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Optical Activity and Absolute Configuration of 2,3 : 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene Derivatives

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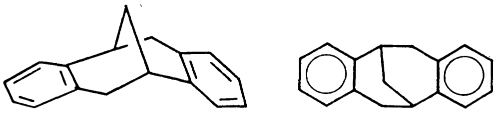
2,3 : 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-diol was synthesized and resolved *via* (−)-menthoxyacetate. Several kinds of optically active derivatives with the same absolute configuration were prepared from the (−)-diol and their chiroptical properties were recorded. The absolute configuration of this series of compounds was determined to be 1*R*, 5*R* by a chemical correlation with (*R*)-(−)-3-phenylbutanoic acid *via* (−)-1,3-diphenylglutaric acid and (−)-2,4-diphenylpentane.

A part of the present authors (members of Faculty of Science) has studied the relationship between structure and chiroptical properties of various triptycene derivatives1) and related compounds.2) The absolute configuration of optically active 2,5-dimethoxy-7- or 8-substituted or 2,7-disubstituted triptycenes1) and 1,5-disubstituted 9,10-dihydro-9,10-etheno- and ethanoanthracenes2) have been studied by either or both X-ray analyses and chemical correlations. However, exciton theoretical analyses of their CD spectra led to antipodal absolute configurations.2,3)

The group of title compounds, 2,3: 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (XII) and its derivatives, having fairly rigid and well-defined strainless cage structure, can be regarded as one of the most appropriate dissymmetric compounds for the study of relationship between structure and optical activity.

The other authors (members of Faculty of Engineering Science) have studied on the stereochemistry of cage compounds such as twistane and related compounds,4) and have been interested in the preparation of 2,3: 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (XII) as a precursor of optically active dibenzotwistane.

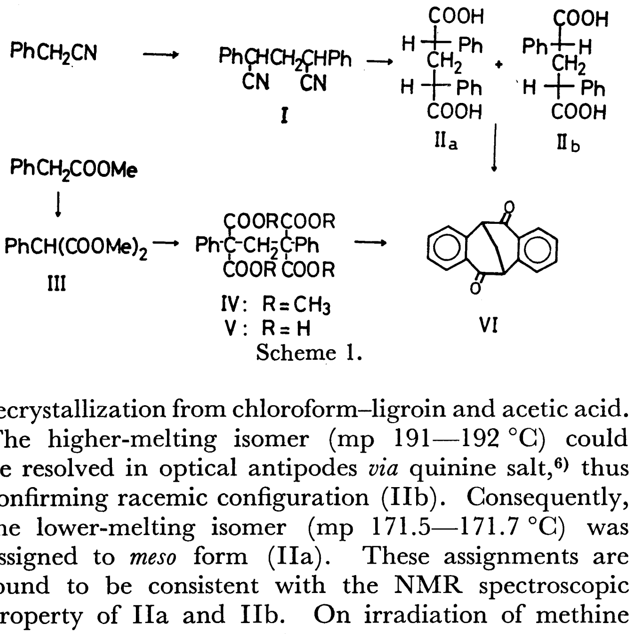


XII

The present paper deals with the synthesis, optical resolution and determination of absolute configuration by chemical means of dibenzobicyclononadiene (XII) and its derivatives.

Results and Discussion

Synthesis and Optical Resolution. The route of synthesis which followed a reported method5) with considerable modification was outlined in Scheme 1. 1,3-Diphenylglutaronitrile (I) was prepared as a mixture of racemic and *meso* forms by the reaction of phenylacetonitrile with methylene iodide and powdered sodium hydroxide. The mixture of I was converted into a mixture of (±)- and *meso*-1,3-diphenylglutaric acids by an alkaline hydrolysis. (±)- and *meso*-1,3-Diphenylglutaric acids could be separated by repeated fractional recrystallization from chloroform–ligroin and acetic acid. The higher-melting isomer (mp 191—192 °C) could be resolved in optical antipodes *via* quinine salt,6) thus confirming racemic configuration (IIb). Consequently, the lower-melting isomer (mp 171.5—171.7 °C) was assigned to *meso* form (IIa). These assignments are found to be consistent with the NMR spectroscopic property of IIa and IIb. On irradiation of methine protons, triplet of methylene protons in the spectrum



Scheme 1.

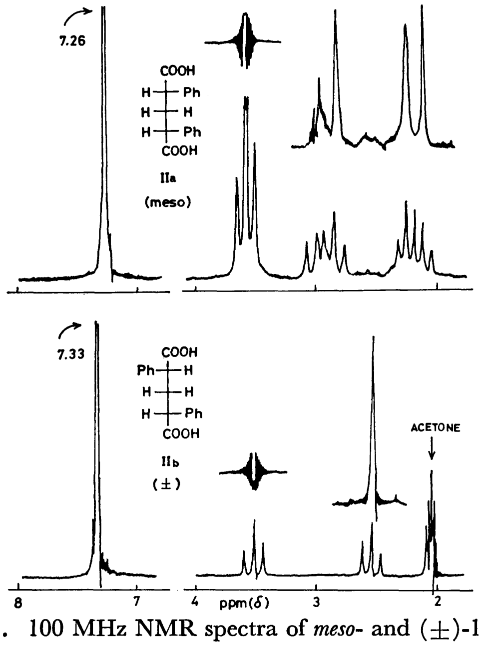
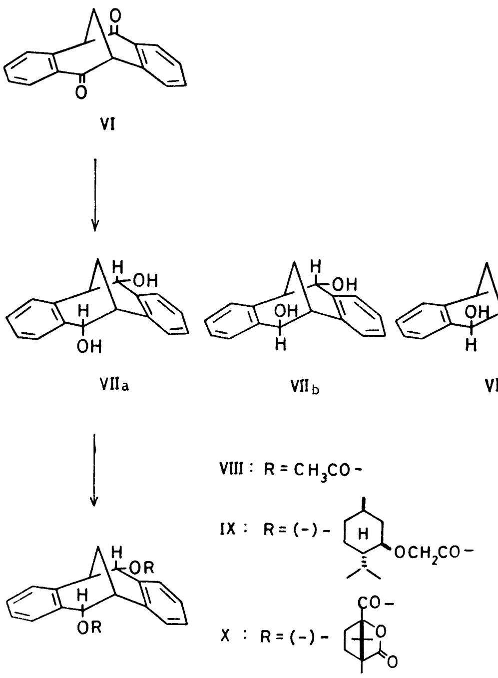


Fig. 1. 100 MHz NMR spectra of *meso*- and (±)-1,3-diphenylglutaric acids (IIa in $CDCl_3$ and IIb in acetone-d_6).

of higher-melting isomer collapsed to a singlet and multiplet of methylene protons of lower-melting isomer changed to double doublets (Fig. 1). These results indicate that the methylene protons in the higher-melting and in the lower-melting isomers situate in a magnetiacally equivalent and in an unequivalent environments, respectively. Consequently, the higher-melting isomer has a C_2 axis of symmetry passing through the methylene carbon, that is characteristic of racemic form (IIb), and the lower-melting isomer has a mirror symmetry of *meso* form (IIa). Both forms of 1,3-diphenylglutaric acid were converted into cyclic diketone (VI) with concentrated sulfuric acid. Diastereomeric mixture of the acids obtained by alkaline hydrolysis of a mixture of diastereomers of nitrile could be cyclized to the diketone (VI) directly without purification or fractionation under the same reaction conditions.

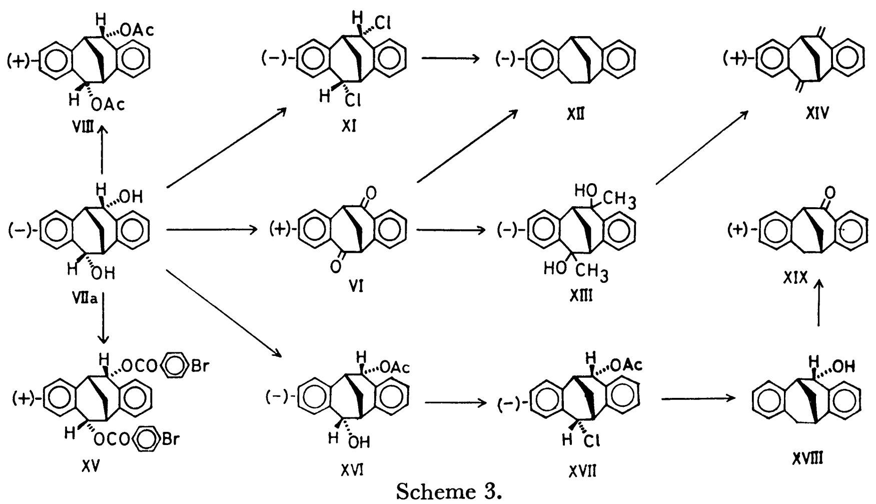
The same diketone (VI) could be prepared from methyl phenylacetate in a moderate yield *via* methyl phenylmalonate (III), methyl 1,3-diphenyl-1,1,3,3-tetracarboxylate (IV) and its hydrolysis product. The hydrolyzate consisting of mainly V was treated with polyphosphoric acid to give diketone (VI). From the diketone (VI) an identical glycol was obtained stereospecifically either by catalytic hydrogenation over platinum oxide catalyst or by reduction with lithium aluminum hydride in tetrahydrofuran. As shown in Scheme 2, three isomeric structures (VIIa,b,c) are possible in the glycol. But the formation of VIIb is excluded on the basis of NMR spectrum of the glycol and its diacetate which is prepared by a direct acetylation of the reduction product without any fractionation. The diacetate (VIII) shows doublet (J=6 Hz, 2H) at τ 3.73 (carbinyl protons) and a sharp singlet (6H) at τ 7.78 (methyl protons of acetyl groups). Therefore, the most probable structure seemed to be the one (VIIa) in which hydrogen atoms are delivered from the sterically less hindered, methano-bridge, side to generate two pseudo-axial hydroxyl groups. The inference was confirmed by the X-ray crystal structure analysis carried out on a single crystal of (+)-bis-*p*-bromobenzoate of (—)-glycol.2)



Scheme 2.

