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115. The Absolute Configuration of 1-Methylindane

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Summary

It is shown unequivocally by chemical correlations *(cf. Schemes 1–3)* and *Raman* optical activity spectra *(cf. Fig. 1* and *2)* that the (*R*)-configuration has to be attributed to (+)-1-methylindane ((+)-**1**). This is in contradiction to an earlier assignment of the (*R*)-configuration to (−)-**1** [2] which was based on the (*R*)-configuration of (+)-indane-1-carboxylic acid (**3**) [11].

[1]) Part of the planned thesis of *H.-R. Sliwka*.

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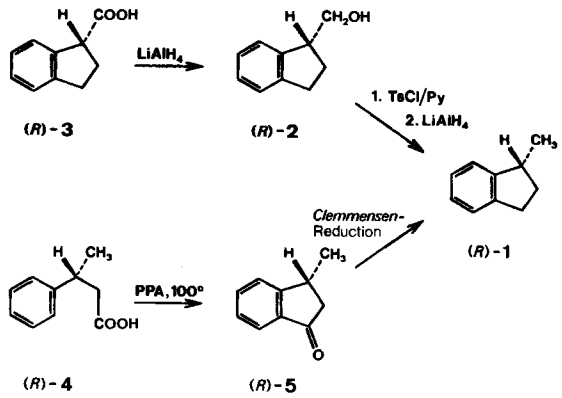
1. Introduction. – 1-Methylindane (**1**) is considered a key compound to the understanding of the optical activity of the electronic transitions of the chirally perturbed benzene chromophore. It is a pure hydrocarbon and conformationally more restricted than analogous open chain molecules. Thus, *Caldwell & Eyring* [1] chose it to discuss the electronic optical activity of the benzene chromophore even before the (*R*)-configuration of (–)-**1** was assigned by a chemical correlation by *Brewster & Buta* [2]. This assignment was recently found to be at variance with their own work by *H. E. Smith et al.* [3]. Even earlier, the route taken by *Allen & Schnepp* [4] to synthetize (+)-1-methylindane ((+)-**1**) had inicated that the (*R*)-configuration of (–)-**1** as given by *Brewster & Buta* [2] might need closer inspection. Yet, the authors of [4] retained the (*S*)-configuration of (+)-**1**, and they found it to be compatible with the results of their calculations.

The measurement of the vibrational *Raman* optical activity of (+)-1-phenylethylamine by one of the authors [5] has focussed attention to the chiral interaction of the methyl and phenyl group. In *Raman* optical activity both groups may be considered vibrational chromophores, and (+)-**1** was chosen as the simplest model compound with a defined relative position of these groups, in order to study their interaction. Obviously, the absolute configuration has to be established unequivocally to derive useful conclusions. In view of this and in connection with other investigations (*cf.* [6]) a detailed chemical study to establish the absolute configuration of (+)-**1** was undertaken.

Scheme 1



2. Absolute Configuration of (+)-1-Methylindane. – 2.1. *Chemical Correlations.* As given in *Scheme 1* optically active 1-methylindane (**1**) can be synthetized without involving the centre of chirality by at least two independent routes. *Brewster & Buta* [2] obtained (–)-**1**[2]) starting with (+)-indane-1-carboxylic acid ((+)-**3**) which was transformed into (–)-**1** *via* the dextrorotatory hydroxymethyl compound **2**. *Allen & Schnepp* [4], and *Smith et al.* [3][3]) chose (–)-3-phenylbutyric acid ((–)-**4**) as starting material, which was cyclized to yield laevorotatory 3-methyl-1-

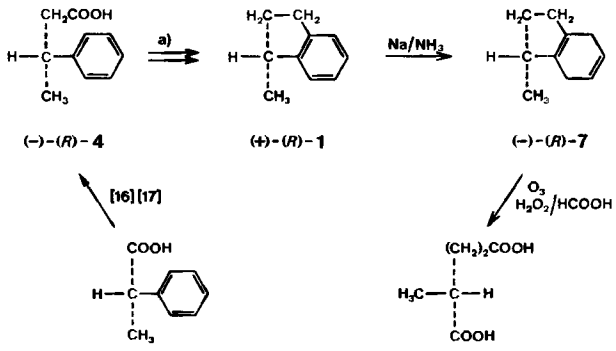
[2]) Unless otherwise stated the sign of rotation refers to the sodium D line.

