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Synthesis, Atropoisomerism and Chemistry of the Dimers of *R*-(–)-Carvone, *R*-(–)-Hydrocarvone, 1*R*,5*R*-(+)-Pinocarvone and Other Monoterpenic Ketones

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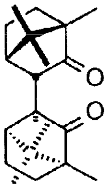
Abstract: Oxidative homocoupling of *R*-(–)-carvone **4**, *R*-(–)-hydrocarvone **21**, 1*R*,5*R*-(+)-pinocarvone **25** and other monoterpenic ketones leads to the respective C_2-symmetric dimers **6**, **20** and **26** in most cases as single diastereoisomers. Subsequent reactions of dimeric compounds were investigated in detail. Other monoterpenes (menthone, pulegone) undergo homocoupling in low yields and poor diastereoselectivity.

The importance of chelation provided by molecules with C_2 symmetry is well recognized[1] and compounds such as binaphthol[2] or hydrobenzoin[3] and their derivatives are popular chiral auxiliaries in asymmetric synthesis. A viable approach to enantiopure compounds with C_2 symmetry is the dimerization of suitable optically active natural products. For example, molecules such as **1**[4] and **2**[5] obtained from dimerizations of camphor are C_2 symmetric and can function as, or can be transformed into, effective ligands.



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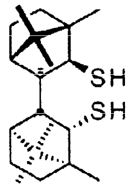

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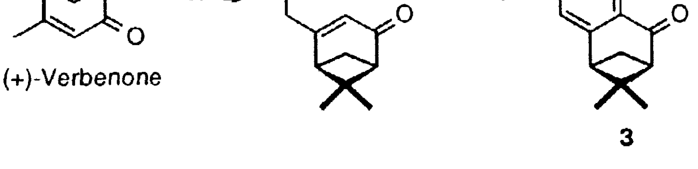
The lack of popularity of these molecules in asymmetric synthesis is probably due to the poor diastereoselectivity of the dimerization or of other steps in their preparation. Our interest in this area was to provide new enantiopure C_2-symmetric molecules with versatile functionalities, such as the carbonyl group, amenable to the synthesis of ligands utilizable in asymmetric catalysis. A similar goal was recently addressed by Paquette *et al.*[6] in research aimed at defining methods for the synthesis of C_2-symmetric molecules such as **3** *via* dimerization of *R*-(+)-verbenone (Eq 1).



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(1)

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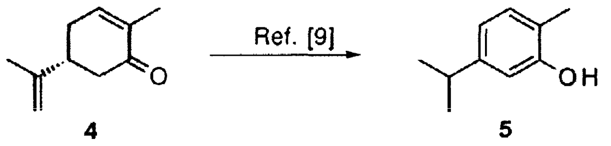
We were intrigued by the idea of devising a ligand featuring the elements of central chirality[7] (due to the presence of asymmetric carbons) together with elements of axial chirality (due to the geometry of the whole molecule) and of devising a method for the synthesis of aromatic atropoisomeric diols (*e.g.* binaphthol) by converting the central chirality of appropriate dimers into the axial chirality of biphenols.[8] For this latter reason we chosed to dimerise carvone **4** because its dimer **6** may be supposed to aromatize into dicarvacrol **7** with the same ease with which carvone itself is aromatized to carvacrol **5** (Eq 2 and 3).[9]



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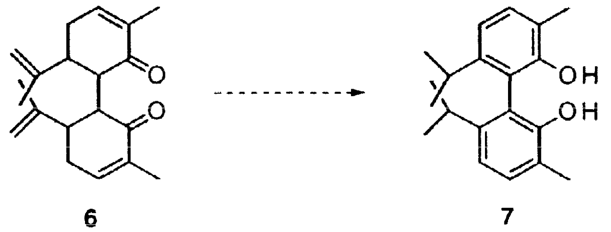
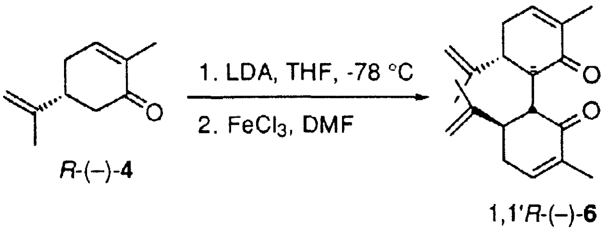


(3)

The molecule **7** should possess all the favourable requirements for configuration stability[10] and high efficiency in chiral transfer.[11] We report here our efforts along these lines, describing the synthesis and transformations of the dimer of carvone **6** and a few other related monoterpene dimers.

Results and Discussion

Dicarvone. The oxidative dimerization of the enolate ion of *R*-(–)-carvone **4** into dicarvone **6** was reported several years ago,[12] without specifying the number of diastereoisomers produced. In our hands the anion of carvone **4** generated by LDA in THF and treated with anhydrous $FeCl_3$ in DMF affords a crude reaction mixture consisting uniquely of dicarvone **6** and unreacted carvone **4** (Eq 4).



(4)

The reaction is remarkably clean. Dicarvone **6** crystallizes from MeOH in 60% yield (95% based on recovered starting material) as long colorless needles leaving the unreacted carvone **4** in solution.

The X-ray structure of **6** (Figure 1) shows that the C1-C11 junction is equatorial and that the carvone rings are encompassed in planes which are mutually orthogonal. Therefore the dihedral angle H1-C1-C11-H11 should be close to 90°. The configuration of the asymmetric carbons of the carvone and the steric hindrance of the two isopropenyl groups forces the molecule into the *P* helicity.

Careful inspection of the ^1H NMR spectrum of **6** suggests that the rotameric preference and the helicity are conserved in the solution phase. The methine protons H1 and H11 at the junction resonate as a doublet at 2.50 ppm, while the methine protons H6 and H16 geminal to the isopropenyl unit are represented by a triplet of doublets at 3.50 ppm. The relevant vicinal constant $J_{1,6}$ = 12.0 Hz indicates that protons H1 and H11 are axially oriented, so that the junction is equatorial also in solution. Discarding the couplings with other protons, H1, H11, H6 and H16 constitute an AA'XX' system where H1 and H11 are chemically equivalent but magnetically non-equivalent protons. Therefore the constant $J_{1,11}$ should appear, provided that it exceeds a threshold that can be put at 0.5 Hz. The coupling between H1 and H11 should also split the ^{13}C side-bands of the ^{1}H resonance at 2.50 ppm. In neither case was coupling observed, which puts its value at the bottom of the Karplus curve and the dihedral H1-C1-C11–H11 angle at about 90°. The selectivity of the transformation from central to axial chirality also requires that the interconversion barrier between the rotamers of dicarvone **6** will occur with a sufficient energy to resist the reaction conditions. No line broadening was observed in the ^{1}H NMR spectra of **6** recorded at temperatures as low as –70 °C; this fact is however not significant, as it may be attributed either to a low interconversion energy or to the exclusive presence of a single rotamer. An answer can be found only by theoretical estimates: molecular mechanics calculations with the PM3 procedure[13] give about 30 kJ mol^{-1} for the interconversion among the three possible atropoisomers of **6**, in agreement with the reported low energy for atropoisomerization around an *sp*^{3}-*sp*^{3} hybridized bond.[7]

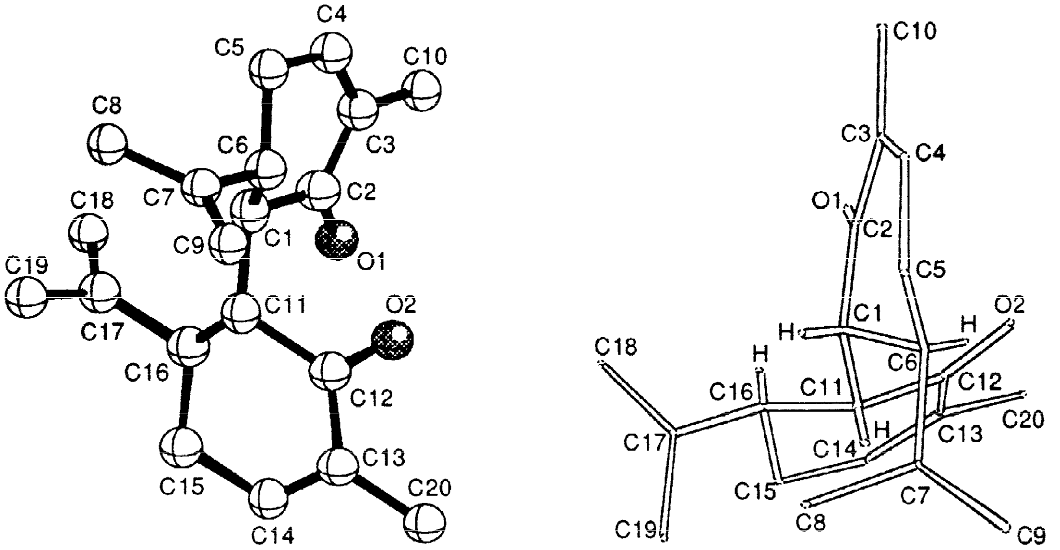
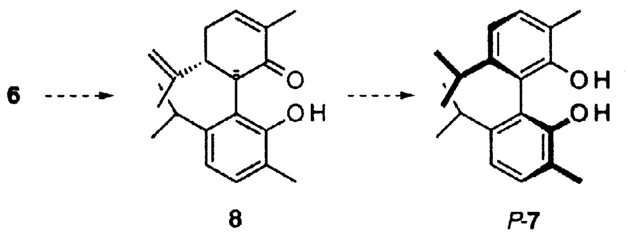


