PREPARATION OF THREE DIASTEREOISOMERS OF 2-(1-METHYL-1-PHENYLETHYL)-5-METHYLCYCLOHEXAN-1-OL FROM (*R*)-(+)-PULEGONE*

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New isolation of (1*R*,2*S*,5*R*)-(−)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexan-1-ol ((−)-8-phenylmenthol, *Ia*), prepared from (*R*)-(+)-pulegone, is described. The method consists in the preparation of phenylcarbamate of *Ia* and its transesterification with ethanol. Further two diastereoisomers of (−)-8-phenylmenthol were isolated: the (1*S*,2*R*,5*R*)-isomer *IIa* and the (1*R*,2*R*,5*R*)-isomer *IIIa*. Compounds *Ia*, *IIa* and *IIIa* were converted into their respective glyoxylates *Ic*, *IIc* and *IIIc*.

Enantioselective Diels–Alder reaction represents now a method which with appropriate chiral reagents leads to compounds of high optical purity[1]. High enantioselectivity[2,3] was achieved particularly with (1*R*,2*S*,5*R*)-(−)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexan-1-ol ((−)-8-phenylmethanol, *Ia*). Compound *Ia* is available from (*R*)-(+)-pulegone; however, this route gives a mixture[2] which, in addition to compound *Ia* (85%), contains about 15% of stereoisomers *IIa* and *IIIa* whose separation is difficult. The originally employed separation by column chromatography[2] has been improved by preparative HPLC which gave also pure diastereoisomer *IIa* (ref.[4]).

Difficulties which we encountered during preparation of greater amounts of compound *Ia*, prompted us to elaborate a suitable method of its isolation from stereoisomeric mixtures. The mixture of alcohols *Ia*, *IIa* and *IIIa*, obtained by reduction of the equilibrated ketone mixture[2], was converted into benzoates, *p*-nitrobenzoates and phenylcarbamates. Only the latter derivatives on crystallization from hexane gave a stereoisomerically uniform product, m.p. 105–106·5°C, $[\alpha]_D^{20}$ +4·0°, identified by spectral methods as phenylcarbamate of (−)-8-phenylmenthol (*Ib*).

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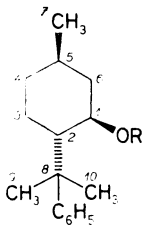
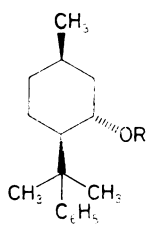
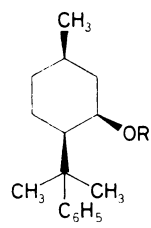
Crystallization of the mother liquors afforded another phenylcarbamate, *IIb*, m.p. 108–110·5°C, $[\alpha]_D^{20}$ 32·0°, markedly differing from *Ib* in the crystal shape. Compound *Ib* crystallized from light petroleum as well-developed plates whereas the phenylcarbamate *IIb* formed long needles. This behaviour was utilized for a crude mechanical separation of crystals. Column chromatography of mother liquors from crystallizations of *Ib* and *IIb* afforded another stereoisomeric phenylcarbamate *IIIb*, $[\alpha]_D^{20}$ −18·9°.



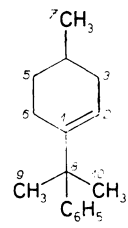
Ia – Ie



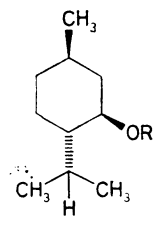
IIa – IIe



IIIa – IIIe



IV



Vb – Vd

In formulae *I–V*: *a*, R = H *b*, R = $CONHC_6H_5$ *c*, R = COCHO *d*, R = $COCH_2Br$ *e*, R = $COCH_2ONO_2$

Attempted liberation of alcohol *Ia* from phenylcarbamate *Ib* by reduction with zinc in acidic medium or with lithium aluminium hydride was completely unsuccessful, also alkaline hydrolysis in the presence of crown ethers gave the desired alcohol only in low yields. The only one preparatively usable method proved to be transesterification in absolute ethanol, catalyzed with 10 equivalents of sodium ethoxide.

