slightly waxy, white solid, $[\alpha]^{22}_{\mathrm{D}}$ +14.9° (*c* 1.0, absolute ethanol). This material was recrystallized from *n*-hexane followed by 95% ethanol to yield white crystals: m.p. 108.0–109.0°, lit. m.p. 109.0–110°,[14] 108.5–110.0°[2a]; $[\alpha]^{23}_{\mathrm{D}}$ +12.7° (*c* 1.2, absolute ethanol), lit. $[\alpha]^{20}_{\mathrm{D}}$ −6.2° for the enantiomer (alcohol),[14] $[\alpha]^{30}_{\mathrm{D}}$ +11.7° (absolute ethanol).[2a]

The infrared spectrum was identical with that of (+)-2,2'-dibromo-6,6'-dimethylbiphenyl prepared from (+)-**2**.[2a,13]

(+)-2-Nitro-6,6'-dimethylbiphenyl (6).—A mixture of optically impure (−)-2-amino-2'-nitro-6,6'-dimethylbiphenyl [**1**, 2.40 g., m.p. 110.0–111.2°, $[\alpha]^{27}_{\mathrm{D}}$ −67.6° (*c* 1.3, 95% ethanol)], 2.5 ml. of concentrated hydrochloric acid, and 10 ml. of water was heated on a steam bath until solution was complete. The mixture was cooled in an ice bath (the amine salt precipitated out at this point) and a solution of 0.76 g. of sodium nitrite in 1.5 ml. of water was added dropwise with vigorous stirring. To the resulting cherry-red solution was added 20 ml. of 50% hypophosphorous acid, previously cooled to 0°; there was considerable evolution of nitrogen. After 24 hr. the mixture was diluted with water and extracted with ethyl ether. The combined ether extracts were washed with water and dried, the ether was filtered and evaporated, and about 20 ml. of 15% sodium hydroxide solution was added to the red residue. The mixture was steam distilled, and the distillate was saturated with sodium chloride and extracted with ethyl ether. The ether extracts were combined, dried, filtered, and evaporated. The residue was recrystallized from 95% ethanol to give 1.48 g. (65.3%) of very pale yellow crystals, m.p. 64.0–67.4°. Recrystallization from 95% ethanol to a constant melting point gave white crystals: m.p. 67.4–68.0°, $[\alpha]^{25}_{\mathrm{D}}$ +153.5° (*c* 0.82, 95% ethanol).

Subsequent preparations employing essentially optically pure 2-amino-2'-nitro-6,6'-dimethylbiphenyl gave virtually the same physical constants.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76; N, 6.16. Found: C, 73.75; H, 5.91; N, 6.34.

(−)-2-Amino-6,6'-dimethylbiphenyl (**7**).—A solution of (+)-2-nitro-6,6'-dimethylbiphenyl [**6**, 1.004 g., m.p. 65.5–67.3°, $[\alpha]^{27}_{\mathrm{D}}$ +146° (*c* 1.0, 95% ethanol)] in 60 ml. of absolute ethanol was hydrogenated at atmospheric pressure and room temperature, in the presence of platinum dioxide as catalyst. The mixture was filtered and the solvent was evaporated to give an oily white residue. Trituration with a small amount of 4 *N* HCl gave white crystals of amine salt. The amine salt was filtered, the filtrate was extracted with ether, and the amine salt was washed with ether. The aqueous acid filtrate and the amine salt were combined and enough water was added to dissolve all of the amine salt. The solution was cooled in an ice bath, made alkaline with 10% sodium hydroxide, and extracted several times with ether. The combined ether extracts were washed with water, dried, filtered, and evaporated to give an oily residue. After drying *in vacuo* over concentrated sulfuric acid this material solidified to give 0.693 g. of colorless product. Recrystallization from petroleum ether (b.p. 30–60°) afforded white crystals: m.p. 53.2–54.2°, $[\alpha]^{26}_{\mathrm{D}}$ −26.3° (*c* 1.1, 95% ethanol).

Anal. Calcd. for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.17; H, 7.57; N, 7.31.