The optical resolution was carried out with (—)-methoxyacetyl chloride. Crude menthoxyacetate prepared from (±)-glycol (VIIa) and the chloride in pyridine was fractionally recrystallized eleven times from benzene–ethanol to give optically pure ester of (—)-enantiomer. The process of resolution could be traced by both polarimetry and IR spectroscopy. Optically pure menthoxyacetate was hydrolyzed by ethanolic potassium hydroxide to obtain optically pure (—)-glycol (VIIa). Attempts of optical resolution *via* camphanate showed poor reproducibility and the highest optical purity of (—)-glycol (VIIa) was 79.8%.

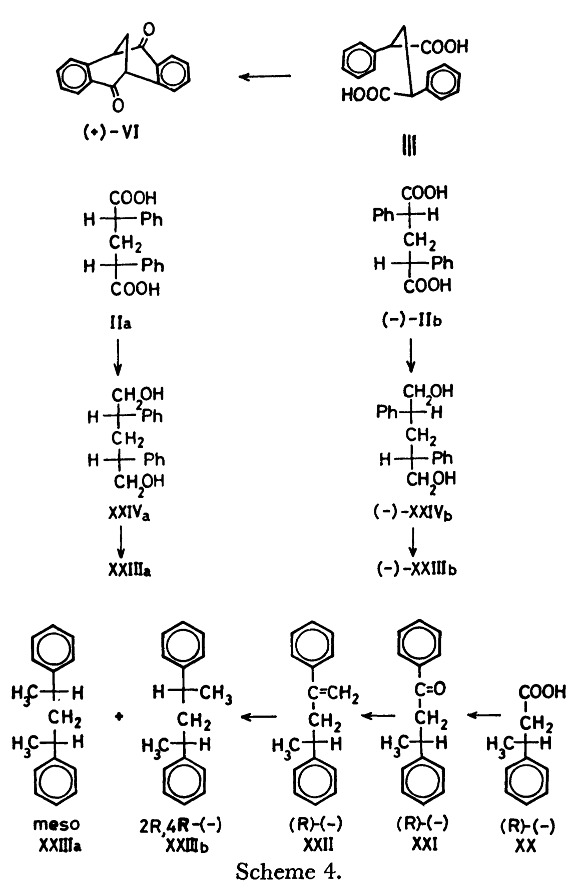
Starting from (—)-glycol (VIIa) several optically active derivatives with an identical configuration were prepared (Scheme 3). (—)-Glycol (VIIa) was oxidized by chromium trioxide-pyridine complex or by chromium trioxide in acetic acid to yield (+)-diketone (VI). The Clemmensen reduction of (+)-diketone (VI) yielded (—)-hydrocarbon (XII) in 33% yield. The same hydrocarbon was obtained quantitatively by lithium aluminum hydride reduction of (—)-dichloride



Scheme 3.

(XI) in tetrahydrofuran which is prepared from (−)-glycol (VIIa) by the usual method. The reaction of (+)-diketone (VI) with methylmagnesium iodide yielded (−)-*tert*-glycol (XIII). The configuration of carbinyl carbons could not be decided yet, but the Grignard reagent probably attacked from the side of methano-bridge to give pseudo-axial hydroxyl groups just as in the case of reduction of diketone (VI). Dehydration of (−)-*tert*-glycol (XIII) with phosphoryl chloride in pyridine gave (+)-diene (XIV) with styrene type chromophores. (−)-Glycol (VIIa) was converted into (+)-diacetate (VIII) and (+)-bis-*p*-bromobenzoate (XV) with acetic anhydride and *p*-bromobenzoyl chloride in pyridine, respectively. A single crystal of (+)-XV was submitted to the X-ray crystal structure analysis. (−)-Glycol (VIIa) was converted into (−)-monoacetate (XVI) with acetic anhydride in pyridine under a milder condition. (−)-Monoacetate (XVI) was treated with thionyl chloride in benzene to yield (−)-chloro-acetate (XVII). Lithium aluminum hydride reduction of (−)-XVII in tetrahydrofuran yielded alcohol (XVIII) which was oxidized without purification to (+)-monoketone (XIX) by the Jones reagent.

Absolute Configuration and Optical Activity. The absolute configurations of the compounds of dibenzobicyclo[3.3.1]nonadiene series were determined by chemical correlation with (*R*)-(−)-3-phenylbutanoic acid (XX).7) The route was outlined in Scheme 4. (−)-1,3-Diphenylglutaric acid (IIb) was converted into (+)-diketone (VI) on dehydrative cyclization with concentrated sulfuric acid at 85 °C. (−)-2,4-Diphenylpentane-1,5-diol (XXIVb) was obtained by lithium aluminum hydride reduction of (−)-diphenylglutaric acid (IIb). Bis-methanesulfonate of (−)-XXIVb was reduced with lithium aluminum hydride in refluxing tetrahydrofuran to yield (−)-2,4-diphenylpentane (XXIIIb). *meso*-2,4-Diphenylpentane (XXIIIa) was obtained with essentially the same sequence of reactions from *meso*-1,3-diphenylglutaric acid (IIa). On the other hand, (*R*)-(−)-3-phenylbutanoic acid (XX) was converted into acid chloride and treated with diphenyl cadmium to give (*R*)-(−)-3-phenylbutyrophenone (XXI). The reaction of methylenetriphenylphosphorane with (*R*)-(−)-XXI gave (*R*)-(−)-2,4-diphenyl-1-pentene (XXII). Catalytic hydrogenation of (*R*)-(−)-XXII over the Adams catalyst yielded almost equimolar mixture of *meso*- and (*R*)-(−)-2,4-diphenylpentane (XXIIIa and XXIIIb) which were analyzed and identified by NMR spectroscopy.



Scheme 4.

(−)-2,4-Diphenylpentane obtained from (−)-1,3-diphenylglutaric acid (IIb) showed an identical CD spectrum with that of the mixture of XXIIIa and (*R*)-(−)-XXIIIb obtained from (*R*)-(−)-XX after correction of optical purity.

From the combined results of the above-mentioned sequence of reactions, it can be clearly concluded that all of optically active compounds shown in Scheme 4 have (*R*)-absolute configuration. The conclusion was consistent with the result of X-ray analysis carried out on a single crystal of (+)-2,3:6,7-dibenzobicyclo[3.3.1]-nona-2,6-diene-4,8-diol-bis-*p*-bromobenzoate (XV).8)

(+)-Diketone (VI) showed a strong positive CD band with well-developed fine structure in the longest wavelength region and a beautiful positive-negative couplet in 37000—44000 cm^{-1} region (Fig. 2). The longest wavelength band can be assigned to $n \rightarrow \pi^*$ transition of conjugated ketone on the basis of solvent effect and a considerably large anisotropic factor (Table 1). The strong couplet centered at near 40000 cm^{-1} was attri-

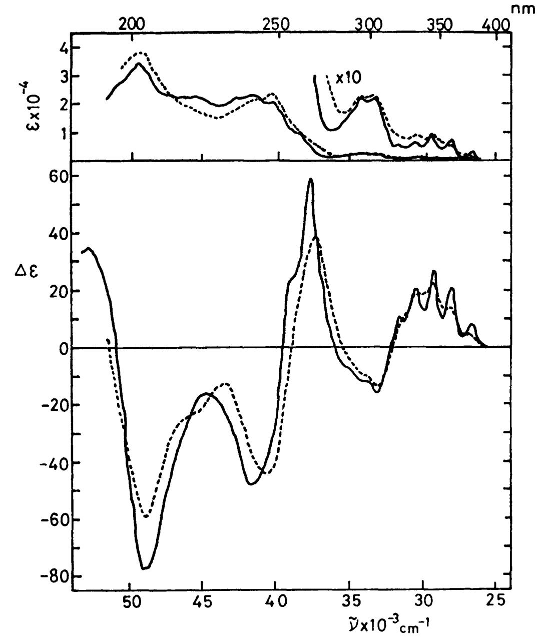


Fig. 2. UV and CD spectra of (+)-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione (VI) in cyclohexane (——) and in 99% ethanol (······).

TABLE 1. UV SPECTRA OF VI AND CD SPECTRA OF (+)-VI, (−)-VIIa, (−)-XII AND (+)-XIV

UV spectra of VI

Solvent	λ_{max} in nm (ε) * Shoulder
Ethanol	372*(200), 355(580), 340(900), 329(880), 300(2290), 293*(2230), 249(23410), 243(21930), 207*(31720), 203.5(38060)
Cyclohexane	376(310), 358(740), 342(940), 328(740), 315(540), 301(2250), 292(2190), 260*(9760) 249(20780), 241(22640), 236(22100), 221*(22140), 203(34420), 197*(26550)

