Macromolecules **1986**, *19*, 509–516

trans isomer. In fact, the anomeric proton signals appeared at δ 6.04 (triplet) and 5.85 (doublet–doublet) with an intensity ratio of 1:~2. Therefore the former signal was definitely assigned to the anomeric proton in the cis isomer and the latter signal to that in the trans isomer.

(25) As clearly shown in the expanded spectrum in Figure 5, the lower peaks of signals b and c are split into two peaks of different intensities. Presumably, such splittings arise from the different diad placements of the cis and trans units and/or from those of the D,L-enantiomeric monomeric units in a polymer chain. Okada, M.; Sumitomo, H.; Komada, H. *Macromolecules* **1979**, *12*, 395. Okada, M.; Sumitomo, H.; Sumi, A. *Macromolecules* **1982**, *15*, 1238.

(26) Eliel, E. L.; Hargrave, K. D.; Pietrusiewicz, K. M.; Monoharan, M. *J. Am. Chem. Soc.* **1982**, *104*, 3635.

(27) Eliel, E. L.; Pietrusiewicz, K. M. *Pol. J. Chem.* **1981**, *55*, 1265.

(28) Anderson, C. B.; Sepp, D. T. *Chem. Ind. (London)* **1964**, 2054.

(29) Okada, M.; Sumitomo, H.; Yamada, S.; Atsumi, M.; Hall, H. K., Jr.; Chan, R. J. H.; Ortega, R. B. *Macromolecules*, in press.

(30) Details of the crystal structure determination can be obtained from Dr. Michael Bruck, Molecular Structure Laboratory, The University of Arizona.

Selective Step-Growth Phenol–Aldehyde Polymerization. 4.[1] Regio-, Enantio-, and Diastereocontrolled Entry to Chiral Nonracemic All-Ortho Novolacs

Giovanni Casiraghi,*[2a] Mara Cornia,[2a] Giuseppe Casnati,[2a]
Giovanni D. Andreetti,[2b] Gianluca Calestani,[2b] and Lucia Zetta[2c]

Istituto di Chimica Organica dell'Università, I-43100 Parma, Italy, Istituto di Strutturistica Chimica and Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., I-43100 Parma, Italy, and Istituto di Chimica delle Macromolecole del C.N.R., I-20130 Milano, Italy. *Received May 29, 1985*

ABSTRACT: The enantiodifferentiating reaction of substituted phenols with racemic α-substituted 2-hydroxybenzyl alcohols assisted by chiralized aluminum chlorides provides a viable entry into optically active binuclear phenolic compounds. The ethylmagnesium bromide promoted condensation of optically active dimers with *rac*-α-methyl-2-hydroxybenzyl alcohol then produces optically active trimers threospecifically (>95% diastereomeric excess) with virtually complete chirality transfer from the existing chiral bridge to the newly created one. A chelate mechanism involving the intermediacy of prochiral *o*-quinone methides is suggested to account for the regio-, enantio-, and diastereoselective reaction behavior.

Introduction

There exists an intense interest in the synthesis of well-defined, molecularly uniform oligonuclear phenolic compounds due to their occurrence in important synthetic resins and unique structural features.[3]

The previous paper of this series[1,4] described highly regiocontrolled syntheses of linear all-ortho methylene- and alkylidene-bridged polyphenols exploiting the use of nontransition metal complexes as organizing agents and selectivity factors. We now report a study directed toward the synthesis of optically active low molecular weight oligomers related to novolacs by using chirally modified organometallic promoters as a source of chirality.[5,6]

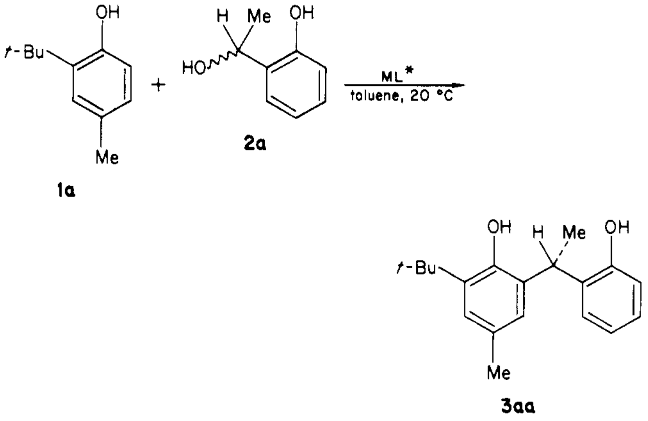
Results and Discussion

Preliminary Experiments. The asymmetric benzylation reaction in Scheme I leading to substituted binuclear compound **3aa** was chosen as a model for the preliminary optimization experiments.

The reaction was carried out under varied conditions by using aluminum(III) or titanium(IV) organometallics chiralized by suitable optically active ligands. In favorable instances, a fairly good chirality transfer from the chiral environment of the metallic promoter to the newly created chiral bridge occurred. Selected results are summarized in Table I.

Inspection of the data in Table I reveals a substantial ligand effect upon the asymmetric induction. Among tested aluminum auxiliaries (runs 1–11), (–)-menthol gave the best asymmetric induction, producing levorotatory **3aa** as the sole reaction product with 28% enantiomeric excess (enantiomer ratio, 64:36), and, as expected, an equal and opposite bias in favor of dextrorotatory **3aa** was observed by using the (+)-menthol-based organometallic.

Scheme I[a]



[a] ML* = the metal with its chiral environment.

Precise observance of the following reaction protocol is required to obtain good enantiocontrol. (a) In situ preparation of the chiralized promoter via ligand-exchange reaction between diethylaluminum chloride and the selected optically active auxiliary; (b) equilibration (30 min) and then addition of the phenol **1a**; (c) equilibration (30 min) and then addition of **2a**. Changing the sequence order by reversing (b) and (c) steps or conducting them simultaneously gave inferior results as far as the chemical and optical yield is concerned.

In a second set of experiments (runs 12–14), titanium(IV)-based chiralized promoters were investigated. Only

0024-9297/86/2219-0509$01.50/0

Table I
Ligand Effect in the Asymmetric Synthesis of 3aa[a]

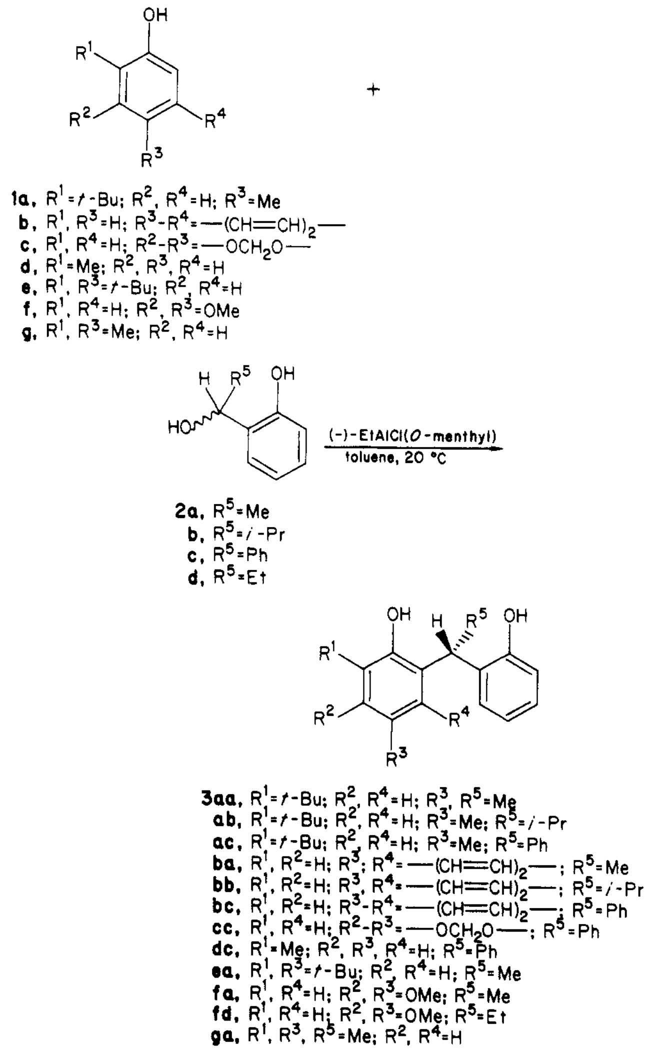
entry	catalyst	ligand[b]	% yield[c]	$[\alpha]^{20}_{D}$,[d] deg	ee,[e] %
1	Et_2AlCl	(-)-menthol	76	-7.2	28
2	Et_2AlCl	(+)-menthol	74	+7.6	31
3	Et_2AlCl	(-)-8-phenylmenthol	51	-6.5	26
4	Et_2AlCl	(-)-borneol	71	+5.7	23
5	Et_2AlCl	(-)-*N*-methylephedrine	60	0.0	0.0
6	Et_2AlCl	(-)-2,2′-dihydroxy-1,1-binaphthyl	51	-2.5	10
7	Et_2AlCl	(-)-cinconidine	51	+4.5	18
8	Et_2AlCl	L-arginine	70	+7.5	30
9	Et_2AlCl	L-valine	61	+5.5	22
10	Et_2AlCl	L-Z-serine	62	+4.2	18
11	Et_2AlCl	L-proline	64	+2.1	9
12	Ti(O-*i*-Pr)$_4$	(-)-menthol	26	0.0	0.0
13	Ti(O-*i*-Pr)$_4$	(-)-2,3-*O*-isopropylidene-D-threitol	19	+2.2	9
14	Ti(O-*i*-Pr)$_4$	L-2-(hydroxymethyl)pyrrolidine	21	+4.3	17