Figure 1. X-ray structure representations of dicarvone **6** with hydrogen atoms partially omitted. *a*: "ball and stick" representation; *b*: "wire frame" representation highlighting the perpendicular relationship of the two cyclohexyl units.

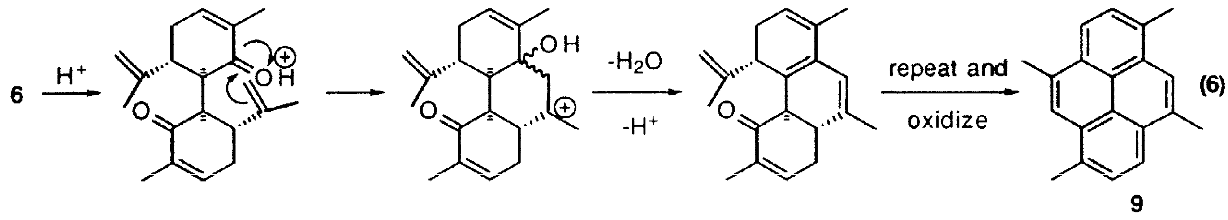
The transformation of dicarvone **6** into dicarvacrol **7** (Eq 5) occurs *via* an aromatization process which is a double bond migration from the external isopropenyl group to the cyclohexenyl ring. The aromatization of the two rings will not occur synchronously, but will likely proceed through the intermediate carvone-carvacrol **8**, where one substructure is aromatized and the other preserves the stereogenic centers of carvone. The atropoisomerization around a *sp*^{3}-*sp*^{2} bond is generally higher, and in fact PM3 analysis reveals the presence of two ground-state rotamers of **8** with an interconversion barrier of *ca.* 100 kJ mol^{-1}. Finally, the PM3 analysis confirms that dicarvacrol **7** is most resistant to atropoisomerization: the calculated energy barrier for the rotation around the *sp*^{2}-*sp*^{2} bond is *ca.* 120 kJ mol^{-1}.

The possibility of hydrogen bonding in **8** and **7** was not taken into account in the molecular mechanics computations and therefore the energies for the corresponding atropoisomerization processes may be somewhat higher. The critical point for converting the central chirality of **6** into the axial chirality of **7** is the low energy barrier for atropoisomerization of dicarvone **6** where no hydrogen bonding is possible. It is then evident that the synthetic method performing the conversion from dicarvone **6** into dicarvacrol **7** must be carried out at a reasonably low temperature.



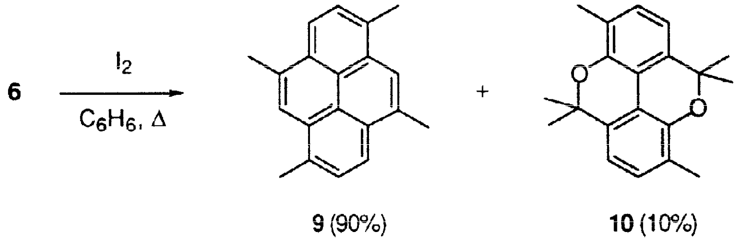
(5)

In order to determine the mildest conditions, we have tested many different reaction procedures. At the outset, acidic conditions (either with Lewis acids such as $BF_3{\cdot}OEt_2$ and $AgBF_4$ or with Brönsted acids such as HCl and H_2SO_4) appeared the most appropriate because they are highly effective in the isomerization of carvone **4** to carvacrol **5**.[9c] However, these same procedures applied to dicarvone **6** yielded 1,4,6,9-tetramethylpyrene **9**. The structure of **9** was assigned on the basis of mass spectrometry (M^+ at 258 *m/z*) and NMR spectroscopy (see Experimental Section). The formation of pyrene **9** may derive from the attack of the carbocation generated by the acid with the isopropenyl residue, followed by water elimination and spontaneous oxidation in the air (Eq 6).



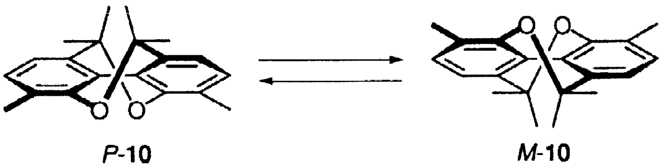
(6)

With I_2 in refluxing benzene dicarvone **6** is converted into pyrene **9** as the major product and to the new chromene derivative **10** (Eq 7). The structure of **10** was determined by mass spectrometry (M^+ at 294 *m/z*) and by ^1H and ^{13}C NMR data.



(7)

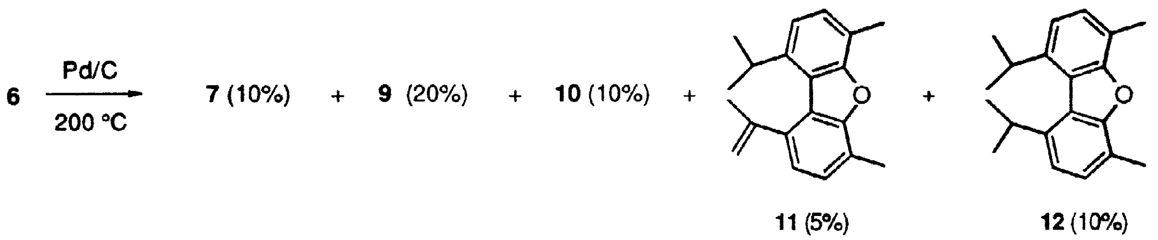
The PM3 analysis of compound **10** shows that the pyrane rings are not planar and that the aromatic rings are not coplanar. The compound therefore exists in the form of the enantiomers *P*-**10** and *M*-**10** (Eq 8). However, the energy for the interconversion between the two enantiomers is so low (PM3 calculations give an energy barrier of about 2 kJ mol^{-1}) that we could not detect any evidence of achronicity of the geminal methyls of the pyran ring in the ^1H NMR spectrum even at the lowest experimentally possible temperature (–70 °C).



(8)

One of the most popular methods for the conversion of cyclohexenones into phenols involves the oxidation with dichlorodicyanoquinone (DDQ).[14] However, dicarvone **6** did not react with DDQ even after refluxing in benzene for a few days. Also the utilization of metal catalysts[15] such as $RuCl_2(PPh_3)_3$ or $RhCl_3{\cdot}3H_2O$,[9d,e] known to aromatize carvone **4**, proved ineffective with dicarvone **6**.

Although the reaction with palladium on carbon represents one of the most efficient conversions of carvone **4** into carvacrol **5**,[9a,b] it necessitates high temperatures and for this reason this reaction was considered in a later step. When neat dicarvone **6** was heated at 200 °C in a sealed Pyrex test tube in the presence of 10% Pd/C, a complex mixture was obtained. The components were separated and identified (Eq 9).



(9)

One of the products was the desired dicarvacrol **7**, while the other products were identified as pyrene **9**, ether **10** and the two furans **11** and **12**. The yield of **7** was disappointingly low and could not be improved by changing the reaction conditions. The number of signals in the ^1H and ^{13}C NMR spectra of **7** clearly establishes the C_2 symmetry of the molecule. On the other hand, the isopropyl methyls appear in the ^1H NMR spectrum as partially overlapping doublets at 1.10 and 1.07 ppm, and they also give rise to distinct ^{13}C NMR signals at 24.88 and 23.54 ppm. The achronicity of the isopropyl methyls can only be accounted for by the presence and the thermal stability of the stereogenic atropoisomerism of **7**. The thermal stability on the NMR timescale is consistent with the calculated PM3 barrier for the rotation around the sp^2-sp^2 bond. The structure was unequivocally determined by X-ray analysis on crystals grown in methanol. Figure 2 shows the ORTEP representation.