CD spectra

Compound	Solvent	λ_{max} in nm ($\Delta\varepsilon$) * Shoulder
(+)-VI	Cyclohexane	377*(+7.9), 375(+8.2), 357(+20.2), 342(+26.5), 328.5(+20.2), 316.5 (+10.0), 302(−15.9), 292.5(−11.5), 280(−3.2), 265.5(+58.6), 257* (+23.8), 248*(−36.0), 241(−48.2), 204(−77.6), 190(+34.8)
	Ethanol	372(+4.7), 354(+13.7), 340(+22.1), 329(+19.1), 318*(+9.7), 302 (−13.3), 290*(−8.0), 268(+38.4), 246(−44.2), 222*(−21.3), 205(−58.9)
(−)-VIIa	Ethanol	272(+0.36), 264(−0.51), 257*(−0.42), 251*(−0.31), 219*(−31.35), 205 (−86.01), 195(+22.30)
(−)-XII	Isooctane	273(+2.7), 266(+2.6), 260(+1.6), 254*(+0.9), 246*(+0.4), 226(−0.8), 222(+2.5), 218 (−8.6), 214 (−9.0), 197(−82.1)
(+)-XIV	Isooctane	299(+1.9), 291(+2.3), 260*(+65.1), 245(+83.2), 227*(−62.7), 216 (−152.4), 203(−78.6)
	Ethanol	298(+1.8), 290*(+2.2), 247(+66.0), 227*(−51.4), 215(−127.3), 205* (−78.2)

buted to an exciton couplet due to the interaction of two conjugated phenyl ketone chromophores. This compound (VI) is unique in the sense that it might be regarded as an α,β- and β,γ-unsaturated ketones at the same time. In applying the octant rule, a different conclusion came out by considering which of α,β- or β,γ-unsaturation contributed stronger to the observed optical activity.[9] It is easily shown by the Dreiding molecular model that molecular framework of this ketone (VI) brings about closely similar spatial disposition of carbonyl and phenyl groups as those in dimethylbenzsuberone and related typical β,γ-unsaturated ketone (Fig. 3).[10] Observed highly positive rotational strength of n→π* transition is consistent with 1*R*,5*R* absolute configuration for (+)-diketone (VI) (Fig. 3). On the other hand, if the diketone (VI) is considered to be an α,β-unsaturated ketone, a small negative n→π* Cotton effect may be expected for the above 1*R*,5*R* configuration on the ground of fairly good coplanarity of phenyl-carbonyl grouping[11] being the dihedral angle of distortion less than 10 degrees as estimated from the Dreiding model (Fig. 4). We concluded that the contribution of β,γ-unsaturation is predominant and that of α,β-unsaturation is negligibly small in this ketone (VI).

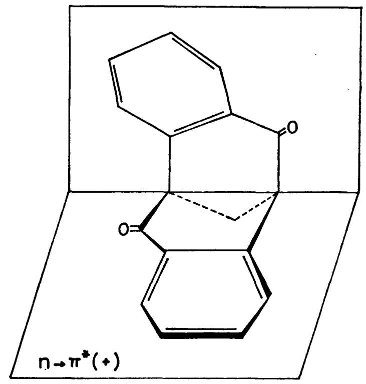


Fig. 3. Octant projection of (+)-1*R*,5*R*-2,3 : 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione (VI) as regarded as a β,γ-unsaturated ketone.

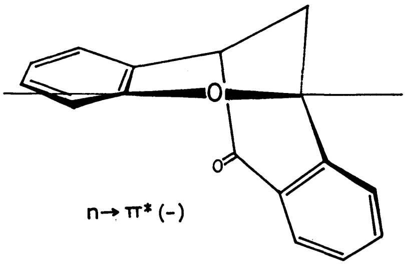


Fig. 4. Octant projection of (+)-1*R*,5*R*-2,3 : 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione (VI) as regarded as an α,β-unsaturated ketone.

With regard to the couplet in the $^1B_{1u}$ type π→π* absorption region of (+)-diketone (VI), we assumed an exciton coupling of C_2 symmetry and the same 1*R*,5*R* configuration as shown in Fig. 5 could be deduced.

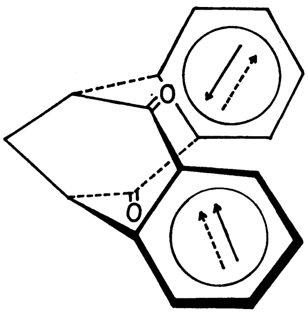


Fig. 5. Exciton coupling of $^1B_{1u}$ band of (+)-1*R*,5*R*-2,3: 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione (VI).

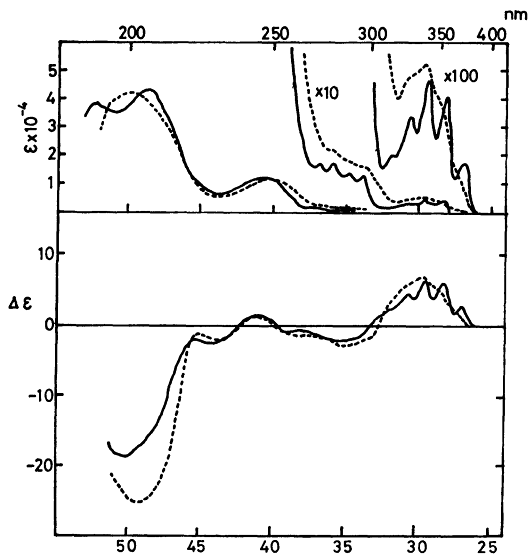


Fig. 6. UV and CD spectra of (+)-2,3 : 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4-one (XIX) in cyclohexane (——) and in 99% ethanol (······).

The positive and negative bands can be assigned to transitions from ground to excited states with A and B symmetry, respectively, based on usual calculations. These assignments are consistent with intensity relationship of the corresponding isotropic absorption band and the absence of a CD couplet in the n→π* band region of (+)-monoketone (XIX) (Fig. 6). In the region of $^1B_{2u}$ type absorption, the situation is not so clear. A small positive-negative couplet is similarly anticipated for the same 1*R*,5*R* absolute configuration. Observed result seems to be consistent with this prediction, if we consider that long wavelength positive band is significantly overlapped with n→π* carbonyl band (*cf.*, solvent effect, Table 1 and Fig. 2). Combining the above-stated consistent results, we concluded that (+)-diketone (VI) has 1*R*,5*R* absolute configuration.

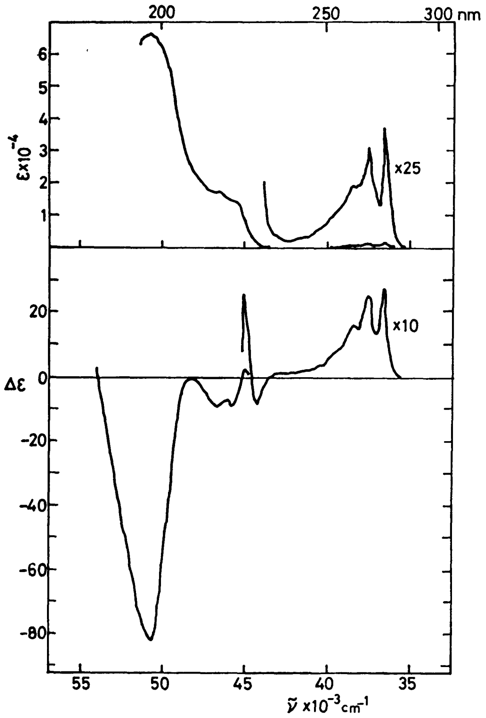


Fig. 7. UV and CD spectra of (−)-2,3 : 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (XII) in isooctane.

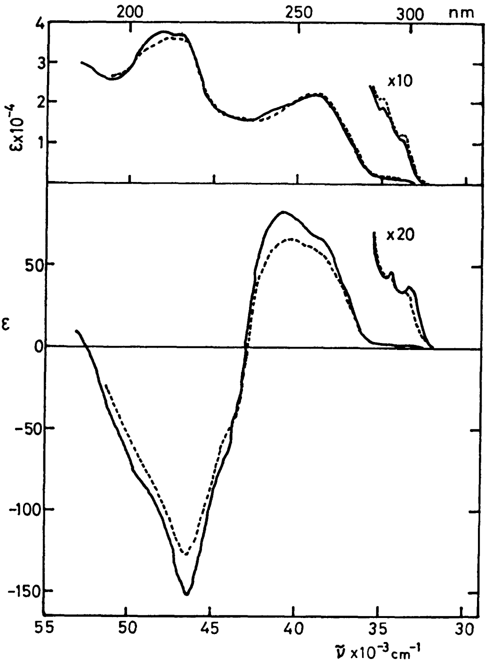


Fig. 8. UV and CD spectra of (+)-4,8-bis(methylene)-2,3 : 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (XIV) in isooctane (——) and in 99% ethanol (······).

The CD and electronic spectra of (−)-hydrocarbon (XII) are shown in Fig. 7. Complexity of the spectra might result from significant overlap of $^1B_{1u}$ and two degenerate $^1E_{1u}$ type bands and low absorption intensity of $^1B_{2u}$ band.

(+)-Diene (XIV) with styrene type chromophores showed a very interesting CD spectrum. In the π→π* spectral region, no couplet pattern could be observed (Fig. 8) in sharp contrast with (+)-diketone (VI). It is difficult to give a definite explanation, but one possible reason is that the direction of polarization of conjugation band of the styrene chromophore and position of its transition moments are considerably different from those of phenyl alkyl ketone.[12]

Experimental

The melting points were measured on a Mettler FP2 apparatus and a Shimadzu Kohfler micro hot stage, and are uncorrected. Purified and anhydrous solvents were used, unless otherwise stated. The IR spectra were obtained on a Hitachi EPI-2, EPI-G3 or a JASCO DS-301 spectrometers, electronic spectra on a Hitachi EPS-3T and a Zeiss PMQIIM4QIIId spectrometers, NMR spectra in deuteriochloroform, unless otherwise stated, on a Varian XL-100 or A-60D spectrometer using TMS as an internal standard and given in δ-unit. The optical rotations were obtained on a Yanagimoto ORD-185 spectropolarimeter or a Union Giken High Precision Polarimeter PM-71 or a JASCO DIP-SL polarimeter at 20 °C, unless otherwise stated. CD spectra were obtained on a JASCO J-20 spectrometer. Shoulders and inflections are denoted by an asterisk.