[a] All these reactions were carried out at 20 ± 0.5 °C as described in the Experimental Section. [b] Ligand/catalyst ratio, 1:1. [c] Isolated yield. [d] *c* 0.5 (ethanol). [e] Enantiomeric excess, determined by ^{1}H NMR in $CDCl_3$, using Eu(hfc)$_3$ chiral shift reagent.

those complexes that are derived from bifunctional ligands such as (−)-2,3-*O*-isopropylidene-D-threitol and L-2-(hydroxymethyl)pyrrolidine gave acceptable enantiocontrol, but the chemical yields of produced **3aa** were disappointingly very low.

Synthesis of Binuclear Compounds. In order to develop synthetic applications of this asymmetric approach we found among the systems investigated those based on a stoichiometric diethylaluminum chloride/menthol combination particularly attractive because of the commercial availability of both Et_2AlCl and optically active menthol (*l* and *d* enantiomers available), the easy recovery of the optically active ligand, and our previous experience with this system as an asymmetric catalyst in the hydroxyalkylation reaction of phenols.[5] The synthesis of the optically active binuclear oligomers **3** bearing CH(Me), CH(Et), CH(*i*-Pr), and CH(Ph) bridges proceeded as in Scheme II.

Scheme II



1a, R^1=*t*-Bu; R^2, R^4=H; R^3=Me
b, R^1, R^3=H; R^3-R^4= —(CH=CH)$_2$—
c, R^1, R^4=H; R^2-R^3= —OCH$_2$O—
d, R^1=Me; R^2, R^3, R^4=H
e, R^1, R^3=*t*-Bu; R^2, R^4=H
f, R^1, R^4=H; R^2, R^3=OMe
g, R^1, R^3=Me; R^2, R^4=H

2a, R^5=Me
b, R^5=*i*-Pr
c, R^5=Ph
d, R^5=Et

3aa, R^1=*t*-Bu; R^2, R^4=H; R^3, R^5=Me
ab, R^1=*t*-Bu; R^2, R^4=H; R^3=Me; R^5=*i*-Pr
ac, R^1=*t*-Bu; R^2, R^4=H; R^3=Me; R^5=Ph
ba, R^1, R^2=H; R^3; R^4= —(CH=CH)$_2$—; R^5=Me
bb, R^1, R^2=H; R^3, R^4= —(CH=CH)$_2$—; R^5=*i*-Pr
bc, R^1, R^2=H; R^3-R^4= —(CH=CH)$_2$—; R^5=Ph
cc, R^1, R^4=H; R^2-R^3= —OCH$_2$O—; R^5=Ph
dc, R^1=Me; R^2, R^3, R^4=H; R^5=Ph
ea, R^1, R^3=*t*-Bu; R^2, R^4=H; R^5=Me
fa, R^1, R^4=H; R^2, R^3=OMe; R^5=Me
fd, R^1, R^4=H; R^2, R^3=OMe; R^5=Et
ga, R^1, R^3, R^5=Me; R^2, R^4=H

Reaction of phenols **1** with racemic α-substituted salicyl alcohols **2** went smoothly with 3 mol equiv of ((−)-menthoxy)ethylaluminum chloride generated in situ by mixing equimolar amounts of Et_2AlCl and (−)-menthol. This treatment, followed by aqueous acidic quenching, resulted in the formation of optically active dimers **3**, whose chemical and optical yields are recorded in Table II.

Inspection of the data in Table II reveals a substantial dependence of the extent of the asymmetric induction upon the steric requirements of the bridging moiety. The data for the reactions involving methyl-, ethyl-, and phenyl-substituted alcohols **2a**, **2d**, and **2c** reveal a good bias in favor of levorotatory products, while reactions starting with isopropyl-substituted alcohol **2b** exhibit only a modest bias in favor of dextrorotatory dimers. Furthermore, by comparing the related experiments 1 and 3 and 4 and 6, one can see that the optical yields of benzylidene-linked dimers are always superior to those of ethylidene-bridged

Table II
Asymmetric Synthesis of Binuclear Oligomers 3[a]

entry	reactants	product	time, days	% yield[b]	$[\alpha]^{20}_{D}$,[c] deg	ee,[d] %
1	**1a + 2a**	**3aa**	2	76	-7.2	28
2	**1a + 2b**	**3ab**	5	57	+2.1	12
3	**1a + 2c**	**3ac**	2	60	-14.4	41
4	**1b + 2a**	**3ba**	5	39	-6.0	28
5	**1b + 2b**	**3bb**	5	45	+3.2	18
6	**1b + 2c**	**3bc**	5	49	-8.8	36
7	**1c + 2c**	**3cc**	1	85	-6.0	33
8	**1d + 2c**	**3dc**	2	74	-4.1	29
9	**1e + 2a**	**3ea**	2	88	-8.7	37
10	**1f + 2a**	**3fa**	2	24	-3.3	25
11	**1f + 2d**	**3fd**	2	28	-3.5	23
12	**1g + 2a**	**3ga**	6	32	-4.2	17

[a] All these reactions were carried out under comparable conditions by using Et_2AlCl/(−)-menthol chiral catalyst. [b] Isolated yield of >98% pure material (by HPLC). [c,d] See notes *d* and *e* in Table I.

Scheme III

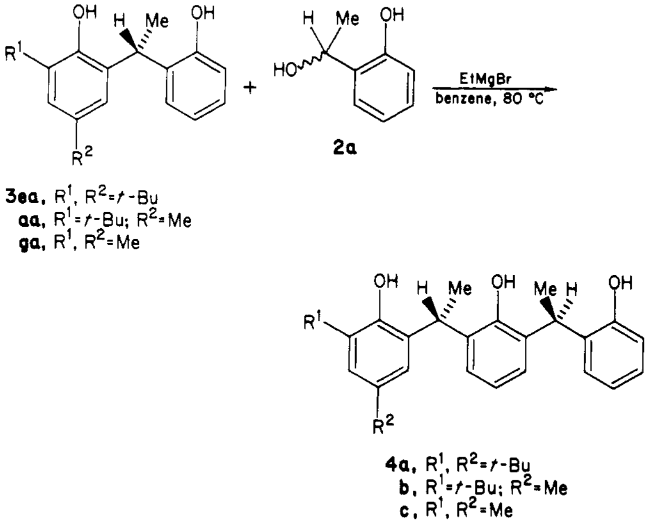


Table III
Asymmetric Synthesis of Trinuclear Oligomers 4[a]

entry	product	% yield[b]	$[\alpha]^{20}_{D}$,[c] deg	de,[d] %	ee,[e] %	confign[f]
1	**4a**	61	−22.7	>95	38	*R*,R**
2	**4b**	44	−12.1	>95	30	*R*,R**
3	**4c**	39	−4.8	>95	14	*R*,R**

[a] Conditions, see the Experimental Section. [b,c] See notes *c* and *d* in Table I. [d] Determined by HPLC. [e] See note *e* in Table I. [f] Based on the relative configuration of (±)-**4a**, determined by X-ray analysis.

compounds, suggesting that, when equally substituted phenols are involved, the steric congestion around the chiral bridging carbon is the more decisive factor in determining stereocontrol.

