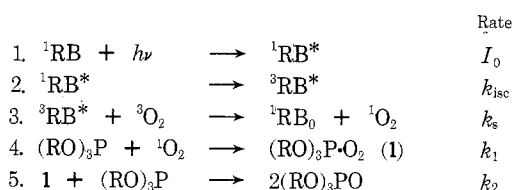


Figure 1. Stern-Volmer plot of  $\beta$ -carotene quenching of the photooxidation of trimethyl phosphite, 0.051 M in benzene-methanol (4:1 by volume) using Methylene Blue sensitizer.

the addition of hydroquinone, as expected for a singlet oxygen oxidation.<sup>5</sup> The intermediacy of singlet molecular oxygen in dye-sensitized photooxidations has frequently been inferred from competition between the substrate and known singlet oxygen acceptors, or from the observation of an identical reaction brought about by singlet oxygen formed by nonphotochemical means.<sup>6</sup> Such methods are inapplicable in this case, since phosphites are oxidized by the oxidation products (hydroperoxides and endoperoxides) of the usual singlet oxygen acceptors and also by the reactants (hydrogen peroxide, phosphite ozonides) usually used to prepare singlet oxygen in the dark.<sup>7</sup> Therefore we turned to the specific quenching by energy transfer of singlet oxygen by  $\beta$ -carotene and by 1,4-diazabicyclo[2.2.2]octane (Dabco).<sup>5,6</sup> Phosphate formation was quenched cleanly by both quenchers, and linear Stern-Volmer plots (see Figure 1) were observed in every case attempted. Singlet oxygen is thus confirmed as the oxidizing agent in this reaction.

The most attractive reaction mechanism is shown in Scheme I. The lack of reversibility of step 4 was shown by a linear plot of relative  $\phi^{-1}$  (phosphate) vs. [phosphite]<sup>-1</sup>, but the possibility of quenching by phosphite cannot be eliminated. Since  $k_d$  for singlet oxygen and the rate constants for  $\beta$ -carotene quenching of singlet oxygen are known for the solvent used, the rates of step 4 can be obtained from the slopes of the Stern-Volmer plots and are included in Table I. These rates are comparable to the rates of reaction of singlet oxygen with tetrasubstituted olefins and correlate with the electron-releasing ability of the alkoxy groups.

#### Scheme I



The structure of the intermediate 1 cannot be deduced from the information available at this time. An intermediate of the same stoichiometry was proposed for the direct

oxidation of phosphites and phosphines by phosphite ozonides,<sup>8,9</sup> and similar intermediates were proposed for the singlet oxygen oxidations of disulfides<sup>10</sup> and sulfides.<sup>11</sup> In the latter case, a zwitterionic structure ( $\text{R}_2\text{S}^+-\text{O}-\text{O}^-$ ) was suggested based on solvent effects. A similar intermediate may be expected in the photooxidation of phosphites.

We are continuing to explore the scope of this reaction and seeking evidence for the structure of the intermediate.

**Acknowledgment.** The authors thank the University of Notre Dame for financial support for this work, the National Science Foundation for a Graduate Traineeship for P.R.B., and Dr. G. F. Hennion for helpful discussions.

#### References and Notes

- (1) Taken in part from the Ph.D. dissertation of P. R. Bolduc.
- (2) A bank of 16 white fluorescent lamps, General Electric F15T8-W, were used as the light source; a merry-go-round was used in relative quantum yield experiments.
- (3) Other solvents and Methylene Blue (MB) sensitizer were used with similar results.
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University of Notre Dame  
Notre Dame, Indiana 46556

Paul R. Bolduc  
Gerald L. Goe\*<sup>12</sup>

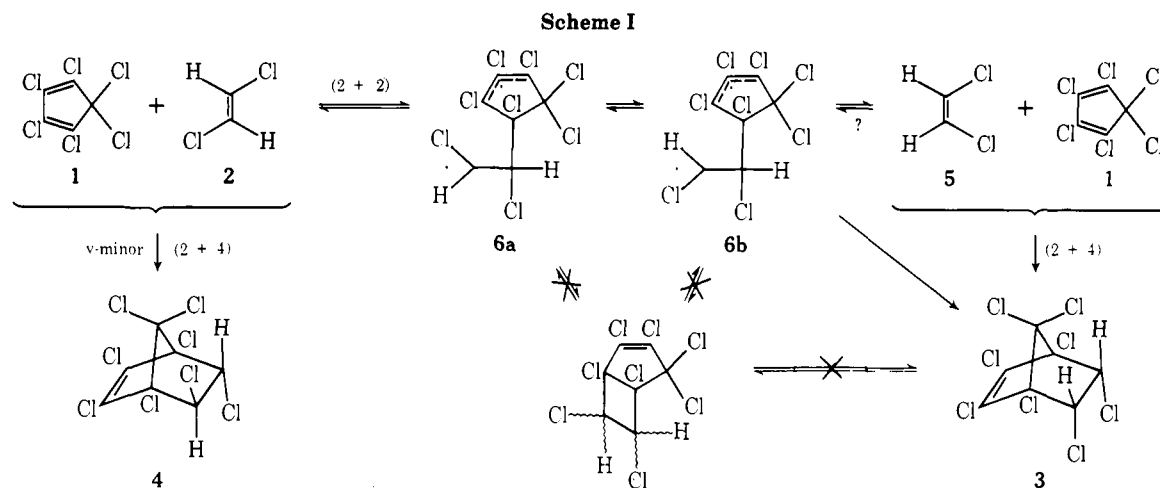
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#### Nonstereospecific Diels-Alder Reactions. I. Reaction of Hexachlorocyclopentadiene with 1,2-Disubstituted Ethylenes

