C. Common-Ion Studies. The required amount of sodium methoxide solution was added to a 5-mL aliquot of the diazonium salt solution to generate the *anti*-arylazo methyl ether in situ. α-Naphthol solution was then added and the solution was then diluted to 50 mL with methanol. The reaction was followed by UV–vis spectrophotometry. For the 2-cyano compound, a stopped-flow technique was required.[5] One syringe of the stopped-flow apparatus contained the α-naphthol solution which was equilibrated to 30 °C in the drive syringe of the stopped-flow apparatus. Solutions of the diazonium salt and sodium methoxide were equilibrated to 30 °C in an external thermostat bath. These solutions were mixed and rapidly added to the other syringe of the stopped-flow apparatus which was then triggered. Three reactions were carried out for each concentration of NaOMe, and the rate constant was calculated from the mean value of the half-life for the three runs.

Heterogeneous Catalytic Racemization of 4,4'-Disubstituted 1,1'-Binaphthyls by Active Carbons and by Modified Carbon Catalysts

Larry G. Hutchins and Richard E. Pincock*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6

The racemization of four 4,4'-disubstituted 1,1'-binaphthyls is heterogeneously catalyzed by active carbon or carbon black suspended in chloroform solutions. In the presence of 1 mg/mL of Norit SG1 in chloroform the observed first-order rate constants for racemization of 0.025 M substrate were increased over the uncatalyzed rate constants by factors of 2.9, 6.7, 8.3, 8.1, and 14 for disubstituents NH₂, CH₃, Br, NO₂, and H, respectively. The rates of uncatalyzed racemization of these binaphthyls are electronically influenced by the para substituents (giving a Hammett ρ of −0.88) and the catalyzed racemization rates show a similar but slightly decreased substituent effect (ρ = −0.57). However, a small steric effect is indicated for the catalyzed reaction since all substituted compounds are less sensitive to catalysis than is 1,1'-binaphthyl itself. Bromination or chlorination of a carbon black results in increased catalytic activity, and potassium–graphite intercalate is an effective, but irratic, racemization agent. An electron-accepting binaphthyl molecule, loosely bound on electron-donor sites of the graphitic basal planes of carbon catalysts, is suggested as an intermediate complex in the catalyzed racemization.

The chiral aromatic hydrocarbon 1,1'-binaphthyl (1, X = H) is sufficiently restricted in rotation around the central bond so that its racemization proceeds only slowly near room temperature in solution.[1] However, the rate of loss of optical activity is dramatically increased by the presence of various active carbons and by industrial carbon blacks.
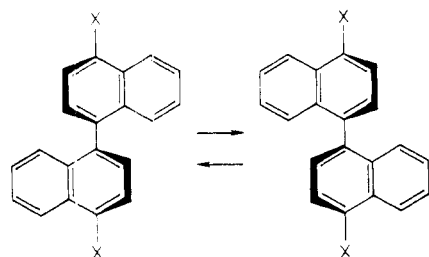
(R)-1,1'-binaphthyl　　(S)-1,1'-binaphthyl

1, X = H; 2, X = NH₂; 3, X = CH₃; 4, X = Br; 5, X = NO₂

The kinetic characteristics of this heterogeneous reaction fit a rate relationship involving adsorption to form a catalyst–binaphthyl surface complex,[3] and an attractive possibility for this complex is a flattened binaphthyl molecule adsorbed on the basal planes of the graphitic carbon surfaces. Such a racemization mechanism would involve a close and simultaneous approach of both naph-thalene rings of binaphthyl to the planar surface, and this specific interaction might therefore be greatly hindered, if not prevented, by the steric effect of *any* substituent such as, for example, the 4,4'-disubstituents of compounds 2–5 with X equal to NH₂, CH₃, Br, and NO₂, respectively.

The work reported was begun with the intention of establishing whether or not the observed catalyzed racemization of binaphthyl could be more generally observed with some of its derivatives. It was then extended to determine what effect a variety of different substituents would have on the rates of both the catalyzed and the uncatalyzed racemizations. With a study of substituent effects we hoped to characterize the polarity of the binaphthyl molecule bound to the carbon surface and also to define the electronic and steric sensitivity of the active sites on carbon.

