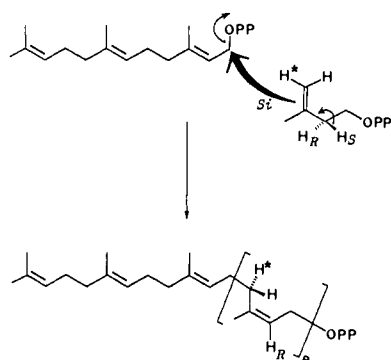


## Scheme II



HPLC to give 5.2 mg of [4,8,12,16,20,24,28-<sup>2</sup>H<sub>7</sub>]-(*E,E*)-farnesyl-(*all-Z*)-heptaprenol (decaprenol),  $[\alpha]_{320} + 5.9 \pm 1.2^\circ$ , <sup>2</sup>H content 93%, and 14.2 mg of [4,8,12,16,20,24,28,32-<sup>2</sup>H<sub>8</sub>]-(*E,E*)-farnesyl-(*all-Z*)-octaprenol (undecaprenol),  $[\alpha]_{320} + 6.3 \pm 0.5^\circ$ , <sup>2</sup>H content 93%. These polyprenols were combined and subjected to ozonolysis. The levulinic acid thus obtained showed a positive Cotton curve ( $[\alpha]_{320} + 42 \pm 14^\circ$ ,  $[\theta]_{280} + 81 \pm 9^\circ$ ), indicating that the configuration was *S*. Conversely, (*R*)-[3-<sup>2</sup>H]levulinic acid ( $[\alpha]_{320} - 51 \pm 14^\circ$ ,  $[\theta]_{280} - 74 \pm 14^\circ$ ) was obtained by similar experiments using **2** in place of **1**. Therefore, it was evidenced that the C–C bond formation took place at the *si* face of the double bond of IPP.

The present observations, taken in conjunction with the previous finding that the 2-*pro-S* hydrogen of IPP is eliminated during the undecaprenyl-pyrophosphate synthetase reaction,<sup>5</sup> indicate that the stereochemical course of the condensation forming *Z* double bonds is similar to that of (*E,E*)-farnesyl-pyrophosphate synthetase reaction in that the C–C bond is formed on the same side as the C–H bond to be cleaved (Scheme II).

### Asymmetric Induction in Diarylcarbene Cyclopropanations

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The mechanism of addition of carbenes to olefins is a subject of historical and current interest.<sup>2</sup> These mechanisms range from a concerted one involving a symmetric transition state (path A of Figure 1) to a stepwise one involving either prior complex formation or diradical formation (path B of Figure 1). We have developed a direct method for distinguishing between synchronous and asynchronous mechanisms based upon a geometric relationship between the asymmetric induction produced when a reacting partner bears one or two chiral prosthetic groups.<sup>3</sup> We now report that application of this method to cyclopropanation of fumarate esters by (triplet) fluorenylidene and diphenylmethylene implicates a nonconcerted mechanism involving a reversible first step.

The substrates in our reactions were dimethyl, methyl 1-bornyl, and di-1-bornyl fumarate. Our principle of cooperativity<sup>3a</sup> requires

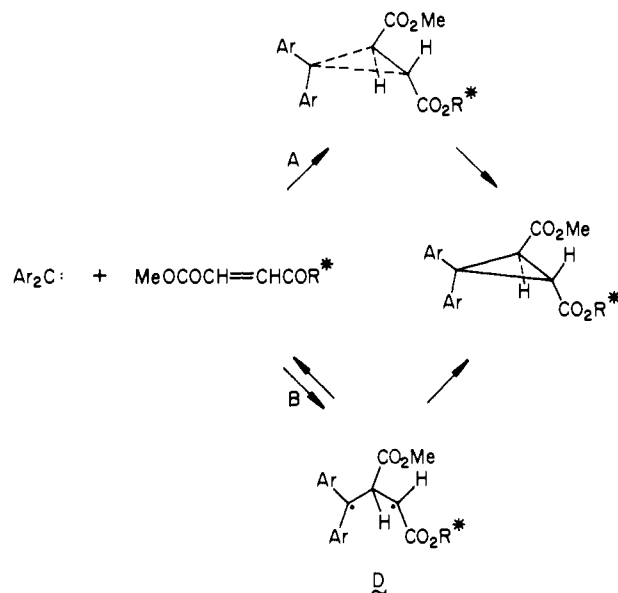


Figure 1. Synchronous vs. asynchronous pathway.

