The Isomeric *trans,trans*-Bicyclo[6.1.0]non-4-enes[1,2]

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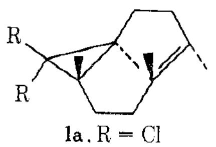
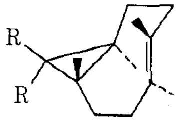
cis,trans-Bicyclo[6.1.0]non-4-enes have been prepared *via* two different routes and photoisomerized to the "parallel" and "perpendicular" isomers of *trans,trans*-bicyclo[6.1.0]non-4-enes. Structures for these isomers were confirmed and assigned by chemical and spectral means. Most noteworthy properties of these isomers include distortion from true perpendicularity in the "perpendicular" isomer and apparent severe distortion from planarity of the "parallel" isomer's double bond. The latter property apparently facilitates a remarkable thermal cis-trans isomerization of an isolated double bond. A comparison of the ultraviolet spectra of the two isomers also supports the postulated interaction between the cyclopropane and the π bond. Other chemistry of these isomers is discussed.

The consequences of cyclopropane ring interactions with proximate reacting centers and unsaturated groups have evoked considerable experimental and theoretical study. In an attempt to probe yet another facet of such interactions, we undertook syntheses of the "parallel" (**1**) and "perpendicular" (**2**) *trans,trans*-bicyclo[6.1.0]non-4-enes. Molecular models of these two isomers showed that the π and the transannular cyclopropane bonds possessed a common axis and that these two bonds were in extremely close proximity to each other. Thus, as viewed from the perspective offered by molecular models, the structural features of these isomers might provide a unique opportunity to study interactions between cyclopropanes and alkenes (as well as other alkene derived products) as a function of two closely related and possibly optimum geometries.

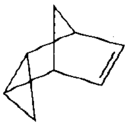


1a, R = Cl
b, R = H



2a, R = Cl
b, R = H

Effects of geometry and distance have been noted on through-space cyclopropane–alkene interactions in other systems (*e.g.*, **3–5**).[3] In contrast to these previous studies, the interfunctional distances of **1** and **2** appeared to be significantly shorter. In addition, the parallel orientation of the p orbitals and the cyclopropane ring in **1** forces maximum possible interactions between these two structural entities.



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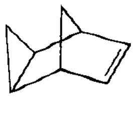

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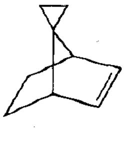

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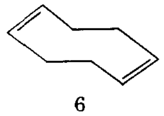
A hint at the potential importance of such orientation–distance factors can be found in a previous study by Cope and Whitesides.[4] In this study, photochemical isomerization of the Cu_2Cl_2 complex of *cis,cis*-1,5-cyclooctadiene (**6**) formed a product in low (1–2%) yield which was assigned the 1,5-*trans,trans*-cyclooctadiene structure. Although these authors were unable to determine whether their product was **7**, **8**, or a mixture of both, they did note chemical instability and ultraviolet spectral properties apparently indicative of transannular interactions. By contrast, **6** is relatively unremarkable in its chemical reactivity.



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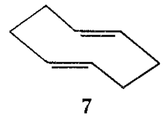

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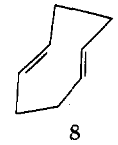

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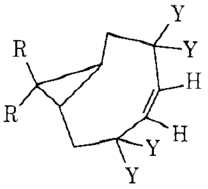
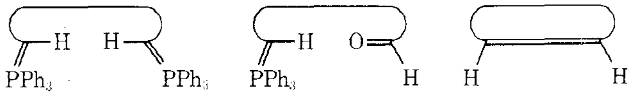
Synthesis. Cyclization Approach. Since the *trans*-alkene moiety was expected to be the most reactive component of the desired structures, we focused on synthetic approaches in which its formation would be the final step. Although an isomerization of the cis isomer **9** appeared to be the simplest approach, the low yields obtained by Cope and Whitesides in the synthesis of *trans,trans*-1,5-cyclooctadiene (**6** or **7**) made this approach initially less desirable.



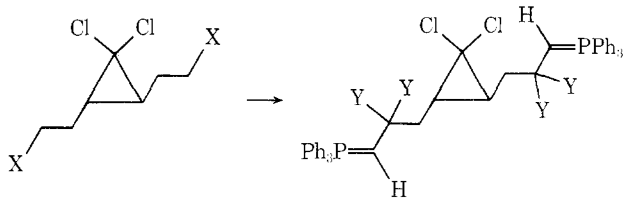
9a, R = Cl; Y = H
b, R = Cl; Y = D
c, R = H; Y = H

An apparently attractive alternative was found in an adaptation of Bestman's symmetrical alkene synthesis.[5] This synthesis involves the oxidation of diphosphonium ylides by molecular oxygen (Chart I). Under favorable circumstances the ylide–aldehyde reacts intramolecularly more rapidly than further oxidation or intermolecular reaction can occur. The appropriate precursor **13e** was prepared in a number of steps (Scheme I) from **13b**. Compound **13b** was

Chart I



Scheme I

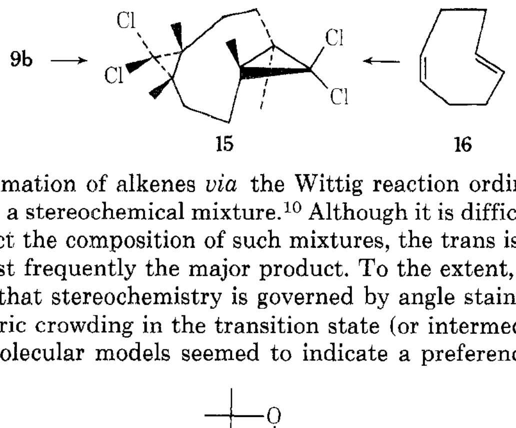


13a, $X = CO_2C(CH_3)_3$
b, $X = CO_2CH_3$
c, $X = CH_2OH$
d, $X = CH_2OTs$
e, $X = CH_2I$
f, $X = CH_2P^+(Ph)_3X^-$
g, $X = CO_2H$

11a, Y = H
b, Y = D

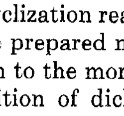
in turn synthesized by addition of dichlorocarbene to the corresponding trans unsaturated ester.[6] Simultaneous high dilution addition of **13e** and 2 equiv of sodium methylsulfinyl methide to oxygenated dimethyl sulfoxide yielded a single product of the desired molecular weight in 22% yield.[7] The general structure of this product was established *via* ozonolysis to **13g.** This ozonolysis product was identical in all respects with a product obtained by chromic acid oxidation of **13c.**

In order to establish the stereochemistry of the cyclization product, **13a**[6] was deuterated by exchange with $(CH_3)_3COD$–$(CH_3)_3COK$. This product was transesterified, the tetradeuterio dimethyl ester was then carried through steps outlined in Scheme I, and the resultant tetradeuterio diylide **14b** was cyclized to **9b** as described above. A ^{13}C satellite nmr spectrum was obtained on the olefinic protons of this product and this spectrum revealed a coupling constant $J_{C^{13}\text{-H},C^{12}\text{-H}}$ of 11.5 Hz. Comparison of this coupling constant with coupling constants obtained for other normal and medium-sized rings[8] established that the cyclization product had the cis stereochemistry about the double bond. Chemical confirmation of this assignment was obtained from the observed total unreactivity of the cyclization product toward 1,3-dipoles such as phenyl azide.[9] Final proof of structure was obtained by the reaction of the cyclization product **9b** with 1 mol of dichlorocarbene to give **15.** This product was identical in all respects with one prepared directly from **16.**



15 16

Formation of alkenes *via* the Wittig reaction ordinarily yields a stereochemical mixture.[10] Although it is difficult to predict the composition of such mixtures, the trans isomer is most frequently the major product. To the extent, however, that stereochemistry is governed by angle stain and/or steric crowding in the transition state (or intermediate) **17,** molecular models seemed to indicate a preference for



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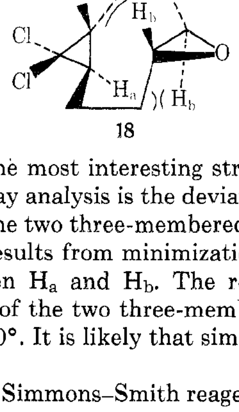
the desired trans isomers. From our observed results it is clear that these factors do not dictate stereoselectivity in this cyclization. This result is all the more interesting in view of the fact that a mixture of **1** and **2** (*vide infra*) was unaltered in composition (although partially destroyed) when subjected to the cyclization reaction conditions.

