

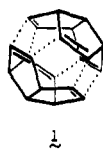
meso- and *dl*-Bivalvane (Pentasecododecahedrane). Enantiomer Recognition during Reductive Coupling of Racemic and Chiral 2,3-Dihydro- and Hexahydrotriquinacen-2-ones

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Abstract: Pinacolic reduction of both optically pure and racemic hexahydrotriquinacen-2-one (**6**) proceeds with *exo,exo* carbon-carbon bond formation. Coupling of enantiomerically pure **6** produces diol **11** exclusively. Formation of comparable amounts of **11** and **12** from (\pm)-**6** shows that the diastereomeric transition states involved are of comparable energy. Studies with chiral and racemic 2,3-dihydrotriquinacen-2-one (**13**) gave analogous results. The various 1,2-glycols are identified by their ¹³C NMR (symmetry is thereby revealed), ¹H NMR (shielding of the endo protons at C₃ and C_{3'} by hydroxyl is witnessed), and ir spectra, in tandem with the method of synthesis. Conversion of the four diols to their thionocarbonates, and subsequent treatment with triethyl phosphite at the reflux temperature, provides the structurally related olefins stereospecifically. Catalytic hydrogenation of **17** provides *dl*-bivalvane (**2**), whereas reduction of **19** gives rise to the *meso*-bivalvane isomer **3**. Other aspects of these transformations and conformational possibilities for **2** and **3** are discussed.

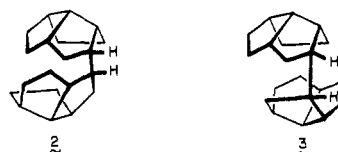
The dodecahedron is one of the five perfect solids (the others are the tetrahedron, cube, octahedron, and icosahedron) and consequently has been a source of fascination for mathematicians since the time of Pythagoras and Plato. Only recently, however, has the dodecahedrane molecule attracted the attention of synthetic chemists. Notwithstanding, this (CH)₂₀ polyhedron, which is endowed with most intriguing geometry, remains an unknown substance.²⁻⁶ Although several approaches to dodecahedrane are currently under investigation in these laboratories, attention is focused specifically herein on the fundamental aspects of that scheme which involves effective "dimerization" of two triquinacene halves. The essence of this concept is not new, it having been advanced earlier in singular form by Woodward, Fukunaga, and Kelly² who viewed dodecahedrane as composed of two triquinacene subunits which when properly arranged might be coaxed into sixfold carbon-carbon bond formation as illustrated in **1**. That efforts along this



line have consistently failed is not surprising, for the requirement of a highly ordered transition state which can maintain strict stereochemical control simultaneously (or nearly so) at 12 trigonal carbon atoms is certain to be overwhelmingly endothermic. Moreover, the added restriction that all six bonds must form from the heavily encumbered endo direction at both termini will surely be most prohibitive. The further need to impinge any given π bond upon lobes of two different noninteracting⁷ double bonds constitutes a process for which chemical analogy is lacking if concerted or metal catalyzed.⁸

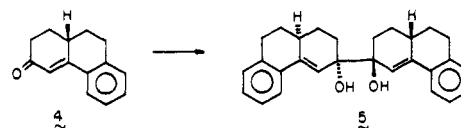
Despite the disadvantages intrinsic to the above model, it is apparent that initial endo,endo coupling of two monomeric triquinacene units at C₂ could go far in setting the stage for the ultimate construction of the desired polyhedron. Such a synthetic plan requires that there exist a reaction sequence which can lead readily to **2** as well as to more highly functionalized derivatives of this hydrocarbon. As we have noted earlier,⁵ a problem immediately presents itself, for

the dissymmetry of the necessarily derivatized triquinacene precursors is such that a pair of coupling products having the structural features of **2** and **3** can arise if the monomer



is a racemic mixture. Only when bonding between chiral triquinacenes results can it be guaranteed that unwanted formation of "dimer" **3** will be precluded.

These conditions presuppose that reductive coupling of racemic triquinacenes will produce diastereomeric products with comparable facility. However, no information is available with which to formulate a reliable prediction. On a promising note, Touboul and Dana have recently reported that electrolytic reduction of racemic **4** proceeds in rigorously enantio-selective fashion with formation of *cis*-threo-*cis* diol **5** to the exclusion of the *cis*-erythro-*cis* and other

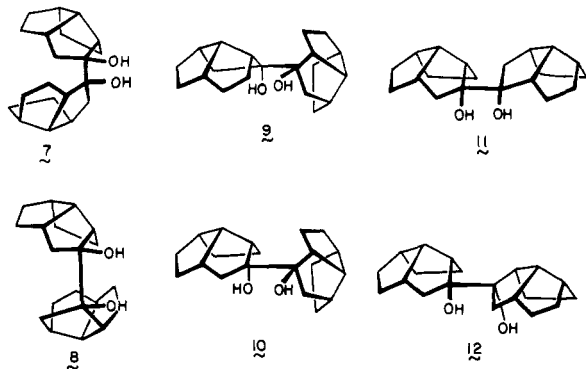


possible isomers.⁹ For the present study where 2,3-dihydrotriquinacen-2-one and its tetrahydro derivative serve as pivotal compounds, the prevailing steric factors are recognized to be generally inimical to bonding from the endo direction.¹⁰ Because adherence to an *exo,exo* bonding scheme would necessitate ultimate inversion of configuration at C₂ in both triquinacene segments, the synthetic methodology of choice should be one which is capable of achieving this transform readily.

