References and Notes

(1) Chemistry of Enol Silyl Ethers. 5. For Part 4, see ref 11.
(2) Chan, T. H.; Brownbridge, P. *J. Chem. Soc., Chem. Commun.* **1979,** 578.
(3) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977,** *16,* 817.
(4) It is possible that a trans trimethylsilylation has taken place.
(5) The dominant tautomer of benzoylacetone in $CDCl_3$ is **4**: Sardella, D. J.; Heinert, D. H.; Shapiro, B. L. *J. Org. Chem.* **1969,** *34,* 2817. A similar conclusion has been drawn in the crystalline state: Semmingsen, D. *Acta Chem. Scand.* **1972,** *26,* 143.
(6) It has been reported that the dianion of *tert*-butyl acetoacetate condenses with the monoanion of formylacetone to give *tert*-butyl 6-methylsalicylate, presumably in an analogous manner: Harris, T. M.; Murray, T. P.; Harris, C. M.; Gumulka, M. *J. Chem. Soc., Chem. Commun.* **1974,** 362.
(7) The relative reactivity of acetal vs. ketone toward titanium tetrachloride has been noted by Mukaiyama.[3]
(8) Mukaiyama, T.; Hayashi, M. *Chem. Lett.* **1974,** 15.
(9) Kende, A. S.; Curran, D. P. *J. Am. Chem. Soc.* **1979,** *101,* 1857.
(10) Brownbridge, P.; Chan, T. H., unpublished results.
(11) Brownbridge, P.; Chan, T. H. *Tetrahedron Lett.* **1979,** 4437.
(12) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969,** *34,* 2324.
(13) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974,** *96,* 7807.
(14) Burlachenko, G. S.; Baukov, Y. I.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1970,** *40,* 97; *Chem. Abstr.* **1970,** *72,* 132859h.
(15) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Chem. Lett.* **1978,** 649.
(16) It should be noted that, although **1** bears a formal resemblance to 1,1-dimethoxy-3-trimethylsiloxybuta-1,3-diene,[17] there is a considerable contrast in their reactions, since **1** is a very poor Diels-Alder diene.[2,10,15]
(17) Banville, J.; Brassard, P. *J. Chem. Soc., Perkin Trans. 1* **1976,** 1852. Danishefsky, S.; Singh, R. K.; Gammill, R. B. *J. Org. Chem.* **1978,** *43,* 379. Danishefsky, S.; Etheredge, S. J. *Ibid.* **1978,** *43,* 4604.
(18) West, R. *J. Am. Chem. Soc.* **1958,** *80,* 3246.
(19) Howe, J. J.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1969,** *91,* 5378.
(20) Kantlehner, W.; Kugel, W.; Bredereck, H. *Chem. Ber.* **1972,** *105,* 2264.
(21) Hellberg, L. H.; Juarez, A. *Tetrahedron Lett.* **1974,** 3553.
(22) This compound has been prepared previously but no physical or spectroscopic details were reported: Murai, S.; Aya, T.; Sonoda, N. *J. Org. Chem.* **1973,** *38,* 4354.
(23) Ansell, M. F.; Nash, B. W.; Wilson, D. A. *J. Chem. Soc.* **1963,** 3028.
(24) (a) Peltier, D. *C. R. Acad. Sci.* **1953,** *236,* 1972. (b) Compound **11** is reported to be an alarm pheromone of various species of ant: Duffield, R. M.; Blum, M. S. *Experientia* **1975,** *31,* 466, and references cited therein.
(25) Anschütz, R.; Post, F.; Corty, E.; Riemer, K.; Inderhees, R.; Lüssem, A. *Justus Liebigs Ann. Chem.* **1924,** *439,* 8.
(26) Workup at this point gives **16**.[8]
(27) Schroeter, G.; Svanoe; Einbeck, H.; Geller, H.; Riebensahm, E. *Justus Liebigs Ann. Chem.* **1922,** *426,* 83.
(28) Hunsberger, I. M.; Gutowsky, H. S.; Powell, W.; Morin, L.; Bandurco, V. *J. Am. Chem. Soc.* **1958,** *80,* 3294.
(29) Previously reported as a component of a mixture: Sarkar, A. K.; Chatterjee, A. *Tetrahedron* **1976,** *32,* 73.
(30) Mosettig, E.; Stuart, A. H. *J. Am. Chem. Soc.* **1939,** *61,* 1.

The Bicycle Rearrangement. Relationship to the Di-π-methane Rearrangement and Control by Bifunnel Distortion. Mechanistic and Exploratory Organic Photochemistry[1,2]

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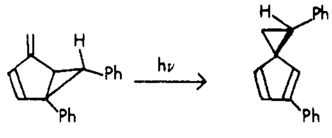
Abstract: The generality of the bicycle rearrangement was extended and the mechanism was further investigated by study of the photochemistry of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene, 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene, 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene, 2,2-dimethylspiro[cyclopropan-1,1′-indene], and 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene. Direct irradiation of the benzobicyclohexene led to the spiroindene as the major product with a quantum yield of 0.040. The minor photoproduct was the 2,2-dimethyldihydronaphthalene, formed with a quantum yield of 0.0033. Both products arise from a mechanism in which the isopropylidene moiety bicycles along the 1-methylenindene π system. The 2,2-dimethyldihydronaphthalene derives from an intermediate cyclopropyldicarbinyl diradical, arising in the bicycling process, opening its three ring. Irradiation of the 2,2-dimethyldihydronaphthalene led exclusively to the benzobicyclohexene without formation of the spiroindene isomer; the efficiency here was 0.086. This reaction is only formally the reverse of the benzobicyclohexene photolysis and utilizes a different state of the cyclopropyldicarbinyl diradical as an intermediate. The lack of formation of spiroindene product from the 2,2-dimethyldihydronaphthalene is discussed in terms of a distorted bifunnel effect. The photolysis of the 4,4-dimethyldihydronaphthalene led to the benzobicyclohexene with an efficiency of 0.22; here, again, a bicycle mechanism is used. The spiroindene isomer and the 1,1-dimethyldihydronaphthalene were unreactive. Also, the triplets throughout were unreactive. Singlet excited state rate constants were derived for each of the reactions. Correlation diagrams, consisting of a triptych with benzobicyclohexene, dihydronaphthalene, and spiro compound at the three branches, reveal a HOMO–LUMO crossing on the benzobicyclohexene branch. The positioning of the crossing, again, accounts for the unidirectionality of the reactions. At the SCF-CI level a distorted bifunnel was encountered and the hypersurfaces concur in predicting the photochemistry. The distorted funnel concept was developed along with other related photochemical theory.

Introduction

Present-day photochemistry has two main objectives. One is the quest for new and general types of photochemical reactions. The other is the search for theory elaborating the factors controlling excited-state transformations. Among the reactions we have been subjecting to study, the bicycle rearrangement[3] is one of the most fascinating, both because of its generality and also because of its utility in defining new photochemical theory.

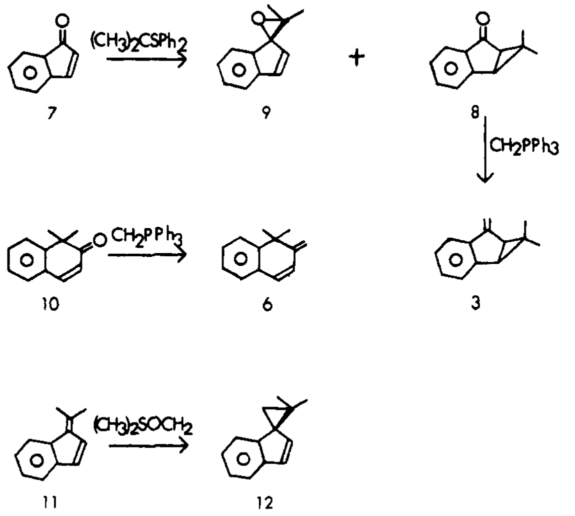
Equation 1 describes a typical example of the photochemical bicycle rearrangement, an example of particular interest because the reaction is seen to be stereospecific. One of our main



1 2

(ref 3b) (1)

Scheme I. New Syntheses of Photochemical Reactants and Products



objectives was to extend the generality of this reaction.

For the present study we selected 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene (**3**) for study. Additionally, the photochemistry of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene (**4**) was of concern since this type of molecule and benzobicyclohexenes had been found[2b] to be photochemically interrelated. Our study extended to the photochemistry of two related systems, that of 4,4-dimethyl-1-methylene-1,2-dihydronaphthalene (**5**) and 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene (**6**).

Results

Synthesis of Photochemical Reactants and Potential Photochemical Products. Our synthetic efforts are summarized in Scheme I. Two points are of special interest. The first is the synthesis of benzobicyclohexene **3**. For this the tricyclic ketone **8** was required and this was approached by reaction of indenone (**7**) with diphenylsulfonium isopropylide.[5a] Typically, for enones without β substitution, the predominant reaction is Michael addition-displacement.[5a-d] The reaction of indenone (**7**) is unique in affording a predominance of epoxide product (i.e., **9**, 51%) and a lesser amount (22%) of desired cyclopropane **8**.