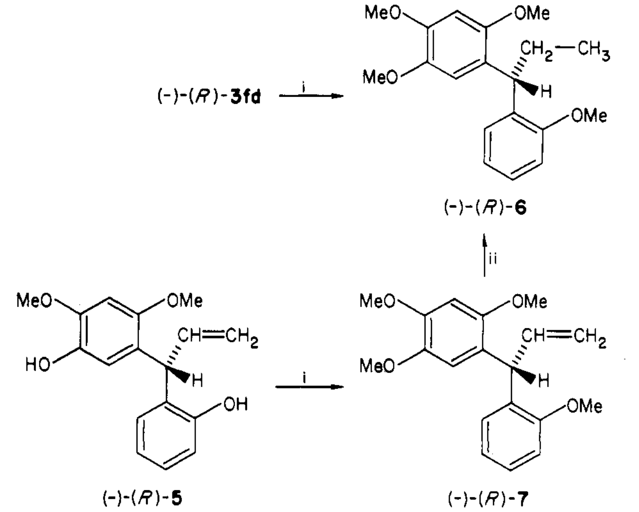
Synthesis of Trinuclear Compounds. Recent studies from this laboratory[1,7] have shown that the stereochemical outcome of non-transition-metal-assisted condensation of alkylidene-bridged binuclear phenolic compounds with α-substituted salicyl alcohols leading to trinuclear diastereoisomers can be controlled by a proper combination of catalysts and reactants. On this basis, we focused our attention on the reaction in Scheme III in order to provide a stereocontrolled entry into optically active trimers.

Rather fortunately, for the three selected examples, with 3 mol equiv of EtMgBr in benzene, the reactions behaved regio- and diastereospecifically, producing threo trimers **4** as predominant products with virtually complete chirality transfer from the existing chiral bridge to the newly formed one. Thus, treatment of enantiomerically enriched (−)-**3ea** (37% ee) in refluxing benzene with (±)-**2a** in the presence of the Grignard reactant gave rise to *threo*-(−)-**4a** in 37% isolated yield with >95% diastereomeric excess and essentially complete retention of the optical purity. Similarly, (−)-**3aa** led to *threo*-(−)-**4b** and (−)-**3ga** led to *threo*-(−)-**4c** (Table III).

The most striking feature in the asymmetric synthesis outlined here is that the enantiomeric purity of the final products **4** is essentially the same of the starting dimers **3**. This means that the chirality transfer proceeds with nearly 100% efficiency throughout the growth sequence.

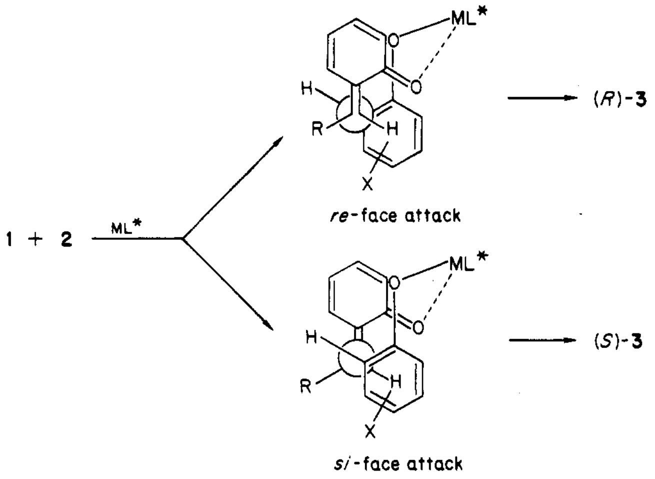
Configurational Assignments of 3 and 4. (−)-Latifolin (**5**), a naturally occurring hydroxylated diphenylmethane from *Dalbergia latifolia* is known to possess *R* chirality at the bridging carbon.[8] In order to determine the absolute configuration of at least one of the enantiomerically enriched dimers in this study, (−)-**3fd** was correlated to (−)-(*R*)-latifolin (Scheme IV). Thus (−)-**3fd** was methylated to dihydrolatifolin dimethyl ether (**6**), whose rotation in ethanol is (−). Since the absolute configuration of (−)-**6** was established as *R* by chemical correlation to (−)-(*R*)-latifolin, we assigned with confidence *R* absolute configuration to levorotatory **3fd**.

Scheme IV
Chemical Correlations between (−)-(*R*)-3fd and (−)-(*R*)-Latifolin (5)[a]



[a] Conditions: (i) $(CH_3)_2SO_4$ in aqueous NaOH at room temperature; (ii) H_2, C/Pd in ethanol.

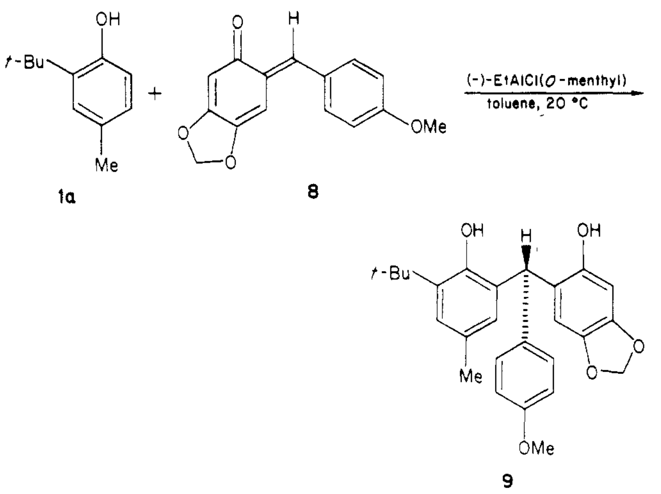
Scheme V



In order to assign the relative topicity to the 7,7′ bridges of the trimeric diastereoisomers, a single crystal of **4a** was subjected to X-ray analysis (see next section). Suitable crystals were obtained from only (±)-**4a** prepared by starting with (±)-**3ea**. The analysis unambiguously showed the anti location of the two 7,7′-methyls, and, therefore, the relative stereochemistry was assigned as *R*,R**, or like or threo.[9] By analogy, we also assigned *R*,R** topicity to both (−)-**4b** and (−)-**4c**, owing to the threo preference of our synthetic methodology.

Mechanistic Considerations. In the related papers of this series[1,4,7] we suggested chelate mechanisms involving metal phenolates and *o*-quinone methide intermediates to account for both the regio- and stereoselective outcome of the condensation reactions leading to all-ortho alkylidene-linked oligonuclear phenolic compounds. If the key reaction really includes metal-controlled interaction between the phenol molecule and the prochiral quinonic species we can obtain, in principle, an enantiocontrolled

Scheme VI



(and regiospecific) reaction when a metal bearing a suitable chiral periphery is involved.

As can be seen in Scheme V, in the presence of a chiral component (L*) two diastereomeric transient complexes are formed for *si*- and *re*-face attacks, respectively, whose activation free energies can differ in such a way that enantiodifferentiation occurs. The results herein showing fairly good enantioselection strongly support such a chelate mechanism involving the intermediacy of prochiral *o*-quinone methides.

In addition, two crucial experiments were carried out supporting this mechanistic picture. First, the asymmetric reaction of experiment 1 in Table I leading to (-)-(*R*)-**3aa** was stopped at ca. 20% and 50% substrate conversion. Recovery of the starting unreacted alcohol **2a** as a racemate rules out a kinetic resolution mechanism via direct enantiomer differentiation of (±)-**2a** by means of the chiralized aluminum phenolates, suggesting preliminary transformation of both the enantiomers of **2a** into a common prochiral intermediate (e.g., *o*-quinone methide) and subsequent enantioface-discrimination reaction.

