PREPARATION OF BOTH ENANTIOMERS OF (1*R**, 2*S**)-1--CYCLOHEXYL-1,2-PROPANEDIOL FROM THE COMMERCIAL NEUBERG'S KETOL*

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Both the optically pure enantiomers of (1*R**,2*S**)-1-cyclohexyl-1,2-propanediol (*II*) were prepared from commercial (*R*)-(−)-1-phenyl-1-hydroxy-2-propanone (*I*; Neuberg's ketol). (1*R*,2*S*)-(+)--1-Cyclohexyl-1,2-propanediol((+)-*II*) was obtained in 19% total yield, its (1*S*,2*R*)-enantiomer ((−)-*II*) in 8% yield. Both diols, as well as their precursors, enantiomeric (1*R**,2*S**)-1-phenyl-1,2--propanediols (*IIIa*), are suitable chiral synthons.

Chiral optically active 1,2-diols and compounds derived from them have found application in various stereoselective reactions[1]. Their use depends not only on how effectively they influence the stereoselectivity of the given process but also on the availability expressed by their price or method of preparation. For these reasons, most of them are available only in one enantiomeric form, usually configurationally related to the original natural material whereas the other enantiomer is much more difficult to obtain. In this communication we describe a simple preparation of both enantiomers of (1*R**,2*S**)-1-cyclohexyl-1,2-propanediol, (+)-*II* and (−)-*II*, and of (1*R**,2*S**)-1-phenyl-1,2-propanediol, (−)-*IIIa* and (+)-*IIIa*, starting from (*R*)-(−)--1-phenyl-1-hydroxy-2-propanone (*I*). Compound *I*, called the Neuberg's ketol[2], is used in the manufacturing of (−)-ephedrine (*VII*), and is obtained by biochemical conversion of benzaldehyde and molasses with the *Saccharomyces coreolanus* strain[3,4]. Although the ketol *I*, isolated from the industrially prepared mixture, has a lower optical purity (80−95%), the subsequent purification methods enable the preparation of optically pure diols *II* and *IIIa*.

The ketol *I* was isolated from the industrially prepared butyl acetate solution using the already described procedure[5]. The residue after distillation of compound *I* contained a crystalline residue which was assumed by Ježo[6] to be 2,6-diphenyl-4--methyl-1,3,5-trioxane (*V*). However, this structure is not compatible with the

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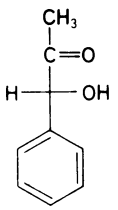
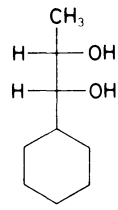
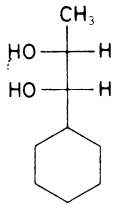


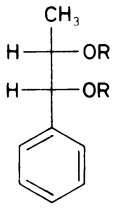
I



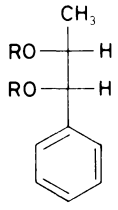
(+) – *II*



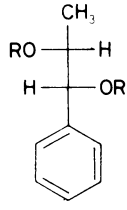
(–) – *II*



(–) – *IIIa*, R = H
(+) – *IIIb*, R = COC_6H_5

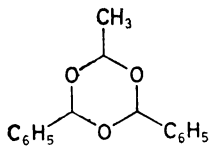


(+) – *IIIa*

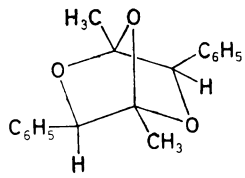


(–) – *IVa*, R = H
IVb, R = COC_6H_5

obtained ^1H and ^{13}C NMR spectra. On the basis of their analysis we suggest that the compound is the hitherto undescribed 3,6-diphenyl-1,4-dimethyl-2,5,7-trioxabicyclo[2.2.1]heptane (*VI*). Our suggested structure with both the phenyl groups in position *exo* corresponds to the relative configuration (1*R**,3*S**,4*R**,6*S**) and has been confirmed by X-ray diffraction analysis[7]. The formation of the bicyclic ether *VI* can be explained by dehydration of the product of dimerization of the ketol. Similar compounds, arising from acyloins, have already been studied[8].