In addition, we have also investigated a variety of other carbon-derived catalysts to determine their ability to racemize binaphthyl. From previous studies the most catalytically active carbons are those with the greater surface areas of less organized character, and it is possible that the racemization takes place not on graphitic planar areas but on disorganized edge sites.[3] The functional groups (i.e., largely oxygen-containing groups)[4] that are present on the edges of the graphitic planes may be involved. To help establish the location and nature of the active sites we have also determined the catalytic efficiency that modified carbons (produced by oxidation, reduction, halogenation,

(1) A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 2365 (1963).

(2) R. E. Pincock, W. M. Johnson, K. R. Wilson, and J. Haywood-Farmer, *J. Am. Chem. Soc.*, **95**, 6477 (1973).

(3) R. E. Pincock, W. M. Johnson, and J. Haywood-Farmer, *Can. J. Chem.*, **54**, 548 (1976).

(4) J. B. Donnet and A. Voet, "Carbon Black: Physics, Chemistry, and Elastomer Reinforcement", Marcel Dekker, New York, 1976, Chapter 4.

Table I. First-Order Rate Constants for Racemization of 4,4'-Disubstituted 1,1'-Binaphthyls[a]

substituent	$10^5 k_{cat}$,[b] s^{-1}	$10^5 k_{uncat}$,[b] s^{-1}	k_{cat}/k_{uncat}
NH_2[c]	20.0	6.8	2.9
CH_3	11.0	1.6	6.9
Br	6.0	0.72	8.3
NO_2	3.0[d]	0.37[d]	8.1
H	28.0	2.0	14.0

[a] In chloroform at 23.8 °C. Substrate concentration 0.025 M, Norit SG1 at 1.0 mg/mL of solution. [b] Average of at least two runs. [c] In acetone. [d] By extrapolation of the $\ln k$ vs. $1/T$ curve determined at 48.9 and 35.0 °C.

and intercalation) have on the catalyzed racemization of 1,1'-binaphthyl.

Results and Discussion

Synthesis of Optically Active 4,4'-Disubstituted Binaphthyls. Among the required optically active binaphthyl compounds 2–5, only one, the diamino compound **2**, is readily available by a classical resolution through separation of diastereomeric salts.[5] For the others, with X = CH_3, Br, and NO_2 substituents, no direct means of resolution are available. The ability to obtain optically active binaphthyl in quantity[6] suggested that aromatic substitution on previously resolved binaphthyl, at sufficiently low temperatures to avoid appreciable racemization, would be a practical way to produce both **4** (X = Br) and **5** (X = NO_2).

Bromination of optically active binaphthyl proceeded rapidly in chloroform at 0 °C, and optically active dibromide **4** was easily produced. However, the nitration of binaphthyl at low temperatures did not effectively proceed to completion with a variety of nitrating agents. A two-stage nitration, the first yielding mainly the 4-nitro derivative, finally gave the dinitro compound, **5**, with low but sufficient optical rotation.

For the production of the optically active dimethyl compound **3**, an unusual resolution of racemic samples of this substituted binaphthyl is possible.[7] When induced by a single crystal of naphthidine (i.e., compound **2**, with X = NH_2, picked at random from a racemic sample), a melted but supercooled sample of the dimethyl compound tends to predominately grow crystals of one enantiomorph from the liquid pool of its rapidly inverting enantiomers. After separation of the naphthidine, samples of dimethylbinaphthyl from many small-scale resolutions having the same sign of rotation were combined. This resolution, which is an example of the rarely observed transfer of chirality of crystals from one compound to another, yields small but adequate amounts of resolved hydrocarbon **3**.

Catalyzed Racemization of 4,4'-Disubstituted Binaphthyls. For kinetic studies of the racemization of binaphthyls, the standard conditions chosen were 0.025 M substrate with 1 mg/mL of carbon (Norit SG1) in chloroform at 24 °C. Both catalyzed and uncatalyzed reactions of substituted binaphthyls gave good straight lines in first-order kinetic plots over 3 half-lives. However, a reaction of chloroform with the amino group of naphthidine required a change to acetone as solvent, and the relatively slow rate of racemization of the dinitro com-
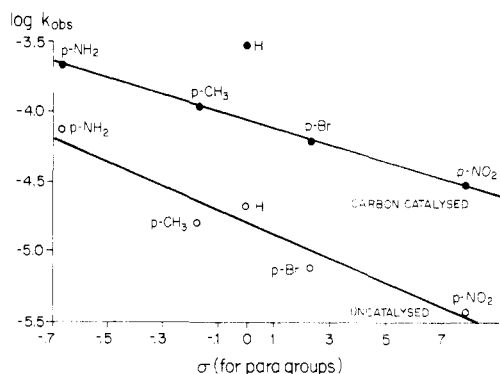