[3]) We undertook our work, also relying on **4**, before the communication of *Smith et al.* was published.

indanone ((−)-**5**; *cf.* [7–10]). The *Clemmensen* reduction of this compound led to (+)-**1**.

According to *Fredga* [11] (+)-indane-1-carboxylic acid ((+)-**3**) is correlated chemically with (−)-2-phenylsuccinic acid, to which the (*R*)-configuration is attributed [12–15]. *Brewster & Buta* [2] therefore assigned the (*R*)-configuration to (−)-**1** synthetized from (+)-**3** (*cf. Scheme 1*). On the other hand, (−)-3-phenylbutyric acid ((−)-**4**) is connected with (+)-(*S*)-hydratropic acid ((+)-**6**; *Scheme 2*) [16] [17],

Scheme 2



a) See *Scheme 1*.

i.e. (−)-(*R*)-**4** should also lead to (−)-(*R*)-**1** according to *Scheme 1*. The experiments (*cf.* exper. part as well as [3] [4]) show, however, that (−)-**4** on cyclization is transformed into (−)-**5**, the *Clemmensen* reduction of which yields dextrorotatory **1**[4]). Thus, in the light of the secured configuration of **4** the assignment of the (*S*)-configuration to (+)-**1** by *Allen & Schnepp* based on *Brewster & Butas* work is questionable.

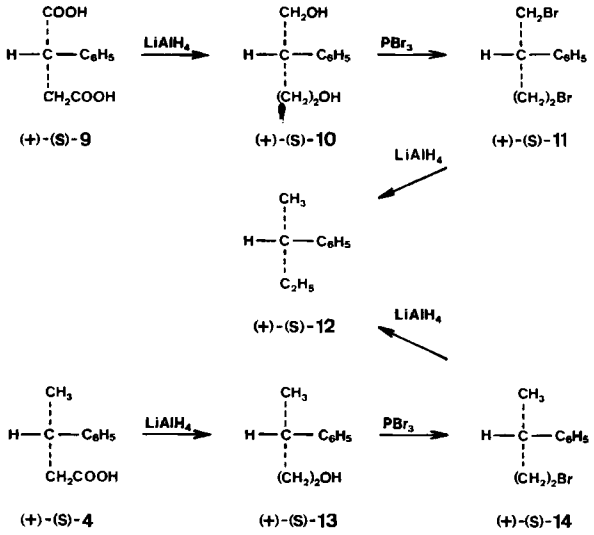
To elude any doubt concerning the absolute configuration of (+)-**1**, obtained from (−)-**4**, we reduced (+)-**1** by the *Birch* method (*cf.* [18]) to (−)-1-methyl-4,7-dihydroindane (**7**; *Scheme 2*). Ozonolysis of this compound and oxydative work-up led to (−)-2-methylglutaric acid (**8**) in 16% chemical yield[5]). According to its correlation with (+)-(*S*)-lactic acid [19] (*cf.* also [20]) (−)-**8** must possess the (*R*)-configuration. Therefore, the synthesis of (+)-**1** from (−)-**4** and its degradation to (−)-**8** is without contradiction, *i.e.* (+)-**1** must possess (*R*)-configuration. This means that the (*S*)-configuration has to be attributed to (−)-**1** as well as to (+)-indane-1-carboxylic acid ((+)-**3**; *Scheme 1*) provided that there is no trivial mistake in *Brewster & Butas* work [2]. This is, however, at variance with *Fredgas* [11] correlation of (+)-indane-1-carboxylic acid ((+)-**3**) with (−)-(*R*)-2-phenylsuccinic acid (**9**). To remove any possible doubt about the configuration of (−)-**9** we connected its antipode

[4]) To eliminate any experimental uncertainty we also reduced (+)-**5**, but using the method of *Huang-Minlon*. The result was pure (−)-**1**.