The Absolute Configuration of 2,2'-Dichloro-6,6'-dimethylbiphenyl-4,4'-diamine[1a]

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On the basis of a theoretical model the (*S*) configuration had been assigned by previous workers to (+)-2,2'-dichloro-6,6'-dimethylbiphenyl-4,4'-diamine (**3**). In an attempt to verify this assignment, (−)-**3** was deaminated to (−)-2,2'-dichloro-6,6'-dimethylbiphenyl (**5**). Since this reaction can only proceed with retention of configuration and since (−)-**5** has the (*S*) configuration, it has therefore been shown that (−)-**3** has the (*S*) configuration. Attempts to resolve **3** failed in our hands and optically active **3** was instead prepared by a series of transformations starting with optically active 2,2'-dimethyl-6,6'-dinitro-4,4'-diphenic acid (**4**).

In the course of previous investigations in these laboratories on the relative and absolute configurations of biphenyls,[2] the (*R*) configuration had been assigned to the dextrorotatory forms of 6,6'-dinitro-2,2'-diphenic acid (**1**)[3] and 6,6'-dimethylbiphenyl-2,2'-diamine (**2**).[4] These results reversed the absolute configurations predicted for these compounds by Kuhn and collaborators, which were based on qualitative[5] and semiquantitative[6] theoretical arguments. It thus became desirable to confirm the absolute configuration of 2,2'-dichloro-6,6'-dimethylbiphenyl-4,4'-diamine (**3**), which had been similarly assigned on theoretical grounds.[6]

An attempt to repeat the reported[6] resolution of racemic **3** was unsuccessful.[7] Synthesis of optically active **3** from optically active precursors was therefore undertaken. The starting material for this sequence was (−)-2,2'-dinitro-6,6'-dimethyl-4,4'-diphenic acid (**4**), which was converted into (−)-**3** and thence into (−)-(*S*)-2,2'-dichloro-6,6'-dimethylbiphenyl (**5**) by the steps outlined in Chart I and discussed in detail below. The product, (−)-(*S*)-**5**, also served as the absolute configurational standard in this series.[4]

Results and Discussion

The starting acid **4** was prepared and resolved according to a modification of the procedure developed by Mix,[8] who recorded a rotation of −20° for the presumably optically pure compound. In the present work, rotations no higher than −16.2, −16.3, and −16.3° were obtained in three separate resolutions; these samples therefore had an optical purity of 81% based on the figure reported by Mix. An incompletely resolved sample of **4**, $[\alpha]_{\mathrm{D}}$ −7.0° (optical purity 35%), was converted to 2,2'-diamino-6,6'-dimethyl-4,4'-diphenic acid (**6**) by catalytic hydrogenation; the crude product had $[\alpha]_{\mathrm{D}}$ −12.6°. Replacement of the amino groups of (−)-**6** by chlorine atoms using the Sandmeyer reaction, followed by esterification with diazomethane, gave **7**, $[\alpha]_{\mathrm{D}}$ −7.2°.

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[1] (a) Partial support by the National Science Foundation (GP-757) is gratefully acknowledged. (b) To whom correspondence should be addressed: Department of Chemistry, Princeton University, Princeton, N. J. 08540.

[2] K. Mislow, *Angew. Chem.*, **70**, 683 (1958); *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962), and references cited therein.

[3] P. Newman, P. Rutkin, and K. Mislow, *J. Am. Chem. Soc.*, **80**, 465 (1958).

[4] F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci, and K. Mislow, *ibid.*, **80**, 476 (1958).

