**Abstract:** Pinacolic reduction of both optically pure and racemic hexahydrotriquinacen-2-one (6) proceeds with exo,exo carbon-carbon bond formation. Coupling of optically pure 6 produces diol 11 exclusively. Formation of comparable amounts of 11 and 12 from 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 $^{13}$C NMR (symmetry is thereby revealed), $^1$H NMR (shielding of the endo protons at $C_3$ and $C_7$ 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 phosphate 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.

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 Kelly who viewed dodecahedrane as composed of two triquinacene subunits which when properly arranged might be coaxied 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 stereoc hemical 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 $\pi$ bond upon lobes of two different noninteracting double bonds constitutes a process for which chemical analogy is lacking if concerted or metal catalyzed.

Despite the disadvantages intrinsic to the above model, it is apparent that initial endo,endo coupling of two monomeric triquinacene units at $C_2$ could go far in setting the stage for the ultimate construction of the desired polyhedron. Such a synthetic scheme 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, 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 enanti-selective fashion with formation of cis-threo-cis diol 5 to the exclusion of the cis-erythro-cis and other possible isomers. 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.

Because adherence to an exo,exo bonding scheme would necessitate ultimate inversion of configuration at $C_2$ 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".

*Leo A. Paquette,* Isamu Itoh, and William F. Barnham

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210.

Received March 28, 1975

Journal of the American Chemical Society / 97:25 / December 10, 1975
Results

After several unsuccessful attempts to couple (±)-6 by means of a thia-diazolidine intermediate, recourse was made to pinacolic reduction. Upon gradual addition of (±)-6 to a mixture of magnesium amalgam and trimethylchlorosilane in dry tetrahydrofuran at 25 °C, 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 C2. Diols 7 and 11, in contrast, possess axial symmetry only (point group C3) 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 C1 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 C2 or C3 symmetry or with a single isomer of the C1 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 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 °C) isolated from racemic 6. This compound is necessarily 7 or 11. As a result of chemical correlation studies involving tetrane 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 tetrane diol 15, the somewhat simpler 1H NMR spectrum of which fully supported the indicated stereochemical assignment (vide infra).

Following the above scheme, (+)-2,3-dihydrotriquinacen-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 enantioomerically pure (+)-(S)-13 led exclusively to (S,S)-14 ([α]25D +142° (c 0.13, ethanol)). This result provides independent evidence confirming the enantiomeric purity of 6 and 12. 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-dihydrotriquinacen-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-dihydrotriquinacen-2-ol arises from intramolecular hydrogen bonding to a double bond (cf. A). A totally analogous situation can be expected to prevail in 14 and 15. However, as can be seen from B, “dimers” having exo hydroxyl 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. 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 Hendo and Hendo, and their chemically equivalent-primed counterparts are clearly evident and together indicate the configurational features at C3 and C3' in the case of 14, the pair of methylene protons at C3 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 Hendo and Hend. For the endo protons at C3 and C3', the dihedral angle relationship with Hendo, respectively, now approaches 120 instead of 0°, and a...
decrease in the H$_{3endo}$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$_{3exo}$ and
H$_{3endo}$ (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$_{3exo}$
and H$_{3endo}$ appear at δ 1.92 (J$_{gem}$ = J$_{vic}$ = 13.0 Hz) and
H$_{3endo}$/H$_{3exo}$ are seen at 2.37 (J$_{vic}$ = 8.0 Hz) is remark-
ably 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 struc-
tures, chemical transformations of the meso “dimers” 12
and 15 have been studied in order to provide appropri-
ately contrasting $^{13}$C NMR reference spectra. Because
certain tungsten reagents appeared to offer a potentially
simple and convenient method for the stereoselective deoxy-
genation of vicinal dialkoxides,18 the dilithio salt of a 50:50
mixture of 11 and 12 was treated with a tetrahydrofuran so-
lution of tungsten hexachloride-n-butyllithium (1:3). After
work-up and chromatography, 50% of the diol was recov-
ered. 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 (±)-6 to 17 and 19 with the titanium trichlo-
ride–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 thiono-
carbonate methodology.20 Because formation of the dio-
potassium salts of 11 and 12 using potassium metal proved
rather sluggish even in refluxing dioxane, and owing to ap-
parent arresting of dialkoxide formation short of comple-
tion, 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 tetrahy-
drofuran at room temperature. In this way, efficient conver-
sions to thionocarbonate salts 16, 18, 20, and 22 were realized
conveniently and in good yield. These more geometrically
rigid cyclic esters unexpectedly show 11 line $^{13}$C NMR spec-
a in agreement with maintenance of C$_2$ (16 and 20) and
C$_1$ symmetry (18 and 22).

