Cycloaddition. XII. The Photosensitized Cycloaddition of the *cis*- and *trans*-2-Butenes to Cyclopentadiene

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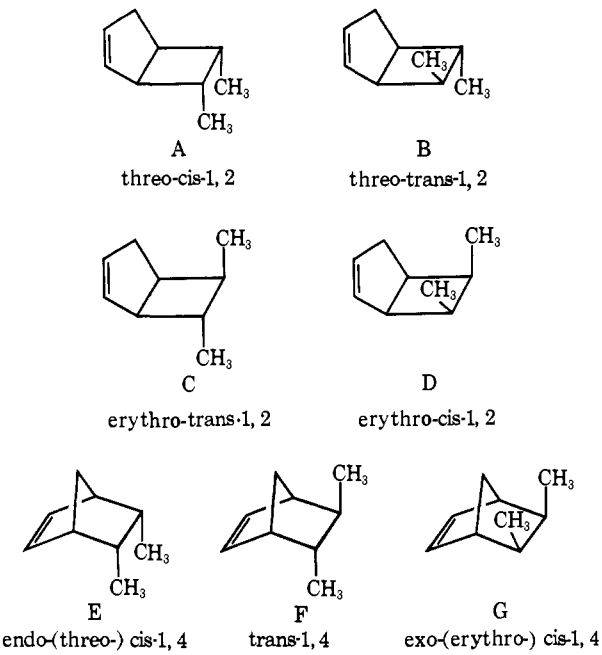
Abstract: Cycloaddition of *cis*- or *trans*-2-butene to cyclopentadiene photosensitized by β-acetonaphthone yields mixtures of three stereoisomeric 5,6-dimethylnorbornenes and four stereoisomeric 6,7-dimethylbicyclo[3.2.0]heptenes. Both butenes yield the same ratio of total cis isomers to trans isomers and of 1,4 adducts to 1,2 adducts. They differ in the relative amounts of products having erythro and threo configurations with respect to C-5 and C-6 of the bicyclo[3.2.0]hept-2-enes or C-1 and C-6 of the norbornenes, the configuration that is fixed at the moment of formation of the triplet biradical. The ratio (threo/erythro) is 1.70 from *cis*- and 3.48 from *trans*-2-butene at 30°, the ratios at −15° being 1.10 and 3.59, respectively. It is shown from the product compositions that the trans 1,4 cycloadduct, F (Chart I), which might arise from either an erythro or a threo biradical, is actually formed almost exclusively from the threo biradical at 30°, and chiefly so at −15°. After the initial formation of the two diastereomeric triplet biradicals in unequal amounts, rotational equilibrium is established in each biradical before spin inversion makes the final ring closure possible.

As a substrate for photosensitized cycloadditions, cyclopentadiene represents the simplification that it exists only in a cisoid conformation and, unlike butadiene,[1] yields cycloadduct mixtures that do not depend upon the nature of the photosensitizer used.[2] Of several stereochemical studies that have been made in this laboratory of photosensitized cycloadditions to cyclopentadiene, including the *cis*- and *trans*-1,2-dichloroethylenes,[2] *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylenes,[3,4] and *cis*- and *trans*-1-chloropropenes,[5] the reaction with *cis*- and *trans*-2-butenes represents a point of reference with a still more subtle simplification[6-8] in that it can be shown that all the internal rotations of the intermediate biradical which affect the configurations of the seven isomeric cycloadducts attain equilibrium before ring closure occurs. This does not mean that identical cycloadduct mixtures are obtained from cis and trans starting materials but that the mixture of threo products as defined below is identical from *cis*- and from *trans*-2-butene, and the mixture of erythro products is similarly identical coming from either isomer. Only the relative amounts of erythro and threo differ.

Chart I



Synthesis of Reference Compounds

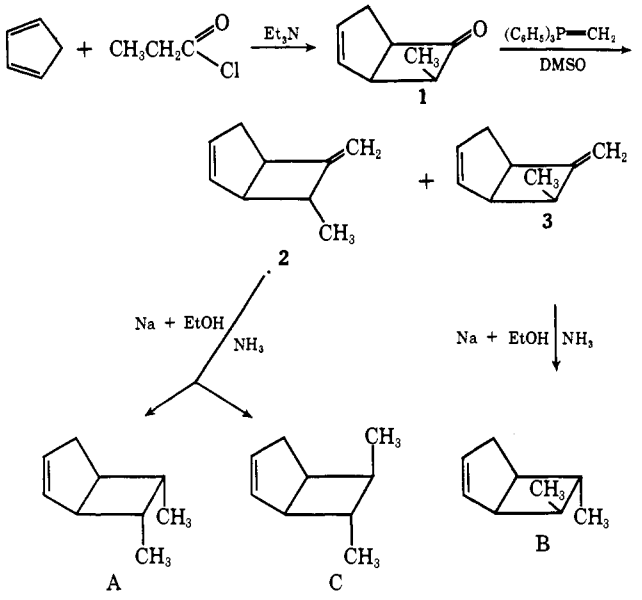
Chart I shows the four possible 1,2 cycloadducts and the three possible 1,4 cycloadducts of 2-butene to cyclopentadiene in which only cis ring fusion is present. The single letter designations of these products will be convenient in discussing both these and other sets of similar cycloadduct structures.[7] The isomeric 5,6-dimethyl-2-norbornenes, E, F, and G, were prepared as described by Miller and Greenlee[9] from Diels–Alder adducts of maleic anhydride and fumaryl chloride with cyclopentadiene, lithium aluminum hydride being used to convert the carboxyl groups to hydroxymethyl groups and again to replace toluenesulfonate groups with hydrogen.

