needles of $[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}^-)_2]_2$, mp 227–231° dec, were collected. The yield was 3.80 g (4.25 mmol, 85%). The 60-MHz ^1H nmr spectrum in deuterioacetone consisted of a triplet of triplets of intensity 3 at τ 8.59 ($J = 7.1, J' = 1.8$) and a quartet of intensity 2 at τ 6.50 ($J = 7.1$), corresponding to the cation methyl and methylene protons, respectively. The 32.1-MHz ^{11}B nmr spectrum consisted of a set of overlapping doublets centered at +7.4 ppm. Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

Acknowledgment. This research was supported in part by the Office of Naval Research. The authors also wish to thank Drs. F. A. L. Anet and R. Wiersema for the 77- and 80-MHz ^{11}B nmr spectra.

Addition Reactions on Coordinated Olefinic Ligands. IV. Stereoselective Synthesis between Dichloro(1,5-hexadiene)platinum(II) and Enantiomeric (*S*)-α-Methylbenzylamine[1]

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Abstract: Interaction between dichloro(1,5-hexadiene)platinum(II) and (*S*)-α-methylbenzylamine has been investigated. The addition reaction leads to a derivative containing a carbon–platinum σ bond. It is possible to obtain an equimolar mixture of two diastereoisomeric forms, or a single one, depending on reaction conditions. The reaction involving the formation of binuclear products from the crude diastereoisomeric mixture has been found to be highly stereoselective. Circular dichroism spectra of monomeric and binuclear products are discussed.

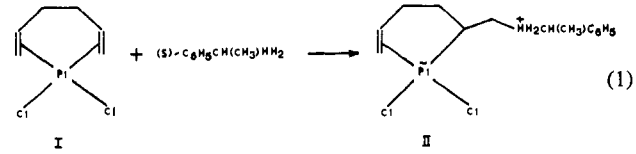
In a previous report[2] we described the addition reactions of ammonia and aliphatic amines on diene complexes of Pt(II) and Pd(II). Such reactions, as well as the ones involving the addition of other nucleophiles, follow a stereospecific mechanism.[3,4] Furthermore, in cases where optically active reagents were present, it was possible to find some stereoselectivity.

Indeed, enantiomeric complexes of disymmetric olefins, as (+)-dichloro(*endo*-dicyclopentadiene)platinum(II) and (−)-dichloro(*endo*-dicyclopentadiene)palladium(II), react with *dl-sec*-butyl alcohol[5] in the presence of bases in a quite stereospecific way, showing a stereoselectivity of about 10–20%. A still higher stereoselectivity was also found[6] in the reaction between the racemic complex dichloro(4-vinylcyclohexene)platinum(II) and (*S*)-α-methylbenzylamine.

In this paper we report the reaction between an optically active nucleophilic agent, (*S*)-α-methylbenzylamine, and a Pt(II) complex with a prochiral diene (that is, having prochiral[7] or enantiotopic[8] faces), dichloro(1,5-hexadiene)platinum(II) (I, Figure 1). The organic moiety of this complex is coordinated to the metal so that carbon atoms C-2 and C-5 are opposite in configuration. That is the same as saying that both the enantiotopic faces of a double bond are coordinated to the same metal atom. The results of the X-ray crystal structure analysis of the analogous Pd(II) complex[9] support our assumptions.

The choice of such a substrate was suggested in order to extend our previous investigations[10] on the molecular asymmetry in prochiral olefins and transition metal complexes. This substrate enables us to study the possible stereochemical features of processes involving some stereospecificity and stereoselectivity (*e.g.*, biological and enzymatic reactions, stereospecific polymerization, etc.) on a simple molecular model.

