of diastereomers from the methyl bornyl adduct to the corresponding dibornyl diastereomer by simple consideration of chemical shift additivities in the proton NMR spectrum.[7] Thus the chemical shift of the exo proton from diastereomer **2**α was the sum of the chemical shift of the exo proton of dimethyl adduct **1** and the incremental shift for the two corresponding methyl bornyl diastereomers **3**α**exo** and **3**β**endo**. The predicted and measured chemical shifts are given in Table I. From integration of the exo proton absorptions, it was further possible to obtain the relative yields of all isomers in each cycloaddition and thus to correlate the extent of asymmetric induction obtained with two chiral groups to that obtained with one. Multiplication of the relative rates of enantioselection for the exo and endo methyl bornyl diastereomers gave the predicted values for enantioselection in the dibornyl case for comparison with the measured values (see Table II). Within experimental error, we see that they are the same.

Cooperativity in enantioselection has several important implications. First, we have further evidence of concert in the Diels–Alder reaction. Second, the fact that the relative rates are multiplicative illustrates what happens in enzymatic systems, where the net result of many chiral centers is optical yields approaching 100%. Finally, we suggest a method for increasing optical yields in asymmetric induction for natural product synthesis. Where a concerted reaction is involved in the synthesis, we may study the effect of individual chiral prosthetic groups at different sites in the molecule and predict which combination will lead to the highest optical yield. Thus we may systematically improve asymmetric induction without relying on chance.

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(7) Such additivity properties constitute a free energy relationship not unrelated to that observed for the asymmetric induction itself.

Production of Orbitally Forbidden Products in the IR-Laser-Induced Isomerization of *cis*-3,4-Dichlorocyclobutene

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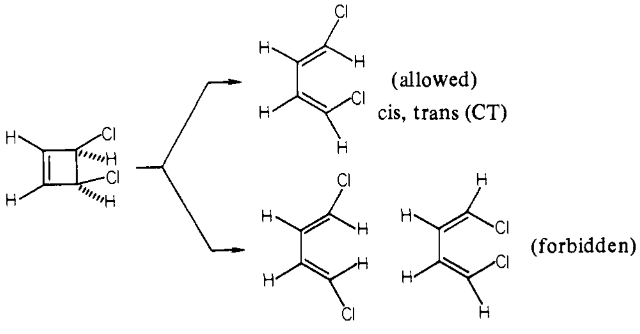
Conservation of orbital symmetry is a powerful tool for predicting the stereochemical course of concerted electrocyclic reactions.[1] Although symmetry-forbidden products can be formed, the "nonallowed" pathways generally have much larger activation energies, resulting in greatly reduced yields. One might expect, however, that vibrational excitation of the reactants in the ground electronic state by an intense infrared laser could substantially increase the yield of the symmetry forbidden products. We report here the first instance of such a laser-induced reaction, namely, the electrocyclic ring opening of *cis*-3,4-dichlorocyclobutene (DCCB) to produce the symmetry-allowed (conrotatory) *cis,-trans*-1,4-dichloro-1,3-butadiene (CT) and the forbidden (disrotatory) cis,cis and trans,trans (CC and TT) isomers:[2-5]



A pulsed CO_2 laser tuned to the 10.812 P(40) line was used to irradiate DCCB in a static Pyrex cell equipped with NaCl and quartz windows. The total yield of products was measured by UV absorption (232.5 nm), while the isomeric composition of the products was determined by GC.[6] A typical chromatogram of the reactant and product mixture is shown in Figure 1. The fractional conversion per laser pulse and the branching ratio for each product were measured as functions of laser fluence ϕ, DCCB pressure, and added buffer gas pressure. Full details of these experiments will be reported in a later publication.[7]

Our principal findings are as follows: (i) At fluences below 3.5 J/cm^2 the only observed product was the allowed CT isomer. At higher fluences the branching ratio for the forbidden products, $\Gamma = ([CC] + [TT])/([TT] + [CT])$, was found to increase linearly with ϕ, as shown in Figure 2. The ratio of CC (the most stable isomer) to TT (the least stable one) was always greater than unity and decreased with increasing fluence. Our findings are consistent with the observation by Danen et al.[8] of only the allowed product at $\phi = 3.5$ J/cm^2 in their study of the IR-laser-induced isomerization of DCCB. (ii) The fractional conversion per pulse was found to increase quadratically with neat DCCB pressure, over a range of 0.020–2.5 torr. The branching ratios, Γ and CC/TT, were essentially independent of DCCB pressure. (iii) The effects of He, Ar, N_2, and O_2 buffer gases were to decrease the fractional conversion per pulse, decrease Γ, and increase the CC/TT ratio.