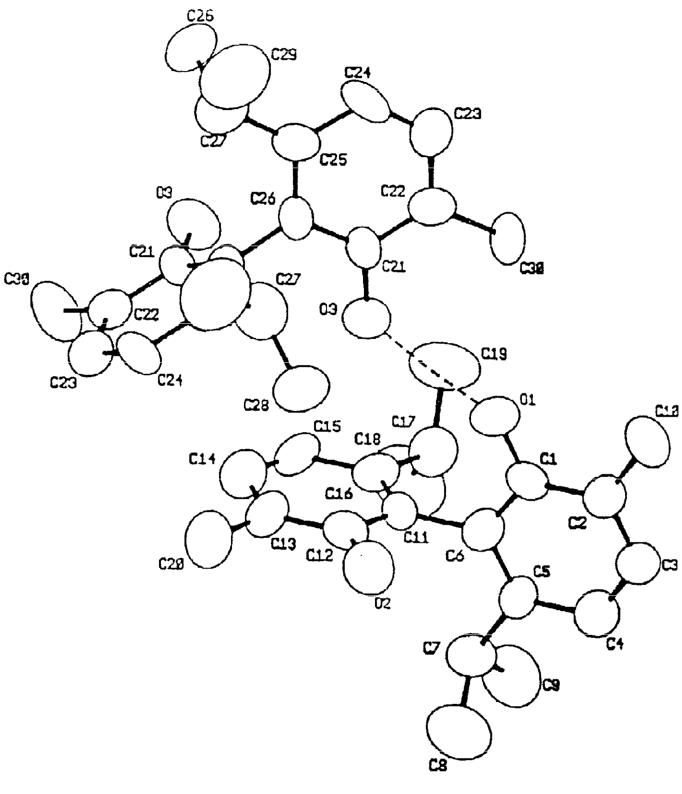
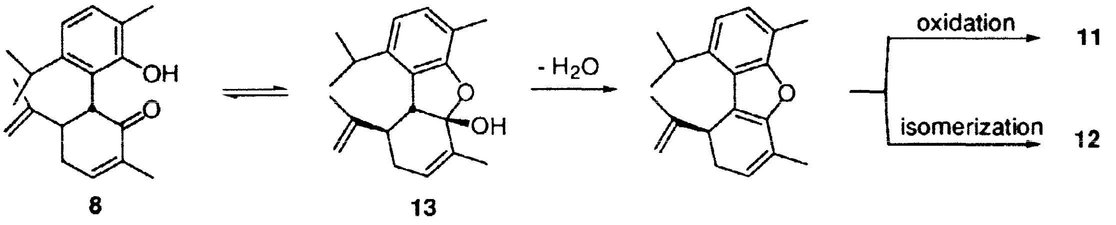


Figure 2. ORTEP representation of the X-ray structure of dicarvacrol **7**.

The crystal lattice is *P* (centric) with a center of symmetry. In other words, the crystals are formed by molecules of opposite chirality, crystallized from a racemic mixture. Indeed the optical rotation of the product showed a very low value ($[\alpha]_D^{25}$ = +8-10 (c = 0.8)) suggesting a small enantiomeric excess, if any. Thus, it appears that the conversion from central to axial chirality occurs with no selectivity.

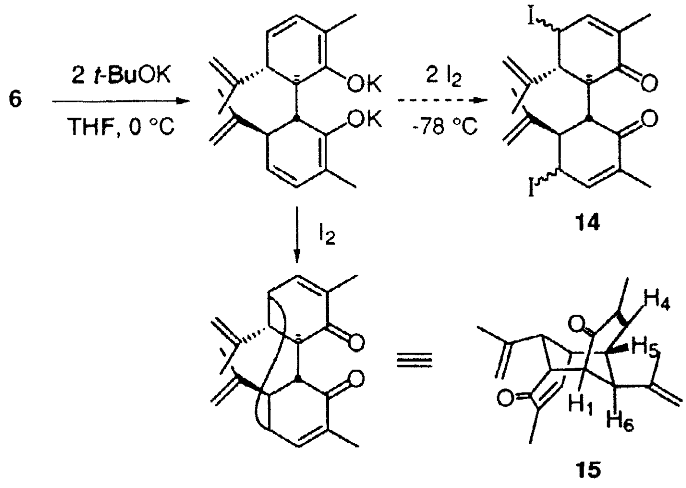
Compounds **9** and **10** have just been described. The structures of **11** and **12** were deduced from mass spectrometry and NMR spectroscopy data (see Experimental Section). The geometry of compound **12**, minimized with the PM3 procedure, highlights the non-planarity of the dibenzofuran ring, so that the molecule exists as two enantiomers. As in the case of molecule **10**, but differently from dicarvacrol **7**, the low calculated energy barrier for interconversion (2 kJ mol^{-1}) prevents the observation of diastereotopic methyls in the isopropyl groups.

The formation of products **11** and **12** may be rationalized by the formation of carvone-carvacrol **8** and it is a relevant hint for its intermediacy. As described in Eq 10, the hemiacetal **13** may be postulated to form by a nucleophilic intramolecular attack of the hydroxy group of the aromatized ring onto the carbonyl group of the adjacent not yet aromatized ring. Subsequently, elimination of water preceeds the oxidation to **11** or the tautomeric isomerization to **12**.



(10)

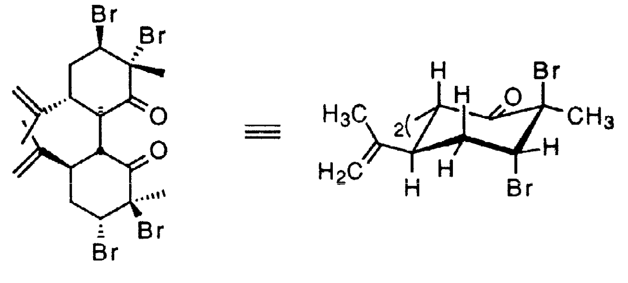
We thus turned to the reaction sequence entailing deprotonation, quenching with iodine and elimination of HI with bases. In dicarvone **6** deprotonation may occur at the α,α' positions or at the γ,γ' positions to the carbonyl groups.[16] The γ,γ' deprotonation appears sterically less hindered and the conjugated base is also thermodynamically more stable because of the wider mesomeric resonance. In agreement with this assumption, the deprotonation actually occurred at the γ,γ' positions, but the subsequent treatment with iodine did not afford the expected diodo derivative **14**. Rather, a compound was formed quantitatively with a molecular weight (from mass spectrometry: M^+ at 296 *m/z*) smaller by 2 dalton than that of dicarvacrol **7**. The exact structure **15** was determined by ^1H and ^{13}C and especially by NOEDS NMR spectroscopy. The resonance at 6.56 ppm belongs to the endocylic vinyl H4. Dipolar correlations were found between this resonance and a resonance at 2.79 ppm, to be attributed to H5. In turn this latter resonance correlates with a resonance at 2.67 (H6) and this latter with a resonance at 2.96 (H1). Compound **15** may be postulated to form *via* an oxidative coupling between the γ,γ' positions of dicarvone **6** mediated by iodine (Eq 11).



(11)

Compound **15** is a chiral enantiopure molecule with C_2 symmetry which may be used to prepare ligands or catalysts for asymmetric synthesis.

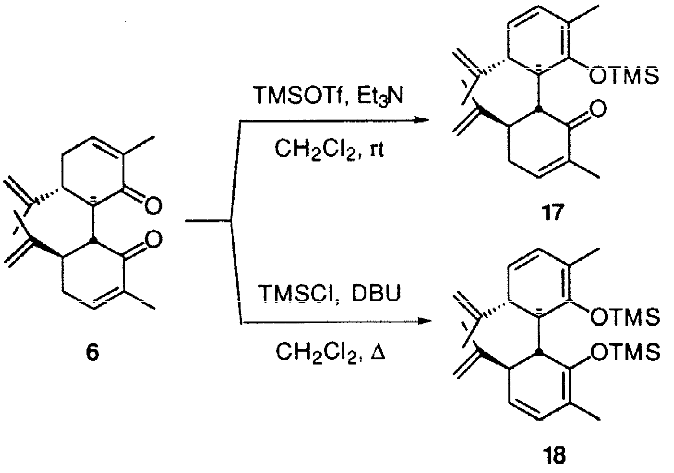
The reaction of dicarvone **6** with two equivalents of Br_2 leads to the clean production of the tetrabromo derivative **16**. From the addition of more than two equivalents of Br_2 an intractable mixture of diastereoisomers was obtained.