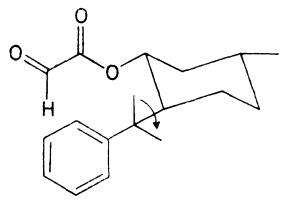
Alcohol *IIa* was liberated analogously as its isomer *Ia*. Phenylcarbamate *IIIb* was extraordinarily unreactive and after twice repeated reaction gave only 52% of compound *IIIa*. This low reactivity may be caused by *cis*-orientation of the sterically bulky groups on the C-1 and C-2 atoms in compound *IIIb*. The enantiomeric purity of alcohols *Ia* and *IIa* was determined by ^{1}H NMR spectroscopy (Mosher's method[5]) and HPLC and was higher than 98% for both substances. In the case of alcohol *IIIa* we obtained only the olefin instead of the Mosher's ester.

The configuration of the liberated alcohols was determined using the NMR spectroscopy. Proton as well as carbon NMR spectra of compound *IIa* are identical with those of the alcohol isolated by Whitesell[4]. As indicated by coupling constants in the spectrum of *IIIa*, the compound has an axial hydroxyl and *cis*-relation between the groups on C-1 and C-2. To distinguish between the (1*R*,2*R*,5*R*)- and (1*S*,2*S*,5*R*)-configuration, we employed the in situ reaction with trichloroacetyl isocyanate (TAI). Table I shows the changes in chemical shifts of the studied alcohols in the TAI-experiment. In the spectrum of *IIIa* the signal of methyl on C-5 is shifted upfield

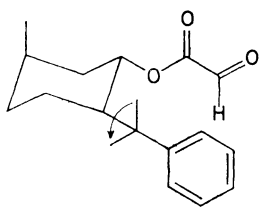
due to the 1,3-diaxial interaction with the hydroxy group[6]. We therefore assume that the alcohol *IIIa* has the (1*R*,2*R*,5*R*)-configuration.

For a study of enantioselective reactions we converted the alcohols *Ia*–*IIIa* into glyoxylates *Ic*–*IIIc*. Bromoacetates *Id*–*IIId* were transformed into nitrates *Ie*–*IIIe* which on reaction with dimethyl sulfoxide in the presence of sodium acetate afforded mixture containing predominantly hydrated glyoxylates. Distillation under reduced pressure gave pure glyoxylates *Ic*–*IIIc*. Azeotropic esterification of the alcohols with bromoacetic acid, catalyzed with *p*-toluenesulfonic acid, led to considerable amounts of elimination product *IV*. Its proportion in the reaction mixture depended on the amount of the catalyst and also on the configuration of the alcohol (Table II). In alcohol *IIIa* the hydroxyl group is in *trans*-relation to the easily cleavable hydrogen on the tertiary carbon atom C-2 and therefore the elimination of water is so facile.

The aldehyde proton signal in the ^{1}H NMR spectra of glyoxylates *Ic*–*IIc* is shifted upfield compared with the analogous signal in (–)-menthyl glyoxylate (*Vc*), the shift being of unusual magnitude. An analogous upfield shift was observed for protons in the ester and phenylcarbamate derivatives of alcohols *Ia* and *IIa* (Table III, the protons in question are underlined). This phenomenon was observed on similar compounds also by other authors[7–9]. It is caused by shielding of protons by the phenyl nucleus situated in derivatives *Ic* and *IIc* as described by formulae *A* and *B*, respectively. These conformers are stabilized by dipole–dipole interactions



A



B

and therefore we neglect other rotamers arising by rotation of the 1-methylphenylethyl group about the C-2—C-8 bond[7–9]. The assumption that the studied protons are shielded by the aromatic nucleus has been verified by measurement of compounds *Ic* and *Vc* in hexadeuterobenzene which forms complexes with electron-deficient groups[10]. For compound *Vc* the difference between the δ values in deuterochloroform and hexadeuterobenzene is considerable ($\Delta\delta$ = 1·00 ppm) whereas for *Ic* it is negligible ($\Delta\delta$ = 0·10 ppm) because in the preferred conformation *A* the shielding of the glyoxylate proton is so great that the effect of hexadeuterobenzene is practically negligible (Table III). For glyoxylate *IIIc* and other derivatives of alcohol *IIIa* the upfield shift of the above-mentioned protons is not so pronounced. This relates to the axial position of the groups –OR and equatorial position of the 1-methyl-1-phenylethyl group. Therefore, no sandwich structure like in conformations *A* or *B*

TABLE I

Comparison of ^{1}H NMR chemical shifts (δ, ppm) of selected protons in alcohols *Ia*—*IIIa* with those observed after treatment with trichloroacetyl isocyanate (TAI)

Proton	δ, ppm			$\Delta\delta^a$, ppm		
	Ia	*IIa*	*IIIa*	*Ia*	*IIa*	*IIIa*
H-1	3·53	3·76	3·83	+1·30	+1·28	+1·19
H-7	0·87	0·91	1·11	+0·03	+0·09	−0·11
H-9	1·29	1·30	1·38	+0·04	−0·06	−0·01
H-10	1·41	1·42	1·40	0	−0·06	−0·02

[a] Change in the chemical shift of the given proton after addition of TAI.