Compound **9** could be prepared more efficiently by controlled selective addition to the more reactive trans double bond of **16.** Thus, addition of dichlorocarbene or diazomethane (followed by photolysis) yielded **9a** and **9c,**[11] respectively. The more cumbersome oxidative cyclization route did make **9b** available and this compound proved to be exceptionally useful, as will be described subsequently.

Isomerization Approach. Since the results of the oxidative cyclization suggested that any nonstereospecific alkene formation might also yield **9,** we reconsidered the possibility that **9** could be photochemically isomerized to the desired structures **1** and **2.** The two major problems with this approach were the prospects for low yields (*vide supra*) and the lack of a stable complex between **9** and cuprous chloride. After some experimentation it was found that a preformed cuprous chloride complex was unnecessary. Observations concerning this procedure and its application to the synthesis of *trans*-cyclooctene have already been published.[12] In brief, the cuprous chloride functions both as a sensitizer for the isomerization and also displaces the equilibrium by virtue of the greater stability of the complex with the more strained *trans*-alkene.

Irradiation of **9a** and cuprous chloride at 2537 Å in hexane for 27 hr produced a mixture which had three components with similar glc retention times. Extraction of this mixture with aqueous silver nitrate left the major component behind in the organic phase. This component was shown to be identical with starting material **9a.** Addition of aqueous ammonia to the silver nitrate solution liberated the two minor products in 43% yield. These two minor products were present in a 5 to 1 ratio before and after the silver nitrate extractions. They were separated by preparative glc and shown by mass spectroscopy to be isomeric with **9a.** Gross structure and the location of the double bond were confirmed by ozonolysis. In a similar manner isomerization of **9c** gave a mixture of two silver nitrate soluble isomers in 20% yield. These isomers which were present in a 7 to 1 ratio were also separable by preparative glc.

In order to distinguish between **1** and **2,** the major isomer from **9a** was converted to its epoxide and submitted for X-ray diffraction analysis.[13] This analysis established structure **18** for the epoxide and proved that the predominent isomer was **2a.** The most interesting structural feature revealed by the X-ray analysis is the deviation from true perpendicularity of the two three-membered rings. This deviation apparently results from minimization of transannular repulsions between H_a and H_b. The resultant angle between the planes of the two three-membered rings is thus 70.3° instead of 90°. It is likely that similar factors pertain to **2.**[14]



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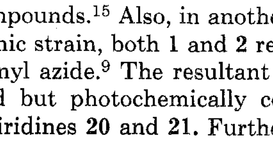
Addition of the Simmons–Smith reagent converted **2a** to **19.** The same product was obtained by addition of dichlorocarbene to the major product from **9c.** In this way both major products were assigned the "perpendicular" structure and the "parallel" structure was attributed to the minor isomers.



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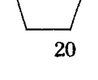
Chemical and Spectral Properties. The fact that **1** and **2** (in contrast to **9**) are soluble in aqueous silver nitrate confirms the presence of strained trans double bonds in both of these compounds.[15] Also, in another reaction characteristic of olefinic strain, both **1** and **2** reacted extremely rapidly with phenyl azide.[9] The resultant triazolines were not characterized but photochemically converted to the corresponding aziridines **20** and **21.** Further important in-



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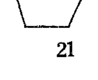

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EXPERIMENTAL SECTION

General Methods: Unless otherwise noted all melting points were determined in glass capillaries and are uncorrected. Liquid samples of less than 6 g were generally distilled using a hot air bath and the boiling point reported was the temperature of the air bath. Irradiations at 2537 Å were done in a Southern New England Ultraviolet Co. (Middletown, Conn.) "Rayonet" Model RS Preparative Photochemical Reactor. Irradiation at longer wavelengths was carried out using a Hanovia 550w medium pressure quartz mercury arc lamp equipped with a water-cooled Pyrex immersion well (Ace Glass Co., Vineland, N.J.). Routine infrared spectra were measured with a Perkin-Elmer (Norwalk, Conn.) Model 137 "Infracord" instrument and ultraviolet spectra were measured using a Cary Model 15 recording spectrophotometer (Applied Physics Corp., Monrovia, California). Vacuum ultraviolet spectra were recorded on a MacPherson Model 665 (MacPherson Instrument Co., Acton, Massachusetts) recording spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian Associates (Palo Alto, California) type A-60 instrument. Carbon-13 Satellite Spectra were recorded using a Varian Associates type XL-100 instrument. Chemical shifts (δ) are expressed in ppm using tetramethylsilane as an internal standard. Preparative gas chromatographic separations were performed on a Hewlett-Packard (Palo Alto, California) Model 700 gas chromatograph using the Model 5795 A preparative attachment. Analytical gas chromatographs were obtained on a Varian Associates (Palo Alto, California) Aerograph Hy-Fi Model 600-D analytical gas chromatograph using 6' x 1/8" columns. Peak areas were measured by disc integration. Mass spectra were recorded on a Perkin-Elmer Hitachi (Norwalk, Conn.) Model RMU-6E mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc. (Knoxville, Tennessee) and by Atlantic Microlabs, Inc. (Atlanta, Georgia).

3,3-Dichloro-*trans*-1,2-cyclopropane Dipropionic Acid Dimethyl Ester (13b)

A solution of 31.5 g (0.157 mole) of dimethyl *trans*-4-octene-1,8-dioate[6b] in 100 ml of 1,2-dimethoxyethane (glyme), which had been dried over molecular sieves, and 29.0 g (0.157 mole) of sodium trichloroacetate was refluxed for 12.0 hours. A slow addition of crystalline sodium trichloroacetate from a bottle attached to the apparatus was then begun. The liberated CO_2 was allowed to vent from a $CaCl_2$ drying tube attached to the top of the condenser. The reaction was monitored by gas chromatography (SE-30) and required 5 days for completion. At this point, the addition was 96% complete and a 16-fold molar excess of sodium trichloroacetate had been used. Workup consisted of diluting the very black and viscous reaction mixture with ether, filtering off the precipitated NaCl, and evaporating the filtrate down to a very black oil. Analysis of this oil by gas chromatography showed only product and a small amount of starting material as the only volatile materials. Vacuum distillation of this oil at 135°/1.5 mm gave 31.8 g (76%) of product. Triturating the residue in boiling acetone, followed by filtration through Florex, evaporation of the filtrate to an oil and vacuum distillation of the oil gave an additional 9.1 g of material. A total yield of 41.9 g (94%) of dichloro cyclopropane 13b was thus obtained. $\delta^{tms}_{CDCl_3}$ 3.75 (singlet, 6H); 2.52 (multiplet, 4H); 1.93 (multiplet, 4H); and 1.37 (multiplet, 2H).

3,3-Dichloro-*trans*-1,2-di(3-hydroxypropyl)Cyclopropane (13c)

A mixture of 22.4 g (0.558 mole) of $LiAlH_4$, 41.7 g (0.147 mole) of 13b and 400 ml of anhydrous ether was refluxed for 5 hours. The mixture was then cooled in an ice bath, stirred, and to it was cautiously added 22.5 ml of H_2O, 22.5 ml of 15% aqueous NaOH, followed by 67.5 ml more H_2O. The mixture was then allowed to stir in the ice bath for 0.5 additional hours. The inorganic salts were then filtered off, the filtrate dried over $MgSO_4$ and evaporated to give a quantitative yield of the diol 13c (33 g). $\delta^{tms}_{CDCl_3}$ 3.70 (multiplet, 4H); 3.42 (singlet, 2H); 1.71 (multiplet, 8H); and 1.18 (multiplet, 2H). Washing the $CDCl_3$ solution of this material once with D_2O completely eliminated the singlet at 3.42δ.