With these considerations in mind, convenient preparations of **2**, **3**, and several related unsaturated congeners have presently been realized. In structural terms, **2** is recognized to be one of a number of possible pentasecododecahedranes. Because of the striking physical similarity of this molecule to that group of mollusks having dorsally hinged lateral shells (clams, oysters, etc.), we have named this hydrocarbon "*dl*-bivalvane" and refer to **3** as "*meso*-bivalvane".

Results

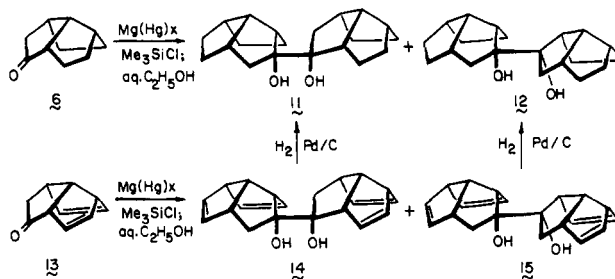
After several unsuccessful attempts to couple (\pm)-**6** by means of a thiadiazolidine intermediate,¹¹ recourse was made to pinacolic reduction. Upon gradual addition of (\pm)-**6** to a mixture of magnesium amalgam and trimethylchlorosilane in dry tetrahydrofuran at 25°, followed by stirring for 24 hr and mild desilylation, there was obtained, in 76% yield, a white crystalline solid. The infrared, ¹H NMR, and mass spectra of this crude product were consistent with a dimeric diol formation but provided little additional structural evidence. Excluding enantiomers, six isomers (**7–12**) are capable of being produced in this reaction.



These fall into three pairs of compounds depending upon whether endo,endo (**7, 8**), endo,exo (**9, 10**), or exo,exo (**11, 12**) carbon-carbon bond formation has transpired. Inspection of these structures reveals that **8** and **12** are meso and belong to point group C_s . Diols **7** and **11**, in contrast, possess axial symmetry only (point group C_2) and have nonsuperimposable mirror image forms. Both members of the endo,exo series (**9** and **10**) lack all symmetry elements and are consequently of the C_1 type. These differentiating features gain considerable importance when it is recognized that the ¹³C NMR spectra of **7, 8, 11**, and **12** would individually be characterized by a set of only ten signals. On the other hand, diols **9** and **10** would each exhibit 20 carbon resonances.

The ¹³C NMR spectrum of the crystalline diol product consisted of 18 lines. With the assumption that two peaks represent pairs of overlapping signals, the spectrum is consistent either with the presence of two diastereomers having either C_2 or C_s symmetry or with a single isomer of the C_1 class. Fractional recrystallization and column chromatography failed to separate components. However, high pressure liquid chromatography on silica gel using 10% ethyl acetate in petroleum ether as eluent readily provided two pure crystalline diols. Each of these substances exhibited only ten peaks in their ¹³C NMR spectra; the 1,2-glycols **9** and **10** are thereby immediately excluded from further consideration.

To distinguish further between the pairs of *dl*- and meso "dimers", enantiomerically pure (+)-(*S*)-**6**^{5b} was likewise subjected to the coupling reaction. In this instance, the single diol which was obtained proved identical in its physical and spectral properties to the more rapidly eluted product (mp 110–111°) isolated from racemic **6**. This compound is necessarily **7** or **11**. As a result of chemical correlation studies involving tetraene diol **14** for which ¹H NMR spectral data convincingly support endo orientation of the hydroxyl groups (vide infra), the structural assignment **11** is considered secure. Logically, the second diol would be expected to arise via exo,exo bonding of two ketone molecules of dissimilar configuration. This conclusion was likewise corroborated by the independent synthesis of **12** involving catalytic reduction of related tetraene diol **15**, the somewhat simpler



¹H NMR spectrum of which fully supported the indicated stereochemical assignment (vide infra).

Following the above scheme, (\pm)-2,3-dihydrotriquinacene-2-one (**13**) was reductively coupled with magnesium amalgam. High pressure liquid chromatography of the resulting pair of diols led to isolation of pure **14** and **15**, the ¹³C NMR spectra of which were each characterized by ten signals. Assignment of structure in this instance was guided by several considerations. First, pinacolic reduction of enantiomerically pure (+)-(*S*)-**13** led exclusively to (*S,S*)-**14** ($[\alpha]_D^{25} +142^\circ$ (*c* 0.13, ethanol)). This result provides independent evidence confirming the enantiomeric purity of **6** and **13**.^{5b} Secondly, catalytic hydrogenation of **14** and **15** over palladium on charcoal at atmospheric pressure led exclusively to **11** and **12**, respectively, as noted previously. The infrared spectra of the unsaturated diols show no peaks due to free hydroxyl groups; rather, the sharp intense absorptions which are seen at 3525 cm^{-1} implicate intramolecular hydrogen bonding between the -OH function and the π bonds. Although such a bond also characterizes the infrared spectrum of endo-2,3-dihydrotriquinacene-2-ol (3548 cm^{-1}) and is absent in that of the epimeric exo alcohol, caution must be exercised in utilizing these findings for the purpose of configurational assignment. Examination of molecular models supports the conclusion that hydrogen bonding in endo-2,3-dihydrotriquinacene-2-ol arises from intramolecular hydrogen bonding to a double bond (cf. A).¹³ A totally analogous situation can be expected to prevail in **14** and **15**. However, as can be seen from B, "dimers" having exo hy-



