and placed in the NMR probe, as described above for the kinetic samples.

All spectra were acquired and stored under computer control, in such a manner as to obtain 10–25 spectra over the course of 3–4 reaction half-lives. For the reaction between **9** and **10**, disappearance of the methyl signal of **10** at δ 1.673 was monitored; the product methyl signal of **11** grew in at δ 1.625. The higher field signal due to the residual hydrogen in the THF-d_8 solvent was used as an internal integration standard (see below). For the reactions of **1** with phosphines, DMAD, and **10**, the disappearance of the Cp singlet of **1** relative to ferrocene as the internal standard (except as noted below) was monitored. For the high-concentration runs using DMAD, the intense DMAD signal precluded accurate monitoring in the Cp region, so in these cases the rate of disappearance of the methylene singlet of **1** relative to the residual THF protons was monitored. The rates could be measured in both ways for the low-concentration DMAD runs, and they were the same, confirming the accuracy of the THF internal standard. Dioxane was used as the internal standard in the low-temperature reaction between **1** and **10**, while the THF residual signal was again used in the room-temperature reactions. Least-squares fitting of the data to first-order plots of the disappearance of **1** gave straight lines generally having standard deviations of ±1–4%.

UV–Visible Kinetics. Two standard stock solutions of **1**, 1.1×10^{-4} and 2.5×10^{-3} M, in THF were prepared and stored, without detectable decomposition, at −40 °C. THF solutions of DMAD and $P(OMe)_3$ were prepared by adding THF to weighed amounts of each compound in volumetric flasks at room temperature. The densities of these solutions were then determined, after which they were cooled to −40 °C.

Immediately prior to use, cold solutions of **1** and DMAD or $P(OMe)_3$ were weighed (in the drybox) into a 1-cm path-length quartz UV cuvette that was fused to a Teflon-brand vacuum stopcock. Room-temperature concentrations were calculated from the known weights and densities. After closing the stopcock, the cuvette was rapidly removed from the box and stored in a −15 °C cold bath. No detectable decomposition occurred at this temperature. The reactions were initially examined with the Hewlett-Packard instrument and appeared well-behaved; the DMAD reaction exhibited isosbestic points at about 310, 450, and 600 nm. For kinetic runs the Carey was used, by monitoring at a single wavelength as described in the text. Temperatures were measured with a calibrated thermometer inserted into a similar quartz UV cell containing THF; it was found that 1 min of shaking the sample cell in a water bath held at the same temperature as the cell holders was necessary for equilibration.

Generally about 30 absorbance readings over 4–5 half-lives were used to determine the reaction rate; for most reactions the rates were sufficiently rapid that end-point readings could be made after 10 half-lives without removing the cuvette from the machine. First-order reaction rates were obtained by plots of ln $(A_t - A_\infty)$ vs. time. The end point used (except as noted below) was that which gave the minimum standard deviation from the least-squares fit to a straight line, but these calculated end points did not differ appreciably from the observed values. The observed standard deviations of the first-order reaction rates were ±0.1–1.0%. For the 0.5 M DMAD, 0.001 M **1** sample, as well as the other 0.001 M **1** samples, which were not first order, the observed end points were used, since varying these end points did not result in minima in the standard deviations; even so the deviations were only ±0.4–1.7%.

Acknowledgment. Financial support for this work was provided by National Science Foundation Grant CHE79-26291. W.H.H. acknowledges an NIH National Research Service Award (F32-GM-07539) from the National Institute of General Medical Sciences. R.G.B. acknowledges a Research Professorship (1982–1983) from the Miller Institute for Basic Research at U. C. Berkeley.

Registry No. 1, 79931-94-5; **4a**, 1460-59-9; **4b**, 4968-91-6; **5**, 86364-95-6; **9**, 58496-39-2; **10**, 86364-96-7; **11**, 86455-89-2; **12**, 79931-95-6; **13**, 12078-25-0; **14**, 86437-13-0; **15**, 56306-55-9; **16**, 86437-14-1; **17**, 21507-95-9; **17**·HCl, 86437-17-4; **20**, 13152-89-1; **20**·HCl, 86437-12-9; $MeCpCo(CO)_2$, 75297-02-8; $Na[CpCo(CO)]_2$, 62602-00-0; $Na[MeCpCo_2(CO)_2]$, 86437-15-2; $Na[MeCpCo(CO)]_2$, 86364-94-5; $MeCp_2Co_2(CO)_2$(DMAD), 86437-16-3; Co, 7440-48-4; $PPhMe_2$, 672-66-2; PPh_3, 603-35-0; PCy_3, 2622-14-2; PMe_3, 594-09-2; $P(OMe)_3$, 121-45-9; DMAD, 762-42-5; (η^5-methylcyclopentadienyl)carbonyl(dimethylphenylphosphine)cobalt, 86364-98-9; α,α'-dibromo-*o*-xylene, 91-13-4; α,α'-dibromo-*o*-xylene-d_8, 86437-11-8; *o*-xylene-d_{10}, 56004-61-6.

Accessibility of Triplet Indenylidene in Solution

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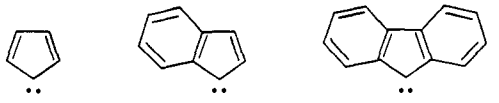
Abstract: Photolysis of diazoindene generated indenylidene (**2**), which reacted with isobutene, *cis*-butene, and *trans*-butene, forming adducts **5a–c** and insertion products **6a–c**. NMR-based configurational assignments to cyclopropanes **5b**-*syn*, **5b**-*anti*, and **5c** permitted detailed analysis of the stereochemistry of addition of **2** to *cis*- and *trans*-butene. The stereochemistry was studied as a function of dilution of the alkenes with *c*-C_4F_8 or 2,3-dimethylbutadiene. These experiments clarified the product-forming roles of singlet and triplet **2**. In the presence of 97 mol % *c*-C_4F_8, ~47% of the cyclopropanes derived from **2** and *cis*-butene came from triplet **2**. Triplet reactions were almost entirely eliminated in the presence of 25 mol % of 2,3-dimethylbutadiene. The reactions of the butene olefins with **2** were compared to similar reactions with cyclopentadienylidene (**1**) and fluorenylidene (**3**).