Second, we synthesized the stable *o*-quinone methide **8**[10] whose *E* geometry has been recently established by X-ray analysis,[11] and then we submitted this prochiral reactant to asymmetric condensation with **1a** by using (-)-EtAlCl(*O*-menthyl) at room temperature. After an aqueous workup, levorotatory triphenylmethane **9** was isolated in 36% chemical yield with 16% ee (Scheme VI).

Taken together these results provide strong support to the chelate mechanism depicted in Scheme V, establishing firmly the occurrence of incipient *o*-quinone methides in condensation involving *o*-hydroxybenzyl alcohols and metal phenolates.[12]

X-ray Analysis. Solid-state studies of phenol–aldehyde resins of the novolac type and related linear oligomers have been carried out only in recent years by using either ^{13}C CP/MAS spectroscopy[13] or single-crystal X-ray analysis.[4,14] In order to assign unambiguously the relative configuration of at least one of the trimers of this study and, especially, to achieve information about the hydrogen bonding and solid-state conformational arrangement in these molecules, a single crystal of racemic **4a** was subjected to X-ray analysis. The related dimer (±)-**3aa** was analyzed too, in order to provide additional data on the molecular association in the crystal when bulky substituents are involved.

Bond distances, bond angles, and selected torsion angles of the two compounds **3ea** and **4a** are comparable in the two molecules and, as expected for these types of systems, nonsignificantly deviate from average values in the literature.[15] Figure 1 shows a projection of the dinuclear oligomer **3aa** on the plane defined by the atoms O1, O1′, and C7. Figure 2 shows a projection of the trimer **4a**.

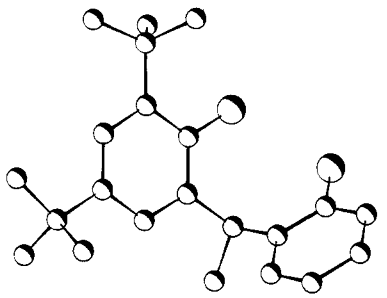


Figure 1. Molecular structure of compound **3ea**.

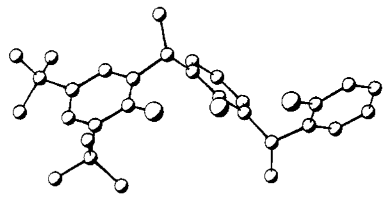


Figure 2. Molecular structure of compound **4a**.

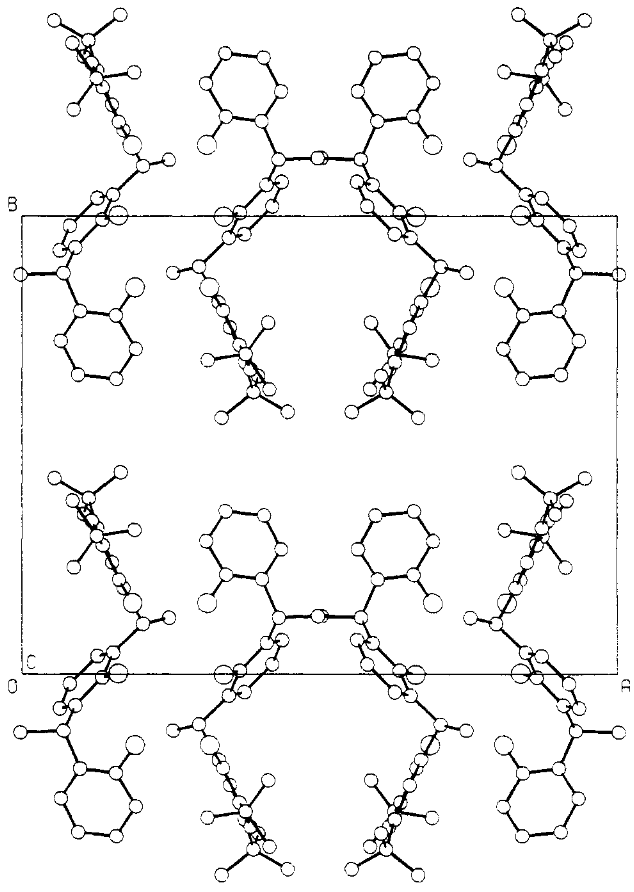


Figure 3. Compound **4a**. Molecular packing seen along [001].

As can be noted, **4a** shows an anti conformation (chairlike), in the sense that the two external phenolic rings are placed in an anti position as observed for trinuclear phenol–formaldehyde and racemic phenol–acetaldehyde oligomers.[1,4] In the solid state the conformation of both the molecules is mainly determined by the intramolecular H-bond system involving the OH groups: the preferential conformations are those in which the H-bond system runs at the opposite side with respect to the CH_3 group.

Table IV
Intramolecular and Intermolecular Hydrogen Bonding in Compounds 3ea and 4a[a]

3ea	4a
Intramolecular Bonding	
O1-HO1 = 0.89 (4)	O1···O1′ = 2.732 (7)
O1···O1′ = 2.867 (3)	O′···O1″ = 2.734 (7)
HO1···O1′ = 1.98 (4)	O1···O1′···O1″ = 143.0 (2)
O1-HO1···O1′ = 168 (3)	
O1′-HO1′ = 0.81 (4)	
Intermolecular Bonding[b]	
	$O1''\cdots O1^{i}$ = 2.742 (9)
	$O1'\cdots O1''\cdots O1^{i}$ = 104.0 (2)
	$O1''\cdots O1^{i}\cdots O1'^{i}$ = 99.5 (2)

[a] Bonding in angstroms or degrees. [b] $i = {}^{1}/_{2} - x, -y, z$.

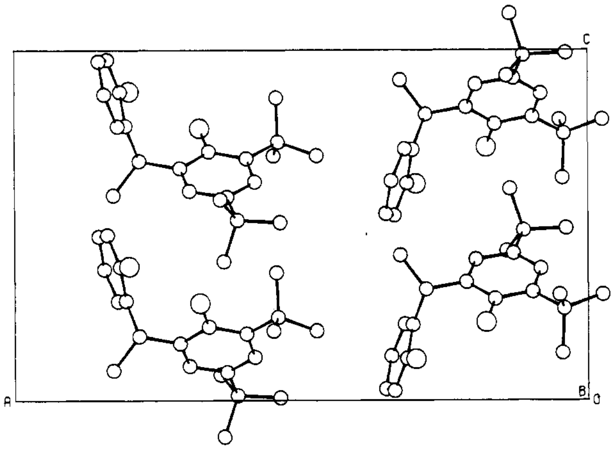


Figure 4. Compound **3ea**. Molecular packing seen along [010].

In the solid state the **4a** molecules are joined in cyclic dimeric units by intermolecular H bonding (Figure 3). The H-bond system is an isodromic system, each OH being a donor and an acceptor at the same time in an ordered sequence. This characteristic is clearly shown by the O···O intra- and intermolecular distances given in Table IV together with the other geometrical parameters involving the H bonding.

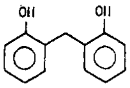
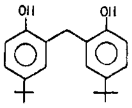
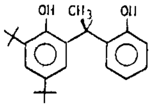
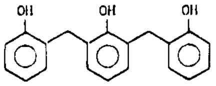
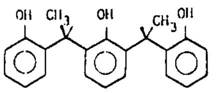
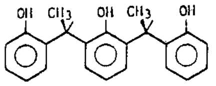
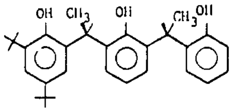
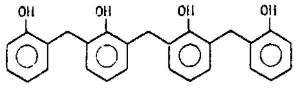
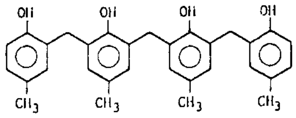
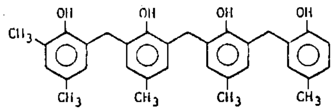
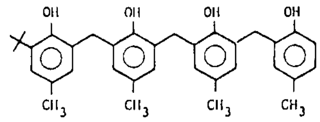
Since in the ΔF map residual electron density peaks to be assigned to the OH hydrogens were found in positions equidistant from two oxygen atoms, a reasonable model for the description of the hydrogen bonding is to consider a random distribution in the crystal of two ordered O–H···O sequences.

