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(45) For TMPD dimers, the most important steric interactions would involve the methyl-group hydrogens (CH_3–N(1)) and the edge carbons (C(3′),C(5′)) on the adjacent cation radical. The molecular models show that these interactions should be minimized, since they would require the involvement of intramolecular high-energy eclipsed hydrogen configurations between the methyl-group hydrogens (CH_3–N(1)) and the H atoms on the neighboring carbons C(2) and C(6). However, it should also be pointed out that an indirect type of steric effect, via changes in van der Waals distances, could result from rehybridization at the nitrogen atoms or ring carbons as a function of substitution. As previously discussed, the loss of methyl substituents in these systems leads to spin-density distributions, indicating increased contributions from quinoidal resonance forms II and III. These structures can be expected to have shorter van der Waals distances than the benzenoid forms I, but it is difficult to estimate how important this electronically induced steric effect is in these systems.
(46) Both bromides are orthorhombic with *Cmcm* space group. Unit-cell dimensions (cf. ref 9,10) are, $\text{TMPD}\cdot^{+}\text{Br}^{-}$: $a = 9.54$, $b = 19.27$, $c = 7.03$ Å. $\text{DMPD}\cdot^{+}\text{Br}^{-}$: $a = 6.38$, $b = 22.48$, $c = 6.21$ Å.
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Absolute Configuration of an Ansa Compound: Gentisic Acid Nonamethylene Ether[1]

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Abstract: The absolute configuration of gentisic acid nonamethylene ether is determined by a chemical correlation method. The levorotatory isomer is concluded to have the *S* configuration.

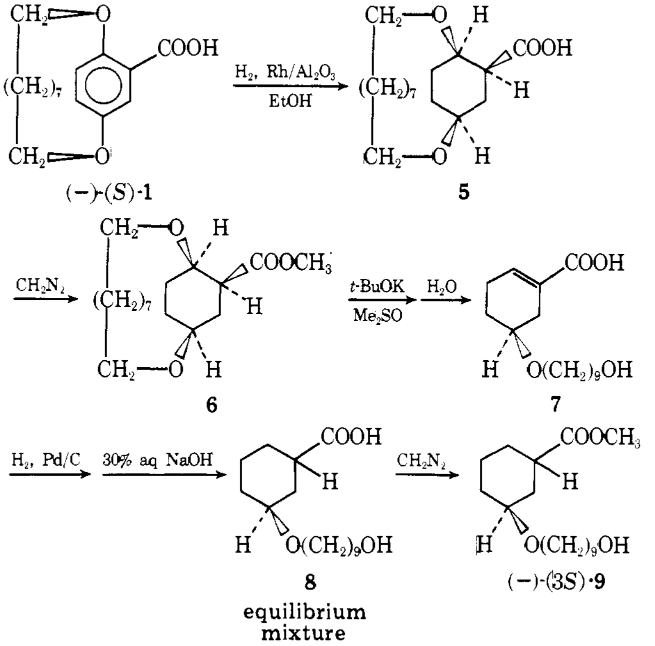
The determination of the absolute configuration of a variety of cyclophanes have been reported in recent years.[2] Three general methods have been used: (1) the interpretation of the stereochemical course of an asymmetric synthesis. This has included the treatment of a racemic cyclophane anhydride with a limited quantity of (−)-α-phenylethylamine and the reaction of an optically active alcohol, derived from an optically active cyclophane, with an excess of racemic α-phenylbutyric anhydride. (2) A comparison of NMR chemical shifts of diastereomeric cyclophanes. (3) A correlation of the sign of the ^1L_b Cotton effect of the benzene chromophore with the absolute configuration.

