

(m, 3 H), 8.12 (s, 1 H), and 8.25 (m, 1 H); MS, m/z (relative intensity) 286 (8.7), 285 (20.8), 284 (parent and base), 191 (14), 143 (17), 131 (59), 115 (29); IR (KBr) 3360 cm^{-1} . **20** is freely soluble in dilute hydroxide and precipitates upon acidification.

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Synthesis of Optically Active 2,2'-Dihalo-1,1'-binaphthyls via Stable Diazonium Salts

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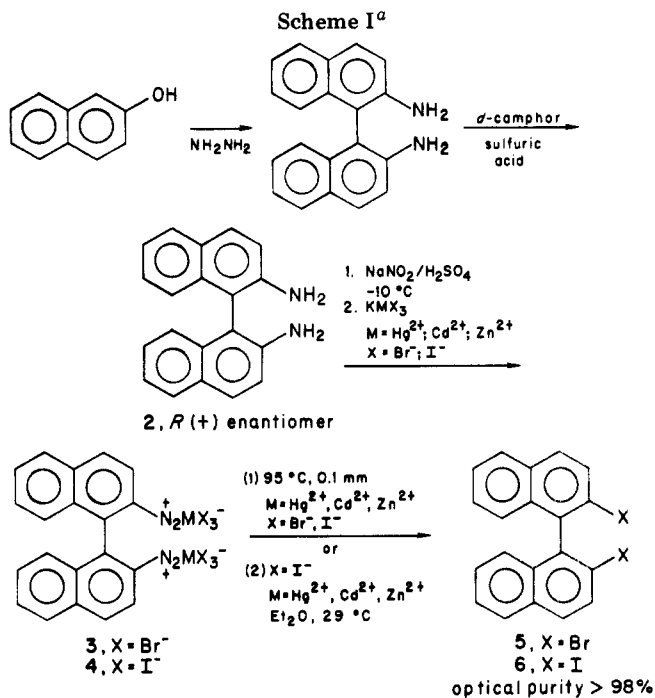
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Optically pure 2,2'-dibromo-1,1'-binaphthyl (DBBN) (**5**) and optically pure 2,2'-diiodo-1,1'-binaphthyl (DIBN) (**6**) are synthesized in preparative quantities starting from 2-naphthol. These compounds are useful for the preparation of chiral, bidentate ligands based on the 1,1'-binaphthyl system. The synthesis proceeds through a common optically active precursor, 2,2'-diamino-1,1'-binaphthyl ((*R*)-(+)-DABN) (**2**), and involves the preparation and subsequent decomposition of stable diazonium metal complexes (**3** and **4**). The effect of several variables, including the nature of the metal *M*, on these reactions is discussed, and comparison to related procedures reported in the literature is made.

Previous reports^{1,2} have described the preparation of 2-lithio-2'-halo-1,1'-binaphthyl and 2,2'-dilithio-1,1'-binaphthyl intermediates and their reaction with electrophiles such as ClPPh_2 , MeOH, or H_2O and aromatic aldehydes to form optically active 2- and/or 2'-substituted 1,1'-binaphthyl derivatives. The usefulness of this synthetic method lies in its ability to produce a wide variety of symmetrical or unsymmetrical chiral, bidentate ligands which all derive from a common optically active precursor (2,2'-diamino-1,1'-binaphthyl) and thus do not require the development of separate, specialized resolution methods. The value of the product ligands and of the lithiated intermediates from these reactions in the study of asymmetric synthesis has been discussed.^{1,2}

Success of this method depends on the ability to obtain samples of optically active 2,2'-dibromo-1,1'-binaphthyl (DBBN) and 2,2'-diiodo-1,1'-binaphthyl (DIBN). Racemic DBBN has been synthesized in 45% yield by treating 2,2'-dihydroxy-1,1'-binaphthyl with Br_2/PPh_3 at $320\text{ }^\circ\text{C}$ ³ and in 55% yield by treating 2-bromonaphthalene with $\text{Pb}(\text{O}_2\text{CCH}_3)_4$.⁴ Another preparation of racemic DBBN by a method which is similar to the one reported in the present work (vide infra) resulted in yields of 80%.⁵ A synthesis of racemic DIBN has also been reported in the literature,⁶ and yields are on the order of 18%. However, none of these methods³⁻⁶ has been shown to be applicable to the direct synthesis of optically active biaryls. We now describe detailed procedures for obtaining optically pure DBBN and DIBN via two novel modifications to the classical Sandmeyer reaction.