1,3-Diphenylglutaronitrile (I). Phenylacetonitrile (93.6 g, 0.799 mol), methylene iodide (107.2 g, 0.400 mol) and powdered sodium hydroxide (32.0 g, 0.800 mol) were mixed and heated to 165—170 °C for 30 min under stirring. Cooled mixture was diluted with water and extracted with ether. Combined organic layer was washed with water and concentrated undre reduced pressure. After volatile material had been removed by steam distillation (distillate, *ca.* 6 l), the residue was extracted with ether and dried over sodium sulfate. A black oil (66.1 g) obtained on concentration of the extract under reduced pressure was chromatographed on alumina (650 g) and fractions eluted with benzene (total 3.3 l) and benzene–ether (1: 1, total 1.5 l) were combined and concentrated under reduced pressure. The oily residue was crystallized from ethanol. Repeated recrystallization from the same solvent yielded analytically pure I as orange yellow crystals, mp 64.9—65.6 °C, IR (nujol mull): 2250 ($\nu_{C\equiv N}$) cm^{-1}, NMR (CCl$_4$): 7.33 (s, 10H, aromatic), 4.03, 3.63 (both t, J=8 Hz, 2H, methine), 2.33 (m, 2H, methylene).

The crude nitrile obtained by chromatography could be used directly for further reaction.

1,3-Diphenylglutaric Acid (II). Crude acid (II) obtained by an alkaline hydrolysis of the nitrile (I)[4] was converted into diethyl ester (see below). The purified ester was refluxed with 10% ethanolic potassium hydroxide. Colorless oil obtained on working up the reaction mixture crystallized gradually on standing, mp 147.5—163 °C (a mixture of *meso*- and *rac*-isomers), IR (Nujol mull): 1710 ($\nu_{C=O}$) cm^{-1}.

Diethyl 1,3-Diphenylglutarate. Crude carboxylic acid (II, 14.42 g) was refluxed with ethanol (100 ml) and concentrated sulfuric acid (5 ml). The reaction mixture was worked up as usual and the oily residue was distilled under reduced pressure to give pure ester, faintly yellow liquid (10.85 g, 62.8%), bp 182—186 °C/133 Pa, IR (neat): 1740, 1730 ($\nu_{C=O}$) cm^{-1}, NMR: 7.25, 7.23 (both s, 10H, aromatic), 3.88—4.33 (m, 4H, methylene of ethyl), 3.33—3.68 (m, 2H, methine), 2.58 (m, 2H, methylene), 1.17, 1.13 (both t, J=7 Hz, 6H, methyl).

meso- *and* rac-*1,3-Diphenylglutaric Acids (IIa and IIb).* Crude crystals of the acid mixture (29.7 g) were recrystallized from chloroform–ligroin. Crystals obtained (4.68 g) were recrystallized further three times from the same mixed solvent to yield colorless needles of pure racemate (IIb, 3.2 g), mp 191—192 °C, IR (Nujol mull): 1710*, 1690 ($\nu_{C=O}$) cm^{-1}, NMR (CD$_3$COCD$_3$): 7.26 (s, 10H, aromatic), 3.50 (t, of d, J=7 Hz and 1 Hz, methine), 2.52 (t, of d, J=7 Hz and 1 Hz, methylene).

Found: C, 71.70; H, 5.68%. Calcd for C$_{17}$H$_{16}$O$_4$: C, 71.82; H, 5.61%.

Crude crystals obtained by drying up the initial mother liquor *in vacuo* were recrystallized from 50% aqueous acetic acid. First crop of crystals enriched in racemate was removed by filtration. Water was added to the hot mother liquor till the mixture became 20% aqueous acetic acid solution. Precipitates obtained on cooling the mixture were recrystallized eight times from 20% aqueous acetic acid to yield pure *meso*-isomer (IIa, 1.224 g), mp 171.5—171.7 °C, IR (Nujol mull): 1710, 1700 ($\nu_{C=O}$) cm^{-1}, NMR: 7.26 (s, 10H, aromatic), 3.57 (dd, 2H, methine), 3.07—2.76 (q, 1H, methylene), 2.31—2.04 (q, 1H, methylene).

Found: C, 71.89; H, 5.66%. Calcd for C$_{17}$H$_{18}$O$_4$: C, 71.82; H, 5.67%.

Optical Resolution of rac-*1,3-Diphenylglutaric Acid (IIb).* The racemic acid (IIb, 1.204 g) dissolved in 99% ethanol (20 ml) was mixed with a 99% ethanol solution of quinine (1.374 g in 10 ml) and stood overnight at room temperature. Colorless crystals (1.578 g) deposited were collected and dried *in vacuo*, mp 215—219 °C. The mother liquor and washings were combined and concentrated under reduced pressure to give colorless residue (1.161 g).

The crystalline salt was decomposed by 3 M hydrochloric acid and extracted with ether. The extract was worked up in the usual way and concentrated under reduced pressure to yield (+)-acid (0.471 g, $[\alpha]_D$ +70.72 ° (*c* 0.2828, 99% EtOH). Enantiomeric (−)-acid (0.7068 g, $[\alpha]_D$ −48.16 ° (*c* 0.2824, 99% EtOH)) was obtained from the residue of mother liquor by the same procedure.

The quinine salt was found thermally unstable and seemed to be difficult to fractionate diastereomers by the usual recrystallization. Optically pure salt could be obtained by repetition of formation and decomposition of the quinine salt for six times at room temperature. The extent of resolution was checked by polarimetry of acid obtained from each mother liquor.

Optically pure salt (0.814 g), mp 219—223 °C (dec.), consisted of two molecules of quinine per a molecule of (+)-acid and contained one molecule of ethanol as a solvent of crystallization.

Found: C, 71.21; H, 7.21; N, 5.54%. Calcd for C$_{61}$H$_{76}$N$_4$O$_{10}$: C, 71.46; H, 7.47; N, 5.47%.

Optically pure (+)-1,3-diphenylglutaric acid (IIb, 0.238 g) was obtained from this salt, mp 197—198.5 °C (from chloroform–*n*-hexane), $[\alpha]_D$ +95.8 °, $[\alpha]_{546}$ +114.8 °, $[\alpha]_{436}$+204.2 ° $[\alpha]_{405}$ +260.1 °, $[\alpha]_{365}$ +375.7 ° (*c* 0.179, 99% EtOH).

Found: C, 71.85; H, 5.66%. Calcd for C$_{17}$H$_{16}$O$_4$: C, 71.82; H, 5.67%.

Tetramethyl 1,3-Diphenylpropane-1,1,3,3-tetracarboxylate (IV). To a mixture of methanol (150 ml) and sodium methoxide (60 g) was added successively methyl phenyl acetate (150 g) and dimethyl oxalate (118 g). The mixture was allowed to stand overnight. After refluxing for 2 hr under stirring, the mixture was decomposed with water and hydrochloric acid, and extracted with ether. Combined extracts, after washing with water and drying over magnesium sulfate, were concentrated to remove solvent and volatile material. The oily residue was distilled under reduced pressure to yield dimethyl phenylmalonate (III. 178.4 g), bp 159—163 °C/3325 Pa. A mixture of dimethyl phenylmalonate (147.8 g) and methylene iodide (96.0 g) was added dropwise to a stirred solution of sodium methoxide (41 g) in methanol (180 ml), and the mixture was refluxed for 32 hr. Cooled reaction mixture was poured into water and extracted with ether. The extract, after washing and drying over calcium chloride, was concentrated, and the residue was distilled under reduced pressure to give pure tetraester (III, 67.3 g), bp 178—180 °C/133 Pa.

Found: C, 64.05; H, 5.72%. Calcd for C$_{23}$H$_{24}$O$_8$: C, 64.48; H, 5.65%.

2,3: 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione (VI). *From the Mixture of Racemic and Meso Forms*: To 1,3-diphenylglutaronitrile (I, 40.0 g) dissolved in 99% ethanol (450 ml) was added a solution of potassium hydroxide (120 g) in water (330 ml) and the mixture was heated to 70 °C for 8 hr. The reaction mixture was mixed with water (550 ml) and washed with ether. Aqueous layer was acidified with concentrated hydrochloric acid and extracted with ethyl acetate. The extract was washed with brine and dried over sodium sulfate. Crude mixture of (±)- and *meso*-1,3-diphenylgluratic acids was obtained as a yellow oil on evaporating the solvent under reduced pressure. The mixture of acids (46.2 g) was dissolved in concentrated sulfuric acid and heated to 85 °C for 30 min. The reaction mixture was poured onto ice and extracted with benzene. The extract was washed with 3% aqueous potassium hydroxide and water successively and dried over sodium sulfate. On evaporating the solvent *in vacuo* was obtained colorless solid (24.3 g), which was recrystallized twice from methanol to yield pure diketone (VI) as colorless needles, mp 147.7—147.8 °C, IR (Nujol mull): 1680 ($\nu_{C=O}$) cm^{-1}, NMR: 8.17—7.82 (m, 2H, aromatic protons adjacent to carbonyl group), 7.55—7.15 (m, 6H, aromatic), 4.01 (t, J= 3 Hz, 2H, bridgehead), 2.98 (t, J=3 Hz, 2H, methylene bridge).

Found: C, 81.99; H, 4.82%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

From Racemic and Optically Active Forms (IIb): By essentially the same cyclization procedure, identical (±)-diketone (VI) was obtained from (±)-IIb in 84% yield. The (−)-acid (IIb, 0.1411 g, $[\alpha]_D$ −48.2 ° (c 0.2824, 99% EtOH), optical purity 50.4%) yielded (+)-diketone (VI, 0.1054 g, $[\alpha]_D$ +139.5 ° (c 0.02108, 99% EtOH) by the same reaction conditions. Optical purity of the (+)-diketone (VI), estimated from the values of ORD peaks and troughs, was *ca.* 45%. A minor extent of racemization seemed to occur during the course of ring closure reaction.

From meso *Form (IIa)*: The *meso*-acid (IIa) yielded the identical (±)-diketone (VI) in 77% yield under the same reaction conditions.