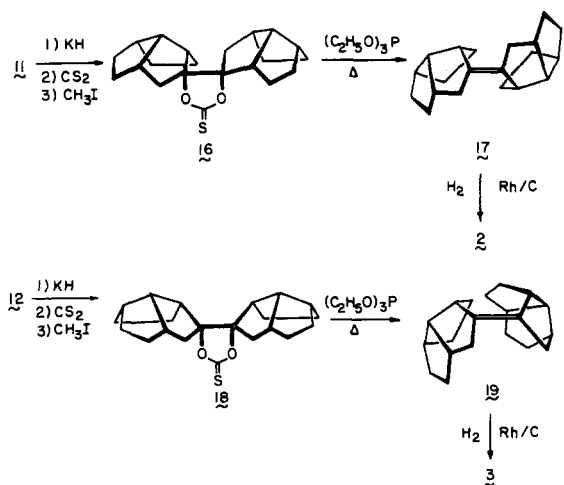
droxyl groups can partake equally well in efficient intramolecular hydrogen bonding (now utilizing the second dihydrotriquinacene moiety) provided that proper conformational features are adopted and these appear qualitatively to be exceptionally favorable. The infrared datum per se is therefore incapable of resolving the central stereochemical issue.

Lanthanide-induced shifting of the ¹H NMR spectra of **14** and **15** was not particularly revealing, perhaps because of the availability of two sites for possible complexation and access by the diols to various conformations.¹⁴ Notwithstanding, data pertaining to the stereochemical nature of each "dimer" were derivable from the ¹H NMR spectra of the pure diols. As regards **14** and **15** specifically, the emergent patterns for $H_{3\text{exo}}$ and $H_{3\text{endo}}$ and their chemically equivalent-primed counterparts are clearly evident and together indicate the configurational features at C_2 and C_2' . In the case of **14**, the pair of methylene protons at C_3 are separated by 0.45 ppm. Because the high-field signal (δ 1.93) exhibits equivalent geminal and vicinal spin-spin interactions of substantial magnitude ($J = 13.0$ Hz), this peak is assignable to $H_{3\text{exo}}$ and $H_{3'\text{exo}}$. For the endo protons at C_3 and C_3' , the dihedral angle relationship with H_4 and H_4' , respectively, now approaches 120 instead of 0°, and a

decrease in the $H_{3\text{endo}}, H_4$ coupling constant should result if the Karplus relationship holds; the observed value is 8.0 Hz in agreement with theory. The chemical shift of $H_{3\text{endo}}$ and $H_{3'\text{endo}}$ (δ 2.37) points furthermore to the existence of a substantial deshielding effect commonly observed when such oxygen functionality is positioned in close proximity to a proton.^{16,17} Since the hydroxyl groups are required to be endo to exert this paramagnetic effect, the stereochemistry of **14** is made evident. The spectrum of **15** in which $H_{3\text{exo}}$ and $H_{3'\text{exo}}$ appear at δ 1.92 ($J_{\text{gem}} = J_{\text{vic}} = 13.0$ Hz) and $H_{3\text{endo}}/H_{3'\text{endo}}$ are seen at 2.37 ($J_{\text{vic}} = 8.0$ Hz) is remarkably similar to that of **14** and similarly establishes the endo hydroxyl configuration of this "dimer".

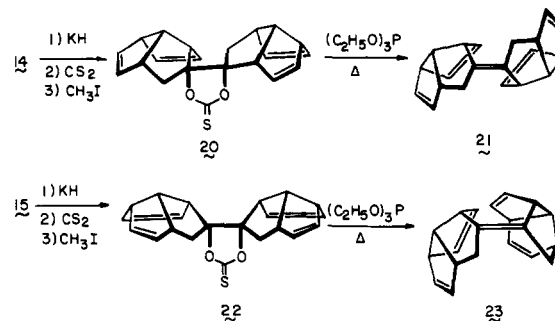
Although only *dl*-diols **11** and **14** are properly disposed for the further elaboration of dodecahedrane type structures, chemical transformations of the meso "dimers" **12** and **15** have been studied as well in order to provide appropriately contrasting ¹³C NMR reference spectra. Because certain tungsten reagents appeared to offer a potentially simple and convenient method for the stereoselective deoxygenation of vicinal dialkoxides,¹⁸ the dilithio salt of a 50:50 mixture of **11** and **12** was treated with a tetrahydrofuran solution of tungsten hexachloride-*n*-butyllithium (1:3). After work-up and chromatography, 50% of the diol was recovered. VPC analysis of the olefin fraction (40%) revealed the presence of at least four components instead of the expected two. It is not known whether these peaks correspond to all four possible diastereomeric olefins since the separation problem generated by this technique was considered so major as to render access to **17** impractical. This result is reminiscent of our experience with the attempted direct conversion of (\pm)-**6** to **17** and **19** with the titanium trichloride-lithium aluminum hydride reagent.¹⁹ In this event, the transition metal hydride produced a mixture of olefins in only 4% yield while providing substantial amounts of the monomeric endo alcohol derivable from **6**.