We report herein our results on the determination of the absolute configuration of gentisic acid nonamethylene ether (**1**). This substance belongs to the family of optically active gentisic acid derivatives studied by Lüttringhaus et al. in their classic investigation of atropisomerism in ansa compounds.[3] To our knowledge this is the first elucidation of the absolute configuration of a cyclophane by a chemical correlation method which relates the cyclophane directly to a compound of known absolute configuration containing an asymmetric carbon atom. Such an approach seems inherently less prone to error than those previously used for cyclophanes, which required interpretation of physical data or the structural factors that influence an asymmetric synthesis.[4]

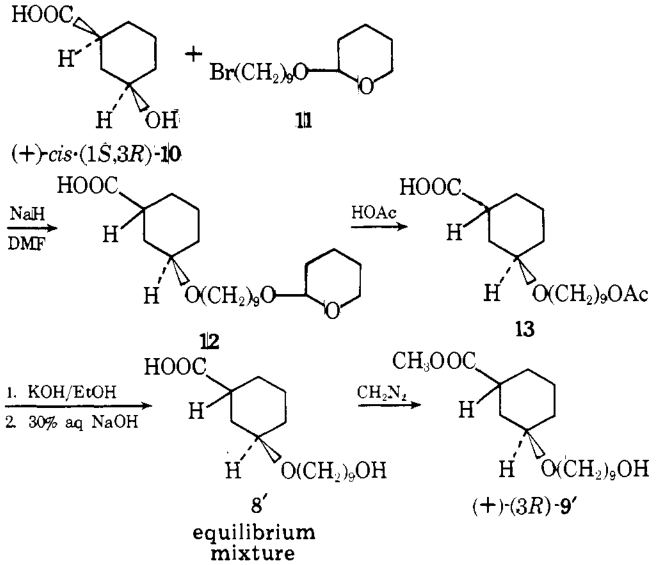
Results and Discussion

We have determined the absolute configuration of **1** by relating it to *cis*-3-hydroxycyclohexanecarboxylic acid (**10**), whose absolute configuration has been established by Noyce and Denney.[8] Our correlation route is outlined in Schemes I and II. Scheme I shows the conversion of (−)-(*S*)-**1** to the relay compound, **9**, of 3*S* configuration. Scheme II shows the conversion of (+)-*cis*-(1*S*,3*R*)-**10** to the same relay compound, **9′**, of 3*R* configuration. In order to avoid unnecessary loss of material, an intermediate was purified only to the extent required for a subsequent step in the correlation scheme. The NMR and ir spectra of each of the intermediates agreed with the proposed structure.

Scheme I



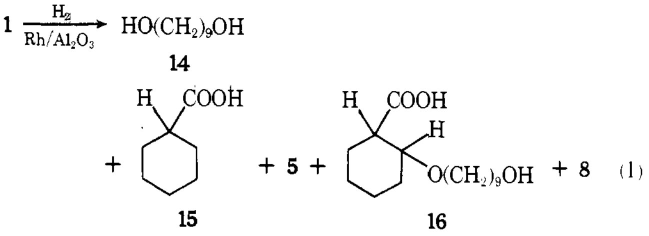
Scheme II



The key step in the correlation scheme is the conversion of atropisomeric **1** to **5**, a compound containing three asymmetric carbon atoms. In order to relate the configurations of **1** and **5**, it is necessary to know the direction of addition of hydrogen to the aromatic ring. We have pictured this step as occurring in a cis manner to the least-hindered side of the aromatic ring, i.e., from the side opposite the nonamethylene chain.

Under relatively mild conditions, the products of the heterogeneous catalytic hydrogenation of carbon-carbon double bonds and aromatic rings arise mainly by way of cis addition of hydrogen.[9] Arenes generally yield a predominance of the all-cis product. These products do not necessarily arise during a single residency on the catalyst.[10] The intermediate cycloalkenes appear to be able to desorb and readsorb before final hydrogenation. Various workers have argued that the favored hydrogenation pathway involves the addition of hydrogen from the catalyst surface to the least-hindered side of the double bond or aromatic ring.[11] The unsaturated substrate is pictured as coordinating with the catalyst surface in such a way as to minimize steric effects between substituents and the surface atoms. On the basis of the available evidence, the conversion of **1** to **5**, as pictured in Scheme I, seems thoroughly reasonable.