The behavior of the dinuclear oligomer **3ea** in the molecular packing is singular (Figure 4). The presence of the ortho substituent inhibits the formation of cooperative chains, and, on the other hand, the formation of dimeric units is not possible mainly due to the geometrical requirements of the OH···OH···O angles, usually in the 110°–145° range. So the oligomer remains monomeric in the molecular packing. The hydrogen-bonding system is fully described with O1 as donor and O2 as acceptor.

The amount of structural data available for this type of compound is now sufficient for a first attempt to rationalize their behavior in the solid state in terms of the dependence on the substitution at the bridges and at the phenolic rings. Table V summarizes the conformations and the molecular packing of di-, tri-, and tetranuclear oligomers studied up to now.

The influence of the substituent at the bridging carbon on the molecular conformation was discussed in a previous paper.[1] A general rule was formulated that assigns a staggered conformation (anti) of the external rings to racemic diads and an eclipsed conformation (syn) to meso diads. The molecular packing of **4a** is in agreement with this rule. The ortho substitution at the phenolic rings plays an important role in determining the molecular packing. The steric hindrance of the ortho substituent always inhibits the formation of infinite cooperative chains, so that only small discrete units (at maximum dimers) can be present. Moreover the ortho substitution influences the conformation of the tetranuclear oligomers since only a syn–anti conformation permits the formation of these dimeric units. The molecular packing of the trinuclear oligomers seems, on the other hand, not to be influenced by conformations and substitutions. All the trimers studied up to now present, in the solid state, dimeric units which are probably related to the energy minimum of the system.

Table V
Solid-State Conformational Arrays and Packing Mode of All-Ortho Oligonuclear Phenolic Compounds

compd	conformation	packing	ref
		infinite chains	4
		hexameric units	4
		monomeric units	a
	anti	dimeric units	4
	anti	dimeric units	1
	syn	dimeric units	1
	anti	dimeric units	a
	syn–anti	infinite chains	4
	anti–anti	infinite chains	14
	syn–anti	dimeric units	14
	syn–anti	dimeric units	14

[a] This work.

Summary and Conclusions

We have reported a synthetic approach to chiral optically enriched novolac-type oligomers based on enantiodifferentiating condensation of phenols with in situ generated prochiral *o*-quinone methides assisted by metal ions bearing a chiral environment (chiralized cations).

The synthesis of binuclear compounds proceeded well with variable stereochemical biases according to the nature and the periphery of the employed metal promoter as well as the steric requisites of the reactants. Thus, with a variety of optically active binuclear synthons available, the stereocontrolled growth reaction to trinuclear oligomers was further made viable with high diastereocontrol (>95% threoselectivity) and essentially complete retention of the starting optical purity.

This work convincingly demonstrates that *o*-quinone methides are the true electrophilic species in the condensation reactions between phenols and salicyl alcohol derivatives when Lewis acid organometallics are involved.

In closing, we are confident that this stereocontrolled condensation will be valuable in the synthesis of chiral polyphenol targets, and, of course, studies directed toward incorporating chirality into all-ortho linked novolacs will be the subjects of future reports.

Experimental Section

General. All melting points are uncorrected. The ^{1}H NMR spectra were obtained on a Bruker CXP 200 spectrometer at 200 MHz. Chemical shifts are expressed in ppm relative to Me_4Si as internal standard. UV spectra were recorded on a Jasco UVIDEC 505 instrument and were run in 95% ethanol solution, IR spectra on a Perkin-Elmer 298 spectrophotometer, and mass spectra on a Varian MAT CH-5 spectrometer with a direct insertion probe (70 eV). Optical rotations were recorded on a Autopol III polarimeter in 95% ethanol solution (*c* 0.5, 1-dm cell). CD spectra were measured by using a Jasco J-500A spectropolarimeter with a DP-500 N data processor in 95% ethanol solution (*c* 10^{-3}, 0.1-cm cell). The enantiomeric purity (ee) of all dinuclear and trinuclear compounds in this study was determined by direct ^{1}H NMR analysis (200 MHz, $CDCl_3$) by using tris[((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III) (Aldrich).

Materials. All chemicals were reagent grade and were used without further purification. Toluene and benzene were dried and stored over molecular sieves. Diethylaluminum chloride (1 M hexane solution) was purchased from Aldrich, and titanium tetraisopropoxide was from Carlo Erba. *rac*-2-Hydroxy-α-methylbenzyl alcohol (**2a**) was prepared by $NaBH_4$ reduction of 2-hydroxyacetophenone in methanol solution. *rac*-2-Hydroxy-α-isopropylbenzyl alcohol (**2b**), *rac*-2-hydroxy-α-phenylbenzyl alcohol (**2c**), and *rac*-2-hydroxy-α-ethylbenzyl alcohol (**2d**) were prepared by the reaction of 2-hydroxyacetophenone with isopropyl-, phenyl-, and ethylmagnesium bromide respectively in diethyl ether. The chiral auxiliaries in this study were commercially available: (−)-menthol (Carlo Erba); (+)-menthol (Aldrich); (−)-borneol, L-arginine, L-valine, Z-L-serine, (−)-*N*-methylephedrine, and (−)-2,3-*O*-isopropylidene-D-threitol (Fluka); (−)-cinconidine, (−)-2,2′-dihydroxybinaphthyl, and L-2-(hydroxymethyl)pyrrolidine (EGA-Chemie); L-proline (Merck). (−)-8-Phenylmenthol was synthesized from (+)-pulegone (EGA-Chemie) following the reported procedure.[16]

(−)-4-Methyl-6-*tert*-butyl-2,2′-ethylidenediphenol (3aa). Typical Procedure. To 15 mL (15 mmol) of a 1 M Et_2AlCl solution in hexane a solution of (−)-menthol (2.34 g, 15 mmol) in toluene (10 mL) was added dropwise at 0 °C over a period of 10 min. After stirring at room temperature for 30 min, a solution of 2-*tert*-butyl-4-methylphenol (**1a**) (0.82 g, 5 mmol) in 10 mL of toluene was added, and the mixture was stirred for 30 min. To this a solution of (±)-α-methylsalicyl alcohol (**2a**) (0.83 g, 5 mmol) in 5 mL of toluene was added, and the light yellow solution was stirred at room temperature for 2 days. The mixture was then quenched with an excess of an aqueous ammonium chloride solution and extracted with diethyl ether (3 × 50 mL). The ethereal extract was washed (water), dried (Na_2SO_4), and concentrated. Chromatography (150 g of SiO_2, 85:15 hexane/acetone) of the residue gave (−)-**3aa** (1.08 g, 76%) as a white solid: mp 126–129 °C; $[\alpha]^{20}_{D}$ −7.2°; $[\Theta]_{271}$ −1985; MS, *m/e* 284 (M^+); IR (KBr) 3230, 2960, 1460, 1220, 760 cm^{-1}; UV, λ_{max} 280 nm (ϵ 4432); ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H, *t*-Bu), 1.64 (d, 3 H, CH*Me*), 2.28 (s, 3 H, Me), 4.60 (q, 1 H, C*H*Me), 5.51 (s, 1 H, OH), 5.98 (s, 1 H, OH), 6.72–7.41 (m, 6 H, Ar H). Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.32; H, 8.71. The following dimers, listed in Table II, were prepared in a similar way:

(+)-4-Methyl-6-*tert*-butyl-2,2′-isobutylidenediphenol (3ab): mp 154–156 °C; $[\alpha]^{20}_{D}$ +2.1°; $[\Theta]_{277}$ −1181; MS, *m/e* 312 (M^+); IR (KBr) 3250, 2960, 1460, 1240, 1200, 760 cm^{-1}; UV, λ_{max} 284 nm (ϵ 5770); ^{1}H NMR ($CDCl_3$) δ 0.85 (m, 6 H, CH*Me*$_2$), 1.36 (s, 9 H, *t*-Bu), 2.20 (s, 3 H, Me), 2.55 (m, 1 H, C*H*Me$_2$), 4.01 (d, 1 H, C*H*-*i*-Pr), 6.02 (s, 1 H, OH), 6.43 (s, 1 H, OH), 6.6–7.4 (m, 6 H, Ar H). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.85; H, 9.09.