3,3-Dichloro-*trans*-1,2-cyclopropane Dipropionic Acid (13g)

A chromic acid oxidizing solution[21] was prepared by adding 2.3 ml (0.044 mole) of conc. H_2SO_4 to 2.67 g (0.027 mole) of chromium trioxide and diluting the resulting mixture to a volume of 10 ml with H_2O. A solution of 0.55 g (0.0024 mole) of diol 13c in 40 ml of acetone was then prepared, stirred and cooled in an ice bath. To the solution was then added, under a N_2 atmosphere, a sufficient quantity of the oxidizing solution (*ca.* 3.5 ml) to cause a persistence of yellow color. The mixture was then stirred at room temperature for 20 hours. Methanol (0.5 ml) was then added, followed by filtration and evaporation. Ether was added to the residue and then saturated aqueous NaCl. The mixture was shaken and separated. The ether layer was dried over $MgSO_4$ and evaporated to an oil. The oil was picked up in ether-petroleum ether and crystallized at -20° to give material (13g) melting at 100-101.5°. One recrystallization gave an analytical sample (mp 101-102°). $\delta^{tms}_{CDCl_3}$ 11.3 (singlet, 2H); 2.56 (triplet, 4H); 1.85 (multiplet, 4H); and 1.30 (multiplet, 2H). ir: 3,000 (broad); 1,705; 1,415; 1,270; 1,218; 919 and 824 cm^{-1}.

Analysis: Calcd. for $C_9H_{12}O_4Cl_2$: C, 42.37; H, 4.74.

Found: C, 42.59; H, 4.84.

3,3-Dichloro-*trans*-1,2-di-(3-tosylpropyl)Cyclopropane (13d)

This compound was first prepared by dissolving 5.8 g (0.025 mole) of diol 13c in 125 ml pyridine (distilled over CaH_2) followed by the addition of 19.1 g (0.100 mole) of *p*-toluenesulfonyl chloride (recrystallized from $CHCl_3$ petroleum ether). The flask was then stoppered and cooled to -20° for 43 hours. The mixture was then added to 500 ml of rapidly stirred ice and H_2O. After 15 minutes the mixture was then extracted 3 times with ether. The ether layers were washed twice with cold 1:1 HCl and once with H_2O, dried over $MgSO_4$, clarified with Norit and evaporated. The residue was picked up in 60 ml ether and crystallized (mp 53-54°) at -78° in a dry ice-acetone bath. Two crops afforded 8.15 g (62%) of ditosylate 13d. Attempts to scale up this reaction, however, resulted in a marked decrease in yield. $\delta^{tms}_{CDCl_3}$ 7.25-7.95 (quartet, 8H); 4.08 (triplet, 4H); 2.46 (singlet, 6H); 1.67 (multiplet, 8H) and 1.01 (multiplet, 2H).

Analysis: Calcd. for $C_{23}H_{28}O_6S_2Cl_2$: C, 51.59; H, 5.27; Cl, 13.24.

Found: C, 51.32; H, 5.43; Cl, 13.42.

A more efficient large-scale preparation consisted of dissolving 20.0 g (0.088 mole) diol 13c in 400 ml benzene followed by the addition of 12.5 g (0.65 mole) of sodium hydride (prepared from 25.0 g of the 50% dispersion by three washings with pentane). The whole mixture was cooled in an ice bath (in order to keep foaming down to a minimum), and was mechanically stirred for about 10 minutes. A solution of 38.0 g (0.18 mole) of freshly purified *p*-toluene sulfonyl chloride dissolved in 100 ml benzene was added dropwise over a period of 45 min. Once addition was complete, the ice bath was removed and the mixture allowed to stir at room temperature for 18 hours. The mixture was then cooled in an ice bath and water was very cautiously added to the stirred mixture. Once the excess NaH was destroyed, the mixture was washed three times with water, dried over $MgSO_4$ and evaporated to an oil (37.0 g, 90%) which could not be crystallized. This oil, however, gave an nmr spectrum identical to the material prepared earlier and appeared quite free from impurities and, hence, was used without further purification.

3,3-Dichloro-*trans*-1,2-di-(3-iodopropyl)Cyclopropane (13e)

This compound was prepared by dissolving 30.2 g (0.19 mole) of NaI in 200 ml of acetone and adding this solution to 25.5 g (0.048 mole) of ditosylate 13d dissolved in 100 ml of acetone. The flask was then swirled to give solution, flushed with nitrogen, stoppered and placed in the dark at room temperature for 42 hours. The solvent was then evaporated and to the mushy crystalline residue was added first ether and then water. The mixture was shaken and then separated. The aqueous layer was extracted twice more with ether, the ether solutions combined, dried over $MgSO_4$ and evaporated to an oil (21.0 g, 99%) which could not be crystallized. $\delta^{tms}_{CDCl_4}$ 3.25 (triplet, 4H); 1.45-2.3 (multiplet, 8H); 1.20 (multiplet, 2H).

3,3-Dichloro-*trans*-1,2-di-(3-triphenylphosphonio-propyl)-cyclopropyl Diiodide (13f; X=Cl)

The reaction was carried out by refluxing a mixture of 37.0 g (0.141 mole) of triphenylphosphine, 21.0 g (0.046 mole) of the diiodide (13e) and 100 ml of acetonitrile for 31.5 hours. The mixture was then evaporated until the oily residue began to foam. The foaming oil was then dissolved in acetone and refluxed. After approximately one hour a crystalline precipitate appeared which was filtered off. Another crop obtained in this manner from the filtrate afforded a total of 40.3 g (91%) of crystalline phosphonium salt mp 215-217 (dec.). $\delta^{tms}_{CDCl_3}$ 7.80 (multiplet, 30H); 3.70 (very broad singlet, 4H); 1.50-2.31 (broad multiplet, 10H).

Analysis: Calcd. for $C_{45}H_{44}P_2Cl_2I_2$: C, 55.64; H, 4.57.

Found: C, 55.86; H, 4.69.

This material was then converted to the corresponding dichloride salt (13f; X=Cl) by eluting it with ethanol through a column containing Dowex 21K chloride anion exchange resin. Recovery of material was quantitative and testing the product with dilute aqueous $AgNO_3$ indicated that the exchange was >97% complete. The evaporation of the ethanol solvent left an oil which foamed lightly. Pumping on the oil at high vacuum (0.02 mm) converted it into a very hygroscopic solid amorphous mass. Although it was used at that point without further purification, extreme care had to be used in handling it due to its extremely hygroscopic nature.

9,9-Dichloro-*trans*-bicyclo [6.1.0] non-*cis*-4-ene (9a)

A 0.27 N solution of sodium methylsulfinyl methide[22] was prepared and filtered through sintered glass under vacuum in order to obtain a clear solution.

The following apparatus for oxidative cyclization was constructed: a 250 ml 3-neck RB flask was fitted with two Hershberg dropping funnels and an oxygen bubbler. A stopcock was attached to the pressure equalization tube on each of the dropping funnels. The oxygen bubbler consisted of a straight tube with a sintered glass (medium fritted) disc attached to the end through which oxygen could be admitted. Attached to the upper part of the joint holding the tube was a vent leading to a mercury bubbler. Addition to the dropping funnels were made *via* syringe and serum stopper; and when the funnels were filled, the stopcocks on the pressure equalization tubes were closed and the reservoirs connected to a balloon filled with argon. Magnetic stirring was used and the reaction flask was heated by means of an oil bath. Once the apparatus was assembled it was twice evacuated to 0.4 mm, flamed and filled with argon.