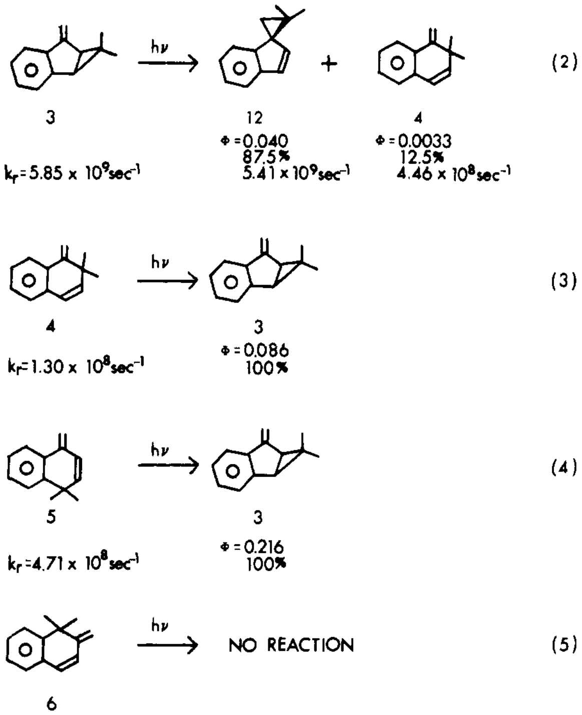
Secondly, our synthesis of spiroindene **12** utilized the addition of dimethylsulfoxonium methylide to the polarized benzofulvene-type π bond in indene **11**. This has single precedent in our previous study.[2b]

Exploratory Photochemistry. Our first objective was to ascertain the gross course of the photochemistry for the compounds of interest. Irradiation of benzobicyclohexene **3** proceeded to afford a single isomeric photoproduct in excellent (>95%) yield. The photoproduct's structure was suggested by its spectral characteristics (note the Experimental Section), and this product proved identical with the independently synthesized spiroindene **12**. It was found that the exclusive formation of this photoproduct depended on long irradiation.

In photolyses made to lower conversions, a second photochemical product was formed. This, too, proved to be an isomer of benzobicyclohexene **3** and was identified as the 2,2-dimethyldihydronaphthalene **4**. The kinetic distribution of products and gross course of the photolysis are given in Scheme II, eq 2. It is seen that the 2,2-dimethyldihydronaphthalene is a minor product even with lower conversion under kinetically controlled conditions.

The absence of the minor product in the more extended photolyses, coupled with the very high mass balance, suggested that secondary photochemistry of this initially formed product was involved. Independent experiments irradiating the 2,2-dimethyldihydronaphthalene **4** revealed that it is isomerized to the benzobicyclohexene **3**. This, too, is depicted in Scheme II (note eq 3).

Scheme II. Photochemical Transformations with Kinetic Distributions, Quantum Yields, and Excited-State Rates



Thus, the benzobicyclohexene **3** and 2,2-dimethyldihydronaphthalene **4** are interconverted photochemically in a pseudo-steady state disturbed by the irreversible conversion to the spiroindene **12**.

A third reactant investigated was the 4,4-dimethyldihydronaphthalene **5**, of interest because of its structural similarity to its isomers discussed above. Irradiation of this reactant led to the benzobicyclohexene **3**, again in excellent yield. Note eq 4 of Scheme II.

Finally, a last isomer, namely, the 1,1-dimethyldihydronaphthalene **6**, was irradiated. In contrast to the examples described above, this reactant proved to be photochemically stable (cf. Scheme II, eq 5).

Quantum-Yield Determinations. These were obtained using the Black Box apparatus described in earlier work[6] which utilizes inorganic filter solutions (note the Experimental Section). The electronic actinometer[7a] used was calibrated for each run with ferrioxalate actinometer[7b] to correct for wavelength dependency. Product analysis was by VPC with an internal standard. Reassurance about the composition of the observed peaks was derived from preparative VPC runs in which product from each peak was characterized. Runs were made at varying conversions, with the lowest conversions being in the 1.5–4.0% range, and the results were extrapolated to 0%. The quantum-yield results are compiled in Scheme II.

Single Photon Counting Determination of Excited Singlet Rates. In our previous work we have noted that excited-state rate constants are more validly used than quantum yields to correlate with excited-state structure and mechanism. These rates are most conveniently obtained by the method of single photon counting with on-line minicomputer data accumulation and deconvolution as described in our earlier accounts.[8,9] The method has proven of considerable versatility in a variety of our previous studies.[10]

The excited state of decay, lifetimes, magic multipliers, and low-temperature reaction rates are compiled in Table I while the room-temperature rates are included in Scheme II.

Table I. Summary of Singlet Rates and Lifetimes[a,b]

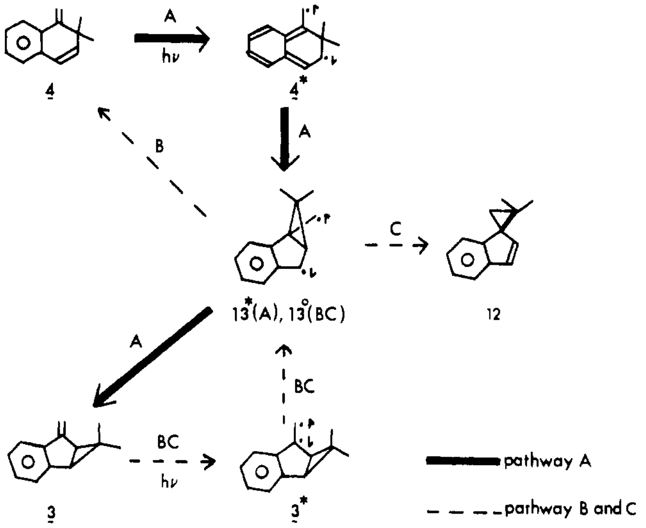
compd	M^c	temp, K	τ, ps	${}^1k_{dt}$, s^{-1}	${}^1k_r$, s^{-1} [d]
benzobicyclohexene **3**	10.2	293	7.40	1.35×10^{11}	5.72×10^8
		77	83.8	1.32×10^{10}	
2,2-dimethyldihydronaphthalene **4**	10.8	293	661	1.51×10^9	1.20×10^7
		77	7136	1.40×10^8	
4,4-dimethyldihydronaphthalene **5**	10.1	293	459	2.18×10^9	4.67×10^7
		77	4636	2.16×10^8	

M = magic multiplier = $({}^{77}\Phi_f)/({}^{RT}\Phi_f)$

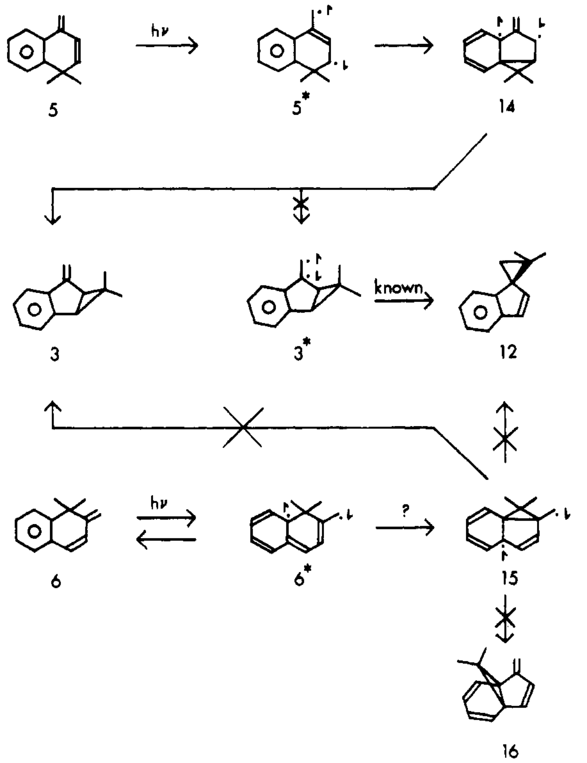
$\tau^{RT} = \tau^{77}/M \quad {}^1k^{RT}{}_r = \Phi_r {}^1k^{RT}{}_{dt}$

[a] See Experimental Section for full details. [b] All runs were made in methylcyclohexane–isopentane (4:1). [c] Average value of several runs. [d] Estimated probable error limits ±10%.

Scheme III. Qualitative Resonance Mechanisms for the Rearrangements



Scheme IV. Mechanisms for the 4,4-Dimethyl and 1,1-Dimethyl Reactants



Interpretative Discussion

A Qualitative Resonance Mechanism for the Reactions. Scheme III provides a qualitative description of the mechanisms leading from benzobicyclohexene **3** and from 2,2-dimethyldihydronaphthalene **4**. These mechanisms are labeled A, B, and C.

There are several intriguing facets apparent at this juncture. The first is that diradical species **13** exhibits behavior which is a function of its source. Thus, beginning with 2,2-dimethyldihydronaphthalene **4**, diradical **13** proceeds to afford only benzobicyclohexene **3**. In contrast, species **13** generated from benzobicyclohexene **3** proceeds onward to form both 2,2-dimethyldihydronaphthalene **4** and spiroindene **12** with the latter being favored 7:1 over the former (i.e., C:B = 7:1).