Attention was next directed to the application of thionocarbonate methodology.²⁰ Because formation of the dipotassium salts of **11** and **12** using potassium metal proved rather sluggish even in refluxing dioxane, and owing to apparent arresting of dialkoxide formation short of completion, the levels of recovered diol usually exceeded 50%. However, the substitution of potassium hydride²¹ led to rapid (1–2 hr) generation of dialkoxide using dry tetrahydrofuran at room temperature. In this way, efficient conversions to thionocarbonates **16**, **18**, **20**, and **22** were realized



conveniently and in good yield. These more geometrically rigid cyclic esters expectedly show 11 line ¹³C NMR spectra in agreement with maintenance of C₂ (**16** and **20**) and C_s symmetry (**18** and **22**).

When heated with triethyl phosphite, these thionocarbonates were transformed stereospecifically to the structurally related alkenes in yields ranging from 72 to 87%. Interestingly, while **16** and **18** had to be heated at the reflux temperature for 3 days to be completely converted to **17** and **19**, respectively, the controlled degradations of **20** and **22** re-



quired only 30 hr. Each of the four hydrocarbon products is nicely crystalline and exhibits ten distinctive ¹³C NMR peaks.

Catalytic hydrogenation of **17** and **19** at 50 psig in the presence of 5% rhodium on carbon proceeded very slowly at room temperature (5–8 days) with exclusive formation of *dl*- and *meso*-bivalvane. The unreactive nature of olefins **17** and **19** can be rationalized in terms of the steric hindrance about the tetrasubstituted π bond and the enormous levels of steric compression which develop as C₂ and C_{2'} elaborate sp³ character. In fact, molecular models suggest that saturation of the double bonds in **17** and **19** from the exo face leads to an enmeshing of the ten endo protons in a fashion which could possibly hinder subsequent rotation about the single bond common to both rings. Were this so, then **2** would be locked into the dodecahedryl conformation used herein for illustration purposes. In an attempt to gain information on this point by spectroscopic methods, the infrared and ¹H NMR spectra of **2** and **3** were examined closely. Previous investigations by Winstein and co-workers have provided evidence that opposed methylene hydrogens which are highly compressed in rigid molecular frameworks give rise to anomalously high infrared C–H stretching frequencies.²² Steric compression is also known to affect chemical shifts²³ and coupling constants in such molecules,²⁴ particularly when an oxygen function is strongly compressed against the methylene group.

The infrared spectra of **2** and **3** recorded as 10% solutions in carbon tetrachloride were compared with that of perhydrotriquinacene (**24**).³ Both "dimers" resemble the model hydrocarbon closely in the C–H stretching region, all three compounds showing a pair of bands at 2955 and 2865 cm⁻¹. No peaks at higher wavenumber were in evidence.

The ¹H NMR spectrum of **24** (CDCl₃ solution) is characterized by two broad but well-separated multiplets at δ 2.0–3.0 (area 4) and 1.1–2.0 (area 12) ascribable to the methine and methylene protons. Direct extrapolation of this information to *dl*- and *meso*-bivalvane leads to the prediction that two broad multiplets should be displayed having relative areas of 10 H (downfield) and 20 H (upfield). In point of fact, the very similar spectra of **2** and **3** display three broad multiplets at δ 2.0–2.8, 1.15–1.9, and 0.6–1.1 having peak areas of 8, 18, and 4. Taking the four apical protons of the triquinacene halves as internal reference (δ 2.0–3.0), certain of the remaining protons are seen to be shielded. While this effect is small and not yet understood, it is interesting to note that no comparable upfield shifting was encountered in the several "dimeric" intermediates synthesized earlier in the study.

The lack of high frequency infrared bands can be rati-

alized in terms of the absence of enhanced force constants as the direct result of inadequate steric compression. Models show that the bivalvanes are much less rigid structures than bird-cage hydrocarbons even if they adopt the most congested conformation possible. If a second axial C-C bond were inserted between the rings in **2** or **3**, the situation would be drastically altered; the structures would become much more rigid and a sharp increase in steric compression would very likely result.

The ^1H NMR data support the idea that the "equilibrium structures" adopted by **2** and **3** do generate recognizable nonbonded interactions between opposing hydrogens. However, this assumption of an increase in total potential energy must be viewed as hypothetical since only the resultant shielding effects exerted on certain (presumed) exo protons are observable.²³ We hope to provide definitive evidence relating to the conformations adopted by **2** and **3** in the solid state by three-dimensional x-ray analysis of their crystal structures. Such studies are currently in progress.

Discussion

From the identification of (-)-(S,S)-**11** as the sole dimeric product of pinacolic reduction of (+)-(S)-**6** and the entirely analogous conversion of (+)-(S)-**13** exclusively to (+)-(S,S)-**14**, it is clear that these coupling reactions are strikingly stereoselective. The absence of the remaining two possible diastereomers (**7** and **9** or their tetrahydro analogs) can be attributed to the energetic advantages attending C-C bond formation from the exo surfaces, the steric demands generated by magnesium alkoxide formation on the concaved interior notwithstanding. Consequently, given optically pure triquinacenone derivatives and the restriction that interaction can occur only with an identical enantiomer, substantial reliance can now be placed on the expectancy that exo,exo coupling will prevail.