16

The structure and the stereochemistry of compound **16** was determined by ^1H NMR spectroscopy. The aliphatic resonance at 4.78 ppm is easily attributed the the methine proton geminal to the bromine. This proton is weakly coupled (3.0 Hz) with the two vicinal methylenic protons resonating at 3.01 and 2.13 ppm. This fact would suggest the axial orientation for both bromine atoms, so that both of them possess at least one hydrogen atom in an *anti*-coplanar relationship. Unfortunately the reaction with *t*-BuOK reverts **16** back to the starting material **6**, while with other bases (*t*-BuLi, LDA) complex mixtures of products formed.

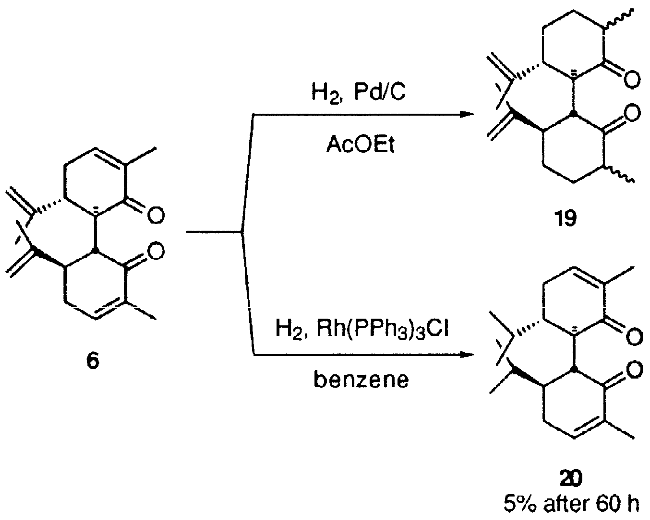
The analysis of the results so far described leads to the conclusion that many reactions result from the interactions of the isopropenyl double bond with the carbonyl group of the adjacent carvone ring. This reactivity may be suppressed by converting the carbonyl group into the silyl enol ether. The consequent greater ring unsaturation should also favor the tendancy towards aromatization. The reaction of dicarvone **6** with several silylating agents in the presence of amines (Et_3N, DBU)[17] leads to the formation of mono and disilyl enolethers (Eq 12).



(12)

The poor stability of the silyl enol ethers **17** and **18** prevented their isolation, so that their structure was obtained uniquely from the analysis of the NMR spectroscopic data. The spectroscopic data are consistent with the formation of silyl enol ethers **17** and **18** rather than with the unconjugated systems derived from the abstraction of the α-proton at the junction. The ^1H NMR spectrum of **18**, displays two endocyclic vinyl resonances at 5.65 and 5.12 ppm, with a mutual $J = 10$ Hz, and two endocyclic aliphatic resonances at 2.56 and 2.2 ppm, with unitary intensity ratios. The system derived from α deprotonation would give rise to one vinyl and three aliphatic endocylic resonances. Compounds **17** and **18** are very sensitive to moisture and readily revert back to the starting material. None of the many attempts to aromatize **17** and **18** was successful. In the reactions with metals (Pd on C, $RhCl_3$) and oxidants (DDQ) only pyrene **9** could be detected, beside variable amounts of starting dicarvone **6**.

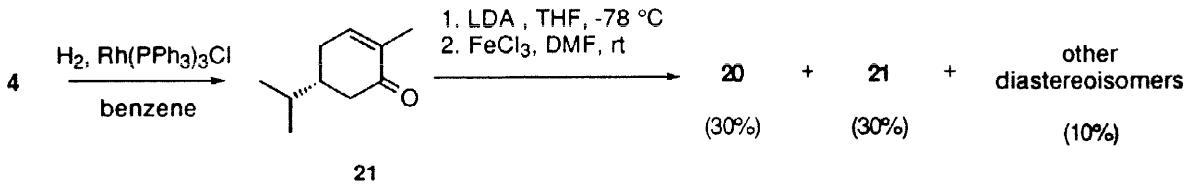
Dihydrocarvone. As protection of the carbonyl for suppressing reactivity between the oxygen of one ring and the isopropylene of the other proved inefficient, we tried reduction of the isopropenyl double bond. Hydrogenation with Pd on C did not succeed to produce **20**, as only the reduction of the endocyclic olefin was obtained with formation of **19** (Eq 13).



(13)

The use of a homogeneous catalyst for the chemoselective reduction of the exocyclic double bond[18] gave rise after several days to traces of the desired product **20**. This low reactivity is indicative of the unusually high steric hindrance given to this functional group by the geometry of dicarvone **6**. This fact can be appreciated by inspection of the X-ray structure (see Figure 1).

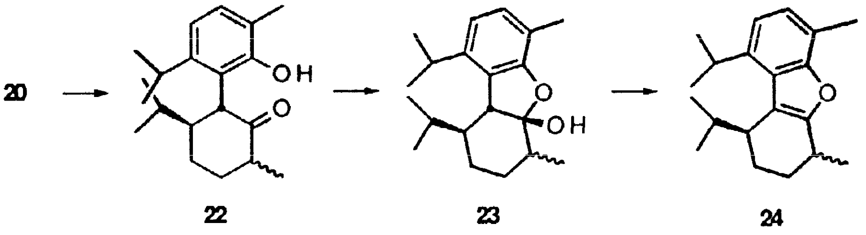
As an alternative we tried to dimerize dihydrocarvone **21**, readly prepared from carvone **4** by established procedures (Eq 14).[18]



(14)

The reaction of **21** with LDA and the coupling with $FeCl_3$ turned out to be less efficient than with carvone **4**, both in conversion and in selectivity. The ^1H NMR spectrum of the crude reaction mixture showed the presence of product **20** together with other diastereoisomers of the dimer. This result may be attributed to the diminished rigidity of dihydrocarvone **21** with respect to carvone **4**. Isolation of the desired dimer **20** with C_2 symmetry was obtained by column chromatography, with a total yield of *ca.* 30%. As in the case of dimer **6**, the relevant coupling constant between the proton at the junction and that geminal to the isopropyl group (J = 6.2 Hz) is indicative of their mutual axial orientation, so that the α,α' junction is also equatorial.

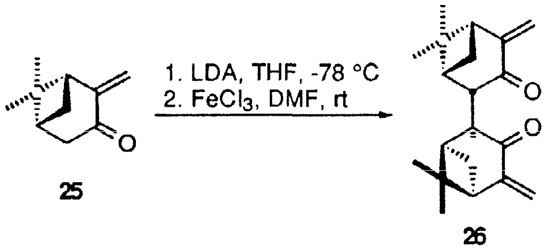
The oxidative reaction of **20** with iodine or DDQ again did not lead to any product. On the other hand, Pd on C generated the product **24** in a good yield (Eq 15). The assignment of structure **24** rests on the analysis by mass spectrometry (M^+ at 284 m/z) and NMR spectroscopy. In the ^1H NMR spectrum, an isolated AB system is found at about 7.00 ppm, indicative of vicinal aromatic or vinylic protons, spectroscopically isolated from the remaining protons. In the aliphatic region, one singlet at 2.47 ppm integrating for 3H is attributed to the methyl at the aromatic ring, while 5 doublets between 1.4 and 0.8 ppm are assigned to the diastereotopic isopropyl methyls and to the methyl at the cyclohexyl ring. Compound **24** may be thought to derive from the intermediate **22**, obtained from **20** *via* a disproportionation process catalyzed by Pd. The dehydration in **23** occurs with the hydrogen at the junction, with formation of the benzofuran skeleton of **24**.



(15)

Dipinocarvone. Pinocarvone **25** is (as the trivial name suggests) the polycyclic isomer of carvone **4**. It can be transformed into carvacrol **5** by the action of acids or radicals.[19] In the context of the present work it was utilized for two reasons: pinocarvone **25** does not possess the isopropenyl function and associated reactivity, and also lacks a position which may undergo γ deprotonation.