To the reaction flask was then added *via* syringe, 20 ml of dimethyl sulfoxide (dried over calcium hydride for 5 days) and the flask heated to 50°. One dropping funnel was then filled with a solution of 2.42 g (3.1 mmoles) of the diphosphonium chloride (13f; X=Cl) in 30 ml of dried dimethyl sulfoxide. The other funnel was then charged with 30 ml of the 0.27 N solution of sodium methylsulfinyl methide prepared above. Stirring was then started and oxygen (passed first through conc. H_2SO_4 and then KOH pellets) was allowed to bubble at a moderate rate through the stirring liquid. Dropwise addition from both funnels was then started and regulated so that at all times an equal quantity of liquid was being added from each funnel with the rate of addition remaining constant. Approximately 30 minutes were required for complete addition, after which oxygen was allowed to continue bubbling through the stirring dark red mixture for an additional 15 minutes. Workup consisted of diluting the reaction mixture 3-fold with water and extracting the resulting mixture 3 times with pentane. The pentane extracts were combined, dried over $MgSO_4$, and concentrated to *ca.* 15 ml by distillation using a wire gauze column. The concentrated solution was then filtered and evaporated at 0° to an oily residue. The residue was then distilled (60°/0.2 mm) to give 130 mg (22%) of a very pungent oil (9a). Analysis by gas chromatography (Fluorosilicone, QF-1) showed this oil to consist of a single product. $\delta^{tms}_{CCl_4}$ 5.65 (multiplet, 2H); 2.19 (multiplet, 6H); and 1.21 (broad singlet, 4H). Mass spectrum, 191 m/e (M^+).

Analysis: Calcd. for $C_9H_{12}Cl_2$: C, 56.56; H, 6.33.

Found: C, 56.58; H, 6.46.

di-*t*-butyl 2,2,7,7-Tetradeutero-*trans*-4-octene-1,8-dioate

To a solution of 21.2 g (0.025 mole) of di-*t*-butyl *trans*-4-octene-1,8-dioate in 75 ml of deuterated *t*-butanol was added *ca.* 0.5 g potassium-*t*-butoxide. The magnetically stirred mixture was then heated to 60° in an oil bath for 21 hours. After evaporation of the solvent to *ca.* 25% of its original volume, ether was added, followed by filtration using $MgSO_4$ as a filter-aid. The filtrate was then evaporated to dryness whereupon crystallization commenced. The crystals were then dried under vacuum (0.05 mm) for 4 hours. Recycling the material three more times using 50 ml, 40 ml and 35 ml deuterated-*t*-butanol, respectively, as solvent afforded a quantitative yield of the diester in 96% isotopic purity (nmr). $\delta^{tms}_{CCl_4}$ 5.41 (multiplet, 2H); 2.20 (triplet, J=1Hz, 4H); 1.39 (singlet, 18H).

9,9-Dichloro-3,3,6,6-tetradeutero-*trans*-bicyclo [6.1.0] non-*cis*-4-ene (9b)

Starting with 20.0 g (0.07 mole) of di-*t*-butyl 2,2,7,7-tetradeutero-*trans*-4-octene-1,8-dioate and carrying out the previously described synthetic sequence for the synthesis of 9a, 400 mg (3% overall yield) of the tetradeuterated bicyclic product 9b was obtained. $\delta^{tms}_{CCl_4}$ 5.64 (singlet, 2H); 2.19 (multiplet, 2H); and 1.19 (multiplet, sharp, 4H). $J_{C^{13}\text{-H to }C^{12}\text{-H}}$ of the olefinic protons was 11.5 Hz.

Ozonolysis of 9,9-Dichloro-*trans*-bicyclo [6.1.0] non-*cis*-4-ene

Approximately 50 mg (0.262 mmole) of 9a were dissolved in 5 ml of absolute methanol, and cooled to -78° in a dry ice-acetone bath. A mixture of 1-2% ozone in oxygen (Welsbach Ozone Generator Model t-408) was bubbled through the solution until the blue color persisted (*ca.* 15 min.). The excess ozone was then flushed out with oxygen and the methanol solution evaporated at room temperature to a clear colorless syrup. To the syrup were added 3 ml of 90% formic acid and 1.5 ml of 30% H_2O_2. Gentle heat from a flame was then applied until the exothermic reaction started; this lasted approximately 15 min. The solution was then refluxed for an additional 25 min. and then cooled to -20°. From the solution, 66 mg (97%) of crystals (mp 103-105°) were obtained. This material had identical infrared and nmr spectra to 13g. In addition, a mixture melting point of the two samples gave no depression.

Attempted Addition of *p*-Methoxyphenyl Azide to 9a

Approximately 250 mg (1.3 mmole) of 9a and 199 mg (1.4 mmole) of *p*-methoxyphenyl azide were dissolved in 1 ml of ether and placed in the dark under a N_2 atmosphere for 3.0 days at room temperature. At the end of this time tlc and nmr spectroscopy showed no reaction had taken place. The ether was then evaporated to an oil and the oil heated to 60° in an oil bath for 5.5 hours. Again, tlc and nmr spectroscopy showed that no reaction had taken place.

9,9,10,10-Tetrachloro-*cis*,*trans*-tricyclo [6.1.0.1^{4,5}] Decane (15) A: From 9a

To 10 ml of pentane (reagent grade) were added 100 mg (0.52 mmole) of 9a and 0.27 mg (5.0 mmole) of sodium methoxide. The mixture was then cooled to 0° in an ice bath, magnetically stirred, and placed in an argon atmosphere. From a dropping funnel was then added, over a period of one hour, 0.5 ml (0.69 g, 3.62 mmoles) of ethyl trichloroacetate. After the addition, the orange mixture was allowed to stir 6 hours additional at 0° and then overnight at room temperature. Water was then added and the mixture shaken and separated. The aqueous layer was then extracted twice with pentane. All pentane extracts were then combined, dried over $MgSO_4$, and evaporated to an oil. Distillation (80-90%/0.2 mm) of this oil gave 131 mg (90%) of a clear oil that crystallized (mp 73-78°). One recrystallization from ethanol gave needles (mp 94-95°). $\delta^{tms}_{CCl_4}$ 1.90-2.60 (multiplet, 4H); and 0.65-1.80 (multiplet, 8H).

Analysis: Calcd. for $C_{10}H_{12}C_4$: C, 43.93; H, 4.41.

Found: C, 43.98; H, 4.47.

B: From Authentic *cis*, *trans*-1,5-Cyclooctadiene (16)

The reaction of 100 mg (0.92 mmoles) of *cis*,*trans*-1,5-cyclooctadiene (16) with 0.54 g (10.0 mmoles) of sodium methoxide and 1.38 g (1.0 ml, 7.24 mmoles) of ethyl trichloroacetate was carried out in the manner described above. Distillation of the crude oily product (80-90°/0.2 mm) gave a clear oil which crystallized in the bulb (mp 84-90°). The infrared and nmr spectra of this material were identical with those of the materials prepared from 9a. In addition, a mixture melting point gave no depression. Yield: 144 mg (59%).

9,9-Dichloro-*trans*-bicyclo [6.1.0] non-*cis*-4-ene Oxide

A solution of 121 mg (0.6 mmoles) of 9a in 10 ml of methylene chloride was mixed with 0.24 g of 85% *m*-chloroperbenzoic acid (corresponds to 1.2 mmoles of the peracid). When solution was complete, the flask was stoppered and cooled to 2-3° for 20 hours. The insoluble material formed was then filtered off and the filtrate washed twice with *sat'd.* Na_2CO_3, once with water, dried over $MgSO_4$ and evaporated at room temperature to a crystalline residue. Distillation (60-80°/0.15 mm) of the residue afforded 118 mg (90%) of a white solid (mp 68-70°). $\delta^{tms}_{CCl_4}$ 1.95-2.90 (multiplet, 6H); and 0.60-1.70 (multiplet, 6H). Mass spectrum: 207 m/e (M^+).

Analysis: Calcd. for $C_9H_{12}Cl_2O$: C, 52.19; H, 5.84.