The triad of carbenes cyclopentadienylidene (**1**), indenylidene (**2**), and fluorenylidene (**3**) invites investigation because connec-



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tions between structure, spin state, and reactivity might be particularly clear. All these carbenes are ground-state triplets, as shown by electron spin resonance studies.[2] Cyclopentadienylidene, generated as the singlet by photolysis of diazocyclopentadiene, is a highly reactive, electrophilic species that displays low selectivity in its reactions with alkanes, alkenes, and sulfides.[3] Reactions

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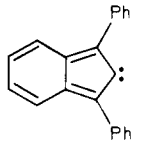
of its triplet ground state are readily detected in solution.[4]

In contrast, ground-triplet-state chemistry of **3** is observable in both solutions[5] and matrix[6] environments because the rate of intersystem crossing between singlet and triplet **3** appears to be comparable to the rates of reaction of the singlet with alkanes or alkenes. Recently, the chemistry of **3** has been intensively scrutinized by laser flash photolysis.[7]

Alone among the carbenes **1–3**, only the chemistry of **2** has not been systematically studied. It is known that **2** adds to benzene, forming an equilibrium mixture of spironorcaradiene and spirocycloheptatriene derivatives.[8] Additionally, the 2,3-diphenyl derivative of **2** cyclopropanates methyl acrylate in low yield,[9] and parent **2** adds in acceptable yield to isobutene.[10] Triplet **2** (in contrast to **3** but similarly to **1**) cannot be trapped with NO to afford an iminoxyl radical.[11] Recently, two reports described the generation and chemistry of 1,3-diphenylisoindenylidene (**4**).[12]



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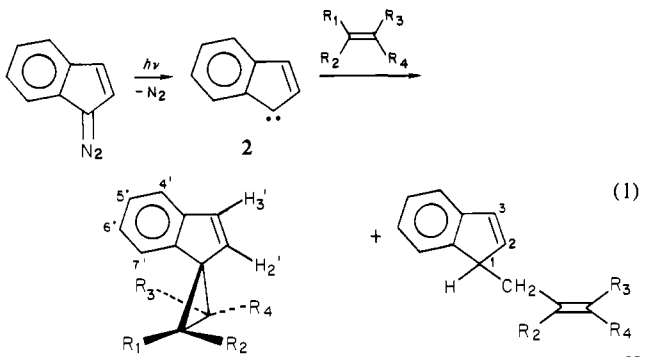
We now report a study of the reactions of **2** with several alkenes. Because of a unique stereochemical phenomenon, we are able to render a particularly detailed account of the accessibility of triplet **2** in solution.

Results

Syntheses and Structures. Diazoindene was prepared from indene and *p*-toluenesulfonyl azide,[13] purified by chromatography on basic alumina, and characterized by IR and NMR spectroscopy.[8] In photolytic work we used diazoindene containing up to 30% indene, diluted with 30% of pentane.

Preparative photolyses ($\lambda > 300$ nm, 25–35 °C) were carried out in isobutene, *cis*-butene, and *trans*-butene, eq (1). Products



(1)

5a, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
5b-*syn*, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
5b-*anti*, $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
5c, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$

6a, $R_2 = CH_3$; $R_3 = R_4 = H$
6b, $R_3 = CH_3$; $R_2 = R_4 = H$
6c, $R_4 = CH_3$; $R_2 = R_3 = H$

Table I. Chemical Shifts of $H_{2'}$ in Spiro[cyclopropane-1,1'-indenes] 5

R_i in structure 5	no. of methyl groups proximal to $H_{2'}$	chemical shift of $H_{2'}$, δ
$R_1 = CH_3$; $R_2 = R_3 = R_4 = H$	0	5.98[a]
$R_1 = R_2 = R_3 = R_4 = H$	0	6.03[a]
$R_1 = R_3 = CH_3$; $R_2 = R_4 = H$	0	6.11[b]
$R_2 = CH_3$; $R_1 = R_3 = R_4 = H$	1	6.28[a]
$R_1 = R_2 = CH_3$; $R_3 = R_4 = H$	1	6.31[a,c]
$R_1 = R_4 = CH_3$; $R_2 = R_3 = H$	1	6.43[b]
$R_2 = R_4 = CH_3$; $R_1 = R_3 = H$	2	6.48[b]

[a] Reference 10, solvent CCl_4. [b] This work, solvent $CDCl_3$. [c] This work, solvent CCl_4.

were isolated by preparative GC on a 5% Carbowax 20M + 5% SE-30 column.

From isobutene and **2**, we isolated 27% of adduct **5a**[10] and 4% of an earlier-eluted material to which we assigned structure **6a**. The proton NMR spectrum of **5a** was identical with that reported by Staley; in particular, $H_{2'}$ and $H_{3'}$ appeared as an AB quartet at ~δ 6.31 and 6.77 ($J = 6$ Hz), respectively.[10] The higher field resonance was assigned to $H_{2'}$, the vinyl proton closest to the (shielding) cyclopropyl ring.[10]

The structure of "insertion" product **6a** rests upon its mass spectrum (M^+ at *m/e* 170), elemental analysis, and proton NMR spectrum. The last clearly revealed the allylic CH_3 (δ 1.84, s), the terminal methylene (δ 4.80, d, $J = 2$ Hz), and other key structural components (see Experimental Section).

Photolysis of diazoindene in neat *cis*-butene led to four isolable 1:1 products: the isomeric *cis*-butene adducts **5b**-*syn* (methyl groups syn to the benzo substituent) and **5b**-*anti*, *trans*-butene adduct **5c**, and alkene **6b**. GC enabled isolation of **5b** (as a syn/anti mixture) in 25% and **6b** in 6% yields. Adduct **5c** was present in ~3.6% yield; its identity was confirmed by GC and HPLC spiking experiments using authentic material prepared from **2** and *trans*-butene (cf. below).

Assignments of structures to the *cis*-butene adducts rest upon elemental and NMR analyses. The **5b** isomers were separable under analytical HPLC conditions (affording their ratio), but they were inseparable by preparative GC, so that NMR spectra were determined on the mixture. The 80-MHz proton spectrum clearly supported structure **5b** revealing CH_3, aromatic, and cyclopropyl resonances as well as two $H_{2'}$–$H_{3'}$ AB quartets. The syn and anti isomers of **5b** were differentiated at higher field.

In the 300-MHz spectrum of the mixture, the high-field ($H_{2'}$)[10] "doublets" of the two isomers appeared at δ 6.11 and 6.48. Staley suggested that methyl groups *proximal* to $H_{2'}$ *deshield* this proton.[10] On this basis, the higher-field $H_{2'}$ doublet at δ 6.11 belongs to **5b**-*syn* in which both methyl groups are *distal* to $H_{2'}$, whereas the lower-field $H_{2'}$ doublet at δ 6.48 belongs to **5b**-*anti*, where the methyl groups are *proximal* to $H_{2'}$. As shown in Table I, chemical shift data for Staley's derivatives of **5**, combined with our data for **5a–c**, form a consistent series, characterized by increased deshielding of $H_{2'}$ with each introduction of a proximal methyl group on the cyclopropyl ring.

To substantiate our assignments a nuclear Overhauser effect (NOE) experiment was performed on the **5b** isomer mixture. Framework molecular models indicate an internuclear "separation" of ~2 Å for closest approach of a methyl proton and $H_{2'}$ in **5b**-*anti*. This is slightly less than the sum of van der Waals radii, so that irradiation of the methyl groups might induce a NOE in the $H_{2'}$ doublet of **5b**-*anti*. Indeed, irradiation of the cluster of CH_3 resonances at δ 1.3–1.4 caused an 11.3–12.6% increase (depending on pulse delay time) in the $H_{2'}$ doublet at δ 6.48. The doublet at δ 6.11 was unaffected. Accordingly, the δ 6.48 resonance must be assigned to $H_{2'}$ of **5b**-*anti*, in agreement with the conclusion based solely on chemical shift. From the integral areas of their respective $H_{2'}$ resonances, the **5b**-*anti*/**5b**-*syn* product ratio was ~1.5, whereas the HPLC product ratio was 1.48.