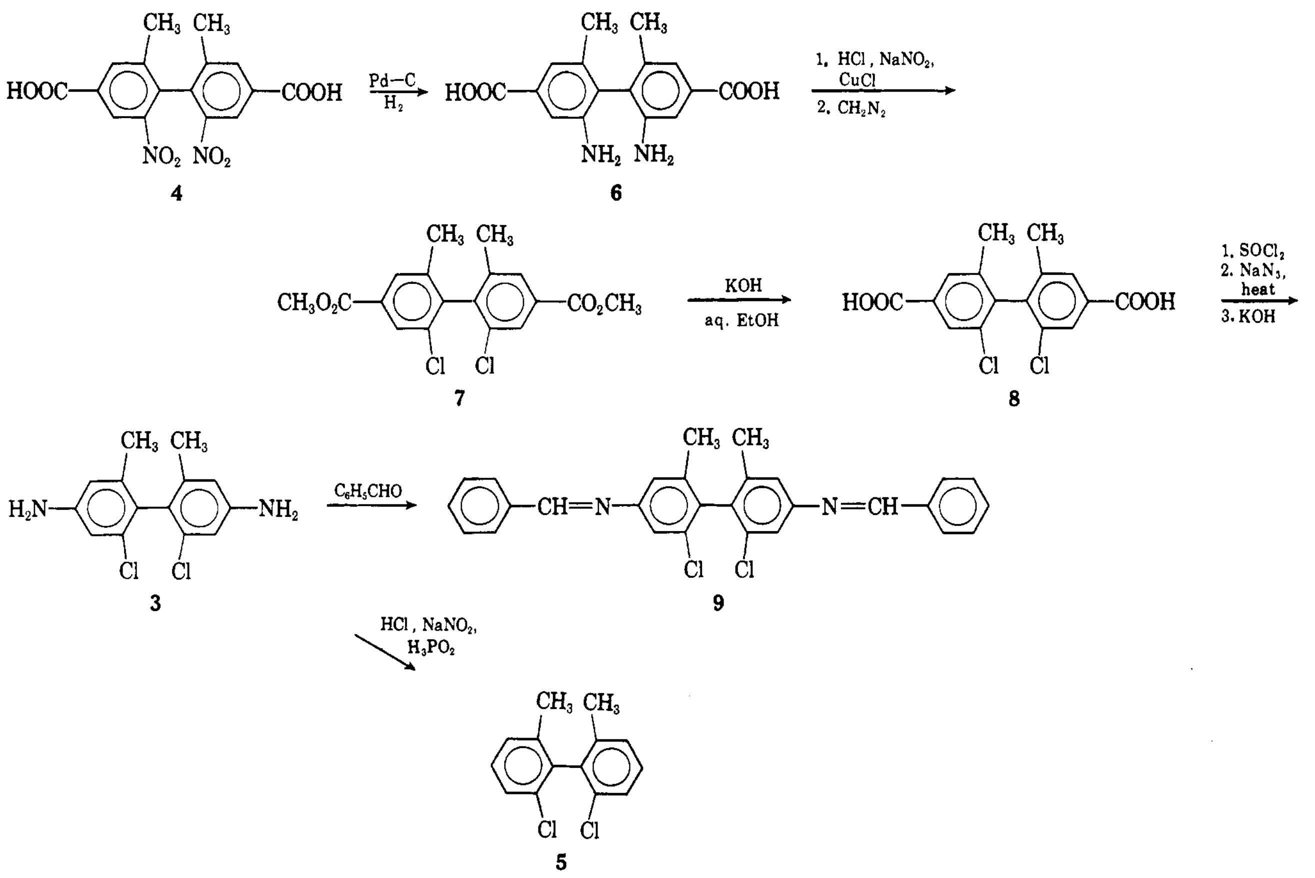
[5] W. Kuhn and K. Bein, *Z. physik. Chem.*, **B24**, 335 (1934).

[6] W. Kuhn and R. Rometsch, *Helv. Chim. Acta*, **27**, 1080, 1346 (1944); W. Kuhn, *Z. Elektrochem.*, **62**, 28 (1958).

[7] F. A. McGinn, M.S. Thesis, New York University, 1957.

[8] H. Mix, *Ann.*, **592**, 146 (1955).