Figure 1. Log of observed first-order rate constant for racemization of 4,4'-disubstituted 1,1'-binaphthyls (at 24 °C in chloroform) against Hammett substituent constants: ●, 0.025 M binaphthyl with 1.0 mg/mL of Norit SG1; ○, 0.025 M binaphthyl, uncatalyzed.

pound **5** made runs at 35 and 49 °C more convenient. Rate constants were extrapolated by the Arrhenius equation to the standard temperature of 24 °C.

The first-order rate constants obtained for 24 °C are given in Table I where it is shown that, for this standard amount of carbon catalyst, the ratio of observed rate constants, k_{cat}/k_{uncat}, varies from 3 (for X = NH_2) to a maximum of 14 (for X = H). A catalytic effect evidently occurs with all the substituted binaphthyls but is most effective with unsubstituted binaphthyl itself. A rate-retarding steric effect of any group (larger than hydrogen) seems apparent, but since these substituents still allow a surface-catalyzed reaction to occur, the observed steric hindrance is small, and a loose and not very stereocritical binding of binaphthyl substrate to the carbon catalyst is indicated.

Insensitivity of the carbon–binaphthyl surface complex to a potentially large steric effect also shows up in Hammett plots (see Figure 1). Steric effects at the 4-positions would be nonexistent for the uncatalyzed reaction, but if a close approach to graphitic planes is involved in the catalyzed reaction, a steric effect should show up in a lack of Hammett correlation. Except for binaphthyl itself, the logarithms of observed rate constants vs. para substituent constants for the carbon-catalyzed racemization of substituted binaphthyls actually fall on a better straight line than do the rate constants for the uncatalyzed racemizations. The uncatalyzed reaction (with a ρ value of –0.88) shows the same electronic effect of substituents that has been classically observed for racemization of 4,4'-disubstituted biphenyls; i.e., electron donors increase the rate of reaction.[8] A generally satisfying explanation of this electronic effect does not seem to be available.[9] In any case, this same pattern of electronic effects is also observed for the carbon-catalyzed reaction but it is diminished in magnitude (i.e., ρ is –0.57). The relative change in the two values of the reaction constant ρ is consistent with the expected electron-donor properties of the planar aromatic surfaces of carbon particles.[10] If adsorption on the catalyst surface involves some electron donation from the surface toward the binaphthyl substrate, a lower sensitivity to any donation from the substituents would result (i.e., a lower

(5) W. Theilacker and R. Hopp, *Chem. Ber.*, **92**, 2293 (1959).

(6) R. E. Pincock and K. R. Wilson, *J. Am. Chem. Soc.*, **97**, 1474 (1975).

(7) Unpublished results of M. Lu and F.-N. Fung, University of British Columbia.

(8) R. L. Shriner, R. Adams, and C. S. Marvel in "Organic Chemistry, An Advanced Treatise", H. Gilman, Ed., Wiley, New York, 1943, Chapter 4, p 368.

(9) Cf.: E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p 126. L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry", Prentice-Hall, Englewood Cliffs, NJ, 1962, p 283.

(10) R. W. Coughlin, *Proc. Int. Congr. Catal., 4th*, **2**, 322 (1971).

Table II. Effect of Catalyst[a] Modification on Rate Constant for Catalytic Racemization of 1,1'-Binaphthyl[b]

treatment	$10^4 k_{obsd}$,[c] s⁻¹	treatment	$10^5 k_{obsd}$, s⁻¹
LiAlH₄ reduced	4.8	brominated	58.0
blank	4.7	brominated, then LiAlH₄ reduced	5.8
HNO₃ oxidized[d]	12.0	blank	7.2
blank[d]	13.0	chlorinated	15.0[e]
		chlorinated, then LiAlH₄ reduced	6.0
		blank	7.2

[a] Spheron 6 at 1.5 mg/mL in acetone was used except where noted. [b] At 25 °C unless specified otherwise. [c] At 45 °C. [d] Norit SG1 at 1.0 mg/mL of solution. [e] At 0 °C.

