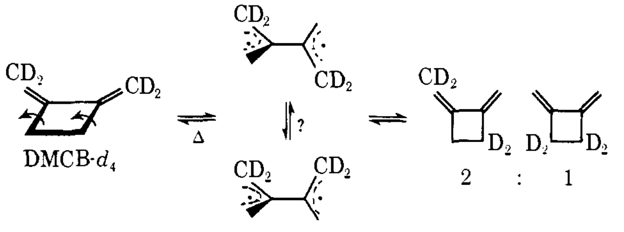
Stereochemical Evidence for Interconversion of Planar and Orthogonal 2,2′-Bisallyl Biradicals in the Pyrolysis of *trans*-3,4-Dimethyl-1,2-dimethylenecyclobutane. Antiaromaticity in Bisallyl Singlet Biradicals

Joseph J. Gajewski

Contribution No. 2622 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401.
Received August 24, 1974

Abstract: Pyrolysis of optically active *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane gave racemic *anti*-1-ethylidene-2-methylene-3-methylcyclobutane as well as partially racemized starting material. The rate constant ratio for structural isomerization to racemization of starting material is 2.2. A number of mechanistic possibilities are discussed in connection with other results leading to the conclusion that an orthogonal 2,2′-bisallyl species is formed initially by conrotatory motions and can undergo central bond rotation faster than ring closure. The relatively high activation energy for the degenerate rearrangement of 1,2-dimethylenecyclobutanes suggests destabilization or antiaromaticity in the bisallyl biradical, a suggestion justified by consideration of electron repulsion in the various geometries of the bisallyl species.

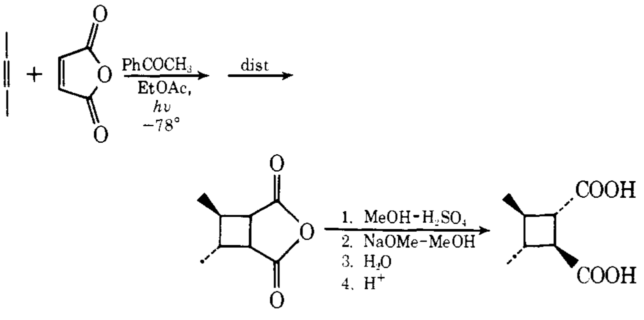
The 2,2′-bisallyl biradical (BA) appears to be the intermediate or transition state in the thermal self-interconversion of 1,2-dimethylenecyclobutanes (DMCB's)[1] and may be involved in the thermal dimerization of allenes.[2] Previous studies have established that ring opening of DMCB's is conrotatory and gives either a fixed orthogonal, perhaps spiroconjugated,[3] BA species or a central bond rotating biradical in which planar and orthogonal forms are rapidly interconverted. In an effort to determine the rate of central bond rotation vs. that for reclosure, optically active *trans*-3,4-dimethyl-DMCB (T) was prepared and pyrolyzed. This study was undertaken with the hope of testing the results of Hoffmann's EHT and CNDO calculations[4] which indicated little conformational preference for the biradical, and secondly to provide evidence on the question of whether the biradical was an intermediate or a transition state in the degenerate rearrangement of DMCB's.



BA

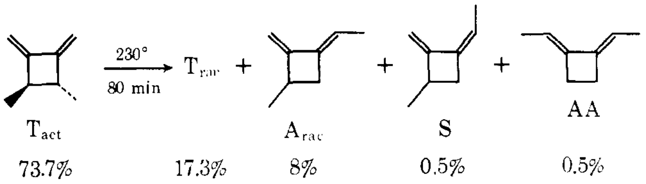
Results

Preparation of Optically Active T. Low temperature acetophenone sensitized photolysis of maleic anhydride and 2-butene in ethyl acetate[5] followed by solvent removal and spinning-band distillation gave *trans*-3,4-dimethyl-*cis*-1,2-cyclobutanedicarboxylic acid anhydride (TA), free of its cis,anti isomer. Methanolysis catalyzed by sulfuric acid and epimerization by sodium methoxide in methanol followed by addition of water and acid gave *trans,trans,trans*-3,4-dimethyl-1,2-cyclobutanedicarboxylic acid. Recrystallization of the brucine salts of the diacid from ethanol followed by acidification, esterification, reduction, tosylation, iodide displacement, elimination, and VPC purification gave T_{act}, $[\alpha]_D$ −87.2° (c 4.11 CHCl$_3$).