Found: C, 52.24; H, 5.81.

cis,*trans*-1,5-Cyclooctadiene (16)

This compound was first prepared from the Di-μ-chlorobis (*cis*, *cis*,1,5-cyclooctadiene) dicopper (I) complex using published procedures.[4]

A more convenient preparation consisted of adding 5.0 g (0.046 mole) commercial (*cis*,*cis*-1,5-cyclooctadiene followed by 200 ml of reagent grade pentane, 5.0 g of commercial cuprous chloride (0.05 mole) and 300 ml more pentane to a 1.5 l quartz irradiation vessel fitted with a condenser leading to a mercury bubbler. The entire apparatus was flushed with dry nitrogen and irradiated at 2537 Å, using vigorous magnetic stirring, for 24 hours. The solid material was then filtered off and stored in the dark under N_2 at room temperature. Approximately 45 g of this material (the result of 5 runs) was worked up by shaking it with pentane and conc. ammonia until all the solid had dissolved. To the mixture was then added ice and sufficient sodium cyanide to decolorize the solution. The solution was then shaken again and separated. The aqueous layer was then extracted twice more with pentane, and the pentane solutions were combined and dried over $MgSO_4$. Analysis of this solution by gas chromatography (SE-30) showed approximately equal amounts of *cis*,*cis*-1,5-cyclooctadiene and *cis*,*trans*-1,5-cyclooctadiene along with a small amount of (*ca.* 1%) *trans*,*trans*-1,5-cyclooctadiene. The solution was then concentrated by distillation, using a wire gauze column, to *ca.* 200 ml. To this solution was added an equal amount of water containing sufficient $AgNO_3$ (usually 10-13 g was required) to eliminate the product peak from a gas chromatogram of the pentane solution. The aqueous layer was then washed once with pentane and to it was added excess conc. ammonia in order to liberate the olefin. The mixture was extracted 3 times with pentane, the pentane solutions combined, dried over $MgSO_4$ and concentrated to about 100 ml by distillation of the pentane through a wire gauze column. Analysis of this solution by gas chromatography showed 99% pure *cis*, *trans*-1,5-cyclooctadiene (16) and integration data gave a yield of 8-10 g (30-40%). The product was then stored in solution at -20° until used.

9,9-Dichloro-*trans*-bicyclo [6.1.0] non-*cis*-4-ene (9a)

To a solution of 10 g (0.093 mole) of *cis*,*trans*-1,5-cyclooctadiene in 100 ml of pentane was added 9.0 g (0.165 mole) of sodium methoxide. A dropping funnel on the flask was then charged with 14.2 g (0.074 mole) of ethyl trichloroacetate. The mixture was then cooled in an ice bath and flushed with argon for 15 minutes after which the ethyl trichloroacetate was added, with magnetic stirring, to the cold mixture for 2 hours. After the addition was complete, the mixture was allowed to stir an additional 2 hours in the ice bath. Workup consisted of adding water to the mixture and 2 extractions with pentane. The pentane solution was then dried over $MgSO_4$ and evaporated to an oil. Distillation of this oil at 60°/0.25 mm afforded 6.1 g (30%) of 9,9-dichloro-*trans*-bicyclo [6.1.0] non-e-ene 9a. δ^{tms}_{CCl4} 5.65 (multiplet, 2H); 2.19 (multiplet, 6H); and 1.21 (broad singlet, 4H).

formation concerning the nature of **1** and **2** was obtained by preparing tetradeuterio analogs **22** and **23** from **9b**. The small amounts of material available precluded separation of **22** and **23**. It was possible, however, to resolve the olefinic peaks in the mixture by high-resolution nmr spectroscopy and to determine $J_{\mathrm{HC=CH}}$ from the carbon-13 satellites.

These coupling constants are summarized in Table I. It is clear from Table I that, while the values for **9b** and **23** fall within accepted limits for the cis and trans coupling constants, respectively, the coupling constant of **22** is highly unusual for a trans double bond.[8] Since it is known that coupling constants are maximal when C–H single bonds are

9,9-Dichloro-*trans,trans*-bicyclo[6.1.0]non-4-ene (**1a** and **2a**)

The mixture of isomers was prepared from **9a** by adding 2.0 g (0.0105 mole) of **9a** followed by 2.0 g (0.05 mole) of freshly prepared cuprous chloride[23] and 15 ml of pentane to a 60 ml quartz vessel, fitted with a condenser and mercury bubbler. The entire apparatus was flushed with nitrogen and irradiated at 2537 Å for 27.0 hours. Vigorous magnetic stirring prevented material from adhering to the sides of the vessel. Workup consisted of adding the entire mixture to conc. ammonia, decolorizing with sodium cyanide and extracting the mixture 3 times with pentane. The pentane solutions were then dried over $MgSO_4$ and concentrated to *ca.* 50 ml and extracted with 30 ml of 20% aqueous $AgNO_3$. A gas chromatogram (Fluorosilicone, QF-1) of the pentane solution showed only starting material remained and no evidence of side reactions was seen. The aqueous layer was then washed once with pentane and then treated with excess conc. ammonia and extracted 3 times with pentane. Analysis of these extracts by gas chromatography showed two compounds in a ratio of 5:1.

The pentane extracts were then evaporated at 0° to an oil. Distillation (50°/1.2 mm) of this oil afforded 0.789 g (43%) of the isomer mixture of **1a** and **2a**. Degassing the reaction mixture prior to irradiation failed to change the yield.

Analysis: Calcd. for $C_9H_{12}Cl_2$: C, 56.56; H, 6.33.
Found: C, 56.43; H, 6.25.

This mixture was then separated by preparative gas chromatography on a 20' by 3/8" 10% Fluorosilicone (QF-1) column to give the perpendicular isomer (**2a**) as the major product, and the parallel isomer (**1a**) as the minor product.

2a: $\delta^{\mathrm{tms}}_{\mathrm{CCl_4}}$ 5.35 (multiplet, 2H); 2.40 (multiplet, 6H); 1.25 (broad multiplet, 2H); and 0.5 (multiplet, 2H).
ir: 846; 895 (weak); 1,005; 1,030; 1,080 and 1,170 cm^{-1}.
uv: $\lambda^{\mathrm{hexane}}_{\mathrm{max}}$ 1.92 nm.

1a: $\delta^{\mathrm{tms}}_{\mathrm{CCl_4}}$ 5.50 (multiplet, 2H); 2.48 (multiplet, 6H); 1.65 (multiplet, 2H); and 0.9 (multiplet, 2H).
ir: 820; 937; 1,048; 1,115 and 1,147 cm^{-1}.
uv: $\lambda^{\mathrm{hexane}}_{\mathrm{max}}$ 200 nm.

Ozonolysis of Isomer Mixture (**1a** and **2a**)

A solution of 100 mg (0.52 mmoles) of the 1:5 isomeric mixture of **1a** and **2a** in 5.0 ml of absolute methanol was cooled in a dry ice-acetone bath and oxygen containing 1-2% ozone (Welsbach Model t-408) was bubbled through the solution until the blue color persisted (*ca.* 1.0 min.). Oxygen was then bubbled through the solution to remove the excess ozone. The methanol solution was then evaporated at room temperature to a clear colorless syrup. The syrup was then refluxed in 3 ml 90% formic acid and 1.5 ml hydrogen peroxide for 40 minutes. Water was then added to the mixture and the mixture extracted 3 times with ether. The ether was then dried over $MgSO_4$ and evaporated to a pale yellow oil. The oil was then taken up in 10 ml of ether and dried into two 5 ml portions.

Portion A was esterified with diazomethane and a gas chromatogram (SE-30) of the crude product showed that only one substance was present. The retention times correlated well with **13b**. Evaporation of the solution to an oil gave 61 mg (85%) of the diester. Comparison of the nmr spectra of this material and **13b** confirmed the identity of this material as **13b**.