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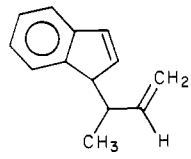
Table II. Photolysis of Diazoindene in Mixtures of *cis*-Butene and Octafluorocyclobutane at 25–35 °C

run	mole fraction of c-C_4F_8	relative yield, %[b] 5b-syn	5b-anti	5c	5b-syn/5b-anti
1	0.000	38.7	48.3	13.0	0.80
2	0.270	39.2	47.4	13.4	0.83
3	0.535	37.7	46.4	15.9	0.81
4	0.750	34.6	46.4	19.0	0.75
5	0.774	35.1	45.6	19.3	0.77
6	0.829	32.8	43.2	24.0	0.76
7	0.870	36.1	42.7	21.2	0.85
8	0.874	32.1	43.0	24.9	0.75
9	0.905	34.2	45.9	19.9	0.74
10	0.915	25.4	34.5	40.0	0.74
11	0.928	23.8	31.4	44.8	0.76
12	0.947	32.3	36.5	31.2	0.88
13	0.967	24.8	35.4	39.8	0.70
14	0.250[c]	46.1	53.5	0.40	0.86
15	0.520[c]	45.8	51.5	2.7	0.89

[a] Diazoindene (~0.009 M) was photolyzed, for 3 h, $\lambda > 411$ nm. Analysis by HPLC on a C-18 reverse-phase column with 55% CH_3CN/45% H_2O as eluent. [b] Reproducibilities are ~±5% of the tabulated value. These are single experiments with duplicate or triplicate HPLC analyses of product distributions by electronic integration. [c] The diluent is 2,3-dimethylbutadiene.

The structure of **6b**, isolated from reaction of **2** with *cis*-butene was tentatively assigned on the basis of its mass spectrum and its 80-MHz NMR spectrum. Particularly important in the latter was the two-proton vinyl multiplet at δ 5.4–5.6, consistent with the internal double bond of **6b** but not with isomer **7**, which would



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feature a higher field terminal methylene absortion. For example, in the fluorenylidene CH "insertion" products analogous to **6b** and **7**, the respective vinyl proton signals appear at δ 5.23–5.53 and 4.93–5.10.[6] Because the reaction of **2** with neat *cis*-butene occurs mainly from the carbene's singlet state (see below), **6b** is most reasonably formulated as a "direct" insertion product of **2** into an allylic C–H bond. In this process, the cis stereochemistry of the alkene substrate would be preserved in the product. Alkenes **6b** and trans isomer **6c** (see below), are differentiable by HPLC.

Photolysis of diazoindene in neat *trans*-butene also gave four GC-isolable 1:1 products: *trans*-butene adduct **5c** (21%), *cis*-butene adducts **5b**-*anti*/**5b**-*syn* (traces), and an alkene tentatively identified as **6c** (6%). The **5b** isomers were identified by HPLC spiking experiments.

Structures were assigned to **5c** and **6c** on the basis of 80-MHz proton NMR spectra, elemental analysis, and mass spectroscopy; details appear in the Experimental Section. The position and geometry of the **6c** alkenic double bond (two-H vinyl multiplet at δ 5.4–5.6) were assigned by considerations parallel to those employed for **6b**.

Stereochemistry of Additions of 2. In neat *cis*-butene, **2** photogenerated from diazoindene mainly gave stereochemically preserved adducts **5b**-*syn* and **5b**-*anti*. Some nonstereospecific, *trans*-dimethyl adduct (**5c**) was formed, however; the **5b**/**5c** ratio was ~7:1. The effect on reaction stereochemistry of substrate concentration was studied with octafluorocyclobutane (c-C_4F_8) as an inert diluent. In these experiments, photolyses were conducted through a Corning 3-72 sharp cut filter (opaque below 411 nm), so that light was absorbed only by the diazoindene. The results (Table II) show that dilution with c-C_4F_8 caused a significant increase in the nonstereospecificity of the reaction, particularly at diluent mole fractions between 0.75–0.97 (runs 4–13), where the relative yield of **5c** (i.e., percent nonstereospecificity) increased from ~19 to 40%.

Table III. Photolysis of Diazoindene in Mixtures of *trans*-Butene and Octafluorocyclobutane at 25–35 °C

run	mole fraction of c-C_4F_8	relative yield, %[b] 5b-syn	5b-anti	5c
1	0.000	1.1	4.2	94.7
2	0.000	0.3	3.7	96.0
3	0.955	0.0	10.8	89.2
4	0.968	0.0	14.7	85.3

[a] For photolytic and analytical conditions, see Table II. [b] Errors are ~±2%, except for relative yields <10%, where reproducibilities are ~±10% of the tabulated values.

Table IV. Photolysis of Diazoindene in Isobutene[a]

run	temp, °C	% yield[b] 5a	6a	6a/5a[b]
1[c]	0	68.5	10.3	0.15 ± <0.01
2[d]	−78	43.3	7.9	0.18 ± 0.01
3[d,e,f]	−78	27.0	2.3	0.085
4[c]	−120	57.6	15.2	0.26 ± 0.01

[a] Diazoindene, 0.014 M, was photolyzed for 6–8 h, $\lambda > 411$ nm at the indicated temperature (maintained by an appropriate cooling bath). Analysis by HPLC (see Table II, note *a*) employed toluene as an internal standard. [b] Yields are based on diazoindene and are averages of duplicate experiments; reproducibilities are ~±2% (5a) and ~±1% (6a). The product ratios are averages of the ratios from each experiment. [c] No unreacted diazoindene remained after photolysis (IR). [d] Some unreacted diazoindene remained after photolysis (IR). [e] The isobutene was diluted with 93 mol % of 1,2-dichlorotetrafluoroethane. [f] Single run.

These photolyses were not run to completion, so that absolute product yields based on diazoindene were low. Relative to an internal toluene standard, total cyclopropane yields by HPLC were ~29% in neat *cis*-butene, 18% in run 4, 16% in run 9, and 15% in run 11; i.e., the absolute product yields decreased with dilution. Control experiments established the purity of the *cis*-butene (>99%) before and after photolyses. Cyclopropanes **5b** and **5c** were shown to be stable to the photolytic and analytical conditions.

The nonstereospecific formation of **5c** from *cis*-butene is most reasonably attributed to reactions of triplet **2**. Dilution with an inert solvent is a classic method of enhancing (nonstereospecific) triplet carbene addition reactions by providing collisional deactivation channels for the conversion of singlet to triplet carbenes.[5] Moreover, dilution of the substrate with 2,3-dimethylbutadiene greatly suppressed the reaction nonstereospecificity (runs 14 and 15, Table II). In run 14, the addition of 25 mol % of diene almost eliminated the formation of **5c**; the absolute yield of adducts **5b** was ~14% in this experiment. 1,3-Dienes are known scavengers of triplet carbenes.[5,14]

The observed ratio of isomeric *cis*-butene adducts, **5b**-*syn*/**5b**-*anti* varies from a low value of 0.70 in the presence of 97 mol % c-C_4F_8 (run 13) to a high value of 0.89 at 52 mol % 2,3-dimethylbutadiene (run 15). We take the latter value to be the *stereoselectivity of singlet* **2** in addition to *cis*-butene. As will be seen below, the diradical intermediate, formed during the addition of triplet **2** to the 2-butenes, selects *against* formation of **5b**-*syn*, so that the **5b**-*syn*/**5b**-*anti* ratio decreases as *cis*-butene is diluted with c-C_4F_8, and the participation of triplet **2** increases.