It should also be noted that while this is the first reported synthesis of optically pure 2,2'-dihalo-1,1'-bi-



^a For **3** and **4**: (a) $M = \text{Hg}^{2+}$; (b) $M = \text{Cd}^{2+}$; (c) $M = \text{Zn}^{2+}$.

naphthyls, there have been reports of the partial resolution of small quantities of DBBN by HPLC^{7a} and by fractional crystallization.^{7b}

The synthesis proceeds via 2,2'-diamino-1,1'-binaphthyl (DABN), which is efficiently resolved with *d*-camphor-sulfonic acid, (*d*-CSA) and then converted to the bis(diazonium) salts **3** and **4** (Scheme I). The dry salts, when mixed with a large excess of KX , can be pyrolyzed under vacuum to yield DBBN or DIBN. Although the isolation

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and subsequent solid-state decomposition of diazonium salts has been extensively used in the preparation of aryl fluorides,⁸ this technique has been much less frequently employed in the synthesis of the other aryl halides.^{5,9-12} The method used in the present work is based upon a technique originally developed by Schwechten⁹ for the preparation of dichloro- and dibromobiphenyls and 2-bromonaphthalene, involving the pyrolysis of arenediazonium trichloromercurates or bromomercurates in the presence of excess potassium chloride or potassium bromide to yield the corresponding aryl halides. The method has subsequently been used (with some modification) in other preparations of 2-bromonaphthalene¹⁰ and 2,2'-dibromo-1,1'-biphenyl,¹¹ in the synthesis of the bromo- and chlorophenanthrenes,¹² and in a preparation of racemic 2,2'-dibromo-1,1'-binaphthyl.⁵ The present report details the extension of this procedure to the preparation of optically pure 2,2'-dihalo-1,1'-binaphthyls through the simple expedient of carrying out the pyrolysis step under reduced pressure in the presence of a metal halide matrix. In addition, the effect on this reaction of varying the metal ($M = \text{Hg(II)}, \text{Cd(II)}, \text{Zn(II)}$) in the iodide complexes (4) has also been studied.

It was discovered that the bis(diazonium metal iodide) complexes 4 can also be decomposed by washing with dry ether at room temperature to yield DIBN after chromatographing the filtrate. Again, little or no loss of optical activity occurs in the recovered diiodide. Other aryl halides have been synthesized via diazonium salts which are isolated and then suspended in a solvent and thermally decomposed.^{8,13-15} Many examples are known in which this technique is used for the preparation of aryl fluorides.⁸ In addition, *o*-toluenediazonium triiodide dihydrate decomposes in aqueous suspension above 40 °C to yield *o*-iodotoluene,¹³ a variety of arenediazonium tetrachloroborates and tetrabromoborates decompose to the corresponding aryl halides in high boiling (bp 110–115 °C) petroleum ether suspensions at temperatures ranging from 35 °C to 134 °C,¹⁴ and the diazonium trichloromercurate and diazonium tribromomercurate salts from (aminocyclopentadienyl)manganese tricarbonyl decompose in petroleum ether (bp 100–120 °C) suspensions at 70 °C to yield the (halocyclopentadienyl)manganese tricarbonyls.¹⁵ Thus, the current work presents a variation of these methods which is both convenient and rapid and is accomplished at low temperature with preservation of optical purity.

The significance of these findings is placed in perspective by considering the reported failure^{7b} of standard Sandmeyer conditions to yield substantial quantities of optically active material.

Results

Synthesis of DABN is accomplished by reaction of a 2:1 ratio of 2-naphthol and hydrazine in a sealed bomb at 180 °C. The diamine is best recovered and purified as the hydrochloride salt. It was found that carefully purified samples (see Experimental Section) of the salt give best results in the subsequent reactions and can be stored for long periods (months) under argon at -30 °C.

After conversion to the neutral amine, the racemic material is resolved by gentle mixing of concentrated solutions of *d*-10-camphorsulfonic acid (*d*-10-CSA) in EtOH/H₂O and DABN in CH₂Cl₂. The *d*-10-CSA salt of (*R*)-(+)-DABN¹⁶ is recovered in chemical yields of 80–90% (based on a single enantiomer) and optical yields of 95–100%¹⁷ after just a single crystallization. The resolved amine can be kept in the salt form and stored at -30 °C for indefinite periods.