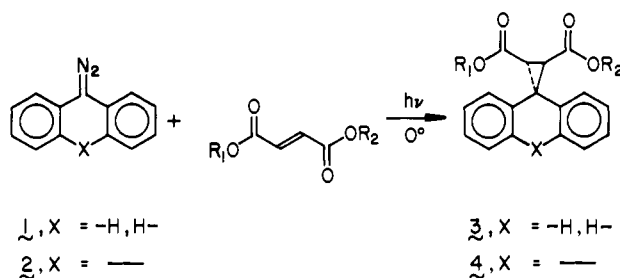


Figure 2. Products of diaryldiazomethane photoinduced cyclopropanation.

Table I. Asymmetric Ratios

cyclopropane-dicarboxylate	diazofluorene	diazodiphenylmethane
dimethyl	1.00 ± 0.05	1.00 ± 0.04
methyl 1-bornyl	1.26 ± 0.06	1.49 ± 0.07
di-1-bornyl (exptl)	1.30 ± 0.05	1.56 ± 0.07
di-1-bornyl (predicted)	1.59 ± 0.10	2.43 ± 0.14
di-1-bornyl (unirrad)	1.00 ± 0.05	

that the asymmetric ratio produced by the bischiral fumarate be the square of the monochiral ratio for the synchronous pathway (path A). When 0.031 M acetonitrile solutions of each fumarate containing either diazofluorene or diazodiphenylmethane maintained at 0 °C were irradiated using 0.1 M K<sub>2</sub>CrO<sub>4</sub> filtered Hanovia light, diarylcyclopropane dicarboxylates were formed in 20–35% yield (see Figure 2), as well as unidentified polar products. The 1-bornyl esters were hydrolyzed in aqueous HCl and reesterified with diazomethane to yield the known dimethyl 3,3-diarylcyclopropane-1,2-dicarboxylates.<sup>4</sup> The enantiomeric ratios determined by NMR using the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphora]europium(III) are reported in Table I. With both diaryl carbene precursors, the asymmetric induction produced with two chiral groups was nearly the same as that produced with one. Experimentally identical asymmetric yields were obtained when the fumarate concentration was reduced by a factor of 20. In a control experiment, an unirradiated solution of diazofluorene and di-1-bornyl

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(4) (a) *trans*-2,3-Dicarbomethoxyspiro[cyclopropane-1,9'-fluorene]: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.26–8.00 (m, 8 H), 3.60 (s, 6 H), 3.43 (s, 2 H); mp (uncorr) 137.0–139.0 °C (lit.<sup>4b</sup> mp 135.5–136 °C). Dimethyl *trans*-3,3-diphenyl-1,2-cyclopropanedicarboxylate: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.13–7.50 (m, 10 H), 3.43 (s, 6 H), 3.23 (s, 2 H); mp (uncorr) 179.5–181.0 °C (lit.<sup>4c</sup> mp 174–174.5 °C). (b) Braun, A. M.; Cassidy, H. G.; Schulz, R. C.; Tanaka, H. *Makromol. Chem.* **1971**, 146, 195. (c) Jones, W. M. *J. Am. Chem. Soc.* **1959**, 81, 3776.

fumarate produced the cyclopropane in only 2% yield but of a sufficient quantity to determine that no asymmetric induction resulted.

The asymmetric ratios produced from both diazoalkanes are reminiscent of our results on photochemical 2 + 2 cycloadditions.<sup>3b</sup> That is, the asymmetric induction observed is almost entirely due to the first chiral group. Since cooperativity is not observed, a synchronous mechanism cannot be operative. Moreover, the order of effects is also inconsistent with an asynchronous but concerted mechanism, which is operationally equivalent to rate-limiting single-bond formation followed by rapid collapse of the 1,3-biradical. Since the presence of asymmetric induction minimally requires a discrimination between the two ends of a molecule, such single-bond formation would be expected to occur preferentially at the less-hindered methyl end of the monochiral fumarate to yield diradical D (Figure 1), with asymmetric induction increasing when the bischiral fumarate forces first-bond formation at a chiral end. That the asymmetric ratio does *not* increase suggests that the second bond-forming step is rate limiting and that the first step is reversible.<sup>5</sup> This first step could either be intermediate complex formation, which has been invoked for singlet carbenes,<sup>2</sup> or bond formation to a trimethylene diradical. A minimal condition for such reversibility is that the heat of reaction have a positive or small negative value. A Benson calculation on addition of triplet diphenylcarbene<sup>9</sup> to dimethyl fumarate to yield the diradical provides a reaction enthalpy of ca. -4 kcal/mol, a figure permissible for, though not requiring, reversible diphenylcarbene addition.