The hydrogenation of **1** was best carried out in 95% ethanol at 3 atm pressure using a 5% Rh on alumina catalyst. A mixture of materials was obtained which included **5** and a number of hydrogenolysis products (eq 1). Use of other conditions, such



as a Pt catalyst or lower H_2 pressures, resulted in an increase in the proportion of hydrogenolysis products. The crude mixture of products was separated into neutral and acidic fractions. The neutral fraction was identified as 1,9-nonanediol (**14**) by comparison with an authentic sample. The acidic portion was chromatographed on silica gel to yield four fractions. Fraction 1 was identified as cyclohexanecarboxylic acid (**15**) by conversion to the methyl ester and comparison with an authentic sample of methyl cyclohexanecarboxylate. The formation of **15** is consistent with the isolation of **14**. Fraction 2 was identified as **5** by conversion to **9** as outlined in Scheme I and discussed in the next paragraph. Fraction 3 was assigned structure **16** on the basis of conversion to the methyl ester, treatment with $NaOCH_3$ in CH_3OH at 70–75 °C for 21 h, hydrolysis, and catalytic hydrogenation to yield **14** and **15**. Fraction 4 was identified as 3-(9-hydroxynonamethyleneoxy)cyclohexanecarboxylic acid (**8**) by equilibration with 30% aqueous NaOH and conversion to the methyl ester. The resulting product was identical with **9′**, synthesized from **10** (Scheme II).

The dealcoholation of **5** to **7** (Scheme I) did not proceed directly, in good yield. This conversion was achieved in two steps by formation of the methyl ester and treatment with *t*-BuOK in Me_2SO, followed by the addition of water. The formation of **7** was indicated by its NMR spectrum which showed vinyl-H absorption at δ 7.12 and an exchangeable singlet corresponding to two hydrogens, and its ir spectrum which exhibited α,β-unsaturated acid and olefin absorptions at 1690 and 1650 cm^{-1}, respectively. Hydrogenation of **7** yielded a saturated acid which probably consisted of a mixture of cis and trans isomers. Equilibration[12] by prolonged heating with 30% aqueous NaOH yielded **8**, which on treatment with CH_2N_2 formed **9**, identical with **9′**, synthesized from **10**. Thus, the conversions outlined in Scheme I were accomplished.

The conversions outlined in Scheme II require no special comments. Details are presented in the Experimental Section.

Levorotatory **1** ($[\alpha]^{25}{}_D$ −4.5°; *c* 3.56, $CHCl_3$)[13] was converted to levorotatory **8** ($[\alpha]^{25}{}_D$ −1.9 ± 0.2°; *c* 1.7, $CHCl_3$) and thence to levorotatory **9** ($[\alpha]^{25}{}_D$ −1.8 ± 0.2°; *c* 0.74, $CHCl_3$) using the route shown in Scheme I. Dextrorotatory **10** ($[\alpha]^{23.6}{}_D$ +9.8°; *c* 4.0, CH_3OH)[14] of 1*S*,3*R* configuration[8] was converted to dextrorotatory **8′** ($[\alpha]^{25}{}_D$ +11.2 ± 0.2°; *c* 3.2, $CHCl_3$) and thence to dextrorotatory **9′** ($[\alpha]^{25}{}_D$ +9,4 ± 0.2°; *c* 1.84, $CHCl_3$) through the route shown in Scheme II. The equilibrations and isolations of **8** and **8′** were carried out under exactly the same conditions. In addition, these materials exhibited virtually identical ir and NMR spectra. On this basis we conclude that both were composed of the same ratio of cis and trans diastereomers. The conversions of **8** to **9** and **8′** to **9′** and the isolations of **9** and **9′** were also carried out under exactly the same conditions.[15] Both **9** and **9′** had virtually identical ir and NMR spectra. We conclude that both **9** and **9′** had identical diastereomeric compositions. The rotations of **8**/**8′** and **9**/**9′** were the same within experimental error. This indicates that the conversions **8** → **9** and **8′** → **9′** proceeded without changes in diastereomeric compositions.[15] Since (−)-**1** led to **9** of opposite rotation to **9′**, we conclude that (−)-**1** has the S configuration.[16] This assignment is in agreement with that previously suggested for gentisic acid polymethylene ethers on the basis of CD measurements.[2]