By conversion of carefully dried and weighed samples of the salt to the free DABN, which was itself carefully dried and weighed, the stoichiometry of the salt was determined to be 1:1 DABN:*d*-10-CSA. In addition, it was found that the resolution could be successfully carried out by using a 1:2 molar ratio of *d*-10-CSA:DABN. The recovered salts showed the same high optical yields as before, but the chemical yields were slightly lower (72% based on one enantiomer), so the resolution is normally carried out with a 1:1 molar ratio of reactants.

Diazotization of the resolved DABN is accomplished with NaNO₂ in H₂SO₄, and the desired bisdiazonium metal halide salts are precipitated from solution by the addition of an aqueous solution containing substantial excesses of the appropriate metal dihalide and potassium halide. Yields and purities of the recovered salts were found to be quite sensitive to several experimental variables (see Experimental Section), most notably, the temperature. Careful control of the temperature at or below -5 °C throughout the reaction was found to be essential for optimum results. In this way, yields of 100–125% (based on the empirical formula⁵ shown for 3 and 4) are routinely achieved and invariably found to be associated with salts of high purity. If these precautions are not followed, the diazonium salts often contain small bits of tarry material, are darker in color, and give lower yields of DIBN and DBBN from the decomposition reactions (vide infra). The diazonium metal halides are conveniently handled in the air at room temperature and showed no tendency toward detonation, even while grinding in a mortar and pestle. However, they are best stored at -30 °C immediately after their preparation, away from light and organic vapors, until just prior to their decomposition to DBBN or DIBN.

Decomposition by the Pyrolysis Method. The transformation of the diamine 2 to the dibromide 5 is similar to one previously reported by Pichat,⁵ in which he decomposed the bis(diazonium) salt 3 in the presence of approximately 2 times its weight of KBr at atmospheric pressure and ~140 °C. Under these conditions, the decomposition leads to rapid evolution of nitrogen, bubbling of the tarry, molten reaction products, and recovery of largely racemic dibromide. However, we have found that at ~0.1 torr of pressure, the decomposition can be carried out smoothly at 95 °C in the presence of a tenfold excess (by weight) of KBr without the formation of molten material and with little or no loss of optical activity in the recovered DBBN. Pichat reports yields of racemic dibromide 5 in the neighborhood of 80% (based on DABN) and we have found that comparable yields of optically pure 5 can be obtained when working on a small scale so that the starting DABN can be carefully purified and the diazotization conditions more closely monitored. When working on a large scale, yields of 60–68% are achieved. Use of much less than a tenfold excess of KBr (e.g., 2× by

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(17) See Experimental Section for values of $[\alpha]_D$ obtained in this work. Compare with those of ref. 20 and 21.

weight) resulted in a vigorous and uncontrolled reaction and a significantly reduced yield of DBBN, while use of greater than a tenfold excess did not improve the results.

Conditions for decomposition of bis(diazonium) salt **4a** to DIBN (**6**) are essentially the same as for the formation of DBBN (**5**), except that KI replaces KBr as the matrix material and the reaction times are somewhat longer. Yields of optically pure DIBN are approximately 45%.

In another experiment, the bis(diazonium) mercury(II) tribromide salt **3** was decomposed under the usual conditions in the presence of a tenfold excess of KI. Mass spectral analysis of the crude product showed intensities of 7.2%, 29.9%, and 57.6% for the molecular ion peaks of diiodobinaphthyl, bromiodobinaphthyl, and dibromobinaphthyl, respectively. This result indicates that the majority of the halogen incorporated into the product 2,2'-dihalo-1,1'-binaphthyls originates from the trihalomercurate anion. A similar experiment, involving the dry decomposition of a mixture of aryl fluoroborates also supports an intramolecular mechanism for fluorination.¹⁸

Decomposition by the Ether-Wash Methods. An alternative preparation of DIBN (**6**) is accomplished by placing the bis(diazonium) salt **4** atop a sintered glass funnel and washing the salt with anhydrous Et₂O. After workup of the filtrate and chromatography of the recovered residue (see Experimental Section), DIBN is recovered in yields of ~50% and with no detectable loss of optical activity. The only other reported synthesis of DIBN (racemic) gives a yield of 18%.⁶ Part of the reason for the increased yield in our preparations over the normal Sandmeyer reaction probably lies in the fact that the bis(diazonium) complexes can be decomposed in the absence of water, thereby minimizing phenol formation and diazo coupling reactions.