**Summary:** The Diels-Alder reaction of hexachlorocyclopentadiene and related dienes with a variety of trans-substituted ethylenes takes place with partial to extensive, *de facto* violation of the cis principle, including in one instance the loss of the structural integrity of the dienophile; two concurrent mechanisms, one involving concerted cycloaddition and the other biradical intermediates, are considered for the products.

**Sir:** The immense success of the Diels-Alder reaction in synthesis is due to a great extent to its stereospecificity whereby the steric integrity of the reactants is preserved in the adducts. This behavior, known as the cis rule, is considered to be the cardinal stereochemical principle of the Diels-Alder reaction.<sup>1</sup> We wish to report now on an extensive series of Diels-Alder reactions of hexachlorocyclopentadiene (1) in which the steric integrity of the dienophile was lost in the adduct, often extensively, in a clear, *de facto* violation of the cis rule.

To develop a rationale for the failure of 1 to form a Diels-Alder dimer on heating,<sup>2</sup> a possible result of steric hindrance between the chlorines of the incipient bridge and the exo positions, we investigated the reaction of 1 with *trans*-1,2-dichloroethylene (2). Heating the pure reactants



in equimolar proportions in a stirred, closed glass container for 67 hr at 163–165° yielded in 47% conversion an adduct which consisted of 95% of *cis-endo*-octachloronorborene (3, mp 190–192°)<sup>3</sup> and 5% of the *trans* isomer (4).<sup>3</sup> The unreacted olefin contained 39% of *cis*-dichloroethylene (5).<sup>4,5</sup>

Heating 1 with equimolar amount of 5 at 163–165° for 62 hr gave in 62% conversion a product which consisted of 99.9% of 3 and 0.1% of *cis-exo*-octachloronorborene (mp 96–98°).<sup>3a,b</sup> The unreacted olefin contained only the amount of 2 that was originally present (2%) in 5.

Control experiments with neat 2, 3, 4, and 5 showed that, when heated separately, neither of them underwent any isomerization under the above conditions. Even in the presence of HCl gas, a possible by-product and catalyst, 2 failed to yield any 5 at all at 165°. Since 2 underwent isomerization only in the presence of 1, it is tempting to postulate that the two reactants formed a biradical intermediate akin to the free radicals invoked in the neat<sup>7</sup> or iodine<sup>8</sup> and benzoyl peroxide<sup>8c</sup> catalyzed isomerization of 2 and 5.<sup>9</sup> Scheme I is proposed to account for the products.

While in Scheme I 3 can most simply be derived from 1 and 5 by the (2+4) cycloaddition process, the diastereomeric biradical 6b, whose intermediacy is necessary for the isomerization of the olefin,<sup>10</sup> could also conceivably yield 3 directly by a simple coupling mechanism.<sup>13</sup> Although our present data do not allow a gauging of the energy requirements of the various steps (concerted 2+4 addition, biradical formation, radical epimerization,  $\beta$  scission, and ring closure), the latter three processes certainly have considerably lower energy requirements than the first two, and at the relatively high temperature of the reaction they readily could occur. The formation of 3 by a dual pathway thus appears permissible. However, competition between the facile steps of 6b still could yield preferentially the  $\beta$  scission rather than coupling product.<sup>14</sup> The data also suggest that steric repulsion is the major underlying cause for the loss of the stereochemical integrity of the dienophile in the adduction process.<sup>16,17</sup> This view is supported by examples in which steric hindrance is reduced. Thus 2 yielded with 5,5-dimethoxytetrachlorocyclopentadiene (7) and tetrachlorofuran (8) only 10 and 5% of *cis* adducts, respectively, while with cyclopentadiene 2 yields only the *trans* adduct.<sup>13a,21</sup> Consonant with these results, 1, 7, and 8 produced with 5 increasingly more *exo-cis* adducts, 0.1, 2.0 and 9.4%, respectively, further confirming the effect of the incipient norbornene bridge on the stereochemistry of the adducts.