Experimental Section

NMR (60 MHz, Me_4Si internal standard) and mass spectra (70 eV) were recorded on Varian A-60 and CH-5 spectrometers, respectively. Ir spectra were recorded on Perkin-Elmer 137 and 247 spectrometers. Optical rotations were taken on a Perkin-Elmer 141 polarimeter. Melting points were determined in open capillary tubes and are corrected. Boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(+)-3-(9-(2-Tetrahydropyranyloxy)nonamethyleneoxy)cyclohexanecarboxylic Acid (12). A solution of 20 g of **11**[17] in 20 ml of DMF was added over a period of 25 min to a mixture of 2.0 g of (+)-*cis*-(1*S*,3*R*)-**10**,[8,14,18] $[\alpha]^{23.6}{}_D$ + 9.8° (*c* 4.0, CH_3OH) [lit.[14] $[\alpha]^{23.6}{}_D$ +9.82° (c 4, CH_3OH)], 25 ml of DMF, and 3.5 g of 57% NaH-oil suspension under a nitrogen atmosphere. The reaction mixture was heated at 75–80 °C for 2½ h, cooled, and decomposed by the addition of ice, followed by water. Nonacidic materials were removed by extraction with ether. The aqueous layer was acidified to pH 1 and extracted with ether. The ether layer was dried, and the solvent was evaporated to yield 1.6 g of a viscous oil (**12**): $[\alpha]^{25}{}_D$ +13.4° (*c* 3.1, $CHCl_3$); NMR ($CDCl_3$) δ 0.9–2.6 (complex, CH, CH_2), 2.9–4.2 (complex, OCH, OCH_2), 4.57 (broad s, OCHO), 9.57 (broad s, COOH).

(+)-3-(9-Acetoxynonamethyleneoxy)cyclohexanecarboxylic Acid (13). A solution of 1.5 g of (+)-**12**, above, in 60 ml of HOAc was heated at reflux for 26 h. Ether was added, and the resulting solution was thoroughly extracted with water. The ether layer was dried, and the solvent was evaporated to yield 1.2 g of an oil (**13**): $[\alpha]^{25}{}_D$ +12.5° (*c* 3.99, $CHCl_3$); NMR ($CDCl_3$) δ 0.9–2.8 (complex, sharp singlet at 2.0, CH, CH_2, CH_3), 2.8–3.8 (complex, OCH, OCH_2), 4.03 (t, *J* = 6 Hz, $COOCH_2$), 10.4 (broad s, COOH).

(+)-3-(9-Hydroxynonamethyleneoxy)cyclohexanecarboxylic Acid (8′). A solution of 1.2 g of **13**, above, in 50 ml of 1.25 M ethanolic KOH was heated at reflux for 3 h. Water (50 ml) was added, and nonacidic impurities were removed by extraction with ether. The aqueous layer was acidified to pH 1 and extracted with ether. The combined ether layers were dried and evaporated to yield an oil, which was chromatographed on silica gel. Elution with 30% ether–benzene gave 0.48 g (center cut) of an oil (unequilibrated **8′**): $[\alpha]^{25}{}_D$ +10.8° (*c* 4.70, $CHCl_3$); NMR ($CDCl_3$) δ 0.9–2.9 (complex, CH, CH_2), 2.9–3.8 (complex, OCH, OCH_2), 7.70 (broad s, COOH and OH, exchangeable with D_2O).

Equilibration was accomplished by heating with 50 ml of 30% aqueous NaOH at reflux for 72 h. The cooled reaction mixture was diluted with water, acidified to pH 1, and extracted with ether. Evaporation of the dried ether layer yielded 0.32 g of a viscous oil (equilibrated **8′**): $[\alpha]^{25}{}_D$ +11.2 ± 0.2° (*c* 3.2, $CHCl_3$); NMR ($CDCl_3$) virtually identical with unequilibrated **8′**.