CHART I



Replacement of the two amino groups in diamine **2** by the Sandmeyer reaction had been shown to occur with essentially complete retention of optical purity, as well as configuration.[4,9] By analogy, it follows that in the present case the optical purity of (−)-**7** ($[\alpha]_D$ −7.2°) is 35%, a figure which is based on the presumed optical purity of the starting material **4** and on the assumption that no optical fractionation occurred in the course of work-up of products. This diester, (−)-**7**, was saponified to crude diacid (−)-**8**, which was in turn converted by the Curtius degradation route to the desired benzidine **3**, $[\alpha]_D$ −9.4° (ethanol). Since the work-up procedure was designed to minimize the possibility of optical fractionation, the isolated sample of **3** was presumably 35% optically pure, corresponding to a maximum rotation of $[\alpha]_D$ −26.9° (ethanol). The previously reported[6] value for the rotation of "optically pure" **3**, $[\alpha]_D$ −1.32° (ethanol), which referred to a sample obtained by resolution of (±)-**3** *via* the tartrate salt, thus corresponds in fact to material whose optical purity is maximally 5%. This figure is substantiated by our observation that a sample of **3**, $[\alpha]_D$ −9.4°, yields a dibenzal derivative **9**, $[\alpha]_D$ +10.4° (benzene). Assuming no optical fractionation, the maximum rotation of **9** is $[\alpha]_D$ +29.7° (benzene). The previous workers[6] reported a rotation of $[\alpha]_D$ +1.33° (benzene) for **9** which had been obtained from **3** having $[\alpha]_D$ −1.32° (ethanol); this is roughly consistent with our figure of 5% for the optical purity of the earlier[6] materials. An adequate explanation of the negligible optical enrichment of **3** observed in the resolution of **3** (and an explanation of the difficulties experienced by ourselves in attempts[7] to resolve **3**) may be found in the possibility of solid solution formation between the diastereomeric salts formed from (±)-**3** and (−)-tartaric acid: since the group volumes of methyl and chlorine do not differ significantly,[10] the diastereomers are expected to be isomorphous.

Deamination of (−)-**3**, $[\alpha]_D$ −9.40°, was accomplished by hypophosphorus acid reduction of the bisdiazonium salt. In this manner, **3** having $[\alpha]_D$ −9.4° (ethanol) afforded **5** having $[\alpha]_D$ −11.5° (ethanol) and $[\alpha]_D$ −15.5° (hexane). Since the maximum rotation reported[4] for **5** is $[\alpha]_D$ +33° (ethanol) and $[\alpha]_D$ +45° (hexane), the optical purity of the product is 35%. The excellent agreement with the presumed optical purity of precursor **4** supports our contention that no significant optical fractionation took place in the series of transformations starting from **4** (Chart I).

The infrared spectrum of (−)-**5** was superimposable on that of a sample of (±)-**5** which had in turn been prepared by deamination of (±)-**3** obtained from the benzidine rearrangement of 3,3'-dichloro-5,5'-dimethylhydrazobenzene.[4,6] Although the infrared spectra of (−)-**5** and (±)-**5** were indistinguishable, and although the two samples were homogeneous and had identical retention times as measured by g.l.c. on Silastic and Carbowax-on-Chromosorb columns, g.l.c. on a silicone gum rubber column revealed the presence of a contaminant (2%) in the sample of (±)-**5** which was absent in the sample of (−)-**5**. Possibly this 2% contaminant is an isomeric dichlorodimethylbiphenyl derived from the diphenylenes which might be expected

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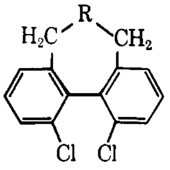
(9) J. T. Melillo and K. Mislow, *J. Org. Chem.*, **30**, 2149 (1965).

(10) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 283.

to accompany in minor quantities the benzidine product (**3**) of the rearrangement of 3,3′-dichloro-5,5′-dimethylhydrazobenzene.[11]

The transformation of (−)-**3** into (−)-(*S*)-**5** unequivocally[2] establishes the (*S*) configuration for (−)-**3**. This result is contrary to the report of Kuhn and Rometsch[6] who claimed the (*R*) configuration for (−)-**3** [or the (*S*) configuration for (+)-**3**] on the basis of theoretical considerations. All three of Kuhn's configurational assignments[5,6] in the biphenyl field (*i.e.*, **1**, **2**, and **3**) have thus been reversed. According to the theoretical model,[6] the angle of torsion (*i.e.*, the dihedral angle between the planes of the two phenyl rings) may affect the sign of rotation in the visible region of the spectrum, and the assumption had been made[6] that in **3**, as well as in **2**, the conformation of the biphenyl is *trans* (*i.e.*, the two chlorine atoms are separated by a distance greater than would be the case if the dihedral angle were $\pi/2$). This assumption is almost certainly unjustified. The *cis* conformation has been established for 2,2′-dichlorobiphenyl[12] and for **2**.[13] Furthermore, although the *trans* conformation had earlier been assigned[4,14] to **2** and **5**, this conformational assignment to **2** was subsequently[15] reversed on the basis of a circular dichroism study of **2**. The conformation of **5** is therefore also most likely *cis*. Since it is highly unlikely that the introduction of two amino groups in the 4,4′ positions would change the average conformation of **5** to any significant extent, the weight of evidence thus points to the *cis* rather than to the *trans* conformation for **3**.