A variety of tests were carried out to eliminate possible artifacts in our experiments. The branching ratios were found to vary only weakly with the number of laser pulses, N, indicating that for small N, CC and TT are not the results of secondary reactions of cold CT building up in the cell. The data points in Figure 2 are extrapolations of Γ to $N = 1$. We further noted that DCCB decayed exponentially with N, with a parallel growth of products, for as much as 70% conversion of all the DCCB in the cell. This observation rules out the possibility that energy pooling collisions between two vibrationally excited DCCB molecules contribute appreciably to the reaction mechanism. In another test, irradiation of DCCB with 8.2 J/cm^2 at 10.285 μm where DCCB absorbs very weakly produced no detectable products. This experiment rules out the possibility of surface catalysis on the cell windows.[9] We also found that at 10.812 μm, the product distribution was independent of cell dimensions.[10]

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(1) (a) Woodward, R. B.; Hoffmann, R. "The Conversion of Orbital Symmetry"; Academic Press: New York, 1970. (b) Zimmerman, H. B. *Acc. Chem. Res.* **1971**, *4*, 272. (c) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761.

(2) *cis*-3,4-Dichlorocyclobutene was synthesized by the method of Pettit and Henery.[5] Gas chromatographic analysis of this product after purification revealed it to be a pure compound. No detectable amounts of the *trans*-3,4-dichlorocyclobutene or the 1,4-dichlorobutadienes were present.

(3) The laser-induced ring opening of hexafluorocyclobutene to hexafluorobutadiene has been carried out, but obviously no stereochemical conclusions may be made in this system: Yogev, A.; Benmair, R. M. J. *Chem. Phys. Lett.* **1977**, *46*, 290.

(4) For studies of related thermal reactions, see: (a) Brauman, J. E.; Archie, W. C., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 4262. (b) Dickens, D.; Frey, H. M.; Skinner, R. F. *Trans. Faraday Soc.* **1965**, *65*, 453 and references cited therein. (c) Hauser, W. P.; Walters, W. D. *J. Phys. Chem.* **1963**, *67*, 1328.

(5) Pettit, R.; Henery, J. *Org. Synth.* **1970**, *50*, 36.

(6) Bartlett, P. D.; Wallbillich, G. E. H. *J. Am. Chem. Soc.* **1969**, *91*, 409. The identity of each peak was confirmed by measuring the retention times under identical conditions of authentic samples of each isomer.

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(8) Danen, W. C.; Koster, D. F.; Zitter, R. N. *J. Am. Chem. Soc.* **1979**, *101*, 4281.

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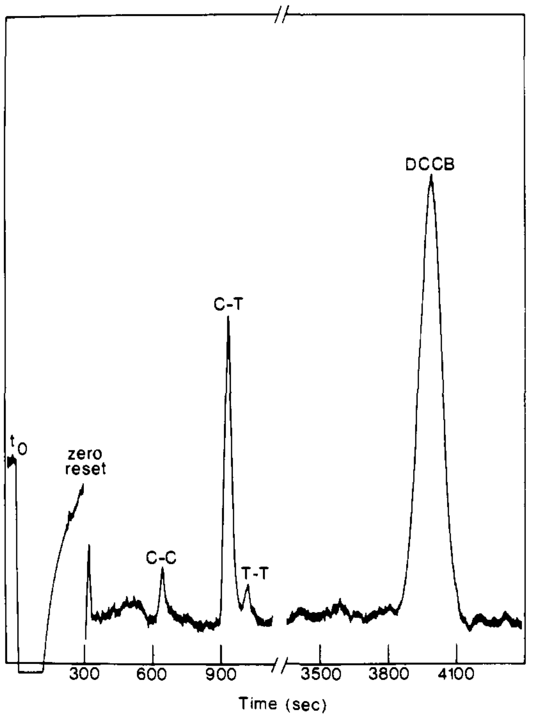

Figure 1. Gas chromatogram of reactant and product mixture after 10 pulses of irradiation at 8.2 J/cm^2 of 0.267 torr of *cis*-3,4-dichlorocyclobutene. The chromatogram was taken on a 10-ft × 0.25-in. β,β'-oxydipropionitrile column at 70 °C, with a detector temperature of 200 °C and an amplifier setting of 2 × 10^{-11} A/mV F.S. Sample was injected at t_0. The peak at 300 s is a column impurity.