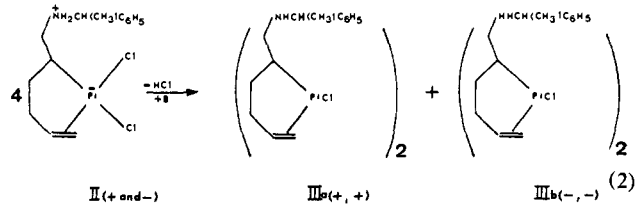
The addition reaction of (*S*)-α-methylbenzylamine to complex I (eq 1) can yield either two diastereoisomeric forms, or a single one, according to the reaction conditions. The crude mixture (II) of the two diastereo-



(1)

I II

isomers, obtained *via* eq 1, can react further (eq 2)



(2)

(1) Part III: A. Panunzi, A. De Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **92**, 3488 (1970).
(2) R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *ibid.*, **91**, 3874 (1969).
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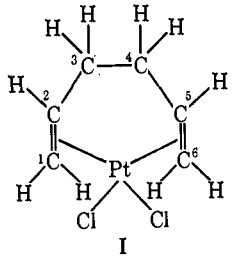


I

Figure 1. Dichloro(1,5-hexadiene)platinum(II), I.

in the presence of base with the loss of hydrochloric acid, giving an equimolar mixture (III) of two diastereoisomeric binuclear products (IIIa and IIIb). These binuclear products are formed by condensing two monomeric units of the same absolute configuration, thus providing a highly stereoselective process.

Results and Discussion

Resolution of Product II. Complex II was obtained as white crystals by reaction of equimolar amounts of (*S*)-α-methylbenzylamine and complex I in methylene chloride solution (eq 1). This product was previously[2] described as a zwitterion-type compound with a carbon–metal σ bond, in which the amine addition occurred on the terminal carbon atom of a vinyl group. Indeed complex II gave, on destructive reduction with $NaBH_4$ in THF, only *N*-*n*-hexyl-(*S*)-α-methylbenzylamine. The presence of the carbon–platinum σ bond in the product (II) gives rise to a different type of asymmetric center at carbon atom C-2 (or C-5) in the five-membered ring. Therefore, from a topological viewpoint the formation of four diastereoisomeric forms would be possible. Nevertheless, several attempts at fractional crystallization of product II from the same reaction solvent, or different ones, gave only two fractions (IIa and IIb) which had optical activities: IIa $[\alpha]^{20}_{578}$ −23° (*c* 0.28, CH_3OH); IIb, $[\alpha]^{20}_{578}$ +24° (*c* 0.35, CH_3OH).

These experimental data can be explained on the basis of results previously reported[1,3,4] on the stereochemistry of the addition reactions of several nucleophilic agents (alkoxides, acetate ion, amines, and carbanions) to coordinated double bonds in Pt(II) and Pd(II) complexes. In all these cases the stereospecific mechanism of the addition reaction pathway was proved. Therefore, in our case, the configurations of the double bond coordinated to the metal and the one of the carbon atom bonded to the platinum remain unchanged[11] (Figure 2). The electronic and CD spectra of IIa and IIb, recorded in the 400–200-mμ range, are shown in Figure 3. By analysis of the CD spectra, IIa and IIb appear to be enantiomeric as far as the asymmetric atoms bound to platinum atom are concerned, the contribution of (*S*)-α-methylbenzylamine being almost negligible. Indeed the amine has no typical absorption bands in the spectral range explored and, as it is not coordinated to the metal, does not affect the electronic transitions responsible for the recorded absorption bands. CD spectra of IIa and IIb are characterized by four bands centered approximately at 380, 330, 295, and 240 mμ, respectively, which are visible as shoulders in the electronic spectra.

(11) Preliminary data on the X-ray structures of IIa and IIb are in agreement with the conclusions achieved on the basis of our experimental results: C. Pedone and E. Benedetti, private communication.

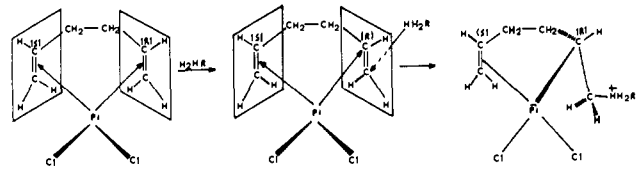


Figure 2. Stereospecific addition mechanism of (*S*)-α-methylbenzylamine to complex I.

