

- center and substituent takes on special importance as in σ^+ and σ^- correlations and that $\epsilon \sim 0.65$ corresponds to a σ^o correlation.
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 - (21) Implicit in this study is the assumption of similar transition states in reactions 1, 2, and 3. The high regioselectivity of each reaction, the comparable rates of cycloadditions (Table III) and activation parameters (Table I), and the observation of good Hammett correlations (a not-too-common observation in 1,3-dipolar additions) provide justification of this assumption.
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 - (30) The relative rates of addition of phenyl azide to 1-ethoxy-, 1-morpholino-, and 1-pyrrolidinocyclopentene are 1:5300:230,000, respectively.⁹ The rates of addition of phenyl azide to 1-heptene and *n*-butyl vinyl ether differ by a factor of less than 2.⁸ Electron-withdrawing substituents on the aryl azide appear to magnify the rate difference; ethyl vinyl ether adds picryl azide 290 times faster than 1-pentene.⁷
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Cycloaddition. XVII. The Twelve Products of Photosensitized Addition of 1-Chloropropene to Cyclopentadiene

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cis- and *trans*-1-chloropropene have been added to cyclopentadiene both thermally at 200° and with β -acetophenone as a photosensitizer. As in other similar cases, the thermal reaction is a stereospecific Diels–Alder process. The photosensitized cycloaddition leads to mixtures of the same four 1,4 and eight 1,2 cycloadducts from both geometrical isomers of 1-chloropropene. Structures were established by a set of syntheses, identities, and correlations involving the thermal and photosensitized cycloadducts of 1,1-dichloropropene to cyclopentadiene, their dechlorination with tributyltin hydride, catalytic hydrogenation of the bicyclo[3.2.0]heptenes to the bicycloheptanes, and close comparison of NMR spectra.

In connection with our studies of cycloaddition reactions proceeding through biradical intermediates, we have studied the thermal and photosensitized cycloaddition of both *cis*- and *trans*-1-chloropropene to cyclopentadiene. This paper describes the isolation and identification of the products of those reactions.

Results

Isolation of Pure *cis*- and *trans*-1-Chloropropene. Commercial technical grade "1-chloropropene" (Columbia Organic Chemicals Co., Inc., Columbia, S.C.) as received was a mixture of about 10% 2-chloropropene, bp 23–24°, 25% *cis*-1-chloropropene, bp 31–32°, and 65% *trans*-1-chloropropene, bp 35–36°.²

Several workers have separated the above compounds by distillation and VPC, and established the structures of the *cis* and *trans* materials by NMR,³ ir correlation,^{4a} and dipole moment.^{4b}

Isolation of pure *cis*- (98+%) and *trans*-1-chloropropene (98+%) was accomplished by distillation using a spinning band column. Because of the great difficulty of the separation, however, a mixture consisting of 15% *cis* and 85% *trans* was used for generating photoadduct mixtures for preparative VPC.

Isolation and Identification of the 1,4 Adducts. The 1,4 adducts of cyclopentadiene and *cis*- and *trans*-1-chloropropene were produced by thermal reaction of a mixture

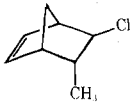

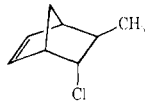
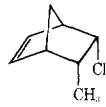
of the 1-chloropropene isomers (15:85, respectively) with cyclopentadiene at 200° in a sealed tube. VPC analysis of the product on a β,β' -oxydipropionitrile (β,β' -ODPN) column indicated the presence of four peaks of retention times greater than those of dicyclopentadiene. From pure *trans*-1-chloropropene (99+%) and cyclopentadiene, olefin was recovered unisomerized and the product mixture consisted of dicyclopentadiene and two fractions (ratio 67.5:32.5) of retention time corresponding to the first and third peaks in the chromatogram from the mixed olefin isomers and cyclopentadiene. Therefore the first and third peaks correspond to the thermal *trans*-1-chloropropene–cyclopentadiene adducts and the second and fourth peak correspond to the *cis*-1-chloropropene–cyclopentadiene adducts. Each component in the *cis*, *trans* thermal reaction was collected preparatively on β,β' -ODPN.

The assignment of the structures is based chiefly on the NMR spectra and some chemical evidence to follow. The assumptions relied upon were (a) 1,4 Diels–Alder addition with retention of configuration in common with dichloroethylene^{4a} and alkylethylenes;⁵ (b) that endo substituents (proton⁶ or methyl⁵) are shifted upfield (shielded) relative to exo substituents; (c) that C₇ protons couple in a W pattern with endo protons.^{6a,7}

The NMR peaks of the Diels–Alder addition compounds are listed in Table I with their structural assignments.

Chemical evidence that further confirms the identity of

Table I

VPC peak	Compd	NMR		Mult	Assignment	J, Hz
		τ	Number of H's			
$\Delta 1$		9.05	3	d	CHCH ₃	7
		8.30	1	d of q	Anti C ₇ H	9, 2
		8.04	1	d of t	Syn C ₇ H	9, 1
		7.77	1	t of q	CHCH ₃	7, 3
		7.35	1	m	Ring junction	
		7.13	1	m	Ring junction	
		6.88	1	d of d	CHCl	3, 2
$\Delta 2$		3.90	2	m	Olefin	
		8.85	3	d	CHCH ₃	7
		8.49	1	d of qn	Anti C ₇ H	9, 2
		8.10	2	m	Syn C ₇ H, CHCH ₃	
		7.55	1	m	Ring junction	
		7.08	1	m	Ring junction	
		6.15	1	d of d	CHCl	7, 2
		4.02	1	d of d	Olefin	6, 3
		3.75	1	d of d	Olefin	6, 3
$\Delta 3$		8.82	3	d	CHCH ₃	7
		8.44	3	m	CHCH ₃ , C ₇ H's	
		7.56	1	m	Ring junction	
		6.97	1	m	Ring junction	
		6.26	1	t	CHCl	3
		3.94	1	d of d	Olefin	6, 3
		3.64	1	d of d	Olefin	6, 3
$\Delta 4$		9.13	3	d	CHCH ₃	7
		8.68	1	d	Syn C ₇ H	9
		8.46	1	d of t	Anti C ₇ H	9, 2
		7.68	1	m	CHCH ₃	7
		7.28	1	m	Ring junction	
		6.89	1	m	Ring junction	
		5.56	1	d of d	CHCl	8, 3
3.85	2	m	Olefin			

the thermal 1,4 adducts is based on the known *exo* hydride donation preference of tri-*n*-butyltin hydride.⁸

The thermal reaction of 1,1-dichloropropene and cyclopentadiene (200°, 24 hr) yields material that on isolation gives a single peak on several VPC columns. The NMR, however, displays two methyl doublets at τ 8.99 and 8.73 in the ratio of about 60:40 and therefore the material consists of at least two separate compounds, presumably *exo*- and *endo*-5,5-dichloro-6-methyl-2-norbornene. Reduction of this mixture with 1 equiv of tri-*n*-butyltin hydride yields a mixture of compounds. VPC analysis on β,β' -ODPN indicates the results listed in Table II on the basis of the above NMR assignments.