ρ value for the catalyzed reaction). Activation of a substrate, chemisorbed on carbon, by a process of charge transfer is an established mode of action by catalytic carbon.[11]

The similar electronic effects observed for both the catalyzed and uncatalyzed reactions makes it likely that similar transition states occur in both cases. Even though adsorption by carbon may promote planarity of binaphthyl, a completely planar binaphthyl molecule is not an absolute requirement in the racemization process. The uncatalyzed racemization is believed to proceed through a transition state having a nonplanar meso configuration.[1] It is not so easy to envision how adsorption might aid this type of racemization process but, consistent with the small steric effects mentioned above, the adsorption involved would likely have less specific steric requirements than that for a completely planar transition state.

Effects of Modification of Catalysts. Many different oxygen-containing functionalities have been shown or suggested to occur on the edge surfaces of carbon catalysts.[4] A general oxidative or reductive treatment of a carbon catalyst would modify the number and type of these oxygen goups, and the relative catalytic activities of the resulting carbons could be used to implicate (or exempt) these groups in the process of catalytic racemization of binaphthyl. For example, the oxidation of activated carbons by refluxing nitric acid is known to greatly increase the concentration of phenolic, carboxylic acid, lactone, and other carbonyl groups,[12] while lithium aluminum hydride reduction has been used to quantitatively identify such groups.[13] The reduction apparently does not greatly affect the more aromatic (i.e., graphitic) part of the carbon surfaces, and these graphite-like basal planar surfaces are also the least sensitive to oxidation. If edge groups on carbons are directly involved in binaphthyl racemization, oxidized or reduced catalysts should show modified catalytic activities.

On the other hand, the polyaromatic basal planes of carbon black surfaces readily adsorb molecular bromine or chlorine[14] and may react to form covalent carbon-halogen bonds.[15] If carbon-catalyzed racemization occurs by adsorption on these planes, a halogen-treated carbon

would be expected to have changed (presumably reduced) activity.

Table II shows the observed rate constants for catalytic racemization by various treated carbons. The blank runs refer to carbon samples treated in an identical manner with the reduced (LiAlH₄), oxidized (HNO₃), or halogenated (Br₂ or Cl₂) carbon but without actually introducing the specific reagent. After oxidative or reductive treatment of the carbon catalyst, the rate constants were essentially the same as those obtained from the respective blanks. Modification of oxygen functions has no relative effect on the activity of this carbon, and catalytic racemization therefore does not apparently involve such edge sites.

In contrast, Table II shows that halogenation of Spheron 6 significantly increased its catalytic activity. For example, chlorination produced a carbon catalyst that was too active to allow measurement of the racemization rate under the standard conditions given in Table II; even at a temperature of 0 °C the observed rate constant was twice that of the blank at 25 °C. This change in activity when carbon has adsorbed halogen indicates that the basal planes of the catalysts are sites of adsorption. It is surprising, however, that there is an *increase* in activity. Possibly the electron-donor properties of the carbon surface are accentuated by the addition of molecular halogen. An increased density of electrons from halogen atoms or new carbon–halogen bonds on the surface could make areas of the basal planes better electron donors. Other possibilities are that the presence of halogen has increased the mobility of binaphthyl or of competing solvent molecules on the surface of the carbon[15] or that completely new active sites have been created by a "cleaning" action of halogen on carbon surfaces. The effect seems quite specifically related to the presence of halogen since, as shown in Table II, reduction with hydride, which may be expected to lead to their partial removal,[16] restores the catalysts to approximately their original activity.

Other catalysts for both heterogeneous and homogeneous racemization of binaphthyl were briefly investigated. A graphitic surface with a high ability to donate electrons is present in the potassium–graphite intercalate compounds where potassium metal has given up an electron to the graphite basal planes.[17,18] Preparations[18] of intercalate with a stoichiometry of approximately $C_{22}K$ gave active catalysts that often individually showed good first-order racemization kinetics but also showed great sensitivity to impurities and irratic and irreproducible rates. An electron-withdrawing graphite compound, the ferric chloride–graphite intercalate C_6FeCl_3, also showed somewhat increased activity over the very weakly active graphite from which it was prepared. Small increases in the rate of homogeneous racemization of binaphthyl in the presence of electron-accepting charge-transfer compounds have been reported.[19]