TA

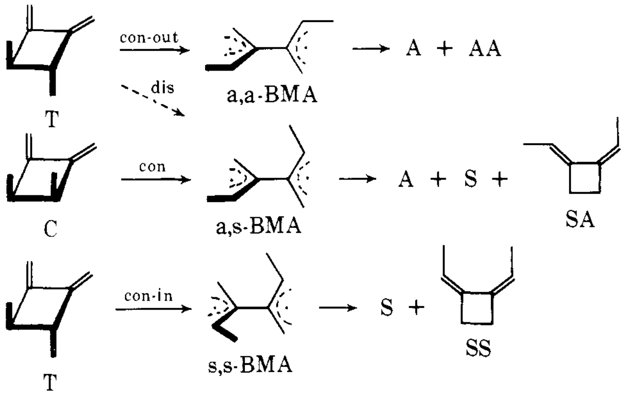
Pyrolysis of Optically Active T. Vapor phase pyrolysis of 30 μl samples of T_{act} in a well-conditioned 2-l. bulb at 230.7° for 80 min gave 9% conversion to a 18:1:1 mixture of *anti*-1-ethylidene-2-methylene-3-methylcyclobutane (A), *syn*-1-ethylidene-2-methylene-3-methylcyclobutane (S), and *anti,anti*-1,2-diethylidenecyclobutane (AA), respectively.[6] Pyrolysis of 360 μl of T_{act} in 30-μl portions followed by VPC isolation of T and A gave sufficient material for optical rotations. Recovered T had $[\alpha]_D$ −70.75° (c 1.26 chf), and A had $[\alpha]_D$ +0.06 ± 0.1° (c 1.0 CHCl$_3$). T was, therefore, 19% racemized under conditions of 9% conversion to A, and A appears to be racemic.



Discussion

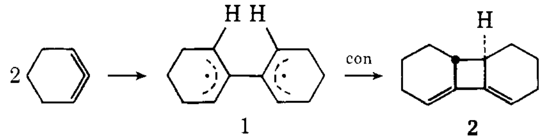
Three Gross Pathways or a Single BA Intermediate. Before examining the optical result, the various reaction pathways for the degenerate rearrangement of DMCB's should be considered. Because three types of products are formed in the thermolysis of DMCB-d_4,[1] a 3,3 sigmatropic shift product, a 1,3 sigmatropic shift product, and presumably starting material, it is possible to invoke three different pathways for the reaction. The observed 1:2 ratio of the 3,3 and 1,3 sigmatropic shift products is a necessary condition for involvement of a single, effectively orthogonal D_{2d} or rapidly central bond rotating BA species (ignoring isotope effects on the statistics). Multiple pathways with fortuitously the appropriate energetics are sufficient to explain the observations, but this must be viewed as unlikely.

Stereochemistry of the Ring Opening. Examination of the pyrolysis products from *trans*- and *cis*-3,4-dimethyl-DMCB, T and C respectively reveals a preference for conrotatory motions about the C_1–C_4 and C_2–C_3 bonds. With the trans compound, there are two conrotatory motions: one (con-out) leads to the *anti,anti*-bismethallyl species (a,a-BMA); the other (con-in) leads to s,s-BMA. The former can give only *anti,anti*-1,2-diethylidenecyclobutane (AA) and *anti*-1-ethylidene-2-methylene-3-methylcyclobutane (A), while the latter can give only *syn,syn*-1,2-diethylidenecyclobutane (SS) and *syn*-1-ethylidene-2-methylene-3-methylcyclobutane (S), assuming allyl radical isomerization is slow compared with ring closure. The observation of less than 5% S in the pyrolysis of T verifies the assumption and sets a minimum value for ratio of involvement of the two conrotatory paths as 18:1. The small amount of the S product could also be due to disrotatory opening of T to give an s,a-BMA which could close to S as well as A and to *syn,anti*-1,2-diethylidenecyclobutane (SA), as was observed in the pyrolysis of C which must give the s,a-BMA species by conrotatory opening. The observation of small amounts of SA[6] indicates that the disrotatory pathway is traversed to some extent.