V



VI

Reduction of the carbonyl group in ketol *I* affords a mixture of (1*R*,2*S*)-*erythro*- and (1*R*,2*R*)-*threo*-1-phenyl-1,2-propanediol ((–)-*IIIa* and (–)-*IVa*, respectively). The relative amounts of both diastereoisomers depend on the reducing agent used: with lithium aluminium hydride[9] the ratio was 80 : 20, with zinc borohydride[10]

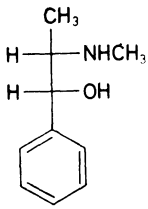
90 : 10 and with sodium borohydride[11] 65 : 35, the isomer (−)-*IIIa* predominating in all cases. The highest diastereoselectivity was achieved with bakers' yeasts[12] which reduced the ketol *I* to the diol (−)-*III* in 94% diastereoisomeric excess.

In our present work we used the catalytic hydrogenation because the previously described reduction of the ketol *I* by this method[13] did not study its stereoselectivity. As expected, we have found that the catalytic hydrogenation is highly stereoselective: in experiments performed under various conditions the *erythro* : *threo* ratio never dropped below 10 : 1. The minor amounts of (−)-*IVa* could be separated by affinity chromatography[14] which, however, was not suitable for work with larger quantities. In such cases fractional crystallization of the corresponding dibenzoates[12,15] (+)-*IIIb* and *IVb* was satisfactory affording the *erythro*-isomer *IIIb* in the optical purity up to 95–97%. Alkaline hydrolysis of the ester (+)-*IIIb* was accompanied by partial racemization and the racemate formed had to be removed by fractional crystallization[16,17]. Therefore, we replaced this hydrolysis by reduction with lithium aluminium hydride which led to higher yields of the diol (−)-*IIIa*.

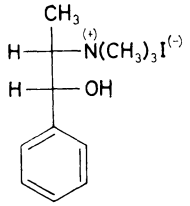
The thus-obtained optically pure (1*R*,2*S*)-(−)-1-phenyl-1,2-propanediol ((−)-*IIIa*) was reduced to the corresponding cyclohexyl analogue described in a racemic form previously[18]. Replacement of the phenyl group at the chirality centre by cyclohexyl (whose steric requirements correspond to an isopropyl group) may influence significantly the stereoselectivity of the studied process. Of the reduction methods employed the best results were obtained with hydrogenation over 5% Rh/C in methanol containing some acetic acid, at room temperature and 0·4–0·65 MPa, which proceeded without racemization[19]. Raney nickel-catalyzed high-pressure hydrogenation according to Urushibara[20] afforded an optically inactive product. Hydrogenation over 2% Ru/Al_2O_3 in methanol was sufficiently rapid only at 9 MPa and 45°C and was accompanied by partial racemization. The above-mentioned procedure afforded (1*R*,2*S*)-(+)-1-cyclohexyl-1,2-propanediol ((+)-*II*) in an overall yield of 19% (related to the starting ketol *I*).

As seen from the literature, the enantiomeric (1*S*,2*R*)-(+)-1-phenyl-1,2-propanediol ((+)-*IIIa*) can be prepared from (1*R*,2*S*)-(−)-ephedrine *VII* by the procedure elaborated by Fischer[17]. Because of the facile conversion[21] of the ketol *I* into the amino alcohol *VII*, this procedure, combined with the described reduction of the aromatic nucleus, can be utilized for the preparation of the enantiomeric (1*S*,2*R*)-(−)-1-cyclohexyl-1,2-propanediol ((−)-*II*). Ephedrine (*VII*) was methylated on the nitrogen atom and the obtained quaternary salt *VIII* was converted by reaction with silver oxide into the hydroxide which on thermal degradation at 100–105°C afforded *trans*-(1*R*,2*R*)-(+)-1-phenyl-1,2-epoxypropane (*IX*). Whereas acid hydrolysis of the epoxide *IX* led to a 2 : 1 mixture of diols *IIIa* and *IVa* and was accompanied by considerable racemization, alkaline hydrolysis afforded only partially (up to 10%) racemized diol (+)-*IIIa*. As already mentioned, the racemate may be removed by fractional crystallization. The analogous reduction of the aromatic nucleus afforded

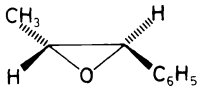
(1*S*,2*R*)-(−)-1-cyclohexyl-1,2-propanediol ((−)-*II*) in 8% yield (related to the starting ketol *I*).