The loss of the stereochemical integrity of the dienophile in the formation of thermal adducts with 1 was encountered in various degrees with a multitude of other olefins

**Table I**  
Distribution of Isomers in Adducts of 1 with  
Trans Olefins

X	Y	Composition of adducts, %		
		A	B	C
CN	CN	57	..	43
COOCH <sub>3</sub>	COOCH <sub>3</sub>	73	..	27
COCl	COCl	84	..	16
Ph	Ph	71	..	29
CH <sub>3</sub>	CH <sub>3</sub>	~100	..	~0
CH <sub>3</sub>	COOCH <sub>3</sub>	84	4	12
CH <sub>3</sub>	Ph	74	20	6
CH <sub>3</sub>	COCl	23	3	74
CH <sub>3</sub>	CN	12	31	57
CH <sub>3</sub>	Cl	30	13	57
CH <sub>2</sub> Cl	Cl	13		38 <sup>a</sup>
Ph	Cl	5	14	81

<sup>a</sup> Adduct contained also 49% of 1,2,3,4,7,7-hexachloro-5-*endo*-(dichloromethyl)norborene.

(Table I), with 5-methylpentachlorocyclopentadiene and, to a lesser extent, with 7 and 8 as the dienes as well.

With allylic *trans* olefins as dienophiles, not only their stereochemical but also their structural integrity may be lost in the adduction process. Thus, while *trans*-1-chloropropene (9) and 1 yielded adducts differing only in stereochemistry, the adducts of 1 and *trans*-1,3-dichloropropene (10) contained structurally isomeric products as well (Table I). Neither 9 nor 10 showed any sign of isomerization when heated separately at the same temperature range in control experiments. A scheme analogous to that outlined above can account both for the stereochemical and structural isomerization of the olefins, and, consequently, for the structure of the adducts as well.

## References and Notes

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- (4) Since **2** contained 0.7% of **5**, 19.9% of it underwent isomerization.
- (5) Although the reaction of **1** and **2** at 190–210° for 48 hr was claimed to give **4**,<sup>6a</sup> repetition of the experiment yielded aromatic breakdown products only.<sup>3c</sup> The products of another experiment at 200° were not identified.<sup>6b</sup> A 37.7% yield of **3** was secured when **1** was heated at 200° with a 9:1 mixture of **5** and **2**.<sup>9c</sup>
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- (9) Although on heating at higher temperature (240–250°) **1** yields chlorine, chlorinated **1**, and various C<sub>9</sub>, C<sub>15</sub>, and C<sub>20</sub> chlorocarbons presumably via a dissociative process involving C<sub>5</sub>Cl<sub>5</sub><sup>•</sup> and Cl<sup>•</sup>,<sup>2</sup> no products of these radicals were detected in the reaction mixtures of **1** with **2** or **5** at 165°, suggesting that these radicals are not involved in the isomerization of **2**. Furthermore, both **7** and **8**, which are less likely sources of radicals than **1**, also yielded significant amounts of cis adducts. Also, the presence of oxygen (air) had no apparent effect on the rate of isomerization, as did neither that of anhydrous potassium carbonate (to intercept HCl). Attempts to use conventional radical inhibitors, such as phenols and anilines, were frustrated by their high reactivity with **1**.
- (10) Significantly, these reactions yielded no **2** + **2** adducts, which, based on the analogy of 1,2,3,4,4,5,6,7,7-nonachlorobicyclo[3.2.0]-2-nonene,<sup>11</sup> are thermally stable under the reaction conditions. The reason for their absence may well be due to the dominance of competing epimerization, β scission, and radical coupling processes of lower energy requirements,<sup>12</sup> resulting in **5**, and **3** as end products.
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- (14) A monitoring of the products from the beginning indicates that in the reaction of **1** with **2** the rate of adduct formation (**3**) increases as the concentration of **5** increases. Since the rate of disappearance of **5** is higher than that of **2** in their reactions with **1**, the appearance of a sigmoid segment in the rate of formation of **3** in the latter reaction can readily be rationalized.<sup>15</sup>
- (15) I thank a referee for his helpful comments, which elicited this and several other footnotes and references.
- (16) These considerations do not apply, of course, when the olefins (e.g., 1,2-dibromoethylene, *trans*-1,4-dichloro-2-butene) can undergo isomerization *per se* under the reaction conditions.
- (17) The fact that, contrary to the conclusion of an earlier study,<sup>6b</sup> 1,1-dichloroethylene does yield a **2** + **4** adduct with **1**,<sup>16</sup> indicates that, if the reaction evolves stepwise, a biradical analogous to **6** can undergo ring closure to the octachloronorborene, presumably because in the absence of competing isomerization steps ring closure to the **2** + **4** adduct remains its only forward option. Significantly, tetrachloroethylene does not yield an adduct with **1** under the above conditions, even though perchloronorborene is a stable chlorocarbon, readily accessible by another route.<sup>19</sup> These olefins thus parallel the behavior of the sterically hindered systems described by Newman, for which he proposed that the Diels-Alder reaction can proceed by a stepwise mechanism.<sup>20</sup>
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- (20) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).<sup>15</sup>
- (21) J. B. Lambert and J. D. Roberts, *Tetrahedron Lett.*, 1457 (1965).
- (22) Address correspondence to Engineering Polymer Products Department, General Electric Co., Mt. Vernon, Ind. 47620.