Where the racemic mixtures of ketones of **6** and **13** are concerned, the energy differences in the diastereomeric transition states for reductive coupling of identical or opposite antipodal forms acquire significance. The results with both **6** and **13** indicate that these dimerizations possess no significant selectivity. Insofar as reliance of a quantitative nature can be placed upon ^{13}C NMR peak heights, the evidence points to formation of entirely comparable quantities of **11/12** and **14/15**. The relative amounts of pure diols actually isolated also agree with their production at comparable levels. We conclude that the diastereomeric energy barriers associated with each pinacolic reduction are closely matched.

Our findings contrast with those of Touboul and Dana for the controlled potential (1.35 V) electrochemical reduction of α,β -unsaturated ketone **4** at pH 6.⁹ While the dimerizations involving optically pure (+)-**4** or (-)-**4** led in turn uniquely to (+)-**5** and (-)-**5**, racemic **4** underwent fully comparable conversion exclusively to (\pm)-**5** and to no other possible diastereomer. Consequently, this last reductive coupling seemingly operates only between molecules of the same absolute configuration with amazing selectivity. If this is correct, it could mean that reduction of **6** and **13** by electrochemical techniques might result in an increase in enantioselectivity. Numerous factors are of course involved, not the least of which is the widely different steric demands of the triquinacenes compared with those of **4**. In any event, this alternative method of reductive coupling remains to be studied.

In conclusion, we point out that access to *dl*-bivalvane (**2**) can be gained conveniently at the present time. Attempts to elaborate the dodecahedrane nucleus by chemical manipulation of **2**, **17**, **21**, and more highly functionalized

derivatives of these "dimers" comprise an area of currently active investigation.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian A-60A, Varian HA-100, and Jeolco MH-100 instruments, while carbon magnetic resonance spectra were obtained with a Bruker 90 spectrometer. Apparent splittings are given in all cases. Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were obtained with a AEI-MS9 instrument at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Reductive Coupling of (\pm)-6**. (\pm - and *meso*-exo,exo-Hexadecahydro[1,1'-bicyclopenta[*cd*]pentalene]-1,1'(2*H*,2'*H*)-diol (**11** and **12**).** To a mixture of magnesium amalgam (from 1.15 g (48.2 mg-atoms) of magnesium and 150 g of mercury), anhydrous tetrahydrofuran (25 ml), and trimethylchlorosilane (2.60 ml, 19.8 mmol) was added a solution of racemic tricyclo[5.2.1.0^{4,10}]decan-2-one²⁵ (**6**, 0.70 g, 4.66 mmol) in 5 ml of the same solvent. The resulting mixture was stirred at room temperature under nitrogen for 24 hr, at which point the organic phase was decanted and the remaining metal was washed several times with tetrahydrofuran. The combined organic layers were evaporated, and the residues from three such reactions were treated with ethanol (15 ml) and water (40 ml). The resulting mixture was heated to reflux on a steam bath for 45 min. After acidification with dilute hydrochloric acid, the mixture was treated with dichloromethane and suction filtered, and the layers were separated. The aqueous phase was saturated with sodium chloride and extracted with dichloromethane. The combined organic layers were washed with brine, dried, and evaporated to leave a residue which when triturated with pentane provided 1.60 g (76%) of white solid, mp 93–98°, whose mass spectrum featured peaks at *m/e* 302, 284, 223, 151, and 150; *m/e* (calcd for C₂₀H₃₀O₂, 302.2246) 302.2248. The ^{13}C NMR spectrum of this substance in CDCl₃ solution exhibited 18 lines.

A 500-mg sample of this material was subjected to high pressure liquid chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether). There were obtained pure **11** (180 mg, 36%), a mixture of **11** and **12** (160 mg, 32%), and pure diol **12** (140 mg, 28%). The impure fractions were routinely recycled. Both diols were recrystallized from hexane to analytical purity.

For **11**: mp 111.5–112°; ^{13}C NMR (CDCl₃) 29.05, 31.65, 33.00, 33.10, 41.78, 42.41, 45.63, 49.38, 56.40, and 89.72 ppm.

Anal. (C₂₀H₃₀O₂) C, H.

For **12**: mp 119–119.5°; ^{13}C NMR (CDCl₃) 29.02, 31.59, 32.82, 33.05, 41.60, 42.60, 45.45, 49.53, 56.27, and 89.72 ppm.

Anal. (C₂₀H₃₀O₂) C, H.