If one excludes chemical-momentum arguments for a species constrained to one energy surface, the same species cannot exhibit memory of its source and thus cannot react differently depending on mode of generation. Hence, we conclude that two diradicals with the gross structure **13** are involved. The diradical derived from 2,2-dimethyldihydronaphthalene **4** is assigned the excited singlet structure (i.e., $\mathbf{13}^*$) while the diradical derived from benzobicyclohexene is assigned a ground state S_0 configuration (i.e., **13**). We have previously made the observation[11] that ground-state 1,4 biradicals, especially of the cyclopropyldicarbinyl type, tend to undergo a 1,4 diradical 2,3 fragmentation (i.e., Grob fragmentation).[12] By analogy the unexcited structure $\mathbf{13}^0$ (i.e., S_0) is assigned to the diradical derived from benzobicyclohexene **3** by mechanisms BC. This point is considered from another viewpoint below.

We further note that electronically excited **13** (i.e., $\mathbf{13}^*$) fails to afford any spiroindene **12** but rather is quite specific in leading to benzobicyclohexene **3**. In contrast, ground-state $\mathbf{13}^0$ leads predominantly to spiroindene **12** and also to 2,2-dimethyldihydronaphthalene **4**.

Finally, the lack of reactivity of spiroindene is of interest. This does not derive from lack of competitive absorption and thus is indeed characteristic of the excited-state reactivity.

We now turn our attention to the photochemical behavior of 4,4-dimethyldihydronaphthalene **5** and 1,1-dimethyldihydronaphthalene **6**; note Scheme IV. The formation of benzobicyclohexene **3** from irradiation of 4,4-dimethyldihydronaphthalene **5** is seen to require benzo–vinyl bridging to afford biradical **14**, which then undergoes a single bicycle step to give benzobicyclohexene **3**. Furthermore, we know that the benzobicyclohexene formed in this last step is electronically unexcited, since otherwise it would proceed onward to afford spiroindene **12**.

1,1-Dimethyldihydronaphthalene **6** and 2,2-dimethyldihydronaphthalene **4** differ only in the location of the fused benzo ring. Thus, strict analogy predicts that the 1,1-dimethyl isomer **6** should rearrange to afford the nonaromatic product **16**. That 1,1-dimethyldihydronaphthalene **6** proved to be photochemically unreactive merely means that another example is found where disruption of aromaticity is an energetically unfavorable factor. Bicycling onto an aromatic ring has been avoided in the mechanisms we previously investigated.[2b,13,14] This is not in disagreement with the observation

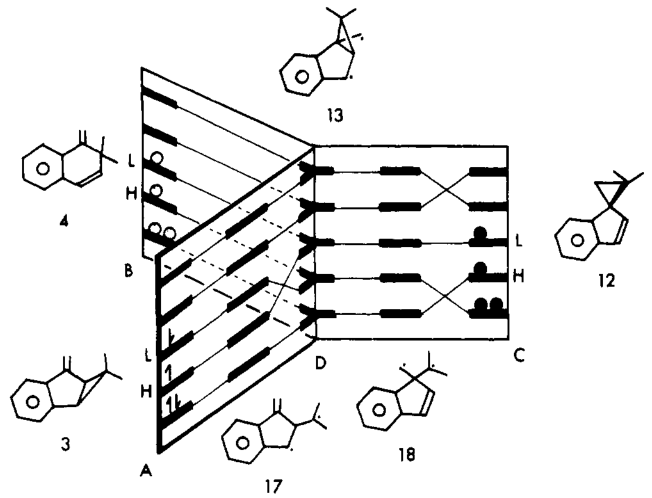


Figure 1. Triptych MO correlation diagram interconnecting the three species under study. Electronic configurations are those for the first excited state of each species of interest.

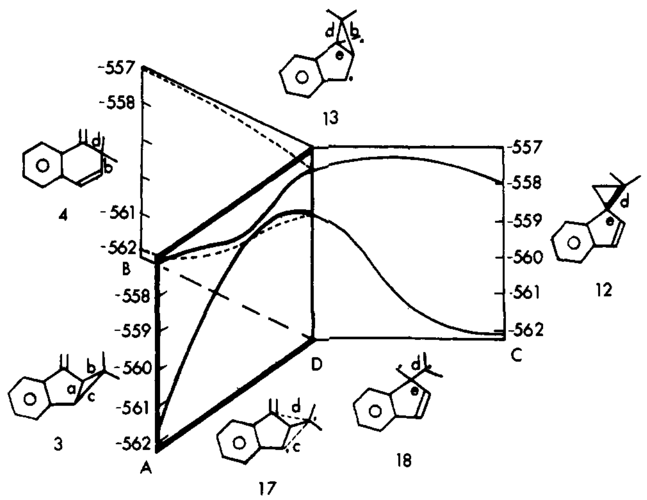


Figure 2. Triptych state diagram interconnecting the three species under study. State energies are given in eV.

that benzenoid systems sometimes are disrupted in photochemical reactions. For example, benzo-ring disruption does occur in species **14** derived from the photochemistry of 4,4-dimethyldihydronaphthalene **5**. Also in various aryl migration reactions in excited states disruption occurs. However, rate inhibition[14] is a common consequence, and benzo bridging seems to occur most readily where this moiety has participated heavily in the excitation process.

One last point concerns the gross reaction course in bicycle transformations. Our previous studies have shown the reaction to be stereospecific when the two moieties on the bicycling carbon are different.[2b,3a] This was one piece of evidence against a mechanism involving carbene expulsion to give a fulvene system followed by intermolecular recombination. The present study provides further evidence on this point. If the reaction did involve dissociation to afford indene and isopropylidene, the same product mixture should result independent of which reactant is involved. The above chemistry shows that this is not the case.

SCF-Derived Correlation Diagrams and Comparison of One-Electron Prediction with Experiment. Our presently studied system differs from those for which our earlier calculations were performed. The difference consists of the absence of a C-6 phenyl group and the presence of a fused benzo ring (for example, note reactant **3** vs. the previously studied **1**). The present calculations were carried out as before[2b] using a truncated set of basis orbitals consisting of those of the π system and those in σ bonds which are altered during the rearrangements. Strikingly, the presently and previously derived one-electron correlation diagrams were qualitatively similar for the highest bonding MOs and lowest antibonding MOs, although owing to different additional chromophores the diagrams were indeed different otherwise.

The correlation diagrams are incorporated into a triptych; note Figure 1. At each branch of the triptych is one of the three compounds of interest. The branches are labeled A, B, and C corresponding to the mechanisms forming the compound at each branch. Focussing attention first on branch A, corresponding to the benzobicyclohexene reactant, we note a crossing of HOMO and LUMO prior to arrival at the intersection D of the three branches where cyclopropyldicarbinyl diradical **13** has been formed. This crossing is of the "intended type" and is discerned by matching of the wave functions before and after the crossing as described in our MO following treatment.[15] Thus, HOMO before the crossing has an MO very close in character to that of LUMO after the crossing and vice versa. However, in energetic terms the crossing is avoided by HOMO-LUMO splitting of the degeneracy at the crossing point.[15b] Such a crossing corresponds to a maximum opportunity to generate ground-state singlet as we noted many years ago.[16] Paraphrased in state terminology this corresponds to approach of ground- and excited-state surfaces; these surface approaches have been termed funnels and conical intersections.[17,18] Bifunnels seems a compromise.

To the extent that the reacting species, having started at A in the triptych in the excited state, arrives at C as a ground-state species, the remainder of the conversion along the remaining two branches of B and C is ground state allowed as seen from the triptych of Figure 1. This is consistent with the observed formation of 2,2-dimethyldihydronaphthalene **4** (at B) and spiroindene **12** (at C).

In contrast an excited state originating at point B of the triptych arrives at the central axis D still excited (i.e., no HOMO-LUMO crossing encountered). This cyclopropyldicarbinyl diradical **13** then can proceed along triptych branch A leading to ground-state benzobicyclohexene **3** at A with the decay to S_0 resulting as a consequence of the HOMO-LUMO crossing in branch A. This is consistent again with observation, since benzobicyclohexene **3** is, indeed, formed from 2,2-dimethyldihydronaphthalene **4**. The same excited cyclopropyldicarbinyl diradical **13**, having reached the triptych axis D, may attempt to proceed onward toward spiroindene **12** at C. However, along branch C there is a HOMO-next to HOMO crossing which leads the species to a still more highly (doubly) excited species, and this reaction is forbidden. This, too, is in accord with observation, since irradiation of 2,2-dimethyldihydronaphthalene **4** affords no spiroindene **12** but only benzobicyclohexene **3**.

Experiment and theory concur in the intriguing conclusion that the cyclopropyldicarbinyl diradical **13** (at axis D of the triptych) is generated in the ground state from photolysis of the benzobicyclohexene **3** in the first excited state when generated from photolysis of 2,2-dimethyldihydronaphthalene **4**. This accounts for the differing behavior of the cyclopropyldicarbinyl diradical species depending on its mode of generation.