Portion B was evaporated to an oil that slowly crystallized (mp 94-102°) to give 62 mg (93%) of crystalline material. This material gave an identical infrared spectrum to authentic **13g**. Crystallization of this material from ether-petroleum ether gave crystals, mp 104-105°. A mixture melting point of this material with **13g** gave no depression. In addition, the infrared spectrum of this material was not changed by crystallization.

trans-Bicyclo[6.1.0]non-*cis*-4-ene[11] (**9c**)

An ethereal solution of diazomethane was added to a solution of 10 g (0.093 mole) *cis,trans*-1,5-cyclooctadiene in *ca.* 50 ml of ether until the yellow color persisted for 30 minutes. The solution was then boiled on the steam bath to remove the excess diazomethane after which it was evaporated to an oil that would not crystallize. The oil was picked up in 500 ml of pentane and irradiated for 12 hours using a 550 w Hanovia medium pressure Hg lamp and Pyrex filter. Distillation of the pentane using a vigreaux column followed by rotary evaporation at 0° gave a yellow oil. Distillation of the oil at 70°/29 mm gave 6.0 g (53%) of *trans*-bicyclo[6.1.0]non-*cis*-4-ene (**9c**).

trans,trans-Bicyclo[6.1.0]non-4-ene (**1b** and **2b**)

The isomer mixture of **1b** and **2b** was prepared in a similar fashion to that described earlier for **1a** and **2a**. To a 60 ml quartz vessel was added 2.0 g (0.0105 mole) of freshly prepared cuprous chloride[23] followed by 1.0 g (8.2 mmoles) of **9c** and 10 ml of pentane. After flushing the entire apparatus with nitrogen, the stirred mixture was irradiated at 2537 Å for 28 hours. Workup was accomplished as before using conc. ammonia and sodium cyanide. Analysis of the pentane extracts by gas chromatography (Nitrile Silicone, XF-1150) showed 85% starting material and 20% isomerized products as the only volatile materials present. Separation of the isomerized products was performed as before using 20% aqueous $AgNO_3$. In this case, the product ratio was found by gc to be 1:7. The pentane solution was first distilled using a wire gauze column and then evaporated to an oil. Distillation of the oil at 50°/29 mm afforded the **1b** and **2b** mixture in 20% yield. Again, degassing the reaction mixture prior to irradiation failed to change the yield.

Analysis: Calcd. for C_9H_{14}: C, 88.45; H, 11.55.
Found: C, 88.18; H, 11.66.

Separation of the two isomers by preparative gas chromatography was achieved using a 12' x 1/2" 20% Nitrile Silicone (XF-1150) column to give **2b** as the major product and 1b as the minor product.

2b: $\delta^{\mathrm{tms}}_{\mathrm{CCl_4}}$ 5.30 (multiplet, 2H); 2.34 (multiplet, 8H); 0.6-1.2 (broad multiplet, 2H); and 0.51 (triplet, 2H).
uv: λ_{max} 197 nm (vacuum).

1b: $\delta^{\mathrm{tms}}_{\mathrm{CCl_4}}$ 5.52 (unresolved multiplet, 2H); 2.38 (multiplet, 8H); 0.85-1.5 (multiplet, 2H); and 2.27 (quartet, 2H).
uv: λ_{max} 205 nm (vacuum).

9,9-Dichloro-*trans,trans* bicyclo[6.1.0]non-4-ene Oxide (**18**)

To a solution of 180 mg (0.95 mmoles) of **2a** and **1a** (5:1 isomer ratio) in 10 ml of methylene chloride was added 0.35 g (1.72 mmoles) of 85% *m*-chloroperbenzoic acid. When solution of materials was complete, the flask was stoppered and cooled to 3° for 24 hours. The insoluble material was filtered and the methylene chloride filtrate was washed twice with saturated aqueous Na_2CO_3, once with water and dried over $MgSO_4$. Evaporation at room temperature gave a quantitative yield of crystalline residue. Sublimation of the residue at 75°/0.2 mm gave a crystalline product, mp 98-104°. A gas chromatogram (Fluorosilicone, QF-1) of the crystalline product showed two products in a 5:1 ratio. After 4 recrystallizations from hexane, the major product (mp 114-116°) was obtained pure (gc) and a crystal submitted for X-ray analysis.

Analysis (mixture): Calcd. for $C_9H_{12}Cl_2O$: C, 52.19; H, 5.84.
Found: C, 52.31; H, 5.84.

10,10-Dichloro-*trans,trans* tricyclo[6.1.0.$1^{4,5}$]Decane (19) from **2a**

Granular zinc copper couple was prepared as before.[64] Five grams (1.5 ml, 0.02 mole) of methylene iodide was added, over a period of 15 minutes, to a mixture of 100 mg **2a** and 2.0 g (0.08 mole) of couple in 20 ml of anhydrous ether. Once the exothermic reaction was over, the mixture was refluxed for 17 hours. The mixture was then worked up by pouring it into ice and 1N HCl and shaking and separating the ether layer. The ether layer was washed again with 1N HCl, once with water, dried over $MgSO_4$ and evaporated at room temperature to an oil (**19**) that would not crystallize. A gas chromatogram (SE-30) of this material showed only 85% purity. The oil was finally purified by preparative gas chromatography on a 8' x 1/2" 30% silicone rubber (UC-W) column. $\delta^{\mathrm{tms}}_{\mathrm{CCl_4}}$ 2.33 (multiplet, 6H); 1.10 (multiplet, 6H); and 0.3 (multiplet, 21H). ir: 780; 805; 908; 1,005; 1,061; 1,220; and 1,445 cm^{-1}.

Analysis: Calcd. for $C_{10}H_{14}Cl_2$: C, 58.55; H, 6.88.
Found: C, 58.34; H, 7.01

From **2b**

To a solution of 40 mg (0.33 mmoles) of the major isomer of the mixture of **1b** and **2b** in 7 ml pentane was added 0.4 g (7.4 mmoles) of sodium methoxide. The magnetically stirred reaction mixture was placed under an argon atmosphere and cooled in an ice bath. Over a period of 45 minutes, 0.68 g (3.63 mmoles) of ethyl trichloroacetate was added. The mixture was allowed to stir in the ice bath for 4 hours and then overnight at room temperature. Water was then added followed by 2 extractions with pentane. The pentane solutions were then combined, dried over $MgSO_4$ and evaporated at room temperature to an oil. Distillation of the oil at 60°/0.2 mm gave a clear product that would not crystallize. Analysis by gas chromatography (SE-30), however, indicated pure material. Both the nmr and ir spectra of this oil were identical with those of **18** from **2a**.

Irradiation of **2a** With Cuprous Chloride

The 60 ml quartz tube was charged with 0.27 g (1.41 mmoles) of **2a**, 0.3 g (2.9 mmoles) of freshly prepared cuprous chloride[65] and 5.0 ml of pentane. After flushing the entire apparatus with nitrogen, the stirred mixture was irradiated at 2537 Å for 31 hours. Treatment of the entire reaction mixture with conc. ammonia and sodium cyanide was followed by pentane extraction. Analysis of these pentane extracts by gas chromatography (Fluorosilicone, QF-1) showed that 60% of the material had been re-isomerized back to **9a**. The remaining 40% was found to be a 5:1 mixture of **2a** and **1a**, respectively. Only trace quantities of any other volatile materials were detected. A quantitative yield of **9a**, **1a** and **2a** was recovered by distillation (60°/0.2 mm).

Irradiation of **1a** and **2a** without Cuprous Chloride

To a 3 mm quartz tube was added *ca.* 10 mg (0.053 mmoles) of **1a** and **2a** (5:1 ratio of isomers) and 0.5 ml of pentane. The tube was sealed and irradiated at 2537 Å for 22 hours. At the end of this time, a grey amorphous precipitate had formed. Analysis by gas chromatography (Fluorosilicone, QF-1) of the supernatant solution showed only **9a**. Both isomers of the starting material had been completely eliminated.

Irradiation of **9a** without Cuprous Chloride

A 3 mm quartz tube which contained *ca.* 10 mg (0.053 mmoles) of **9a** and 0.2 ml pentane was first filled with argon and then sealed and irradiated at 2537 Å for 15 hours. At the end of this time, the light yellow solution showed no evidence of polymer formation. Analysis by gas chromatography (Fluorosilicone, QF-1) showed only starting material was present.

Thermal Stability of **9a**

The determination was made by adding 40 mg (0.21 mmoles) of **9a**, 0.5 ml C_6D_6 and *ca.* 0.2 mg of hydroquinone to a thick-wall nmr tube. The tube was then filled with argon, sealed, and heated at 250° for 12 hours. Both nmr and gc (Fluorosilicone, QF-1) showed no change had occurred.