The theoretical discussion[6] of the optical rotatory power of compounds such as **3** and **5** has in any event been rendered more tenuous by the results of later findings which could not have been anticipated at the time of the original work.[6] Thus, in the two *bridged* 2,2′-dichlorobiphenyls **10**, which are closely analogous to the unbridged dichlorobiphenyls **3** and **5**, but which are rigidly locked into the *cis* conformation by the bridge, the dextrorotatory (in the visible) isomer has the (*S*) configuration[16] apparently in agreement with the model of Kuhn and Rometsch. However, it has been shown[16] that this rotation does *not* correspond to the sign of the nearest Cotton effect, but to the sign of a high-amplitude positive [for the (*S*) configuration] Cotton effect which is centered at short wave lengths and whose tail dominates the whole of the visible region; actually, the Cotton effect closest to the visible is *negative* for the (*S*) configuration of **10**.[15]



10, R = $C(CO_2C_2H_5)_2$ or $[N^+(CH_2)_5]Br^-$

Kuhn and Rometsch[6] examined the optical rotatory dispersion (O.R.D.) of (−)-**3** and reported a trough at *ca.* 400 mμ, with $[\phi]_{400}$ −28°. We have found that the O.R.D. curve exhibits a trough at 320 mμ, rather than 400 mμ, with $[\phi]_{320}$ −225° (or −643° when corrected to optical purity). Spectropolarimetric examination below 310 mμ, where the O.R.D. curve crosses the zero line, was prevented by the relatively high absorbance and the low optical rotation in that region of the spectrum.

Experimental[17]

Optical Activation of 2,2′-Dimethyl-6,6′-dinitro-4,4′-diphenic Acid (4).[8]—A solution of racemic 2,2′-dimethyl-6,6′-dinitro-4,4′-diphenic acid (40.2 g., m.p. 335–343° dec., lit.[8] m.p. above 340° dec.) in 800 ml. of boiling acetone was mixed with a solution of brucine (43.8 g.) in 1 l. of boiling acetone. The resulting crystals were recrystallized six times from 80% aqueous ethanol to give 14.3 g. of diastereomeric salt, $[\alpha]^{25}D$ −13° (*c* 0.795, dioxane). A slurry of the brucine salt (14.0 g.) in 100 ml. of water was warmed on the steam bath and 25 ml. of a 7 *M* solution of aqueous ammonia was added. The resulting yellow solution slowly deposited crystals of brucine upon standing in the refrigerator. The cold solution was filtered and the clear filtrate was acidified with 20% aqueous hydrochloric acid. The white precipitate was collected by filtration and was purified by dissolution in dilute Na_2CO_3 solution, followed by filtration and acidification of the filtrate with dilute aqueous hydrochloric acid. The resulting product after drying consisted of 6.0 g. of a white powder: m.p. 330–332° dec. (with some evidence of decomposition beforehand), $[\alpha]^{25.5}D$ −16.3° (*c* 1.23, 95% ethanol), lit.[8] $[\alpha]^{20}D$ −20° (ethanol). The infrared spectrum of a sample of (−)-**4** was superimposable on that of the racemic modification. The spectrum was dominated by a strong band at 5.88 μ, corresponding to the carbonyl stretching vibration, and by two bands at 6.50 and 7.45 μ, corresponding to the asymmetric and symmetric vibrations, respectively, of the nitro group.

A second resolution of racemic **4** gave 13.4 g. of optically active acid: m.p. 321–335° dec., $[\alpha]^{24}D$ −7.0 (ethanol). This was the sample of (−)-**4** which was subsequently used as the starting material in the synthesis described in Chart I.

Anal. Calcd. for $C_{16}H_{12}N_2O_8$: C, 53.34; H, 3.36; N, 7.78. Found: C, 53.87; H, 3.75; N, 7.62.