Compounds A, B, and C were prepared as shown in Scheme I, beginning with an addition of methylketene generated *in situ* to cyclopentadiene to yield more than 90% of *endo*-7-methylbicyclo[3.2.0]hept-2-en-6-one (**1**).

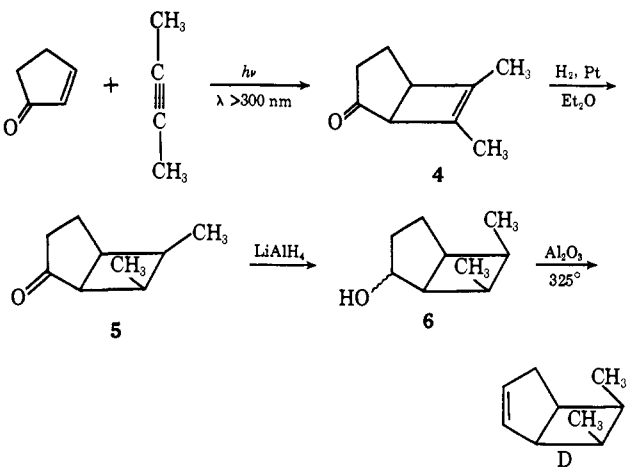
The assignment of the carbonyl group to the 6 position is based on analogy to the adducts of ketene[10] and dimethylketene[11] with cyclopentadiene. The nmr spectrum of **1** shows a three-proton doublet at τ 9.05 corresponding to the more shielded of the two methyls of the dimethylketene cycloadduct (τ 8.72 and 9.07).[12]

(1) R. S. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, 87, 3406 (1965).
(2) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968), Table 3.
(3) R. Wheland, Thesis, Harvard University, 1970.
(4) R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 3822 (1970).
(5) L. A. Hull, Thesis, Harvard University, 1970.
(6) P. D. Bartlett, *Quart. Rev., Chem Soc.*, **24**, 473 (1970), Figure 6.
(7) P. D. Bartlett, Lecture at 23rd International Congress of Pure and Applied Chemistry, Boston, Mass.; *Pure Appl. Chem., Suppl.*, **4**, 281 (1971).
(8) B. D. Kramer, Thesis, Harvard University, 1968.
(9) H. N. Miller and K. W. Greenlee, *J. Org. Chem.*, **26**, 3734 (1961).
(10) J. D. Roberts and W. F. Gorham, *J. Amer. Chem. Soc.*, **74**, 2278 (1952).
(11) T. L. Dawson and G. R. Ramage, *J. Chem. Soc.*, 3523 (1950).
(12) J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

Scheme I



Scheme II



This assignment is in agreement with the report of Dreiding, *et al.*,[13] that the cycloadduct from cyclopentadiene and methylketene generated *in situ* is 98% endo and 2% exo. Brady, *et al.*,[14] identified only the endo isomer in the product.

Reaction of **1** with methylenetriphenylphosphorane in dimethyl sulfoxide[15] led to a 42% yield of a mixture of two hydrocarbons which were separated by preparative vapor chromatography. The configuration of **3** was assigned on the basis of its nmr spectrum (multiplets at τ 4.3 (2 H), 5.3 (2 H), 6.7 (3 H), and 7.7 (2 H) and a doublet at τ 9.05 (3 H)). Isomer **2** showed a singlet at τ 4.3 (2 H), multiplets at 5.2 (2 H), 6.5 (1 H), and 7.4 (4 H), and a doublet at τ 8.8 (3 H).

Appropriately to these structures, **3** gave about an 80% yield of the single product **B** on reduction with sodium and ethanol in liquid ammonia.[16,17]

Similar reduction of **2** gave the two products (A and C) in a combined yield of 80%. Catalytic hydrogenation of B and C gave the same saturated compound.

The erythro-cis-1,2-cycloadduct D was prepared as shown in Scheme II. Irradiation through Pyrex of Δ^2-cyclopentenone in excess 2-butyne as described by Eaton[18] gave the bicyclic ketone **4**. As expected for cis catalytic hydrogenation of the double bond in **4**, the sequence **4** → **5** → **6** → D gave a fourth bicyclo[3.2.0]-heptene with an nmr spectrum consisting of a multiplet at τ 4.3 (2 H), a complex multiplet at τ 6.5 to 7.8 (6 H), and two superposed doublets centered at τ 9.2 (6 H). The signal at τ 4.3 is characteristic of the compounds A, B, and C while the norbornenes E, F, and G gave signals at τ 4. The absorptions of the methyl groups at τ 9.2 are at higher field than any seen in the other isomers, as might be expected for the endo-cis structure.

The mass spectra of compounds A to G are all virtually identical. All show a parent peak at *m/e* 122 with a base peak at *m/e* 66 (cyclopentadiene). Despite crowding of the signals that prevented detailed analysis of the 60-MHz nmr spectra, these were sufficiently individual for characterization and confirmatory identification of vapor chromatography fractions.