(+)-Methyl 3-(9-Hydroxynonamethyleneoxy)cyclohexane carboxylate (9′). A solution of 0.32 g of equilibrated **8′**, above, in ether was treated with an excess of CH_2N_2 in ether at 0 °C and allowed to remain at room temperature overnight. The reaction mixture was dried and evaporated, and the residual oil was distilled, using a short-path apparatus,[15] at 0.1 mm and a heating bath temperature of 180–210 °C to yield 0.18 g of **9′** (some loss of material occurred on the walls of the distillation assembly): $[\alpha]^{25}{}_D$ +9.4 ± 0.2° (*c* 1.84, $CHCl_3$); NMR ($CDCl_3$) δ 0.8–2.9 (complex, CH, CH_2, OH (at 2.01, exchangeable with D_2O)), 2.9–3.9 (complex with a sharp singlet at 3.65, OCH, OCH_2, OCH_3); ir (liquid film) 3375 (OH), 1730 (ester) cm^{-1}; mass spectrum *m/e* 300, 282, 269, 241.

Anal. Calcd for $C_{17}H_{32}O_4$: C, 67.96; H, 10.74. Found: C, 67.81; H, 10.49.

Hydrogenation of Racemic Gentisic Acid Nonamethylene Ether (1). Identification of the Products. A mixture of 1.42 g of **1**,[3c] 235 ml of acetic acid, and 1.49 g of 5% Rh on Al_2O_3 was hydrogenated in a Parr low-pressure apparatus for 16 h. The catalyst was filtered off, and the filtrate was evaporated. The residue was heated at reflux overnight with 10% ethanolic KOH, cooled, and extracted with ether. Evaporation of the dried ether layer yielded a white solid, mp 46–47 °C, which was identified as 1,9-nonanediol (**14**) by comparison with an authentic sample. The aqueous layer was acidified to pH 1 and extracted with ether. Evaporation of the dried ether solution yielded an oil (1.32 g) which was chromatographed on 300 g of silica gel, using 10% ether–benzene as the eluent. Four major fractions were obtained.

Fraction 1 was identified as cyclohexanecarboxylic acid (**15**) by conversion to the methyl ester and comparison with an authentic sample of methyl cyclohexanecarboxylate.

Fraction 2 (0.61 g, 43%) was recrystallized from CCl_4: mp 138–139 °C; NMR ($CDCl_3$) δ 1.0–2.6 (complex, CH, CH_2), 3.2–4.2 (complex, OCH, OCH_2), 9.41 (broad s, COOH).

Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.93. Found: C, 67.71; H, 9.93.

Fraction 2 was identified as 2,5-(1,9-nonamethylenedioxy)cyclohexanecarboxylic acid (**5**) by conversion to **9**, which compared exactly with **9′** synthesized by the route outlined in Scheme II. The conversion of **5** to **9** was achieved by the path outlined in Scheme I, which is described below for (−)-**5** obtained from (−)-**1**.

Fraction 3 (0.22 g, 15%) appears to have consisted mainly of 2-(9-hydroxynonamethyleneoxy)cyclohexanecarboxylic acid (**16**) on the basis of the following evidence. Its NMR and ir spectra resembled that of **8′**. Fraction 3 was converted to the methyl ester with CH_2N_2, which was heated at 70–75 °C for 21 h with methanolic $NaOCH_3$, followed by hydrolysis with aqueous KOH. The crude reaction product was separated into acidic and neutral fractions. The neutral fraction was identified as 1,9-nonanediol (**14**). Chromatography of the acidic fraction on silica gel yielded cyclohexenecarboxylic acid which was positively identified by catalytic hydrogenation to **15**.

Fraction 4 (0.38 g, 27%) was identified as 3-(9-hydroxynonamethyleneoxy)cyclohexanecarboxylic acid (**8**) by equilibration with 30% aqueous NaOH and conversion to the methyl ester, as described above for the conversion of **8′** to **9′**. The resulting product had ir and NMR spectra virtually identical with **9′**.