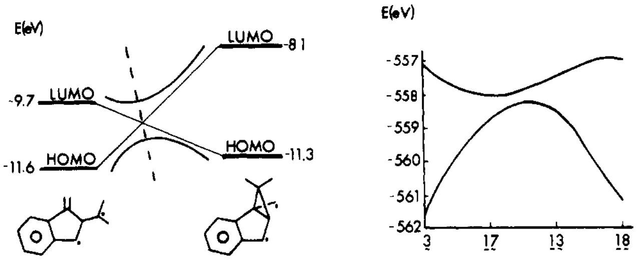
Finally, in our discussion at the one-electron level, we find that the correlation diagram leading from branch C affords an excited state forbidden reaction as a consequence of HOMO-(HOMO − 1) crossing.

Configuration Interaction Derived Potential Energy Surfaces. The Canted and Displaced Funnel Hypothesis. Quite commonly in our previous investigations we have utilized MO correlation diagrams for photochemical reactions.[19,20,21] However, excited-state surfaces have also proven useful[22,23]

Table II. Distribution of Electronic Excitation in Species **3**, **17**, and **13**[a]

benzobicyclohexene 3				17				13			
orbitals r,t	ΔP_{rt}	ΔE_{rt}	bond	orbitals r,t	ΔP_{rt}	ΔE_{rt}	bond	orbitals r,t	ΔP_{rt}	ΔE_{rt}	bond
2,7	−0.0247	0.0000		2,7	0.1015	−0.4759	d	2,6	0.0223	−0.1438	e
2,14	0.0042	0.0001		2,14	0.0044	−0.1420		2,7	−0.0057	0.0364	d
5,6	−0.0566	0.3773	a	5,7	−0.3176	1.9095	c	2,11	0.0014	0.0062	e
5,7	−0.0681	0.4457	c	5,13	0.0268	0.0201		2,14	−0.0003	0.0013	d
5,12	−0.0136	0.0611	a	5,14	0.0368	−0.1114		5,7	0.0093	−0.0049	
5,13	0.0072	−0.0001		6,7	0.0013	0.0000		5,14	−0.0341	0.0099	
5,14	−0.0260	0.1158	c	6,14	−0.0110	0.1473		6,7	−0.0046	0.0288	b
6,7	−0.0291	0.1910	b	7,10	−0.0208	0.0821		6,10	0.0065	−0.0292	e
6,13	0.0035	−0.0157	a	7,13	0.0036	−0.0143		6,14	0.0049	−0.0211	b
6,14	−0.0077	0.0340	b	10,11	0.0085	−0.1915		7,10	−0.0032	0.0138	d
7,12	−0.0131	0.0577	b	10,14	0.0229	−0.2101		7,11	0.0033	−0.0145	b
7,13	−0.0109	0.0480	c	11,14	0.0031	−0.0098		10,11	−0.0007	0.0134	e
12,13	0.0004	−0.0076	a	13,14	−0.0117	0.1090		10,14	−0.0006	0.0115	d
12,14	0.0036	−0.0688	b					11,14	−0.0022	0.0421	b
13,14	−0.0023	0.0439	c								
				Bond Excitation Energies							
bond a		0.415		bond c		1.910		bond b		0.035	
bond b		0.214		bond d		−0.476		bond d		0.063	
bond c		0.653						bond e		−0.166	

[a] Note Figure 4.



a. Canting towards 17; from SCF level calculations.

b. Displacement towards 3; from CI level calculations.

Figure 3. Energetics, canting, and displacement of the bifunnel.

as an alternative description. The two types of presentations are basically equivalent[24a] with exceptions arising primarily where there are unusually heavy weightings of upper excited configurations in the final wave function. Nevertheless, for quantitative purposes state diagrams have an advantage.

Figure 2 presents the state counterpart to the MO treatment of Figure 1. The same three bridges are again labeled A, B, and C. Here two features are of special interest. We note that the forbidden excited state reaction for the spiroindene **12**, cited above in connection with the MO treatment, has an energy barrier. This barrier arises from the HOMO-(HOMO − 1) crossing of the one-electron approximation. Similarly, the formation of spiroindene **12** from 2,2-dimethyldihydronaphthalene S_1 by utilization of only bridges B and C is seen to be inhibited by the same S_1 barrier in bridge C; also this would require formation of the excited-state product followed by decay, a process rare in photochemistry where appreciable motion is involved[24b] and where the reaction is not exceptionally exothermic. Why the bifunnel in bridge A is not used to form spiroindene **12** from 2,2-dimethyldihydronaphthalene **4** is discussed below.

Of still greater interest is the situation in bridge A of the triptych of Figure 2. We focus attention on the region of the LUMO-HOMO one-electron degeneracy, however, using state surfaces. Here we do find a near degeneracy of S_1 and S_0. Two features of this part of the surface are particularly important. The first is that the bifunnel so often observed in photochemistry, is canted with the top toward D and the bottom toward axis A. Such canting would dispose an excited-state molecule in the upper cone of the bifunnel to decay in the direction of A rather than D. Such a consequence is in accord with the observed photochemistry whereby the quantum yield of formation of product from benzobicyclohexene **3** (i.e., motion from A) totals $\phi = 0.043$ compared with the quantum yield of formation of **3** (i.e., motion toward A) from 2,2-dimethyldihydronaphthalene **4**, which is $\phi = 0.086$.

An additional especially important point is the momentum effect originally considered by Teller[25] in which a reacting species tends to remain on the same conical surface after the crossing. Thus an excited-state molecule originating at A would tend to cross toward axis D while an excited-state molecule originating at axis D would tend to cross toward edge A. Such a momentum effect would not apply to a molecule which has time to equilibrate in a bifunnel, a situation most likely being cases where the degeneracy is split with an appreciable energy gap.

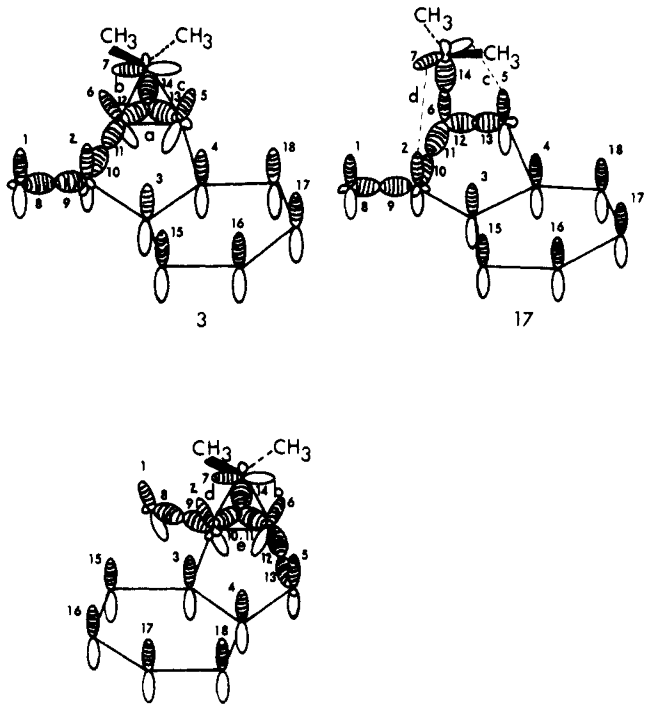


Figure 4. Basis sets for SCF-CI calculations for species **3**, **17**, and **13**.

There still remains the point that no spiroindene **12** is formed on irradiation of 2,2-dimethyldihydronaphthalene **4**. One might consider utilization of the bifunnel of bridge A to arrive at ground state followed by conversion toward spiroindene. In molecular terms, this is a mechanism in which the 2,2-dimethyldihydronaphthalene undergoes a di-π-methane bridging to give excited cyclopropyldicarbinyl diradical **13** (at axis D) followed by partial unzipping toward the 1,3 diradical **17** followed by decay and reclosure to give ground-state cyclopropyldicarbinyl diradical and then bicycling onward to the spiroindene **12**. One weakness of this mechanism is the momentum effect discussed above.

A second point is found from our calculations of the near intersection. Not only is the bifunnel canted, but also the minimum of the upper cone is displaced appreciably toward A relative to the maximum of the lower cone. This can be termed a "displaced bifunnel" and is illustrated in Figure 3. Interestingly, the canted effect arises at the SCF level while the displacement effect is found only after configuration interaction to give state surfaces.

The net result of such a displaced bifunnel is assistance of decay in the direction of triptych edge A. We suggest that successful photochemistry is often influenced by favorable canted bifunnel and displaced bifunnel surfaces.

ΔP and ΔE Analysis. Previously[2b,10e,g,18a,b] we have described a method allowing assignment of electronic excitation to portions of a reacting excited-state molecule. This used the difference in bond orders between excited and ground state. In unexcited portions of a molecule ΔP is near zero, while in portions which are heavily excited the excited- and ground-state wave functions differ and ΔP is nonzero. Where the molecule is more antibonding in the excited state than ground state ΔP is negative, while in portions where the molecule has become more bonding a positive value is observed. An alternative approach is to use the dissected energy differences, or ΔE values. Here "hot" portions of the molecule have positive values, while negative regions have been drained of energy.