A mixture of 3.3 mol of *trans*-2-butene, 0.09 mol of β-acetonaphthone, and 0.38 mol of cyclopentadiene was irradiated through Pyrex for 12 hr at −17°. After the addition of another 0.38 mol of cyclopentadiene and a further 12 hr of irradiation, the product mixture was separated into fractions by bulb-to-bulb distillation and found to contain a mixture of cross adducts in about 3% yield. Preparative vapor chromatography in column 1 (see Table I) yielded four main fractions of

Table I. Retention Times in Vapor-Phase Chromatography

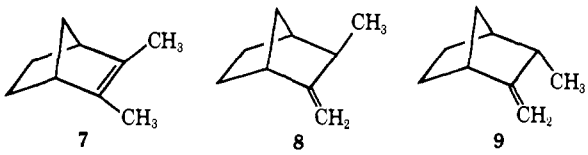
Compound	Retention times, min (on analytical columns) Column 1[a,d]	Column 2[b,d]	Column 3[c]
trans-2-Butene	4.8	2.8	15.0
cis-2-Butene	4.8	2.8	16.2
F	44.8	39.2	
B	44.8	42.4	
C	53.2	48.0	
A	58.0	50.8	
E	67.6	54.0	
G	70.8	54.0	
D	99.2	78.0	

[a] Analytical column 1: 45 ft × 1/8 in. column of 20% Carbowax 20M on Chromosorb P. [b] Analytical column 2: 25 ft × 1/8 in. column of 10% SF 96 on Chromosorb P. [c] Column 3: 45 ft × 1/8 in. column of 15% dimethylsulfolane on Chromosorb P. [d] Preparative version of column 1: 24 ft × 0.25 in.; preparative version of column 2: 30 ft × 0.25 in.

which three proved to be identical by retention time and nmr spectra with A, C, and G. The first of the four fractions was rechromatographed on preparative column 2, and B and F were identified as two of the components by their retention times and nmr spectra. Adducts D and E, present in very small amounts, were not isolated preparatively and were identified in the cycloadduct mixtures by their retention times.

The separation on column 2 also yielded a third fraction which proved to be a mixture of santene (**7**) and the two isosantenes (**8** and **9**).[19]

(13) M. Rey, S. M. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chem. Acta*, **53**, 417 (1970).
(14) (a) W. T. Brady and E. F. Hoff, Jr., *J. Org. Chem.*, **35**, 3733 (1970); (b) W. T. Brady, E. F. Hoff, Jr., R. Roe, Jr., and F. H. Parry, III, *J. Amer. Chem. Soc.*, **91**, 5679 (1969).
(15) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 28, 1128 (1963).
(16) A. P. Krapcho and M. E. Nadel, *J. Amer. Chem. Soc.*, **86**, 1096 (1964).
(17) H. Greenfield, R. A. Friedel, and M. Orchin, *ibid.*, **76**, 1258 (1954).
(18) P. Eaton, *Tetrahedron Lett.*, 3695 (1964).



7 8 9

It was shown that the santenes were not present in the original cycloadduct mixture, that they could be formed by partial isomerization of synthetic F on the preparative column 2, but that they were not produced by a similar column used in the analytical vapor chromatography. Thus the results of Tables II and III were obtained under conditions in which santene and the isosantenes were not present.

Table II. Dependence of Product Distribution upon Length of Irradiation in Photosensitized[a] Cycloaddition of *trans*-2-Butene to Cyclopentadiene

Adduct	% after irradiation for 4 hr	8 hr	16 hr
A	17.9	17.9	19.6
B	23.9	23.3	22.8
C	13.6	13.3	14.2
D	1.2	1.1	1.1
E	0.9	0.9	1.1
F	35.6	34.6	33.8
G	6.9	8.9	7.3

[a] β-Acetonaphthone (E_T = 59.3 kcal/mol) was used as sensitizer. T = 25°.

Table III. Product Distribution from Photosensitized[a] Cycloaddition of *cis*- and *trans*-2-Butene to Cyclopentadiene

Adduct	% present in cycloadduct mixture: 30 ± 2°, From cis	30 ± 2°, From trans	−15 ± 2°, From cis	−15 ± 2°, From trans
A	13.9	17.6	12.8	18.4
B	20.3	25.0	17.8	27.1
C	22.2	13.5	25.1	11.7
D	1.2	1.2	1.4	0.6
E	1.2	1.1	1.1	0.9
F	27.7	33.6	26.9	34.9
G	13.6	7.9	14.8	6.4
2-Butene isomerized	1.9	~1	0.3	~1

[a] β-Acetonaphthone as sensitizer.

Composition of the Photocycloadduct Mixtures

By the use of the three analytical vpc columns of Table I on a vapor chromatograph with flame ionization detection, it was possible to determine the extent of isomerization of the *cis*- or *trans*-2-butene used and the relative amounts of the seven cycloadducts in the product mixture. Column 1 cleanly separated adducts A, C, E, and G from each other and from the other adducts. Column 2 was used to determine the relative amounts of B, D, and F. There was no evidence that F underwent any isomerization on this column. Column 3 was used to determine the relative amounts of *cis*- and *trans*-2-butenes present. With this column it was possible to measure accurately small quantities of *trans*-2-butene in a large amount of the cis isomer. Because of tailing, the determination of *cis*-2-butene in the trans isomer was less accurate, although changes of the order of 1% could be observed.