Hydrogenation of (−)-1. A mixture of 2.75 g of (−)-**1** ($[\alpha]^{25}{}_D$ −4.5°; *c* 3.56, $CHCl_3$ (lit.[3c] $[\alpha]^{20}{}_D$ −16.73°; *c* 4.06, $CHCl_3$)), 2.8 g of 5% Rh on Al_2O_3, and 120 ml of 95% ethanol was hydrogenated as above for racemic **1**. TLC (silica gel, 20% dioxane–benzene with 1% acetic acid) showed the crude acidic portion of the product to be composed of the same reaction products as obtained from racemic 1. Chromatography on silica gel yielded 0.89 g of (−)-**5**: $[\alpha]^{25}{}_D$ −4.5° (*c* 2.81, $CHCl_3$).

(−)-Methyl 2,5-(1,9-Nonamethylenedioxy)cyclohexanecarboxylate (6). (−)-**5** (0.89 g), above, was treated with an excess of CH_2N_2 in ether at 0 °C. The solution was allowed to remain at room temperature overnight, dried, and evaporated to yield (−)-**6** (0.94 g) as a clear colorless oil: $[\alpha]^{25}\mathrm{D}$ −4.9° (c 3.38, $CHCl_3$); NMR ($CDCl_3$) δ 1.0–2.8 (complex, CH, CH_2), 3.1–4.3 (complex, with a sharp singlet at 3.70, OCH, OCH_2, OCH_3); ir (liquid film) 1740 (ester) cm^{-1}.

(−)-5-(9-Hydroxynonamethyleneoxy)-1-cyclohexenecarboxylic Acid (7). A mixture of 0.94 g of (−)-**6**, above, 0.98 g of *t*-BuOK, and 40 ml of dry Me_2SO was stirred under a nitrogen atmosphere for 46 h at room temperature. Ice was added to the cooled reaction mixture, which was then thoroughly extracted with ether. The remaining aqueous solution was acidified to pH 1 and extracted with ether. This ether solution was extracted with H_2O, dried, and evaporated to give 0.76 g of (−)-**7** as a tan oil: $[\alpha]^{25}\mathrm{D}$ −5.3° (c 1.76, $CHCl_3$); NMR ($CDCl_3$) δ 0.9–2.8 (complex, CH_2), 3.2–3.9 (complex, OCH, OCH_2), 7.12 (broad s, vinyl H), 7.30 (broad s, COOH and OH, exchangeable with D_2O); ir (liquid film) 1690 (C=O, α,β-unsaturated acid), 1650 (C=C) cm^{-1}.

(−)-8. A mixture of 0.76 g of (−)-**7**, above, 0.37 g of 5% Rh on C, and 150 ml of 95% ethanol was hydrogenated in a Parr low-pressure apparatus for 2 h. After filtration of the catalyst and evaporation of the solvent, the crude product was chromatographed on silica gel, using 40% ether–benzene as the eluent to yield 0.56 g of an oil (unequilibrated **8**).

Equilibration was accomplished as for **8′** to yield **8**: $[\alpha]^{25}\mathrm{D}$ −1.9 ± 0.2° (c 1.7, $CHCl_3$). Its ir and NMR spectra were virtually identical with those of **8′**.

(−)-9. (−)-**8**, above, was converted to (−)-**9** using exactly the same procedure as for **8′** to **9′**. The product had $[\alpha]^{25}\mathrm{D}$ −1.8 ± 0.2° (c 0.74, $CHCl_3$). Its NMR and ir spectra were virtually identical with those of **9′**.

Acknowledgment. The method of determining the absolute configuration of a gentisic acid polymethylene ether embodied in this work was first suggested to L.H.S. in 1957 by Professor Kurt Mislow. We thank Messrs Ching Chen, Jack Landis, and Joseph LaRubbio for their technical assistance.

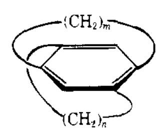
References and Notes

(1) This work was supported in part by the National Science Foundation, the Research Corporation, and the General Faculty Research Committee of the City College.

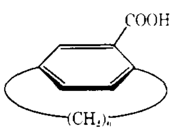
(2) For examples and leading references, see E. Langer, H. Lehner, and K. Schlögl, Tetrahedron, **29**, 2473 (1973).