From Tetramethyl Ester (IV): Tetramethyl ester (IV, 14.2 g) was mixed with 5% alcoholic potassium hydroxide and refluxed for 2 hr. The mixture was diluted with water and neutral material was removed by extraction with ether. Aqueous layer was acidified with hydrochloric acid and extracted with ether. The extract was washed with water and dried over magnesium sulfate. A partly crystallized residue (V, 5.0 g) obtained on evaporating the solvent under reduced pressure was mixed with polyphosphoric acid (150 g) and heated to 100 °C under stirring for 2 hr. The reaction mixture was poured onto ice water and extracted with ether. Organic layer was washed with 5% aqueous sodium carbonate and water, and dried over magnesium sulfate. Crystalline residue obtained by evaporating the solvent *in vacuo* was recrystallized from benzene–ligroin to yield the same (±)-diketone (VI).

2,3: 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-diol (VIIa). By Lithium Aluminum Hydride Reduction: The diketone (VI, 0.5 g) in tetrahydrofuran (8 ml) was added under stirring to an ice-cooled suspension of lithium aluminum hydride (0.63 g) in the same solvent (16 ml). After stirring for further 1 hr under ice-cooling, the reaction mixture was worked up in the usual way, and extracted with ether. The extract was washed successively with water, aqueous potassium carbonate and saturated sodium chloride, and dried over sulfate. Evaporation of the solvent under reduced pressure yielded the crude glycol (VIIa), mp 225 °C (with sublimation), IR (Nujol mull): 3280 (broad), 3550, 3575 (ν_{O-H}) cm^{-1}.

Found: C, 80.66; H, 6.35%. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39%.

By Catalytic Reduction: The diketone (VI, 0.1228 g) in ethyl acetate (10 ml) was catalytically reduced over the Adams catalyst, yielding identical glycol (VIIa) in quantitative yield.

4,8-Diacetoxy-2,3: 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (VIII). Crude glycol (VIIa, 0.2081 g) dissolved in pyridine (3 ml) was mixed with acetic anhydride (4 ml) and heated to 90 °C for 5.5 hr. The reaction mixture was worked up in the usual way to give colorless solid (0.2247 g) which showed single spot on a silica gel TLC plate developed with benzene or benzene–ether. The solid was recrystallized from benzene–methanol to give colorless needles of VIII, mp 220.9—221.6 °C, IR (Nujol mull): 1730 ($\nu_{C=O}$) cm^{-1}, NMR: 7.32—6.87 (m, 8H, aromatic), 6.27 (d, J=6 Hz, 2H, methine), 3.55 (q, 2H, bridgehead), 2.43 (t, J=3.5 Hz, 2H, methylene), 2.22 (s, 6H, methyl).

Found: C, 74.97; H, 5.96%. Calcd. for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

Optical Resolution of 2,3: 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-diol (VIIi). Via *Bis-(−)-menthoxyacetate (IX)*: (−)-Menthoxyacetyl chloride (2.18 g) was added to a stirred solution of (±)-glycol (VIIa, 1.00 g, 3.96 mmol) in pyridine (8 ml). After stirring overnight at room temperature, the mixture was poured into water and extracted with benzene. The extract was washed successively with 2 M hydrochloric acid, aqueous potassium carbonate and saturated aqueous sodium chloride, and dried over sodium sulfate. A brown solid obtained on evaporating the solvent under reduced pressure was chromatographed on silica gel (30 g). Elution with benzene–ether (4: 1) yielded light yellow solid (2.32 g), mp 179.7—189.4 °C, (Nujol mull): 1760, 1740 ($\nu_{C=O}$) cm^{-1}.

The crude bis-(−)-menthoxyacetate was recrystallized eleven times from benzene–ethanol (1: 1) to give an optically pure enantiomer as colorless needles (0.25 g), mp 215.7—216.3 °C, IR (Nujol mull): 1750 ($\nu_{C=O}$) cm^{-1}, ORD: $[\alpha]_D$ −41.4 °, $[\alpha]_{546}$ −49.7 °, $[\alpha]_{405}$ −119.4 ° (c 0.313, dioxane).

Found: C, 76.45; H, 8.74%. Calcd for $C_{41}H_{56}O_6$: C, 76.36; H, 8.75%.

Optically pure IX (0.217 g) thus obtained was dissolved in benzene and mixed with ethanolic potassium hydroxide (0.09 g in 5 ml). After the mixture had been refluxed for 2 hr, water was added. Precipitate formed, after being washed with water, was recrystallized from benzene to give optically pure (−)-glycol (VIIa), mp 189.5—189.8 °C, IR (Nujol mull): 3390 (ν_{O-H}) cm^{-1}, ORD: $[\alpha]_D$ −84.9 °, $[\alpha]_{546}$ −101.4 °, $[\alpha]_{500}$ −132 °, $[\alpha]_{450}$ −185 °, $[\alpha]_{436}$ −204 ° (c 0.4065, 99% EtOH), $[\alpha]_{405}$ −261 °, $[\alpha]_{350}$ −487 °, $[\alpha]_{320}$ −771 °, $[\alpha]_{250}$ −5400 °, $[\alpha]_{230}$ −19150 ° (c 0.2185, 99% EtOH), UV: $\lambda_{max}^{99\%EtOH}$ (ε) 272 (320), 269(360), 264(470), 275*(390), 255*(280), 249*(230), 244*(150), 215*(17300), 199(59100) nm, CD: see Table 1.

Via *Bis-(−)-camphanate (X)*: The crystals (0.4183 g) obtained from (±)-glycol (VIIa, 0.1754 g), (−)-camphanyl chloride (0.375 g) and pyridine (5 ml) were recrystallized five times from benzene–ligroin to give (+)-bis-camphanate (32 mg) with constant rotation, colorless needles, mp 281—285 °C, $[\alpha]_D$ +38.9 ° (c 0.4834, dioxane).

Found: C, 72.55; H, 6.59%. Calcd for $C_{27}H_{40}O_8$: C 72.53; H, 6.58%.

(−)-Glycol (VIIa, mp 187.9—188.3 °C (from benzene), $[\alpha]_{350}$ −388.5 ° (c 0.02059, 99% EtOH), optical purity 79.8%) was obtained on alkaline hydrolysis of the (+)-bis(−)-camphanate (X) with constant optical rotation.

(+)-4,8-Diacetoxy-2,3: 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (VIII). (−)-Glycol (VIIa,104.4 mg) was acetylated with acetic anhydride (2 ml) and pyridine (1.5 ml) on heating to 90 °C for 5.5 hr. The reaction mixture was worked up in the same way as racemate to give colorless crystals (129.3 mg) of (+)-VIII, which showed identical NMR spectrum and the same tlc-Rf value with those of the racemate. The crystals were recrystallized from methanol to give pure (+)-VIII, colorless needles, mp 242.6—243.0 °C, IR (Nujol mull): 1730 ($\nu_{C=O}$) cm^{-1}, ORD: $[\alpha]_D$ +10.7 °, $[\alpha]_{474}\approx 0$ °, $[\alpha]_{436}$ −12.4 °, $[\alpha]_{405}$ −31.4 °, $[\alpha]_{365}$ −83.0 ° (c 0.541, dioxane).

Found: C, 74.82; H, 6.03%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

(+)-2,3: 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione (VI). Chromium trioxide (0.1 g) in acetic acid (1 ml) was added under stirring to an ice-cooled solution of (−)-VIIa (20.1 mg) in acetone (3 ml) and acetic acid (0.5 ml). After stirring for further 19 hr at room temperature, the mixture was worked up in the usual manner. Light brown solid (13.4 mg) obtained was dissolved in benzene

and passed through a short column of silica gel (1.5 g). The material obtained from the filtrate was recrystallized from ligroin to give (+)-VI, colorless needles, mp 194.—194.5 °C, IR (Nujol mull): 1685 ($\nu_{C=O}$) cm^{-1}, ORD: $[\alpha]_D$ +343 °, $[\alpha]_{546}$ +419 °, $[\alpha]_{436}$ +1370 °, $[\alpha]_{405}$ +2570 °, $[\alpha]_{372}$ +9140 °, $[\alpha]_{355}$ +12600 °, $[\alpha]_{341}$ +7480 °, $[\alpha]_{320}$ −9340 °*, $[\alpha]_{316}$ −23700 °*, $[\alpha]_{306}$ −29100 °, $[\alpha]_{274}$ +14600 °, $[\alpha]_{253}$ −77200 ° (*c* 0.0198, 99% EtOH), UV and CD: see Table 1.

Found: C, 82.23; H, 4.90%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

(−)-4,8-Dichloro-2,3 : 6,7-dibenzobicyclo[3. 3. 1]nona-2, 6-diene (XI). (−)-Glycol (VIIa, 117.8 mg) in benzene (10 ml) was refluxed with thionyl chloride (1.3 ml) for 17.5 hr. The reaction mixture was treated in the usual way, and faintly yellow oil obtained on evaporating the solvent under reduced pressure was dissolved in benzene and passed through a short column of silica gel. Colorless oil (140.9 mg) obtained from the filtrate was crystallized from methanol to give pure (−)-XI, colorless leaflets, mp 130.4—132.1 °C, NMR (CCl_4): 7.30—7.10 (m, 8H, aromatic), 4.96 (d, *J*=2 Hz, 2H, methine), 3.52 (m, 2H, bridgehead), 2.55 (t, *J*=3 Hz, 2H, methylene), ORD (at 25 °C): $[\alpha]_{365}$ −428 °, $[\alpha]_{276}$ −2420 °, $[\alpha]_{271}$ −391 °* $[\alpha]_{250}$ −6770 ° (*c* 0.02148, 99% EtOH), UV: $\lambda_{max}^{99\%EtOH}$ (ε) 278(450), 273*(540), 270(580), 266*(560), 261*(500), 211.5 (26700), 206(25800), 202*(28100), 195(41700) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 278(−2.96), 270(−3.18), 264*(−1.88), 234 (+24.2), 218(+32.3), 198.5(−68.3) nm.

Found: C, 70.81; H, 4.91; Cl, 24.65%. Calcd for $C_{17}H_{14}Cl_2$: C, 70.60; H, 4.88; Cl, 24.52%.