Degassed mixtures of β-acetonaphthone, cyclopentadiene, and *trans*-2-butene in sealed Pyrex tubes were irradiated at 25° for periods of 4, 8, and 16 hr by means of a 450-W Hanovia lamp. The molar ratio of the components was approximately 0.1:1.0:6.2. The results of the analyses are shown in Table II.

The cycloadduct mixture after 16 hr of irradiation was not significantly different from that after 4 or 8 hr. Since about 75% of the cyclopentadiene was consumed in the first 4 hr, these experiments constitute a test of the stability of the cycloadducts under the conditions of the photosensitized cycloaddition.

Table III shows the results of irradiation of degassed mixtures of *cis*- or *trans*-2-butene, cyclopentadiene, and β-acetonaphthone in the approximate molar ratio of 10:1:0.1 in Pyrex tubes for 8–10 hr at 30 and at −15°. All seven cycloadducts are present, although the two endo-cis products D and E are unfavored, together making up no more than 2.5% of the product mixture. Although the relative amounts of the individual isomers are not the same in the products from *cis*- and *trans*-2-butene, yet the fraction of the total product consisting of cis isomers is the same from both olefins. Likewise, the sum of the 1,4-addition products is the same fraction of the whole whether *cis*- or *trans*-2-butene be taken as starting materials.

Discussion

The following steps are involved in the photosensitized cycloaddition of cyclopentadiene to 2-butene: (1) photoexcitation of sensitizer; (2) intersystem crossing of excited singlet sensitizer to triplet; (3) transfer of triplet energy from excited sensitizer to cyclopentadiene; (4) formation of triplet biradical from excited cyclopentadiene and 2-butene; (5) stereochemical equilibration of biradical by internal rotation; (6) spin inversion of one of the odd electrons in biradical; and (7) ring closure to product.

In principle, there are other processes competing with each of these steps. In step 1, the sensitizer can be made essentially the sole absorber of light by excluding wavelengths absorbed by other components of the system. Step 2 is rapid for β-acetonaphthone and suffers essentially no competition.

In step 3, cyclopentadiene is the only component of the mixture with a low enough triplet state to serve as an acceptor of the transferred energy, although direct formation of an excimer by energy transfer to a pair of cyclopentadiene molecules, or of an exciplex involving one cyclopentadiene and one butene, would also be possible.

Collisional quenching of the sensitizer triplet can lower the overall quantum efficiency without modifying the mechanism. Quantum efficiencies were not determined in this study.

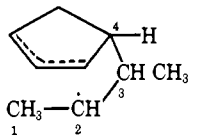
The evidence that step 4 occurs is the total loss of the original olefin configuration during cycloaddition. An imaginable mechanism, wherein a triplet exciplex, held together by donor–acceptor forces, eventually undergoes spin pairing and forms a (2 + 2) cycloadduct concertedly, would be expected to retain configuration. The stereochemical randomization must mean that the

(19) We are indebted to Dr. L. M. Stephenson for identifying this mixture and for preparing authentic samples of 7, 8, and 9.

intermediate exists as a biradical during a number of cycles of intramolecular rotation.

Since the biradical formed from two cyclopentadiene molecules[20] is allylic at both sides, it is formed with relative ease and cyclopentadiene is a serious competitor for 2-butene in step 4. The yields suggest that cyclopentadiene must be more than 500 times as reactive toward the excited triplet as is 2-butene.

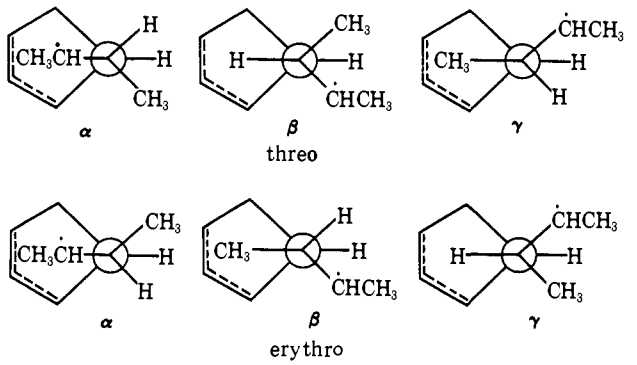
Consideration of step 5 shows that the stereochemical history of the biradicals is potentially complex. The orientation in addition of 1,1-dichloro-2,2-difluoroethylene and of vinylidene chloride[21] to cyclopentadiene shows that the cyclopentadiene reacts in such a way as to produce an allylic radical in the ring. Hence, the biradical formed between 2-butene and cyclopentadiene triplet will have the gross structure **10**.