Table II gives the results for bonds of interest in benzobicyclohexene **3**, for 1,3 biradical **17**, and for cyclopropyldicarbinyl diradical **13**. Several points are of interest. The first is the distribution of excitation in the benzobicyclohexene **3** reactant. Perusal of Table II reveals excitation energy to be distributed in bonds a, b, and c of the three ring. Additionally, equally large contributions are found in the benzo ring, although these are not tabulated. It is found that the ΔE values are of most use.[2b,10e]

The second point of interest is that it is the "rear wheel" (i.e., bond c) of the bicycle which is highest in energy (note bond excitation energies in Table II), and this is the bond which is selectively broken to reach the excited state–ground state funnel (note Figure 2).

Furthermore, in the 1,3 biradical **17**, the more energetic bond is c while bond d is actually energy deficient. This agrees with formation of bond d in arriving at the funnel and breakage of bond c.

Finally, focusing attention on electronically excited cyclopropyldicarbinyl diradical **13**, the highest energy three-ring bond is d, and this is the bond broken in proceeding toward the funnel and the benzobicyclohexene **3**.

Conclusion

Photochemistry is a field being expanded in utility and interest by the addition of new reactions. It is clear from the present investigation that the bicycle reaction is another transformation of particular generality and with a mechanism common to the many examples we have studied thus far. The reaction also provides an illustration of the accessibility of an understanding of the intimate details of the forces controlling excited-state reactions.

Experimental Section[26]

3,4-Benzo-6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one. A suspension of diphenylisopropylsulfonium iodide in 500 mL of anhydrous dimethoxyethane was prepared according to the method of Corey[5a] from 10.06 g (33.3 mmol) of diphenylethylsulfonium fluoroborate, 33.3 mmol of lithium diisopropylamide (from 4.77 mL of diisopropylamine and 22.2 mL of 1.50 M *n*-butyllithium in hexane) dissolved in 150 mL of anhydrous dimethoxyethane, 2.13 mL (33.3 mmol) of dichloromethane, and 2.08 mL (33.3 mmol) of methyl iodide. To this another 33.3 mmol of lithium diisopropylamide in 150 mL of anhydrous dimethoxyethane was added. The entire procedure was carried on at −78 °C under nitrogen. To a solution of diphenylsulfonium isopropylide at −78 °C was added 3.61 g (27.8 mmol) of freshly prepared indenone in 100 mL of anhydrous dimethoxyethane dropwise with vigorous stirring. After addition the mixture was stirred for 1.0 h at −78 °C, warmed to −15 °C over 3 h, and stirred at −15 °C for 20 h. The mixture was then poured into water, ether extracted, dried, and concentrated in vacuo, leaving a brown oil. Chromatography on a 3.0 × 200 cm silica gel column slurry packed in hexane with elution in 250-mL fractions gave fractions 1–20, hexane, 8.48 g of diphenyl sulfide; 21–25, changed to 2.0% ether in hexane, nil; 26–28, 2.81 g (16.3 mmol, 50.6%) of 2,2-dimethyl-3-oxospiro[cyclopropan-1,1′-indene]; 29–30, nil; 31–33, 1.06 g (6.16 mmol, 22.2%) of 3,4-benzo-6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one.

The spectral data for the dimethyl epoxide: NMR ($CDCl_3$) τ 2.52–2.83 (m, 4 H, aromatic), 3.02 (d, 1 H, J = 6 Hz, vinyl), 3.65 (d, 1 H, J = 6 Hz, vinyl), 8.36 (s, 3 H, methyl), 8.40 (s, 3 H, methyl); IR (thin film) 3.26, 3.38, 6.87, 7.27, 10.20, 10.40, 13.25, 13.61, 13.79 μ.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.59; H, 7.16.

The spectral data for 3,4-benzo-6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one: NMR ($CDCl_3$) τ 2.51–2.67 (m, 4 H, aromatic), 7.49 (d, 1 H, J = 7 Hz, cyclopropyl), 7.93 (d, 1 H, J = 7 Hz, cyclopropyl), 8.49 (s, 3 H, methyl), 9.94 (s, 3 H, methyl); IR (thin film) 3.27, 3.31, 3.37, 3.43, 3.50, 5.94, 6.91, 7.27, 8.01, 9.14, 9.46, 9.66, 11.24, 11.91, 13.25 μ.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.51; H, 7.20.

Indenone. A solution of 5.00 g (28.7 mmol) of indenone ethylene ketal[27a] and 10 mg of *p*-toluenesulfonic acid in 100 mL of water and 100 mL of anhydrous tetrahydrofuran was stirred in the dark under nitrogen at room temperature for 6 h. The reaction mixture was diluted with water and ether extracted, and the combined ethereal extracts were washed with saturated sodium bicarbonate and brine, dried, and concentrated in vacuo, leaving 3.61 g (27.8 mmol, 96.6%) of indenone, bp 76–78 °C (1.5 mm), lit. bp 75–77 °C[27b] (1.5 mm), 61–63 °C[27c] (0.9 mm), 69–70 °C[27d] (0.35 mm). This was used immediately after preparation. The spectral data were identical with those reported previously.[27b,c]

3,4-Benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene. To a stirred suspension of 1.86 g (5.22 mmol) of methyltriphenylphosphonium bromide in 100 mL of anhydrous ether under nitrogen was added 3.5 mL of 1.50 M *n*-butyllithium (5.22 mmol) in hexane. After stirring for 15 min the solution was cooled to 0 °C and 0.500 g (2.9 mmol) of 3,4-benzo-6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one in 5 mL of anhydrous ether was added dropwise. The mixture was stirred at 0 °C for 4 h, poured into water, and ether extracted. The ethereal extracts were washed with water and brine, dried, and concentrated in vacuo, leaving a yellow oil. Chromatography on a 3.0 × 50 cm silica gel column slurry packed in hexane with elution with hexane in 100-mL fractions gave fractions 1–3, nil; fraction 4–5, 152 mg (0.894 mmol, 30.5%) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene.

The spectral data: NMR ($CDCl_3$) τ 2.45–2.82 (m, 4 H, aromatic), 4.38 (bs, 1 H, vinyl), 4.79 (bs, 1 H, vinyl), 7.43 (d, 1 H, J = 6.0 Hz, cyclopropyl), 7.70 (d, 1 H, J = 6.0 Hz, cyclopropyl), 8.79 (s, 3 H, methyl), 9.35 (s, 3 H, methyl); IR (thin film) 3.27, 3.32, 3.42, 6.90, 7.25, 8.06, 9.44, 9.72, 11.13, 12.02, 13.25 μ; UV (95% EtOH) 260 nm (ϵ 9101), 270 (6292), 295 (2022); MS *m/e* 170.1094 (calcd for $C_{13}H_{14}$, *m/e* 170.1096.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.62; H, 8.34.

1-Oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene. This material was prepared according to a modification of the method of Klemm and Shabtai[28b] from 5.00 g (3.42 mmol) of 2-tetralone in 100 mL of anhydrous tetrahydrofuran, 11.4 g (102 mmol) of potassium *tert*-butoxide, and 8.47 mL (136 mmol) of methyl iodide. The yield was 5.43 g (31.2 mmol, 91.8%) of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene, bp 88-90 °C (1.0 mm), lit. bp 86-88 °C[28a] (1.0 mm), 88-89 °C[28b] (1.0 mm), 124-126 °C[28c] (11 mm), 137 °C[28d] (15 mm). The spectral data were in agreement with those reported.[28b,c]

1-Oxo-2,2-dimethyl-1,2-dihydronaphthalene. This material was prepared according to the method of Klemm and Shabtai[28b] from 5.20 g (29.9 mmol) of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene to yield 3.60 g (20.9 mmol, 70.0%) of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene, bp 80-81 °C (0.5 mm), lit. bp 72-74 °C[28b] (0.4 mm), 123-125 °C[28c] (12 mm). The spectral data were in agreement with those reported.[28b,c]

2,2-Dimethyl-1-methylene-1,2-dihydronaphthalene. This material was prepared by a modification of the method of Wittig[29] from 3.57 g (10.0 mmol) of methyltriphenylphosphonium bromide, 6.80 mL (10.0 mmol) of 1.50 M *n*-butyllithium in hexane, and 945 mg (5.50 mmol) of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene. Purification was accomplished by chromatography on a 2.0 × 40 cm silica gel column slurry packed in hexane. Elution with hexane in 100-mL fractions gave fractions 1-3, nil; 4-6, 798 mg (4.96 mmol, 85.3%) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene, bp 65-66 °C (0.5 mm), lit. bp 55.5-57 °C[29] (0.3 mm).

The spectral data: NMR ($CDCl_3$) τ 2.37-2.57 (m, 1 H, aromatic), 2.72-3.08 (m, 3 H, aromatic), 3.65 (d, 1 H, J = 10 Hz, vinyl), 4.20 (d, 1 H, J = 10 Hz, vinyl), 4.56 (bs, 1 H, $=CHH$), 4.80 (bs, 1 H, $=CHH$), 8.80 (s, 6 H, methyls); IR (thin film) 3.25, 3.29, 3.33, 3.40, 3.45, 3.52, 6.17, 6.23, 6.78, 6.87, 6.90, 7.42, 7.99, 8.46, 9.13, 9.71, 11.30, 12.42 μ; UV (95% EtOH) 282 nm (ϵ 14 350), 323 (1930), 337 (561); MS *m/e* 170.1090 (calcd for $C_{13}H_{14}$, *m/e* 170.1096).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.80; H, 8.38.