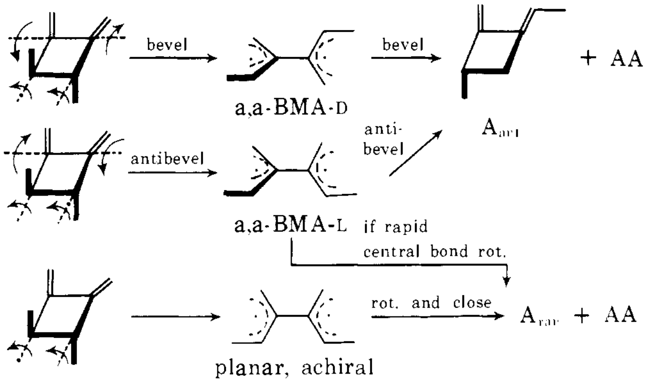
In other conrotatory electrocyclic openings, particularly of cyclobutenes, there is also a large preference for con-out over con-in pathways,[7] although the preference in the DMCB case should be less since a third rotation involving the C_1–C_2 bond could occur separating the originally bound atoms, C_3 and C_4, much more than in the cyclobutene case. Support for this derives from the fact that T and C rearrange at similar rates, while *trans*-3,4-dimethylcyclobutenes rearrange 20–40 times faster than the corresponding cis-disubstituted cyclobutenes.[7]

It should be noted that confusion persists in the literature over the preferred mode of closure of bisallyl biradicals.[8] Most of this confusion results from unwarranted conclusions over the source of products obtained from the thermal dimerization of substituted allenes. Without going into a lengthy analysis of all the reports, it is clear that no information about the mode of ring closure of bisallyl can be obtained from the stereochemistry of the products without knowing the stereochemistry of the presumed bisallyl intermediate. In only one allene dimerization can that stereochemistry be implied, namely in the dimerization of 1,2-cyclohexadiene which gives the trans-tricyclic compound **2**.[9] In the presumed intermediate biradical **1**, only the all-cisoid allyl radicals are possible, and **2** can only result from conrotatory closure of **1**. However, Moore points out that the cis isomer of **2** is more strained than **2**, and so disrotatory closure of **1** may be prevented on grounds of energetics. Thus, the only experiment that reveals the stereochemical course of closure of bisallyl species is that which examines its microscopic reverse, namely ring opening of 1,2-dimethylenecyclobutanes which clearly occurs via conrotatory motions. This is not to say, however, that disrotatory opening is energetically inaccessible. The facts presented herein indicate that disrotatory opening accounts for roughly 5% of the degenerate isomerization of DMCB's, but this is a maximum value.[6] The formation of S and AS from T may result from isomerization about the allyl radical moieties in the a,a-BMA biradical subsequent to its formation via conrotatory opening of T but prior to ring closure.



Direction of Central Bond Rotation. In the conrotatory ring opening of T, there are two possible directions of rotation or twist about the C_1–C_2 bond. These are termed "bevel" or "anti bevel" depending on the relative rotations at the intersections of the rotation axes at C_1 or at C_2 as either meshed bevel gears or as "clashed" bevel gears.

The lack of precision in the definition of the terms bevel and anti bevel is obvious upon close inspection, yet the terms are sufficiently descriptive for emphasizing the difference between the two twist modes.



There is a third possibility shown above involving no C_1–C_2 rotation, giving instead a planar form which later rotates rapidly into an orthogonal form but must give racemic products. This mechanism will explain the optical results but not the observed similarity in the rates of reaction of C and T. If the transition state for ring opening were planar, greater steric interactions would develop with the cis compound opening conrotatory, and it should react much slower just as in the *cis*- vs. *trans*-3,4-dimethylcyclobutene case. Thus direct formation of a planar BA is unlikely.

Shown above are the possible stereochemical results from reactions via bevel and antibevel pathways. The bevel pathway from one enantiomer of T will give a single enantiomer of the chiral orthogonal a,a-BMA-D. If this species closes to A by the microscopic reverse of its formation faster than it undergoes central bond rotation through 180°, then optically active A of the configuration shown must result; further if it closes back to T under these conditions, T must retain its optical purity. Since this is not consistent with the facts, the a,a-BMA species derived by the bevel pathway must undergo ring closure slower than central bond rotation so that racemized A will result, and whatever T is reformed will be racemic.

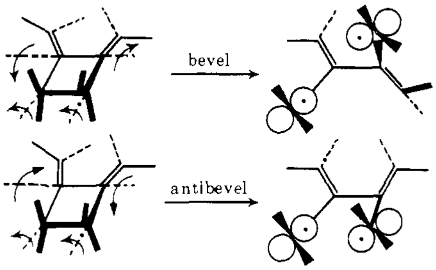
Antibevel opening of optically active T will give the opposite enantiomer of the chiral intermediate a,a-BMA-L. Closure of a,a-BMA-L to A faster than central bond rotation will lead to the *same* enantiomer of A as obtained via the bevel pathway provided microscopic reversibility applies.

Since this too is not consistent with the facts, rapid central bond rotation in the intermediate must be involved to explain the results.