The solvated electron, in the form produced from sodium in hexamethylphosphoramide,[20] acts as a very effective agent for homogeneous racemization of binaphthyl. For example, essentially complete and immediate racemization is observed on mixing equimolar solutions of sodium and binaphthyl in hexamethylphosphoramide at

(11) D. E. Weiss, "Proceedings of the 5th Congress on Carbon", Vol. 1, Pergamon Press, New York, 1962, p 65.
(12) A. Voet, J. B. Donnet, P. A. Marsh, and J. Schultz, *Carbon*, 4, 155 (1966).
(13) J. B. Donnet, *Carbon*, 6, 161 (1968).
(14) B. R. Puri and R. C. Bansal, *Indian J. Chem.*, 5, 381 (1967).
(15) A. I. Medalia and D. Rivin in "Characterization of Powder Surfaces", G. D. Parfitt and K. S. W. Sing, Eds., Academic Press, London, 1976.

(16) D. Rivin and J. Aron, 7th Conference on Carbon, Cleveland, OH, June 1965; see *Carbon*, 3, 358 (1965).
(17) D. E. Bergbreiter and J. M. Killough, *J. Am. Chem. Soc.*, 100, 2126 (1978).
(18) J. M. Lalancette, G. Rollin, and P. Dumas, *Can. J. Chem.*, 50, 3058 (1972).
(19) A. K. Colter and L. M. Clemens, *J. Am. Chem. Soc.*, 85, 114 (1963); 86, 3106 (1964).
(20) H.-L. J. Chen and M. Bersohn, *J. Am. Chem. Soc.*, 88, 2663 (1966); G. Fraenkel, S. H. Ellis, and D. T. Dix, *ibid.*, 87, 1406 (1965).

room temperature. The rapid racemization of the binaphthyl radical anion has been previously observed[21] and is consistent with calculations which show that the radical anion prefers a planar configuration.[22] On the basis of the observed rapid homogeneous racemization of the binaphthyl radical anion, the reversible formation of an anionic binaphthyl species, loosely bound on carbon, seems a reasonable possibility for the heterogeneous racemization. As with most heterogeneous catalytic reactions, the structure of the active site and the stereochemistry of the bound molecular species cannot be yet interpreted in terms of a very explicit mechanism. However, the effects of catalyst modification together with the effects of substituents give rise to a picture involving a loose binding of binaphthyl to the graphitic planes of the carbon catalyst, with these surfaces acting as weak electron donors toward the binaphthyl molecule.

Experimental Section

Binaphthyl was synthesized according to the method of Sakellarios and Kyrimis[23] and resolved by the solid-state method.[6] Spheron 6 was obtained from Cabot Corp. and Norit SG1 from Matheson Coleman and Bell. Infrared spectra were recorded on a Perkin-Elmer 137 infrared spectrophotometer. Mass spectra were recorded on an Atlas CH-46 spectrometer at an ionizing potential of 70 eV. Elemental microanalysis were performed by Mr. Peter Borda, University of British Columbia. Melting points were determined with a Thomas Unimelt capillary melting point apparatus using open-tube capillaries and are corrected. Gas-liquid chromatography (GLC) was performed with a Hewlett-Packard 5830A gas chromatograph equipped with a flame-ionization detector and using nitrogen as carrier gas with a 182 cm × 3 mm diameter stainless-steel column packed with 3% OV-17 on Chromosorb W AW-DMCS, 80/100 mesh. Optical rotations were determined on either a Perkin-Elmer 141 or 241 MC polarimeter using a 1-dm or a 1-cm quartz-faced jacketed cell.

4,4'-Dibromo-1,1'-binaphthyl. Optically active binaphthyl (0.25 g, 1.0 mmol; $[\alpha]^{23}_{589}$ +191) was stirred in 8 mL of chloroform cooled in an ice bath at 0 °C. Bromine (0.25 mL, 4.7 mmol) was syringed into the stirred solution and the reaction followed by GLC (270 °C). After the first new peak had completely disappeared and a second new peak had appeared (40 min), the reaction was quenched by the addition of 10 mL of saturated NaHSO₃. After removal of the aqueous phase, the solution was rinsed with 10 mL of saturated NaHSO₃, twice with 10 mL of 10% NaOH, twice with 10 mL of H₂O, and once with saturated NaCl and was dried over MgSO₄. The red solution was evaporated in vacuo to give light brown crystals. These were dissolved in 25 mL of CH₂Cl₂, treated once with 50 mg of decolorizing Norit, and washed down a 25 mm × 13 mm diameter alumina column. The solvent was removed in vacuo to give 0.34 g (82%) of **4** as a fine white powder: mp 215.0–217.0 °C (lit.[24] mp 217.5 °C, racemic); $[\alpha]^{23}_{589}$ +47 (c 9.1 mg/mL in CHCl₃); IR (CHCl₃) 1600, 1560 cm⁻¹ (1,2,3,4-substitution); mass spectrum, parent peak at *m/e* 414.