Pinocarvone **25** is readily obtained in high yield by singlet oxygenation of α-pinene.[20] As with carvone **4**, deprotonation with LDA and oxidative dimerization led specifically to the diastereoisomer **26** in *ca.* 60% yield (Eq 16). The identity of compound **26** was determined by X-ray crystallography and NMR spectroscopy (see Experimental Section).



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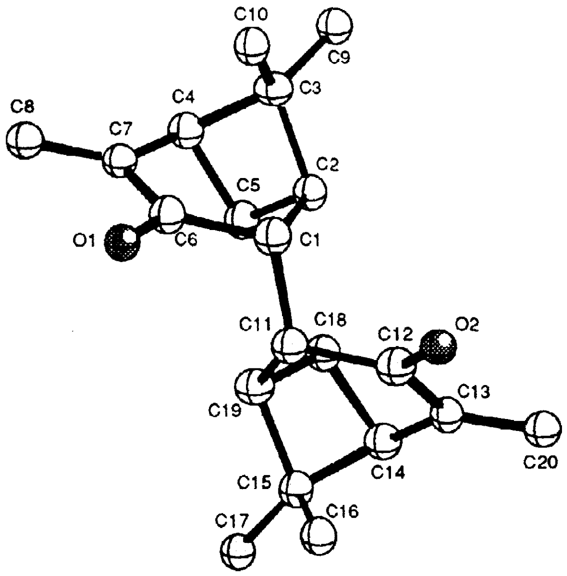
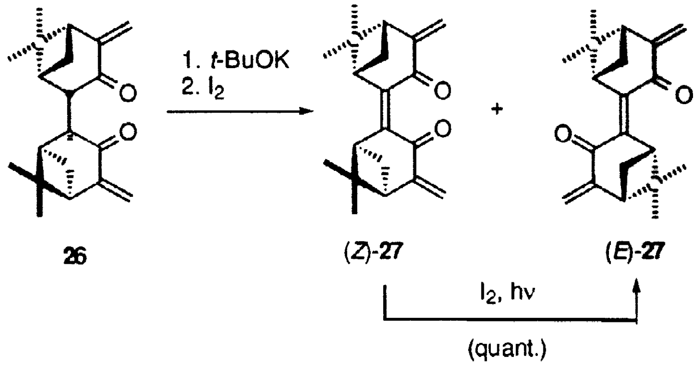


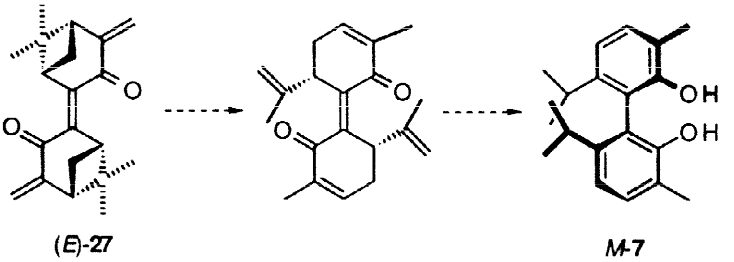
Figure 3. Representation of the X-ray structure of dipinocarvone **26** with hydrogen atoms omitted.

Deprotonation of **26** with *t*-BuOK and quenching with I_2 lead to the formation mixture of *Z* and *E* stereoisomers **27** in a kinetic 2.5:1 ratio (Eq 17). The most revealing feature of the ^1H NMR spectrum of the kinetic mixture is the presence of two triplets at 2.99 and 4.59 ppm, assigned to the bridghead protons vicinal to the double-bond junction. The low-field signal is assigned to the *E* diastereoisomer, by virtue of the strong deshielding caused by the neighbouring carbonyl group.



(17)

Upon standing in light in the presence of iodine, compound *Z*-**27** is converted into *E*-**27**. The conversion into *E*-**27** may be monitored by ^{1}H NMR spectroscopy. The conversion is reasonable, as the *E* diastereoisomer should suffer less from the nonbonding interaction between the two carbonyls. We could record the ^{13}C NMR spectrum of this more stable isomer only.



(18)

The ring opening reaction of **27** to **7** was attempted under the various conditions that are known to convert pinocarvone into carvacrol (AcOH, $BF_3{\cdot}OEt_2$, CF_3COOH, H_2SO_4, $HSnBu_3$),[19] but with no successful results.

Other di-monoterpenes: Dimenthone, Dipulegone, Dicamphor. The oxidative coupling reaction was tested with other readily available terpenes, in order to examine a wider range of natural substances containing the carbonyl function. The results are summarized in Table 1.

Table 1. Conversion, number of diastereoisomers, diastereomeric ratio and yields in the oxidative coupling of some monoterpenes.

#	Monoterpene	Conversion	Number of Diastereoisomers (Diastereomeric ratio)	Main or exclusive diastereoisomer	Yield
1	Carvone	60%	1	**6**	60%
2	Dihydrocarvone	70%	3 (9 : 0.5 : 0.5)	**20**	30%
3	Pinocarvone	30%	1	**26**	30%
4	Menthone	<5%	not determined	not determined	not isolated
5	Pulegone	<5%	1	not determined	not isolated
6	Camphor (see ref 4)	60%	3	not reported	not reported
7	Dibromocamphor	<5%	1	not determined	not isolated

So far, only carvone, pinocarvone and verbenone can be readily dimerized, while the other natural monomers require new methods as yet undetermined. The yields of the dimers of menthone, pulegone and dibromocamphor are very poor. Camphor has been oxidatively dimerized by Saegusa *et al.* giving a complex mixture of diastereoisomers.[4]

Conclusions. The work performed so far has lead to the synthesis, from inexpensive and readly available natural products, of new molecules with C_2 symmetry, which are promising precursors for the preparation of ligands of interest in asymmetric synthesis. The most ambitious target described in the Introduction, *i.e.* the stereoselective conversion of di-monoterpenes with central chirality into dicarvacrol **6** with axial chirality only, was not achieved. Nevertheless, some useful considerations emerge from the present study: (*i*) the aromatization of dicarvone **6** is difficult, and requires conditions too harsh for preserving chirality; (*ii*) a number of reactions can occur between the hydroxy or carbonyl functions on one ring and the isopropenyl group on the adjacent ring; (*iii*) the formation of dimeric diastereoisomers possessing a double bond junction is promising, because they appear to convert specifically to the single more stable isomer.

Experimental Section

The reactions were carried out using standard techniques under nitrogen, the glassware was flame-dried and cooled under nitrogen. Commercial high purity reagents were employed without further purification. Tetrahydrofuran and benzene were dried over potassium and benzophenone, diisopropylamine, dimethylformamide and dichloromethane were dried over calcium hydride and distilled before use. The progress of the reactions was monitored by TLC or ^1H NMR spectroscopy. Flash chromatography was performed with 230-400 mesh silica-gel Merk 60 with standard tecniques.[21] Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC200 spectrometer and on a Varian Unity 400 spectrometer. The NOE spectra were obtained in the differential mode (NOEDS)[22] on a Varian Unity 400 spectrometer. The lines of the selected multiplet were 0.05 s cyclically saturated for a total time of 10 s with the proper attenuation of the decoupling power. Mass spectra were recorded with a Hewlett-Packard 5890-II apparatus. IR spectra were collected on a BIO-RAD FTS-40 spectrometer. Optical rotations were measured on a Perkin Elmer 638 polarimeter. X-Ray diffraction data were collected on a Philips PW1100 instrument. The structure was solved by SHELX 86 program and refined by block full matrix least squares using the SHELX 76 program. The H atoms were located on a DF map and isotropically refined.