The two compounds which predominate are the two with the *endo* chloro structures in accord with *exo* hydride donation by the tin hydride. The ratio of *exo* donation of a hydrogen atom to *endo* donation in the *endo* methyl compounds is 9.7:1. This corresponds to a small *trans/cis* directive factor of 1.3 by neighboring methyl, superposed on a normal *exo/endo* preference of 7.4.

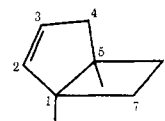
The thermal reaction of 1,1-dichloropropene and cyclopentadiene on the basis of the above analysis yields a 58:42 mixture of 5,5-dichloro-*endo*-6-methyl-2-norbornene and 5,5-dichloro-*exo*-6-methyl-2-norbornene. The ratio corresponds to the 60:40 ratio of the methyl doublets at τ 8.99 and 8.73, with the *endo* material again being the more upfield of the two.

Designation of Isomers. The 12 isomeric cycloadducts obtained from photosensitized addition of the 1-chloropropenes to cyclopentadiene are resolved by β,β' -ODPN and TCEP columns into nine fractions, the order of elution

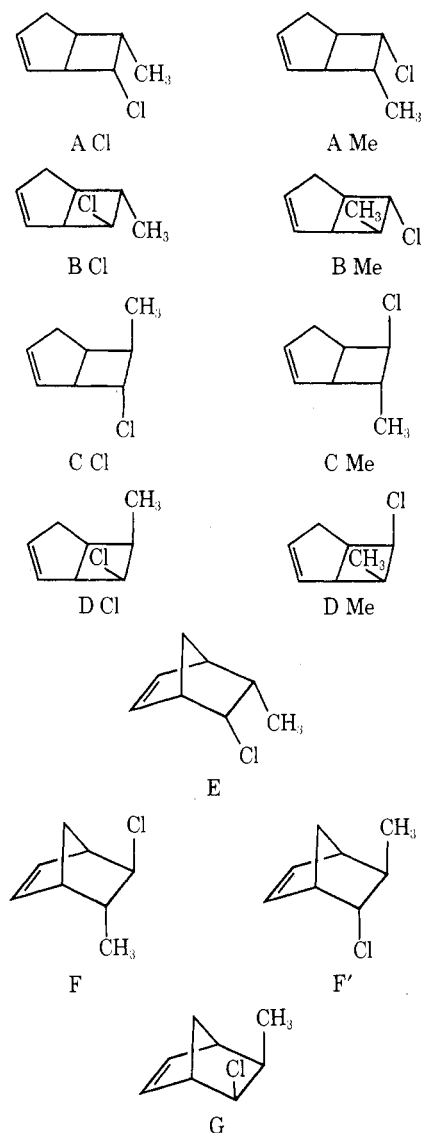
Table II
Results of Reaction of *exo*- and *endo*-5,5-Dichloro-6-methyl-2-norbornene with (*n*-Bu)₃SnH

	$\Delta 1$	$\Delta 2$	$\Delta 3$	$\Delta 4$
% reduced material	5.4	6.3	36.2	52.1

being the same on both columns. In discussing the steps in the identification of the isomers, the VPC fractions will be named *h* ν 1 through *h* ν 9, with no implication as to the number of components in each fraction. In the course of the study the isomers will be matched with the possible four 1,4 cycloadducts (Table I) and the eight 1,2 cycloadducts. Since these correspond in structure and configuration to the 2-butene cycloadducts previously studied,^{9,10} the structures are designated by an adaptation of the same scheme previously used (Scheme I). For example, the names A Cl or A Me refer to structure A with the chlorine and methyl, respectively, at position 7. For consistency with other papers from this laboratory we depict the bicyclo[3.2.0]hept-2-enes with the 4 ring in a horizontal plane and the 5 ring joined to it along the left side, inclined upward, with the double bond in front.



Scheme I
The 12 Photocycloadducts of 1-Chloropropene to Cyclopentadiene



Synthesis. The synthetic and correlative sequence adopted is shown in Scheme II.

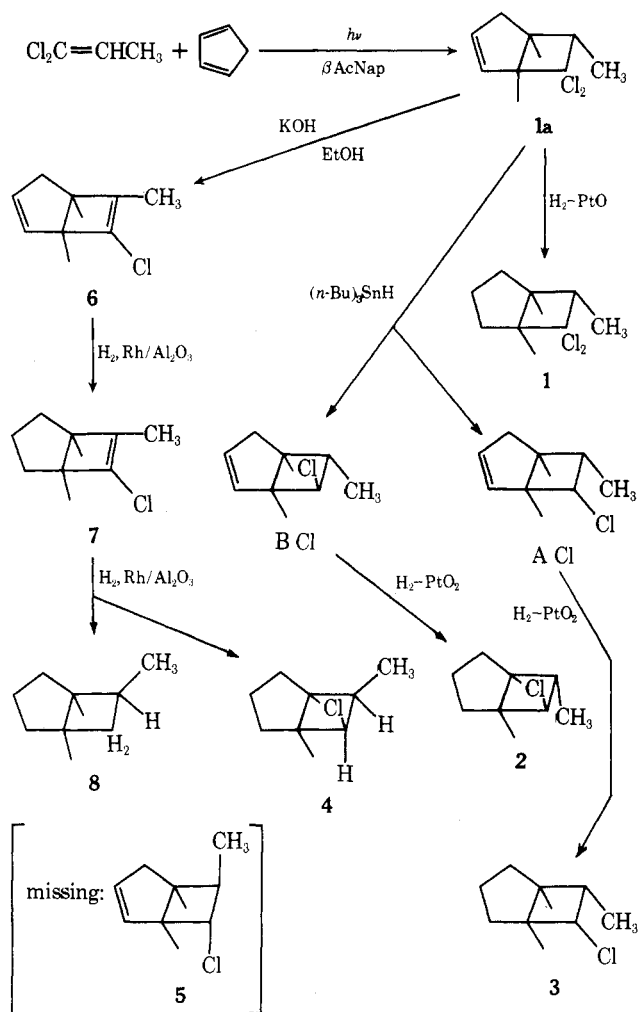
Photosensitized Cycloaddition of 1,1-Dichloropropene and Cyclopentadiene. The photoreaction of 1,1-dichloropropene and cyclopentadiene was carried out with β -acetonaphthone as sensitizer. The ratio of cross adducts to photodicyclopentadiene was about 1:6. The cyclopentadiene dimers were separated from the cross adducts by distillation with the dicyclopentadienes distilling at the lower temperature. The higher boiling fraction revealed four peaks on VPC analysis (Carbowax 20 M column).