TABLE II

Amounts of compound *IV* formed in azeotropic esterification of alcohols with bromoacetic acid

Alcohol	*p*-TsOH.H_2O, mole%	*IV*, %
Ia	5	traces
Ia	12	12
IIa	0·8	5·7
IIIa	1·2	82

TABLE III

Chemical shifts of proton signals (δ, ppm) in ^{1}H NMR spectrum of the ester part of compounds *I*—*III* and *V*

Derivative	*I*	*II*	*III*	*V*
b, R = $CONHC_6H_5$	5·30	5·42	6·23	6·60
c, R = COCHO	8·40 (8·30[a])	8·50	9·18	9·40 (8·40[a])
d, R = $COCH_2Br$	3·00	3·06	3·63	3·80
e, R = $COCH_2ONO_2$	—	4·05	4·70	—

[a] Measured in C_6D_6.

is possible. This arrangement is assumed[3,4,9] to be the cause of the marked stereodifferentiation in the case of the alcohols *Ia* and *IIa*. For this reason we do not expect a considerable asymmetric induction in reactions of derivatives of alcohol *IIIa*.

EXPERIMENTAL

Melting points (measured on a Kofler block) and boiling points are uncorrected. The reaction course was monitored by thin-layer chromatography (TLC) on Silufol UV (Kavalier). Column chromatography was performed on silica gel "Herrmann" (Köln-Ehrenfeld). NMR spectra were measured on a Tesla BS-467 (^{1}H at 60 MHz) and a Varian XL-200 (^{1}H at 200 MHz, ^{13}C at 50·31 MHz) instrument in deuterochloroform with tetramethylsilane as internal standard. Chemical shifts (in ppm) and coupling constants (in Hz) were obtained by first order analysis. The in situ acylations with trichloroacetyl isocyanate (TAI) were carried out by addition of a small amount of TAI into a solution of the compound in an NMR cell. IR spectra were measured on a UR 20 spectrometer (Carl Zeiss, Jena) and optical rotations on a Perkin–Elmer 141 polarimeter. Mass spectra were obtained with a ZAB EQ spectrometer (VG, Great Britain) at 70 eV. HPLC analyses were performed on an HP 1090 (Hewlett–Packard) instrument combined with an HP 85B microcomputer. The data were evaluated using a DAD UV-detector with an 8-channel integrator DPU. Compounds were separated on four 150 × 3·2 (i.d.) mm columns (connected in series) packed with Separon SIX, particle size 5 μm. Flow rate 0·5 ml/min, mobile phase light petroleum containing 2·5% of ether and 0·05% of ethanol.

Phenylcarbamates *Ib*, *IIb* and *IIIb*

A mixture of stereoisomeric alcohols *Ia*, *IIa* and *IIIa* (193 g, 830 mmol; 77 : 7·5 : 15·5 as determined by column chromatography on silica gel; prepared by the known procedure[2] from (*R*)-(+)-pulegone), phenyl isocyanate (110 g, 920 mmol), 4-dimethylaminopyridine (3 g) and benzene (750 ml) was heated to 70—75°C for 23 h. After cooling to room temperature, the reaction mixture was washed successively with water, saturated sodium hydrogen carbonate solution, 10% sodium hydroxide and water, and dried over sodium sulfate. Evaporation of the solvent and addition of hexane (300 ml) yielded a crude mixture of carbamates *Ia* and *IIb* (165 g). Chromatography of the mother liquors on silica gel (600 g) in light petroleum with 5% of ether afforded phenylcarbamate *IIIb* (16 g); $[\alpha]_D^{20}$ −18·9° (*c* 0·22, ethanol). For $C_{23}H_{29}NO_2$ (351·2) calculated: 78·59% C, 8·32% H, 3·99% N; found: 78·84% C, 8·60% H, 3·96% N. ^{1}H NMR spectrum: 1·00 d, 3 H (H-7, J(7, 5) = 6·6); 1·39 s, 3 H (H-9); 1·40 s, 3 H (H-10); 5·00 m, 1 H (H-1); 6·23 bs, 1 H (NH); 6·8—7·5 m, 10 H (arom. H). IR spectrum: 3 445 (NH); 1 740, 1 558, 1 541, 1 215 (O=CON); 1 606, 695 (N-atom); 703 (C-arom).