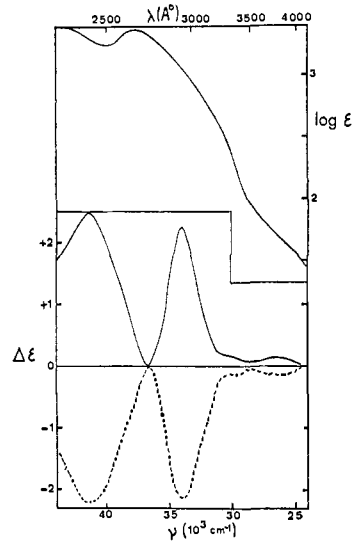


Figure 3. Electronic and CD spectra of IIa (—) and IIb (---) (*c* 0.1, methanol).

The magnitude of the dichroism enables us to attribute the 380- and 330-mμ bands to d–d transitions, activated by the presence of the olefinic ligand coordinated in an enantiomeric way. Consequently, the sign of these bands should be correlated to the chirality of the ligand. The 295- and 240-mμ bands are, by their intensity, typical charge-transfer bands and could be attributed to d–π* transitions, too sensitive to the chirality of the coordinated ligand.[12]

A negligible amount of steroselectivity was observed if the addition reaction between complex I and (*S*)-α-methylbenzylamine was performed in such a way as to obtain product II in the solid state, as soon as possible. Indeed CD spectra of several samples of II, obtained from different solvents and at different temperatures in a period of time <15 min, do not show absorption bands of meaningful intensity in the 400–220-mμ region.

Resolution of Complex II *via* Asymmetric Synthesis. If the interaction between complex I and (*S*)-α-methylbenzylamine is performed in such a volume of solvent as to prevent the precipitation of product II, it is possible to note that the optical activity of the solution increases. After some time, it was found, surprisingly, that the diastereoisomer IIb was prevailingly present in solution. The same result was obtained, after a comparable period of time, dissolving the other diastereoisomer IIa in methylene chloride solution. The CD spectrum of the complex IIb, obtained in such a way, was quite like that reported above. This absolute resolution *via* a first-order asymmetric trans-

(12) Attempts to relate the sign of the absorption bands in the CD spectra with the absolute configuration of IIa and IIb, as well as for analogous complexes, are actually in progress.

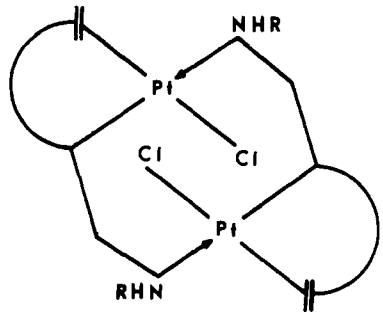


Figure 4. A proposed schematic structure for the binuclear species IIIa and IIIb.

formation can be called *antiracemization*,[13] according to the term proposed by Bosnich.

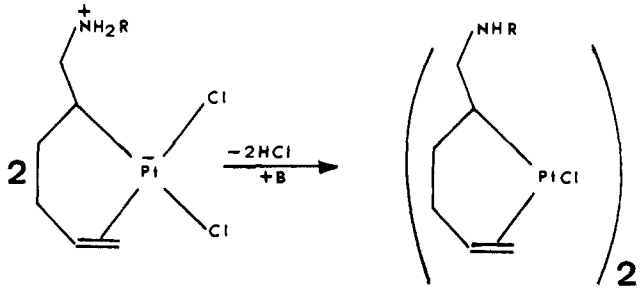
The mechanism of this transformation can be explained in terms of the existence of the equilibrium

$$\text{IIa} \rightleftharpoons \text{I} + \text{Am} \rightleftharpoons \text{IIb}$$

which leads to the formation of IIb that must be thermodynamically more stable in solution. Evidence of the existence of these equilibria is centered on the isotopic exchange reaction with (*S*)-α-methylbenzylamine labeled with ^{14}C. Indeed, it was found that isotopic exchange between product II and the ^{14}C-labeled amine hydrochloride in methylene chloride solution was complete in a period of time comparable to that of the antiracemization.

It is very likely that the reasons for the different thermodynamic stabilities in solution of IIb and IIa are related to the effective presence of different nonbonded interactions. It will be of interest to observe possible interactions between the ammonium group and the metal atom.

Stereoselective Synthesis of Binuclear Products IIIa and IIIb. The diastereoisomeric compounds IIa and IIb, in the presence of bases, lose hydrochloric acid, giving rise to complexes IIIa and IIIb, according eq 3.