VII



VIII



IX

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. NMR spectra were measured on a Tesla BS-567 (100 MHz for ^{1}H) and on a Bruker AM-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) instrument in deuteriochloroform using tetramethylsilane as internal standard. The chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. The multiplicity in the ^{13}C NMR spectra was determined using the APT method. Optical rotations were measured on an objective polarimeter Zeiss Opton LEP A2, accuracy 0·01°. Gas-liquid chromatographic analyses were carried out on a Chrom 5 chromatograph with a flame-ionization detector. Thin-layer chromatography was performed on Silufol UV 254 sheets (Kavalier, Votice, Czechoslovakia).

Isolation of (*R*)-(−)-1-Phenyl-1-hydroxy-2-propanone (*I*)
From an Industrial Solution[5]

An industrially prepared solution of *I* in butyl acetate (276·0 g; content of ketol *I* 0·94 mol) was dissolved in ether (1 000 ml) and rapidly extracted with saturated solution of sodium carbonate (2 × 150 ml) and with water (5 × 200 ml). To the stirred and ice-cold organic portion was added dropwise during 1 h a solution of sodium pyrosulfate (130·0 g; 0·68 mol) in water (350 ml). The mixture was stirred for 2 h and the separated crystals were filtered and washed with ether (3 × 100 ml). The thus-obtained adduct was dissolved in water (600 ml) and solid sodium hydrogen carbonate was added until the evolution of carbon dioxide ceased. The mixture was saturated with sodium chloride and extracted with ether (7 × 150 ml). The combined organic portions were dried over sodium sulfate overnight, the solvent was evaporated and the oily residue was fractionated in vacuo; yield 89·2 g (63%) of a yellowish liquid, b.p. 72—74°C/33 Pa; $[\alpha]_D^{20}$ −164·7° (*c* 2·2; ethanol). Reported[5] b.p. 124—125°C/1·6 kPa, $[\alpha_D^{20}]$ −181·9° (*c* 2·0; ethanol). ^{1}H NMR spectrum (100 MHz): 2·03 s, 3 H (CH_3); 4·29 bs, 1 H; 5·02 s, 1 H (CH); 7·29 m, 5 H (H-arom.). For $C_9H_{10}O_2$ (150·2) calculated: 71·97% C, 6·71% H; found: 72·1% C, 6·76% H.

The distillation residue which crystallized during the distillation, was twice crystallized from ethanol to give 9·5 g of compound *VI* as white needles, m.p. 150·0—150·5°C; $[\alpha]_D^{20}$ −9·2° (*c* 5·8; chloroform). Reported[6] m.p. 149·5—150·0°C. ^{1}H NMR spectrum (100 MHz): 1·42 s, 6 H (CH_3); 4·95 s, 2 H (CH); 7·32 m, 10 H (H-arom.). ^{13}C NMR spectrum (100·61 MHz): 15·19 (CH_3); 86·77 (C-3, C-6); 108·96 (C-1, C-4); 127·06 (C-arom.); 128·27 (C-arom.); 128·35

(C-arom.); 137·64 (C-arom.). IR spectrum ($CHCl_3$): 835, 895, 1 000, 1 100, 1 165, 1 250, 1 390, 1 455, 1 495, 2 950, 3 010, 3 040, 3 075, 3 100. For $C_{18}H_{18}O_3$ (282·3) calculated: 76·59% C, 6·41% H; found: 76·62% C, 6·30% H.