Racemate was obtained as colorless needles, mp 173.4—174.2 °C (from methanol).

(−)-2,3: 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene (XII). *From (−)-Dichloride (XI)*: (−)-Dichloride (XI, 267 mg) in tetrahydrofuran (5 ml) was added to a stirred suspension of lithium aluminum hydride (0.37 g) in the same solvent (12 ml), and the mixture was refluxed for 24 hr. The reaction mixture was worked up in the usual manner. Light yellow oil obtained was dissolved in carbon tetrachloride–benzene (1: 1) and passed through a short column of silica gel (14 g). Colorless oil (180.9 mg) obtained from the filtrate was crystallized from methanol to yield (−)-XII, colorless needles, mp 100.8—102.2 °C, NMR: 7.28—6.85 (m, 8H, aromatic), 3.52—2.55 (m, 6H, methine and methylene), 2.92 (t, *J*=3 Hz, 2H, methano-bridge), ORD: $[\alpha]_D$ −247 °, $[\alpha]_{404}$ −635 °, $[\alpha]_{365}$ −900 °, $[\alpha]_{282}$ −2010 °, $[\alpha]_{268}$ −987 ° (*c* 0.02188, isooctane), UV: $\lambda_{max}^{isooctane}$ (ε) 273(1480), 266(1230), 262(790), 260(770), 258*(740), 252*(430), 246*(230), 219(14450), 214(17200), 196(66100) nm, CD: see Table 1.

Found: C, 92.40; H, 7.28%. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32%.

Racemate: mp 71.7—73.5 °C.

By the Clemmensen Reduction of (±)-VI: A mixture of (±)-diketone (VI, 218 mg), toluene (3 ml), concentrated hydrochloric acid (1.75 ml), water (0.75 ml) and granulated zinc (1.2 g) activated with mercuric chloride and diluted hydrochloric acid was refluxed for 24 hr under stirring. The reaction mixture was worked up in the usual way to yield light yellow oil. The oil in carbon tetrachloride was passed through a short column of alumina and silica gel, successively. Colorless oil (64.3 mg) obtained from the filtrate was crystallized from 99% ethanol to give pure (±)-XII, colorless plates, mp 72.1—73.5 °C, which showed identical IR and NMR spectra with those of (±)-XII obtained from (±)-VIIa.

Found: C, 92.55; H, 7.43%. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32%.

(−)-4,8-Dihydroxy-4,8-dimethyl-2,3 : 6,7-dibenzobicyclo[3.3.1]-nona-2,6-diene (XIII). To an ice-cooled solution of methylmagnesium iodide (magnesium 0.9 g, methyl iodide 5.5 g and ether 30 ml) a solution of (+)-VI (511.3 mg) in tetrahydrofuran (25 ml) was added under stirring. After 1.5 hr, the mixture was refluxed for 5 hr. Brown oil (584.4 mg) obtained on treatment of the reaction mixture in the usual manner was dissolved in benzene and passed through a short column of silica gel (3 g). Colorless solid obtained from benzene and benzene–ether eluates was recrystallized once from benzene and twice from petroleum ether to give pure (−)-XIII, mp 115.1—116.0 °C, IR (Nujol mull): 3750, 3480 (ν_{O-H}) cm^{-1}, NMR: 7.65—7.05 (m, 8H, aromatic), 3.04 (t, *J*=3 Hz, 2H, bridgehead), 2.57 (t, *J*=3 Hz, 2H, methylene), 1.65 (s, 6H, methyl), 1.63 (s, 2H, OH), ORD (at 25 °C): $[\alpha]_{365}$ −349 °, $[\alpha]_{300}$ −1040 °, $[\alpha]_{260}$ −3010 ° (*c* 0.020645, 99% EtOH), UV: $\lambda_{max}^{99\%EtOH}$ (ε) 272(240), 268(200), 262.5 (400), 275.4*(330), 252*(250), 245*(150), 218*(15050), 214* (17900), 196.5(69400) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 274(+0.05), 271.5(−0.07), 265(−0.12), 256(−0.16), 251(−0.16), 216 (−35.3), 203(−85.6) nm.

Found: C, 81.27; H, 7.20%. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19%.

Racemate was prepared similarly and recrystallized twice from benzene–ligroin, mp 165.5—166.2 °C, IR (Nujol mull): 3570 (ν_{O-H}) cm^{-1}.

When just two equivalents of the Grignard reagent was added to (±)-VI, only 44.3% of (±)-XIII was obtained and a ketoalcohol, 4-hydroxy-4-methyl-2,3 : 6,7-dibenzobicyclo-[3.3.1]nona-2,6-dine-8-one, was isolated in 37.6% yield. The ketoalcohol was recrystallized three times from acetone to yield pure crystals, which contained a molecule of acetone as a solvent of crystallization, IR (Nujol mull): 3460 (ν_{O-H}), 1690, 1683 ($\nu_{C=O}$), 1712 ($\nu_{C=O}$, acetone) cm^{-1}, NMR: 7.85 (m, J_o= 7 Hz, J_m=3 Hz, J_p=1.5 Hz, 1H, aromatic *ortho* to carbonyl), 7.58—7.03 (m, 7H, other aromatic), 3.78 (t, *J*=3 Hz, 1H. bridgehead vicinal to hydroxyl), 3.28 (t, *J*=3 Hz, 1H, bridgehead vicinal to carbonyl), 2.66 (t, *J*=3 Hz, 2H, methylene), 2.09 (s, 6H, acetone), 1.98 (s, 1H, OH), 1.75 (s, 3H, methyl),

Found: C, 78.37; H, 6.85%. Calcd for $C_{18}H_{16}O_2 \cdot C_3H_6O$: C, 78.23; H, 6.88%.

(+)-4,8-Bis(methylene)-2,3 : 6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (XIV). (−)-Dimethyl glycol (XIII, 467.4 mg) in pyridine (6 ml) was heated to 50—65 °C with phosphoryl chloride (1.8 ml) for 1.5 hr. The reaction mixture was worked up in the usual way. A benzene solution of light yellow oil obtained on evaporating the solvent under reduced pressure was passed through a short column of silica gel (7.5 g) to yield colorless crystals (231.1 mg) which were recrystallized from methanol to give pure (+)-XIV, colorless needles, mp 124.2—124.6 °C, IR (Nujol mull): 1620 ($\nu_{C=C}$) cm^{-1} NMR: 7.70—6.95 (m, 8H, aromatic), 5.44 (d, *J*=0.5 Hz, 2H, olefin *syn* to benzene), 5.25 (d, *J*=0.5 Hz, 2H, olefin *anti* to benzene), 3.88 (t, *J*=3 Hz, 2H, bridgehead), 2.32 (t, *J*=3 Hz, 2H, methylene), ORD (at 25 °C): $[\alpha]_D$ +392 °, $[\alpha]_{546}$ +703 °, $[\alpha]_{405}$ +1460 °, $[\alpha]_{365}$ +2390 °, $[\alpha]_{330}$ +4410 ° (*c* 0.01964, 99% EtOH), UV: $\lambda_{max}^{99\%EtOH}$ (ε) 296.5(1210), 286.5 (2130), 258(22100), 251*(21000), 230*(16000), 213.5(35650), 209(36000) nm, $\lambda_{max}^{isooctane}$($\varepsilon$) 296.5(1130), 286.5(1930), 266* (16200), 258.5(22100), 251*(21000), 230*(16100), 213.5 (37200), 208.5(37900), 192*(27400) nm, CD: see Table 1.

Found: C, 93.20; H, 6.62%. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60%.

Racemate: mp 81.2—81.5 °C (from *n*-pentane).

*(+)-2,3 :6, 7-Dibenzobicyclo[3.3.1]nona-2, 6-diene-4,8-diol-bis-*p*-bromobenzoate (XV).* To a stirred solution of (−)-VIIa (0.5 g) in pyridine (7 ml) *p*-bromobenzoyl chloride (0.5 g) was added at room temperature and the mixture was heated to 60 °C under stirring for 20 hr. The reaction mixture was

worked up in the usual way. A viscous oil (0.45 g) obtained was dissolved in benzene and chromatographed twice on silica gel (34 g each) very carefully. Colorless solid obtained from the benzene eluates was recrystallized from methanol to give (+)-XV, mp 212.7—213.7 °C, IR (Nujol mull): 1720 ($\nu_{C=O}$) cm^{-1}, NMR: 7.97 (d, J=8.4 Hz, 4H, *ortho* protons of *p*-bromobenzoyl groups), 7.34—6.88 (m, 8H, other aromatic protons), 6.60 (d, J=6 Hz, 2H, methine), 3.70 (q, 2H, bridgehead), 2.58 (t, J=3 Hz, 2H, methylene), ORD: $[\alpha]_D$ +192 °, $[\alpha]_{546}$ +231 °, $[\alpha]_{436}$ +424 °, $[\alpha]_{405}$ +532 °, $[\alpha]_{365}$ +753 ° (*c* 0.587, acetone), UV: $\lambda_{max}^{cyclohexane}$ (ε) 283(1410), 271*(3630), 255*(31000), 247(41200), 218*(23800), 200(116500) nm, CD: $\lambda_{max}^{cyclohexane}$ ($\Delta\varepsilon$) 287(+0.24), 284(−0.40), 278*(+2.25), 255(+46.8), 235(−3.04), 212(−63.9) nm.

Found: C, 60.44; H, 3.58; Br, 25.79%. Calcd for $C_{31}H_{22}O_4Br_2$: C, 60.21; H, 3.59; Br, 25.85%.

Single crystals of (+)-XV for the X-ray crystallographic analysis were prepared on standing an acetone solution (200 mg in 25 ml) in a loosely stoppered ground joint flask for three months in a dark place.

When the above-mentioned procedure was applied to (±)-VIIa, the (±)-diester (XV) was obtained only in 51% yield and mono-*p*-bromobenzoate was isolated in 40,6% yield.