Effect of Varying the Metal in Bis(diazonium) Salts **4.** The success of both the pyrolysis and ether-wash methods for the formation of DIBN (**6**) were then studied as a function of the metal, M, in the complexes **4**. In each of four separate experiments, a solution of diazotized DABN was divided into three equal portions. One portion was reacted with excess ZnI₂/KI, the second portion with excess HgI₂/KI, and the third portion with excess CdI₂/KI to form the bis(diazonium) complexes **4c**, **4a**, and **4b**, respectively. Half of each of these stable salts was then decomposed by the pyrolysis method and the other half by the ether wash method (vide supra) to form DIBN **6**. The yields from these reactions are presented in Table I. Note that all six reactions in a given experiment involve the same batch of diazotized amine and that all of the decomposition products are worked up in identical fashion so that any differences in the results are due to changes in the metal or the decomposition method. From Table I it can be seen that the mercuriodide complexes give the best yield (46 ± 7%) for the pyrolysis method, while the yields observed for the iodomercurate and iodocadmate complexes using the ether-wash technique are comparable (46 ± 3% and 49 ± 3%, respectively).

Purification of DBBN and DIBN. Recrystallization of optically active DBBN from 95% ethanol leads to two distinct crystal forms which differ greatly in their optical purity (see Experimental Section). The high-rotating crystals (mp 155 – 157 °C, corrected) consistently give specific rotations between 32 °C and 34 °C, and it has been demonstrated¹ that such samples of DBBN have optical purities in excess of 98%. Sublimation of the recrystallized DBBN (0.01 torr, 112 – 118 °C, 12–48 h) results in *no* loss

Table I. Yields (%) of DIBN (6**)^d Recovered from the Decomposition of Bis(diazonium) Salts **4a-c****

exp ^a	M = Zn (4c)		M = Hg (4a)		M = Cd (4b)	
	pyrolysis ^b	ether-wash ^c	pyrolysis ^b	ether-wash ^c	pyrolysis ^b	ether-wash ^c
1	37.4	37.5	56.2	43.9	40.3	53.1
2	52.5	35.2	44.6	45.1	47.4	46.2
3	35.9	40.8	40.8	46.0	31.7	46.5
4	35.8	39.6	43.6	50.5	37.1	49.1

^a Each experiment used a single preparation of diazotized DABN which was split into 3 equal portions (see text). ^b Decomposition of **4** accomplished via the pyrolysis method (see text and Experimental Section). ^c Decomposition of **4** accomplished via the ether-wash method (see text and Experimental Section). ^d Recovered DIBN from every experiment gave maximum rotation¹ after 1 recrystallization and 1 sublimation (see Experimental Section); thus all reactions ultimately yield product with complete retention of optical activity.

of optical purity and gives a white, powdery substance which is free of H₂O, EtOH, and other protonic impurities and is thus suitable for use in the metal-halogen exchange reactions.¹

The crude DIBN is generally recrystallized once from 80% hexane/20% xylene and then sublimed (150 °C; 0.01 torr; 24 h) to yield a white powder with a pale yellow tint. Twelve such samples had an average [α]_D²⁵ of 16.2 ± 0.2°, which was shown¹ to represent an optical purity of >98%. All 12 samples melted sharply over a range of 1 °C to 2 °C (mp 215 – 217 °C, corrected) and were successfully employed in the subsequent metal-halogen exchange reactions.¹

Summary

In the present paper, methods for the preparation of optically pure 2,2'-dibromo-1,1'-binaphthyl and 2,2'-diiodo-1,1'-binaphthyl have been described. These methods are highly efficient, yielding preparative quantities of DBBN and DIBN from the simple starting material, 2-naphthol. The routes involve preparation and subsequent decomposition of stable diazonium salts with complete retention of optical purity, and thus these techniques represent significant extensions¹ of earlier procedures⁸⁻¹⁵ used for preparing racemic compounds.