Hydrogenation of Ketol *I* over Adams Catalyst

A mixture of purified ketol *I* ($[\alpha]_D^{20}$ −164·7°; 104·9 g; 0·7 mol), platinum oxide according to Adams (1·2 g; 5·28 mmol) and methanol (350 ml) was shaken in a hydrogen atmosphere at 0·1–0·3 MPa and 20°C for 3 h. After filtration of the catalyst and evaporation of the solvent, the crude product was distilled in vacuo. The main fraction (89·9 g; 86%) consisted of the diastereoisomeric 1-phenyl-1,2-propanediols *IIIa* and *IVa*, b.p. 115–116°C/0·12 kPa, $[\alpha]_D^{20}$ −19·2° (*c* 5·0; ethanol). The ratio *erythro* : *threo*, as determined from the ^{1}H NMR spectrum, was 10 : 1. ^{1}H NMR spectrum (100 MHz) of the mixture: 0·98 d (H-3 *threo*, J = 6·8); 1·01 d (H-3 *erythro*, J = 6·2); 3·04 bs (OH); 3·78–4·07 m (H-2); 4·28 d (H-1 *threo*, J = 7·5); 4·62 d (H-1 *erythro*, J = 4·0); 7·32 m (H-arom.).

(1*R*,2*S*)-(−)-1,2-Dibenzoyloxy-1-phenylpropane ((+)-*IIIb*)

The title compound was prepared by reaction of the mixture of diols (−)-*IIIa* and (−)-*IVa* with an excess of benzoyl chloride in pyridine[17]. The reaction product was recrystallized from methanol to a constant melting point and optical rotation (yield 71%); m.p. 93·5–95·0°C, $[\alpha]_D^{20}$ +61·0° (*c* 4·40; chloroform); reported[17] m.p. 95·5–97·0°C, $[\alpha]_D^{20}$ +62·8° (chloroform) and m.p. 93·5°C, $[\alpha]_D^{20}$ +62·2° (*c* 1·20; chloroform)[12]. ^{1}H NMR spectrum (100 MHz): 1·43 d, 3 H (H-3, J(3, 2) = 6·0); 5·62 dq, 1 H (H-2, J(2, 3) = 6·0, J(2, 1) = 4·0); 6·34 d, 1 H (H-1, J(1, 2) = 4·0); 7·30–8·22 m, 5 H (H-arom.). For $C_{23}H_{20}O_4$ (360·4) calculated: 76·65% C, 5·59% H; found: 76·65% C, 5·61% H.

(1*R*,2*S*)-(−)-1-Phenyl-1,2-propanediol ((−)-*IIIa*)

A) Dibenzoate (+)-*IIIb* (42·8 g; 0·119 mol) was hydrolyzed with a solution of potassium hydroxide in aqueous methanol using a procedure described previously[16]. The crude product was fractionally crystallized from ether–cyclohexane to separate the less soluble racemic diol *IIIa* (3·9 g) m.p. 90–92°C (reported[23] m.p. 91–92°C). The mother liquors gave 11·5 g (64%) of pure diol (−)-*IIIa*, m.p. 40–42°C, $[\alpha]_D^{20}$ −18·1° (*c* 4·0; ethanol); reported[16] m.p. 40–41°C, $[\alpha]_D^{20}$ −18·1° (*c* 3·8; ethanol). ^{1}H NMR spectrum (400 MHz): 1·01 d, 3 H (H-3, J(2, 3) = 6·4); 2·96 bs, 2 H (OH); 3·94 dq, 1 H (H-2, J(2, 3) = 6·4; J(1, 2) = 4·1); 4·62 d, 1 H (H-1, J(1, 2) = = 4·1); 7·31 m, 5 H (H-arom.). For $C_9H_{12}O_2$ (152·2) calculated: 71·03% C, 7·95% H; found: 71·24% C, 8·01% H.