The statement that both the bevel and antibevel pathways lead to the same enantiomer of A via enantiomeric BMA species which close faster than they rotate is correct so long as microscopic reversibility applies in the ring closure step. Therefore, involvement of either pathway via a fixed D_{2d} biradical is excluded by the data. However, if both pathways are involved to the same extent; i.e., the bevel and antibevel pathways have the same activation free energy for product formation, racemic product must result.

Comparison of Bevel and Antibevel Pathways. Implication of Rapid Central Bond Rotation in 2,2′-Bisallyl. The previous discussion allows for three interpretations for the formation of racemized product from optically active T: (1) bevel; or (2) antibevel ring opening to a rapidly rotating BMA species; or (3) equienergetic formation and reaction of a nonrotating D_{2d} BMA via both bevel and antibevel pathways.

Examination of the bevel and antibevel paths reveals that the antibevel pathway destroys C_3–C_4 overlap to a much greater extent to achieve the same amount of overlap with the diene π system as the bevel pathway indicating that the antibevel pathway is higher in energy than the bevel pathway. For instance, assuming a 45° conrotatory motion about the C_1–C_4 and the C_2–C_3 bond (giving 70% of maximum overlap between the p orbitals of rehybridized C_3 and C_4 with the p orbitals on C_1 and C_2) and assuming the same distance between C_3 and C_4 during a bevel or an antibevel twist, the overlap between C_3 and C_4 decreases much faster with an antibevel motion since the residual C_3–C_4 overlap increases in π,π character while, with the bevel motion, the decreasing overlap has more σ,σ character. At all C_3–C_4 distances greater than 2.0 Å, σ,σ overlap is much more important than π,π overlap. For instance, at a 45° twist of C_1–C_2 and a distance of 2.4 Å between C_3 and C_4, $S(\sigma,\sigma) = 0.17$, while $S(\pi,\pi) = 0.046$.[10] Moreover at that distance, the nonbonded H–H distance is only 1.0 Å in the antibevel pathway resulting in severe steric repulsion forcing the C_3–C_4 distance to be still longer, therefore, further reducing the overlap.



Thus it is bevel opening to a rapidly rotating BA species that is the pathway for the reaction.

Geometry of 2,2′-Bisallyl. The optical results in the pyrolysis of *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane make it clear that a 2,2′-bisallyl biradical is formed by conrotatory motions, and it undergoes central bond rotation faster than ring closure.

Unfortunately these results have no direct bearing on the preferred geometry of the biradical or the energy gap separating various confirmations, because the activation energy for ring closure is unknown.

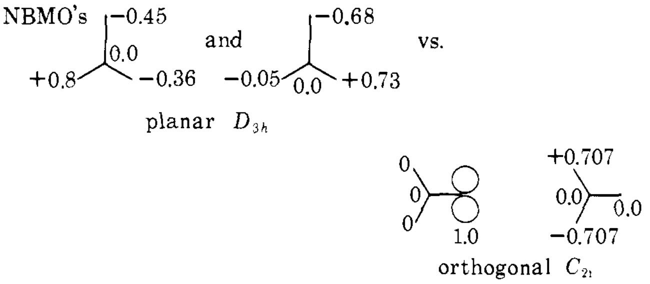
From group contributions to thermodynamic parameters and the known activation energy for the DMCB degenerate rearrangement,[1b] the activation energy for the ring closure can be estimated to be 10 kcal/mol if the value of the resonance energy of the allyl radical is 10 kcal/mol.[11] This activation energy could not be greater than the value of the allyl radical resonance energy, or rapid rotation within the allylic moieties could occur resulting in nonstereospecific product formation.[11,12] However, rotation around the central bond could have an activation energy only a few kcal/mol less than that for reclosure leaving open the possibility of the orthogonal form being as much as 7 kcal/mol more stable than the planar form. It must also be recognized that the planar form suffers more nonbonded interactions than the orthogonal form. Indeed, application of Bartell's relatively hard potential functions[13] to the system assuming trigonal hybidization and a central bond length of 1.50 Å with 1.40 Å lengths for all other C–C bonds reveals 10 kcal/mol destabilization of the planar form relative to the orthogonal one. If this were the case, it is remarkable that racemization occurred at all! However, it is true that these functions may overemphasize the nonbonded repulsions,[13b] and further it is not clear that olefinic carbons can be assumed to be isotropic. Nonetheless, the planar form should be more destabilized on steric grounds and, to whatever extent this is true, the differences in electronic energy of the planar and orthogonal π system are smaller than the maximum allowed by the ring closure activation energy.