Experimental Section

2,2'-Diamino-1,1'-binaphthyl (DABN). Hydrazine monohydrate (Aldrich) and 2-naphthol (Aldrich) are mixed in a 1:2 ratio, placed in a Parr bomb, and heated at 180 °C for 78 h. While still warm (~60 °C), the mixture is dissolved in a hot solution of 80% methanol and 20% concentrated HCl (v/v). To this dark solution is added a large quantity of ether (approximately 6 L of Et₂O per 1 L of MeOH/HCl solution). The resulting green/brown precipitate is collected by filtration and dissolved at room temperature in a minimum amount of methanol which contains a small amount of HCl (to insure complete conversion to the HCl salt). The salt is then precipitated with ether. This recrystallization is repeated until a snow-white powder is obtained. Yield after two recrystallizations = 60–65%. The amine (as the HCl salt) is generally stored under argon at ca. -30 °C. The neutral amine is prepared from 43 g of DABN·2HCl, 3200 mL of ether, and 1000 mL of 1 M NaOH which are stirred until no more solid is present. The two layers are separated, and the aqueous layer is extracted with ether (2 × 200 mL). The ether extracts are combined, dried over Na₂SO₄, and rotovapped, yielding a white powder which is stored at ca. -30 °C under argon (mp 186–187 °C, uncorrected; mp 193.2–194.5 °C, corrected; lit.⁵ mp 193 °C). The yield of highly purified diamine is 40% to 55% based on 2-naphthol (250 g to 600 g of starting material). High resolution mass spectra of the diamine show a molecular ion corresponding to *m/e* 284.1313. C₂₀H₁₆N₂ requires *m/e* 284.1323. Clemo and Dawson¹⁹ report a

(18) See ref 8, pp 7 and 22; Brunton, J. C.; Suschitzky, H.; *J. Chem. Soc.* 1955, 1035.

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45% yield of brown precipitate (mp 185–187 °C) and an unspecified yield of material recrystallized from benzene/petroleum ether (mp 191 °C).

Resolution of DABN. Although rigorous, inert atmosphere techniques are not strictly necessary, it has been found that yields and purity of the final product are improved if the solvents are degassed by boiling and then cooled under a stream of argon.

D-10-Camphorsulfonic acid (*d*-10-CSA, Aldrich; 21 g, 0.0904 mol) is placed in a 125-mL flask, which is sealed with a septum and flushed with argon. Degassed EtOH (21 g) is added via syringe to dissolve the *d*-10-CSA at a temperature of 50–60 °C. To the cooled solution (room temperature) is added 12.0 mL of degassed H₂O (36% w/w; 0.67 mol).

DABN (26 g, 0.0914 mol) is placed in a 1-L flask which is sealed with a rubber stopper containing a polyethylene tube which is capped by a septum. The flask is flushed with argon, and 500 g of degassed CH₂Cl₂ are transferred into the flask via the polyethylene tube under argon pressure. The resulting solutions are clear and light copper to gold in color. The *d*-10-CSA solution is carefully added via syringe and with only gentle mixing to the DABN/CH₂Cl₂. The flask is placed in the dark and left undisturbed for 12 to 24 h. The resulting white precipitate is filtered from the bright yellow supernatant, washed with CH₂Cl₂, pumped dry, and stored under argon at ca. –30 °C. The DABN-*d*-10-CSA melts at 235–236 °C, uncorrected; 246–47 °C, corrected (lit.²⁰ mp 243 °C): [α]_D²⁰ +105.3° (pyridine, *c* 1.225) (lit.²⁰ [α]_D²⁰ +95.3° (pyridine, *c* 1.123)). Yields of DABN-*d*-10-CSA range from 80% to 89%, based on 1 enantiomer. The opposite enantiomer is recoverable in comparable yields and optical purity. The resolved amine is generally stored in the salt form (DABN-*d*-10-CSA). The amine is freed in the same manner as described for DABN-2HCl. Recovery of (*R*)-(+)-DABN is quantitative: mp 231–233.5 °C, uncorrected; 242–244.5 °C, corrected (lit.²⁰ mp 242.5–243 °C); [α]_D^{21.4} +155.5° (pyridine, *c* 1.00) (lit.²⁰ [α]_D²¹ +144.5° (pyridine, *c* 3.82) and lit.²⁰ [α]_D²⁰ +149.5° (pyridine, *c* 1.482) and lit.²¹ [α]_D³⁰ +154° (pyridine, *c* 3.58)).