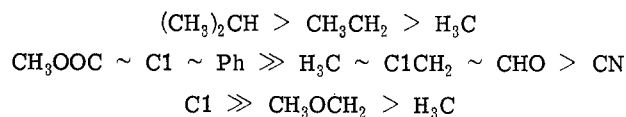
## Nonstereospecific Diels-Alder Reaction. II. Reaction of Hexachlorocyclopentadiene with 1,1-Disubstituted and Monosubstituted Ethylenes

**Summary:** The major epimers in the adducts of hexachlorocyclopentadiene, and related dienes, with unsymmetrical 1,1-disubstituted ethylenes are those in which the bulkier substituents are endo, irrespective of secondary orbital interaction considerations; similar results obtain with monosubstituted ethylenes as well, where the cyano and aldehyde substituents yield significant proportions of the novel exo adducts.

**Sir:** In the preceding communication we described the Diels-Alder reaction of hexachlorocyclopentadiene (**1**) with a variety of 1,2-disubstituted ethylenes, which takes place with a *de facto* violation of the cis principle, and suggested that steric hindrance may be the main underlying cause for the anomalous behavior.<sup>1</sup> To gain a better insight into the role of various substituents in these reactions, we examined the behavior of 1,1-disubstituted olefins as well.

The experiments were carried out by heating **1** with the olefin in a stirred and sealed, all glass system at the lowest temperature at which the reaction proceeded at a convenient rate and quantitatively analyzing the crude product by proton nmr before any subsequent separation, purification, and identification steps. To facilitate structure assignment, adducts of **1** with symmetrically 1,1-disubstituted ethylenes have also been prepared as model compounds; the pertinent 1,2,3,4,7,7-hexachloronorborenes yielded the following nmr parameters: 5,5-dimethyl- (**2**) δ, H<sub>exo</sub> 2.499, H<sub>endo</sub> 1.963 (*J*<sub>gem</sub> = -13.0 Hz), CH<sub>3,exo</sub> 1.50, CH<sub>3,endo</sub> 1.02; 5,5-diphenyl- (**3**), H<sub>exo</sub> 3.633, H<sub>endo</sub> 3.158 (*J*<sub>gem</sub> = -13.6 Hz); 5,5-dichloro- (**4**), H<sub>exo</sub> 3.497, H<sub>endo</sub> 3.114, (*J* = -14.7 Hz), CDCl<sub>3</sub> solution. Isomer distribution data in adducts of representative, 1,1-dissimilarly substituted ethylenes are shown in Table I.

The results of these kinetically controlled<sup>2</sup> experiments indicate the following competitive relationships for the less hindered endo position.



While the alkyl series underlines the role of size in the competition, and it apparently can be extended to include the aldehyde and cyano substituents, several of the cases reflect the results of opposing forces. Thus, while secondary orbital interaction<sup>3</sup> between the π system of **1** and the dienophile can be invoked with phenyl, methoxycarbonyl, and perhaps even chlorine,<sup>4</sup> to rationalize their endo selectivity, it cannot account for the preferentially exo pattern of the aldehyde and cyano substituents.<sup>5</sup> However, size and secondary attractive forces, when considered jointly, seem to accommodate the results. When in competition, size appears to dominate over secondary interactions (methyl *vs.* the planar aldehyde and the linear nitrile substituents) and, expectedly, the two effects reinforce each other when not in opposition (phenyl *vs.* methyl).<sup>6</sup>

The results of the reaction of **1** with α-methylstyrene (**5**) differ from literature data in two respects.

(a) The structure assigned<sup>7</sup> to the crystalline adduct<sup>8</sup> (**6A**) of **1** and **5** had the phenyl group exo and was derived from the nmr spectrum of its deuterium-labeled analog based on the assumption that the exo proton resonates downfield from the endo proton. Exact repetition of the reaction conditions<sup>7</sup> yielded in our hands a crystalline ad-

Hooker Research Center  
Niagara Falls, New York 14302

Victor Mark<sup>22</sup>

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