Their relative amounts in order of increasing retention time were 61.8:27.8:1.1:9.2. Peaks 1, 2, and 4 (comprising 99% of the mixture) were each collected preparatively.

The last peak was not of cross-adduct origin, since it did not contain any olefinic hydrogens. It was tentatively identified as photodimers of 1,1-dichloropropene.

The second peak collected corresponded in retention time to the mixture of 1,4 adducts previously obtained in the thermal reaction of 1,1-dichloropropene and cyclopentadiene. The NMR indicated two doublets centered at τ 8.99 and 8.73 in the ratio of 2.6:1 and therefore a mixture of the endo and exo methyl 1,4 compounds in that ratio. This

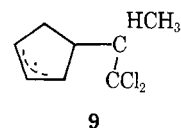
Scheme II



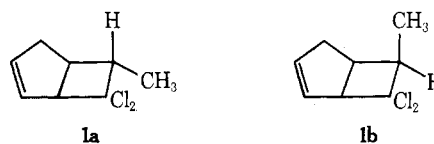
fraction also contained about 5% impurity from peak 1 of the photomixture.

Peak 1, which comprised about 62% of the mixture and 68% of the cross adducts, appeared to be a single compound. It had a single methyl doublet centered at τ 8.82, a multiplet at τ 7-8, a broad peak at τ 6.2, and a sharp singlet at τ 4.11 in the ratio of 3:4:1:2, respectively. It was assigned the structure 1a, 7,7-dichloro-6-exo-methylbicyclo[3.2.0]hept-2-ene, for several reasons.

Accumulated experience indicates that a chlorine atom on a C=C double bond is more activating than a methyl group toward capture of a cyclopentadiene triplet, and more stabilizing to a free radical at the carbon to which the Cl is attached. There is no doubt that the prevalent biradical,^{11,12} in photocycloaddition of 1,1-dichloropropene to cyclopentadiene will have the structure 9, and the strongly

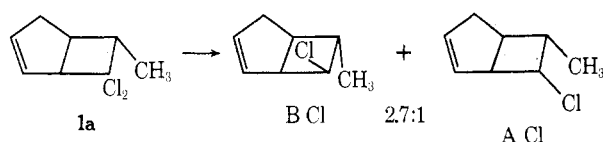


predominant *non*-1,4 adduct must therefore be either 1a or 1b.



The far downfield position of the methyl NMR signal, τ 8.83, supports the *exo* assignment which would be made on the basis of experience with photosensitized cycloadditions. The assignment of structure **1a** is also uniquely compatible with the reactions of this adduct.

Compound **1a** was reduced with tri-*n*-butyltin hydride (1.1 equiv). Two monochloro materials were obtained in about 80% yield. The isomers were in the ratio of 2.7:1 and were therefore assigned structures B Cl and A Cl, respectively. The well-known *exo* preference for hydrogen atom donation by tri-*n*-butyltin hydride to a free radical is the basis of the assignment.¹³



The mass spectra of both B Cl and A Cl indicated the correct molecular weights and the nmr indicated the correct hydrogen ratios. The methyl resonances were shifted only slightly upfield from **1a** to τ 8.85 and 8.84, respectively. The downfield hydrogen at the ring junction shifted upfield in both cases to τ 6.42 and 6.70, respectively, as would be expected on removing an electronegative substituent. There appeared in each a new signal attributable to a chloromethyl hydrogen which is split by two adjacent hydrogens. Both B Cl and A Cl can be hydrogenated quantitatively over Adams catalyst in ethyl acetate solvent, to compounds **2** and **3**, respectively. The mass spectra of **2** and **3** indicated the correct molecular weights and the NMR spectra indicate no olefin resonances, a chloromethyl hydrogen and a ring junction hydrogen (α to the chlorine), and a doublet methyl group, as well as eight indistinguishable saturated hydrogens.

Compound **1a** can also be hydrogenated and the product **1** has a molecular weight indicating the addition of two hydrogens. The NMR shows a doublet methyl group at τ 8.78 and a single broad hydrogen at τ 6.75. When **1** is reduced with 1 equiv of tri-*n*-butyltin hydride, **2** and **3** are produced in the ratio of 4.7:1. The increased stereoselectivity is to be expected since the *endo* side of **1** is now more hindered than the *endo* side of **1a**. This further confirms the *endo-exo* relationship to the chlorines in compounds B Cl and A Cl.

Compound **1a**, the dichloro-*exo*-methyl adduct, was dehydrohalogenated in KOH-ethanol to the diene **6** in about 70% yield. The mass spectrum of **6** indicated a molecular weight of 140, corresponding to loss of HCl from **1a**. The NMR showed two distinct olefinic hydrogens at τ 4.15 and 4.3, two distinct ring-junction hydrogens at τ 6.7 and 6.85, two allylic hydrogens at τ 7.3, and an olefinic methyl signal at τ 8.23. The methyl signal appeared to be a triplet coupled to two hydrogens with a coupling constant of about 1 Hz.