1,1'-Binaphthyl-2,2'-bis(diazonium triiodomercurate). Concentrated H₂SO₄ (450 mL) is cooled to –5 to –10 °C by an ice/NaCl/N₂ slush. To this cooled solution is slowly added NaNO₂ (13.5 g, 0.1956 mol) with constant stirring. No NO₂ (reddish-brown gas) should evolve. Once the NaNO₂ is added, the ice bath is removed, and the solution is allowed to come to room temperature. Once the NaNO₂ is dissolved, the solution is again cooled to between –5 and –10 °C, with constant stirring. DABN (11.75 g, 0.04133 mol) is dissolved in pyridine (80 mL) to obtain a straw to light gold solution.²² This solution is added dropwise (syringe pump) to the stirring NaNO₂/H₂SO₄ solution, being careful to guide the drops straight into the reaction mixture so that they do not run down the walls of the flask. The addition takes approximately 2–3 hours, and it is important to maintain the temperature below –5 °C and to maintain efficient stirring throughout the reaction. The resulting dark, molasses colored solution is then stirred for an additional hour to ensure complete diazotization.

Chunks (1 cc) of ice are then added to the stirring mixture very slowly, keeping the temperature below –5 °C. Addition of ice is continued until no rise in temperature is observed (≥2 h). An ice-cooled mixture of urea (11.8 g, 0.1965 mol) in H₂O (300 mL) is then added dropwise, again maintaining the temperature below –5 °C, as heat and gas are evolved in destroying the excess NaNO₂. When the addition is complete, the solution is stirred for 30 min or until no more gas is evolved.

A solution of mercuric iodide (52.8 g, 0.1162 mol) and KI (58.44 g, 0.3520 mol) in H₂O (120 mL) is swirled until the solids dissolve and then placed on ice until ready for use. The salt solution (KHgI₃) is then added to the diazonium mixture, causing the immediate formation of a light brown precipitate. The precipitate is filtered without washing and is stored at ca. –30 °C. The

reaction is typically run with 10 g to 50 g of DABN as starting material.

1,1'-Binaphthyl-2,2'-bis(diazonium triiodozincate) and 1,1'-Binaphthyl-2,2'-bis(diazonium triiodocadmate). These complexes are prepared in exactly the same manner as the analogous mercury complex just described except that ZnI₂ or CdI₂ replaces HgI₂ during the final precipitation step.

2,2'-Diiodo-1,1'-binaphthyl (DIBN). The bis(diazonium) salts from above are converted to DIBN either by the pyrolysis method or by the ether-wash method (see Results section and Table I).

A. Pyrolysis Method The bis(diazonium) salt is ground with 5 to 10 times its weight of KI until a fine, intimate mixture is obtained. This mixture is placed in a sublimator and heated at 95 °C (0.1 torr) for 2 h. The resulting residue at the bottom of the sublimator is extracted with CH₂Cl₂. The combined CH₂Cl₂ extracts are washed with aqueous sodium bisulfite, dried over anhydrous sodium sulfate, and rotovapped to dryness. The recovered residue is redissolved in CCl₄, placed on a column packed with silica gel (70–230 mesh), and eluted with CCl₄. A large first fraction is collected and rotovapped to dryness, yielding a granular white/yellow precipitate. This product is recrystallized from a solution of 20% xylene/80% hexane (v/v), giving pale to light yellow needles. No significant changes in the crystal's appearance, their melting range (vide infra), or their optical purity (vide infra) are noted after a second recrystallization. Sublimation of the once-recrystallized diiodide at 0.01 torr and 150 °C for 24 h yields a white powder with a very pale yellow tint. Average yield of purified material is approximately 45% (for Hg complexes; see Table I): mp of (*R*)-(+)-2,2'-diiodo-1,1'-binaphthyl is 206.5–208 °C, uncorrected, 215.2–216.8 °C, corrected; mp of racemic 2,2'-diiodo-1,1'-binaphthyl is 215.5–217.5 °C, uncorrected; 225–227 °C, corrected. Cava⁶ reports an 18% yield of racemic DIBN (orange crystals, mp 222–225 °C). [α]_D²³ +16.4 (pyridine, *c* 1.725) for (*R*)-(+)-DIBN. The specific rotations of crude DIBN (residues from chromatography eluent) are generally in the neighborhood of 20° and level off at 16.0° to 16.4° after one recrystallization/sublimation cycle. High resolution mass spectrum gives a molecular ion peak at *m/e* = 505.9057 (C₂₀H₁₂I₂ requires *m/e* = 505.9027). Fragments corresponding to loss of one iodine atom (M⁺ - 127) and to loss of two iodine atoms (M⁺ - 254) are also prominent in the mass spectra of DIBN.