Thus the degenerate rearrangement of DMCB's stands in contrast to that of methylenecyclopropanes where the intermediate orthogonal trimethylenemethane singlet biradical (TMM) undergoes ring closure roughly ten times faster than rotation through a planar species (or a bisorthogonal one).[14] There are now MINDO[15] and ab initio[16] calculations on the various forms of the singlet TMM biradical which indicate a 25 and 52 kcal/mol instability respectively of the planar form over the orthogonal one. Thus the calculations support the gross experimental observations recognizing that ring closure of TMM biradical cannot have activation energies as high as 24 kcal/mol. Similar sophisticated calculations on a 2,2′-bisallyl would be most welcome.

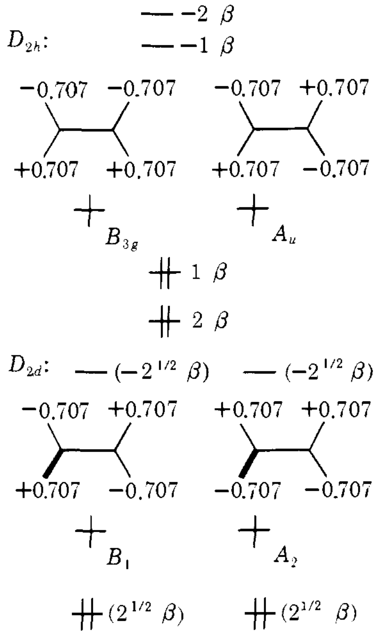
Antiaromaticity of Planar and Orthogonal 2,2′-Bisallyl. The above stated comparison of 2,2′-bisallyl with trimethylenemethane deserves further comment and leads to interesting predictions of geometries of other π-conjugated biradicals.

The preference for orthogonal over planar geometry in singlet trimethylenemethane can be understood in terms discussed by Salem and Borden.[17]

Electron repulsion as calculated from orbital coefficients in planar singlet TMM is roughly 2 eV (~45 kcal/mol) higher than in the orthogonal singlet.[17] Qualitatively this is because each of the two nonbonding, degenerate MO's of planar TMM have orbital density on some of the same atoms regardless of which of the infinite sets of pairs of MO's are chosen while, in the orthogonal form, the nonbonding accidentally degenerate orbitals do not have orbital density on the same centers. This is analogous to the reason for the difference in singlet–triplet splitting of planar olefin and diene π–π^* and carbonyl n–π^* excited states. In the former, the splitting is large while, in the latter, it is small.[18]



In 2,2′-bisallyl, a different situation obtains. The NBMO's of both orthogonal and planar bisallyl are only accidentally degenerate (in the orthogonal form, the NBMO's belong to the B_1 and A_2 representations of D_{2d} and, in the planar form, they belong to A_u and B_{3g} representations of D_{2h}). Therefore, the MO's must preserve the symmetry of the molecular framework, implying that each NBMO has orbital density on the same atoms, suggesting substantial electronic destabilization of the singlet states of both geometries. Indeed in quantitative terms, the extent of electronic destabilization should be the same in both forms, and so the relative energies of the two should depend on the total π energies and steric effects. On the former basis, the planar form would be favored ($E_\pi^{D_{2h}} = 6\alpha + 6\beta$ vs. $E_\pi^{D_{2d}} = 6\alpha + 5.656\beta$), which may counter balance the nonbonded repulsions of the planar form.



Importantly, the prediction of destabilization of both forms of the 2,2′-bisallyl biradical is borne out by the relatively high activation energy for the degenerate rearrangement (46.8 kcal/mol) reported by Dolbier and Doering.[1b] By comparison, the activation energy for the cleavage of cyclobutane to ethylene is 63.2 kcal/mol[19] and, since cyclobutane cleaves more rapidly than it undergoes geometric isomerization,[20] this activation energy would appear to reflect the ease of opening one bond of the cyclobutane ring. When allylic stabilization of one radical site is possible as in the degenerate rearrangement of methylenecyclobutane, the activation energy drops to 49.5 kcal/mol[21] and, since this rearrangement is not concerted[22] (or not completely so), the 13.7 kcal/mol activation energy difference between this reaction and the cyclobutane cleavage reflects the extent of allyl radical stabilization in the transition state for cyclobutane ring cleavage. Addition of another *exo*-methylene, in the form of 1,2-dimethylenecyclobutane (DMCB), might reasonably be expected to lead to a further reduction in the activation energy, perhaps as much as 13.8 kcal/mol down to 35.8 kcal/mol. The actual value is 11 kcal/mol higher and may well represent the electronic destabilization or antiaromatic of the bisallyl singlet being reflected in the transition state for ring opening of DMCB. This hypothesis applies to other π-conjugated biradicals such as vinyl and the two divinyl trimethylenemethanes and bisallyls and numerous other systems, many of which are under study in our laboratory.