In ethyl acetate over platinum oxide **6** was hydrogenated to a single material with a molecular weight of 110 and an NMR spectrum whose only distinctive feature was an upfield methyl doublet at τ 9.17. Since it is known that Pt in polar solvents can hydrogenolyze vinylic chlorines, this reduced material is probably **8**, 6-*endo*-methylbicyclo[3.2.0]heptane.¹⁴

Hydrogenation of **6** in hexane with 5% Rh/Al₂O₃ under about 3 atm produced three materials, all separable by VPC. Besides 55% of **7** and 5% of **8** there was 40% of a product assigned the structure **4**, 6-*endo*-chloro-7-*endo*-methylbicyclo[3.2.0]heptane, on the basis of *exo* hydrogenation, a molecular weight of 144 with one chlorine, an NMR spec-

trum with an upfield methyl doublet (τ 9.07), and a downfield chloromethyl hydrogen at τ 5.25.

The above sequence constitutes a chemical proof of the configuration of the methyl group in **1a**. Since **2** and **3** represent the possible configurations about the chloromethyl carbon with the unchanged fixed methyl configuration of **1**, and **4** has the *endo* methyl configuration (*exo* hydrogenation) with a specific chloro configuration, and since **2** and **3** are distinct from **4**, their methyl configurations must be different from that of **4** and hence they must have an *exo*-methyl configuration. Thus **1a** must have an *exo*-methyl configuration in accord with its assignment and the assignments of the structures based on it.

With the four possible 1,4 adducts, Δ 1-4, the two 1,2 adducts, B Cl and A Cl, and the three hydrogenated 1,2 adducts, **2**, **3**, and **4**, it became possible to isolate and identify the compounds produced in the photoreaction of 1-chloropropene and cyclopentadiene.

Isolation of Photoadducts. The photosensitized reaction of a mixture of 1-chloropropene isomers and cyclopentadiene at about 0-10° produced a mixture of cyclopentadiene photodimers and cross-adducts. As has been mentioned, analysis of the mixture on a β,β' -ODPN column or TCEP column indicated nine peaks, *h* ν 1-9, in addition to photodimers of cyclopentadiene, which had shorter retention times than the cross-adducts. Fractions *h* ν 1-6 were collected preparatively on a 20 ft \times 0.25 in. column of 20% β,β' -ODPN on 60/80 mesh Chromosorb P at about 95°. The fractions *h* ν 7-9 were collected on a 20 ft \times 0.25 in. column, 20% TCEP on 60/80 mesh Chromosorb P at about 120°. The latter peaks were very small and of very long retention times. The eventual analysis was performed at higher temperature on a TCEP column and it was shown by injection of the collected samples from the β,β' -ODPN collections that the relative retention times as well as separations were identical on the two columns.

The peak *h* ν 3 could be separated into two closely overlapping peaks only on a 0.125 in. analytical TCEP column. On all 0.25 in. and preparative columns the best that could be obtained was a somewhat unsymmetrical peak, and hence in the collected material no appreciable separation of *h* ν 3 was obtained.

From the NMR spectra of the collected materials it was immediately obvious that some peaks were pure compounds and others were mixtures. The criterion used in the above analysis was the appearance of a single methyl doublet and a single chloromethyl hydrogen. By this criterion *h* ν 1, *h* ν 2, and *h* ν 6-9 were all single-component peaks. The peak *h* ν 1 was pure Δ 1(F), peak *h* ν 6 was pure B-Cl, and peak *h* ν 7 was pure Δ 4(E). In addition the peaks *h* ν 3-5 also contained as one of their components some of the compounds previously synthesized. The peak *h* ν 3 consisted of A-Cl as the major component with one other minor component. The peak *h* ν 4 contained an unknown material as the major component and Δ 2(G) as the only other component. The peak *h* ν 5 contained Δ 3(F') and one other component.

Hydrogenation reduces the eight possible 1,2 adducts to four, of which three have been independently synthesized. In addition, given compounds A Cl and B Cl, it is immediately possible to assign their double bond isomers by finding the other compounds that hydrogenate to **2** and **3**.

Hydrogenation of *h* ν 5 gives two overlapping peaks on TCEP. Each was collected on the 0.25 in. TCEP column. The first peak consisted of nearly pure **2** (impurity being the second peak) and the second peak was the hydrogenation product of Δ 3(F'). Since *h* ν 5 consisted of Δ 3 and an unknown adduct, the unknown material must have been C Me, 6-*endo*-chloro-7-*exo*-methylbicyclo[3.2.0]hept-2-ene.

Table III
Identities of the Hydrogenated VPC Peaks^a

VPC peak	Product
<i>hν</i> 2	5
<i>hν</i> 3	3
<i>hν</i> 4	5 + dihydro-G
<i>hν</i> 5	2 + dihydro-F
<i>hν</i> 8	4
<i>hν</i> 9	4

^a Platinum oxide, 1 atm hydrogen, 25°, in ethyl acetate.

*hν*3 was hydrogenated to give pure 3 with no other compounds present as judged by VPC or NMR. The other minor component therefore must be A Me, the double bond isomer of A Cl, 6-*exo*-chloro-7-*exo*-methylbicyclo[3.2.0]hept-2-ene.

When the pure materials *hν*8 and *hν*9 are hydrogenated they yield the identical product 4 and are therefore the two possible olefin isomers from which 4 can be derived, namely D Cl and D Me, whose structural assignments will be discussed.

The only remaining unidentified materials are *hν*2 (a pure compound) and *hν*4, which contains as a minor component Δ2(G) plus an unidentified material. When *hν*2 is hydrogenated it yields a single material, 5. The peak *hν*4 gives on hydrogenation two peaks on TCEP in the approximate ratio 3:1. The larger peak was collected and shown to be identical with 5, the hydrogenation product from *hν*2. The second peak had the same retention time as the hydrogenation product of Δ2 since Δ2 was a component of the original mixture.

The above is summarized in Table III.

NMR Assignments. The position of the ring-junction hydrogen in the NMR that is both allylic and α to the chloromethinyl group offers a means of differentiating between two double-bond isomers in this series of compounds. Allylic character and proximity to -CHCl- have deshielding effects that are approximately additive. Within any two double bond isomers the shielding or deshielding effects of *exo* and *endo* adjacent chlorines or methyl will be fixed, since the configurations of the chlorine and methyl are identical. Within isomeric pairs there are four kinds of ring-junction hydrogens. They are (a) α to methylmethinyl group and nonallylic; (b) α to chloromethinyl group and nonallylic; (c) allylic and α to methylmethinyl group; (d) allylic and α to chloromethinyl group.