[5]) Ozonolysis of indane itself does not lead to glutaric acid [21]. In accordance with this observation we were not able to isolate **8** after ozonolysis (CH_2Cl_2, 0°) and oxydative work-up of **1**. Only homophthalic acid could be isolated in 5% yield.

chemically with our starting material (+)-3-phenylbutyric acid (**4**) without involving the chiral centre, as given in *Scheme 3*. The transformation of (−)-(*R*)-**4** *via* **13** and **14** into (−)-(*R*)-2-phenylbutane (**12**) has already been performed by *Cram* [22]. Reduction of (+)-(*S*)-**9** with $LiAlH_4$ gave the dextrorotatory diol **10** (*cf.* [23]), which

Scheme 3



on treatment with PBr_3 yielded the dibromide (+)-**11**. Refluxing this compound in tetrahydrofurane with $LiAlH_4$ in the presence of a catalytic amount of $CoCl_2$ (*cf.* [24]) lead to (+)-**12** without loss of optical purity. This clearly demonstrates that (+)-**9** and (+)-**4** have the same configuration at C(2) and C(3), respectively, namely (*S*)[6]).

2.2. *Spectroscopic Evidence from Vibrational* Raman *Optical Activity.* The above stereochemical correlations are corroborated by data provided by this new method. It is shown elsewhere [25] in more detail that the absolute configuration of many 1-substituted arylethanes is reflected in *Raman* optical activity spectra. We here used the potential inherent in this fact to correlate, *via* the vibrational optical activity spectra, the absolute configuration of (+)-(*R*)-1-methylindane ((+)-**1**) directly with that of (+)-(*R*)-1-phenylethylamine (**15**) determined by an X-ray analysis [26].

Two components can be sampled in *Raman* optical activity, namely a polarized and a depolarized one [27]. So far it was found, however, that for depolarized bands their signs are identical. For the present purpose of merely correlating absolute configurations, the measurement of the more readily obtainable depolarized component was therefore considered sufficient. Adjustment steps and checks required

[6]) The correlation of (+)-**3** with (−)-(*R*)-**9** by an $AlCl_3$-catalyzed cyclization of the acid chloride of the latter (prepared at 100° from (−)-(*R*)-**9**) seems to be on a weak foundation, since extensive racemization was observed [11]. After *Clemmensen* reduction of the keto acid, (+)-**3** could only be isolated in a yield of 3% after seeding with independently prepared (+)-**3**.