10

Since in forming the bond C_3–C_4 two new chiral centers are generated, each biradical will be permanently of either threo or erythro type, regardless of its passage through the rotamers α, β, or γ (Scheme III). In the

Scheme III



biradical **10** there are two internal rotational modes that affect the configuration. Rotation about the bond C_3–C_4 should have a barrier typical of a tetrasubstituted ethane, while that about C_2–C_3 should have the lower barrier characteristic of the bond between an sp^2- and an sp^3-hybridized carbon atom in a 3,3-disubstituted propylene, at least 1 kcal/mol less.[22] Since the cis or trans configuration of the butene is one of the factors determining the relative energies of the transition states leading in step 4 to the six rotamers of the two diastereomeric biradicals of Scheme III, it is to be expected that these rotamers will be formed in characteristically different proportions from *cis*- and *trans*-2-butene; normally this would result in the erythro and threo biradicals being formed in different total amounts from the two configurations of starting material. If the lifetime of the triplet biradical is long before spin inversion, the three ethane-like conformations of each biradical will attain equilibration, and in that case the six propylene-like conformations of each rotamer of each diastereomer

(20) N. J. Turro and G. S. Hammond, *J. Amer. Chem. Soc.*, 84, 2841 (1962).
(21) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, 30, 1849 (1965).
(22) E. B. Wilson, Jr., *Advan. Chem. Phys.*, 2, 367 (1959).

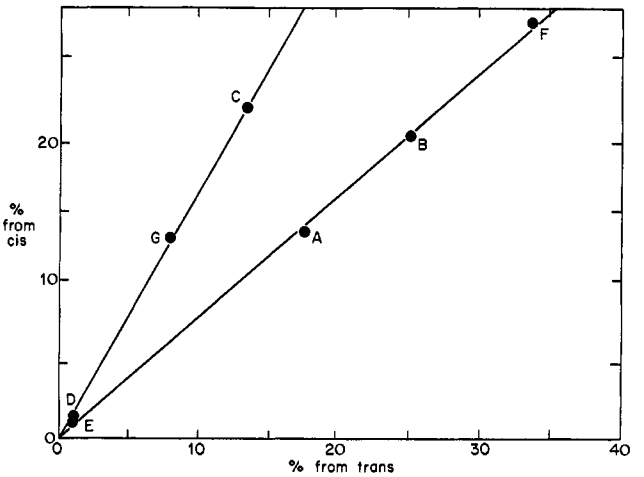


Figure 1. Product distribution in the photosensitized cycloaddition of cyclopentadiene to *cis*- and *trans*-2-butene at 30°, showing grouping into the erythro family C–D–G and the threo family A–B–E.

will also reach equilibration. If this happens, the product distributions will meet a condition for which it is possible to test: all products arising from the threo biradical will be formed in the same proportions relative to each other from *cis*-2-butene as from *trans*-2-butene, and the same will be true of the products arising from the erythro biradical. Of the seven products in the photocycloadduct mixtures, A, B, and E can result only from closure of the threo biradical, while C, D, and G must come from the erythro biradical. Only F is of uncertain origin, its formation from either diastereomeric biradical being possible.

The test for complete rotational equilibration of the biradicals may be stated as follows. If *cis*-2-butene leads to the fraction x of threo biradical and the fraction $(1 - x)$ of erythro biradical, while *trans*-2-butene leads to the fraction y of threo and $(1 - y)$ of erythro biradical, then the known threo and erythro cycloadducts will be formed in the amounts shown in Table IV.

Table IV. Expected Product Distribution on Assumption of Rotational Equilibration

Isomer	Fraction from cis	Fraction from trans
A	$x f_A$	$y f_A$
B	$x f_B$	$y f_B$
E	$x f_E$	$y f_E$
C	$(1 - x) f_C$	$(1 - y) f_C$
D	$(1 - x) f_D$	$(1 - y) f_D$
G	$(1 - x) f_G$	$(1 - y) f_G$

A plot of the abundance of each isomer in the product from *cis*-2-butene as ordinate against the abundance of the same isomer in the product from *trans*-2-butene as abscissa must, then, by the hypothesis of rotational equilibration, show the threo products A, B, and E on a straight line through the origin with slope $\lambda_T = x/y$ and the erythro products C, D, and G on another straight line through the origin with slope $\lambda_E = (1 - x)/(1 - y)$. Such a plot is shown in Figure 1 for the products at 30°, and it is evident that the condition being tested for is accurately met. From the slopes of the lines we can evaluate x and y.

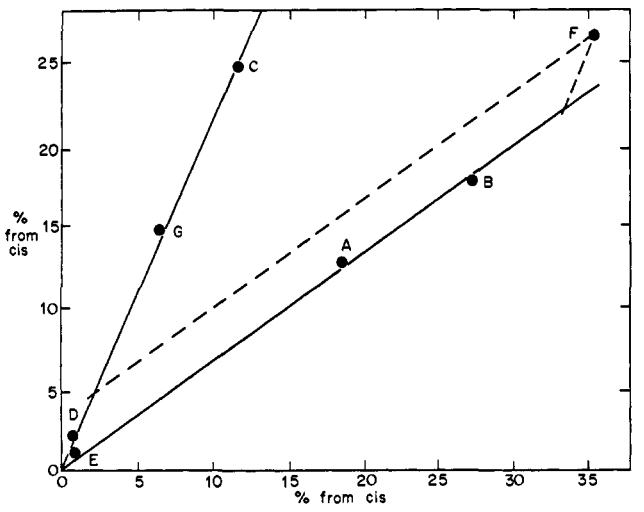


Figure 2. Product distribution in the photosensitized cycloaddition of cyclopentadiene to *cis*- and *trans*-2-butene at −15°. Dashed lines indicate possible apportionment of F between formation *via* erythro and threo biradicals.

$$y = (1 - \lambda_E)/(\lambda_T - \lambda_E)$$

$$x = \lambda_T y = \lambda_T(1 - \lambda_E)/(\lambda_T - \lambda_E)$$

At 30° the least-squares slopes are $\lambda_T = 0.810$ and $\lambda_E = 1.662$, and the mean square deviations (msd) of points from the lines are 0.26 and 0.56, respectively: $x = 0.630, y = 0.777$.