2,2-Dimethylspiro[cyclopropan-1,1′-indene]. To 60.0 mg (2.50 mmol) of solid mineral oil free sodium hydride and 50.7 mg (2.30 mmol) of trimethylsulfoxonium iodide[30a] was added cautiously under nitrogen 6.0 mL of anhydrous dimethyl sulfoxide dropwise. After hydrogen evolution had ceased, the mixture was stirred for 10 min and then 347 mg (2.22 mmol) of 1-propylidene[1*H*]indene[30b] in 10 mL of anhydrous dimethyl sulfoxide was added dropwise. After stirring for 10 min, the mixture was poured into water and extracted with ether. The ether extracts were washed with water and brine, dried, and concentrated in vacuo, leaving 381 mg of brown oil. Chromatography on a 2.5 × 30 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1-3, nil; 4, 341 mg (2.00 mmol, 90.1%) of 2,2-dimethylspiro[cyclopropane-1,1′-indene].

The spectral data were identical with those reported previously.[30c] UV (95% EtOH): 230 nm (ϵ 30 402), 263 (11 769), 298 (2288).

4,4-Dimethyl-1-methylene-1,4-dihydronaphthalene. This material was prepared according to the method of Wittig[29] from 3.74 g (10.5 mmol) of methyltriphenylphosphonium bromide, 7.00 mL (10.5 mmol) of 1.50 M *n*-butyllithium in hexane, and 1.00 g (5.81 mmol) of 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene.[28b,e] Purification was accomplished by chromatography on a 3.0 × 30 cm silica gel column slurry packed in hexane. Elution with hexane in 100-mL fractions gave fractions 1-4, nil; 5-6, 517 mg (3.04 mmol, 52.3%) of 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene, bp 70-71 °C (0.3 mm), lit. bp 54-54.5 °C[29] (0.1 mm).

The spectral data: NMR ($CDCl_3$) τ 2.14-2.31 (m, 1 H, aromatic), 2.49-2.93 (m, 3 H, aromatic), 3.68 (d, 1 H, J = 10 Hz, vinyl), 4.29 (d, 1 H, J = 10 Hz, vinyl), 4.38 (bs, 1 H, methylene), 5.01 (bs, 1 H, methylene), 8.63 (s, 6 H, methyls); IR (thin film) 3.23, 3.27, 3.31, 3.38, 3.42, 3.50, 6.04, 6.29, 6.73, 6.80, 6.85, 6.90, 7.35, 7.56, 7.68, 8.47, 8.85, 9.24, 9.52, 11.43, 12.82, 13.16, 14.29, 17.71 μ; UV (95% EtOH) 260 nm (ϵ 6673), 228 (1965), 299 (1280); MS *m/e* 170.1095 (calcd for $C_{13}H_{14}$, *m/e* 170.1096).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29, Found: C, 91.81; H, 8.19.

1,1-Dimethyl-2-oxo-1,2-dihydronaphthalene. This material was prepared according to the method of Marvell et al.[31a] from 2.10 g (12.1 mmol) of 1,1-dimethyl-2-oxo-1,2,3,4-tetrahydronaphthalene[31b] to yield 1.48 g (8.60 mmol, 71.1%) of 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene, bp 98-100 °C (0.4 mm), lit. bp 136-141 °C[31a] (16 mm), 146-150 °C[31c] (18 mm), 100 °C[31d] (0.5 mm).

The spectral data were identical with those reported previously.[31e]

1,1-Dimethyl-2-methylene-1,2-dihydronaphthalene. Procedure 1. To a stirred suspension of 3.45 g (9.66 mmol) of methyltriphenylphosphonium bromide in 100 mL of anhydrous ether under nitrogen was added 6.44 mL of 1.50 M *n*-butyllithium (9.66 mmol) in hexane. After the mixture was stirred for 15 min, 923 mg (5.37 mmol) of 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene in 10.0 mL of anhydrous ether was added dropwise. The mixture was stirred for 2 h, poured into water, and ether extracted. The ethereal extracts were washed with water and brine, dried, and concentrated in vacuo, leaving a yellow oil. Chromatography on a 3.0 × 50 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1-4, hexane, nil; 5-6, hexane, 571 mg (3.36 mmol, 62.6%) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene.

The spectral data were identical with those reported previously for a rearrangement product of 1,1,2-trimethyl-1,2-dihydronaphthalene.[32] MS: *m/e* 170.1095 (calcd for $C_{13}H_{14}$, *m/e* 170.1096).

Anal Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.90; H, 8.10.

1,2-Dihydro-1,1,2-trimethyl-2-naphthalenol. To a stirred solution of 500 mg (2.94 mmol) of 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene in 30 mL of anhydrous ether under nitrogen was added 2.73 mL (4.37 mmol) of a 1.6 M ether solution of methyllithium. The reaction mixture was stirred at room temperature for 30 min, quenched with 100 mL of cold water, and ether extracted. The ethereal extracts were washed with water and brine and concentrated in vacuo, leaving a yellow oil. Chromatography on a 3.0 × 50 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1-4, 1% ether in hexane, nil; 5, 2% ether in hexane, nil; 6-7, 0.541 g (2.88 mmol, 98.9%) of 1,2-dihydro-1,1,2-trimethyl-2-naphthalenol.

The spectral data: NMR ($CDCl_3$) τ 2.58-3.02 (m, 4 H, aromatic), 3.63 (d, 1 H, J = 9.0 Hz, vinyl), 4.16 (d, 1 H, J = 9.0 Hz, vinyl), 7.47 (bs, 1 H, OH), 8.68 (s, 3 H, C-2 methyl), 8.74 (s, 3 H, C-1 methyl), 8.77 (s, 3 H, C-1 methyl); IR (thin film) 2.89, 3.25, 3.28, 3.34, 3.40, 6.67, 6.83, 7.19, 7.29, 8.20, 8.55, 8.66, 9.13, 9.35, 9.54, 10.70, 12.53, 12.78 μ; MS *m/e* 188.1207 (calcd for $C_{13}H_{16}O$, *m/e* 188.1201).

Anal Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.90; H, 8.69.

1,1-Dimethyl-2-methylene-1,2-dihydronaphthalene. Procedure 2. Using a modification of Schmid et al.,[33] a solution of 500 mg (2.69 mmol) of 1,2-dihydro-1,1,2-trimethyl-2-naphthalenol in 15 mL of 5% aqueous hydrochloric acid and 20 mL of THF was allowed to stir under nitrogen at room temperature for 12 h. The solution was poured into water and ether extracted, and the ethereal extracts were washed with sodium bicarbonate, water, and brine and concentrated in vacuo, leaving a yellow oil. Chromatography on a 3.0 × 50 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1-4, 1% ether in hexane, nil; 5-6, 2% ether in hexane, 0.453 g (2.66 mmol, 98.9%) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene.

The spectral data were identical with those above but different from those reported in ref 33, where ethylmagnesium bromide was reported as a reactant.

General Procedure for Exploratory Photolyses. All direct and sensitized exploratory irradiations were performed using a 450-W medium-pressure mercury lamp immersion apparatus or the Black Box apparatus[6] as specified for each run. All runs were purged with purified nitrogen[34] for 1 h before and during photolysis.

Exploratory Photolysis of 3,4-Benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene. High-Conversion Run. A solution of 100 mg (0.588 mmol) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene in 100 mL of *tert*-butyl alcohol was irradiated for 6 h through a Corex filter and then concentrated in vacuo, leaving 101 mg of a yellow oil. Chromatography on a 3.0 × 100 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1-4, hexane, nil; 5-6, 2% ether in hexane, nil; 7, 3% ether in hexane, 98.6 mg (0.580 mmol, 98.6%) of 2,2-dimethylspiro[cyclopropan-1,1′-indene]. This material was identical with independently synthesized spiroindene (GC, IR, NMR, UV).

Exploratory Photolysis of 3,4-Benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene. Product Isolation. A solution of 300 mg (1.76 mmol) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene in 300 mL of *tert*-butyl alcohol was irradiated for 20 min through a Corex filter and then concentrated in vacuo, leaving 304 mg of a yellow oil. Chromatography on a 3.0 × 100 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1-5, hexane, nil; 6-7, hexane, 217 mg (1.28 mmol, 72.3%) of 3,4-benzo-

2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene; 8, hexane, nil; 9, 9.00 mg (0.053 mmol, 3.0%) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene; 10–11, 2% ether in hexane, nil; 12, 64.0 mg (0.376 mmol, 21.3%) of 2,2-dimethylspiro[cyclopropan-1,1′-indene] (mass balance, 98.3%). The starting material was unchanged (IR, NMR, UV) and the bicyclo[3.1.0]hexene and 1,2-dihydronaphthalene photoproducts had spectral data (IR, NMR, UV) identical with that of independently synthesized material (vide supra).