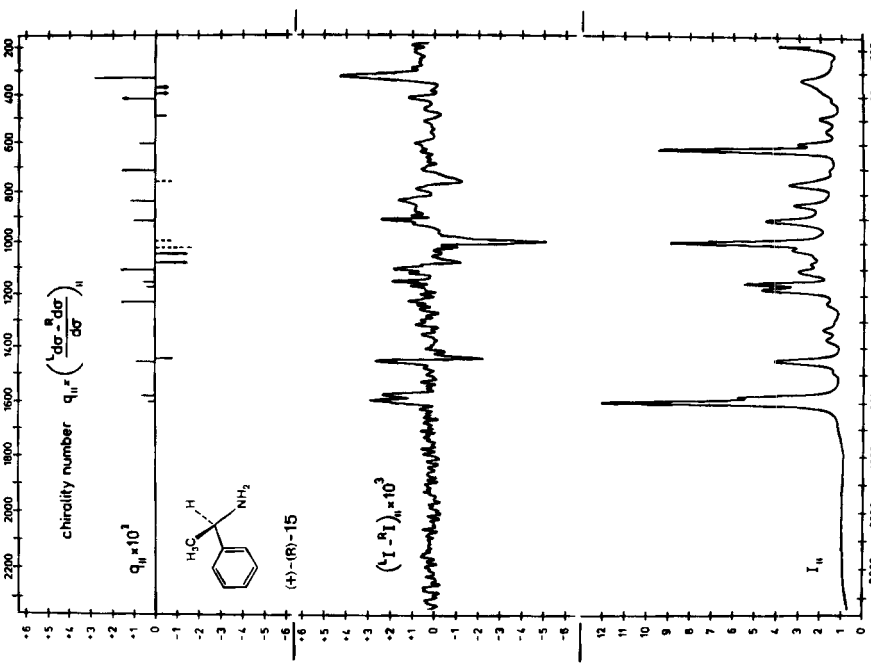


Fig. 1. *The depolarized (measured in parallel polarization* (||) Raman *and circular difference* Raman *spectrum of* (+)-R-*1-methylindane* (**1**; p = 1.00). The data are not corrected for instrument response. Slitwidth is 9 cm^{-1}. $^{L}d\sigma$ and $^{R}d\sigma$ denote differential scattering cross sections for left and right circularly polarized light, respectively; see [27]. q-Numbers of strongly polarized bands are indicated by dashed lines; see text.

Fig. 2. *The depolarized* Raman *and circular difference* Raman *spectrum of* (+)-R-*1-phenylethylamine* (**15**; p = 1.00). The data are not corrected for instrument response. Slitwidth is 9 cm^{-1}. q-Numbers of strongly polarized bands are indicated by dashed lines; see text.

for the reliable measurement of the polarized component were omitted, and strongly polarized bands in *Figures 1* and *2* may thus show slight artefacts (which is due to the fact that finite light collection angles have to be used). Such bands have been identified by a dashed representation of their chirality numbers [27].

Three spectral regions in *Figures 1* and *2* are of particular interest here. These are the vibrations 8a and 8b (*Wilson* notation) which are degenerate in benzene and are found in the vicinity of 1600 cm^{-1}, the doubly degenerate antisymmetric deformation mode of the methyl group at 1450 cm^{-1}, and at least two bands between 300 and 400 cm^{-1} which have not yet been clearly identified, but seem to involve components from benzene vibrations [25], methyl torsions [28], and possibly deformations on the asymmetrically substituted carbon atom.

The two benzene vibrations at 1600 cm^{-1} are split in the spectra of both substances and have both the same sign, which is positive for (+)-(*R*)-1-phenylethylamine (**15**) and negative for (+)-(*R*)-1-methylindane ((+)-**1**)[7]. In contrast, the two components of the antisymmetric methyl deformation mode lead to couplets, which also have opposite signs for the two molecules. The vibrations in the 300 to 400 cm^{-1} region again have opposite signs in the two spectra, which is best seen from a comparison of the corresponding chirality numbers. As the exact magnitude of the chirality numbers is difficult to evaluate in this low frequency regions, they are represented by arrows instead of bars, meaning that they are probably larger than drawn. Based on our work reported in [25] it must therefore be concluded that the methyl group and the hydrogen atom at the asymmetrically substituted carbon atom are interchanged in (+)-**1** as compared to (+)-(*R*)-**15**. The configuration of (+)-**1** should therefore be as drawn in *Figure 1*, namely (*R*), in agreement with the results obtained by chemical correlations.

We wish to thank Mr. *F. Nydegger* and Dipl.-Chem. *W. Bernhard,* Institute of Organic Chemistry of the University of Fribourg, for elemental analyses and mass spectra, respectively. One of us *(H.-R. S.)* also thanks the '*Friedrich-Naumann*-Stiftung' for a scholarship. We gratefully acknowledge support of this work by the *Swiss National Science Foundation.*

Experimental Part

General Remarks. See [29] [30]. Polarimetric measurements (c = g/ml, l = 1 dm) were performed with a *Perkin Elmer* polarimeter, model 241 MC. All known compounds were characterized by their IR.-, NMR.- and mass spectra (MS.) and their purity also determined by gas chromatography (GC.).

1. (−)-*(R)- and* (+)-*(S)-3-Phenylbutyric acid* ((−)- and (+)-**4**). The menthol esters of the racemic acid were separated as described [31]. The crystalline menthol ester (m.p. 45°) of (−)-(*R*)-**4** provided after saponification [31] pure (−)-(*R*)-**4** with $[\alpha]_{589}^{25} = -57.2°$ (neat; −56.5° [22] and −57.3° [8]), *i.e.* optical purity (p) = 1.00. From the mother liquor of the menthol ester of (−)-(*R*)-**4** the antipode (+)-(*S*)-**4** was obtained after saponification; $[\alpha]_{589}^{25} = +36.5°$ (neat; p = 0.64).