The deshielding one would expect for the above ring-junction hydrogens (for a fixed *endo,exo* chlorine-methyl series) would be d > c ≅ b > a. Hence it is possible to assign the allylic α chloromethinyl hydrogen given the NMR spectra of the two isomers, since it is simply the most downfield hydrogen, other than the chloromethinyl hydrogen, from which it can be easily differentiated. For example, B Cl has its most downfield saturated hydrogen other than the chloromethinyl hydrogen at τ 6.42. The most downfield ring-junction hydrogen in B Me is at τ 6.8, a difference of 0.38 ppm.

The compounds *hν*8 and *hν*9 are double bond isomers since they both hydrogenate to 4. The compound *hν*9 has its most downfield ring-junction hydrogen at τ 6.3, clearly differentiated from the other saturated hydrogens. The compound *hν*8 has an indistinguishable collection of hydrogens at τ 6.6-7.7, two of which are its ring-junction hydrogens and both of which are considerably more shielded than τ 6.3. Therefore *hν*9 has a hydrogen which is both allylic and α to a chloromethinyl group. On this basis it can be assigned structure D Cl, 7-*endo*-chloro-6-*endo*-methyl-

Table IV
NMR Characterization of Hydrogenation Products 2-5

Compd	Position of chloromethinyl hydrogen, τ	No. cis adjacent alkyl groups and ring
5	6.62	2
3	6.00	1
2	5.99	1
4	5.25	0

Table V
Identities of the Components of the VPC Peaks on TCEP Produced in the Photosensitized Cycloaddition of Cyclopentadiene and *cis*- and *trans*-1-Chloropropene

VPC peak	Identity
<i>hν</i> 1	F
<i>hν</i> 2	CCl
<i>hν</i> 3	ACl + AMe
<i>hν</i> 4	G + BMe
<i>hν</i> 5	F' + CMe
<i>hν</i> 6	BCl
<i>hν</i> 7	E
<i>hν</i> 8	DMe
<i>hν</i> 9	DCl

bicyclo[3.2.0]hept-2-ene, and *hν*8 can be assigned structure D Me, 6-*endo*-chloro-7-*endo*-methylbicyclo[3.2.0]hept-2-ene.

The assignment of structure 5 to the hydrogenation product from *hν*2 was made for several reasons. First, it was not identical with 4, the diendo compound, and did not correspond to either 2 or 3, the *exo*-methyl possibilities. Second, its upfield methyl doublet (τ 9.03) is closer to that of 4 (τ 9.07) than that of 2 or 3 (τ 8.84 and 8.81). Hence, since it must have an *endo* methyl group and it is not 4, it must be 5. Also, since a methyl group is shielding relative to a hydrogen and *endo* hydrogens are more shielded than *exo* hydrogens, the chloromethinyl hydrogen of 5 should be the most shielded of all the chloromethinyl hydrogens, the effects being additive, in the series 2, 3, 4, and 5. In Table IV are listed the positions of the chloromethinyl hydrogens in the NMR for the above compounds; also listed are the number of cis adjacent alkyl groups in each case.

The position of the ring-junction hydrogen in the nmr that is both allylic and α to the chloromethinyl group again permits the assignment of structure to the two compounds that hydrogenate to 5. The most downfield ring-junction hydrogen is *hν*2 at τ 6.6, and it is clearly differentiable from the other allylic hydrogens. On the other hand, in the major component of *hν*4 the corresponding hydrogens are more upfield (above τ 6.7) and not clearly differentiable. Therefore *hν*2 has the structure C Cl, 7-*exo*-chloro-6-*endo*-methylbicyclo[3.2.0]hept-2-ene, and the 1,2 component of *hν*4 has the structure B Me, 6-*exo*-chloro-7-*endo*-methylbicyclo[3.2.0]hept-2-ene.

In Table V are listed the final assignments for *hν*1-9, and in Table VI are listed the nmr peaks of the 1,2 adducts.

Experimental Section

Thermal Reaction of Cyclopentadiene and a Mixture of *cis*- and *trans*-1-Chloropropene. The olefin mixture (85.4% *trans*, 14.6% *cis*, 7.2 g, 0.094 mol) and freshly distilled cyclopentadiene (3.85 g, 0.058 mol) was degassed and sealed in a thick-walled tube. The tube was heated in a tube oven to 200° for 24 hr and then let cool for 7 hr. The tube was opened and some of the material was

Table VI

Compd	NMR, τ	H's	Mult ^a	Assignment	J, Hz
DC1	8.96	3	d	Methyl	7
	7.60	2	m	Methylene	
	7.10	2	m	Bridge-methinyl	
	6.3	1	m	Bridge- α CHCl-allyl	
	5.3	1	t	CHCl	
	4.2	2	m	Olefinic	
DMe	9.06	3	d	Methyl	7
	6.5-7.9	5	m	Bridge-allylic-methinyl	
	5.25	1	t	CHCl	
	4.3	2	m	Olefinic	
	8.85	3	d	Methyl	
BC1	7.2-8.0	4	m	Bridge-allylic-methinyl	8
	6.4	1	m	Bridge- α CHCl-allyl	
	6.0	1	t	CHCl	
	4.15	2	s (br)	Olefinic	
CMe	8.8		d	Methyl	7
	6.7-7.9		m	Bridge-allylic-methinyl	
	5.85		t	CHCl	
	4.2		s (br)	Olefinic	
	8.85	3	d	Methyl	
AC1	7.2-8.0	4	m	Bridge-allylic-methinyl	8
	6.7	1	m	Bridge- α CHCl-allyl	
	5.85	1	d of d	CHCl	
	4.2	2	s (br)	Olefinic	
AMe	8.8		d	Methyl	7
	7.2-8.0		m	Bridge-allylic-methinyl	
	5.9		m	CHCl	
	4.2		m	Olefinic	
CC1	8.98	3	d	Methyl	7
	6.9-7.7	4	m	Bridge-allylic-methinyl	
	6.6}	2	m	Bridge- α CHCl-allyl	
	6.5}		d of d	CHCl	
	4.2	2	m	Olefinic	
BMe	8.95		d	Methyl	7
	6.8-8.0		m	Bridge-allylic-methinyl	
	6.5		d of d	CHCl	
	4.2		s	Olefinic	

^a s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

analyzed on a 0.25 in. \times 16 ft 20% TCP column in order to ascertain the purity of the recovered olefin. It was found to be the same as the initial mixture. The olefin was distilled off and the residue was bulb-to-bulb distilled. Analysis and collection of the material was performed on a 0.25 in. \times 20 ft 20% β,β' -ODPN column at 90°, flow rate about 80 cm³/min. The retention times of the four compounds were 69.4, 74.6, 101.4, and 132.2 min.