In Table III are adduct distributions observed upon photolysis of diazoindene in *trans*-butene. In the absence of diluent (runs 1 and 2), the reaction was ~95% stereospecific with **5c**/**5b** ~ 19. Addition of 95–96 mol % of c-C_4F_8 enhanced the yield of **5b**, which rose to ~15% of **5b**-*anti* at 96.8 mol % of diluent, lowering **5c**/**5b** to 5.8. Most strikingly, at high c-C_4F_8 dilutions (runs 3 and 4), where there was substantial involvement of triplet **2**, *essentially no* **5b**-*syn was formed*. Nonstereospecificity in the addition of triplet **2** to *trans*-butene was expressed by formation

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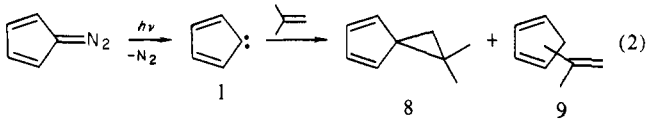
of only one of the two possible *cis*-dimethyl adducts, **5b**-*anti*.

Alkene Formation in Addition to Isobutene. Photolysis of diazoindene in isobutene gave adduct **5a** and alkene **6a**. Their distribution was examined as a function of temperature in the liquid phase, with the results shown in Table IV. Alkene formation was modestly enhanced, relative to cyclopropanation, as temperature decreased (runs 1, 2, and 4). An opposite trend appeared upon dilution of the −78 °C reaction solution with 93 mol % ClF_2CCF_2Cl (run 2 vs. 3).

For comparison purposes, cyclopentadienylidene (**1**) was generated in isobutene by photolysis of diazocyclopentadiene[3a] (eq 2). The spiro[2.4]heptadiene adduct **8** and alkene **9** were isolated



(2)

by GC and identified by NMR spectroscopy and appropriate comparisons to authentic samples.[15,16] After photolysis at 0 °C, HPLC gave the alkene/adduct (**9**/**8**) ratio as 0.14; photolysis at −120 °C led to an increase in alkene, with **9**/**8** = 0.29 (reproducibilities were better than ±0.01).

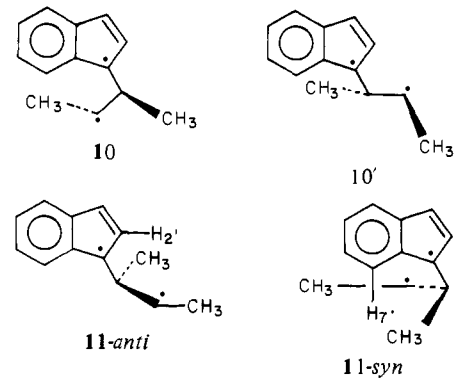
Discussion

The principal hypothesis used to interpret the stereochemical phenomena that accompany carbenic additions to alkenes is that of Skell and Woodworth,[17] which maintains that singlet carbenes add stereospecifically and triplet carbenes add nonstereospecifically. This theory, now often considered a "rule", requires that the triplet add to the alkene in a stepwise fashion, initially producing a triplet 1,3-diradical. Here, if the rates of bond rotations are comparable to or faster than the rate of spin inversion/ring closure, the original relative geometry of the alkenic substituents will be at least partially lost upon formation of the product cyclopropane. A singlet carbene, in contrast, is believed to add concertedly to an alkene, forming the cyclopropane with conservation of the original alkene substituent geometry.[17,18]

An important illustration of these principles, closely related to the chemistry of **2**, was the demonstration that singlet **3**, photogenerated from diazofluoroene, added to *cis*-butene with approximate stereospecificity when 1,3-butadiene was added to scavenge triplet **3**.[5] On the ther hand, when triplet **3** was generated from singlet **3** by collisional deactivation with hexafluorobenzene, grossly nonstereospecific addition was observed.[5] Recently, laser flash photolytic studies of the reactions of **3** with *cis*- and *trans*-pentene were interpreted as demonstrating *nonstereospecific* additions of singlet **3**.[7c] However, revised assignments of the spectroscopically observed intermediates, together with reinterpretation of the kinetic data, make it clear that there is no cogent evidence for nonstereospecific singlet fluorenylidene additions.[7a]

In view of its general success[18] and specific applicability to the chemistry of **3**,[5] we will use the Skell–Woodworth rule[17] to analyze the additions of **2** to *cis*- and *trans*-butene. Specifically, nonstereospecific addition will be attributed to the intervention of triplet **2**. The peculiar stereochemical properties exhibited by triplet **2**, particularly the nonformation of **5b**-*syn* during its addition to *trans*-butene, make possible a quite detailed analysis of the competitive additions of singlet and triplet **2**.

A concise interpretation of the data in Tables II and III is achieved with the following postulates: (a) Addition of triplet **2** to *trans*-butene affords *trans*-dimethyl triplet diradicals **10** and **10′**; addition to *cis*-butene yields *cis*-dimethyl triplet diradicals



11-*syn* and **11**-*anti*. (b) Interconversions among these conformationally different triplet diradicals are rapid, relative to spin inversion/closure, so that the same or nearly the same set of diradicals is formed from either *cis*- or *trans*-butenes. (c) Product formation does not competitively occur from **11**-*syn* (i.e., **5b**-*syn* is not formed from this diradical). (d) Formation of **5c** from **10** (**10′**) exceeds formation of **5b**-*anti* from **11**-*anti* by a factor of ~3–5.5. Let us see how this set of ideas both arises from and can be used to interpret the data.

At the qualitative level, the data indicate that photolysis of diazoindene generates mainly singlet **2**, which adds to *cis*- or *trans*-butene, mainly affording **5b** or **5c**. However, significant quantities of triplet **2** also form upon direct photolysis of the diazo compound, even in undiluted alkenes. The extent of triplet involvement can be enhanced upon dilution of the alkenes with *c*-C_4F_8.

One can make semiquantitative estimates of triplet addition under the various reaction conditions. Crucial to these estimates are runs 14 and 15 of Table II and runs 3 and 4 of Table III. The former examples show that dilution with radical scavenger 2,3-dimethylbutadiene essentially eliminates nonstereospecific addition of **2** and, consequently, formation of **5c** from *cis*-butene. Not only does this implicate triplet **2** as the principal source of nonstereospecificity, but one can take the observed **5b**-*syn*/**5b**-*anti* ratio of ~0.88 as characteristic of *singlet* **2** addition to *cis*-butene. From runs 3 and 4 (Table III), we see that addition of triplet **2** to *trans*-butene gives only the **5b**-*anti* nonstereospecific product and essentially none of its **5b**-*syn* isomer. Taking this to be a property of the set of triplet diradical intermediates **10**, **10′**, **11**-*anti*, and **11**-*syn* (points a and c) and assuming rapid bond rotations within these intermediates (point b), then it follows that the **5b**-*syn* *formed from* **2** *and cis-butene comes nearly exclusively from singlet* **2**.