It might be argued that steric inhibition of allyl radical resonance in the transition state for cleavage is responsible for the relatively high activation energy of the DMCB degenerate rearrangement. Since neither the methylenecyclopropane[14b,c] or the methylenecyclobutane[21,22] degenerate nonconcerted rearrangements appear retarded, there seems to be no compelling reason for involving an 11 kcal/mol steric inhibition in the DMCB case.

Finally the presumed destabilization of bisallyl lessens the force of the argument for bevel over antibevel opening. Indeed, if the intermediate is destabilized, the greater overlap of the C_3 and C_4 orbitals with the diene system in the bevel opening is inhibitory and not salutary. Pursuit of this question can only lead to performance of difficult and perhaps overly exotic experiments but does not diminish the essential conclusion of conjugative destabilization in the non-4n, noncyclic π system, 2,2′-bisallyl.

Experimental Section

General.—Nuclear magnetic resonance spectra were recorded on a Varian HR220 spectrometer. Chemical shifts are reported in δ values in parts per million downfield from Me_4Si. Infrared spectra were obtained with Perkin-Elmer Model 137 and 137G spectrophotometers in the indicated phase. Vapor phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using dibutyl tetrachlorophthalate (DBTCP) as liquid phase. Exact masses were taken on an AEI MS-9 mass spectrometer operating at 70 eV. Melting points were measured with a Thomas-Hoover capillary melting point apparatus without correction.

***trans*-3,4-Dimethyl-1,2-cyclobutanedicarboxylic Acid Anhydride (TA).** A 1-l. solution of 35 g (0.36 mol) of maleic anhydride and 3 g of distilled acetophenone in spectral grade ethyl acetate, which was degassed with a nitrogen stream, was cooled to −78°. To this solution was added 50 g of *trans*-2-butene, and the solution was irradiated with a 450-W Hanovia medium-pressure Hg arc for 44 hr under a nitrogen atmosphere with the reaction vessel immersed in a Dry Ice–acetone bath. The arc lamp was housed in a double-walled immersion well which was cooled by tap water and insulated from the solution by a vacuum jacket. After irradiation, the solvents were removed in a rotatory evaporator, and the residue was distilled rapidly through a 12 in. Vigreux column at 0.5 Torr to remove unreacted maleic anhydride and gave 15 g of a clear liquid, bp 40–100°. The distillate contained two anhydrides, and so 50 g of this material collected from three photolyses was distilled through a 20 in. spinning-band column at 0.25 Torr. A 21-g fraction, bp 72–74° (0.25 Torr), of *trans*-3,4-dimethyl-1,2-cyclobutanedicarboxylic acid anhydride (TA) was collected: NMR of TA (CCl_4) δ 1.15 (d, J = 7 Hz, 3 H), 1.35 (d, J = 7 Hz, 3 H), 2.27 (sextet, J = 7 Hz, 1 H), 2.50 (mult 1 H), 2.92 (t, J = 7 Hz, 1 H), 3.42 (d of d, J = 7, 1 Hz, 1 H); ir (neat) 2950, 1850, 1780, 1450, 1250, 1210, 1100, 1015, 910, and 750 cm^{-1}; m/e (calcd for TA 154.0631) 154.0632.

Dimethyl *trans*-3,4-Dimethyl-*cis*-1,2-cyclobutanedicarboxylate. A solution of 21 g (0.136 mol) of TA in 350 ml of methanol containing 5 ml of concentrated sulfuric acid was heated at reflux for 5 hr. After cooling, the methanol was removed on a rotary evaporator, and water was carefully added with cooling followed by extraction with 200 ml of diethyl ether. After the water layer was removed and after the ether layer was washed with portions of 5% aqueous sodium bicarbonate solution until the washings were basic, the ether solution was dried and evaporated giving 25.4 g (93.5%) of dimethyl *trans*-3,4-dimethyl-*cis*-1,2-cyclobutanedicarboxylate which was used without further purification; NMR (CCl_4) δ 0.94 (d, J = 6 Hz, 3 H), 1.10 (d, J = 6 Hz, 3 H), 2.03 (m, 1 H), 2.55 (m, 2 H), 3.27 (m, 1 H), 3.58 (s, 3 H), 3.63 (s, 3 H); ir (neat) broad 1735 cm^{-1}; m/e (calcd 200.1050) 200.1030.