Reductive Coupling of (+)-(S)-6**. (-)-(S,S)-exo,exo-Hexadecahydro[1,1'-bicyclopenta[*cd*]pentalene]-1,1'(2*H*,2'*H*)-diol (**11**).** The procedure described above was followed. After 80 mg of optically pure (+)-**6**²⁵ had been allowed to react for 12 hr, the organic layer was removed, and the black residue was washed with ether (3 × 10 ml) and ethyl acetate (2 × 10 ml). The combined organic layers were washed with 1 *N* hydrochloric acid (10 ml) and saturated sodium bicarbonate solution (10 ml), dried, and concentrated to leave 125 mg of residue. Crystallization from hexane gave 30 mg of white solid; chromatography of the filtrate on silica gel afforded an additional 20 mg of diol (total yield 62%), the ir and ^{13}C NMR spectra of which were identical with those of **11**. Further recrystallization from hexane gave (*S,S*)-**11** as white crystals: mp 110–111°; [α]₂₅³⁶⁵ -25°; [α]₂₅⁴³⁶ -11°; [α]₂₅⁵⁴⁶ -7°; [α]₂₅^D -5° (c 0.10, ethanol).

Reductive Coupling of (\pm)-13**. (\pm - and *meso*-exo,exo-2*a*,2'*a*,4*a*,4'*a*,6*a*,6'*a*,6*b*,6'*b*-Octahydro[1,1'-bicyclopenta[*cd*]pentalene]-1,1'(2*H*,2'*H*)-diol (**14** and **15**).** Treatment of 2.35 g (16.1 mmol) of racemic **13**²⁶ dissolved in tetrahydrofuran (70 ml) with magnesium amalgam (from 6 g of magnesium turnings and 680 g of mercury) and trimethylchlorosilane (12 ml) at room temperature under nitrogen for 15 hr led after work-up to a yellow residue (2.3 g). Crystallization of this material from hexane provided 200 mg of **15**. The mother liquor was passed through an alumina (activity III) column for initial purification (elution with hexane-ether (8:1)) and then subjected to high pressure liquid chromatography on silica gel (elution with 5% ethyl acetate in petroleum

ether). There were obtained an additional 220 mg of **15** (total yield 18%) and 490 mg (21%) of **14**. Both diols were recrystallized from hexane to analytical purity.

For **14**: mp 72–73°; ¹³C NMR (CDCl₃) 44.19, 48.61, 51.47, 56.11, 58.00, 86.87, 131.00, 134.45, 136.53, and 137.20.

Anal. (C₂₀H₂₂O₂) C, H.

For **15**: mp 155.5–157°; ¹³C NMR (CDCl₃) 43.89, 48.77, 51.34, 56.57, 57.92, 86.70, 131.05, 134.45, 136.45, and 136.91.

Anal. (C₂₀H₂₂O₂) C, H.

Reductive Coupling of (+)-(S)-13. (+)-(S,S)-*exo,exo*-**2a,2'a,4a,4'a,6a,6'a,6b,6'b**-Octahydro[1,1'-bicyclopenta[*cd*]pentalene]-1,1'-(2*H*,2'*H*)-diol (**14**). A 90-mg sample of optically pure (+)-**13**^{5b} was allowed to react with magnesium amalgam as pre-described for (+)-**6**. Purification of the reaction mixture by chromatography on alumina (activity III) furnished 42 mg (46%) of (S,S)-**14**: mp 72–73°; [α]_D²⁵₃₆₅ +533°; [α]_D²⁵₄₃₆ +310°; [α]_D²⁵₅₄₆ +171°; [α]_D²⁵_D +142° (c 0.13, ethanol). The ir and ¹³C NMR spectra of this diol were identical with those obtained earlier for racemic **14**.

Catalytic Hydrogenation of 14. A solution of **14** (120 mg) in ethyl acetate (15 ml) was hydrogenated at atmospheric pressure over 10% Pd/C (30 mg) to give a white solid (120 mg, 100%, mp 110–111°) whose ir and ¹³C NMR spectra were identical with those of **11**.

Catalytic Hydrogenation of 15. A solution of **15** (60 mg) in ethyl acetate (20 ml) was hydrogenated at atmospheric pressure over 10% Pd/C (30 mg) to afford a white solid (60 mg, 100%, mp 118–119°) which proved completely identical with **12**.

(±)-*exo,exo*-Hexadecahydrodispiro[cyclopenta[*cd*]pentalene-1(2*H*),4'-[1,3]dioxolane-5',1''(2''*H*)-cyclopenta[*cd*]pentalene]-2'-thione (**16**). To potassium hydride in oil (ca. 550 mg) was added a solution of **11** (485 mg, 1.66 mmol) in freshly distilled (from LiAlH₄) tetrahydrofuran (15 ml) and this was stirred at room temperature under nitrogen for 2 hr. A solution of carbon disulfide (130 μl) in the same solvent (5 ml) was introduced, and the mixture was stirred at room temperature for 10 min and then at 70° for 15 min. The flask was cooled in ice, and a solution of methyl iodide (130 μl) in tetrahydrofuran (3 ml) was added followed by heating at 60° for 5 min. After cooling to room temperature, the solution was decanted from a yellow residue which was subsequently washed with ether (3 × 15 ml). The combined organic layers were treated with *tert*-butyl alcohol (5 ml) to destroy residual potassium hydride, passed through a short column of silica gel, and evaporated to leave a greenish-yellow residue. Chromatography on silica gel provided 367 mg (67%) of thionocarbonate **16**, mp 138.5–140° (from hexane) and 155 mg (30%) of recovered diol **11**: ¹³C NMR (CDCl₃) 9.05, 31.27, 32.05, 32.53, 37.12, 41.17, 45.40, 48.53, 53.82, 103.35, and 191.08 ppm.