This graphical analysis of the data now permits us to draw conclusions about the proportions of the ambiguous product, F, that arise from erythro and from threo biradicals. It so happens that the point for F in Figure 1 lies on the threo line within experimental uncertainty, indicating that nearly all of the trans-1,4-cycloaddition product is formed, in this case, by way of the threo biradical.

The product composition at −15° is plotted in Figure 2. Again A, B, and E form one straight line through the origin, $\lambda_T = 0.669$, msd = 0.41, and C, D, and G form another, $\lambda_E = 2.184$, msd = 0.55; $x = 0.523$, $y = 0.782$; but this time F occupies a position definitely off the threo line. If this position of F on the graph is simply the result of one part of F coming through threo and another part through erythro biradicals, then there is a unique apportionment which will place the threo part on the threo line and the erythro part on the erythro line, while yielding the correct total amount of F from *cis*- and from *trans*-2-butene. These proportions are indicated by the parallelogram in Figure 2, whose dashed sides are parallel to the erythro and threo lines. The points of intersection of the dotted with the solid lines correspond to the amounts of F resulting from erythro and from threo biradicals: 5.1 and 21.8%, respectively, from *cis*-2-butene and 2.3 and 32.6% from *trans*-2-butene.

Table V summarizes the distribution of the biradicals between erythro and threo, and the relative amounts of the products from each biradical. It would be interesting to know the actual amount of erythro biradical that leads to 1,4-trans adduct at 30°, but we have no way of determining it since it is of the same order as, or less than, the experimental error of the analyses. Except for the paths leading to F, there seems to be little difference between the behavior of the biradicals at 30 and at −15°. At both temperatures internal rotation comes to equilibrium before spin inversion and ring closure occur.

Table V. Stereochemical Distribution in Triplet Biradicals from Cyclopentadiene and *cis*- or *trans*-2-Butene

	30°	−15°
% threo from cis	63.0	52.3
% threo from trans	77.7	78.2
Distribution of threo products, %		
A	22.0	23.9
B	32.2	33.2
E	1.9	2.1
F	43.9	40.8
Distribution of erythro products, %		
C	59.9	54.1
D	3.2	3.0
G	36.9	31.9
F	Small	11.0

Experimental Section

endo-cis- **and** *trans*-**5,6-Dimethyl-2-norbornene (E and F).** In a 250-ml flask were placed 1.0 g (0.125 mol) of lithium hydride, 2.5 g (0.066 mol) of lithium aluminum hydride, and 140 ml of dry tetrahydrofuran. The mixture was heated to reflux and 28.0 g (0.0606 mol) of *endo-cis*-2-norbornene-5,6-dimethanol di-*p*-toluenesulfonate, mp 88–90°,[8] or *trans*-2-norbornene-5,6-dimethanol di-*p*-toluenesulfonate, mp 92–93°,[8] was added in small portions with stirring. After the addition had been completed, the mixture was heated under reflux for 4 hr. Most of the tetrahydrofuran was removed at aspirator pressure and replaced with about 100 ml of ether. The mixture was cooled in ice and carefully hydrolyzed by the addition of cold water followed by dilute sulfuric acid. The aqueous layer was separated and extracted with ether. The extracts were combined with the organic layer which was then dried over anhydrous potassium carbonate. Distillation yielded in the case of E 1.7 g (23%), bp 133–136° [lit.[8] bp 143°]. In the case of F, the yield was 2.2 g (30%), bp 125–127° [lit.[8] bp 132.5°].

exo-cis-**5,6-Dimethyl-2-norbornene (G)** was prepared in the same way on about two-thirds of the scale of the preceding preparation from 19.5 g (0.042 mol) of *exo-cis*-2-norbornene-5,6-dimethanol di-*p*-toluenesulfonate, mp 168–170° dec.[8] The yield of G was 0.9 g (17.5%), bp 138° [lit.[8] bp 144°].

The 60-MHz nmr spectrum of E showed a triplet at τ 3.98, J = 2 Hz (1.9 H); a broad singlet at τ 7.39 (2 H); a broad multiplet from τ 7.6 to 8.2 (2 H); a multiplet from τ 8.4 to 8.9 (2.1 H); and a doublet centered at τ 9.31, J = 7 Hz (6 H). The nmr spectrum of F showed a doublet quartet at τ 3.98, J = 6.3 Hz (2 H), broad unresolved 1-proton signals at τ 7.46 and 7.72, a multiplet from τ 8.38 to 8.79 (3 H), and a series of overlapping signals from τ 8.79 to 9.35 (9 H). The nmr spectrum of G showed a triplet at τ 3.98, J = 2 Hz (2 H), a triplet at τ 7.68, J = 2 Hz (2.4 H), and overlapping multiplets from τ 8.3 to 9.4 (11 H).