(±)-Bis-*p*-bromobenzoate (XV): colorless needles, mp 233.7—234.4 °C (from methanol), IR (Nujol mull): 1714 ($\nu_{C=O}$) cm^{-1}.

(±)-Mono-*p*-bromobenzoate: colorless rods, mp 163.0—163.5 °C, IR (Nujol mull): 3310 (ν_{O-H}), 1728, 1718 ($\nu_{C=O}$) cm^{-1}, NMR (CCl_4): 7.79 (d, J=8.4 Hz, 2H, *ortho* protons of *p*-bromobenzoyl group), 7.46 (d, J=8.4 Hz, 2H, *meta* protons of *p*-bromobenzoyl group), 7.50—6.70 (m, 8H, other aromatic protons), 6.40 (d, J=6 Hz, 1H, methine of ester), 4.89 (q, 1H, methine of alcohol), 3.52 (m, 1H, bridgehead near to ester), 3.27 (m, 1H, bridgehead near to alcohol), 2.43 (broad s, 2H, methylene), 1.46 (d, J=12 Hz, 1H, OH, disappeared on addition of D_2O). Found: C, 66.01; H, 4.44; Br, 18.22%. Calcd for $C_{24}H_{19}O_3Br$: C, 66.22; H, 4.40; Br, 18.36%.

(−)-2,3: 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-diol-monoacetate (XVI). (−)-Diol (VIIa, 3.61 g, $[\alpha]_D^{25}$ −85.2 ° (*c* 0.9240, $CHCl_3$), $[\alpha]_D^{25}$ −48.3 ° (*c* 0.4968, 99% EtOH), optical purity 56.9%) in pyridine was mixed with acetic anhydride (1.46 g) under ice-cooling. The mixture was stirred for further 2 hr at the same temperature and allowed to stand overnight at room temperature. The reaction mixture was worked up in the usual manner. Crystals of recovered (−)-diol (VIIa, 0.563 g) deposited on concentrating the extract were removed by filtration, and the filtrate was chromatographed on alumina (70 g). Recrystallization from ether of the crystals obtained from benzene eluates yielded (+)-diacetate (VIII, 0.850 g), mp 211.0—213.0 °C, $[\alpha]_D^{25}$ +25 ° (*c* 0.2469, $CHCl_3$), Found: C, 74.74; H, 5.90%.

Crystals (1.59 g) obtained from ether–methanol (95:5) eluates were recrystallized from ether to give (−)-monoacetate, mp 129.0—133.0 °C, $[\alpha]_D^{25}$ −27.7 ° (*c* 0.5340, $CHCl_3$).

Found: C, 77.53; H, 6.16%. Calcd for $C_{19}H_{18}O_3$: C, 77.42; H, 6.14%.

(+)-2,3: 6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4-one (XIX). A mixture of (−)-monoacetate (XVI, 1.40 g), thionyl chloride (18 ml) and benzene (120 ml) was refluxed for 17 hr. The reaction mixture was worked up in the usual way and the residue obtained on evaporating the benzene extract *in vacuo* was purified by crystallization from *n*-hexane to yield (−)-8-chloro-4-acetate (XVII), mp 139.0—144.0 °C, $[\alpha]_D^{22}$ −31.0 ° (*c* 0.4974, $CHCl_3$), Found: C, 73.06; H, 5.38; Cl, 11.30%. Calcd for $C_{19}H_{17}O_2Cl$: C, 72.95; H, 5.48; Cl, 11.33%.

(−)-Chloride (XVII, 0.850 g) in tetrahydrofuran (10 ml) was added dropwise to a stirred suspension of lithium aluminum hydride (1.2 g) in the same solvent (60 ml). After the mixture had been refluxed for 24 hr, the reaction mixture was treated in the usual manner and the solvent was removed *in vacuo*. Crude alcohol (XVIII) thus obtained was submitted to oxidation without further purification. To an ice-cooled solution of crude XVIII in acetone (40 ml) was added the Jones reagent dropwise under stirring till red color of the reagent persisted for a while. The mixture was stirred for further 30 min at the same temperature and then mixed with water. Ethereal extract, after being washed and dried, was concentrated *in vacuo*, and the residue dissolved in benzene was passed through a short column of silica gel (15 g). Colorless crystals (440 mg) obtained from benzene eluates were recrystallized from benzene–*n*-hexane to give pure (+)-XIX, mp 112—114 °C, $[\alpha]_D^{22}$ +27.5 ° (*c* 0.2479, $CHCl_3$), UV: $\lambda_{max}^{99\%EtOH}$ (ε) 370*(93.5), 350*(380), 337.5(523), 326*(483), 297*(1620), 290*(1730), 278(2210), 253(11900), 201(41800) nm, $\lambda_{max}^{cyclohexame}$ (ε) 374*(164), 371(176), 355.5(410), 340(464), 326(343), 315(204), 297(1400), 287(1420), 278.5(1790), 271(1710), 251*(11000), 247(11600), 214*(26900), 206(43050), 191.5(37900), 190(38600) nm, CD (corrected for 100% optical purity): $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 370*(+1.50), 352.5*(+5.10), 338.5(+6.93), 327*(+6.18), 315*(+3.85), 303*(−1.50), 283(−1.96), 276*(−1.72), 260*(−1.02), 245*(+1.11), 243(+1.21), 229(−1.71), 203.5(−25.0) nm, $\lambda_{max}^{cyclohexane}$ ($\Delta\varepsilon$) 384*(+0.05), 380*(+0.20), 377*(+1.53), 371(+2.99), 354.5(+6.29), 339.5(+6.65), 325.5(+4.64), 315(+2.58), 303*(+0.904), 298*(+0.86), 275(−1.17), 358(−0.63), 244(+1.31), 225(−2.61), 199(−18.5) nm.

Found: C, 86.89; H, 5.92%. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

(R)-(−)-3-Phenylbutanoic Acid (XX). (±)-XX, bp 134—136 °C/800 Pa, was prepared by the reaction of benzene with crotonic acid in the presence of anhydrous aluminum chloride.13) Optical resolution was carried out with (+)-α-phenylethylamine14) to yield (*R*)-(−)-XX, $[\alpha]_D$ −52.0 ° (*c* 0.042, benzene).

(R)-(−)-3-Phenylbutylphenone (XXI). (*R*)-(−)-XX (3.61 g) was converted into acid chloride with thionyl chloride in ether. A solution of the acid chloride in benzene (50 ml) was added under ice-cooling and stirring to a benzene solution of diphenylcadmium (*ca.* 80 ml), which was prepared from phenylmagnesium bromide (magnesium 0.61 g, bromobenzene 2.6 ml, and ether 20 ml) and anhydrous cadmium chloride (2.5 g suspended in 50 ml of ether). After being refluxed for 3 hr, the reaction mixture was worked up in the usual way. Organic layer and benzene extracts, after being washed and dried, were evaporated under reduced pressure. Viscous brown oil (3.4 g) thus obtained was found to be contanimated with considerable amount of ethyl 3-phenylbutyrate. The crude product (1.3 g) in 99% ethanol (10 ml) was mixed with potassium hydroxide (0.7 g in ethanol 20 ml and water 5 ml) and the mixture was allowed to stand at room temperature overnight. After evaporating the solvent under reduced pressure, the mixture was diluted with water and extracted with benzene. The extract was washed with 5% aqueous sodium hydrogencarbonate, and dried over sodium sulfate. (*R*)-(−)-XX (0.381 g) was recovered from the aqueous layer and sodium hydrogencarbonate washings on acidification. Light yellow oil (0.7311 g) obtained from benzene extract was carefully purified by repeated chromatography on silica gel and alumina. (*R*)-(−)-Ketone (XXI) was obtained as a colorless oil, IR (neat): 1683 ($\nu_{C=O}$) cm^{-1} NMR: 8.0—7.8 (m, 2H, *ortho* protons of benzoyl group), 7.55—7.17 (m, 8H, other aromatic protons), 3.73—3.08 (m, 3H, methylene and methine), 1.31 (d, J=6.6 Hz, 3H, methyl), UV: $\lambda_{max}^{isooctane}$ (ε) 358*(24.5), 355*(26.0), 341*(47.3), 328*(62.5), 319(64.7),

287(724), 279(938), 277.5*(933), 273(891), 268.5(945), 264.7(919), 261*(946), 249*(8480), 240(13300), 205.5*(26900), 200.5(38100), 191.2(67500), 190(69000) nm, ORD: $[\alpha]_D$ −14.8 °, $[\alpha]_{546}$ −19.0 °, $[\alpha]_{436}$ −49.7 °, $[\alpha]_{405}$ −79.5 °, $[\alpha]_{367\cdot5}$ −240.6 °, $[\alpha]_{353}$ −335.1 °, $[\alpha]_{339\cdot5}$ −249 ° (*c* 1.1972, CCl_4), $[\alpha]_D$ +0.66 °, $[\alpha]_{546}$ ≈0 °, $[\alpha]_{436}$ −16.6 °, $[\alpha]_{405}$ −40.8 °, $[\alpha]_{370}$ −170.8 °, $[\alpha]_{355}$ −262.7 °, $[\alpha]_{340\cdot5}$ −183.9 °, $[\alpha]_{335\cdot5}$ ≈0 °, $[\alpha]_{322}$ +96.9 °, $[\alpha]_{317}$ +303.8 ° (*c* 0.609, hexane), CD: $\lambda_{max}^{isooctane}$ ($\Delta\varepsilon$) 371 (−0.0628), 354.5 (−0.204), 340(−0.325), 327.5(−0.339), 316(−0.266), 306* (−0.174), 295*(−0.0876), 287(−0.116), 279.5(−0.0916), 268(−0.174), 261(−0.171), 252(−0.494), 219 (+2.24), 201.5(+8.76) nm.