We can therefore analyze run 1 of Table II (neat *cis*-butene) as follows: the 38.7% **5b**-*syn* from addition of singlet **2** demands that (38.7 ÷ 0.88) or 44.0% of **5b**-*anti* also comes from addition of singlet **2**. This leaves 4.3% of **5b**-*anti* and 13.0% of **5c** as formed by addition of *triplet* **2** to *cis*-butene. The total triplet product from *cis*-butene is then ~17%, formed in a *trans*-dimethyl (**5c**) to *cis*-dimethyl (**5b**-*anti*) ratio of ~3.0. A parallel analysis of run 13 Table I, where the *cis*-butene has been diluted with ~97 mol % of *c*-C_4F_8, indicates that triplet **2** additions now account for ~47% of the products (40% **5c** + 7% **5b**-*anti*). Here, however, the **5c**/**5b**-*anti* ratio from triplet **2** appears to be ~5.5 (point d).

These estimates are in reasonable agreement with an analysis of the *trans*-butene/indenylidene reactions. If in neat *trans*-butene photolysis of diazoindene also affords ~17% of products derived from triplet **2**,[19] then the extent of nonstereospecific product formation (**5b**-*anti*) should be ~3–4% depending on whether we take 5.5 or 3.0 as the **5c**/**5b**-*anti* product ratio associated with addition of triplet **2** to *either cis*- or *trans*-butene. About 4% of **5b**-*anti* is actually observed. Similarly, at high *c*-C_4F_8 dilution of *trans*-butene (Table III, runs 3 and 4), use of the result (derived

(15) Zimmerman, H. E.; Juers, D. F.; McCall, J. M.; Schroder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3662.
(16) Mitchell, R. S.; McLean, S.; Guillet, J. E. *Macromolecules* **1968**, *1*, 417.
(17) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496.
(18) Gaspar, P. P.; Hammond, G. S. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2, p 207f.

(19) We are assuming here that the efficiencies of additions of singlet and triplet **2** are comparable with *cis*- or *trans*-butene. With reactive carbenes such as **2**, we suspect that this assumption is good to within ~10%.[4]

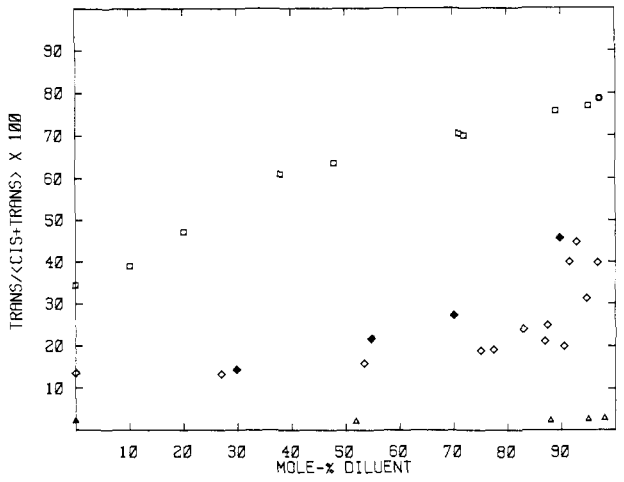


Figure 1. Nonstereospecificity of carbene additions expressed as (percent *trans*-cyclopropane)/(total cyclopropane product) for additions of **1–3** to *cis*-alkenes as a function of added diluent: △, reaction of **1** with *cis*-4-methylpent-2-ene, diluent *c*-C_4F_8;[4] ◇, reaction of **2** with *cis*-butene, diluent *c*-C_4F_8 (◆, diluent C_6F_6[23]); □, reaction of **3** with *cis*-butene, diluent C_6F_6.[5]

above) that ~47% of the adducts come from triplet **2** predicts that ~7–12% of **5b**-*anti* should be formed; 10.8–14% is actually observed.

These semiquantitative analyses derive straightforwardly from points a–d above and lead to conclusions that are in reasonable accord with the data. The apparent applicability to *trans*-butene reactions of the kinetically controlled **5c**/**5b**-*anti* product ratio extracted from the triplet **2**/*cis*-butene data suggests that the same set of diradical intermediates is indeed obtained from triplet **2** and either butene isomer.

Why is only **5b**-*anti* formed from triplet **2** and 2-butene? Molecular models of triplet diradicals **11**-*anti* and **11**-*syn* show significantly greater steric interaction between the "cis" dimethyl groups of the alkyl fragment and the peri aromatic proton ($H_{7'}$) in **11**-*syn* (nearest internuclear approach ~1.4 Å[20]) than between the methyl groups and indenyl proton $H_{2'}$ in **11**-*anti* (~1.9 Å[20]). Consequently, **11**-*syn* is disfavored relative to **11**-*anti*; and spin inversion/closure occurs from the latter, dominant population, affording **5b**-*anti*.[21] A parallel argument suggests that closure to *trans*-dimethyl product **5c** should occur from diradical **10**, rather than **10'**, but stereochemical evidence is not available here. Finally, relief of the vicinal "cis" dimethyl interaction of **11**-*anti* makes **10** the most favored of the diradicals, accounting for the 3–5-fold dominance of **5c** over **5b**-*anti* in product mixtures derived from triplet **2** additions to the 2-butenes.

In Figure 1, we display nonstereospecific product formation (*trans*-dialkyl product) as a function of diluent concentration for addition of cyclopentadienylidene (**1**)[4] to *cis*-4-methylpent-2-ene, and additions of indenylidene (**2**) or fluorenylidene (**3**)[5] to *cis*-2-butene. Quite different behavior is observed for each carbene. Carbene **1**, which is highly reactive and rather unselective,[3] adds with near stereospecificity no matter how much diluent is present, the percent-trans product reaching only 3.1% at 98 mol % *c*-C_4F_8. The marginal nonstereospecificity in this reaction could be attributable to addition of excited diazocyclopentadiene or excited singlet **1** rather than triplet **1**, because nonstereospecificity persisted even in the presence of 60 mol % of 2,5-dimethyl-2,4-hexadiene.[4] Thus, triplet **1** is not readily accessible from singlet **1** in solution by use of collisional deactivation at reasonable diluent concentrations. Reactions of singlet **1** may be too rapid and/or its decay to triplet **1** may be too slow, realtive to those reactions, even after ~100-fold dilution.

On the other hand, triplet **3** is readily obtainable in solution.[5] The percentage of *trans*-dimethyl product from *cis*-butene is ~34% in neat *cis*-butene and rises almost linearly with dilution to ~80% at 98 mol % hexafluorobenzene diluent. Jones and Rettig clearly showed that this diluent-mediated nonstereospecificity is associated with triplet **3**.[5] The dibenzo substitution that formally converts **1** to **3** might function in two ways: it could make singlet **3** less reactive than singlet **1**, so that intersystem crossing to triplet **3** would be more competitive with singlet reactions, or it could accelerate intersystem crossing. Both factors could also operate simultaneously to enhance access to triplet **3**.