(−)- and (±)-2,2′-Diamino-6,6′-dimethyl-4,4′-diphenic Acid (6).[8]—A slurry of partially resolved 2,2′-dimethyl-6,6′-dinitro-4,4′-diphenic acid (**4**, 14.0 g., $[\alpha]^{24}D$ −7.0°) in 150 ml. of glacial acetic acid was hydrogenated at 38 p.s.i. and room temperature using 10% palladium on charcoal as a catalyst. The resulting slurry was filtered, the yellow filtrate was evaporated to dryness, the solid residue was taken up in concentrated Na_2CO_3 solution, and the mixture was filtered. Adjustment of the pH to a value of less than 2 with HCl brought a clear solution; careful readjustment of the pH to 4 with concentrated Na_2CO_3 solution gave a powdery precipitate. The product was collected by filtration and, after it was dried *in vacuo* over potassium hydroxide, consisted of 9.2 g. (79%) of a cream-colored powder: m.p. 314–325° dec., $[\alpha]^{24}D$ −12.6° (*c* 0.95, 95% ethanol), lit.[8] $[\alpha]^{20}D$ −41.2° (ethanol). This material was not further purified for the next step.

In like manner racemic **6** was prepared by the catalytic hydrogenation of (±)-**4**. The yellow product melted at 314–315° dec., lit.[8] m.p. 325° dec.

(−)- and (±)-2,2′-Dichloro-6,6′-dimethyl-4,4′-dicarbomethoxybiphenyl (7).—A solution of sodium nitrite (4.14 g.) in 13 ml. of water was added dropwise to a slurry of 2,2′-diamino-6,6′-dimethyl-4,4′-diphenic acid (9.0 g., $[\alpha]^{24}D$ −12.6°) in 82 ml. of 6 *M* aqueous hydrochloric acid at −12°. The resulting light orange slurry of bisdiazonium salt was added to a solution of cuprous chloride (9 g.) in 42 ml. of concentrated hydrochloric acid over a period of about 1 hr., with stirring and cooling. During this period the temperature of the reaction mixture fluctuated

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[11] M. Večeřa and J. Petranek [*Collection Czech. Chem. Comm.*, **25**, 2005 (1960)] have demonstrated that the rearrangement of 3,3′-dichlorohydrazobenzene gives 85% of 2,2′-dichlorobenzidine and 13% of a mixture of 6,2′- and 4,2′-dichloro-2,4′-biphenyldiamines.

[12] G. H. Beaven and D. M. Hall, *J. Chem. Soc.*, 4637 (1956).

[13] E. Bergmann and L. Engel, *Z. physik. Chem.*, **B15**, 85 (1931); see, however, A. Weissberger, *ibid.*, **B15**, 97 (1931).

[14] D. D. Fitts, M. Siegel, and K. Mislow, *J. Am. Chem. Soc.*, **80**, 480 (1958).

[15] K. Mislow, E. Bunnenberg, R. Records, K. Wellman, and C. Djerassi, *ibid.*, **85**, 1342 (1963).

[16] K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *ibid.*, **84**, 1455 (1962).

[17] We thank Messrs. R. Atkins, J. Derman, K. Friedman, G. M. Gould, P. Shenkin, and D. Sugarman for technical assistance.

between −10 and 15°. Rapid evolution of nitrogen (frothing) was observed. The reaction mixture was filtered and the residue was washed with water and air dried. The orange solid was extracted with ether. Treatment of the red ether extracts with ethereal diazomethane (external cooling) produced vigorous bubbling and ultimately a clear orange solution. The ether was evaporated and a concentrated solution of the residue in benzene was adsorbed on a column prepared with 120 g. of silica gel slurried in hexane. The fraction which was eluted between 1:1 benzene–hexane and pure benzene gave 5.0 g. (45.4%) of an off-white solid which was rechromatographed as above to yield 3.85 g. of a white crystalline compound: m.p. 117–120.5°, $[\alpha]^{24}\mathrm{D}$ −7.2° (*c* 0.97, 95% ethanol).

Anal. Calcd. for $C_{18}H_{16}Cl_2O_4$: C, 58.86; H, 4.40; Cl, 19.31 Found: C, 58.71; H, 4.21; Cl, 19.28.

Racemic **7**, similarly prepared from racemic **6**, melted at 122–122.5° after recrystallization from benzene–hexane.

Anal. Calcd. for $C_{18}H_{16}Cl_2O_4$: C, 58.86; H, 4.40; Cl, 19.31. Found: C, 58.31; H, 4.23; Cl, 19.48.