B) A solution of dibenzoate (+)-*IIIb* (21·6 g; 59·9 mmol) in ether (100 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (2·5 g; 65·9 mmol) in ether (150 ml) so as the mixture boiled gently. The mixture was then refluxed for 1 h, cooled and treated successively with water (30 ml) and 10% sulfuric acid (50 ml). The organic phase was separated, the aqueous one saturated with sodium chloride and extracted with ether (4 × 50 ml). The combined organic portions were dried over sodium sulfate, the solvent was evaporated under diminished pressure and the residue was distilled in vacuo (oil pump). After removal of benzyl alcohol at 48°C/40 Pa the distillation was interrupted and the residue was allowed to crystallize in vacuo for 1 h. The obtained product was twice crystallized from ether–heptane; yield 7·0 g (77%) of colourless crystalline diol (−)-*IIIa*, m.p. 40·5°C, $[\alpha]_D^{20}$ −18·1° (*c* 3·0; ethanol). Its spectra were identical with those of the alkaline hydrolysis product.

(1*R*,2*S*)-(−)-1-Phenyl-2-methylamino-1-propanol ((−)-Ephedrine) (*VII*)

An autoclave, containing platinum dioxide according to Adams (89·3 mg; 0·39 mmol) and methanol (150 ml), was flushed three times with hydrogen and the catalyst was reduced at hydrogen pressure of 0·3 MPa. An industrial solution of ketol *I* in butyl acetate (27·5 g of solution, containing 15·0 g; 0·1 mol of pure compound) and a solution of methylamine in methanol (52·0 g of 10·8% solution; 0·18 mol) were immediately added and the mixture was hydrogenated[21] at initial hydrogen pressure of 0·3 MPa for 60 min. After filtering off the catalyst, the filtrate was concentrated in vacuo to one third of the original volume and acidified to pH 3·0 with hydrochloric acid (1 : 1). Further gradual concentration in vacuo afforded two fractions of crystals which were combined and crystallized twice from aqueous ethanol. Yield 12·9 g (64%) of hydrochloride of the amino alcohol *VII*, m.p. 220–222°C, $[\alpha]_D^{20}$ −34·4° (*c* 5·0; water) (reported[22] m.p. 216–217°C, $[\alpha]_D^{20}$ −34·9° (*c* 9·0; water). Prior to use, the free base was liberated from the hydrochloride with 0·3M sodium hydroxide. The aqueous phase was repeatedly extracted with ether, the ethereal solution was dried over potassium carbonate, the solvent was evaporated and the clear oily *VII* was used immediately in the next reaction step.

N,N-*Dimethylephedrinium iodide* (VIII) was prepared by treatment of amino alcohol *VII* with sodium methoxide and methyl iodide by a described procedure[17]. The obtained quaternary salt was recrystallized from 80% ethanol, m.p. 212–214°C, $[\alpha]_D^{20}$ −22·2° (*c* 3·1; water); reported[17] m.p. 204–206°C, $[\alpha]_D^{20}$ −22·2° (*c* 3·1; water). For $C_{12}H_{20}INO$ (321·2) calculated: 44·87% C, 6·28% H, 39·51% I, 4·36% N; found: 44·55% C, 6·35% H, 39·10% I, 4·16% N.

(1*R*,2*R*)-(+)-1-*Phenyl*-1,2-*epoxypropane* (IX) was obtained in 45% yield by thermal decomposition of the quaternary base prepared from the iodide *VIII* and silver oxide using the procedure of Fischer[17]; b.p. 84–84·5°C/1·33 kPa; $[\alpha]_D^{20}$ +68·9° (*c* 4·0; ethanol). Reported[17] b.p. 82°C/1·33 kPa, $[\alpha]_D^{20}$ +70·7° (*c* 4·0; ethanol). ^{1}H NMR spectrum (100 MHz): 1·42 d, 3 H (H-3, J = 5·0); 3·01 m, 1 H (H-2); 3·55 d, 1 H (H-1, J = 2·0); 7·19 m, 5 H (H-arom.). For $C_9H_{10}O$ (134·2) calculated: 80·56% C, 7·51% H; found: 80·68% C, 7·63% H.