(−)-4-Methyl-6-*tert*-butyl-2,2′-benzylidenediphenol (3ac): mp 178–180 °C; $[\alpha]^{20}_{D}$ −14.4°; $[\Theta]_{272}$ −1151; MS, *m/e* 346 (M^+); IR (KBr) 3500, 2960, 1441, 1240, 1150, 760 cm^{-1}; UV, λ_{max} 279 nm (ϵ 5407); ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H, *t*-Bu), 2.18 (s, 3 H, Me), 4.80 (s, 1 H, C*H*(Me)$_2$), 4.94 (s, 1 H, OH), 5.80 (s, 1 H, OH), 6.5–7.4 (m, 11 H, Ar H). Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.37; H, 7.69.

(−)-1-(2-Hydroxynaphthyl)-1-(2-hydroxyphenyl)ethane (3ba): mp 115–116 °C; $[\alpha]^{20}_{D}$ −6.0°; $[\Theta]_{282}$ +748; MS, *m/e* 264 (M^+); IR (KBr) 3260, 2960, 1490, 1260, 1220, 810, 760 cm^{-1}; UV, λ_{max} 279 nm (ϵ 5130); ^{1}H NMR ($CDCl_3$) δ 1.83 (d, 3 H, CH*Me*), 5.14 (q, 1 H, C*H*Me), 5.67 (s, 1 H, OH), 6.10 (s, 1 H, OH), 6.7–8.3 (m, 10 H, Ar H). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.91, H, 6.33.

(+)-1-(2-Hydroxynaphthyl)-1-[(2-hydroxyphenyl)methyl]propane (3bb): mp 177–179 °C; $[\alpha]^{20}_{D}$ +3.2°; $[\Theta]_{284}$ +915; MS, *m/e* 292 (M^+); IR (KBr) 3260, 2960, 1450, 1260, 1220, 810, 760 cm^{-1}; UV, λ_{max} 280 nm (ϵ 6941); ^{1}H NMR ($CDCl_3$) δ 1.12 (m, 6 H, CH(*Me*)$_2$), 3.20 (m, 1 H, C*H*(Me)$_2$), 4.58 (d, 1 H, C*H*-*i*-Pr), 6.6–8.4 (m, 12 H, Ar H and OH). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.26; H, 7.07.

(−)-α-(2-Hydroxynaphthyl)-α-(2-hydroxyphenyl)toluene (3bc): mp 151–159 C; $[\alpha]^{20}_{D}$ −8.8°; $[\Theta]_{288}$ −572; MS, *m/e* 326 (M^+); IR (KBr) 3500, 1610, 1460, 1240, 1210, 820, 760 cm^{-1}; UV, λ_{max} 280 nm (ϵ 7946); ^{1}H NMR ($CDCl_3$) δ 5.42 (s, 1 H, CH), 5.58 (s, 1 H, OH), 6.5–8.1 (m, 11 H, Ar H and OH). Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64, H, 5.56. Found: C, 84.80, H, 5.71.

(−)-2,2′-Dihydroxy-4,5-methylenedioxytriphenylmethane (3cc): glassy solid; $[\alpha]^{20}_{D}$ −6.0°; MS, *m/e* 320 (M^+); IR (KBr) 3440, 1490, 1180, 760 cm^{-1}; UV, λ_{max} 302 nm (ϵ 6060); ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 2 H, CH_2), 5.10 (bs, 1 H, OH), 5.60 (bs, 1 H, OH), 6.7–8.2 (m, 12 H, ArOH and CH). Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 75.12; H, 5.32.

(−)-2,2′-Dihydroxy-3-methyltriphenylmethane (3dc): mp 119–123 °C; $[\alpha]^{20}_{D}$ −4.1°; MS, *m/e* 290 (M^+); IR (KBr) 3520, 1600, 1500, 1450, 1210, 760 cm^{-1}; UV, λ_{max} 275 nm (ϵ 4665); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H, Me), 3.92 (bs, 1 H, OH), 3.98 (bs, 1 H, OH), 5.92 (s, 1 H, CH), 6.7–7.4 (m, 12 H, Ar H). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.79; H, 6.49.

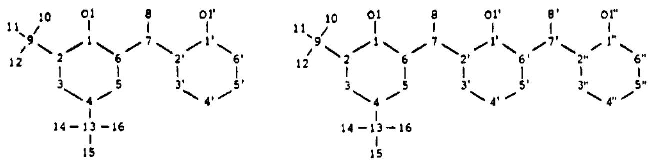
(−)-4,6-Di-*tert*-butyl-2,2′-ethylidenediphenol (3ea): mp 128–131 °C; $[\alpha]^{20}_{D}$ −8.7°; $[\Theta]_{276}$ −1101; MS, *m/e* 326 (M^+); IR (KBr) 3440, 2950, 1590, 1500, 1220, 760 cm^{-1}; UV, λ_{max} 279 nm (ϵ 4617); ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9 H, *t*-Bu), 1.41 (s, 9H, *t*-Bu), 1.67 (d, 3 H, CH*Me*), 4.63 (q, 1 H, C*H*Me), 6.20 (bs, 2 H, OH), 6.6–7.3 (m, 6 H, Ar H). Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 81.09; H, 9.36.

(−)-4,5-Dimethoxy-2,2′-ethylidenediphenol (3fa): oil; $[\alpha]^{20}_{D}$ −3.3°; MS, *m/e* 274 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.60 (d, 3 H, CH*Me*), 3.66 (s, 1 H, OMe), 3.75 (s, 1 H, OMe), 4.51 (q, 1 H, C*H*Me), 6.1 (s, 1 H, OH), 6.32 (s, 1 H, OH), 6.6–7.3 (m, 6 H, Ar H). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.29; H, 6.40.

(−)-4,5-Dimethoxy-2,2′-propylidenediphenol (3fd): oil; $[\alpha]^{20}_{D}$ −3.5°; $[\Theta]_{288}$ −530; MS, *m/e* 288 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH$_2$*Me*), 2.11 (m, 2 H, C*H*$_2$Me), 3.69 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 4.19 (t, 1 H, C*H*CH$_2$), 6.25 (s, 1 H, OH), 6.36 (s, 1 H, OH), 6.7–7.3 (m, 6 H, Ar H). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.99; H, 7.12.

(−)-4,6-Dimethyl-2,2′-ethylidenediphenol (3ga): mp 140–143 °C; $[\alpha]^{20}_{D}$ −4.2°; $[\Theta]_{273}$ +622; MS, *m/e* 242 (M^+); IR (KBr) 3420, 3320, 2980, 1490, 1190, 760 cm^{-1}; UV, λ_{max} 279 nm (ϵ 4226); ^{1}H NMR ($CDCl_3$) δ 1.65 (d, 3 H, CH*Me*), 2.21 (s, 3 H, Me), 2.23 (s, 3 H, Me), 4.61 (q, 1 H, C*H*Me), 5.62 (s, 1 H, OH), 5.97 (s, 1 H, OH), 6.7–7.4 (m, 6 H, Ar H). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.60; H, 7.63.

