

# Communications

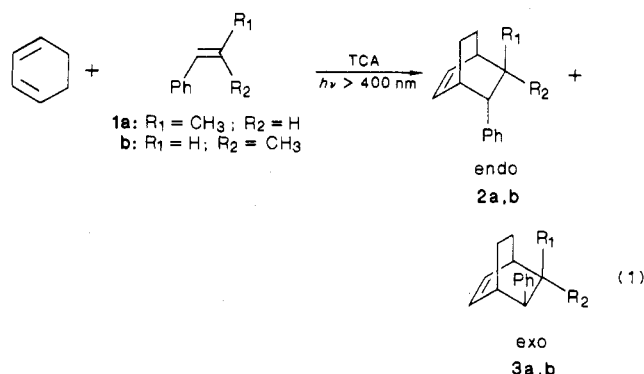
## The Triplex Diels-Alder Reaction: Stereospecific Addition of Methylstyrenes to 1,3-Cyclohexadiene

**Summary:** Irradiation of a benzene or *p*-dioxane solution containing a cyano-substituted arene (tetracyanoanthracene or dicyanonaphthalene, which absorbs the light), 1,3-cyclohexadiene, and *cis*- or *trans*- $\beta$ -methylstyrene gives predominantly *endo*-6-methyl-5-phenylbicyclo[2.2.2]oct-2-enes with retention of styrene configuration in both cases. These reactions occur in useful yield and offer a unique, convenient route for the cycloaddition of an electron-rich diene to an electron-rich dienophile. The mechanism of these reactions was examined and shown to be consistent with the triplex Diels-Alder hypothesis.

**Sir:** The conventional thermal Diels-Alder reaction often provides a convenient, predictable route for the cycloaddition of an electron-deficient dienophile to an electron-rich diene.<sup>1</sup> Various procedures have been devised to accelerate this reaction, but, in general, they are unsuccessful when both the diene and the dienophile are electron-rich. The removal of this restriction seemed imminent in 1981 when Bauld and co-workers discovered that triarylamminium salts initiated the Diels-Alder-like dimerization of 1,3-cyclohexadiene (CHD) and other electron-rich dienes.<sup>2</sup> A radical cation chain reaction mechanism was proposed for this process,<sup>3</sup> and subsequent examinations have supported this path with a few important exceptions. However, the ammonium salt catalyzed reaction is restricted by lack of selectivity to dimerizations of dienes; "crossed" cycloadditions require prodigious excesses of the dienophile. Additional complications with this procedure arise when the ammonium salt initiates the isomerization or polymerization of the dienophile.<sup>4,5</sup>

In 1983, Jones and co-workers<sup>6</sup> described a photosensitized dimerization of CHD under conditions where radical ion formation is thermodynamically impossible. Our investigation and extension of this discovery led to its generalization as the triplex Diels-Alder reaction.<sup>7</sup> Ac-

cording to this hypothesis, the exciplex formed by the excited singlet state of an electron-deficient arene (tetracyanoanthracene, TCA, for example)<sup>8</sup> and a dienophile is trapped by a diene to give a cycloadduct-yielding triplex. Herein we describe application of this procedure to the reaction of *cis*- or *trans*- $\beta$ -methylstyrene with 1,3-cyclohexadiene (eq 1). This crossed cycloaddition does not



occur in useful yield under conventional thermal conditions, in reactions catalyzed by the ammonium salt, or by triplet sensitization. But it proceeds in useful yield and with complete retention of stereochemistry under the triplex conditions. These findings provide new evidence of the utility of the triplex Diels-Alder reaction and expand our view of its mechanism.

Irradiation (450-W Hg lamp, uranium glass filter) of a TCA-saturated dioxane solution of *trans*-styrene **1a** and CHD (0.13 M each) gives one major product and several minor products. The major product is the *endo*-*trans* adduct **2a**, the *exo*-*trans* isomer **3a** is one of the very minor products, and neither of the *cis* adducts **2b** or **3b** could be detected by gas chromatography (<1%).<sup>9</sup> Photolysis of a similar solution containing *cis*-styrene **1b** (0.13 M) gives primarily *endo*-*cis* adduct **2b**; only trace amounts of the *trans* adducts **2a** and **3a** could be detected.<sup>11</sup> Under these photolysis conditions, the only significant side reactions are dimerization of the CHD<sup>12</sup> and addition of CHD to the styrenes to form bicyclo[4.2.0]octenes {[2 + 2] adducts} in yields of ca. 10 and 5%, respectively. In contrast, the radical-cation cycloaddition procedure, initiated either by the aryl ammonium salt<sup>4</sup> or by irradiation of 1,4-dicyanonaphthalene (DCN) in acetonitrile solution,<sup>7</sup> yields overwhelming amounts of CHD dimers. These findings have

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(11) Authentic **2b** was prepared by LiEt<sub>3</sub>BH reduction of the bicyclic tosylate obtained from the alcohol produced by LiAlH<sub>4</sub> reduction of the adduct of CHD to *cis*-ethyl cinnamate.