Thermal Reaction of *trans*-1-Chloropropene and Cyclopentadiene. The reaction was conducted as described above with 4.0 g (0.06 mol) of cyclopentadiene and 5.0 g (0.065 mol) of *trans*-1-chloropropene (99.25% by VPC). The reaction was carried out at 180° for 24 hr. The tube was opened and 4.8 g of olefin was recovered which was still about 99+% pure by VPC. VPC analysis of the product after bulb-to-bulb distillation indicated largely dicyclopentadiene but there were two significant peaks with retention times of 68.3 and 99.8 min in the ratio 67.5:32.5.

Photosensitized Cycloaddition of 1-Chloropropene and Cyclopentadiene. The mixture of 1-chloropropenes (85% *trans*, 15% *cis*, 185 g, 2.42 mol), cyclopentadiene (4 g, 0.061 mol), and β -acetophenone (2 g, 0.012 mol) was irradiated at about 10° in a water bath by means of a water-jacketed 450-W Hanovia lamp. The solution was stirred by nitrogen bubbling through. Every 4 hr another 4 g (0.061 mol) of cyclopentadiene was added (for a total of 20 g, 0.3 mol) and the total irradiation time was 20 hr. The excess olefin was distilled off and the residue was bulb-to-bulb distilled, yielding about 27 g of material. VPC on β,β' -ODPN indicated about 75% dicyclopentadiene and 25% material consisting of six major peaks (78°, 75 cm³/min, on 0.25 in. 20% β,β' -ODPN, 25 ft) of retention times of 97.2, 106, 119.6, 130, 146.2, and 157.6 min, and three minor peaks of longer retention time. The six major peaks were

collected preparatively on β,β' -ODPN, and the three minor peaks were collected on TCEP.

Thermal Reaction of 1,1-Dichloropropene and Cyclopentadiene. A solution of 1,1-dichloropropene (11.1 g, 0.1 mol) and cyclopentadiene (3.3 g, 0.05 mol) with some hydroquinone (0.2 g) was sealed in a thick-walled glass tube after degassing and heated to 200° for 24 hr. The tube was then cooled and opened, the excess olefin was removed on the rotovac, and the residue was bulb-to-bulb distilled at about 0.005 mm. VPC on Carbowax indicated mostly dicyclopentadiene, but there was also a peak of longer retention time that was collected. The VPC retention time was identical with that of the second peak in the photoreaction of the two above components and displayed two methyl doublets in the ratio of 60:40 at τ 8.99 and 8.73, respectively.

Photoreaction of 1,1-Dichloropropene and Cyclopentadiene. Synthesis of 7,7-Dichloro-6-exo-methylbicyclo-[3.2.0]hept-2-ene (1a). A solution of β -acetophenone (4 g, 0.024 mol) in 1,1-dichloropropene (300 g, 2.7 mol) was irradiated with a 450-W Hanovia high-pressure lamp under N₂ with stirring at about 15-20°. To this solution was added, at about 4-hr intervals, 10-g (0.15 mol) portions of freshly distilled cyclopentadiene to a total of about 40 g (0.6 mol) over the course of about 16 hr, and the irradiation was continued overnight to bring the total irradiation time to about 22 hr. The excess dichloropropene was distilled off and the residue (about 40 g) was distilled under vacuum (18 mm) through a 12-in. Vigreux column. The DCPD came off first at about 66-75° followed by the cross adducts at 88-89° (6 g, 0.03 mol). VPC of the undistilled material on Carbowax indicated a DCPD/cross adduct ratio of about 6:1. The distilled material indicated four peaks on Carbowax 20M (10%, 0.125 in., 150°, 40 psi,

flow 2.6) of retention times of 30, 33.5, 40, and 42.5 min. The first, second, and fourth peaks were collected preparatively. Exact mass for **1a**: theory, 176.0159; found, 176.0146.

Reaction of (*n*-Bu)₃SnH and Compound **1a. Synthesis of *exo*-6-Methyl-*endo*-7-chlorobicyclo[3.2.0]hept-2-ene (**B Cl**) and *exo*-6-Methyl-*exo*-7-chlorobicyclo[3.2.0]hept-2-ene (**A Cl**). A mixture of tri-*n*-butyltin hydride (0.429 g, 0.00147 mol) and **1a** (0.237 g, 0.00134 mol) in hexane was refluxed overnight under argon with stirring. The material was bulb-to-bulb distilled (0.005 mm). Evaporation and isolation gave a mixture of isomers by vpc (0.170 g, 0.0012 mol, 89%), **3a:2a** 27:73. The mixture also contained about 5% starting material and about 15% of a material of short retention time, seemingly hydrocarbon. The mixture was separated on β,β' -ODPN preparatively, to give pure **2a** and pure **3a**, of identical retention time with *h* ν 3 and *h* ν 6, respectively. Exact mass for **2a**: theory, 142.0549; found, 142.0546. Exact mass for **3a**: found, 142.0552.**

Reaction of Thermal Dichloropropene-Cyclopentadiene Adducts with (*n*-Bu)₃SnH. Formation of 1,4-Chloropropene Adducts. A mixture of the two thermal adducts from the dichloropropene-cyclopentadiene reaction in the ratio 60:40 endo:exo (0.156 g, 0.00089 mol), tri-*n*-butyltin hydride (0.290 g, 0.001 mol), and hexane was refluxed overnight under argon with stirring and then the material was bulb-to-bulb distilled at about 0.005 mm, giving the product mixture (0.124 g, 0.00088 mol, 99%). The analysis was performed on β,β' -ODPN.