Optically Active Dimethyl *trans,trans,trans*-3,4-Dimethyl-1,2-cyclobutanedicarboxylate. A solution of 25 g (0.125 mol) of the ester above was added to 350 ml of a methanol in solution to which had previously been added 6 g of sodium. The solution was heated at 55° under nitrogen for 2 days after which 20 g of sodium hydroxide dissolved in 50 ml of water was added. After heating at reflux for 6 hr, the solution was cooled, and the solvent was evaporated in a rotary evaporator to dryness. Then 200 ml of water was added, and 6 *N* hydrochloric acid was added with cooling to bring the pH to 1. A solid precipitated during the acidification which, after filtration and drying, gave 16 g of light-yellow crystals, mp 137–141°. After recrystallization from ethyl acetate, 10 g of white crystals of *trans,trans,trans*-3,4-dimethyl-1,2-cyclobutanedicarboxylic acid, mp 140–143°, was obtained: NMR ($CDCl_3$) δ 1.26 (d, J = 6 Hz, 6 H), 2.02 (sym, m, 2 H), 2.82 (sym, m, 2 H) (the acid protons were not observed). A mixture of 9 g of the diacid above and 33 g of brucine was added to 160 ml of not absolute ethanol. After filtration to remove suspended materials, the solution was cooled to 5° to give 18 g of a solid. Three recyrstallizations from ethanol and combination with the head crop from another resolution gave 13.5 g of a brucine salt which, upon treatment with aqueous hydrocloric acid and extraction with diethyl ether followed by drying of the ether solution and evaporation, gave 3.5 g of a moist white solid. After heating with 350 ml of methanol and 3 ml of concentrated sulfuric acid followed by the usual work-up and distillation at 124–126° (25 Torr), 3.8 g of an optically active dimethyl *trans,trans,trans*-3,4-dimethyl-1,2-cyclobutanedicarboxylate was obtained: NMR (CCl_4) δ 1.15 (d, J = 6.54 Hz, 6 H), 2.9 (sym, m, 2 H), 2.67 (sym, m, 2 H), 3.64 (s, 6 H); ir (neat) broad 1735 cm^{-1}; $[\alpha]^{23}D$ −35.6° (c 1.52 MeOH); *m/e* 200.1031.

Optically Active *trans,trans,trans*-3,4-Dimethyl-1,2-cyclobutanedimethanol. An ethereal solution of 3.5 g (0.0175 mol) of the optically active diester above was added slowly to 1.8 g (0.047 mol) of lithium aluminum hydride in diethyl ether. After reaction, a freshly prepared saturated aqueous solution of anhydrous sodium sulfate was added to decompose the excess hydride reagent and cause precipitation of the salts. After filtration, the salts were washed with tetrahydrofuran, and the solvents were combined and dried over anhydrous sodium sulfate. Evaporation of the solvent and distillation at 0.5 Torr gave 2.4 g (86%) *trans,trans,trans*-3,4-dimethyl-1,2-cyclobutanedimethanol; bp 90–93°; NMR (CCl_4) δ 1.03 (d, J = 6 Hz, 6 H), 1.4 (m, 2 H), 1.55 (m, 2 H), 3.2 (broad t, J = 7 Hz, 2 H), 3.55 (broad d, J = 7 Hz), 4.6 (very broad s, 2 H); ir (neat) broad 3300 cm^{-1}; $[\alpha]^{23}D$ +21.45° (*c* 2.5 MeOH); *m/e* (calcd 144.1151) 144.1142.

Optically Active *trans*-3,4-Dimethyl-1,2-dimethylenecyclobutane (T_{act}). The optically active diol (2.3 g) was converted to the ditosylate, then to the diiodide, then dehydroiodinated as described previously[1a] to give 1.25 ml of volatile material which was purified on a 0.25 in. × 6 ft di-*n*-butyl tetrachlorophthalate (DBTCP) column at 100° and 60 ml/min Me flow to give 800 μl of optically active *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane, $[\alpha]^{23}D$ −87.2° (*c* 4.11 chloroform).