Table VI
Crystal Data and Atom Numbering Scheme for Compounds 3ea and 4a



compd	3ea	4a
formula	$C_{22}H_{30}O_2$	$C_{30}H_{38}O_3$
M_r	326.48	446.63
crystal system	orthorhombic	orthorhombic
space group	*Pbca*	*Pcca*
Z	8	8
a, Å	20.586 (3)	21.807 (3)
b, Å	15.453 (2)	16.642 (3)
c, Å	12.513 (2)	14.680 (2)
V, Å^3	3980 (1)	5327 (1)
D_c, g cm^{-3}	1.090	1.114
radiation	Cu *Kα*	Cu *Kα*
temp, °C	22 ± 1	22 ± 1
final *R* value	0.067	0.114

***threo*-(−)-2-(2-Hydroxy-3,5-di-*tert*-butyl-α-methylbenzyl)-6-(2-hydroxy-α-methylbenzyl)phenol (4a). Typical Procedure.** To a solution of ethylmagnesium bromide (3 mmol) in diethyl ether (25 mL) was added with stirring a solution of (−)-4,6-di-*tert*-butyl-2,2′-ethylidenediphenol (**3ea**, 37% ee) (0.33 g, 1 mmol) and *rac*-2-hydroxy-α-methylbenzyl alcohol (**1a**) (0.14 g, 1 mmol) in diethyl ether (25 mL) at room temperature. The ether was removed completely under vacuum, and anhydrous toluene (50 mL) was added. The resulting mixture was refluxed with stirring for 12 h, quenched with an excess of a saturated ammonium chloride solution, and extracted with diethyl ether (3 × 25 mL). The ethereal extract was washed (water), dried (Na_2SO_4), and concentrated. Chromatography (50 g of SiO_2, 70:30 hexane/acetone) of the oily residue gave (−)-**4a** (0.27 g, 61%) as a white solid: mp 175–179 °C; $[\alpha]^{20}_{D}$ −22.7; $[\Theta]_{279}$ −883; MS, *m/e* 446 (M^+); IR (KBr) 3260, 2960, 1590, 1240, 760 cm^{-1}; UV, λ_{max} 279 nm (ε 6630); ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9 H, *t*-Bu), 1.41 (s, 9 H, *t*-Bu), 1.71 (d, 3 H, CH*Me*), 1.73 (d, 3 H, CH*Me*), 3.62 (q, 2 H, C*H*Me), 5.30 (s, 2 H, OH), 6.02 (s, 1 H, OH), 6.29 (s, 1 H, OH), 7.0–7.4 (m, 9 H, Ar H). Anal. Calcd for $C_{30}H_{38}O_3$: C, 80.68; H, 8.58. Found: C, 80.91; H, 8.60. The following trimers listed in Table III were prepared in a similar way:

***threo*-(−)-2-(2-Hydroxy-3-*tert*-butyl-5-methyl-α-methylbenzyl)-6-(2-hydroxy-α-methylbenzyl)phenol (4b)**: mp 176–179 °C; $[\alpha]^{20}_{D}$ −12.1; $[\Theta]_{279}$ −666; MS, *m/e* 404 (M^+); IR (KBr) 3360, 2960, 1590, 1240, 760 cm^{-1}; UV, λ_{max} 279 nm (ε 6871); ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 9 H, t-Bu), 1.60 (d, 6 H, CH*Me*), 2.28 (s, 3 H, Me), 4.68 (m, 2 H, C*H*Me), 6.04 (s, 1 H, OH), 6.30 (s, 1 H, OH), 6.7–7.4 (m, 10 H, Ar H and OH). Anal. Calcd for $C_{27}H_{32}O_3$: C, 80.16; H, 7.97. Found: C, 80.26; H, 8.12.

***threo*-(−)-2-(2-Hydroxy-3,5-dimethyl-α-methylbenzyl)-6-(2-hydroxy-α-methylbenzyl)phenol (4c)**: mp 179–182 °C; $[\alpha]^{20}_{D}$ −4.8; MS, *m/e* 362 (M^+); IR (KBr) 3220, 2980, 1600, 1240, 760 cm^{-1}; UV, λ_{max} 279 nm (ε 6657); ^{1}H NMR ($CDCl_3$) δ 1.50 (d, 3 H, CH*Me*), 1.58 (d, 3 H, CH*Me*), 2.18 (s, 6 H, Me), 4.58 (m, 2 H, C*H*Me), 6.00 (s, 1 H, OH), 6.49 (s, 1 H, OH), 6.6–7.4 (m, 10 H, Ar H and OH). Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.53, H, 7.23. Found: C, 79.68; H, 7.40.

(−)-(*R*)-2,2′,4,5-Tetramethoxy-1,1-diphenylethane (Dihydrolatifolin Dimethyl Ether) (6). To a solution of (−)-4,5-dimethoxy-2,2′-propylidenediphenol (**3fd**) (0.29 g, 1 mmol) in 8 mL of dry acetone containing anhydrous potassium carbonate (1.5 g) was added dimethyl sulfate (0.65 g, 5 mmol), and the mixture was stirred at room temperature for 5 h while a stream of dry nitrogen was passing. After filtration, the excess of dimethyl sulfate was decomposed by the addition of water, and the mixture was extracted with ether. Removal of the solvent gave an oily residue that crystallized on standing (0.24 g, 76%). A pure sample of (−)-**6** was obtained by chromatography (SiO_2; 8:2 hexane/acetone): mp 62–65 °C; $[\alpha]^{20}_{D}$ −3.6 (*c* 1, 95% ethanol); MS, *m/e* 316 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.83 (t, 3 H, CH_2*Me*), 2.04 (m, 2 H, C*H*$_2$Me), 3.79 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 4.24 (t, 1 H, C*H*Et), 6.3–7.4 (m, 6 H, Ar H).

(−)-(2-Hydroxy-3-*tert*-butyl-5-methylphenyl)(2-hydroxy-4,5-methylenedioxyphenyl)(4-methoxyphenyl)methane (9). To an in situ prepared solution of ((−)-menthoxy)ethylaluminum chloride (15 mmol) in 10 mL of toluene was added a solution of 2-*tert*-butyl-4-methylphenol (**1a**) (0.82 g, 5 mmol) in 10 mL of toluene, and the mixture was stirred at room temperature for 30 min. To this was added a solution of (*E*)-6-(4-methoxybenzylidene)-3,4-methylendioxycyclohexa-2,4-dienone[10] (**8**) (1.30 g, 5 mmol) in 5 mL of toluene, and the blue-violet solution was stirred at room temperature for 24 h. After the usual workup (aqueous quenching, extraction, drying, and removal of the solvent), silica gel chromatography of the residue using a 7:3 hexane/acetone solvent mixture gave (−)-**9** (0.75 g, 36%) as a pale yellow viscous oil: $[\alpha]^{20}_{D}$ −3.1 (*c* 1, 95% ethanol); MS, *m/e* 420 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H, *t*-Bu), 2.10 (s, 3 H, Me), 3.75 (s, 3 H, OMe), 4.80 (s, 1 H, OH), 5.51 (s, 1 H, OH), 5.80 (s, 2 H, OCH_2O), 6.25 and 6.37 (2s, 1 H each, 2′-H and 6′-H), 6.40 and 6.95 (2s, 1 H each, 4-H and 6-H), 6.81 and 7.05 (2d, 4 H, 2″-, 3″-, 5″-, and 6″-H). Anal. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.13; H, 6.90.

X-ray Analysis. Compound 3ea. Colorless prismatic crystals were grown from a hexane solution at room temperature. The space group was determined by systematic absences. Precise cell parameters (from 29 high-order reflections) and 4250 three-dimensional intenisty data (*hkl*, $2\theta_{max}$ = 120°) were measured on a General Automation GA Jumbo 220 controlled Siemens diffractometer with Ni-filtered Cu Kα radiation (λ = 1.54178 Å) using the $\omega - 2\theta$ scan mode. Intergrated intensities were obtained by using a profile-analysis program. The reference reflection used for control and scaling of the intensities in the course of the data collection showed no significant variations. Crystal data are summarized in Table VI. The structure was solved by direct methods. The atomic parameters were refined by least-squares procedures, using anisotropic temperature factors. The hydrogen atoms attached to oxygens and carbons were located on a ΔF map; those of the *p*-*tert*-butyl group, for which the electron density peaks were not well resolved, were included in the refinement with geometrically calculated positional parameters. The hydrogen atoms were included in the refinement with isotropic temperature factors. The final *R* value ($R = \sum|F_o| - |F_c|/|F_o|]$) was 0.067 for the 2831 independent observed reflections ($I \geq 3\sigma(I)$) with (number of observations)/(number of refined parameters) of 9.4. The average shift/error ratio at the end of the refinement was 0.015. Fractional coordinates are given in Table VII (Supplementary Material).