6-Methyl-7-chlorobicyclo[3.2.0]hepta-2,6-diene (6). A solution of **1a** (0.5 g, 0.00282 mol) in 5 ml of EtOH with 2.0 g of KOH was refluxed for about 2 days until VPC indicated replacement of the starting material by a product of short retention time (15 min, 150°, 20M 10%, 0.125 in.). Dilution with about 50 ml of water, extraction with ether, drying the ether, and its evaporation yielded the product **6** (0.281 g, 0.002 mol, 71%). Collection on a preparative column gave pure material. Exact mass: theory, 140.0393; found, 140.0398.

Hydrogenation of 2a. Formation of *exo*-6-Methyl-*endo*-7-chlorobicyclo[3.2.0]heptane (2). A solution of **2a** (0.05 g, 0.00035 mol) with PtO₂ (0.001 g) in about 0.5 ml of ether was hydrogenated at room temperature and 1 atm for 24 hr, during which 9 ml of H₂ was absorbed, and the reaction then stopped. By VPC, starting material (retention time 40 min, β,β' -ODPN, 75°, 35 psi) had disappeared to be replaced by product (retention time 30.4 min). Evaporation of the ether after bulb-to-bulb distillation gave product **2** (0.035 g, 0.00025 mol, 70%) whose nmr displayed no vinyl hydrogens. Exact mass: theory, 144.0705; found, 144.0701.

Hydrogenation of 3a. Formation of *exo*-6-Methyl-*exo*-7-chlorobicyclo[3.2.0]heptane (3). A solution of **3a** (0.037 g, 0.00026 mol) and PtO₂ (0.002 g) in CH₂Cl₂ was hydrogenated at 1 atm of H₂ with stirring for 24 hr. The reaction could not be followed by VPC, since starting material and product had the same retention time. However, after 24 hr the material had taken up about 6.5 ml of hydrogen (about 100%) and stopped. The material was bulb-to-bulb distilled and the methylene chloride evaporated. The nmr of the product (0.027 g, 0.00018 mol, 75%) had no vinylic hydrogen signals. Exact mass: theory, 144.0705; found, 144.0711.

Hydrogenation of *h* ν 4. Formation of *endo*-6-Methyl-*exo*-7-chlorobicyclo[3.2.0]heptane (5). A solution of *h* ν 4 (0.0377 g, 0.00027 mol) was hydrogenated over PtO₂ (0.001 g) in ether in the usual manner. Starting material (retention time 36 min, β,β' -ODPN, 75°, 35 psi) was replaced by two peaks in the ratio of 68:32 (retention times 34.8 and 43.2 min). The largest component, **5**, was collected (0.012 g) and its time-averaged nmr spectrum taken by use of the HA-100 spectrometer for 3 hr. Exact mass: theory, 144.0705; found, 144.0709.

Hydrogenation of *h* ν 5. Formation of 2. A solution of 0.096 g of *h* ν 5 in ether was hydrogenated over PtO₂ (0.003 g) in the usual manner with the uptake of about 17 ml of hydrogen. Starting material was replaced by two peaks on TCEP (retention times 61.1 and 63.5 min). Isolation by filtration and evaporation gave product (0.085 g, 0.00059 mol, 87%). Vpc separation and collection indicated **2** as the first peak and the hydrogenation product of the 1,4-*endo*-chloro-*exo*-methyl adduct (dihydro-F') as the second peak.

Hydrogenation of *h* ν 2. Formation of 5. A solution of *h* ν 2 (exact mass: theory, 142.0549; found, 142.0547; 0.011 g, 0.000078 mol) and PtO₂ (0.001 g) in CCl₄ was hydrogenated in the usual manner, taking up about 2 ml of H₂, at which point the reaction stopped. The material was bulb-to-bulb distilled and isolated as CCl₄ solution. It was identified as **5** by NMR and ir.

Hydrogenation of *h* ν 3. Formation of 3. The photopeak *h* ν 3 (0.055 g, 0.00039 mol), which contained **A Cl** and another 1,2 prod-

uct by NMR to the extent of about 15%, was hydrogenated over PtO₂ (0.003 g) in ether, taking up about 10 ml of hydrogen over the course of about 24 hr. Bulb-to-bulb distillation and evaporation of the ether gave a product (0.048 g, 0.00034 mol, 87%) whose NMR and ir indicated it to be a single material, **3**.

Hydrogenation of 6. Formation of 6-Methyl-7-chlorobicyclo[3.2.0]hept-6-ene (7). The diene **6** (0.025 g, 0.00018 mol) was hydrogenated over PtO₂ (0.001 g) in about 0.5 ml of CCl₄. After about 8 hr the material had taken up about 3 ml of hydrogen and the uptake halted. Vpc on β,β' -ODPN indicated disappearance of starting material (retention time 20 min) and the appearance of a new peak (retention time 10 min), compound **7**. Exact mass: theory, 142.0549; found, 142.0556.

Hydrogenation of 6. Formation of *endo*-6-Methylbicyclo[3.2.0]heptane (8). The diene **6** (0.05 g, 0.00036 mol) was hydrogenated over PtO₂ (0.001 g) in about 0.5 ml of ethyl acetate with chlorobenzene as internal standard. After 2 hr the material had taken up about 11 ml of hydrogen (115% of theory) and then the uptake halted. VPC on Apiezon J (15%, 16 ft, 135°, 100 cm³/min) indicated complete disappearance of starting material (retention time 20 min) and appearance of a new peak (retention time 3.0 min) in about 95% yield based on chlorobenzene. The material was collected on the column (0.011 g, 28%). Exact mass: theory, 110.1096; found, 110.1092.