Exploratory Photolysis of 2,2-Dimethyl-1-methylene-1,2-dihydronaphthalene. Product Isolation. A solution of 502 mg (2.95 mmol) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene in 502 mL of *tert*-butyl alcohol was irradiated for 0.75 h through a Pyrex filter and then concentrated in vacuo, leaving 506 mg of a yellow oil. Chromatography on a 3.0 × 100 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1–15, hexane, nil; 16–18, 179 mg (1.05 mmol, 35.6%) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene; 19–20, nil; 21–22, 312 mg (1.84 mmol, 62.2%) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene; 23–27, 2% ether in hexane, nil; 28–29, 6.0 mg (0.035 mmol, 1.19%) of 2,2-dimethylspiro[cyclopropan-1,1′-indene] (mass balance, 99.0%). The starting material was unchanged (GC, IR, NMR, UV) and the bicyclo[3.1.0]hexene and spiroindene photoproducts were identical (GC, IR, NMR, UV) with independently synthesized material (vide supra).

Exploratory Photolysis of 4,4-Dimethyl-1-methylene-1,4-dihydronaphthalene. Product Isolation. A solution of 496 mg (2.92 mmol) of 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene in 500 mL of *tert*-butyl alcohol was irradiated for 1 h through a Pyrex filter and then concentrated in vacuo, leaving 500 mg of a yellow oil. Chromatography on a 3.0 × 100 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1–16, hexane, nil; 17–19, 317 mg (1.86 mmol, 63.9%) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene; 20–22, hexane, nil; 23–24, 163 mg (0.959 mmol, 32.9%) of 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene; 25–29, nil; 30–31, 2% ether in hexane, 6.0 mg (0.035 mmol, 1.21%) of 2,2-dimethylspiro[cyclopropane-1,1′-indene] (mass balance, 98.0%). The starting material was unchanged (GC, IR, NMR, UV) and the bicyclo[3.1.0]hexene and spiroindene photoproducts were identical (GC, IR, NMR, UV) with independently synthesized material (vide supra).

Exploratory Photolysis of 1,1-Dimethyl-2-methylene-1,2-dihydronaphthalene. A solution of 104 mg (0.612 mmol) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene in 100 mL of *tert*-butyl alcohol was irradiated for 24 h through a Pyrex filter and then concentrated in vacuo, leaving 106 mg of a clear oil. Chromatography on a 2.5 × 45 cm silica gel column slurry packed in hexane with elution in 500-mL fractions gave fractions 1–4, hexane, nil; 5–6, 0.5% ether in hexane, 103 mg (0.606 mmol, 99.0%) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene; 7–8, 2% ether in hexane, nil.

An identical irradiation was performed with 100 mg (0.588 mmol) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene through a Corex filter for 24 h. Chromatography as above gave 98.5 mg (0.579 mmol, 98.5%) of starting material.

An identical irradiation was performed with 100 mg (0.588 mmol) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene through a Vycor filter for 24 h. Chromatography as above gave 97.5 mg (0.574 mmol, 97.5%) of starting material. In each irradiation starting material was unchanged (GC, IR, NMR, UV).

Exploratory Photolysis of 2,2-Dimethylspiro[cyclopropan-1,1′-indene]. A solution of 100 mg (0.588 mmol) of 2,2-dimethylspiro[cyclopropan-1,1′-indene] in 100 mL of *tert*-butyl alcohol was irradiated for 4.0 h through a Corex filter under typical exploratory photolysis conditions (vide supra). UV analysis of the crude photolysate showed no internal filter formation. The photolysate was concentrated in vacuo to yield 103 mg of a clear oil. Chromatography on a 2.5 × 45 cm silica gel column slurry packed in hexane with elution in 100-mL fractions gave fractions 1–4, hexane, nil; 5, 2% ether in hexane, nil; 6–7, 98 mg (0.576 mmol, 98.0%) of starting material. The starting material was unchanged by GC, IR, NMR, and UV analysis.

Exploratory Sensitized Photolysis of 3,4-Benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene. A solution of 160 mg (0.941 mmol) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene and 3.11 g (17.1 mmol) of benzophenone in 750 mL of anhydrous *tert*-butyl alcohol was irradiated for 20.6 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 3.32 g of white, crystalline residue. The light absorbed was 18.0 mEinsteins. The residue was chromatographed on a 3 × 100 cm silica gel column slurry packed in hexane. Elution in 100-mL fractions gave fractions 1–6, hexane, nil; 7–8, 157 mg (0.924 mmol, 98.1%) of starting material; 9–14, 2% ether in hexane, nil; 15–24, 3.01 g (16.5 mmol, 96.8%) of benzophenone, mp 47–48 °C. The starting material was unchanged by GC, IR, NMR, and UV analysis. A control mixture containing 0.625% of 2,2-dimethylspiro[cyclopropan-1,1′-indene] and a control mixture containing 0.625% of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene were examined under identical conditions and this conversion would have been measurable. Therefore, conversion was <0.625%, $\Phi < 3.3 \times 10^{-4}$.

Exploratory Sensitized Photolysis of 2,2-Dimethyl-1-methylene-1,2-dihydronaphthalene. A solution of 151 mg (0.888 mmol) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene and 2.79 g (15.3 mmol) of benzophenone in 750 mL of anhydrous *tert*-butyl alcohol was irradiated for 8.3 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 2.95 g of white, crystalline residue. The light absorbed was 14.6 mEinsteins. The residue was chromatographed on a 3 × 100 cm silica gel column slurry packed in hexane. Elution in 100-mL fractions gave fractions 1–10, hexane, nil; 11–12, 150 mg (0.882 mmol, 99.3%) of starting material; 13–19, 2% ether in hexane, nil; 20–30, 2.71 g (14.9 mmol) of benzophenone, mp 47–48 °C. The starting material was unchanged by GC, IR, NMR, and UV analysis. A control mixture containing 0.66% of 2,2-dimethylspiro[cyclopropan-1,1′-indene] and a control mixture containing 0.66% of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene were examined under identical conditions and this conversion would have been measurable. Therefore, conversion was <0.65%, $\Phi < 4.0 \times 10^{-4}$.

Exploratory Sensitized Photolysis of 4,4-Dimethyl-1-methylene-1,4-dihydronaphthalene. A solution of 153 mg (0.900 mmol) of 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene and 2.89 g (15.9 mmol) of benzophenone in 750 mL of *tert*-butyl alcohol was irradiated for 19.1 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 3.15 g of white, crystalline residue. The light absorbed was 15.0 mEinsteins. The residue was chromatographed on a 3 × 100 cm silica gel column slurry packed in hexane. Elution in 100-mL fractions gave fractions 1–10, hexane, nil; 11–12, 150 mg (0.882 mmol, 98.0%) of starting material; 13–20, 2% ether in hexane, nil; 21–32, 2.81 g (15.4 mmol, 97.2%) of benzophenone, mp 47–48 °C. The starting material was unchanged by GC, IR, NMR, and UV analysis. A control mixture containing 0.65% of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene and a control mixture containing 0.65% of 2,2-dimethylspiro[cyclopropan-1,1′-indene] were examined under identical conditions and this conversion would have been measurable. Therefore, conversion was <0.65%, $\Phi < 3.9 \times 10^{-4}$.

Exploratory Sensitized Photolysis of 1,1-Dimethyl-2-methylene-1,2-dihydronaphthalene. A solution of 150 mg (0.882 mmol) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene and 3.00 g (16.5 mmol) of benzophenone in 750 mL of *tert*-butyl alcohol was irradiated for 19.9 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 3.22 g of white, crystalline residue. The light absorbed was 14.9 mEinsteins. The residue was chromatographed on a 3 × 100 cm silica gel column slurry packed in hexane. Elution in 100-mL fractions gave fractions 1–11, hexane, nil; 12–13, 148 mg (0.871 mmol, 98.7%) of starting material; 14–20, 2% ether in hexane, nil; 21–30, 2.98 (99.3%) of benzophenone, mp 47–48 °C. The starting material was unchanged by GC, IR, NMR, and UV analysis. A control mixture containing 0.67% of 2,2-dimethylspiro[cyclopropan-1,1′-indene] was examined under identical conditions and this conversion would have been measurable. Therefore, conversion was <0.66%, $\Phi < 3.95 \times 10^{-4}$.