(−)- and (±)-2,2'-Dichloro-6,6'-dimethyl-4,4'-diphenic Acid (8).—A mixture of 2,2'-dichloro-6,6'-dimethyl-4,4'-dicarbomethoxybiphenyl (**7**, 3.85 g., $[\alpha]^{24}\mathrm{D}$ −7.2°), absolute ethanol (180 ml.) potassium hydroxide (32.5 g.), and water (120 ml.) was refluxed for 3 hr. Evaporation of the solution produced a white paste which was dissolved in water. Acidification of the solution with concentrated hydrochloric acid gave a white precipitate which was collected by filtration and dried *in vacuo* over potassium hydroxide. Extraction of this material with ether produced 2.80 g. (79%) of a white crystalline solid, m.p. 340–364° dec., $[\alpha]^{29}\mathrm{D}$ −10.6° (*c* 0.94, acetone), whose elemental analysis indicated the presence of impurities.

Anal. Calcd. for $C_{16}H_{12}Cl_2O_4$: C, 56.56; H, 3.57; Cl, 20.91. Found: C, 57.42; H, 3.63; Cl, 19.71.

Racemic **8**, similarly prepared in crude form from **7**, melted at 370–374°.

Anal. Calcd. for $C_{16}H_{12}Cl_2O_4$: C, 56.56; H, 3.57; Cl, 20.91. Found: C, 57.67; H, 3.77; Cl, 20.23.

(−)- and (±)-2,2'-Dichloro-6,6'-dimethylbiphenyl-4,4'-diamine (3).[18]—A mixture of thionyl chloride (53 ml.), crude 2,2'-dichloro-6,6'-dimethyl-4,4'-diphenic acid (**8**, 2.47 g., $[\alpha]^{29}\mathrm{D}$ −10.6°) and anhydrous pyridine (2 ml.) was refluxed for 2 hr. The clear yellow solution was evaporated to dryness and the residue was taken up in carbon tetrachloride. The mixture was filtered and the filtrate was evaporated to dryness. The residual acid chloride was dissolved in 53 ml. of acetone and the solution was treated with a solution of sodium azide (4.22 g.) in 10 ml. of water. The resulting mixture was diluted with 50 ml. of water, the oil was separated, and the aqueous layer was extracted with two 25-ml. portions of toluene. The combined organic layers were dried over magnesium sulfate and heated to 90°. Rapid bubbling ensued. When the bubbling had subsided the bath temperature was raised to about 120° and 50 ml. of 50% potassium hydroxide solution was added. The heterogeneous system was refluxed for 3 hr. At the end of this period the mixture was extracted with dilute hydrochloric acid. Neutralization of the clear, aqueous solution with Na_2CO_3 gave 0.38 g. (18%) of a white powder. Chromatography of the impure diamine on 15 g. of silica gel (elution with 1:10 ether–benzene) afforded (after drying) 0.268 g. of an off-white crystalline solid: m.p. 154–161°; $\lambda_{\max}^{\text{ethanol}}$ 296 mμ (ε 4100), 251 mμ (ε 24,800); $[\alpha]^{29}\mathrm{D}$ −9.4° (*c* 0.905, 95% ethanol); O.R.D.[19] (*c* 0.215–0.0215, 27°) $[\phi]_{583}$ −27°, $[\phi]_{400}$ −62°, $[\phi]_{350}$ −91°, $[\phi]_{320}$ −225° (trough), $[\phi]_{310}$ 0° (end value).

Anal. Calcd. for $C_{14}H_{14}Cl_2N_2$: C, 59.80; H, 5.02; Cl, 25.22; N, 9.96. Found: C, 59.75; H, 5.08; Cl, 24.97; N, 9.80.

Racemic **3**, similarly prepared from racemic **8**, melted at 165–166° (lit.[6] m.p. 167–168°) after recrystallization from 50% aqueous ethanol.

Anal. Calcd. for $C_{14}H_{14}Cl_2N_2$: C, 59.80; H, 5.02; Cl, 25.22; N, 9.96. Found: C, 60.12; H, 5.18; Cl, 25.37; N, 10.35.