Found: C, 85.36; H, 7.18%. Calcd for $C_{15}H_{16}O$: C, 85.68; H, 7.19%.

Racemate was obtained by the same procedure in 71% yield which was recrystallized from methanol to give pure (±)-XXI, colorless leaflets, mp 70.8—71.5 °C, IR (KBr disk): 1680 ($\nu_{C=O}$), 760, 705 (δ_{CH}, monosubstituted benzene) cm^{-1}. In this case contamination with the ethyl ester was not so serious that (±)-XXI could be easily purified by chromatography on silica gel and recrystallization.

*(*R*)-(−)-2,4-Diphenyl-1-pentane (XXII).* Triphenylmethylphosphonium bromide (1.761 g) suspended in ether (30 ml) was converted into triphenylphosphinmethylene with *n*-butyllithium (3 ml of 1.65 M hexane solution).[15] (−)-Ketone (XXI, 0.774 g) in ether (70 ml) was added over 5-min period to the stirred solution of the Wittig reagent and the mixture was refluxed for 11.5 hr under stirring. Solid deposited on cooling the reaction mixture was filtered and washed thoroughly with ether. The filtrate and washings were combined and dried over sodium sulfate. Colorless oil (1.120 g) obtained on evaporating the solvent under reduced pressure was dissolved in *n*-hexane and carefully chromatographed on silica gel (40 g). Evaporation of *n*-hexane eluates gave (−)-XXII, colorless oil (0.519 g, 67.6%), IR (neat): 890 ($\delta_{=CH}$ out of plane) cm^{-1}, NMR: 7.47—7.0 (m, 8H, aromatic), 5.21 (d, *J*=1.6 Hz, 1H, olefinic proton *cis* to phenyl), 4.97 (m, 1H, olefinic proton *trans* to phenyl), 3.07—2.52 (m, 3H, methylene and methine), 2.87 (d, *J*=6.5 Hz, 3H, methyl), UV: $\lambda_{max}^{isooctane}$ (ε) 290* (77.2), 268.5 (1270), 264(2130), 240(9170), 217*(12300), 206(27000), 191.5(67640), 190(68500) nm, ORD: $[\alpha]_D$ −68.1 °, $[\alpha]_{546}$ −83.1 °, $[\alpha]_{436}$ −156.9 °, $[\alpha]_{405}$ −196.6 °, $[\alpha]_{365}$ −279.4 ° (*c* 1.354, *n*-hexane), CD: $\lambda_{max}^{isooctane}$ ($\Delta\varepsilon$) 271.5(−0.121), 267.5(+0.102), 264(−0.160), 235(−3.21), 210(+5.37), 192 (−39.2) nm.

Found: C, 91.90; H, 8.29%. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16%.

A small amount of (−)-ketone (XXI, 0.131 g, 16.9%) was recovered from benzene eluate.

*(*R*)-(−)- and* meso-*2,4-Diphenylpentane (XXIIIb and XXIIIa)* Hydrogenation of (*R*)-(−)-2,4-diphenyl-1-pentene (XXII, 0.422 g) in benzene (50 ml) and ethyl acetate (50 ml) over the Adams catalyst (48 mg) yielded colorless oil (0.407 g). The material in *n*-hexane was chromatographed on silica gel. Ratio of *meso*-(XXIIIa) and (−)-isomers (XXIIIb) could be estimated to be 50.7% and 49.3%, respectively, by the intensities of methyl signals in their NMR spectra of purified reduction product, UV: $\lambda_{max}^{isooctane}$ (ε) 268(330), 264.3(346), 261 (436), 259(443), 254.5*(370), 253.5(377), 248.5(279), 243* (194), 238*(140), 217*(10000), 213*(14300), 209(17600), 205*(17500), 193(89000), 191.8(97500), 190(91800) nm, ORD: $[\alpha]_D$ −39.4 °, $[\alpha]_{546}$ −49.1 °, $[\alpha]_{436}$ −84.4 °, $[\alpha]_{405}$ −105.2 °, $[\alpha]_{365}$ −150.4 ° (*c* 0.5140, isooctane), CD: $\lambda_{max}^{isooctane}$ ($\Delta\varepsilon$) 271(−0.0162), 268(+0.0117), 266*(−0.0208), 263.5 (−0.0483), 257(−0.0616), 251(−0.0485), 245*(−0.0350), 239*(−0.0266), 217(−4.59) nm.

Found: C, 91.28; H, 9.00%. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99%.

(−)-2,4-Diphenylpentane-1,5-diol (XXIVb). (−)-1,3-Diphenylglutaric acid (IIb, 0.548 g, $[\alpha]_D$ −44.1 ° (*c* 0.295, 99% EtOH), optical purity 46%) in tetrahydrofuran (30 ml) was added to a stirred suspension of lithium aluminum hydride (0.1464 g) in the same solvent (20 ml), and the mixture was refluxed for 5 hr. The reaction mixture was worked up in the usual manner and extracted with ether. After washing and drying, the extract was concentrated under reduced pressure. Colorless oil (0.462 g) thus obtained was crystallized from benzene to give pure (−)-XXIVb, mp 72—90 °C, IR (neat): 3350 (very broad, ν_{O-H}) cm^{-1}, NMR: 7.40—6.83 (m, 10H, aromatic), 3.45 (d, *J*=6.2 Hz, 4H, $C\underline{H}_2OH$), 2.68—1.77 (m, 4H, methylene and methine), 2.13 (s, 2H, OH), ORD: $[\alpha]_D$ −39.1 °, $[\alpha]_{546}$ −45.1 °, $[\alpha]_{436}$ −80.9 °, $[\alpha]_{405}$ −99.7 °, $[\alpha]_{365}$ −135.3 ° (*c* 0.8432, 99% EtOH).

Found: C, 79.12; H, 7.85%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%.

meso-*2,4-Diphenylpentane-1,5-diol (XXIVa).* Reduction of *meso*-1,3-diphenylglutaric acid (IIa, 0.514 g) according to the same procedure used for (−)-isomer (IIb) gave *meso*-diol (XXIVa) in a quantitative yield which was recrystallized from benzene–ligroin to give pure material, mp 116.7—117.3 °C, IR (Nujol mull): 3250, 3170* (ν_{O-H}) cm^{-1}, NMR: 7.50—7.00 (m, 10H, aromatic), 3.73 (d, *J*=6.6 Hz, 4H, $C\underline{H}_2OH$), 3.07—1.58 (m, 4H, methylene and methine), 1.74 (s, 2H, OH).

Found: C, 79.52; H, 7.86%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%.

(−)-2,4-Diphenylpentane (XXIIIb). To an ice-cooled and stirred solution of (−)-diol (XXIVb, 0.406 g, optical purity, max. 46%) in pyridine (10 ml) was added dropwise methanesulfonyl chloride (1.0 g). The mixture was stirred for further 4 hr at room temperature and then allowed to stand overnight in a refrigerator. Treatment of the reaction mixture in the usual way gave bis-methanesulfonate (0.625 g) as light brown oil. A solution of the mesylate in tetrahydrofuran (30 ml) was added to a suspension of lithium aluminum hydride (1.0 g) in the same solvent (25 ml) and the mixture was refluxed for 12 hr. The reaction mixture was worked up in the usual manner to yield crude (−)-XXIIIb, faintly yellow oil (0.300 g). A *n*-hexane solution of the crude (−)-XXIIIb was chromatographed on silica gel (20 g), yielding pure (−)-XXIIIb, colorless oil, NMR: 7.47—6.96 (m, 10H, aromatic), 2.83—2.24 (sextet, 2H, methane), 1.96—1.72 (m, 2H, methylene), 1.14 (d, *J*=7 Hz, 6H, methyl), UV: $\lambda_{max}^{isooctane}$ (ε) 268(372), 264(361), 261.2(473), 259(458), 255(391), 253.5 (391), 249(287), 243*(188), 237*(115), 217*(10300), 213* (14600), 209(17700), 205*(17400), 193(82300), 191.5(86800), 190(87100) nm, ORD: $[\alpha]_D$ −34.7 °, $[\alpha]_{546}$ −42.3 °, $[\alpha]_{436}$ −73.4 °, $[\alpha]_{405}$ −91.9 °, $[\alpha]_{365}$ −124.6 ° (*c* 0.5740, isooctane), CD: $\lambda_{max}^{isooctane}$ ($\Delta\varepsilon$) 271 (−0.0164), 268(+0.0126), 266* (−0.0203), 263.5(−0.0580), 257(−0.0696), 251(−0.0464), 245*(−0.0261), 239*(−0.0145), 217(−6.19) nm.

Found: C, 91.03; H, 9.09%. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99%.

meso-*2,4-Diphenylpentane (XXIIIa).* *meso*-Diol (XXIVa, 0.255 g) was converted into *meso*-bis-mesylate (0.396 g) by the reaction with methanesulfonyl chloride (0.274 g) in pyridine (5 ml) performed under the same reaction condition used for the (−)-diol (XXIVb). The *meso*-bis-mesylate was reduced by lithium aluminum hydride (0.9 g) in tetrahydrofuran. Purification of crude product (0.204 g) in *n*-hexane by chromatography on silica gel (25 g) yielded *meso*-XXIIIa, colorless oil, NMR: 7.46—6.98 (m, 10H, aromatic), 2.96—2.37

(sextet, 2H, methine), 2.21—1.48 (m, 2H, aromatic), 2.21—1.48 (m, 2H, methylene), 1.21 (d, J=6.7 Hz, 6H, methyl), UV: $\lambda_{\max}^{\text{isooctane}}$ (ε) 268 (312), 264.5(330), 261.1(416), 259 (432), 255*(356), 253.5(359), 248.8(256), 244*(167), 238* (103), 217(10400), 213*(14200), 209(17400), 205*(17200), 193(87300), 192(95700), 190(94000), 188.5(69200) nm.

Found: C, 90.86; H, 8.95%. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99%.

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