When heated with triethyl phosphite, these thionocarbo-
nates were transformed stereospecifically to the structurally
related alkenes in yields ranging from 72 to 87%. Inter-
estingly, 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 $^{13}$C 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 C$_2$ and C$_2'$ elaborate
sp$^3$ character. In fact, molecular models suggest that satu-
ration 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 dodecahedrane conformation used
herein for illustration purposes. In an attempt to gain infor-
mation on this point by spectroscopic methods, the infrared
and $^1$H 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 frequen-
cies.22 Steric compression is also known to affect chemical
shifts23 and coupling constants in such molecules,24 particu-
larly 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 perhy-
drotriquinacene (24).2 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 $^1$H NMR spectrum of 24 (CDCl$_3$ solution) is char-
acterized 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
methylene and methylene protons. Direct extrapolation of
this information to dl- and meso-bivalvane leads to the predic-
tion 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 ration-
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 $^1$H NMR data support the idea that the "equilibrium structures" adopted by 2 and 3 do give recogniz-able 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. 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 pinacolonic 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 or 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 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 pinacolonic reduction are closely matched.

Our findings contrast with those of Touboul and Dana for the controlled potential (1.35 V) electrochemical reduction of a,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 (−)-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 triquinacenones 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 Scandinaviano Microanalytical Laboratory, Herlev, Denmark.

Reductive Coupling of (±)-6. (±)- and meso-exo,exo-Hexadecahydro[1,1'-bicyclo[6.2.2]tetradecyl]-1,1'-dicarboxylic acid (1) and (±)-6 were treated with sodium amalgam (1.15 g (14.7 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]tridecan-2-one (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 1 hr. 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 triturated with pentane provided 1.60 g (76%) of white solid. mp 93–98°C, whose mass spectrum featured peaks at m/e 302, 284, 223, 151, and 150; m/e (calcd for C$_{20}$H$_{30}$O$_2$, 302.2246) 302.2248. The $^{13}$C NMR spectrum of this substance in CDCl$_3$ 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°C; $^{13}$C NMR (CDCl$_3$) 29.05, 31.65, 33.00, 33.10, 41.78, 42.41, 45.63, 49.38, 56.40, and 89.72 ppm. Anal. (C$_{20}$H$_{30}$O$_2$) C, H.

For 12: mp 119–119.5°C; $^{13}$C NMR (CDCl$_3$) 29.02, 31.59, 32.82, 33.05, 41.60, 42.60, 45.45, 49.53, 56.27, and 89.72 ppm. Anal. (C$_{20}$H$_{30}$O$_2$) C, H.

Reductive Coupling of (±)-(S)-6, (±)-(S,S)-exo,exo-Hexadecahydro[1,1'-bicyclo[6.2.2]tetradecyl]-1,1'-dicarboxylic acid (2) and (±)-6 were treated with sodium amalgam (1.15 g (14.7 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]tridecan-2-one (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 1 hr. 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 triturated with pentane provided 1.60 g (76%) of white solid. mp 93–98°C, whose mass spectrum featured peaks at m/e 302, 284, 223, 151, and 150; m/e (calcd for C$_{20}$H$_{30}$O$_2$, 302.2246) 302.2248. The $^{13}$C NMR spectrum of this substance in CDCl$_3$ 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°C; $^{13}$C NMR (CDCl$_3$) 29.05, 31.65, 33.00, 33.10, 41.78, 42.41, 45.63, 49.38, 56.40, and 89.72 ppm. Anal. (C$_{20}$H$_{30}$O$_2$) C, H.