2. (−)-*(R)- and* (+)-*(S)-3-Methyl-1-indanone* ((−)- and (+)-**5**) [4] [9] [10]. After carefully mixing of 190 g phosphoric acid (85%) with 95 g phosphorus pentoxide, the mixture was kept under stirring at 100°. 19.0 g (0.116 mol) (−)-(*R*)-**4** were added and stirring continued for 3 h. The reaction mixture was cooled, diluted with ice/water, and extracted with ether. The combined extracts were washed with 5%

[7] The measured size of the 1600 cm^{-1} difference bands is unreliable, due to the smallness of the q-numbers.

aqueous $NaHCO_3$-solution and dried. Distillation at 55–61°/0.3 Torr yielded 14.7 g (88%) (−)-(*R*)-**5** as a colourless liquid with $[\alpha]_{589}^{25} = -4.04°$[8]) (neat; −4.08° [8], −4.16° [7]).

$C_{10}H_{10}O$ (146.21) Calc. C 82.16 H 6.90% Found C 82.10 H 6.98%

In the same manner the (+)-(*S*)-acid **4** (p = 0.64) was cyclized to yield (+)-(*S*)-**5** with $[\alpha]_{589}^{25}$ = +2.57° (neat), $[\alpha]_{589}^{25}$ = +10.6° (*c* = 0.028, $CHCl_3$; for p = 1.00, $[\alpha]_{589}^{25}$ = −16.6° (*c* = 0.02) [32]), $[\alpha]_{589}^{25}$ = +13.0 (*c* = 0.029, acetone), $[\alpha]_{589}^{25}$ = −1.1° (*c* = 0.029, benzene).

$C_{10}H_{10}O$ (146.21) Calc. C 82.16 H 6.90% Found C 82.01 H 6.79%

3. (+)-*(R)- and* (−)-*(S)-1-Methylindane* ((+)- and (−)-**1**) [3] [4]. – 3.1. (+)-*(R)*-**1** *by* Clemmensen *reduction of* (−)-*(R)*-**5** (*cf.* [33]). To 60 g amalgamated zinc [34] and 100 ml water, 7.3 g (0.05 mol) (−)-(*R*)-**5** in 350 ml benzene were added. After addition of 55 g of conc. hydrochloric acid the mixture was refluxed. Two further 55 g portions of conc. hydrochloric acid were introduced over a period of 24 h. The aqueous layer was extracted with ether and the etheral extracts combined with the benzene layer. This organic layer was washed with 5% aqueous $NaHCO_3$-solution. Distillation at 68–70°/12 Torr provided 2.8 g (+)-(*R*)-**1** containing 1% **5** (GC. evidence). A second fraction distilling at 118–120°/12 Torr represented unreacted (−)-**5**. (+)-(*R*)-**1** was obtained in a pure state after chromatography on silica gel with hexane as eluant. $[\alpha]_{589}^{25}$ = +11.06° (neat), $[\alpha]_{589}^{25}$ = −2.6° (*c* = 0.019, isooctane), $[\alpha]_{589}^{25}$ = +10.0° (*c* = 0.014, benzene).