endo-**7-Methylbicyclo[3.2.0]hept-2-en-6-one (1).** In a 2-l. three-necked flask fitted with a stirrer, dropping funnel, and Dry Ice condenser were placed 500 g (7.6 mol) of cyclopentadiene and 100 g (1.09 mol) of propionyl chloride. The solution was stirred vigorously under nitrogen while 110 g (1.09 mol) of triethylamine was added dropwise over a period of 2 hr. The reaction mixture warmed spontaneously to gentle reflux. It was stirred at room temperature for 2 hr and then passed through a sintered glass filter. Volatile material was removed on the rotary evaporator at room temperature. The residue by nmr and vpc appeared to be about 35% methylbicycloheptenone with the remainder being dicyclopentadiene. The pure ketone was obtained by chromatographing 28-g portions of the crude material on a 1.625 × 30 in. column packed with 400 g of Florisil, with first petroleum ether and then petroleum ether–ether mixture as eluent, bp 59–60° (15 mm): nmr, narrow signal at τ 4.18 (2 H), a broad multiplet centered at τ 6.43 (3 H), an unresolved signal at τ 7.50 (2 H), and a doublet at τ 9.05 (3 H).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.53; H, 8.26.

endo- and *exo*-6-Methylene-7-methylbicyclo[3.2.0]hept-2-ene (3 and 2, respectively). Into a 500-ml flask was weighed 4.2 g (0.09 mol) of 52% sodium hydride in mineral oil. The oil was removed with pentane and the flask was flushed with nitrogen. To the flask was added 45 ml of dry dimethyl sulfoxide and the mixture heated at 75° for 45 min. The solution was cooled and 34.0 g (0.095 mol) of methyltriphenylphosphonium bromide[23] in 85 ml of dimethyl sulfoxide was added. The mixture was stirred at room temperature for 10 min and a solution of 10 g (0.082 mol) of *endo*-7-methylbicyclo[3.2.0]hept-2-en-6-one (1) was added. The flask was kept at 45° overnight and then the volatile material was drawn out and trapped at aspirator pressure. There was collected 4.1 g (42%) of an approximately 50:50 mixture of the endo and exo hydrocarbons. The isomers were separated by preparative gas chromatography with a $^3/_8$ in. × 20 ft column of 20% FFAP on Chromosorb P at 80°.

exo-6-Methyl-*endo*-7-methylbicyclo[3.2.0]hept-2-ene (B). Into a 25-ml flask fitted with a Dry Ice condenser and a sodium hydroxide drying tube were weighed 0.3 g (0.0025 mol) of 6-methylene-*endo*-7-methylbicyclo[3.2.0]hept-2-ene (3) and 0.60 g (0.0013 mol) of absolute ethanol. About 5 ml of anhydrous ammonia was distilled into the flask and 0.16 g (0.007 g-atom) of sodium was added in small pieces. After each piece was added, the blue color was allowed to fade. After the addition was complete, the mixture was stirred for 0.5 hr. About 7 ml of water was added dropwise with cooling. The aqueous layer was extracted with pentane and the extracts combined with the organic layer. The pentane solution was dried over anhydrous potassium carbonate and the solvent removed with the rotary evaporator. Vpc analysis showed only one component (about 80%) in addition to starting material. Pure B was obtained by preparative gas chromatography with an F and M Model 300 chromatograph and a 0.25 in. × 24 ft column of 20% Carbowax 20M on Chromosorb P.

The 60-MHz nmr spectrum of B showed a singlet at τ 4.28 (2.0 H), a broad one-proton multiplet from τ 6.6 to 7.1, a multiplet from τ 7.3 to 8.3 (4 H), a broad multiplet from τ 8.3 to 8.83 (1 H), and overlapping doublets, J = 6 Hz, at τ 8.90 and 9.12, totaling 5.9 H in area.

endo-6-Methyl-*exo*-7-methylbicyclo[3.2.0]hept-2-ene (C) and *cis*-*exo*-Dimethylbicyclo[3.2.0]hept-2-ene (A). The sodium reduction of 0.3 g (0.0025 mol) of 6-methylene-*exo*-7-methylbicyclo[3.2.0]hept-2-ene (2) was carried out as in the preparation of B. This time an approximate 80% yield of almost 50:50 mixture of A and C was obtained. The two products were isolated by preparative vpc as in the case of B.

The 60-MHz nmr spectrum of A showed a broad singlet at τ 4.3 (1.8 H), a multiplet from τ 7.15 to 8.2 (6 H), and overlapping doublets, J = 7 Hz, at τ 8.96 and 9.09 (6 H).

The 60-MHz nmr spectrum of C showed a singlet at τ 4.3 (2 H), a multiplet from τ 6.85 to 7.5 (2 H), a multiplet from τ 7.5 to 7.82 (2 H), a multiplet from τ 7.82 to 8.75 (2 H), and overlapping doublets at τ 8.89, J = 6 Hz, and 9.05, J = 7 Hz, totaling 6 H.