The properties of indenylidene (**2**) are midway between those of **1** and **3**. The triplet is obtainable in solution but requires high dilution to establish substantial concentrations. The percentage of *trans*-dimethyl product is ~13% from neat *cis*-butene and increases only marginally up to ~80 mol % diluent. Thereafter, a sharp increase in trans-product formation is observed, which reaches ~40% at [*c*-C_4F_8] > 91 mol %.[23a] The relative accessibilities of triplets **1**, **2**, and **3** by collisional deactivation in solution are thus seen to be related to the number of benzo substituents carried by the carbenes, which, in turn, may determine both the reactivities of the singlet carbenes and their rates of intersystem crossing.[23b]

Brief comment is required on two other points. What is the origin of the triplet **2** that gives rise to the 13% nonstereospecificity (17% triplet) observed during photolysis of diazoindene in neat *cis*-butene? We suspect that this triplet probably comes from the diazoindene, possibly via intersystem crossing of excited singlet to triplet diazo compound, from which triplet **2** arises directly upon loss of nitrogen. If the triplet carbene stemmed from intersystem crossing of the singlet carbene, we would have expected the addition of inert diluent to have been much more effective in increasing triplet yield at low diluent concentrations.

Secondly, we have no direct stereochemical evidence bearing on the achievement of equilibration between singlet and triplet **2**. Scatter in the data at high dilution makes it difficult to know if the stereochemistry has become independent of [*c*-C_4F_8] at high dilution, which would be expected for an equilibrated system of singlet and triplet **2**.[23b]

With certain ground-state triplet carbenes, where singlet/triplet equilibrium mixtures can be readily obtained in *solution*, lowering the reaction temperature strongly favors abstraction–recombination reactions of the triplet with olefinic substrates (leading to alkene products) over competitive addition reactions of the singlet (leading to cyclopropanes). For example, the alkene/cyclopropane product ratio for reactions of diphenylcarbene with isobutene changes from 0.24 at 0 °C to 3.07 at −130 °C.[24] The behavior of **1**, **2**, or **3**

(20) Internuclear separations were measured from "custom-cut" Framework Molecular Models (Prentice-Hall).

(21) Closure must occur from singlet 1,3-diradicals corresponding to **11**-*anti* and **11**-*syn*. The energetics, conformational equilibria, and stereoelectronic effects associated with singlet 1,3-diradicals have recently been reviewed.[22] Current calculations suggest that stereoelectronically generated rotational barriers in singlet 1,3-diradicals are very low (<1 kcal/mol). At this level and considering both the extensive substitution of our 1,3-diradicals as well as the delocalization of one electron over the indenyl moiety, it seems impossible to make a cogent analysis of the behavior of diradicals **11** after spin inversion places them on the singlet surface. Presently, we believe that the steric interactions generate considerably higher differential conformational energies on both singlet and triplet diradical surfaces and provide a satisfactory rationale for the observed stereochemistry.

(22) Borden, W. T. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2 p 175f.

(23) (a) Several experiments were also carried out with hexafluorobenzene rather than *c*-C_4F_8 as a diluent (cf. Figure 1, solid diamonds). Although the nonstereospecificity of **2** appears to be slightly greater with C_6F_6, the overall dependence of nonstereospecificity on [diluent] is similar for the two diluents. (b) Recent flash photolytic studies (Brauer, B.-E.; Grasse, P. B.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6814, private communication from Professor Schuster) suggest that intersystem crossing and equilibration of singlet and triplet **3** may be very rapid. In this event, the C_6F_6 dilution effect on the stereochemistry of addition of **3**[5] might not operate by the collisional deactivation mechanism. Rather, C_6F_6 would act by perturbing the spin-state equilibrium so as to favor product formation from triplet **3**. Should this alternative explanation be correct, it might also be applicable to the diluent-mediated stereochemical behavior of the addition reactions of **2**. On the other hand, as shown in Figure 1, the concentration dependence of the diluent-induced nonstereospecific addition of **2** to *cis*-butene is quite similar whether C_6F_6 or *c*-C_4F_8 is the diluent. Because *c*-C_4F_8 would appear to lack obvious low-energy modes of complexation with singlet or triplet **2**, its putative equilibrium perturbation would likely take the form of a polar solvent effect.

is not similar (cf. above and Table IV). Alkene/cyclopropane ratios rise only from 0.15 (0 °C) to 0.26 (−120 °C) with **2** and isobutene and from 0.14 to 0.29 with **1** under similar reaction conditions. With **3** the ratio is only 0.04 at 0 °C and actually declines to 0.014 at −100 °C.[6] We suspect that with **1** and **2** at 0 °C the alkene products are mainly produced by direct insertion of the singlet carbenes. Lowering the temperature to −120 °C may provide access to marginally increased quantities of triplets and somewhat higher alkene yields, but large effects are absent. Apparently, a prior, rapid equilibration of singlet and triplet carbenes in solution, achieved with Ph_2C but not with **1–3**, is necessary if temperature variation is to significantly alter the alkene/cyclopropane product ratio.

Experimental Section

General. Proton NMR spectra were recorded on a Varian T-60 spectrometer in CCl_4 solution with an internal $(CH_3)_4Si$ standard or were measured at 80 MHz in $CDCl_3$ solution using a Varian Model FT-80 spectrometer. Mass spectra were recorded on a Du Pont Model 21-490 mass spectrometer.

Analytical HPLC was carried out on a Waters Associates instrument fitted with a C-18 reverse-phase column. We used a CH_3CN/water mixture as the eluent, with UV detection at 254 nm. The detector was calibrated with known mixtures of pure products. Reaction mixture peaks were identified by augmentation with authentic samples. Separation conditions included: condition A 55% CH_3CN/45% water, flow rate = 2.1 mL/min; condition B 67% CH_3CN/33% water, flow rate = 1.0 mL/min; condition C 70% CH_3CN/30% water, flow rate = 1.5 mL/min. Preparative GC was done on a Varian Aerograph Model 90-P instrument, fitted with a 10 ft × 0.25 in. 5% Carbowax 20M + 5% SE-30 on 60/80 GCR column. All gaseous alkenes were purchased from Matheson Company and were dried by passage through a column of calcium sulfate prior to use. Microanalyses were performed by Robertson Laboratory, Florham Park, NJ.

Diazoalkanes. Diazocyclopentadiene was prepared by the method of Weil and Cais.[3a,25] Diazoindene was prepared by the method of Quinn and Shaver.[13] The crude diazoindene was further purified by chromatography in pentane on basic Al_2O_3, activity grade III. Its UV, ^1H NMR, and IR spectra were in agreement with those reported by Rewicki and Tuchscherer.[8] As used in the present work, the diazoindene contained up to 30% of indene and was diluted with approximately 30% of pentane. Its concentration was determined by ^1H NMR.