The mixture of carbamates *Ib* and *IIb* was twice crystallized from hexane to give phenylcarbamate *Ib* (135 g); m.p. 105—106·5°C, $[\alpha]_D^{20}$ +4·00° (*c* 0·95, ethanol). For $C_{23}H_{29}NO_2$ (351·2) calculated: 78·59% C, 8·32% H, 3·99% N; found: 78·55% C, 8·38% H, 3·92% N. ^{1}H NMR spectrum: 0·89 d, 3 H (H-7, J(7, 5) = 6·5); 1·22 s, 3 H (H-9); 1·31 s, 3 H (H-10); 4·67 dt, 1 H (H-1, J(1a, 2a) = J(1a, 6a) = 10·7, J(1a, 6e) = 4·3); 5·30 bs, 1 H (NH); 6·93—7·35 m, 10 H (arom. H). IR spectrum: 3 425(NH), 1 725 (C=O).

The mother liquors were dissolved in light petroleum (b.p. 45—60°C) and the solvent was allowed to evaporate slowly. Two types of crystals were obtained: well-developed orthogonal crystals of phenylcarbamate *Ib* and long needles of carbamate *IIb*. The crystals were mechanically separated and crystallized from light petroleum. This procedure gave 12·9 g of phenylcarbamate

IIb, m.p. 108–110·5°C, $[\alpha]_D^{20}$ +32·0° (*c* 0·41, ethanol). For $C_{23}H_{29}NO_2$ (351·2) calculated 78·59% C, 8·32% H, 3·99% N; found: 78·34% C, 8·36% H, 3·88% N. ^{1}H NMR spectrum 1·02 d, 3 H (H-7, *J*(7, 5) = 7·3); 1·25 s, 3 H (H-9); 1·35 s, 3 H (H-10); 4·93 td, 1 H (H-1 *J*(1a, 2a) = *J*(1a, 6a) = 10, *J*(1a, 6e) = 4·3); 5·42 bs, 1 H (NH); 6·90–7·40 m, 10 H (arom. H), IR spectrum: 3 440, 3 430 (NH), 1 736 (C=O).

The purity of the obtained substances was checked by HPLC on a 250 × 4·3 (i.d.) mm HP column packed with SIL 100·5 μm; mobile phase hexane with 1% of ethyl acetate, flow rate 0·8 ml/min. Retention times: *Ib* 7·5 min, *IIb* 8·1 min, *IIIb* 11·9 min.

(1*R*,2*S*,5*R*)-(–)-2-(1-Methyl-1-phenylethyl)-5-methylcyclohexan-1-ol ((–)-8-phenylmenthol) (*Ia*)

Phenylcarbamate *Ib* (12 g, 33 mmol) was added to a solution of sodium ethoxide (prepared from 8·5 g of sodium and 150 ml of anhydrous ethanol) and the reaction mixture was refluxed for 28 h. After cooling and neutralization with 10% hydrochloric acid, the ethanol was evaporated, the residue was extracted with dichloromethane (80 ml) and ether (2 × 80 ml) and the combined extracts were dried over magnesium sulfate. Evaporation of the solvents and distillation gave 7·4 g (97%) of product *Ia*, b.p. 85·5°C/1·3 Pa, $[\alpha]_D^{20}$ –24·7° (*c* 1·2, ethanol). For the enantiomeric alcohol reported[2] $[\alpha]_D^{20}$ +26·3° (*c* 2·3, ethanol). For $C_{16}H_{24}O$ (232·4) calculated: 82·70% C, 10·41% H; found: 83·17% C, 10·64% H. ^{1}H NMR spectrum: 0·87 d, 3 H (H-7, *J*(7, 5) = 6·6); 1·29 s, 3 H (H-9); 1·41 s, 3 H (H-10); 3·53 dd, 1 H (H-1, *J*(1a, 2a) = 9·5, *J*(1a, 6a) = 10·7, *J*(1a, 6e) = 4·0); 7·10–7·48 m, 5 H (arom. H).