For 12: mp 119–119.5°C; $^{13}$C NMR (CDCl$_3$) 29.02, 31.59, 32.82, 33.05, 41.60, 42.60, 45.45, 49.53, 56.27, and 89.72 ppm. Anal. (C$_{20}$H$_{30}$O$_2$) C, H.
was treated with potassium hydride (ca. 400 mg and 130 mg (35%) of recovered drofuran, followed by sequential addition of carbon disulfide and 

\[ \text{[cyclopenta[cdjpentane-1(2H),4'-thione} \]

from hexane), and 56 mg (11%) of recovered diol 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

in anhydrous tetrahydrofuran (from acetone); 13C NMR (CDCl3) 29.05, 30.76, 32.11, 32.26, 36.73, 40.71, 47.76, 53.87, 103.09, and 191.24 ppm. 

Anal. (C20H22O2) C, H. 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

meso-\[Z\]-2a,4a,6a,6b,6''-Octahydro-1,1'-bicyclo [cdjpentane (19). A solution of di-thionocarbonate 16 (180 mg, 0.52 mmol) in 2 ml of triethyl phosphite (reflux 70 hr), there was obtained 71 mg (84%) of hydrocarbon 19: mp 82--83.5° (from 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. (C18H18O2S) C, H. 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

for 4 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) 29.51, 34.97, 50.37, 54.68, 58.49, 131.40, 132.39, 133.43, 134.48, and 138.23 ppm. 

Anal. (C18H18O2S) C, H. 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

meso-\[Z\]-2a,4a,6a,6b,6''-Octahydro-1,1'-bicyclo [cdjpentane (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, 132.39, 133.43, 134.48, and 138.23 ppm. 

Anal. (C20H22O2) C, H. 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

Catalytic Hydrogenation of 17. (\(\pm\)-endo,endo-Eicosahydro-

1,1'-bicyclo [cdjpentane, dl-Bivalvane (2). A solution containing 85 mg (0.30 mmol) of 17 in 10 ml of ethyl acetate was hydrogenated at 50 psi over 5% rhodium on carbon (50 mg) for 2 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) 29.51, 34.97, 50.37, 54.68, 58.49, 131.40, 132.39, 133.43, 134.48, and 138.23 ppm. 

Anal. (C18H18O2S) C, H. 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

meso-\[Z\]-2a,4a,6a,6b,6''-Octahydro-1,1'-bicyclo [cdjpentane (21). After heating 115 mg of 21 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. (C20H22O2) C, H. 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

Catalytic Hydrogenation of 19. \(\pm\)-endo,endo-Eicosahydro-

1,1'-bicyclo [cdjpentane, meso-Bivalvane (3). Hydrogenation at 50 psi of 120 mg (0.45 mmol) of 19 in 10 ml of ethyl acetate containing 50 mg of 9% rhodium on carbon during 5 days furnished 95 mg (79%) of 19: mp 153--154° (from acetone) ; 13C NMR (CDCl3) 23.73, 30.86, 31.80, 34.89, 40.66, 45.63, 47.80, 53.87, 103.13, and 191.24 ppm. 

Anal. (C20H22O2) C, H. 

\[ \text{[cyclopenta[cdjpentane-2'-thione} \]

Attention. We are grateful to the National Institutes of Health (Grant AI-11490) and Eli Lilly and Company for their partial support of this research.

References and Notes


Journal of the American Chemical Society / 97:25 / December 10, 1975
An Unusually Weak Carbon–Carbon Single Bond

Tad H. Koch,* John A. Olesen, and James DeNiro

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. Received August 10, 1974

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 8 kcal/mol in ethanol.

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). In solution these dimers possess a weak carbon–carbon single bond and exist in equilibrium with a radical at room temperature. 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 °C 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.

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 °C 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 1 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 1300 and 1735 cm⁻¹, respectively, in the infrared, and a parent ion at m/z 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 °C, 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.