Synthesis of Cyclopropanes and Olefinic Insertion Products. General Procedure. About 15 mL of the desired alkene was condensed and added to a precooled screw-top (Pyrex) Carius tube. The diazo compound (~8 mmol) in pentane solution was then added, the tube was sealed and warmed to 25 °C, and the contents were stirred magnetically and photolyzed for 8–16 h at 25–35 °C with a focused Osram 200XE mercury lamp. After photolysis, the tube was cooled and opened, and the excess olefin was evaporated at 25 °C. The residue was distilled on a Kugelrohr apparatus and the distillate was subjected to GC for product isolation.

syn*- and *anti*-*cis*-2,3-Dimethylspiro(cyclopropane-1,1′-indene) (5b-*syn* and 5b-*anti*).** These products were formed from diazoindene and *cis*-butene and isolated as a mixture in 24% yield by GC: the GC retention time was 7.9 min at a column temperature of 205 °C; on HPLC, **5b-*syn had a retention time of 22.8 min, that of **5b-*anti*** was 26.3 min (condition A);[26] 300-MHz NMR ($CDCl_3$) δ 7.45 (d, $H_{4'}$ syn, $J_{4'5'}$ = 7.3 Hz), 7.40 (d, $H_{4'}$ anti, $J_{4'5'}$ = 7.3 Hz), 7.27–7.15 (m, $H_{5'}$, $H_{6'}$, $H_{7'}$ syn, $H_{5'}$, $H_{6'}$ anti), 7.01 (d, $H_{3'}$ anti, $J_{3'2'}$ = 5.8 Hz, with additional 0.5 Hz coupling), 6.93 (d, $H_{7'}$ anti, $J_{6'7'}$ = 7.6 Hz), 6.77 (d, $H_{3'}$ syn, $J_{2'3'}$ = 5.2 Hz), 6.48 (d, $H_{2'}$ anti, $J_{2'3'}$ = 5.7 Hz), 6.11 (d, $H_{2'}$ syn, $J_{2'3'}$ = 5.4 Hz), 2.20–2.14 (m, anti cyclopropyl protons), 2.14–2.07 (m, syn cyclopropyl protons), 1.35 (d, J = 6.2 Hz, with additional 2.0 Hz coupling, anti CH_3 groups), 1.31 (d, J = 6.1 Hz with additional 1.8 Hz coupling, syn CH_3 groups).[27,28] Integral areas were in accord with assignments.

Anal. Calcd for $C_{13}H_{14}$: C, 91.70; H, 8.30. Found: C, 91.84; H, 7.99.

1-(*cis*-2-Butenyl)indene (6b). This product was also obtained from the reaction of diazoindene and *cis*-butene: it was isolated in 67% yield by GC, column temperature 205 °C, retention time 5.5 min; HPLC retention time 33.7 min (condition A); 80-MHz NMR spectrum ($CDCl_3$) δ 7.05–7.6 (m, 4 H, aromatic), 6.7–6.9 (m, 1 H, H_3), 6.4–6.6 (m, 1 H, H_2), 5.4–5.6 (m, 2 H, butenyl CH=CH), 3.2–3.8 (m, 1 H, H_1), 2.4–2.8 (m, 2 H, butenyl allylic CH_2), 2.6 (d, J = 5 Hz, 3 H, CH_3); mass spectrum, m/e 170 (M^+).

***trans*-2,3-Dimethylspiro(cyclopropane-1,1′-indene) (5c).** This product was isolated in 21% yield from the photolytic reaction of diazoindene and *trans*-butene: GC retention time 6.9 min, column temperature 205 °C; HPLC retention time 24.3 min (condition A); 80-MHz NMR spectrum ($CDCl_3$) δ 7.15–7.70 (m, 4 H, aromatic), 6.98 and 6.43 (AB quartet, J_{AB} = 4 Hz, 2 H, $H_{2'}$, $H_{3'}$), 1.8–2.2 (m, 2 H, cyclopropyl), 1.45 (crude d, J = 4 Hz, 6 H, methyls).[28]

Anal. Calcd for $C_{13}H_{14}$: C, 91.70; H, 8.30. Found: C, 91.89; H, 8.20.

1-(*trans*-2-Butenyl)indene (6c). This product was isolated by GC in 6% yield from the reaction of diazoindene and *trans*-butene: GC retention time 5.3 min at 205 °C; HPLC retention time 37.1 min (condition A); 80-MHz spectrum ($CDCl_3$) δ 7.0–7.5 (m, 4 H, aromatic), 6.3–6.9 (m, [poorly resolved AB quartet], 2 H, H_2, H_3), 5.4–5.6 (m, 2 H, butenyl CH=CH), 3.1–3.7 (m, 1 H, H_1), 1.8–2.6 (m, 2 H, butenyl allylic CH_2), 1.5–1.8 (m, 3 H, CH_3); mass spectrum, m/e 170 (M^+).

2,2-Dimethylspiro(cyclopropane-1,1′-indene) (5a). This product was isolated by GC in 27% yield from the photolytic decomposition of diazoindene in isobutene: GC retention time 7.9 min at 205 °C; HPLC retention time 19.9 min (condition C); its proton NMR spectrum agreed with that reported by Staley.[10,28]

Anal. Calcd for $C_{13}H_{14}$: C, 91.70; H, 8.30. Found: C, 91.66; H, 8.22.

1-(2-Methyl-2-propenyl)indene (6a). This product was isolated by GC in 4% yield from reaction of diazoindene and isobutene: GC retention time 67.3 min at 205 °C; HPLC retention time 26.5 min (condition C); 80-MHz NMR spectrum ($CDCl_3$) δ 7.0–7.5 (m, 4 H, aromatic), 6.5 and 6.8 (AB quartet, J = 4 Hz with additional 2 Hz coupling, 2 H, H_2, H_3), 4.8 (d, J = 2 Hz with additional splitting, 2 H, $=CH_2$), 3.5–3.8 (m, 1 H, H_1), 2.05–5.4 (m, 2 H, propenyl allylic CH_2), 1.8 (s, 3 H, CH_3); mass spectrum, m/e 170 (M^+).

Anal. Calcd for $C_{13}H_{14}$: C, 91.70; H, 8.30. Found: C, 91.56; H, 8.32.

2,2-Dimethylspiro[2.4]hepta-4,6-diene (8). This product was isolated by GC in 15% yield from the photolysis of diazocyclopentadiene in isobutene: GC retention time 6.7 min at 130 °C; HPLC retention time 7.0 min (condition C); its proton NMR spectrum agreed with that reported by Zimmerman.[15] Anal C, H.

Methallylcyclopentadiene (9). This compound was prepared from sodium cyclopentadienide and methallylchloride by the method of Mitchell.[16] Its HPLC retention time was 10.0 min (condition C).

Stereospecificity of Addition of 2 to 2-Butenes. In the general procedure, 40 mg of diazoindene was added to 20 mL of *cis*- or *trans*-butene in a 3.5 × 8 in. Pyrex tube that contained a magnetic stir bar. The sample was then degassed at −196 °C (0.05 mmHg) and blanketed with nitrogen. We used three freeze–thaw cycles; the sample was then sealed under nitrogen at −78 °C and warmed to room temperature in the dark. It was photolyzed at 25–35 °C, with stirring, for 3 h with a focused Osram 200XE mercury lamp with a Corning sharp cut ($\lambda > 411$ nm) glass filter. After photolysis, excess olefin was allowed to evaporate at room temperature. The reaction residue was diluted with acetonitrile, filtered, and analyzed by HPLC (condition A). In some cases, a known weight of toluene was added to the reaction residue as an internal standard before analysis.

Dilution Experiments. A known weight of octafluorocyclobutane (Matheson Co.) and *cis*- or *trans*-2-butene together with 40 mg of diazoindene were mixed in a Pyrex tube. The total solution volume was about 30 mL. The sample was degassed and photolyzed as described above. The excess olefin and diluent were allowed to evaporate and the residue was analyzed by HPLC. 2,3-Dimethylbutadiene and *cis*-2-butene were mixed in known proportions with 40 mg of diazoindene in a Pyrex tube. The reaction mixture was degassed and photolyzed. Excess olefin and dimethylbutadiene were carefully removed at room temperature under reduced pressure. The residue was analyzed by HPLC.