$C_{10}H_{12}$ (132.21) Calc. C 90.85 H 9.15% Found C 90.72 H 9.40%

3.2. (−)-*(S)*-**1** *by* Huang-Minlon *reduction of* (+)-*(S)*-**5** (*cf.* [34] [35]). The mixture of 14.6 g (0.1 mol) (+)-(*S*)-**5** with 11 g K_2CO_3, 10 g hydrazine hydrate (98%), and 10 g diethylene glycol was refluxed for 1 h, distilled at 190° and the condensate extracted with ether. The etheral extracts were washed with 10% aqueous hydrochloric acid. The dark coloured residue of the distillation was heated at 190° for additional 3 h, diluted with 1000 ml water and extracted with ether. The etheral extracts were combined, after washing with 10% aqueous hydrochloric acid, with the extracts of the distillate, washed with water and dried. Distillation at 68–70°/12 Torr yielded 9 g (68%) (−)-(*S*)-**1** which were accompanied by 8% of an olefinic compound (NMR. and GC. evidence). Chromatography on silica gel (impregnated with 10% $AgNO_3$) with pentane provided pure (−)-(*S*)-**1** with $[\alpha]_{589}^{25}$ = −6.52° (neat), $[\alpha]_{589}^{25}$ = −6.5° (*c* = 0.017, benzene), $[\alpha]_{589}^{25}$ = +1.6° (*c* = 0.019, isooctane).

4. (−)-*(R)-2-Methylglutaric acid* (**8**) *by degradation of* (+)-*(R)*-**1**. – 4.1. (−)-*(R)-1-Methyl-4,7-dihydroindane* (**7**). We reduced 3.8 g (28.7 mmol) (+)-(*R*)-**1** with 2 g sodium in 26 ml liquid ammonia and 3 ml methanol according to a procedure described by *Giovannini & Wegmüller* [18]. Since the product contained appreciable amounts of unreacted **1** the procedure was twice repeated to give (−)-(*R*)-**7** with less than 3% of starting material. Distillation at 68–69°/13 Torr gave 2.9 g (76%) in a purity of at least 94% (GC.: 2.8% **1** and two unknown products of 2.7 and 0.5%). $[\alpha]_{589}^{25}$ = −5.6° (*c* = 0.057, hexane), −6.0° (579), −6.65° (546), −11.1° (436), −18.3° (365), −36° (313), −52° (297), −25° (265). – IR. (Film): 3020, 2950, 2840, 2810, 1650 (≻C=C≺), 1455, 1430, 1370, 1070, 950, 915, 660. – ^{1}H-NMR. (CCl_4): 5.63 (*s*, 2 H, H–C(5) and H–C(6)); 2.54 (br. *s*, 4 H, 2 H–C(4) and 2 H–C(7)); 2.2–1.1 (*m*, 5 H, H–C(1), 2 H–C(2), and 2 H–C(3)); 0.96 (*d*, *J* = 7, 3 H, CH_3–C(1)).

$C_{10}H_{14}$ (134.23) Calc. C 89.49 H 10.51% Found C 89.76 H 10.83%

4.2. (−)-*(R)-2-Methylglutaric acid* (**8**). At −78°, a stream of oxygen/ozone was bubbled through the solution of 1.5 g (11.2 mmol) (−)-(*R*)-**7** in 40 ml ethyl acetate/methanol 3:1 until it turned blue. The solvent mixture was evaporated at 0°. The residue was dissolved in 18 ml hydrogen peroxide (30%) and 18 ml of formic acid (98%) and stirred at 40° over night. The excess of H_2O_2 was destroyed at 80° in the presence of catalytic amounts of Pt (10%) on asbestos. After removel of water and formic acid under reduced pressure the residue was chromatographed on TLC. (silica gel, benzene/methanol/glacial acetic acid 11.2:2:1 [36], developing reagent: Bromocresol Green) and (−)-**8** identified using its racemic form. Recrystallisation from benzene provided 0.27 g (16%) (−)-(*R*)-**8**, $[\alpha]_{589}^{25}$ = −22.3° (*c* = 0.02, ethyl acetate; $[\alpha]_D^{25}$ = −24.7°, *c* = 0.02, ethyl acetate [19], *i.e.* p = 0.90), m.p. 70–72°.

$C_6H_{10}O_4$ (146.14) Calc. C 49.31 H 6.90% Found C 49.66 H 7.02%

After treating 0.21 g of the acid with an excess of diazomethane in ether, distillation at 98°/15 Torr gave (−)-(*R*)-dimethyl glutarate (purity 93% by GC.) which showed the same retention time in GC.