Anal. Calcd for C₂₀H₁₂Br₂: C, 58.29; H, 2.94; Br, 38.78. Found: C, 58.46; H, 2.90; Br, 38.66.

4,4'-Dinitro-1,1'-binaphthyl. In order to follow the synthesis by thin-layer chromatography (TLC; Eastman Chromagram 13181 silica gel with fluorescent indicator No. 6060, CCl₄ as eluant), we obtained a sample of racemic **5** by using the method of Schoepfle.[25] Binaphthyl (1.8 g, 7.1 mmol; $[\alpha]^{23}_{589}$ –174) was dissolved in 72 mL of CCl₄ and cooled in an ice bath at 0 °C. Concentrated H₂SO₄ (7.6 mL) was added with rapid stirring, followed by 4.5 g (71 mmol) of concentrated HNO₃. After 15 min the organic layer was decanted and washed with saturated NaHCO₃ until slightly basic, then with water until neutral, and finally with saturated NaCl

before being dried over MgSO₄. Removal of the solvent in vacuo gave 1.8 g of a yellow viscous oil consisting of mostly mononitro compound. This oil was dissolved in 42 mL of acetic acid, followed by the addition of 18 mL of 0.66 M HNO₃ and 90 mL of 3.3 M H₂SO₄. After the mixture was stirred for 1 h, the reaction was judged complete by TLC and quenched by the addition of 5 g of ice. The light yellow crystals which precipitated were rinsed with 100 mL of saturated NaHCO₃, 100 mL of H₂O, and 10 mL of ethanol and were dried in vacuo to give 2.1 g of light yellow powder. This powder was mixed with 6 g of alumina and chromatographed with elution by 20% benzene/petroleum ether (30–60 °C). The second yellow band was treated with decolorizing Norit and quickly filtered to prevent complete catalyzed racemization. The solvent was removed in vacuo to give 0.60 g (34%) of **5** as a fine yellow powder: mp 225–233 °C (lit.[25] mp 246 °C, racemic); $[\alpha]^{23}_{546}$ –11 (c 5.0 mg/mL in CHCl₃); IR (CHCl₃) 1550, 1360 (N=O), 888 (C—N), 890, 845 cm⁻¹ (1,2,3,4-substitution); mass spectrum, parent peak at *m/e* 344.

Anal. Calcd for C₂₀H₁₂N₂O₄: C, 69.77; H, 3.51; N, 8.14; O, 18.59. Found: C, 69.66; H, 3.48; N, 8.03; O, 18.83.

4,4'-Dimethyl-1,1'-binaphthyl. This compound was a generous gift from Dr. Fu-Ning Fung and was resolved as described below without further purification.

A *single crystal* of naphthidine (approximately 2 mg) was added to a clean, dry, 1-mL ampule containing between 2 and 20 mg of pure, racemic **3**. The ampule was sealed and immersed in a 151 °C oil bath for 4 min during which time **3**, but not the naphthidine, **2**, melted. The ampule was then quickly and smoothly transferred to a 100 °C oil bath where the DMB was allowed to crystallize on the naphthidine seed (several hours to several days) to give usually a large opaque crystal. This was repeated with 60 ampules, each being seeded with a different naphthidine crystal. Polarimetric analysis of the ampule contents showed $[\alpha]^{23}_{589}$ in acetone ranging from ±31 to ±157 for the 60 different ampules. The contents of ampules giving the same sign α value were combined to give two batches of brown crystals, 0.26 and 1.18 g. These were each mixed with an equal weight of alumina and eluted with 600 mL of 2–4% benzene/petroleum ether (30–60 °C) to give white crystals: 0.08 g, $[\alpha]^{29}_{589}$ –95 (c 3.7 mg/mL in acetone); 0.89 g, $[\alpha]^{29}_{589}$ +86 (c 5.9 mg/mL in acetone).