Lithiation of DIBN¹ and treatment with CO₂ (dried over CaCl₂) lead to the formation of 1,1'-binaphthyl-2,2'-dicarboxylic acid which gives a molecular ion in the high resolution MS corresponding to *m/e* 342.0894 (C₂₂H₁₄O₄ requires 342.0892). In similar fashion, lithiation of DIBN,¹ followed by quenching with CH₃OD, yields 2,2'-dideuterio-1,1'-binaphthyl. High resolution MS gives a molecular ion corresponding to *m/e* 256.1210 (C₂₀H₁₂D₂ requires *m/e* 256.1221).

B. Ether-Wash Method. The bis(diazonium) salt is placed on a sintered-glass funnel which is connected to vacuum via a filter flask. The salt is washed with anhydrous Et₂O until no more bubbling is observed from the salt. The deep-red ether filtrate is washed with aqueous sodium bisulfite, dried over anhydrous Na₂SO₄, and rotovapped to dryness. The recovered residue is dissolved in CCl₄ and chromatographed on silica gel (70–230 mesh; CCl₄ as eluent), the first large fraction being collected and rotovapped to give DIBN (35%–53%; see Table I). Recrystallization from 80% hexane/20% xylene (v/v), followed by sublimation (0.01 torr, 150 °C) gives a white powder with a pale yellow tint. Physical characteristics and mass spectra of this product were identical with those of DIBN prepared by the pyrolysis method (vide supra).

The diazonium decomposition reactions are typically run by decomposing the diazonium salt prepared from 10 g to 50 g of DABN.

1,1'-Binaphthyl-2,2'-bis(diazonium tribromomercurate). The diazotization proceeds in a fashion which is completely analogous to the preparation of the triiodomercurate complex. An ice-cold aqueous solution containing a 1:1 weight ratio of HgBr₂ and KBr (2 g of solid per 4.5 mL of H₂O; 3.56 g of HgBr₂ per 1 g of DABN) is added dropwise to a diazotized solution of DABN, care being taken that each drop falls directly into the well-stirred reaction mixture. A bright yellow precipitate forms immediately, and the mixture is stirred for an additional 25 min after the addition is complete. The yellow solid is collected by suction filtration and washed with water until the filtrate is no longer

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(21) O'Connor, M. J.; Ernst, R. E.; Holm, R. H.; *J. Am. Chem. Soc.* **1968**, 90, 4561.

(22) A very dark color for the solution of DABN in pyridine indicates that the sample contains significant impurities and will likely lead to poor results (low yield and low purity) in the diazotization reaction.

acidic. After successive washings with methanol (using the minimum necessary to remove the H₂O) and Et₂O, the bright yellow powder is suction dried for approximately 15–20 min. Yields range from 95% to 125% based on the empirical formula⁵ of the title compound. Samples are generally stored immediately in a freezer, but some have been kept at room temperature (away from light) for weeks to months without major decomposition. However, such samples do darken in color (taking on an orange tint) and result in somewhat reduced yields of DBBN in the subsequent decomposition reaction.

2,2'-Dibromo-1,1'-binaphthyl (DBBN). The decomposition of the bis(tribromomercurate) salt is accomplished by grinding it with a tenfold excess of KBr (pre-ground and oven-dried) until an intimate mixture is obtained, and then heating this mixture at 95 °C under a pressure of approximately 0.1 torr. The bright yellow color generally fades within 15 to 30 min to a hue ranging from buff to light olive-green. The color change is accompanied by evolution of N₂(g). The product is extracted with water and CH₂Cl₂, and the CH₂Cl₂ extracts are dried (anhydrous Na₂SO₄), rotovapped, and chromatographed (silica gel, 70–230 mesh; hexane as eluent). After collection of two broad, bright yellow bands, the solid dibromide is eluted from the column. This solid residue is rinsed briefly with cold pentane or cold hexane to remove the bulk of the yellow impurity, leaving an off-white to greenish white powder. Yield of DBBN is generally 60–65% (based on the starting DABN), although yields of 80% and higher can be achieved by using very pure samples of the bis(diazonium) salt (prepared from small-scale diazotization reactions). Recrystallization of the crude dibromide leads to two distinct crystalline forms: type A, large, flat crystalline wedges (orthorhombic) and type B, very tiny needles (triclinic), formed in "fluffy" clusters. Type A crystals have a relatively sharp melting point (1–2.5 °C range at approximately 150 °C) and high $[\alpha]_D$ values (32°–34°). Type B crystals have a very broad melting point (~145–172 °C) and low $[\alpha]_D$ values (10–20°). Samples of the recrystallized material which are mixtures of the two crystal forms give melting point ranges of 3–5 °C and $[\alpha]_D$ values between 28° and 32°. Neither of the two crystal forms will consistently crystallize out first and invariably the other form will eventually come out of solution after a significant portion of the first form has crystallized. However, type A crystals can be obtained from solutions which originally precipitate the type B form by decanting the supernatant from these type B crystals into a clean flask. If type B continue to precipitate first, the process is repeated until the initial precipitate consists of type A crystals.