Hydrogenation of 6. Formation of *endo*-6-Methyl-*endo*-7-chlorobicyclo[3.2.0]heptane (4). The reaction was followed on β,β' -ODPN (90°, 0.125 in. \times 16 ft, 40 psi, flow rate 2.5). The diene **6** (0.1012 g, 0.00072 mol) in about 3-5 ml of hexane was hydrogenated in the Parr hydrogenator at 40 psi hydrogen over 5% Rh/Al₂O₃ (0.03 g). The starting material (retention time 19 min) had disappeared after 30 min, to be replaced by a compound of retention time 9.6 min previously demonstrated to be **8**. Sampling at 1-hr intervals indicated the appearance of a material of short retention time (2.9 min), **8**, and one of long retention time (34 min) at the expense of **8**. The reaction stopped with the composition listed in the discussion of results and could be forced to go no further. Centrifugation to remove catalyst, evaporation to remove solvent, and preparative VPC to remove impurities yielded pure **4** (0.016 g, 0.00011 mol, 32%). Exact mass: theory, 144.0705; found, 144.0708.

Hydrogenation of *endo*-6-Methyl-*endo*-7-chlorobicyclo[3.2.0]hept-2-ene (D Cl). The olefin, **D Cl** (exact mass: theory, 142.0549; found, 142.0554) isolated by preparative VPC as *h* ν 9 (0.027 g, 0.00019 mol) and PtO₂ (0.002 g) in about 0.2 ml of CCl₄ was hydrogenated under 1 atm of hydrogen. The material took up 4.5 ml (95%) in 4 hr and ceased further uptake. Isolation by bulb-to-bulb distillation and evaporation of solvent yielded **4** (0.024 g, 89%) identified by ir and NMR.

Hydrogenation of *endo*-6-Chloro-*endo*-7-methylbicyclo[3.2.0]hept-2-ene (D Me). The olefin, **D Me** (exact mass: theory, 142.0549; found, 142.0545) isolated by preparative vpc of *h* ν 8 (0.0114 g, 0.00008 mol) and PtO₂ (0.001 g) in about 0.1 ml of CCl₄ was hydrogenated under 1 atm hydrogen. The hydrogen uptake ceased after 5 hr. Isolation by bulb-to-bulb distillation as CCl₄ solution was effected and the material was identified as **4** on the basis of ir and NMR spectra.

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Cycloaddition. XVIII. Isomer Distributions in the Photosensitized Addition of 1-Chloropropene to Cyclopentadiene

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cis- and *trans*-1-chloropropene have been added to cyclopentadiene with β -acetonephthone as a photosensitizer at 30.5 and -24.8° . The relative total amounts of *cis* and *trans* photocycloadducts are about the same from *cis*- and *trans*-1-chloropropene, but the composition with respect to individual isomers is different in the two products by amounts outside the experimental error. These differences are smaller than in the similar case of the 1,2-dichloroethylenes and, as in that case, are greater at the lower temperature than at the higher. The observed regioselectivities and relative reactivities of olefins toward excited cyclopentadiene triplet are consistent with direct formation of a triplet biradical, whose time of spin inversion to singlet is appreciably shortened by the presence of chlorine within the biradical.

One of the clearest models of cycloaddition through a biradical intermediate is the reaction initiated by a photosensitizer. Triplet excitation energy is transferred rapidly from the sensitizer to that one of the unsaturated reactants having the lower lying triplet. Attack of this triplet on the second reactant produces a biradical with its electron spins unpaired, longer lived than a singlet biradical. Undergoing extensive intramolecular rotational equilibration, this biradical leads to product distributions characteristically different from those of concerted cycloadditions² from excited singlet state participants. Cyclopentadiene, sensitized by aromatic ketones, gives photocycloadducts to 1,2-dichloroethylene,^{3,4,7,8} 2-butene,^{5,7} and 1,2-dichloro-1,2-difluoroethylene,^{6,7} which are mixtures of all seven possible *cis*-fused 1,2 and bridged 1,4 cycloadducts with extensive loss of configuration.

The comparison of the photocycloadditions of 2-butene and 1,2-dichloroethylene⁷ revealed a striking difference. Six of the seven products are classifiable as belonging to the erythro or threo series,¹⁰ this configurative feature being established at the moment of formation of the biradical. (The *trans* 5,6-disubstituted norbornenes are of ambiguous origin, since they can be formed from both erythro and threo biradicals.) *cis*- and *trans*-2-butene lead to identical ratios of the three erythro products, and to identical ratios of the threo products, although the ratio of total erythro to total threo depends upon the configuration of the starting material. This indicates that the internal rotations of each biradical on which the relative amounts of its products depend have reached statistical equilibrium before the spin inversion which triggers cyclization of the biradical. In the dichloroethylene products, however, although the ratio of total *cis* products to total *trans* products is largely independent of the configuration of the starting material, the actual isomer distribution within the threo series and within the erythro series shows large variation between *cis* and *trans* dichloroethylenes. The product pattern suggested that the sp^2 - sp^3 rotation that equili-

brates the relative configurations of the two chlorine atoms was still proceeding rapidly, but that the sp^3 - sp^3 rotation about the newly formed bond in the biradical must be proceeding less completely. It has recently been established⁹ that this ethane-like rotation approaches equilibration at higher temperatures, so that the dichloroethylene photocycloaddition at 80–100° is comparable in degree of equilibration to the 2-butene cycloaddition at -15° .

In the difference between the cases of 2-butene and of 1,2-dichloroethylene several factors may be involved. Since the steric requirements of the chlorine atom and the methyl group are comparable, it seems likely that the difference is more a matter of rate of spin inversion, converting triplet into singlet biradical (concerted or unconcerted with bond formation) than of the rate of intramolecular rotation in the biradical. Chlorine is not a heavy enough nucleus to cause spectacular effects on rates of spin inversion, but a finite influence of this kind is to be expected and could easily produce the marginal effect observed where ring closure just begins to compete with internal rotation. Other possible differences in the systems being compared include persistence of an exciplex in the formation of the biradical, secondary interaction between chlorine and hydrogen in the biradical, "cogwheel" facilitation of rotation past a methyl group as compared to a chlorine atom, and possible donor-acceptor character in the reaction between cyclopentadiene triplet and dichloroethylene providing a possible bypass to the conservation of spin multiplicity. Since the similarities between the butene and dichloroethylene systems are greater than the differences, the last-named factor cannot be very important. The fact that the product compositions are independent of sensitizer over a considerable range of excitation energy³ makes competition between cyclopentadiene and a dichloroethylene-diene complex as energy acceptor seem unlikely.

Several of the possible influences mentioned here would depend in their operation on whether the chlorine atom, or the methyl group, were at the radical site or at the site of