(–)-8-*Phenylmenthyl bromoacetate* (Id): (–)-8-Phenylmenthol (6·9 g, 30 mmol) was azeotropically esterified by heating with bromoacetic acid (5·15 g, 37 mmol) in benzene (50 ml) in the presence of 5 mol% of *p*-toluenesulfonic acid for 13·5 h. Distillation afforded 9·1 g (87%) of the product, b.p. 145–150°C/9·2 Pa, $[\alpha]_D^{20}$ –21·1° (*c* 0·13, ethanol). For $C_{18}H_{25}O_2Br$ (353·3) calculated: 61·19% C, 7·13% H, 22·62% Br; found: 61·10% C, 7·15% H, 22·99% Br. ^{1}H NMR spectrum: 0·88 d, 3 H (H-7, *J*(7, 5) = 5·0; 1·22 s, 3 H (H-9); 1·32 s, 3 H (H-10); 3·00 s, 2 H (CH_2Br); 4·90 td, 1 H (H-1, *J*(1a, 2a) = *J*(1a, 6a) = 10·0, *J*(1a, 6e) = 4·0); 7·10–7·40 m, 5 H (arom. H).

An experiment with greater amount (12 mole %) of *p*-toluenesulfonic acid afforded, in addition to bromoacetate *Id*, a mixture of nonpolar compounds (14%), containing 73% of racemic 1-(1-methyl-1-phenylethyl)-4-methylcyclohexene (*IV*) which was isolated by column chromatography. B.p. 151–152°C/200 Pa. For $C_{16}H_{22}$ (214·2) calculated: 89·65% C, 10·35% H; found: 89·64% C, 10·19% H. ^{1}H NMR spectrum: 0·92 d, 3 H (H-7, *J*(7, 4) = 6·1); 1·35 s, 3 H (H-9); 1·39 s, 3 H (H-10); 5·66 m, 1 H (H-2); 7·08–7·30 m, 5 H (arom. H).

(–)-8-*Phenylmenthyl glyoxylate* (Ic): A mixture of bromoacetate *Id* (8 g, 22·6 mmol), silver nitrate (8·7 g) and acetonitrile (60 ml) was allowed to stand for 8 days. The separated silver bromide was removed by filtration, the crude nitrate was dissolved in dimethyl sulfoxide (50 ml) and fused sodium acetate (1·85 g, 22·6 mmol) was added into the reaction mixture. After stirring for 2 h, the reaction mixture was poured on ice, extracted with ether (5 × 100 ml) and the solution was dried over magnesium sulfate. The solvent was evaporated and the residue was distilled to give 5·0 g (67%) of product, b.p. 135–140°C/40 Pa. For $C_{18}H_{24}O_3$ (288·4) calculated: 74·96% C, 8·39% H; found: 74·70% C, 8·22% H. For hydrate $[\alpha]_D^{20}$ –169° (*c* 0·51, benzene). ^{1}H NMR spectrum: 0·88 d, 3 H (H-7, *J*(7, 5) = 5·0); 1·23 s, 3 H (H-9); 1·30 s, 3 H (H-10); 4·95 td, 1 H (H-1, *J*(1a, 2a) = *J*(1a, 6a) = 11·0, *J*(1a, 6e) = 4·0); 7·00–7·35 m, 5 H (arom. H); 8·40 s, 1 H (CHO).

(1*S*,2*R*,5*R*)-(+)-(1-Methyl-1-phenylethyl)-5-methylcyclohexan-1-ol
((+)-8-Phenylisomenthol) (*IIa*)

Phenylcarbamate *IIb* (7·6 g, 22 mmol) was added to a solution of sodium ethoxide (prepared from 5·0 g of sodium and 100 ml of anhydrous ethanol) and the mixture was refluxed for 15 h. Chromatography of the crude product followed by distillation afforded alcohol *IIa* (4·9 g, 97%), b.p. 135–138°C/20 Pa; $[\alpha]_D^{20}$ +19·0° (*c* 1·22, ethanol). Spectral data of the product agreed with those published[4].