Pyrolyses of Optically Active *trans*-3,4-Dimethyl-1,2-dimethylenecyclobutane. A total of 360 μl of T_{act}, $[\alpha]^{23}D$ −87.2°, was pyrolyzed in 30-μl portions in a well-conditioned 2-l. vessel at 230.7° for 80 min. Recovery of the pyrolysate on a vacuum line followed by analysis on a 200 ft DBTCP column revealed an average of 9% conversion to *anti*- and *syn*-1-ethylidene-2-methylene-3-methylcyclobutane (A and S) and *anti,anti*-diethylidenecyclobutane (AA) in a ratio of approximately 18:1:1, respectively. After separation on the DBTCP column, the starting material had $[\alpha]^{23}D$ −70.75°, (*c* 1.26 chloroform), and the major product, A, had $[\alpha]^{23}D$ +0.06 ± 0.01°.

Acknowledgment. I thank the National Science Foundation and the Alfred P. Sloan Foundation for support of this work and Jonathan Chasman for preparing large quantities of the photocycloadduct.

References and Notes

(1) (a) J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.*, **94**, 1675 (1972); (b) W. Von E. Doering and W. R. Dolbier, *ibid.*, **89**, 4532 (1967).

(2) (a) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); (b) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970); (c) J. J. Gajewski, *Mech. Mol. Migr.*, **4**, 1 (1971); (d) W. R. Moore, A. D. Bach, and T. M. Ozretich, *J. Am. Chem. Soc.*, **91**, 5918 (1969); (e) W. R. Dolbier, Jr., and S.-H. Dai, *ibid.*, **92**, 1774 (1970); **94**, 3946 (1972).

(3) (a) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

(4) B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1075 (1970).

(5) Performed according to D. O. Owsley and J. J. Bloomfield, *J. Org. Chem.*, **36**, 3768 (1971), whom we thank for providing not only detailed procedures but a sample of the 2-butenemaleic anhydride adduct.

(6) (a) Small amounts of *syn,anti*-1,2-diethylidenecyclobutane SA are also formed in the pyrolysis along with the hydrogen-shifted triene derived from it. The ratio of SA + triene to AA is approximately 1:13.[6b] (b) Bruce Stahly, unpublished observations.

(7) (a) R. Criegee, D. Seebach, R. E. Winter, B. Borretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965); (b) C. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1546 (1966).

(8) See P. W. Dillon and G. R. Underwood, *J. Am. Chem. Soc.*, **96**, 779 (1974), particularly ref 41.

(9) W. R. Moore and W. R. Moser, *J. Am. Chem. Soc.*, **92**, 5469 (1970).

(10) H. J. Kopineck, *Z. Naturforsch.*, *Teil A*, **5**, 2120 (1950), as quoted in J. D. Roberts, "Notes on Molecular Orbital Calculations", W. A. Benjamin, New York, N. Y., 1962.

(11) (a) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Am. Chem. Soc.*, **91**, 2136 (1969); (b) W. Tsang, *Int. J. Chem. Kinet.*, **5**, 929 (1973), reported 12 kcal/mol for the resonance energy of the isobutenyl radical.

(12) Moore's results with 1,2-cyclohexadiene[9] indicate that the bisallyl biradical has a substantial energy barrier for closure to DMCB.

(13) (a) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960). (b) It is also the case that the calculated barrier is made up of many small interactions none of which is more than 2 kcal/mol so slight geometric changes can substantially reduce the barrier height. Professor S. I. Milier has suggested that the barrier to rotation in biphenyl may be analogous to that in bisallyl. The biphenyl barrier has been claimed to be 0.042 eV or less than 1 kcal/mol: T. Sekiya, K. Sakamoto, and W. Yoshio, *Nippon Genshiryoku Kenkyusho Kenkyu Hokoku*, **JAERI-1181**, 75 (1969). See also R. J. Kurland and W. B. Wise, *J. Am. Chem. Soc.*, **86**, 1877 (1964).

(14) (a) E. F. Ullman, *J. Am. Chem. Soc.*, **82**, 505 (1960); (b) J. J. Gajewski, *ibid.*, **90**, 7178 (1968); **93**, 4450 (1971); (c) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970); (d) W. von E. Doering and L. Birladeanu, *ibid.*, **29**, 449 (1973).

(15) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 308 (1971).

(16) W. J. Hehre, L. Salem, and M. R. Willcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).

(17) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973).

(18) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966; (b) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1967 (among many others).

(19) R. W. Vreeland and D. F. Swinehart, *J. Am. Chem. Soc.*, **85**, 3349 (1963).

(20) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

(21) W. von E. Doering and J. C. Gilbert, *Tetrahedron. Suppl.*, **7**, 392 (1966).

(22) J. E. Baldwin and R. H. Fleming, *J. Am. Chem. Soc.*, **95**, 5249, 5256, 5261 (1973).