Reaction of **1a** and **2a** with Sodium Methylsulfinyl Methide

A solution of 183 mg (0.955 mmoles) of **2a** and **1a** (5:1 mixture of isomers) dissolved in 5.0 ml of pentane was prepared and, at room temperature with magnetic stirring, 3.1 ml (one equivalent) of freshly prepared and filtered 0.3 M sodium methyl sulfinyl methide[62] was added. The mixture turned immediately red-black and moderate heat evolution was noted. The mixture was allowed to stir for 90 minutes after which it was diluted 3-fold with water and extracted 3 times with pentane. The pentane extracts were combined, dried over $MgSO_4$ and evaporated to an ice bath to give 145 mg of residue. To the residue was added 5.0 ml of pentane. Comparison of gc integration data (Fluorosilicone, QF-1) between this solution and the original starting solution indicated only 52 mg (28%) of **1a** and **2a** remained. No isomerization of **1a** and **2a** to **9a** was detected and attempts to identify the other components of the complex residue failed.

N-Phenyl-10,10-Dichloro-*trans,trans*-azatricyclo[6.1.0.$1^{4,5}$]-decane

A solution of 1.5 g (7.9 mmoles) of 2a and 1a (5:1 mixture of isomers) in 10 ml of absolute ether was combined with 0.935 g (7.9 mmoles) of phenyl azide also dissolved in 10 ml of absolute ether. The mixture was then swirled and cooled to 3° for 5 hours. The solvent was evaporated to dryness and then further dried by vacuum (0.05 mm) for 12 hours in the dark. The yield of triazoline adduct was quantitative.

To a Pyrex vacuum sublimation apparatus whose cold-finger condenser was cooled by recirculated ice water was added 2.2 g (7.0 mmoles) of the triazoline adduct and 95 ml of anhydrous acetone (the apparatus was filled sufficiently to give considerable immersion of the cold-finger condenser in the solution). The magnetically stirred solution was then photolyzed using a 275w sun lamp for 12 hours. During the photolysis, the temperature of the solution remained below room temperature at all times. From the photolysis, 157 ml (96% of theory) of nitrogen was collected. The yellow solution was then evaporated to an oil which was picked up in pentane, filtered and cooled to 3°. From the filtrate, 1.6 g (80%) of crystals (mixture of isomers) were collected, mp 115.5-119°.

Analysis: Calcd. for $C_{15}H_{17}NCl_2$: C, 63.84; H, 6.07
Found: C, 63.65; H, 6.14

Aziridine **21**

To a solution of 350 mg (1.83 mmole) of pure **2a** in 5 ml of anhydrous ether was added 218 mg (1.83 mmole) of phenyl azide. The resulting solution was cooled in darkness to 3° for 48 hours. Evaporation of the solvent to dryness followed by vacuum drying (0.02 mm) in the dark for 6.0 hours gave the triazoline adduct in quantitative yield.

Photolysis, for 9 hours, of the triazoline in 5 ml anhydrous acetone was carried out as described above.

Evaporation of the acetone solution followed by crystallization of the oil from pentane gave 256 mg (50%) of **21**, mp 124-125°. $\lambda^{\mathrm{hexane}}_{\mathrm{max}}$ 278 nm (ε 1,820); ir: 700; 768; 797; 929; 1,209; 1,450; 1,499 and 1,610 cm^{-1}. $\delta^{\mathrm{tms}}_{\mathrm{CDCl_3}}$ 6.70-7.40 (multiplet, 5H); 2.40 (quartet, 4H); 1.87 (doublet, 2H) and 0.85-1.60 (multiplet, 6H). Mass Spectrum: 282 m/e (M^+).

Aziridine **20**

Preparation of this material from 100 mg (0.525 mmole) of pure 1a and 62 mg (0.525 mmole) of phenyl azide was carried out in the same manner as described earlier for **21**. Subsequent photolysis yielded material which could be crystallized from pentane, 37 mg (27%), mp 72.5-73.5°. $\lambda^{\mathrm{hexane}}_{\mathrm{max}}$ 278 nm (ε 1,800); ir: 700; 770; 805 (broad); 929; 945; 1,209; 1,320; 1,499 and 1,610 cm^{-1}. $\delta^{\mathrm{tms}}_{\mathrm{CDCl_3}}$ 6.70-7.40 (multiplet, 5H); 2.41 (doublet, 4H); 2.09 (doublet, 2H) and 0.85-1.65 (multiplet, 6H). Mass Spectrum: 282 m/e (M^+). The cracking pattern was identical to that obtained for **20**. This material is quite difficult to crystallize.

Thermal Chemistry of **2b**

The procedure was carried out by dissolving *ca.* 100 mg (0.82 mmoles) of **2b** in 1 ml of hexane (which had been shaken with conc. H_2SO_4) and sealing in a 6 mm Pyrex glass tube. The tube and contents were heated at 138° over a stream of refluxing xylene for 84 hours. At the end of this time, gc analysis (silicone nitrile, XF-1150) indicated that no change had occurred in the mixture.

Thermal Chemistry of **1b**

The procedure was carried out using *ca.* 100 mg (0.82 mmoles) of **1b** and 1 ml of hexane in a similar manner to the pyrolysis of **25b**. At the end of 24 hours, gc analysis (silicone nitrile, XF-1150) showed 12% conversion to **9b**. After another 58 hours of heating, 31% of the material had been isomerized to **9b**. No other reaction products were found.

Pyrolysis of **1b** and **2b** in the Presence of Base

To *ca.* 100 mg of **1b** and **2b** (the 7:1 mixture of isomers) was added 1 ml of hexane and 0.5 ml of quinoline. The mixture was then sealed in a 6 mm Pyrex tube and heated at 138° for 35 hours using a stream of refluxing xylene. At the end of this time, a considerable amount of **9b** had been formed.

Pyrolysis of Aziridine **21**

The reaction was carried out by dissolving 50 mg (0.177 mmoles) of **21** in 1 ml of hexane and sealing the mixture in a 6 mm Pyrex tube. The tube and contents were then heated to 138° over a stream of refluxing xylene for 67.0 hours. When the tube had cooled, a crystalline substance appeared (mp 123-124°) and appeared from tlc (50:50 C_6H_6 petroleum ether) to be unreacted starting material.

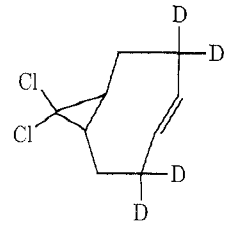
Pyrolysis of **20**

This reaction was carried out using *ca.* 15 mg **20** (0.053 mmoles) and 1 ml of hexane sealed in a 6 mm Pyrex tube. The tube was heated to 138° as before for 60 hours. Upon cooling of the tube, no crystals formed, but tlc (50:50 C_6H_6-petroleum ether) indicated that no change had occurred.

Table I
Olefinic Vicinal Coupling Constants of the Tetradeuterated Trans-Fused Bicyclo[6.1.0]non-4-ene Isomers

Compound	$J_{H-C^{13}=C^{12}-H}$, Hz
9b (cis)	11.5
22 (trans-parallel)	11.0
23 (trans-perpendicular)	16.5

coplanar, we believe that the reduced coupling constant for **22** indicates the presence of noncoplanar olefinic C–H bonds.



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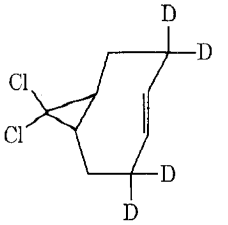
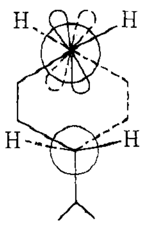


23

Two possible conformations for nonplanar strained double bonds have been proposed, discussed, and experimentally observed in the literature. The first of these, exemplified by structure **24**, retains the sp^2 hybridization and results in a skewing of the substituents.[16a–c] The second of these, **25**, involves the rehybridization of the two olefinic



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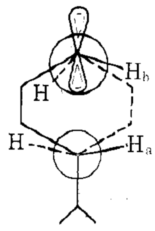


25

carbons and retains the eclipsed arrangement of the substituents.[16c–e] Formation of either structure **24** or **25** would effectively move the π bond further away from the cyclopropane ring and thereby diminish interaction between the π bond and the internal cyclopropane ring bond. Since such repulsions are almost certainly greater in the case of the parallel form, it is not surprising that the parallel isomers show a much greater tendency to relieve such interactions. Although the π–σ interactions may be smaller in structure **25**, it appears that transannular H_aH_b interactions are much less severe in **24**. Unfortunately, the available data do not allow a distinction between **24** and **25**. It is also impossible to relate quantitatively the magnitude of the deviation to the observed coupling constants.