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Table I. Relative Yields of Cycloadducts from Reactions of CHD and  $\beta$ -Methylstyrenes

styrene	M	CHD, M	sens	solvent	endo		exo		[CHD] <sub>2</sub>	[2 + 2]
					trans 2a	cis 2b	trans 3a	cis 3b		
trans	0.13	0.13	TCA	dioxane	81	ND <sup>a</sup>	2	ND	12	5
cis	0.13	0.13	TCA	dioxane	1	61	ND	13	16	10
trans	0.13	0.13	DCN	dioxane	11	ND	tr	ND	83	5
cis	0.13	0.13	DCN	dioxane	tr	8	ND	2	85	4
trans	0.76	0.26	DCN	CH <sub>3</sub> CN	4	ND	tr <sup>b</sup>	ND	95	tr
cis	0.76	0.26	DCN	CH <sub>3</sub> CN	ND	tr	ND	tr	98	tr
trans	0.13	0.25	(Ar) <sub>3</sub> N <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub> <sup>c</sup>	1	ND	tr	ND	99	tr
cis	0.10	0.23	(Ar) <sub>3</sub> N <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	ND	ND	ND	ND	100	ND
trans	0.76	0.26	Ph <sub>2</sub> CO	C <sub>6</sub> H <sub>6</sub>	ND	ND	tr	ND	93	7
cis	0.76	0.26	Ph <sub>2</sub> CO	C <sub>6</sub> H <sub>6</sub>	tr	ND	tr	ND	90	10
trans	3.1	9.8	thermal	none <sup>d</sup>	2	ND	3	ND	95	tr
cis	3.1	9.8	thermal	none <sup>d</sup>	ND	2	ND	tr	97	ND

<sup>a</sup>ND: no peak is detected by capillary GC with the retention time corresponding to this product. <sup>b</sup>Tr: A small peak in the capillary GC trace with the proper retention time is observed, but it represents less than 1% of the product mixture. The error in the relative yields is  $\pm 5\%$  of the reported value. <sup>c</sup>This experiment was run under the radical cation Diels–Alder conditions described by Bauld and co-workers<sup>4</sup> but modified to contain 0.03 M 2,6-di-*tert*-butyl-4-methylpyridine as recommended by Gassman and co-workers.<sup>5</sup> <sup>d</sup>The experiment was run with degassed, sealed tubes of the reactants kept at 180 °C for 40 h.

possible significance beyond the reactions described herein since we demonstrated recently that the triplex process is not restricted to aryl-substituted olefins.<sup>13</sup> The results are summarized in Table I.

The triplex procedure provides a practical route for the preparation of substituted bicyclo[2.2.2]octenes. The TCA-sensitized cycloaddition of *trans*- $\beta$ -methylstyrene (0.17 g) to CHD in dioxane solution gives endo-trans adduct 2a in 75% yield (by gas chromatography) at 50% conversion. Similarly, endo-cis adduct 2b may be obtained in 50% crude yield. The adducts may be isolated simply by distillation of the crude photolysis mixture.

It has been difficult to define the mechanism of the triplex Diels–Alder reaction with certainty. In general, both diene and dienophile components quench the excited singlet state of the sensitizer. This leads to ambiguity of order in the structure of the ternary species that must precede adduct formation: [Sens·Diene·Dienophile] or [Sen·Dienophile·Diene]. Results from the present study provide additional support for the latter formulation. The fluorescence of TCA or DCN is quenched by the methylstyrenes at approximately the diffusion-limited rate in benzene or *p*-dioxane solutions. The quenching process leads to the radical anion of DCN, detected by time-resolved spectroscopy, in acetonitrile solution but not in dioxane or benzene.<sup>14</sup> An exciplex of DCN and *trans*- $\beta$ -methylstyrene is detected by its emission ( $\lambda_{\text{max}} = 450$  nm) in benzene solution. Significantly, the exciplex emission of DCN and the styrene is quenched by CHD ( $k_{\text{obsd}} = 9.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). These findings require formation of a ternary complex with the structure [Sens·Dienophile·Diene] as an intermediate or transition state, but, of course, do not prove that this triplex is on the reaction path leading to the cycloadduct. Finally, we note that the increased yield of CHD dimers when DCN is the sensitizer may be attributed to formation of the diene triplet, a process forbidden energetically when TCA is the catalyst.

The stereochemical findings reported herein are of significance mechanistically and for application of the triplex procedure to synthetic organic chemistry. These cycloadditions give primarily endo adducts with essentially complete retention of configuration of the dienophile. The decrease in endo selection for the *cis*-styrene may be a consequence of steric crowding in the triplex where rigidity beyond that of the normal Diels–Alder transition state is presumed because of “back side” contact between the dienophile and the sensitizer. The stereospecificity provides convincing evidence that the reaction sequence does not proceed through a “one-bond” intermediate where rotation to another conformation is faster than the formation of the second bond.<sup>15</sup>

In summary, irradiation of a benzene or dioxane solution containing a cyano-substituted sensitizer, 1,3-cyclohexadiene, and *cis*- or *trans*- $\beta$ -methylstyrene gives mainly endo-6-methyl-5-phenylbicyclo[2.2.2]oct-2-enes with complete retention of styrene configuration in both cases. These reactions occur in useful yield and offer a unique, convenient route for the cycloaddition of an electron-rich diene to an electron-rich dienophile. The mechanism of these reactions is consistent with the triplex Diels–Alder hypothesis.

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(15) Interestingly, photolysis under radical cation conditions gives Diels–Alder-like adducts with predominantly retained dienophile configuration but in very small amounts. Apparently, under these conditions the methylstyrene radical cation isomers do not interconvert.<sup>16</sup>

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