IIa or IIb IIIa or IIIb (3)

By treating IIIa and IIIb with methanolic hydrochloric acid, it is possible to restore IIa and IIb, respectively. This means that in this reaction the chiral centers are not involved. Chemical and spectroscopic investigation reported in a previous paper[2] led us to attribute the schematic structure shown in Figure 4 to the binuclear species IIIa and IIIb.

By treating the crude product II with bases, a solid yellow compound (III) is obtained, identical, with respect to analysis, molecular weight, and ir and uv spectra, with compounds IIIa and IIIb described above.

(13) B. Bosnich, *J. Amer. Chem. Soc.*, **89**, 6143 (1967).

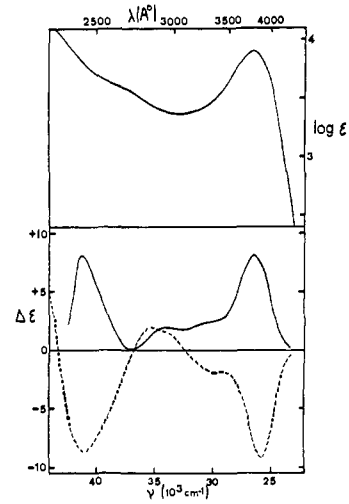


Figure 5. Electronic and CD spectra of IIIa (—) and IIIb (---) (*c* 0.1, methanol).

On fractional crystallization of product III from a chloroform–ether mixture, only two fractions are recovered in practice. Their optical properties are coincident with those of complexes IIIa and IIIb. The total absence of species formed by condensing a IIa monomeric unit with a IIb one unequivocally shows the high degree of stereoselectivity in the formation of binuclear products. Electronic and CD spectra of IIIa and IIIb are shown in Figure 5. The CD spectra of IIIa and IIIb are almost mirror images of one another, apart from the sign of the dichroism in the 300–280-mμ region which is affected by the presence of a Pt-coordinated (*S*)-α-methylbenzylamine group which transforms into diastereoisomers what otherwise would be enantiomers. Owing to their magnitude, the absorption bands at 380 and 330 mμ cannot be assigned to pure d–d transitions. Probably they can be due to d–π* transitions which also reflect the chirality of the organic ligand coordinated to the platinum atom. Particularly, in the case of the maximum at 380 mμ (ε 9000; Δε ±9), the shift of a d–π* transition toward lower energy may be explained by observing the molecular model proposed for complex III. This model shows that the coordination planes of the two platinum atoms are not coplanar. Therefore, it might be possible that the two d_{z^2} orbitals overlap and form the bonding and antibonding combinations $(\varphi_1 + \varphi_2)/\sqrt{2}$ and $(\varphi_1 - \varphi_2)/\sqrt{2}$. The difference in energy between the latter and the isolated d_{z^2} orbital might account for the shift to lower energy of the corresponding transition to olefin π* orbital. Extensive studies on this matter are in progress.

Experimental Section

Infrared and electronic spectra were determined on a Beckman IR-9 spectrophotometer and a Beckman DK 2 spectrophotometer, respectively. The circular dichroism spectra were recorded on a Jouan-Roussel CD 185 dichrograph. Molecular weights were determined in chloroform solution with a Hitachi Perkin-Elmer Model 115 apparatus. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter using 1.00-dm cells. Some of the elemental analyses were performed in this laboratory and others by Mikroanalytisches Laboratorium of the Max Planck Institut fur Kohlenforschung, Mülheim, West Germany.

Materials. The solvents were purified by usual procedures. The other chemical used were of analar grade. (*S*)-α-Methyl-

benzylamine had $[\alpha]^{20}_{589}$ −40.2° (neat). Dichloro(1,5-hexadiene)-platinum(II) was prepared by the Jensen procedure.[14]

Reaction of Dichloro(1,5-hexadiene)platinum(II) with (*S*)-α-Methylbenzylamine. Preparation of Complex II. To a stirred solution of 5.6 g (0.016 mol) of complex I in 40 ml of methylene chloride a solution of 1.94 g (0.016 mol) of (*S*)-α-methylbenzylamine in 10 ml of the same solvent was added dropwise. After 15 min, the solvent was removed *in vacuo* and the residue was washed with ether and dried. This white crude product (II, 7.5 g) had $[\alpha]^{20}_{589}$ −21.5° (*c* 0.4, CH_3OH).