Compound 4a. Colorless prismatic crystals were obtained from a toluene solution at room temperature. Crystal data were determined as before and 3533 three-dimensional data (*hkl*, $2\theta_{max}$ = 120°) were measured on the same diffractometer and with the same procedure.

The reference reflection showed no significant variations. Crystal data are collected in Table VI. The structure was solved by direct methods and refined by least squares using anisotropic temperature factors and with the constraint of C–H = 1.08 Å. Hydroxyl hydrogen atoms were not refined. The final *R* value was 0.110 for the 1850 independent observed reflections ($I \geq 3\sigma(I)$) with (number of observation)/(number of refined parameters) of 5.2. The fractional coordinates are reported in Table VIII (Supplementary Material). All the calculations were executed on a SEL 32/77 Computer of the Institute by using the SHELX system of programs.[17]

Acknowledgment. We are grateful to Dr. Volker Böhmer of Mainz University for suggestions and valuable discussions. This work was supported by the Consiglio Nazionale delle Ricerche, Progetto Finalizzato Chimica Fine e Secondaria.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, selected torsion angles, and anisotropic thermal parameters for compounds **3ea** and **4a** (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 3. Casiraghi, G.; Cornia, M.; Ricci, G.; Casnati, G.; Andreetti, G. D.; Zetta, L. *Macromolecules* **1984**, *17*, 19–28.

(2) (a) Istituto di Chimica Organica, Università di Parma. (b) Istituto di Strutturistica Chimica, Università di Parma. (c) Istituto di Chimica delle Macromolecole, CNR Milano.

(3) Recent reviews: Böhmer, V. *Netsu Kokasei Jushi* **1983**, *4*, 220–235. Böhmer, V. *Netsu Kokasei Jushi* **1984**, *5*, 148–164. Gutshe, C. D. *Top. Curr. Chem.* **1984**, *123*, 1–47.

(4) Casiraghi, G.; Cornia, M.; Sartori, G.; Casnati, G.; Bocchi, V.; Andreetti, G. D. *Makromol. Chem.* **1982**, *183*, 2611–2633. Casiraghi, G.; Cornia, M.; Ricci, G.; Balduzzi, G.; Casnati, G.; Andreetti, G. D. *Makromol. Chem.* **1983**, *184*, 1363–1378.

(5) Bigi, F.; Casiraghi, G.; Casnati, G.; Sartori, G.; Zetta, L. *J. Chem. Soc., Chem. Commun.* **1983**, 1210–1211. Bigi, F.; Casiraghi, G.; Sartori, G.; Soncini, P.; Gasparri Fava, G.; Ferrari Belicchi, M. *Tetrahedron Lett.* **1985**, *26*, 2021–2024.

(6) Casiraghi, G.; Cornia, M.; Casnati, G.; Zetta, L. *Macromolecules* **1984**, *17*, 2933–2934.

(7) Casiraghi, G.; Cornia, M.; Balduzzi, G.; Casnati, G. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 366–369.

(8) Balakrishna, S.; Rao, M. M.; Seshadri, T. R. *Tetrahedron* **1962**, *18*, 1503–1507. Dempsey, C. B.; Donnelly, D. M. X. *Chem. Ind. (London)* **1963**, 491–492. Kumari, D.; Mukerjee, S. K.; Seshadri, T. R. *Tetrahedron Lett.* **1966**, 3767–3772. Donnelly, D. M. X.; Nangle, B. J.; Hulbert, P. B.; Klyne, W.; Swan, R. J. *J. Chem. Soc. C* **1967**, 2450–2452.

(9) For a discussion of nomenclature, see: Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654–660.

(10) Jurd, L. *Tetrahedron* **1977**, *33*, 163–168.

(11) Pochini, A., University of Parma, Italy, personal communication, 1985.

(12) Casnati, G.; Pochini, A.; Terenghi, M. G.; Ungaro, R. *J. Org. Chem.* **1983**, *48*, 3783–3785.

(13) Bryson, R. L.; Hatfield, G. R.; Early, T. A.; Palmer, A. R.; Maciel, G. E. *Macromolecules* **1983**, *16*, 1669–1672.

(14) Paulus, E.; Böhmer, V. *Makromol. Chem.* **1984**, *185*, 1921–1935.

(15) Cambridge Crystallography Data Centre File. Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, O. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35*, 2331–2336. Barnes, J. C.; Paton, J. D.; Damewood, J. R., Jr.; Mislow, K. *J. Org. Chem.* **1981**, *46*, 4975–4979.

(16) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908–6909.

(17) Sheldrick, G. H. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Komingsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, 1976; pp 34–42.

Poly(*N*-acylethylenimines) with Pendant Carbazole Derivatives. 2. Synthesis of 3,6-Dimethoxy-, 3,6-Dihydroxy-, and 2,7-Dihydroxycarbazole-Containing Polymers

Bing R. Hsieh and Morton H. Litt*

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106.

Received September 5, 1985

ABSTRACT: The synthesis and polymerization of 2-[2-(9-(3,6-dimethoxycarbazolyl))ethyl]-2-oxazoline and 2-[4-(9-(3,6-dimethoxycarbazolyl))butyl]-2-oxazoline are described. The former gave a polymer with a high percentage of cross-linking; the latter gave an amorphous polymer in 100% yield. Demethylation of the second polymer and a 2,7-dimethoxycarbazole-containing polymer with boron tribromide gave amorphous 3,6-dihydroxycarbazole and 2,7-dihydroxycarbazole polymers, respectively, in quantitative yields. These polymers showed higher T_g's than those of methoxycarbazole polymers and were insoluble in most organic solvents; strong hydrogen bonding may cause the insolubility.

Introduction

Modification of electrical properties of pendant group polymers through formation of charge-transfer complexes has been studied extensively, especially for carbazole-containing polymers such as poly(*N*-vinylcarbazole) (PVK).[1] Although many complexes of PVK showed semiconducting behavior and EPR signals, the conductivity (σ) remained very low, even at very high dopant concentrations. A more promising approach to improve the conductivities of PVK-based materials was reported in 1977 by Block et al.[2] They introduced unpaired electrons into PVK: partial oxidation of PVK with tris(*p*-bromophenyl)ammonium hexachloroantimonate gave cross-linked material containing 3,3′-dicarbazylium cation radicals having $\sigma_{RT} = 10^{-5}$ $(\Omega\ \mathrm{cm})^{-1}$. These authors also estimated $\sigma_{RT} = 10^{-2}$ $(\Omega\ \mathrm{cm})^{-1}$ for the fully oxidized material. However, this material is undoubtedly highly cross-linked and impossible to process. To avoid the necessity of processing, cross-linked films were recently made by electrochemical oxidation of various carbazole polymers in situ.[3] For example, electrooxidation of PVK gave 50% oxidized films having $\sigma_{RT} = 6 \times 10^{-4}$ $(\Omega\ \mathrm{cm})^{-1}$.

Another way of solving the processing problem is to develop polymers that will not cross-link when oxidized, in other words, to produce redox-reversible carbazole polymers by blocking the reactive 3,6-positions of the carbazole ring.[4] The major objective of this work was to synthesize redox-reversible poly(*N*-acylethylenimines) with pendant carbazole derivatives which could form stable ion radical salts.

In the first paper of this series, we reported the synthesis of poly(*N*-acylethylenimines) with 2,7-dimethoxycarbazole as the side groups from properly substituted oxazoline monomers.[5] Here, we describe the preparation of similar polymers with 3,6-dimethoxycarbazole on the side chain. One important reason for selecting the methoxylated carbazoles as the side groups is the ease of hydrolysis of the methoxy groups to form corresponding hydroxylated carbazole polymers, which are our major interest and which may show reversible electrochemical behavior. The oxazoline ring, however, is relatively basic and can be protonated by a phenoxy proton to a slight extent, if there are any present. The protonated oxazoline is very vulnerable to nucleophilic attack and ends up as an amide ether. Therefore, the methoxys serve as protecting groups, which prevent chain transfer of the phenolic protons on oxazoline rings and make the polymerization possible.

---

*To whom all correspondence should be addressed.