4,4'-Diamino-1,1'-binaphthyl (Naphthidine). Naphthidine was a generous gift from Dr. Keith R. Wilson and was resolved as described.[5] Just prior to a kinetic run the resolved naphthidine was treated with one-fourth its weight of decolorizing Norit, filtered, and dried in vacuo. Failure to treat the naphthidine with Norit gave erratic kinetics, even for the uncatalyzed reaction.

Kinetics Procedures. Kinetic runs for the carbon-catalyzed reactions were performed essentially as previously described.[3] A two-necked flask fitted with an overhead Corning Vibrastir and containing a preweighed amount of the catalyst was equilibrated at the desired temperature. The binaphthyl solution was pipetted into the reaction flask, and when half had been added the Vibrastir and timer were started. Approximately 1-mL samples were removed periodically with a Pasteur pipette and filtered through a Swinny syringe filter. Polarimetric analysis was performed at λ = 589 nm for binaphthyls 1, 3, and 4. For naphthidine (2) and for **5** sufficiently high rotations could be obtained only if λ = 546 nm were used for analysis. For the uncatalyzed reactions samples were periodically removed and analyzed as for the catalyzed reactions.

Nitric Acid Oxidation of Norit SG1. Norit SG1 (1 g, Matheson Coleman and Bell) was refluxed for 4 h in 10 mL of HNO₃ (sp gr = 1.42; bp 83 °C). The HNO₃ was then distilled off by using reduced aspirator pressure (20 mm). The Norit was cleaned further by ten washings with 20 mL of 0.1% NaOH. After each washing the Norit was centrifuged and the centrifugate decanted. The final centrifugate was clear. The charcoal was then refluxed overnight in 0.1% HCl, centrifuged, rinsed with H₂O until neutral, and dried overnight at 100 °C under high vacuum.

Lithium Aluminum Hydride (LAH) Reduction of Spheron 6. Spheron 6 (1 g, Cabot Corp.) was stirred at room temperature with 20 mL of tetrahydrofuran (freshly distilled from LAH) under a dry atmosphere. LAH (1.1 g) was added over 5 min. A mild reaction occurred with the addition of the LAH. The reaction was refluxed for 10.5 h and cooled, approximately 10 g of ice was

(21) O. Ito and M. Hatano, *Chem. Lett.*, 39 (1976).

(22) M. F. M. Post, J. Langelaar, and J. D. W. Van Voorst, *Chem. Phys. Lett.*, **46**, 331 (1977). See also G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **74**, 1525 (1955).

(23) E. Sakellarios and T. Kyrimis, *Chem. Ber.*, **57**, 324 (1924).

(24) A. Corbellini and E. Debendetti, *Gazz. Chim. Ital.*, **59**, 391 (1929); *Chem. Abstr.*, **24**, 360 (1930).

(25) C. S. Schoepfle, *J. Am. Chem. Soc.*, **45**, 1566 (1923).

added, and the clear liquid phase was discarded. The carbon catalyst was then treated for 14 h in 75 mL of refluxing 6 M HCl, rinsed neutral with 250 mL of H₂O, and dried overnight under high vacuum at 82 °C. A blank was prepared by treating 1 g of Spheron 6 in an identical fashion but without the addition of any LAH.

Chlorination of Spheron 6 at 450 °C.[14] Spheron 6 used for chlorination was first washed in the following manner. Spheron 6 (10 g) was refluxed for 12 h in 6 M HCl and subsequently rinsed to neutrality with H₂O. It was then extracted with benzene for 20 h on a Soxhlet extractor and dried for 20 h on a high-vacuum drying pistol at 100 °C. Cleaned Spheron 6 (0.30 g) was spread over 10 cm in the center of a 75-cm Pyrex tube fitted with a gas inlet and outlet. The inlet was connected to a tank of reagent grade chlorine and the outlet to a series of two traps, each containing 200 mL of 20% NaOH. The Pyrex tube was placed into a tube furnace and purged with argon as it came to 450 °C (2 h). Chlorine was then bubbled through the system for 3 h. After this time the chlorine was turned off and the system cooled to room temperature. Air was passed through the tube to evacuate any chlorine, and then the carbon catalyst was rinsed into a beaker and stirred with 100 mL of H₂O for 0.5 h. It was then centrifuged and dried on a high-vacuum drying pistol for 12 h at 100 °C. A blank was prepared by treating 0.30 g of Spheron 6 in an identical manner but without the introduction of any chlorine into the system.