Two optically active samples of 2,2'-dibromo-1,1'-binaphthyl ($[\alpha]_D^{25} +30.1^\circ$ and $[\alpha]_D^{25} +32.4^\circ$; pyridine, *c* 1.00) prepared from

(*R*)-2,2'-diamino-1,1'-binaphthyl ($[\alpha]_D^{25} +147.2^\circ$; pyridine, *c* 1.0) melted at 152.0–152.5 °C, uncorrected; 157.0–157.5 °C, corrected. A third sample ($[\alpha]_D^{25} +34.1^\circ$; pyridine, *c* 1.00) melted at 150.0–151.9 °C, uncorrected; 154.9–156.9 °C, corrected. Melting point of racemic 2,2'-dibromo-1,1'-binaphthyl is 180.5–181.0 °C, uncorrected; 187.3–187.9 °C, corrected; lit.⁵ mp 185 °C. The average specific rotation of seven samples of (*R*)-(+)-DBBN with melting points above 147 °C (151.7 °C, corrected) and melting ranges of less than 3.5 °C was found to be $32.9 \pm 0.8^\circ$. Within this group, the specific rotations ranged from 31.5° to 34.1°, and the maximum specific rotation for DBBN is about $33 \pm 1^\circ$.¹ High resolution MS shows molecular ion peaks at *m/e* 409.9305, *m/e* 411.9277, and *m/e* 413.9269 (C₂₀H₁₂Br₂ requires *m/e* 409.9305, *m/e* 411.9285, and *m/e* 413.9265). The 1:2:1 ratio for the intensities of the molecular ion "triplet" is characteristic of a molecule containing two bromine atoms (due to almost equal abundance of ⁷⁹Br and ⁸¹Br). Fragment ions corresponding to loss of one bromine (M⁺ – 79 and M⁺ – 81) and to loss of two bromines (M⁺ – 158, M⁺ – 160, M⁺ – 162) are also evident.

Decomposition of 1,1'-Binaphthyl-2,2'-bis(diazonium tribromomercurate) in the Presence of Excess Potassium Iodide. A sample of 1,1'-binaphthyl-2,2'-bis(diazonium tribromomercurate) is thermally decomposed by using the pyrolysis method just described for preparation of 2,2'-dibromo-1,1'-binaphthyl (DBBN), except that KI replaces KBr as the matrix material. Reaction proceeds as above and product workup is identical. Mass spectral analysis of the crude product shows peaks at *m/e* 506 (7.2%, diiodobinaphthyl), 458 and 460 (29.9%, bromiodobinaphthyl), 410, 412, and 414 (57.6%, dibromobinaphthyl). Small peaks at *m/e* 380 (2.5%, iodobinaphthyl) and 332 (1.7%, bromobinaphthyl) are also observed. The remaining peaks at *m/e* 280 and 268 were not definitively assigned and total 1.1%. No peak at *m/e* 254 (binaphthyl) is observed.

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Registry No. (*R*)-(+)-2, 18741-85-0; (±)-2, 79082-81-8; (±)-2·2HCl, 97644-73-0; (*R*)-(+)-2-*d*-10-CSA, 93621-61-5; (*R*)-3a, 97654-71-2; (*R*)-4a, 97654-68-7; (*R*)-4b, 97654-69-8; (*R*)-4c, 97654-70-1; (*R*)-(+)-5, 86688-08-6; (*R*)-(+)-6, 86688-06-4; NH₂NH₂, 302-01-2; 2-naphthol, 135-19-3; (*R*)-bromiodobinaphthyl, 97644-74-1.