(*P*)-(4*R*,5*R*)-5-Isopropenyl-4-((1*R*,6*R*)-6-isopropenyl-3-methyl-2-oxo-3-cyclohexenyl)-2-methyl-1-cyclohexen-3-one (Dicarvone 6). A solution of *n*-BuLi in hexanes (2.5 M, 4.8 mL, 12 mmol) was added to a solution of diisopropylamine (1.57 mL, 12 mmol) in dry THF (10 mL) at –78 °C. The resulting slurry was strirred for 15 min and **4** (1.57 mL, 10 mmol) was added at the same temperature. The pale yellow mixture was stirred 30 min and a solution of anhydrous $FeCl_3$ (1.78 g, 11 mmol) in dry DMF (100 mL) was added at –78 °C. The dark slurry was stirred at –78 °C for 2 h and at rt for 12 h. HCl (1M, 10 mL) was added and the solution was extracted with pentane (3x20 mL), washed with 1M HCl (10 mL), H_2O (10 mL), brine (10 mL) and dried over Na_2SO_4. The volatile materials were evaporated and the viscous residue was recrystallized from MeOH to obtain 950 mg (60% yield) of colorless needles: M.p. 107 °C; $[\alpha]_D^{25} = -64.5$ (MeOH, *c* 2.1); ^1H NMR (400 MHz, CD_2Cl_2), δ 6.67 (2H, m), 4.85 (2H, m), 4.77 (2H, m), 3.42 (2H, td, J = 12.0, 4.7 Hz), 2.36 (2H, d, J = 12.0 Hz), 2.36 (2H, m), 2.25 (2H, m), 1.69 (6H, m), 1.63 (6H, s); ^{13}C NMR (100 MHz, CD_2Cl_2), δ 200.37, 146.65, 143.05, 135.89, 114.27, 49.95, 48.70, 31.93, 19.45, 16.10; IR (KBr), ν 3072, 2977, 2917, 2858, 1661, 1448, 1382, 1154, 1066, 893, 513 cm^{-1}.

X-ray data. $C_{20}H_{26}O_2$; mw 298.43; crystal size: 0.3, 0.3, 0.6 mm; crystal system: orthorombic; space group $P2_12_12_1$ Nº19; a = 12.372(2), b = 11.132(2), c = 13.205(2) Å, V = 1818.6(5) $Å^3$, $Z = 4$, D_c = 1.09 g/cm^3; μ = 4.65 mm^{-1}; λ = 1.54180 Å; number of reflections measured 1500; number of reflections unique 1481; number of parameters refined 303. The final conventional R factor for the 1481 considered observed reflections $[F \geq 4\sigma(F)]$ was 0.059 $[R_w = 0.059; w = 1/(\sigma^2(F)+0.013749F^2)]$.

Reaction of ***6*** *with sulfuric acid.* A dispersion of finely powdered **6** (200 mg, 0.66 mmol) in aqueous H_2SO_4 (50% in wt., 1 mL) was stirred at 80 °C for 1 h. The mixture was quenched with a saturated solution of $NaHCO_3$ (10 mL), the aqueous layer was extracted with Et_2O (3x15 mL) and the combined organic layers were dried over $MgSO_4$. The volatile materials were evaporated and the solid residue was purified by flash chromatography (eluant hexanes). Eluate 1: 1,4,6,9-tetramethylpyrene **9**, 100 mg (59% yield) of colorless needless: M.p. 184-186 °C; ^1H NMR (200 MHz, $CDCl_3$): δ 8.15 (2 H, d, J = 7.9 Hz), 8.02 (2 H, s), 7.86 (2 H, d, J = 7.9 Hz), 2.97 (6 H, s), 2.90 (6 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 132.94, 131.24, 129.60, 129.55, 127.65, 124.20, 122.41, 120.36, 20.42, 19.96; IR (KBr): ν 3036, 2963, 2921, 2852, 1613, 1515, 1465, 1433, 866, 813 cm^{-1}. MS (70 eV): *m/z* 258, 243, 226, 119. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.65; H, 7.12. Eluate 2: unreacted **6**, 112 mg.

Reaction of ***6*** *with iodine.* A solution of **6** (200 mg, 0.66 mmol) and I_2 (340 mg, 1.33 mmol) in dry benzene (10 mL) was refluxed for 12 h. The mixture was quenched with a saturated solution of $Na_2S_2O_8$ (10 mL), extracted with Et_2O (3x15 mL) and dried over Na_2SO_4. The volatile materials were evaporated and the solid residue was purified by flash-chromatography (eluant 5% CH_2Cl_2 in hexanes). Eluate 1: 3,5,5,8,10,10-hexamethyl-5,10-dihydrocumeno[5,4,3-*cde*]chromene **10**, 20 mg (10% yield) of colorless oil: ^1H NMR (200 MHz, $CDCl_3$): δ 7.03 (2 H, dd, J = 7.7, 0.5 Hz), 6.69 (2 H, d, J = 7.7 Hz), 2.23 (6 H, d, J = 0.5 Hz), 1.6 (12 H, s); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 148.18, 134.56, 130.32, 124.63, 114.21, 113.28, 77.50, 29.70, 27.80, 15.24; IR (film): ν 3053, 2985, 2920, 2854, 1579, 1401, 1289, 1149, 1111, 935, 806, 657 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.98; H, 7.53. Eluate 2: 1,4,6,9-tetramethylpyrene **9**, 130 mg (84% yield).

Reaction of ***6****with Pd/C at 200 °C.* Finely powdered **6** (100 mg, 0.33 mmol) and 10% Pd on charcoal (10 mg) into a screw-capped Pyrex test tube was purged with nitrogen, sealed and heated in a sand bath at 200 °C for 12 h. The mixture was cooled and purified by flash-chromatography (eluant CH_2Cl_2/hexanes in gradient from pure hexanes to 1 : 1 mixture). Eluate 1: 1,9-diisopropyl-4,6-dimethyldibenzo[*b*,*d*]furan **12**, 10 mg (10% yield) of colorless oil: ^1H NMR (200 MHz, $CDCl_3$): δ 7.26 (2 H, d, J = 8.1 Hz), 7.21 (2 H, d, J = 8.1 Hz), 3.82 (2 H, hept, J = 6.9 Hz), 2.58 (6 H, s), 1.14 (12 H, d, J = 6.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.00, 141.84, 127.60, 122.00, 119.30, 119.00, 31.34, 24.71, 15.04; IR (film): ν 3052, 3027, 2961, 2925, 2869, 1502, 1457, 1387, 1374, 998, 812 cm^{-1}. MS (70 eV): *m/z* 280, 265, 251, 237, 209, 197, 178, 165, 139, 125, 111, 89, 76, 51. Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.96; H, 8.87. Eluate 2: 1-isopropenyl-9-isopropyl-4,6-dimethyldibenzo[*b*,*d*]furan **11**, 5 mg (5% yield) of colorless oil: ^1H NMR (200 MHz, $CDCl_3$): δ 7.29-6.98 (4 H, m), 5.23 (1 H, m), 5.09 (1 H, m), 4.09 (1 H, hept, J = 6.9 Hz), 2.60 (3 H, s), 2.58 (3 H, s), 2.15 (3 H, m), 1.35 (3 H, d, J = 6.9 Hz), 1.11 (3 H, d, J = 6.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.89, 154.80, 148.21, 143.08, 137.55, 128.03, 127.07, 123.10, 121.59, 121.30, 120.29, 119.35, 118.60, 114.07, 25.52, 25.04, 23.18, 15.14, 14.99; IR (film): ν 3077, 3026, 2957, 2922, 2865, 1638, 1566, 1503, 1370, 1255, 1204, 999, 897, 814 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 85.99; H, 7.85. Eluate 3: 1,4,6,9-tetramethylpyrene **9**, 20 mg (20% yield). Eluate 4: 3,5,5,8,10,10-hexamethyl-5,10-dihydrocumeno[5,4,3-*cde*]chromene **10**, 10 mg (10% yield) of colorless oil: ^1H NMR (200 MHz, $CDCl_3$): δ 7.03 (2 H, d, J = 7.7 Hz), 6.69 (2 H, d, J = 7.7 Hz), 2.23 (6 H, b), 1.6 (12 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 148.18, 134.56, 130.32, 124.63, 114.21, 113.28, 77.50, 27.80, 15.24; IR (film): ν 148.18, 134.56, 130.32, 124.63, 114.21, 113.28, 77.50, 29.70, 27.80, 15.24 cm^{-1}. Eluate 5: 2-(2-hydroxy-6-isopropyl-3-methylphenyl)-3-isopropyl-6-methylphenol **7**,[23] 10 mg (10% yield) of colorless needless: M.p. 150-152 °C; ^1H NMR (200 MHz, $CDCl_3$): δ 7.21 (2 H, d, J = 7.9 Hz), 6.94 (2 H, d, J = 7.9 Hz), 4.67 (2 H, s), 2.47 (2 H, hept, J = 6.8 Hz), 2.26 (6 H, s), 1.1 (6 H, d, J = 6.8 Hz), 1.07 (6 H, d, J = 6.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.70, 147.47, 131.77, 121.84, 117.63, 117.55, 30.27, 24.88, 23.54, 15.91; IR (KBr): ν 3514, 3498, 3471, 3046, 3022, 2959, 2923, 2867, 1573, 1453, 1401, 1214.33, 1114, 1022, 814 cm^{-1}.