A final question concerns the identity of the reactive intermediate produced upon irradiation. Recent experimental evidence by Schuster and co-workers<sup>6</sup> and by Scaiano, Griller, and co-workers<sup>7</sup> suggests that singlet fluorenylidene undergoes rapid intersystem crossing to the ground-state triplet. Our fumarate concentrations are such that less than 10% of the singlet can be intercepted even at diffusion control. Scaiano and Griller have observed<sup>7</sup> that triplet fluorenylidene adds to acetonitrile to form a nitrile ylide. Using their activation parameters, we calculate a rate for this process at 0 °C of  $2.3 \times 10^7 \text{ s}^{-1}$ , a rate that is approximately half the pseudo-first-order rate constant of direct addition to 0.031 M diethyl fumarate calculated in a similar fashion, namely,  $(1.37 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})(0.031 \text{ M}) = 4.2 \times 10^7 \text{ s}^{-1}$ . However, the nitrile ylide would form photostable pyrrolines,<sup>10</sup> which are presumably the unidentified additional products of the reaction, rather than cyclopropanes. Finally, the control experiment, which presumably involves 1,3-dipolar addition by the diazofluorene itself, produced no asymmetric induction. We are forced to conclude that the reactive intermediate is triplet fluorenylidene and, by analogy, triplet diphenylmethylene.

That cyclopropanation by triplet diarylcarbenes should prove to be nonconcerted is unsurprising, although we now have direct evidence that this is the case. We also have demonstrated that in our case first bond formation appears to be reversible. This is consistent with, and supportive of, the observation that certain 1,3-biradicals of type D can undergo bond cleavage to form carbenes.<sup>5</sup> Perhaps more important, we have an additional reaction that has proved susceptible to our cooperativity criterion.<sup>11</sup>

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**Supplementary Material Available:** A calculation of the second bond dissociation energy of diphenylmethane (2 pages). Ordering information is given on any current masthead page.

## Large Tunneling Effects in the Migration of Chemisorbed Hydrogen on a Metal

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"The migration of atoms or molecules along the surface is one of the most important steps in surface reactions....Nevertheless only a few experiments provide information about this surface process."<sup>1</sup> Therefore theoretical calculations can play a valuable role. DiFoggio and Gomer have measured surface diffusion coefficients for H and D on a close-packed plane of tungsten and found strong evidence for tunneling at  $T \leq 140\text{--}160 \text{ K}$ .<sup>2,3</sup> Although most theoretical work has been based on classical methods,<sup>4</sup> Valone et al. (VVD),<sup>5</sup> in a Monte Carlo transition-state-theory study of H diffusing on the (100) plane of fcc Cu in the low-coverage limit, included quantal effects by replacing the original pair potential by a temperature-dependent, Gaussian-averaged effective potential derived semiclassically.<sup>6,7</sup> They found non-Arrhenius  $T$  dependences and large differences at low  $T$  from an Arrhenius expression with the activation energy set equal to the classical barrier height. These results are very exciting, but the effective-potential method, which, if valid, could have widespread usefulness for molecular dynamics calculations, has not been tested against a dynamical method of known reliability. We have now calculated the same surface diffusion coefficients using a reaction-path formulation of variational transition-state theory (VTST) with semiclassical adiabatic ground-state (SAG) transmission coefficients,<sup>8-10</sup> a combination that has been tested extensively for gas-phase reactions involving hydrogen.<sup>11-13</sup> This method also has the advantage that it allows us to distinguish quantal effects on bound degrees of freedom from tunneling effects (these effects are not separable in the VVD calculations). This is the first application of reaction-path methods,<sup>14</sup> VTST, or SAG methods to a condensed-phase process, and it extends these powerful tools to the simplest possible elementary step in surface reactions and one that is often<sup>1</sup> rate limiting at low pressure.

We consider the diffusion of a single H atom on a rigid single terrace of Cu. The lattice parameters and interaction potential are the same as used by VVD. The former are based on bulk Cu without surface reconstruction; the latter is based on the pair

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