6,7-Dimethylbicyclo[3.2.0]hept-6-en-2-one (4). A solution of 5.8 g (0.071 mol) of cyclopent-2-enone in 80 ml of 2-butyne was irradiated through Pyrex with a 450-W Hanovia lamp as described by Eaton.[18] The reaction mixture was distilled through a 6-in. Vigreux column to give 3.0 g (31%) of the product, bp 59–65° (12 mm).

endo-*cis*-Dimethylbicyclo[3.2.0]heptan-2-one (5). A solution of 1.7 g (0.0125 mol) of 4 in about 5 ml of ether with a little platinum oxide added was stirred magnetically under hydrogen at 1 atm. The ether solution was decanted away from the catalyst. The resulting solution was used directly in the next preparation.

cis-*endo*-Dimethylbicyclo[3.2.0]heptan-2-ol (6). To a stirred suspension of 0.3 g (0.008 mol) of lithium aluminum hydride in about 10 ml of ether cooled to 0°, the ether solution of the above catalytic hydrogenation product was added dropwise. The resulting mixture was stirred at room temperature for 4 hr and the excess hydride decomposed carefully with cold water. The ether layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed at aspirator pressure to give the crude alcohol.

cis-*endo*-6,7-Dimethylbicyclo[3.2.0]hept-2-ene (D). A 1 × 25 cm Pyrex tube was mounted vertically and fitted at the top with a dropping funnel and at the bottom with a condenser and receiver. The tube was packed with 8 mesh Alcoa F-1 alumina and heated to 325° with a heating tape. The pressure of the system was reduced to 15 mm, and a solution of crude 6 (about 1.5 g) in a little benzene was dropped into the tube. The product was dried over anhydrous magnesium sulfate. Vpc analysis indicated that the crude material consisted of one major product (about 40%) and many minor components. The major fraction was collected on an F and M Model 300 gas chromatograph with a 0.25 in. × 24 ft column of 20% Carbowax 20M on Chromosorb P. This fraction was shown to be D by nmr and mass spectrum analysis.

The 60-MHz nmr spectrum of D showed a singlet at τ 4.27 (2.0 H), a multiplet from τ 6.5 to 7.6 (4 H), a multiplet from τ 7.6 to 7.85 (2 H), and overlapping doublets, J = 7 Hz, at τ 9.10 and 9.21 (6 H).

Photosensitized Cycloadditions. Eastman practical grade dicyclopentadiene was fractionally distilled through a 2-ft column packed with glass helices at aspirator pressure. Material from the center cut was cracked at atmospheric pressure to give cyclopentadiene. Eastman White Label β-acetonaphthone was used as received. Matheson 99 mol % *cis*- and *trans*-2-butene were used as received.

For the irradiations, the desired quantities of β-acetonaphthone and freshly distilled cyclopentadiene were weighed into 13-mm Pyrex test tubes with constricted necks. The tubes were degassed and *cis*- or *trans*-2-butene was distilled in under vacuum. The tubes were sealed under vacuum and weighed to determine the amount of butene present. The tubes were strapped to a Pyrex well immersed in a cooling bath and irradiated with a 450-W Hanovia mercury lamp. For the runs near room temperature, tap water was circulated through the lamp well and the cooling coils of the bath. For the runs at −15°, ethanol at 0° from a Lauda Kryomat Model TK30 was circulated through the lamp well while ethanol at −30° from a Blue M Model WED-100LNC bath was passed through the coils of the cooling bath. Temperature control in each case was ±2°.

For the product analysis, an Aerograph Model 1520 gas chromatograph with flame ionization detection was used. Helium was used as the carrier gas. The butenes were analyzed using a 45 ft × $^1/_8$ in. column of 15% dimethylsulfolane on 60–80 mesh Chromosorb P (column temperature, 30°; carrier gas, maximum flow at 50 psig inlet pressure). Compounds A, C, E, and G were separated from each other and from B, D, and F with a 45 ft × $^1/_8$ in. column of 20% Carbowax 20M on 60–80 mesh Chromosorb P (column temperature 80°; injector, 135°; detector, 145°; carrier gas, maximum flow at 70 psig inlet pressure). The relative amounts of B, D, and F were determined by using a 25 ft × $^1/_8$ in. column of 10% SF 96 on 60–80 mesh Chromosorb P (column temperature, 70°; injector, 135°; detector, 145°; carrier gas, 10% of maximum flow at 65 psig inlet pressure). A Disc integrator was used to determine the area under each peak. The relative sensitivity of the detector to each compound was not determined.

For the preparative photocycloadditions, a mixture of 15 g (0.09 mol) of β-acetonaphthone and 25 g (0.38 mol) of freshly distilled cyclopentadiene was placed in a 300-ml, photolysis apparatus, fitted with a Pyrex well. The apparatus was degassed and 185 g (3.3 mol) of *trans*-2-butene was distilled in under vacuum. The solution was placed under argon and irradiated at −17° for 12 hr using a 450-W Hanovia mercury lamp. At the end of this period, an additional 25 g of cyclopentadiene was added, and the irradiation was continued for 12 hr more. The butene was allowed to boil off and the residue distilled bulb-to-bulb at 0.1 mm. The cross adducts were separated from the photodimers of cyclopentadiene by preparative vpc using a 20 ft × $^3/_8$ in. column of 20% QF-1 on Chromosorb P (column temperature, 135°; helium flow, 200 cc/min). Adducts A, C, and G were separated from each other and the other adducts on an F and M Model 300 gas chromatograph with a 24 ft × 0.25 in. column of 20% Carbowax 20M on Chromosorb P (column temperature, 85°; injector, 140°; detector, 150°; helium flow, 60 cc/min). A 30 ft × 0.25 in. column of 15% Sf 96 on Chromosorb P (column temperature, 90°; injector, 140°; detector, 150°; helium flow, 25 cc/min) was then used to separate adducts B and F from each other and from the mixture of santene and isosantenes produced by isomerization on the column.

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