(+)-8-*Phenylisomenthyl bromoacetate* (IId): Azeotropic esterification of (+)-8-phenylisomenthol (5·1 g, 22 mmol) afforded 6·03 g (80%) of product *IId*, $[\alpha]_D^{20}$ −41·75° (*c* 0·41, ethanol). For $C_{18}H_{25}O_2Br$ (353·3) calculated: 61·19% C, 7·13% H, 22·62% Br; found: 60·86% C, 7·04% H, 22·69% Br. ^{1}H NMR spectrum: 0·95 d, 3 H (H-7, *J*(7, 5) = 6·8); 1·22 s, 3 H (H-9); 1·32 s, 3 H (H-10); 3·06 s, 2 H (CH_2Br); 5·0 td, 1 H (H-1, *J*(1a, 2a) = (1a, 6a) = 9·3, *J*(1a, 6e) = 5·5); 7·23 bs, 5 H (arom. H). IR spectrum: 1 701, 1 270 (OC=O); 703 (arom.).

(+)-8-*Phenylisomenthyl glyoxylate* (IIc): Bromoacetate *IId* (5·50 g, 16·3 mmol) was converted by the above-described procedure into 5·0 g of crude glyoxylate hydrate; $[\alpha]_D^{20}$ −21·9° (*c* 0·22, benzene). ^{1}H NMR spectrum: 0·96 d, 3 H (H-7, *J*(7, 5) = 6·5); bs, 6 H (H-9, H-10); 5·00 m, 1 H (H-1); 7·25 bs, 5 H (arom. H); 8·50 s, 1 H (CHO).

(1*R*,2*R*,5*R*)-(−)-2-(1-Methyl-1-phenylethyl)-5-methylcyclohexan-1-ol
((−)-8-Phenylneoisomenthol) (*IIIa*)

Phenylcarbamate *IIIb* (11·5 g, 33 mmol) was converted into the alcohol *IIIa* (4·0 g) as described for compound *Ib* except that the transesterification was repeated to increase the low yield. B.p. 104–105°C/13 Pa; $[\alpha]_D^{20}$ −44·85° (*c* 1·32, ethanol). For $C_{16}H_{24}O$ (232·4) calculated: 82·70% C, 10·41% H; found: 82·85% C, 10·28% H. ^{1}H NMR spectrum: 1·11 d, 3 H (H-7, *J*(7, 5) = 7·3); 1·38 s, 3 H (H-9); 1·40 s, 3 H (H-10); 3·83 bs, 1 H, (H-1, $\sum J(1,2,6) = 9$; 7·15–7·45 m, 5 H (arom. H). ^{13}C NMR spectrum: 16·36 t (C-3); 21·24 q (C-7); 25·55 q (C-9); 26·40 d (C-5); 27·70 q (C-10); 32·72 t (C-4); 40·38 s (C-8); 40·39 t (C-6); 52·59 d (C-2); 69·10 d (C-1); 125·44 d; 126·15 d, 127·94 d, 149·80 s (arom. C).

(−)-8-*Phenylneoisomenthyl bromoacetate* (IIId): Azeotropic esterification of alcohol *IIIa* (3·5 g) afforded, in addition to compound *IV* (2·65 g, 82%), only minor amount (0·78 g, 15%) of the product *IIId*; $[\alpha]_D^{20}$ +4·33° (*c* 0·39, ethanol). For $C_{18}H_{25}O_2Br$ (353·3) calculated: 61·19% C, 7·13% H, 22·62% Br; found: 61·01% C, 7·25% H, 22·20% Br. ^{1}H NMR spectrum: 0·98 d, 3 H (H-7, *J*(7, 5) = 6·8); 1·33 s, 6 H (H-9, H-10); 3·63 s, 2 H (CH_2Br); 4·93 m, 1 H (H-1); 7·33 bs, 5 H (arom. H).

(−)-8-*Phenylneoisomenthyl glyoxylate* (IIIc): Bromoacetate *IIId* (0·60 g, 1·8 mmol) was converted into glyoxylate *IIIc* (as hydrate, 0·33 g, 60·5%) as described for *Ic*; $[\alpha]_D^{20}$ −39·8° (*c* 0·24, benzene). ^{1}H NMR spectrum: 1·00 d, 3 H (H-7, *J*7, 5) = 7·5); 1·35 bs, 6 H (H-9, H-10); 4·97 m, 1 H (H-1); 7·24 bs, 5 H (arom. H); 9·19 s, 1 H (CHO).

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