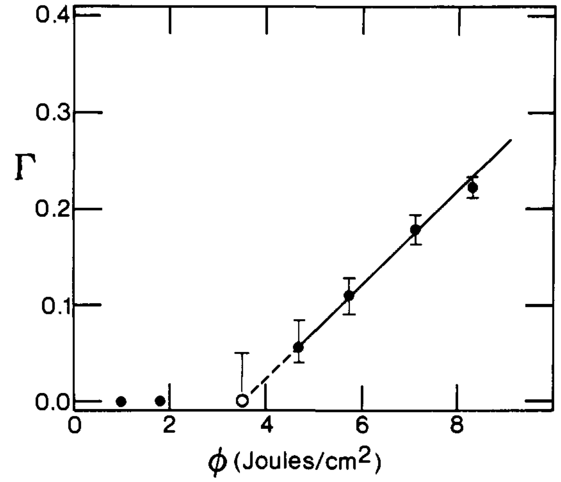

Figure 2. Fraction of forbidden products vs. laser fluence. The open circle is the measurement of Danen et al.[8]

The observation that the conversion per pulse increases with reactant pressure indicates that collisions play a major role in the reaction mechanism. This behavior is expected even at low pressures for the following reason. Isomerization reactions are unique in that, unlike fragmentation reactions, the nascent products cannot dissipate their energy (in excess of 60 kcal/mol for CC and TT)[4] except through collisions and radiation. Collisions of vibrationally hot products with excited reactants lead to further reaction, the products of which are able to continue the "energy chain". The length of this chain, and hence the conversion per pulse, should increase with reactant pressure. The expected effect of the buffer gases is to shorten the chain, reduce Γ, and increase the CC/TT ratio by lowering the energy content of the molecules involved.

It has been conjectured that vibrational excitation of the reactant can result in symmetry forbidden products being formed in a concerted process on the ground electronic surface. The production of a large fraction of the sterically unfavorable CC isomer (CC/TT > 1) argues against such a concerted mechanism in the present study.[4a] More likely explanations for the forbidden products are either direct formation of CC and TT from a biradical intermediate[12] or secondary isomerization of vibrationally hot CT formed in a concerted step. We note that secondary absorption of photons by the nascent primary product is unlikely to be important because of the collisional nature of the mechanism. Additional studies are in progress to elucidate further the mechanism.

Acknowledgment. We thank Professor John Brauman for very helpful discussions. Support by the National Science Foundation (Grant CHE78-07998) is gratefully acknolwedged.

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Erythro-Selective Aldol Reaction via Tris(dialkylamino)sulfonium Enolates[1]

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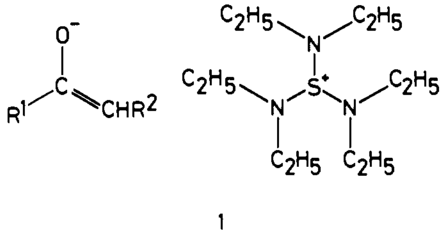
Recently we have demonstrated that reaction of an enol silyl ether and tris(diethylamino)sulfonium (TAS) difluorotrimethylsiliconate as a fluoride ion source, generates the TAS enolate depicted in structure **1**.[2] The anionic moiety in **1** in THF solvent has proved to possess negligible bonding interaction with the TAS countercation and acts as a highly nucleophilic species.[1,2] We report here a stereoselective aldol reaction of such a TAS enolate (Scheme I), which provides a new means for acyclic stereoselection.[3]



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Aldol reaction of the TAS enolate **1** and aldehyde substrates does not take place smoothly, because the equilibrium of eq 2 in Scheme I lies so far to the left.[2,4] In addition, the aldol anion **5** in certain cases reacts with another aldehyde molecule to give the enolate/aldehyde 1:2 condensation product.[5] However, the silyl fluoride **4** or enol silyl ether **2** present in the reaction system can trap effectively the aldol anion **5** to give the aldol silyl ether **6** (eq 3 or 4).[6] Thus, when a mixture of an (*E*)- or (*Z*)-enol silyl

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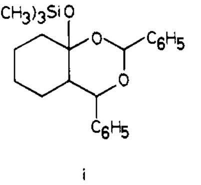
(1) Superanions. 3. Part 2: Noyori, R.; Nishida, I.; Sakata, J. *Tetrahedron Lett.* **1980**, *21*, 2085.

(2) Noyori, R.; Nishida, I.; Sakata, J.; Nishizawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 1223.

(3) Review: Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2.

(4) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, 1969; Chapter 13.

(5) For instance, the reaction of 1-(trimethylsiloxy)cyclohexene and benzaldehyde afforded the adduct i.



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