X-ray data for 7. $C_{20}H_{26}O_2$; mw 298.43; crystal size: 0.2, 0.6, 0.6 mm; crystal system: orthorombic; space group Pbna Nº 60; $a = 16.807(2)$, $b = 26.634(2)$, $c = 11.801(1)$ Å; $V = 5282(1)$ Å^3, $Z = 12$, $D_c = 1.13$ g/cm^3; $\mu = 0.38$ mm^{-1}; $\lambda = 0.71070$ Å; number of reflections measured 6206; number of reflections unique 6206; number of parameters refined 298. The final conventional R factor for the 1481 considered observed reflections $[F \geq 4\sigma(F)]$ was 0.072 $[R_w = 0.075; w = 1/(\sigma^2(F)+0.002240F^2)]$.

(1*R*,2*R*,6*R*,7*R*)-11,12-Diisopropenyl-4,9-dimethyltricyclo[5.3.1.1^{2,6}]dodeca-3,9-diene-5,8-dione (15). To a suspension of *t*-BuOK (112 mg, 1.0 mmol) in dry THF (1 mL) at 0 °C was added dropwise a solution of **6** (150 mg, 0.5 mmol) in dry THF (3 mL). The solution was stirred at the same temperature for 30 min, was cooled to −78 °C and a solution of I_2 (257 mg, 1 mmol) in dry THF (3 mL) was added dropwise. The system was left to reach rt within 2 h. The solution was quenched with saturated $Na_2S_2O_5$ (10 mL), extracted with Et_2O (3x15 mL) and the combined organic layers were dried over Na_2SO_4. The volatile materials were removed by evaporation and the residue was recrystallized from *n*-hexane to obtain 140 mg (95% yield) of colorless prisms: M.p. 256 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 6.56 (2 H, d, J = 6.4 Hz), 4.85 (2 H, m), 4.51 (2 H, m), 2.96 (2 H, m), 2.79 (2 H, d, J = 6.4 Hz), 2.67 (2 H, m), 1.82 (6 H, d, J = 1.6 Hz), 1.61 (6 H, m); ^{13}C NMR (50 MHz, $CDCl_3$): δ 198.27, 144.45, 140.97, 140.53, 112.90, 47.50, 41.87, 35.23, 21.95, 15.51; IR (KBr): ν 3081, 2970, 2936, 2922, 2887, 1665, 1442, 1385, 1351, 1085, 892 cm^{-1}. MS (70 eV): *m/z* 296, 281, 253, 239, 225, 199, 188, 159, 148, 128, 107, 91, 77, 55. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.99; H, 8.23.

(1*R*,2*R*,4*R*,5*R*)-5-Isopropenyl-4-((1*R*,3*R*,4,6*R*)-6-isopropenyl-3,4-dibromo-3-methyl-2-oxocyclohexyl)-1,2-dibromo-2-methylcyclohexan-3-one (16). A solution of Br_2 (0.2 mL, 4.0 mmol) in CCl_4 (10 mL) was added dropwise to a solution of **6** (600 mg, 2.0 mmol) in CCl_4 (5 mL). The mixture was stirred 20 min, the volatile materials were removed by suction and the residue was purified by flash chromatography (eluant hexane) to obtain 900 mg (73% yield) of colorless solid: M.p. 170-173 °C; $[\alpha]_D^{22} = +108.6$ (CH_2Cl_2, *c* 2.0); ^1H NMR (400 MHz, $CDCl_3$): δ 4.95 (2 H, bs), 4.86 (2 H, bs), 4.78 (2 H, t, J = 3.0 Hz), 3.62 (2 H, td, J = 11.8, 3.0 Hz), 3.49 (2 H, d, J = 11.8 Hz), 3.02 (2 H, td, J = 11.8, 3.0 Hz), 2.13 (2 H, dt, J = 11.8 and 3.0 Hz), 2.05 (6 H, s), 1.70 (6 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 200.20, 144.14, 114.95, 63.87, 58.16, 44.74 (two C), 36.14, 28.60, 18.73; IR (KBr): ν 3073, 2928, 1722, 1433, 1061, 903 cm^{-1}. Anal. Calcd for $C_{20}H_{26}O_2Br_4$: C, 38.87; H, 4.24. Found: C, 38.12; H, 4.18.

(4*R*,5*R*)-4-((1*R*,6*R*)-2-(Trimethylsililoxy)-6-isopropenyl-3-methyl-2,4-cyclohexadienyl)-5-isopropenyl-2-methyl-1-cyclohexen-3-one (17). To a solution of **6** (150 mg, 0.5 mmol) and Et_3N (0.21 mL, 1.5 mmol) in dry CH_2Cl_2 (1 mL) TMSOTf (0.28 mL, 1.5 mmol) was added dropwise at 0 °C. After 2 h the volatile materials were removed and a small amount was dissolved in $CDCl_3$. ^1H NMR (200 MHz, $CDCl_3$): δ 5.83 (1 H, dd, J = 9.3, 3.0 Hz), 5.45 (1 H, bs), 5.12 (1 H, d, J = 9.3 Hz), 4.90 (1 H, bs), 4.83 (1 H, bs), 4.73 (1 H, bs), 4.70 (1 H, bs), 3.10-2.15 (6 H, multiplets), 1.8-1.6 (12 H, 4 singlets), 0.15 (9 H, s). Any effort to purify the compound led to the recovery of **6**.

(5*S*,6*R*)-1-(Trimethylsililoxy)-6-((1*R*,6*S*)-2-(trimethylsililoxy)-6-isopropenyl-1,3-dimethyl-2,4-cyclohexadienyl)-5-isopropenyl-2,6-dimethyl-1,3-cyclohexadiene (18). To a solution of **6** (150 mg, 0.5 mmol) and DBU (0.224 mL, 1.5 mmol) in dry CH_2Cl_2 (1 mL) TMSCl (0.19 mL, 1.5 mmol was added dropwise) at 0 °C. The mixture was refluxed for 12 h, the volatile materials were removed and a small amount was dissolved in $CDCl_3$. ^1H NMR (200 MHz, $CDCl_3$): δ 5.65 (2 H, d, J = 10.0 Hz), 5.12 (2 H, d, J = 10.0, 6.0 Hz), 4.83 (2 H, bs), 4.75 (2 H, bs), 2.60-2.10 (4 H, multiplets), 1.80-1.60 (12 H, 4 singlets), 0.15 (18 H, s). Any effort to purify the compound led to the recovery of **6**.

(*P*)-(4*R*,5*R*)-5-Isopropyl-4-[(1*R*,6*R*)-6-isopropyl-3-methyl-2-oxo-3-cyclohexenyl]-2-methyl-1-cyclohexen-3-one (20). To a solution of diisopropylamine (1.57 mL, 12 mmol) in dry THF (10 mL) a solution of *n*-BuLi in hexanes (2.5 M, 4.8 mL, 12 mmol) was added at −78 °C. The slurry was strirred 15 min and **21**[19] (1.57 mL, 10 mmol) was added at the same temperature. The mixture was stirred 30 min and a solution of anhydrous $FeCl_3$ (1.78 g, 11 mmol) in dry DMF (100 mL) was added at −78 °C. The dark slurry was stirred at −78 °C for 2 h and at rt for 12 h. HCl (1M, 10 mL) was added and the solution was extracted with pentane (3x20 mL), washed with 1M HCl (10 mL), H_2O (10 mL), brine (10 mL) and dried over Na_2SO_4. The volatile materials were evaporated and the viscous residue was purified by flash-chromatography (eluant 5% AcOEt in hexanes) to obtain 310 mg (31% yield) of colorless oil: $[\alpha]_D^{22}$ = +26.0 ($CHCl_3$, *c* 2.0); ^1H NMR (200 MHz, $CDCl_3$): δ 6.63 (2 H, m), 2.80 (2 H, m), 2.40-2.05 (6 H, multiplets), 1.75 (6 H, s), 1.73 (2 H, m), 0.92 (6 H, d, *J* = 6.8 Hz), 0.84 (6 H, d, *J* = 6.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.16, 142.34, 135.30, 49.50, 43.26, 27.97, 24.87, 21.30, 17.93, 16.15; IR (film): ν 2955, 2924, 1664, 1464, 1451, 1367 cm^{-1}. Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.80; H, 10.23.