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[8]) On standing over a longer period (~ 1 year) the $[\alpha]_{589}^{25}$-value decreased steadily.

as the racemic ester. $[\alpha]_{589}^{25} = -24.9°$ (neat; (+)-(*S*)-antipode $[\alpha]_{589}^{25} = +25.58°$ [37]; *i.e.* p = 0.97), $[\alpha]_{589}^{25} = -26.2°$ ($c = 0.085$, benzene), $[\alpha]_{589}^{25} = -21.9°$ ($c = 0.09$, ethyl acetate).

$C_8H_{14}O_4$ (174.20) Calc. C 55.16 H 8.10% Found C 55.03 H 8.33%

4.3. *Ozonolysis of* (−)-*(S)*-**1**. The solution of 1.8 g (13.6 mmol) of the indane (p = 0.64) in 50 ml methylene chloride was treated at 0° with an oxygen/ozone stream during 19 h. The residue was refluxed for 2 h in a mixture of 15 ml hydrogen peroxide (30%) and 10 ml glacial acetic acid. The solution was concentrated under reduced pressure, the residue dissolved in 30 ml 1M aqueous H_2SO_4 and the excess of H_2O_2 destroyed at 50° with potassium permanganate (3.5 g). After filtration of manganese dioxide, the filtrate was extracted with ether. From the viscous oil, left (0.7 g) after evaporation of the ether, separated crystals when triturated with benzene. The colourless crystals (0.95 g, *i.e.* 5%) were identified as homophthalic acid (IR. identical with that of an authentic sample; no depression of a mixed m.p. with homophthalic acid; identical retention times in GC. for the dimethylesters).

5. (+)-*(S)-2-Phenylbutane* (**12**) *from* (+)-*(S)-3-phenylbutyric acid* (**4**). – 5.1. (+)-*(S)-3-Phenyl-1-butanol* (**13**) (*cf.* [22]). The reduction of 5.0 g (0.030 mol) (+)-(*S*)-**4** (p = 1.00; prepared according to [38]) with $LiAlH_4$ in the usual manner give 4.4 g (96%) (+)-(*S*)-**13**; $[\alpha]_{589}^{25} = +38.18°$ (neat).

5.2. (+)-*(S)-1-Bromo-3-phenylbutane* (**14**) (*cf.* [22]). We treated 3.0 g (0.020 mol) (+)-(*S*)-**13** with phosphorous tribromide as described for the antipode [39]. After work-up 3.1 g (74%) (+)-(*S*)-**14** were obtained as colourless liquid with $[\alpha]_{589}^{25} = +99.44°$ (neat), $[\alpha]_{589}^{25} = +63.9°$ ($c = 0.018$, methylene chloride), $[\alpha]_{589}^{25} = +61.0°$ ($c = 0.018$, acetone), and $[\alpha]_{589}^{25} = +72.4°$ ($c = 0.03$, ether).

5.3. (+)-*(S)-2-Phenylbutane* (**12**) (*cf.* [22]). We reduced 2.3 g (10.7 mmol) (+)-(*S*)-**14** with $LiAlH_4$ in ether in the presence of catalytic amounts of $CoCl_2$ (*cf.* [24]). Usual work-up provided 1.3 g (87%) pure (+)-(*S*)-**12** with $[\alpha]_{589}^{25} = +24.31°$ (neat; (−)-(*R*)-antipode $[\alpha]_{589}^{25} = -24.3°$ [22]; *i.e.* p = 1.00), $[\alpha]_{589}^{25} = +25.9°$ ($c = 0.026$, methylene chloride).

$C_{10}H_{14}$ (134.22) Calc. C 89.49 H 10.51% Found C 89.41 H 10.50%

6. (+)-*(S)-2-Phenylbutane* (**12**) *from* (+)-*(S)-2-phenylsuccinic acid* (**9**). – 6.1. (−)-*(R)- and* (+)-*(S)-2-Phenylsuccinic acid* (**9**). The racemic acid was resolved *via* its brucine salts as described [40] [41]. The salt of the (+)-(*S*)-antipode was decomposed with diluted hydrochloric acid to yield (+)-(*S*)-**9** with $[\alpha]_{589}^{25} = +161.2°$ ($c = 0.042$, acetone; $[\alpha]_{589}^{25} = +171.1°$ ($c = 0.020$, acetone) [42]; *i.e.* p = 0.94). The mother liquor of the brucine salt of the (+)-(*S*)-acid provided after decomposition (−)-(*R*)-**9** with $[\alpha]_{589}^{25} = -110.5°$ ($c = 0.087$, acetone; p = 0.65).