Bromination of Spheron 6.[26] Spheron 6 (1.0 g, cleaned and degassed as for the chlorination blank) was stirred for 24 h in 100 mL of 0.1 N Br₂ with 0.2 N KBr in distilled H₂O. The suspension was then cooled and centrifuged, the red centrifugate decanted, and the carbon catalyst obtained washed with 300 mL of H₂O until a clear centrifugate was obtained. The carbon was then dried for 12 h on a high-vacuum drying pistol at 100 °C. Chlorinated and brominated Spheron 6 were reduced by lithium aluminum hydride in a manner identical with that for the nonhalogenated Spheron 6 described above.

Racemization of Binaphthyl by Sodium. Hexamethylphosphoramide (HMPA) was heated over barium oxide for 3.5 h at 65 °C and then vacuum distilled [bp 64 °C (0.65 mm)]. It was then degassed by the freeze–thaw method (three cycles) and used immediately. Solutions of solvated electrons were prepared according to the following method and were used immediately. In a typical preparation approximately 100 mg of sodium was cut from the center of a 1-in. cube, rinsed in pentane, and quickly transferred to a clean, dry, and preweighed 25-mL two-necked flask. The flask had been fitted with a glass stopper and rubber septum and contained a magnetic stir bar. The flask was then evacuated for 0.5 h to evaporate the solvent from the sodium and reweighed to give 65 mg of sodium. Freshly degassed HMPA (4 mL) was syringed into the flask and the stirring started. After 10 min the solution took on a dark blue hue. After 30 min of stirring, the sodium had completely dissolved, and the dark blue solution was ready for use.

A dry 10-mL test tube containing 19 mg (0.075 mmol) of binaphthyl was sealed with a rubber septum and purged with nitrogen. Freshly degassed HMPA (3 mL) was added to dissolve the binaphthyl, followed by 20 μL of the solvated electron solution. Under a stream of nitrogen some of the faint yellow solution was syringed into a 1-cm polarimeter cell and the polarimeter reading rapidly taken. Optical rotations were always immediately decreased and to a greater extent with a higher concentration of solvated electrons. The residual optical activity disappeared at a rate close to that of normal uncatalyzed racemization.

Preparation and Kinetics with Graphite Intercalates. Potassium–graphite intercalates were prepared according to the method of Lalancette.[18] All preparations used Fisher acid-washed graphite and Matheson Coleman and Bell reagent grade potassium.

Kinetic runs were performed immediately with a fresh batch of intercalate. In a typical run, a constant-temperature bath was applied to the flask in which 1.2 g of intercalate had been prepared under argon, and the system was allowed 0.5 h to come to thermal equilibrium. A solution of optically active binaphthyl ([α]²³₅₈₉ −132, 30 mL of 0.015 M binaphthyl in distilled spectrograde n-heptane) was thermally equilibrated for 15–30 min at the temperature of the run and then pipetted into the reaction flask. The timer and stirrer were started when half the solution had been added. Kinetics were followed as in the carbon-catalyzed reactions by polarimetry at 365 nm. Runs often showed first-order behavior but appeared to be very sensitive to solvent or other impurities.

FeCl₃–graphite (first stage, C₆FeCl₃), prepared from spectrograde SP-1 graphite (Union Carbide), was a generous gift from Dr. J. G. Hooley.[27] The intercalate was washed free of adsorbed FeCl₃ in the following manner. The intercalate (3 g) was washed five times with 25 mL of acetone and then stirred for 3 h in 100 mL of acetone. It was then filtered and dried in vacuo for 3 h. All filtrates from the washings were yellow. For the intercalate-catalyzed reactions it was also determined whether some soluble compounds were responsible for the catalysis. At the end of a catalytic run the catalyst was allowed to settle to the bottom of the flask, and approximately 2 mL of the supernatant was filtered through a Swinny syringe filter and mixed (1:1) with a 1.0 × 10⁻³ M solution of optically active binaphthyl. The optical rotation of the solution was the same before and after shaking the solution for 10 min.

(26) B. R. Puri, N. K. Sandle, and O. P. Mahajan, *J. Chem. Soc.*, 4880 (1963).

(27) J. G. Hooley and R. N. Soniassy, *Carbon*, **8**, 191 (1970).