(1*S*)-1,8-Diisopropyl-4,5-methyl-1,2,3,4-tetrahydrodibenzo[*b,d*]furan (24). Finely powdered **20** (50 mg, 0.16 mmol) and 10% Pd on charcoal (10 mg) in a screw-capped Pyrex test tube were purged with nitrogen, sealed and heated in a sand bath at 200 °C for 12 h. The mixture was cooled and purified by flash chromatography (eluant hexane) to obtain 20 mg (45% yield) of colorless oil: ^1H NMR (200 MHz, $CDCl_3$): δ 7.10-6.95 (2 H, multiplets), 3.45 (1 H, hept, *J* = 6.8 Hz), 3.06-2.90 (2 H, multiplets), 2.47 (3 H, s), 2.3-1.4 (5 H, multiplets), 1.38 (3 H, d, *J* = 6.8 Hz), 1.21 (3 H, d, *J* = 6.8 Hz), 1.05 (3 H, d, *J* = 6.8 Hz), 0.93 (3 H, d, *J* = 6.8 Hz), 0.83 (3 H, d, *J* = 6.8 Hz); IR (film): ν 3052, 3024, 2959, 2928, 2870, 1733, 1505, 1457, 1384, 1273, 977, 809 cm^{-1}. MS (70 eV): *m/z* 284, 241, 211, 197, 183, 165, 141, 128, 105, 91, 69, 55. Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.77; H, 10.01.

(1*S*,5*S*)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (25). A solution of α-pinene (46 mL, 294 mmol), acetic anhydryde (29 mL, 303 mmol), pyridine (12 mL, 147 mmol), DMAP (716 mg, 6 mmol) and tetraphenylporphyrin (21 mg, 0.034 mmol) in CH_2Cl_2 (270 mL) was irradiated with a halogen lamp (500 Watt) for 2 h under O_2 bubbling. The mixture was diluited in CH_2Cl_2 (270 mL), washed in sequence with saturated aqueous $NaHCO_3$ (2 x 200 mL), 1 M HCl (2 x 100 mL), saturated aqueous $CuSO_4$ (100 mL), brine (200 mL), and dried over Na_2SO_4. The volatile materials were removed by suction and the residue was distilled under reduced pressure with a 10 cm Vigreux to afford 41.9 g (95% yield) of a colorless oil: B.p. 80 °C at 0.1 Torr; $[\alpha]_D^{22}$ = +63 (neat); ^1H NMR (200 MHz, $CDCl_3$): δ 5.95 (1 H, d, *J* = 1.6 Hz), 5.00 (1 H, d, *J* = 1.6 Hz), 2.80-2.60 (3 H, multiplets), 2.46 (1H, m), 2.20 (1H, m), 1.36 (3 H, s), 1.28 (1 H, m), 0.80 (3 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 200.04, 149.04, 117.42, 48.22, 42.47, 40.77, 38.52, 32.40, 25.96, 21.53; IR (KBr): ν 3027, 2967, 2927, 1706, 1624, 1463, 1409, 1369, 1328, 1283, 1263, 889, 860 cm^{-1}.

(1*S*,4*R*,5*R*)-4,4'-Bi(6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one) (26). To a solution of diisopropylamine (1.57 mL, 12 mmol) in dry THF (10 mL) at −78 °C was added a solution of *n*-BuLi in hexanes (2.5 M, 4.8 mL, 12 mmol). The slurry was stirred 15 min and **25** (1.57 mL, 10 mmol) was added at the same temperature. The mixture was stirred 30 min and a solution of anhydrous $FeCl_3$ (1.78 g, 11 mmol) in dry DMF (100 mL) was added at −78 °C. The dark slurry was stirred at −78 °C for 2 h and at rt for 12 h. HCl (1M, 10 mL) was added and the solution was extracted with pentane (3x20 mL), washed with 1M HCl (10 mL), H_2O (10 mL), brine (10 mL) and dried over Na_2SO_4. The volatile materials were evaporated and the viscous residue was recrystallized from MeOH to obtain 150 mg (10% yield) of colorless needles: M.p. 270 °C (dec.); $[\alpha]_D^{25}$ = +175.2 ($CHCl_3$, *c* = 2.3); ^1H NMR (200 MHz, $CDCl_3$): δ 5.99 (2 H, d, *J* = 1.7 Hz), 5.02 (2 H, d, *J* = 1.7 Hz), 3.54 (2 H, bs), 2.71 (2 H, t, *J* = 6.0 Hz), 2.54 (2 H, dt, *J* = 10.6, 6.0 Hz), 2.08 (2 H, t, *J* = 6.0 Hz), 1.33 (6 H, s), 1.32 (2 H, d, *J* = 10.6 Hz), 0.85 (6 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.70, 148.88, 117.87, 51.58, 47.75, 41.80, 41.55, 29.71, 26.03, 21.00; IR (KBr): ν 3096, 2976, 2933, 2882, 1701, 1615, 1398, 1282, 1104, 1063, 1021, 954, 835 cm^{-1}. Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.53; H, 8.91.
X-ray data. $C_{20}H_{26}O_2$; mw 298.43; crystal size: 0.2, 0.4, 0.4 mm; crystal system: orthorombic; space group $P2_12_12_1$ Nº19; a = 13.486(2), b = 14.213(2), c = 8.912(1) Å, V = 1708.2(4) Å^3, Z = 4, D_c = 1.16 g/cm^3; μ = 0.40 mm^{-1}; λ = 0.71070 Å; number of reflections measured 2374; number of reflections unique 2013; number of parameters refined 303. The final conventional R factor for the 1481 considered observed reflections $[F \geq 4\sigma(F)]$ was 0.050 $[R_w = 0.058;\ w = 1/(\sigma^2(F)+0.005982F^2)]$.

(*E*)-(1*S*,5*R*)-4,4'-Dehydro-4,4'-bi(6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one) (27). To suspension of *t*-BuOK (45 mg, 0.4 mmol) in dry THF (1 mL) at 0 °C was added dropwise a solution of **26** (60 mg, 0.2 mmol) in dry THF (1 mL). The solution was stirred at the same temperature for 30 min, then cooled to −78 °C and a solution of I_2 (102 mg, 0.4 mmol) in dry THF (1 mL) was added dropwise. The system was left to reach rt within 2 h. The solution was quenched with saturated $Na_2S_2O_5$ (10 mL), extracted with Et_2O (3x15 mL) and the combined organic layers were dried over Na_2SO_4. The volatile materials were removed by evaporation and a small amount was dissolved in $CDCl_3$ *Z*-**27**. ^1H NMR (200 MHz, $CDCl_3$): δ 6.03 (2 H, d, *J* = 1.4 Hz), 5.13 (2 H, bs), 2.99 (2 H, t, *J* = 6.3 Hz), 2.90-2.65 (4 H, multiplets), 1.46 (6 H, s), 1.40 (2 H, m), 0.97 (6 H, s).
The mixture of isomers was dissolved in $CHCl_3$ (10 mL), I_2 (5 mg) was added and the mixture was irradiated with an halogen lamp (100 Watt) for 2 h. The iodine was destroyed with saturated $Na_2S_2O_5$ (2 mL), the organic layer was washed with water (5 mL), saturated brine (5 mL) and dried over Na_2SO_4. The volatile materials were removed by evaporation and the residue was recrystallized from *n*-hexane to obtain 55 mg (95% yield) of colorless prisms *E*-**27**: M.p. 112 °C; $[\alpha]_D^{22}$ = −210.0 ($CHCl_3$, *c* = 0.8); ^1H NMR (200 MHz, $CDCl_3$): δ 5.95 (2 H, d, *J* = 1.6 Hz), 5.11 (2 H, d, *J* = 1.6 Hz), 4.59 (2 H, t, *J* = 6.4 Hz), 2.81 (2 H, t, *J* = 6.4 Hz), 2.80 (2 H, dt, *J* = 9.6, 6.4 Hz), 1.45 (6 H, s), 1.41 (2 H, d, *J* = 9.6 Hz), 0.77 (6 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 186.44, 150.12, 144.84, 117.82, 48.40, 45.02, 31.66, 29.69, 26.20, 22.82; IR (KBr): ν 2956, 2927, 1674, 1617, 1083, 1018 cm^{-1}; MS (70 eV): *m/z* 253, 225, 221, 197, 173, 159, 145, 128, 115, 91, 77, 65, 65, 53. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.01; H, 8.01.

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