Anal. (C₂₁H₂₈O₂S) C, H.

meso-exo,exo-Hexadecahydrodispiro[cyclopenta[*cd*]pentalene-1(2*H*),4'-[1,3]dioxolane-5',1''(2''*H*)-cyclopenta[*cd*]pentalene]-2'-thione (**18**). A 478-mg (1.62 mmol) sample of diol **12** when treated as above gave a greenish-yellow residue from which 180 mg of **18** could be isolated by direct crystallization (hexane). The mother liquor was chromatographed on silica gel to provide an additional 296 mg (total yield 87%) of **18**, white crystals, mp 153.5–154° (from hexane), and 56 mg (11%) of recovered diol **12**: ¹³C NMR (CDCl₃) 29.05, 30.76, 32.11, 32.26, 36.73, 40.71, 45.48, 47.76, 53.87, 103.09, and 191.24 ppm.

Anal. (C₂₁H₂₈O₂S) C, H.

(±)-*exo,exo*-**2a,2'a,4a,4'a,6a,6'a,6b,6'b**-Octahydrodispiro[cyclopenta[*cd*]pentalene-1(2*H*),4'-[1,3]dioxolane-5',1''(2''*H*)-cyclopenta[*cd*]pentalene]-2'-thione (**20**). Treatment of **14** (380 mg, 1.29 mmol) with potassium hydride (ca. 400 mg) in anhydrous tetrahydrofuran, followed by sequential addition of carbon disulfide and methyl iodide in the pre-described fashion gave 210 mg (50%) of **15** and 130 mg (35%) of recovered **14**. Recrystallization of **15** from acetone-hexane afforded the pure thionocarbonate: mp 184.5–186.5°; ¹³C NMR (CDCl₃) 39.79, 47.07, 49.77, 54.74, 58.58, 103.04, 126.90, 132.68, 133.07, 137.10, and 190.51 ppm.

Anal. (C₂₁H₂₀O₂S) C, H.

meso-exo,exo-**2a,2'a,4a,4'a,6a,6'a,6b,6'b**-Octahydrodispiro[cyclopenta[*cd*]pentalene-1(2*H*),4'-[1,3]dioxolane-5',1''(2''*H*)-cyclopenta[*cd*]pentalene]-2'-thione (**22**). Diol **15** (330 mg, 1.12 mmol) was treated with potassium hydride (ca. 400 mg) in tetrahydrofuran at room temperature under nitrogen for 5 hr and then reacted

in turn with carbon disulfide and methyl iodide as before. Purification of the brownish residue by chromatography on silica gel gave 205 mg (55%) of **22**, mp 135–135.5° (from ether-hexane), and 110 mg (35%) of diol **15**: ¹³C NMR (CDCl₃) 39.56, 46.88, 49.96, 54.16, 58.64, 103.27, 127.29, 132.78, 132.91, 137.04, and 190.63.

Anal. (C₂₁H₂₀O₂S) C, H.

(±)-(E)-**2a,2'a,3,3',4,4',4a,4'a,5,5',6,6',6a,6'a,6b,6'b**-Hexadecahydro-Δ^{1,1'(2*H*,2'*H*)-bicyclopenta[*cd*]pentalene (**17**). A solution of *dl*-thionocarbonate **16** (180 mg, 0.52 mmol) in 2 ml of triethyl phosphite was gently refluxed under nitrogen for 70 hr. The cooled reaction mixture was extracted with hexane (4 × 5 ml), and the combined organic layers were dried and evaporated. The colorless residue was chromatographed on silica gel (hexane elution) to give 112 mg (81%) of olefin **17**: mp 65–66.5° (from ether-acetone); ¹³C NMR (CDCl₃) 31.86, 33.42, 33.80, 34.31, 37.09, 43.51, 45.51, 48.50, 55.30, and 138.09 ppm.}

Anal. (C₂₀H₂₈) C, H.

meso-(Z)-**2a,2'a,3,3',4,4',4a,4'a,5,5',6,6',6a,6'a,6b,6'b**-Hexadecahydro-Δ^{1,1'(2*H*,2'*H*)-bicyclopenta[*cd*]pentalene (**19**). From 110 mg (0.33 mmol) of **18** and 2 ml of triethyl phosphite (reflux 70 hr), there was obtained 71 mg (84%) of hydrocarbon **19**: mp 82–83.5° (from ether-acetone); ¹³C NMR (CDCl₃) 31.78, 33.67, 34.18, 34.45, 36.93, 43.27, 45.51, 48.29, 55.03 and 137.72 ppm.}

Anal. (C₂₀H₂₈) C, H.

