (*R*)-(+)-binaphthol, thus establishing the BNP acids' absolute configuration. This is a convenient access to optically active binaphthols, used by Cram and co-workers[31] to prepare macrocyclic polyethers and by Japanese authors[8] in asymmetric synthesis of cyclic binaphthyl esters.

Racemic and optically active BNP acids (as well as binaphthols) are also available commercially from Aldrich Chemical Company, Inc.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 46
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hexanes

(S)-(+)- AND (R)-(−)-1,1'-BINAPHTHYL-2,2'-DIYL HYDROGEN PHOSPHATE

(±)-Binaphthylphosphoric (BNP) acid

pyridine-solvated binaphthylphosphoric (BNP) acid

(S)-(+)- and (R)-(−)-BNP acid

binaphthylphosphoric (BNP) acid

(S)-(+)-BNP acid

(R)-(−)-BNP ACID

(−)-BNP acid

(+)- and (−)-BNP acid

cephalosporin

o-tyrosine

(S)-(−)- and (R)-(+)-binaphthol

methyl ester derivatives

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ethyl acetate (141-78-6)

methanol (67-56-1)

ether (60-29-7)

2-naphthol (135-19-3)

acetate

acetone (67-64-1)

carbon (7782-42-5)

Phosphorus Oxychloride (21295-50-1)

pyridine (110-86-1)

toluene (108-88-3)

2-propanol (67-63-0)

ferric chloride (7705-08-0)

cinchonidine (485-71-2)

pyridine hydrochloride (628-13-7)

Diazomethane (334-88-3)

strychnine

Tetrahydrofuran (109-99-9)

lithium aluminum hydride (16853-85-3)

phosphorous oxychloride

pyridine, phosphorus oxychloride

binaphthol

(+)-cinchonine,

cinchonine

binaphthylphosphoric acid,
(±)-binaphthylphosphoric acid

2-amino-1,2-diphenylethanol

2-aminobutanol (13054-87-0)

2-amino-1-(4-nitrophenyl)-1,3-propanediol (119-62-0)

α-difluoromethyl-α-aminovaleric acid

dibenzothiepin

1,1'-bi-2-naphthol,
(±)-1,1'-bi-2-naphthol (18531-99-2)

3-hydroxyphenyl-N-propylpiperidine

Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-hydroxy-, 4-oxide (39648-67-4)