Structures **1** and **2** are much more stable than their diene analogs **6** or **7**. They were indefinitely stable when kept at −20° in a dilute hexane solution and reasonably stable in solution at room temperature under nitrogen. It was hoped that the forced close proximity of the π bond and the cyclopropane might force forbidden 2 + 2 cycloadditions. Instead, at elevated temperatures, the parallel isomer **1b** was slowly converted to the cis,trans isomer **9c**. For example, when **1b** was heated at 138° for 84 hr, glc analysis indicated 31% conversion to **9c**. The extent of isomerization was not effected by the presence of quinoline which indicates that the isomerization is not acid catalyzed. By contrast, **2b** and **9c** were unchanged when heated at this temperature for the same period of time.[17] The facility of this unprecedented thermal isomerization of an isolated double bond lends chemical support to the postulated weakened, distorted π bond depicted in **24** (or possibly **25**).

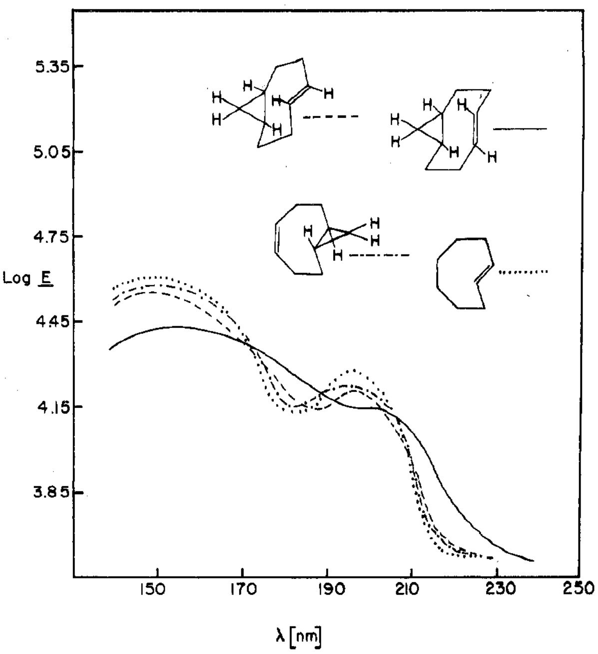
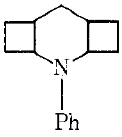


Figure 1.

The photochemistry of **1** and **2** was also briefly investigated for signs of internal cycloaddition. The irradiation at 2537 Å of a mixture of **1a** and **2a** in hexane for 22 hr resulted in conversion to the cis,trans isomer **9a** along with the formation of considerable gray polymer. No starting material or other volatile products were formed. Similar treatment of **9a** resulted in neither change nor polymer. A final attempt at cycloaddition in this system with aziridines **21** and **20** was made. It is known that aziridines undergo thermal conrotatory ring opening to azomethine ylides. Although such intermediates might have added across the cyclopropane ring bond to give products such as **26** and **27**, both **20** and **21** were recovered unchanged when heated at 138° for 60 hr.



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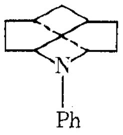

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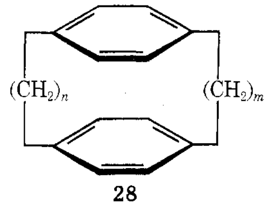
In order to further assess the nature of the transannular interaction, vacuum ultraviolet spectra were obtained for **1b**, **2b**, and **9c**. These spectra are reproduced in Figure 1 along with, for purposes of comparison, *trans*-cyclooctene. From these spectra it can be seen that the parallel form **1b** has the longest wavelength maximum and that both the σ–σ* and π–π* absorption bands are considerably broadened for the parallel form. The shift to longer wavelengths appears to be indicative of transannular resonance stabilization in the excited state. A similar observation has been made by Cram in the paracyclophane series (**28**) where *m* and *n* are small (*e.g.*, when *m* = *n* = 2).[19] It is interesting



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to note that shifts to longer wavelengths in the paracyclophane series were also associated with broadened bands and decreased absorption intensities.

The properties of 1 are thus vastly different from the perpendicular isomer 2 or other analogous *trans*-alkenes. The difference appears attributable to the transannular repulsions between the π bond and the cyclopropane ring. These repulsions distort the π bond and thus greatly alter its chemical reactivity. Further studies on these and related distorted alkenes should clarify the precise nature of the distortion process and the chemical consequences of such distortions. Finally, it is apparent that the unique features of the trans,trans arrangement present in these compounds offer many opportunities for chemical study of previously unavailable molecular arrangements.[20]

Registry No.—**1a**, 36217-82-0; **1b**, 36217-84-2; **2a**, 36217-81-9; **2b**, 36217-83-1; **6**, 1552-12-1; **9a**, 36217-85-3; **9a** oxide, 53447-31-7; **9b**, 53447-32-8; **9c**, 36217-86-4; **13b**, 53384-96-6; **13c**, 53432-89-6; **13d**, 53384-97-7; **13e**, 53384-98-8; **13f** (X = I), 53384-99-9; **13f** (X = Cl), 53385-02-7; **13g**, 36217-87-5; **15**, 53447-33-9; **16**, 5259-71-2; 18, 36217-88-6; **19**, 53447-34-0; **20**, 53385-00-5; **21**, 53447-36-2; **22**, 53447-35-1; **23**, 53447-37-3; phenyl azide, 622-37-7; sodium methylsulfinyl methide, 15590-23-5; cuprous chloride, 7758-89-6; *p*-methoxyphenyl azide, 2101-87-3; di-*tert*-butyl *trans*-4-octene-1,8-dioate, 53432-90-9; di-*tert*-butyl 2,2,7,7-tetradeuterio-*trans*-4-octene-1,8-dioate, 53385-01-6; triphenylphosphine, 603-35-0; sodium iodide, 7681-82-5; *p*-toluenesulfonyl chloride, 98-59-9; dimethyl *trans*-4-octene-1,8-dioate, 32456-97-6; sodium trichloroacetate, 650-51-1.

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Synthesis of Some *cis*- and *trans*-2-Dimethylaminomethyl Cyclic Amines and Related Diamines[1]

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The preparation of *N,N*,2,2-tetramethyl-1,3-propanediamine, *cis*- and *trans*-2-(dimethylaminomethyl)cyclohexylamine, and 3-*exo*-dimethylaminomethyl-2-*endo*-norbornanamine has been accomplished by the Mannich reaction on the appropriate carbonyl compound, followed by oximation and reduction. The reactions of methacrolein and 3-methylene-2-norbornanone with methylhydrazine gave pyrazolines whose methiodides were reduced to *N,N*,2-trimethyl-1,3-propanediamine and 3-*endo*-dimethylaminomethyl-2-*endo*-norbornanamine, respectively.

The dedeuteration of acetone-d_6 has been shown to be catalyzed bifunctionally by the monoprotonated form of *N,N*-dimethyl-1,3-propanediamine.[2,3] Examination of models of the transition state of the rate-controlling step in the reaction showed that in the two most stable conformers the carbon-1–nitrogen bond from the diamine was approximately eclipsed with a carbon-2–hydrogen or carbon-2–carbon-3 bond. The greatly increased bifunctional catalytic activity of both the cis and trans isomers of 2-(dimethylaminomethyl)cyclopentylamine experimentally demonstrated the importance of conformational effects.[2,3] To study such effects in more detail we have synthesized several additional conformationally constrained derivatives of *N,N*-dimethyl-1,3-propanediamine and also two 1,4-diamines.