(±)-(E)-**2a,2'a,4a,4'a,6a,6'a,6b,6'b**-Octahydro-Δ^{1,1'(2*H*,2'*H*)-bicyclopenta[*cd*]pentalene (**21**). Treatment of 110 mg of **20** with triethyl phosphite (1.5 ml) at the reflux temperature under nitrogen for 2 days led to isolation of 61 mg (72%) of **21**: mp 75.5–77° (from acetone); ¹³C NMR (CDCl₃) 38.04, 49.37, 50.37, 54.68, 58.49, 131.40, 132.59, 133.43, 134.48, and 138.23 ppm.}

Anal. (C₂₀H₂₀) C, H.

meso-(Z)-**2a,2'a,4a,4'a,6a,6'a,6b,6'b**-Octahydro-Δ^{1,1'(2*H*,2'*H*)-bicyclopenta[*cd*]pentalene (**23**). After heating 115 mg of **22** in 1.5 ml of triethyl phosphite at the reflux temperature under nitrogen for 2 days, there was obtained 78 mg (87%) of **23**: mp 149–151° (from acetone); ¹³C NMR (CDCl₃) 38.01, 48.99, 50.50, 54.30, 58.35, 132.48 (2C), 133.91, 134.45, and 138.28 ppm.}

Anal. (C₂₀H₂₀) C, H.

Catalytic Hydrogenation of 17. (±)-*endo,endo*-Eicosahydro-1,1'-bicyclopenta[*cd*]pentalene. *dl*-Bivalvane (**2**). A solution containing 85 mg (0.30 mmol) of **17** in 10 ml of ethyl acetate was hydrogenated at 50 psig over 5% rhodium on carbon (50 mg) for 8 days. Removal of the catalyst by filtration and evaporation of solvent gave 75 mg (83%) of **2** as a white solid: mp 85–85.5° (from acetone); ¹³C NMR (CDCl₃) 25.91, 30.02, 32.54 (2C), 36.67, 44.02, 44.51, 46.20, 47.92, and 54.68 ppm.

Anal. (C₂₀H₃₀) C, H.

Catalytic Hydrogenation of 19. *meso-endo,endo*-Eicosahydro-1,1'-bicyclopenta[*cd*]pentalene. *meso*-Bivalvane (**3**). Hydrogenation at 50 psig of 120 mg (0.45 mmol) of **19** in 10 ml of ethyl acetate containing 50 mg of 5% rhodium on carbon during 5 days furnished 95 mg (79%) of **3** as a white solid: mp 134–134.5° (from acetone); ¹³C NMR (CDCl₃) 25.30, 31.05, 32.48 (2C), 36.12, 44.05, 44.51, 46.23, 48.08, and 54.55 ppm.

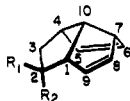
Anal. (C₂₀H₃₀) C, H.

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An Unusually Weak Carbon-Carbon Single Bond

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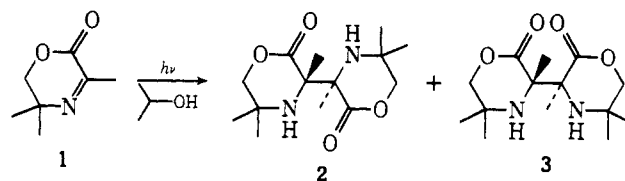
Abstract: The reactivity of the meso and *dl* photoreductive dimers (**2** and **3**) of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**) is described. The meso and *dl* isomers readily interconvert, are air oxidized, and disproportionate. The reactivity results from the fact that the dimers have an unusually weak carbon-carbon single bond and exist in equilibrium with a radical (**5**). Radical **5** is a unique carbon radical in that it is relatively stable and yet has no aromatic or olefinic substituents. The enthalpy of dissociation of the dimers is solvent dependent and ranges from 22 kcal/mol in chloroform to 11 kcal/mol in ethanol. The low enthalpy of dissociation is discussed in terms of the structures of the dimers and the radical.

In our examination of the photochemical reactivity of conjugated imines, we have isolated and characterized stereoisomeric, photoreductive dimers of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**).¹ In solution these dimers possess a weak carbon-carbon single bond and exist in equilibrium with a radical at room temperature.² This facile bond homolysis is unusual, especially since the resulting radical bears no aromatic groups.

Results and Discussion

Irradiation of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**) in 2-propanol solvent at -15° with a 450-W mercury lamp through a Pyrex filter gave a 57% yield of a mixture of reductive type dimers. These were separated by medium-pressure liquid chromatography with a column of neutral alumina and assigned meso and *dl* stereoisomeric structures **2** and **3** from spectroscopic data described separately.¹

The reductive dimers were found to be thermally unstable in solution. When a freeze-thaw degassed, 31% *dl*-69% meso dimer mixture in deuteriochloroform was heated to 80° for 20 min, a stereochemical equilibration occurred giving a 69% *dl*-31% meso mixture as indicated by NMR analysis. In the presence of oxygen, the dimer mixture was



rapidly oxidized to 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**). Prolonged heating of the dimer mixture in the absence of oxygen gave a 50:50 mixture of **1** and 3,5,5-trimethylmorpholin-2-one (**4**), the products of disproportionation. (See Scheme I for a summary of these reactions.) The structural assignment of **4** is based upon the NMR data in the Experimental Section, N-H and carbonyl stretching bands at 3300 and 1735 cm^{-1} , respectively, in the infrared, and a parent ion at m/e 143 (15% of base) in the mass spectrum.

The stereochemical equilibration, air oxidation, and disproportionation reactions of the dimers were suggestive of a radical intermediate. When a degassed sample of the dimer mixture dissolved in benzene, chloroform, or absolute ethanol was warmed to 80° , EPR spectra were observed as given in Table I. Structure **5** was proposed for the radical with hyperfine splitting assignments as indicated in Table I.