The CD spectrum of II, recorded in the 400–220-mμ region, does not show bands of meaningful intensity.

Anal. Calcd for $C_{14}H_{21}NCl_2Pt$: Pt, 41.6; C, 35.8; H, 4.5; N, 2.95. Found: Pt, 41.8; C, 35.7; H, 4.4; N, 2.9.

Resolution of II. Fractional crystallization of the crude product obtained following the procedure reported above was troublesome because of the insolubility of the product in the most of organic solvents. It was sparingly soluble only in methanol and methylene chloride (~4 g/l. at room temperature). Consequently, the following procedure has been employed. To a cold stirred solution of 6.73 g (0.019 mol) of complex I in 60 ml of methylene chloride, a solution of 2.37 g (0.019 mol) of (*S*)-α-methylbenzylamine in 10 ml of the same solvent was added dropwise over a 15–20-min period. During the addition, the temperature of the reaction mixture was maintained between −15 and −20°. The reaction mixture was then allowed to warm to room temperature and stirred for 1 additional hr. Filtration of the precipitate formed provided 4.84 g (IIa, yield 53%) of a white crystalline product which had $[\alpha]^{20}_{578}$ −23° (*c* 0.28, CH_3OH). Further recrystallizations from methanol did not change the optical rotation. After the mother liquor was allowed to stand at 0° for 24 hr, two further fractions were recovered. Recrystallization from methanol afforded 3.12 of a white crystalline product (IIb, 33.5% yield) which had $[\alpha]^{20}_{578}$ +24° (*c* 0.35, CH_3OH).

The analysis of IIa and IIb showed the same elemental composition of II. CD spectra of both diastereoisomers were performed in methanol solution (Figure 3). The magnitude of the main absorption bands led us to assign the same optical purity to IIa and IIb.

Destructive reduction with $NaBH_4$ in THF of the complexes IIa and IIb, as well as of the crude mixture II, gave the same substituted amine *N*-*n*-hexyl-(*S*)-α-methylbenzylamine. Identification of the amine was achieved by comparison with an authentic sample.[2]

Asymmetric Synthesis of IIb. To a solution of 1.0 g (0.0028 mol) of complex I in 250 ml of methylene chloride, 0.34 g (0.0028 mol) of (*S*)-α-methylbenzylamine was added at room temperature. No precipitation occurred. This solution was allowed to stand at room temperature until the optical rotation did not change within 1% (about 4 days). By evaporating the solvent, a white product was obtained which had $[\alpha]^{20}_{578}$ +23° (*c* 0.31, CH_3OH). Its CD spectrum was identical with that of IIb (Figure 3).

Antiracemization of IIa into IIb. A 0.5-g sample of IIa, $[\alpha]^{20}_{578}$ −23° (*c* 0.28, CH_3OH), was dissolved in 200 ml of methylene chloride. Following the same procedure described above, the product recovered had $[\alpha]^{20}_{578}$ +24° (*c* 0.25, CH_3OH). Its CD spectrum was identical with that of IIb (Figure 3).

Isotopic Exchange Reaction of IIa with ^{14}C-Labeled (*S*)-α-Methylbenzylamine. To a solution of 0.235 g (0.0005 mol) of IIa in 100 ml of methylene chloride, 0.0785 g (0.0005 mol) of ^{14}C-labeled (*S*)-α-methylbenzylamine hydrochloride[15] was added. The solution was allowed to stand at room temperature for 4 days. The solvent was removed *in vacuo* and the residue was washed several times with cold methanol to remove the amine hydrochloride. A determination of radioactivity on this residue using a GM thin-window counter showed that the isotopic exchange was complete.

Preparation of IIIa from IIa and of IIIb from IIb. IIa (1.41 g, 0.003 mol), $[\alpha]^{20}_{578}$ −23° (*c* 0.28, CH_3OH), was suspended in 50 ml of acetone. Anhydrous sodium carbonate (0.3 g) was added and the suspension was stirred at room temperature for 7 hr. The resulting clear green-yellow solution was filtered to remove sodium chloride and excess sodium carbonate. After the solvent was evaporated *in vacuo*, a green-yellow solid product was obtained (IIIa, 1.2 g, 92% yield). Attempts at recrystallization from various solvents did not give good crystalline products. The crude product had $[\alpha]^{20}_{578}$ +120° (*c* 0.47, CH_3OH).