(1*S*,2*R*)-(+)-1-Phenyl-1,2-propanediol ((+)-*IIIa*)

Epoxide *IX* (20·7 g; 0·154 mol) was hydrolyzed[17] with potassium carbonate (42·0 g; 0·304 mol) in water (500 ml) at 80–85°C for 15 h. After cooling, the mixture was saturated with sodium chloride and extracted with ether (6 × 150 ml). The combined organic portions were dried over sodium sulfate and the solvent was evaporated in vacuo. The residue was dried over phosphorus pentoxide for 5 days and the obtained crystals were subjected to fractional crystallization from ether–light petroleum which furnished the less soluble racemate (2·3 g), m.p. 90–92°C (reported[23] m.p. 91t72°C). The mother liquors gave 13·7 g (59%) of diol (+)-*IIIa*, m.p. 39–42°C, $[\alpha]_D^{20}$ +18·1° (*c* 3·8; ethanol) (reported[16] m.p. 40–41°C, $[\alpha]_D^{20}$ +18·1° (*c* 4·6; ethanol). ^{1}H NMR spectrum (100 MHz): 1·01 d, 3 H (H-3, J = 6·2); 3·04 bs, 2 H (OH); 3·93 dq, 1 H (H-2, J(2, 3) = = 6·2; J(1, 2) = 4·0); 4·62 d, 1 H (H-1, J = 4·0); 7·32 m, 5 H (H-arom.). For $C_9H_{12}O_2$ (152·2) calculated: 71·03% C, 7·95% H; found: 70·85% C, 7·96% H.

(1*R*,2*S*)-(+)-1-Cyclohexyl-1,2-propanediol ((+)-*II*)

A mixture of diol (−)-*IIIa* (15·2 g; 0·1 mol) and 5% Rh/C (3·1 g) was layered with methanol (150 ml). Glacial acetic acid (2 ml) was added and the mixture was hydrogenated at 0·5 MPa for 6 h. The catalyst was filtered off, the methanol was evaporated and the residue was fractionated in vacuo. The principal fraction (11·8 g of a colourless oil, b.p. 102–103°C/75 Pa) was crystallized from ether–light petroleum affording 9·8 g (62%) of (+)-*II*, m.p. 56–57·5°C, $[\alpha]_D^{20}$ +11·8° (*c* 4·0; ethanol). ^{1}H NMR spectrum (400 MHz): 0·93–1·02 m, 2 H (cyclohexyl);

1·12—1·35 m, 4 H (cyclohexyl); 1·16 d, 3 H (H-3, $J = 6·4$); 1·52—1·76 m, 4 H (cyclohexyl); 2·05 m, 1 H (cyclohexyl); 3·32 dd, 1 H (H-1, $J(1, 2) = 3·7$; $J(1, 1') = 7·7$); 3·40 bs, 1 H (OH); 3·58 bs, 1 H (OH); 3·86 dq, 1 H (H-2, $J(1, 2) = 3·7$; $J(2, 3) = 6·4$). ^{13}C NMR spectrum (100·61 MHz): 15·94 (C-3); 25·75 (C-3′); 25·94 (C-5′); 26·35 (C-4′); 28·88 (C-2′); 29·31 (C-6′); 40·00 (C-1′); 68·00 (C-2); 78·86 (C-1). For $C_9H_{18}O_2$ (158·2) calculated: 68·31% C, 11·47% H; found: 68·55% C, 11·49% H.

(1*S*,2*R*)-(−)-1-Cyclohexyl-1,2-propanediol ((−)-*II*)

The title compound (3·8 g; 56%) was obtained from diol (+)-*IIIa* (6·5 g; 42·7 mmol) by the procedure described in the preceding experiment; m.p. 55·5—57·5°C; $[\alpha]_D^{20}$ −11·6° (*c* 2·3; ethanol). Its spectral characteristics are the same as those of the (+)-enantiomer. For $C_9H_{18}O_2$ (158·2) calculated: 68·31% C, 11·47% H; found: 68·15% C, 11·60% H.

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