6.2. (+)-*(S)-2-Phenyl-1,4-butandiol* (**10**) (*cf.* [23] [43]). We reduced 5.5 g (0.028 mol) (+)-(*S*)-**9** (p = 0.94) in 300 ml ether with 3 g $LiAlH_4$ in 25 ml ether. After 8.5 h refluxing the mixture was cooled and decomposed with ice/water at −15°. Then, diluted sulfuric acid was added until the precipitate was dissolved. The solution was several times extracted with ether. The etheral extracts were combined, washed and dried. Distillation in a 'kugelrohr' (130°/0.03 Torr) provided 4.1 g (88%) (+)-(*S*)-**10** as a colourless, viscous oil with $[\alpha]_{589}^{60} = +28.19°$ (neat), $[\alpha]_{589}^{25} = +31.2°$ ($c = 0.061$, acetone). – IR. (film): 3320 (OH), 3020, 2930, 2880 (CH), 1600, 1495, 1455, 1055, 770, 705. – ^{1}H-NMR. (acetone-d_6): 7.20 (*s*, 5 H); 3.8–3.4 (*m*, 4 H and 2 OH); 3.2–2.8 (*m*, 1 H); 2.3–1.8 (*m*, 2 H).

$C_{10}H_{14}O_2$ (166.23) Calc. C 72.26 H 8.49% Found C 72.01 H 8.40%

6.3 (+)-*(S)-1,4-Dibromo-2-phenylbutane* (**11**). To 3.6 g (0.022 mol) (+)-(*S*)-**10** phosphorus tribromide (3.9 g) was added dropwise at 0°. The reaction mixture was stirred over night at room temperature and then 1 h at 90°. Ice water was added and the organic layer extracted with ether. The etheral extracts were washed and dried. After evaporation of the ether the residue was distilled in a 'kugelrohr' (90°/0.03 Torr). 4.3 g (68%) (+)-(*S*)-**11** were obtained as a colourless liquid with $[\alpha]_{589}^{25} = +92.1°$ (neat), $(\alpha]_{589}^{25} = +51.8°$ ($c = 0.0167$, methylene chloride). – IR. (film): 3020, 2950, 2920 (CH), 1600, 1490, 1450, 1430, 1255, 760, 695. – ^{1}H-NMR. (CCl_4): 7.2 (*s*, 5 H); 3.6–3.0 (*m*, 5 H); 2.7–2.0 (*m*, 2 H).

$C_{10}H_{12}Br_2$ (292.02) Calc. C 41.13 H 4.14% Found C 41.15 H 4.20%

6.4. (+)-*(S)-2-Phenylbutane* (**12**). To 0.62 g $LiAlH_4$ and 0.18 g waterfree $CoCl_2$ 4 ml tetrahydrofurane were added at 0°. The dark coloured mixture was refluxed and 2.1 g (7.2 mmol) (+)-(*S*)-**11**, dissolved in 5 ml tetrahydrofurane, were added dropwise. The mixture was heated for 24 h at reflux[9]). The decomposition of the unreacted $LiAlH_4$ was achieved with aqueous tetrahydrofurane. After usual

[9]) Reduction of (+)-(*S*)-**11** under the same conditions in boiling ether gave **12** only in an yield of 1.5%.

work-up distillation at 55°/15 Torr provided 0.40 g (40%) (+)-(*S*)-**12**. $[\alpha]_{589}^{25} = +23.8°$ (neat), $[\alpha]_{589}^{25} = +24.6°$ ($c = 0.043$, methylene chloride; $p = 0.95$).

$C_{10}H_{14}$ (134.22) Calc. C 89.49 H 10.51% Found C 89.17 H 10.28%

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