Anal. Calcd for $C_{25}H_{40}N_2Cl_2Pt_2$: Pt, 45.1; Cl, 8.2; N, 3.25; mol wt, 865.6. Found: Pt, 44.8; Cl, 8.4; N, 3.1; mol wt, 897.

A similar procedure was employed to obtain IIIb from IIb in 95% yield. The crude product had $[\alpha]^{20}_{578}$ −98° (*c* 0.5, CH_3OH). Recrystallization from methanol did not significantly improve the optical rotation.

Anal. Calcd for $C_{28}H_{40}N_2Cl_2Pt_2$: Pt, 45.1; Cl, 8.2; N, 3.25; mol wt, 865.6. Found: Pt, 45.0; Cl, 8.3; N, 3.2; mol wt, 858.

CD and electronic spectra of IIIa and IIIb are shown in Figure 5.

By dissolving IIIa and IIIb in methanolic HCl, IIa and IIb were obtained about after 3 hr. The identification was obtained by optical rotation and CD spectra.

Preparation and Resolution of Diastereoisomeric Mixture III. Diastereoisomeric mixture II (5.63 g, 0.012 mol), $[\alpha]^{20}_{578}$ −21.5° (*c* 0.4, CH_3OH), and 0.9 g of anhydrous sodium carbonate in 150 ml of acetone were allowed to stand 7 hr at room temperature under stirring. Working the resulting solution as described above, a green-yellow solid product was obtained (III, 5 g, 96% yield), which had $[\alpha]^{20}_{578}$ +28° (*c* 0.68, CH_3OH).

III (4.1 g) was fractionally recrystallized from 30 ml of a chloroform–ether mixture (2:1 ratio). After allowing the solution to stand for 36 hr at −10°, three fractions were recovered. The first fraction (A, 1.63 g) had $[\alpha]^{15}_{578}$ −80° (*c* 0.45, CH_2Cl_2); the second (B, 0.31 g) had $[\alpha]^{15}_{578}$ +41° (*c* 0.72, CH_2Cl_2). The third fraction resulted from removing the solvent from the mother liquor (C, 2.11 g) and had $[\alpha]^{15}_{578}$ +127° (*c* 0.53, CH_2Cl_2). Several recrystallizations of fraction A from the same solvent mixture (until no significant change of the optical rotation occurred) gave 1.4 g of a yellow crystalline product (A′) having $[\alpha]^{20}_{578}$ −112° (*c* 0.58, CH_3OH).

Fractions B and C were recrystallized from a chloroform–ether mixture (1:1 ratio). After the solution was allowed to stand for 24 hr at −10°, 0.23 g of a yellow crystalline solid identical with A′ was obtained, which had $[\alpha]^{20}_{578}$ −106° (*c* 0.55, CH_3OH). By evaporating the mother liquor a solid was obtained which was triturated with ether and dried (C′, 1.9 g), $[\alpha]^{20}_{578}$ +136° (*c* 0.45, CH_3OH).

Several attempts at recrystallization of C′ from other solvents were unsuccessful because only amorphous solids resulted.

Analysis, molecular weight, and ir, electronic, and CD spectra of A′ and C′ were identical with those of IIIb and IIIa, respectively.

Acknowledgments. The authors are indebted to Dr. P. Salvadori (University of Pisa) for recording the CD spectra. G. P. gratefully acknowledges the Italian National Council of Research (C. N. R.) for financial support.

(14) K. A. Jensen, *Acta Chem. Scand.*, 7, 866 (1953).

(15) $C_6H_5{}^{14}CH(CH_3)NH_2$ was prepared from acetophenone-1-^{14}C [A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes," Part I, Interscience, New York, N. Y., 1958, p 662] according to the Ingersoll's modification of Leuckart's method: A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1946, p 503. The racemic amine was resolved by the known method: A. Ault, *J. Chem. Educ.*, 42, 269 (1965).