(3) (a) A. Lüttringhaus and H. Gralheer, *Justus Liebigs Ann. Chem.*, **550**, 67 (1942); (b) *ibid.*, **557**, 108, 112 (1945); (c) A. Lüttringhaus and G. Eyring, *ibid.*, **604**, 111 (1957).

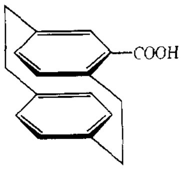
(4) As a case in point, two recent conflicting reports of the absolute configurations of [*m*][n]paracyclophanes (**2**) and substituted [n]paracyclophanes (**3**) can be cited. Langer, Lehner and Schlögl on the basis of CD studies concluded that levorotatory [*m*][n]paracyclophanes and levorotatory [n]paracyclophanes both have the *S* configuration.[2] Prior to this report, the same conclusion had been reached for [10]paracyclophane-12-carboxylic acid (**3b**) through the use of two different asymmetric syntheses.[5] Yamamoto and Nakazaki,[6] by synthesis, related (+)-**2a** and (+)-**3a** directly to (+)-[2.2]paracyclophane-4-carboxylic acid (**4**) whose absolute configuration had previously[7] been established as *S* by an asymmetric synthesis, using the paracyclophane anhydride and (−)-α-phenylethylamine. On this basis, (−)-**2a** and (−)-**3a** would have the *R* configuration, opposite to that proposed by Schlögl et al.[2] The source of the discrepancy between ref 2 and 6 cannot be absolutely established from the published results. The results reported in ref 2 seem to be on a firmer footing since CD and two different asymmetric synthetic methods were involved. The weak link in all the data, which prevents the work presented in ref 2 and 6 from agreeing with each other, appears to be the previously[7] established absolute configuration of **4**, upon which the conclusions of ref 6 are based.



2a, $m = n = 8$



3a, $n = 8$
b, $n = 10$



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(6) K. Yamamoto and M. Nakazaki, *Chem. Lett.*, 1051 (1974).

(7) H. Falk and K. Schlögl, *Angew. Chem., Int. Ed. Engl.*, **7**, 383 (1968).

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(9) For examples, discussions, and additional references, see: (a) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, N.Y., 1967; (b) S. Siegel in "Advances in Catalysis", Vol. 16, Academic Press, New York, N.Y., 1966; (c) R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, N.Y., 1965; (d) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(10) (a) S. Siegel and V. Ku, *Proc. Third Internat. Cong. Catalysis*, Amsterdam, 1964, Contribution I-80, North-Holland Publishing Co., Amsterdam, 1965; H, van Bekkum, *ibid.*, discussion of contribution I-80.

(11) The following references are not intended to be exhaustive. (a) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. P. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942); (b) G. W. Eigenmann and R. T. Arnold, *ibid.*, **81**, 3440 (1959); ref 9d; G. V. Smith, *J. Catal.*, **5**, 152 (1966).

(12) Various reagents and conditions were tested using *cis*- and *trans*-3-methoxycyclohexanecarboxylic acids and the corresponding methyl esters as model compounds. The best results, in terms of the time necessary to reach the equilibrium composition from both isomers and the "cleanness" of the product, were obtained by heating with 30% aqueous NaOH at reflux for 65 h.

(13) The highest rotation that has been reported for this compound is $[\alpha]^{20}\mathrm{D}$ −16.73 (c 4.06, $CHCl_3$).[3c]

(14) D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.*, **74**, 5912 (1952) have reported $[\alpha]^{23.6}\mathrm{D}$ +9.82° (c 4, CH_3OH).

(15) The final distillations of **9** and **9′** were carried out in a short-path small-scale distillation assembly of very low resolving power (Kontes Glass Co., Vineland, N.J., No. K284800), which was chosen in order to minimize losses and lessen the possibility of unequal fractionation of diastereomers.

(16) Nomenclature according to R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew, Chem., Int. Ed. Engl.*, **5**, 385 (1966).

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