The infrared spectrum of (±)-**3** from this preparation was identical with that of (−)-**3**, prepared above, and with that of an analytical sample of (±)-**3** prepared by the benzidine rearrangement of 3,3'-dichloro-5,5'-dimethylhydrazobenzene.[4,6]

(−)- and (±)-2,2'-Dichloro-6,6'-dimethylbiphenyl (5).—A solution of 2,2'-dichloro-6,6'-dimethylbiphenyl-4,4'-diamine (**3**; 0.1136 g., $[\alpha]^{29}\mathrm{D}$ −9.4°) in 0.34 ml. of concentrated hydrochloric acid and 0.10 ml. of water was cooled to −5°. Addition of a solution of sodium nitrite (0.059 g.) in 0.148 ml. of water resulted in a pink solution which was treated dropwise with hypophosphorus acid (1.27 ml.) at −5° over a period of 10 min. A frothy mass was obtained which was left in the freezer for a period of 20 hr. The mixture was then warmed to room temperature and diluted with 25 ml. of water. The resulting pink precipitate was collected by filtration, dried *in vacuo*, dissolved in hexane, and chromatographed on 12 g. of Woelm acid-washed alumina, grade I. Elution with hexane afforded 0.045 g. (44%) of colorless crystals: m.p. 114–117°, $[\alpha]^{26}\mathrm{D}$ −15.5° (*c* 0.90, hexane), $[\alpha]^{26}\mathrm{D}$ −11.5° (*c* 1.04, 95% ethanol). Gas chromatographic retention times on the respective columns follow: Silastic (6 ft., 35 p.s.i., 136 cc./min., 150°), 6.2 min.; 20% Carbowax 1500 on Chromosorb (6 ft., 35 p.s.i., 240 cc./min., 200°), 11.0 min.; and silicone gum rubber (12 ft., 35 p.s.i., 105 cc./min., 200°), 29.4 min.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82; Cl, 28.23. Found: C, 66.70; H, 4.84; Cl, 27.87.

Racemic **5**, similarly prepared[4] from racemic **3** obtained[4] from the benzidine rearrangement of 3,3'-dichloro-5,5'-dimethylhydrazobenzene, had an infrared spectrum which was superimposable on that of (−)-**5** prepared above. Gas chromatographic retention times on the respective columns under the conditions stated above follow: Silastic, 6.1 min.; 20% Carbowax on Chromosorb, 11.0 min.; and silicone gum rubber, 29.6 min. In the last case the main peak was accompanied by a small peak (ratio of peak areas 97.7:2.3) with a retention time of 38.4 min.

(+)- and (±)-N,N'-Dibenzal-2,2'-dichloro-6,6'-dimethylbenzidine (9).[6]—2,2'-Dichloro-6,6'-dimethylbiphenyl-4,4'-diamine (**3**, 0.0476 g., $[\alpha]^{29}\mathrm{D}$ −9.4°) was treated with 2 equiv. of a standardized benzaldehyde solution in 95% ethanol. The solution was warmed slightly, blanketed with nitrogen, and stoppered tightly. In about 10 min., crystals began to form. After several hours the solution was centrifuged. The mother liquor was removed by pipetting and the crystals were pumped down in a vacuum desiccator over wax. The product (0.067 g., 86%) had m.p. 161–171°, $[\alpha]^{23}\mathrm{D}$ +10.4° (*c* 3.65, benzene).

Anal. Calcd. for $C_{28}H_{22}Cl_2N_2$: C, 73.53; H, 4.85; Cl, 15.50; N, 6.12. Found: C, 72.98; H, 4.92; Cl, 15.40; N, 6.55.

Racemic **9**, similarly prepared from racemic **3**, gave 0.108 g. (84%) of product, m.p. 177–180° (lit.[6] m.p. 177–178.5°).

Anal. Calcd. for $C_{28}H_{22}Cl_2N_2$: C, 73.53; H, 4.85; Cl, 15.50; N, 6.12. Found: C, 72.98; H, 4.91; Cl, 15.58; N, 6.12.

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[18] Conditions for this rearrangement followed those described by K. Mislow and P. A. Grasemann [*J. Org. Chem.*, **23**, 2027 (1958)] for the rearrangement of 1,1'-binaphthyl-2,2'-dicarboxylic acid.

[19] Measured on a Cary Model 60 spectropolarimeter.