Low-Temperature Photolyses. In the general procedure, 40 mg of diazoindene or diazocyclopentadiene were added to 20 mL of isobutene in a 3.5 × 15 in. Pyrex tube. The mixture was degassed as described above. The sample was then thawed in the dark and transferred to a quartz-tailed Dewar, containing coolant at the appropriate temperature. The Dewar was placed in the center of a Rayonet photolysis apparatus containing 16, 300-nm lamps, and the sample was irradiated for 6–8 h. After photolysis the tube was cooled to −78 °C and opened, and the excess isobutene was evaporated at room temperature. A known weight of toluene was added to the reaction residue as an internal standard. The

(24) Moss, R. A.; Huselton, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1314.
(25) Weil, T.; Cais, M. *J. Org. Chem.* **1963**, *28*, 2472.
(26) Cyclopropanes **5b-*syn*** and **5b-*anti*** were assumed to have identical HPLC detector response factors because the raw peak area ratio was identical with that obtained by integration of their $H_{7'}$ vinyl proton NMR resonances.
(27) The spectral assignments were made by Dr. Byron H. Arison (Merck, Sharp, and Dohme Research Laboratories), who determined the spectra.
(28) A description of the ^{13}C NMR spectrum will appear in the Ph.D. Dissertation of C. M. Young.

sample was diluted with CH_3CN, filtered, and analyzed by HPLC (condition B was used for the reaction of diazoindene with isobutene; condition C was used for the reaction of diazocyclopentadiene with isobutene). In the dilution experiments, a known mixture of 1,2-dichlorotetrafluoroethane and isobutene together with 40 mg of diazoindene was prepared in a Pyrex tube. The mixture was degassed and photolyzed as described above. The excess olefin was evaporated. The residue was diluted and analyzed by HPLC (condition B).

Control Experiments. *cis*- and *trans*-2-butenes were examined before and after photolysis by GC on a 7 ft × 0.25 in. 40% $AgNO_3$ on 45/60 GCR column at 40 °C. In each case the olefins were greater than 99% pure. The stereochemical stability of the cyclopropane adducts to the photolysis conditions was tested by adding a known mixture of **5b**-*syn*, **5b**-*anti*, and **5c** to a mixture of *trans*-4-methyl-2-pentene and diazoindene and then irradiating the mixture under standard reaction conditions. HPLC analysis showed no change in the cyclopropane distribution after irradiation. Similar control experiments were performed with mixtures of alkene and cyclopropane products from the reactions of diazoindene and diazocyclopentadiene with isobutene. In each case the products were found to be stable to the photolysis conditions.

Acknowledgments. We are grateful to the National Science Foundation for financial support. We sincerely thank Dr. Byron H. Arison of Merck, Sharp, and Dohme Research Laboratories, Rahway, NJ, for 300-MHz proton NMR spectra, for assistance with their interpretation, and for the NOE experiments. We also thank Prof. Joseph D. Rosen (Food Science Department, Cook College, Rutgers University) for the mass spectra and D. Silver for technical assistance.

Registry No. 1, 4729-01-5; **2**, 82539-36-4; **5a**, 60584-81-8; **5b**-*syn*, 86436-88-6; **5b**-*anti*, 86495-12-7; **5c**, 86495-13-8; **6a**, 86436-89-7; **6b**, 86436-90-0; **6c**, 86436-91-1; **8**, 24321-67-3; **9**, 86436-92-2; diazacyclopentadiene, 1192-27-4; diazoindene, 35847-40-6; isobutene, 115-11-7; *cis*-butene, 590-18-1; *trans*-butene, 624-64-6.

X-ray and Theoretical Analysis of the Relationship between Substituent Steric Effects and the Structure of Bicyclo[1.1.0]butane. The Unexpected Flexibility of the Bicyclo[1.1.0]butane Skeleton

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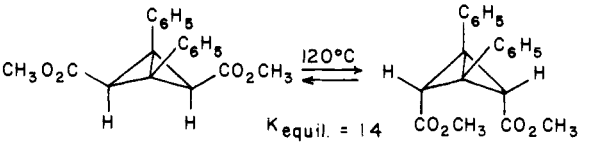
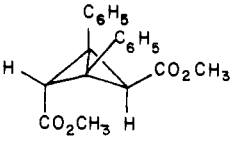
Abstract: Single-crystal X-ray analyses have been run for the three possible stereoisomers of 1,3-diphenyl-2,4-bis(methoxycarbonyl)bicyclo[1.1.0]butane. The endo–endo, exo–endo, and exo–exo diester interflap angles were 127.2°, 121.2°, and 113.4°, respectively, which showed surprising flexibility in the bicyclo[1.1.0]butane skeleton. As the interflap angle decreased, the C1–C3 bond lengths shortened (1.558, 1.498, and 1.455 Å, respectively). The bridgehead phenyl groups moved closer together as the interflap angle increased. This counter-intuitive movement of the bridgehead substituents necessitated that a least-motion discontinuity was required for any process involving flap inversion of the bicyclo[1.1.0]butane skeleton. In order to evaluate this relationship of bridgehead substituent position to the interflap angle of the bicyclo[1.1.0]butane skeleton, a theoretical study of the relationship between the interflap angle and the other bonding parameters was carried out for bicyclo[1.1.0]butane with both fully optimized HF–SCF and a generalized valence bond (GVB) approach in the PRDDO approximation. These calculations covered the range of interflap angles from 99° to 180° (planar bicyclo[1.1.0]butane). Our calculations corroborate the experimentally determined structural relationships and extend beyond what is experimentally determined. Discontinuity occurred at an interflap angle of 150 ± 2°, where the bridgehead substituents ceased their inward migration and subsequently moved outward as the interflap angle proceeded from 150° to 180°. At an interflap angle of 180°, the molecule lacked D_{2h} symmetry with the bridgehead hydrogens being out of the four-carbon plane by approximately 30°. The inversion barrier for a shift of these bridgehead hydrogens from one side of the four-carbon plane to the other side was calculated to be 4 kcal/mol.

Highly strained, polycyclic molecules have attracted considerable attention during the last two decades.[3] Both experimental and theoretical studies have emphasized the unique properties of this class of compounds. Because of its unique chemical reactivity and supposedly rigid structure, the bicyclo[1.1.0]butane system has received the most attention. Among the relatively large number of examples of anomolous behavior noted for this bicyclic ring system was a study of its flap inversion by Woodward and Dalrymple.[4] These workers reported that the stereoisomers **1** and **2** were interconverted at 120 °C.[5] Most curious about this



1 **2**



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report[4] was the finding that the diendo isomer, **2**, was the thermodynamically more stable component of the equilibrium mixture.

(1) Lando Undergraduate Fellow, summer 1975.
(2) A. P. Sloan Fellow, 1977–1979; Camille and Henry Dreyfus Teacher-Scholar, 1978–1983; Du Pont Young Faculty Grantee, 1978.
(3) For a leading reference see: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.
(4) Woodward, R. B.; Dalrymple, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 4612.
(5) D'yakonov, I. A.; Razen, V. V.; Komendantov, M. I. *Tetrahedron Lett.* **1966**, 1127, 1135.

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