Limited Photolysis of 2,2-Dimethyl-1-methylene-1,2-dihydronaphthalene. Product Isolation. A solution of 520 mg (3.06 mmol) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene in 750 mL of *tert*-butyl alcohol was irradiated for 43.7 h through filter solution A on the Black Box apparatus. The photolysis was monitored by VPC using a 0.64 × 150 cm column packed with 10% QF-1 on 100–120 mesh Varaport 30 at 115 °C. The photolysate was concentrated in vacuo to yield 525 mg of colorless oil. The light absorbed was 17.4 mEinsteins. The residue was chromatographed on a 3.0 × 350 cm silica gel column slurry packed in hexane with elution in 100-mL fractions which gave fractions 1–18, hexane, nil; 19–21, 148 mg (0.871 mmol, 28.5%) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo-

Table III. Direct Quantum Yield Photolyses of 2,2-Dimethyldihydronaphthalene **4**, 4,4-Dimethyldihydronaphthalene **5**, and Benzobicyclohexene **3**

run	reactant (mmol)	light absorbed, mEinstein	% conversion	photoproduct (mmol)	Φ
1[a]	**4** (2.45×10^{-1})	1.31×10^{-1}	4.40	**3** (1.08×10^{-2})	8.23×10^{-2}
2[a]	**4** (1.88×10^{-1})	1.92×10^{-1}	7.77	**3** (1.46×10^{-2})	7.60×10^{-2}
3[a]	**4** (2.06×10^{-1})	3.71×10^{-1}	13.0	**3** (2.69×10^{-2})	7.25×10^{-2}
1[a]	**5** (2.35×10^{-1})	2.33×10^{-2}	2.03	**3** (4.77×10^{-3})	2.05×10^{-1}
2[a]	**5** (4.47×10^{-1})	2.31×10^{-1}	8.90	**3** (3.97×10^{-2})	1.72×10^{-1}
3[a]	**5** (1.72×10^{-1})	1.97×10^{-1}	16.1	**3** (2.78×10^{-2})	1.41×10^{-1}
4[a]	**5** (1.85×10^{-1})	3.19×10^{-1}	20.2	**3** (3.74×10^{-2})	1.17×10^{-1}
1[b]	**3** (2.61)	9.38×10^{-1}	1.50	**12** (3.62×10^{-2})	3.86×10^{-2}
				4 (3.05×10^{-3})	3.25×10^{-3}
2[b]	**3** (2.37)	2.58	3.77	**12** (8.53×10^{-1})	3.31×10^{-2}
				4 (6.45×10^{-3})	2.50×10^{-3}
3[b]	**3** (1.05)	4.18	8.84	**12** (8.82×10^{-2})	2.11×10^{-2}
				4 (4.18×10^{-3})	1.00×10^{-3}
4[b]	**3** (9.03×10^{-1})	4.99	10.5	**12** (8.98×10^{-2})	1.79×10^{-2}
				4 (4.82×10^{-3})	9.66×10^{-4}
5[b]	**3** (4.71×10^{-1})	5.73	13.3	**12** (5.79×10^{-1})	1.01×10^{-1}
				4 (4.58×10^{-3})	7.99×10^{-4}

[a] Run in 100 mL of *t*-BuOH. [b] Run in 750 mL of *t*-BuOH.

[3.1.0]hex-3-ene; 22-24, nil; 25-26, 368 mg (2.16 mmol, 70.8%) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene; 27-40, 2% ether in hexane, nil; 41-50, 3% ether in hexane, nil (mass balance, 99.2%). The starting material was unchanged (GC, IR, NMR, UV) and the bicyclo[3.1.0]hexane photoproduct identical (GC, IR, NMR, UV) with independently synthesized material (vide supra). A control mixture containing 0.20% of 2,2-dimethylspiro[cyclopropan[1,1′-indene] was analyzed by VPC as above and this conversion would have been measurable. Therefore, conversion to spiroindene was <0.20%, $\Phi < 3.5 \times 10^{-4}$.

Photolysis Apparatus for Quantum-Yield Determinations. All quantum-yield determinations were run on the Black Box apparatus.[6] Light output was measured for each run by a digital electronic actinometer[7a] calibrated by ferrioxalate actinometry.[7b] For Black Box photolyses the band-pass was controlled by one of a series of filter solution combinations held in a 750-mL total volume three-compartment quartz faced filter solution cell. The filter solutions employed were filter A (cell 1, 2.0 M nickel sulfate hexahydrate in 10% sulfuric acid; cell 2, 0.8 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 2.46×10^{-4} M bismuth trichloride in 40% hydrochloric acid; transmission 0% below 254 nm, 26% at 286 nm, 0% above 307 nm); filter B (cell 1, 0.190 M nickel sulfate hexahydrate in 10% sulfuric acid; cell 2, 0.80 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 1.11 M stannous chloride dihydrate in 60% hydronchloric acid; transmission 0% below 342 nm, 9.0% at 361 nm 0% above 382 nm).

All quantum-yield photolyses were purged with purified nitrogen for 1 h before and during each run.

Direct Quantum Yield Results. All direct runs were analyzed by vapor phase chromatography using a 0.64 × 150 cm column packed with 10% QF-1 on 100-120 mesh Varaport 30 at 115 °C using biphenyl as internal standard. The solvent was anhydrous *tert*-butyl alcohol and irradiation was performed through filter solution A. The data are reported in Table III.

Photoreduction of Benzophenone by Benzhydrol. Control Run. A solution of 2.50 g (13.7 mmol) of benzophenone and 1.01 g (5.47 mmol) of benzhydrol in 750 mL of *tert*-butyl alcohol was irradiated for 18.4 h through filter B on the Black Box apparatus. The light absorbed was 7.50 mEinsteins. The photolysate was filtered leaving 345 mg of a solid which was recrystallized from hexane to give 337 mg (0.920 mmol) of benzopinacol, mp 193.5-195 °C. The filtrate was concentrated in vacuo to yield 3.24 g of a white, crystalline residue. The residue was chromatographed on a 3.0 × 100 cm silica gel column slurry packed in hexane. Elution in 20-mL fractions gave fractions 1-50, 2% ether in hexane, nil; 51-60, 3% ether in hexane, 12.2 mg (0.0333 mmol) of benzopinacol, mp 192-194 °C; 60-70, nil; 71-85, 2.07 g (11.4 mmol, 82.8%) of benzophenone, mp 47-49 °C; 86-150, nil; 151-210, 5% ether in hexane, nil; 211-250, 6% ether in hexane, 81 mg (440 mmol, 8.02%) of benzhydrol, mp 80.5-81 °C; 250-300, 10% ether in hexane, 198 mg (1.07 mmol, 19.6%) of benzhydrol, mp 80-81 °C. The quantum yield of formation of benzopinacol was $\Phi = 0.127$.

Energy-Transfer Test. Quenching of Benzophenone Triplets by 3,4-Benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene. A solution of 122 mg (0.734 mmol) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene, 3.10 g (17.0 mmol) of benzophenone, and 13.2 g (7.16 mmol) of benzhydrol in 750 mL of *tert*-butyl alcohol was irradiated for 24 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 4.63 g of a colorless oil. The light absorbed was 19.6 mEinsteins. The oil was chromatographed on a 3.0 × 100 cm silica gel column slurry packed in hexane. Elution in 20-mL fractions gave fractions 1-40, hexane, nil; 41-70, 122 mg (0.718 mmol, 97.6%) of 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene; 71-121, 0.25% ether in hexane, nil; 122-198, 1% ether in hexane, 13.5 mg (0.0368 mmol) of benzopinacol, mp 193-194 °C; 199-220, 2.96 g (16.2 mmol 95.5%) of benzophenone, mp 48-49 °C; 221-280, 2% ether in hexane, nil; 281-330, 6% ether in hexane, 1.27 g (6.89 mmol, 96.2%) of benzhydrol, mp 80-81 °C; 331-430, 10% ether in hexane, nil. The quantum yield of benzopinacol formation was $\Phi = 1.88 \times 10^{-3}$.

Energy-Transfer Test. Quenching of Benzophenone Triplets by 2,2-Dimethyl-1-methylene-1,2-dihydronaphthalene. A solution of 96.1 mg (0.564 mmol) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene, 2.50 g (13.7 mmol) of benzophenone, and 1.02 (5.55 mmol) of benzhydrol in 750 mL of *tert*-butyl alcohol was irradiated for 20.3 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 3.69 g of a colorless oil. The light absorbed was 18.3 mEinsteins. The oil was chromatographed on a 3 × 100 cm silica gel column slurry packed in hexane. Elution in 20-mL fractions gave fractions 1-41, hexane, nil; 42-80, 0.25% ether in hexane, 95.7 mg (0.562 mmol, 99.6%) of 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene; 81-137, nil; 138-238, 1% ether in hexane, 2.38 g (13.1 mmol, 95.2%) of benzophenone, mp 47-48 °C; 239-300, 2% ether in hexane, nil; 301-350, 6% ether in hexane, 0.984 g (5.34 mmol, 96.2%) of benzhydrol, mp 80-81 °C; 351-450, 10% ether in hexane, nil. No benzopinacol was observed.

Energy-Transfer Test. Quenching of Benzophenone Triplets by 4,4-Dimethyl-1-methylene-1,4-dihydronaphthalene. A solution of 110 mg (0.646 mmol) of 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene, 2.50 g (13.7 mmol) of benzophenone, and 1.00 g (5.43 mmol) of benzhydrol in 750 mL of anhydrous *tert*-butyl alcohol was irradiated for 18.4 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 3.72 g of a white crystalline residue. The light absorbed was 15.0 mEinsteins. The residue was chromatographed on a 3.0 × 100 cm silica gel column slurry packed in hexane. Elution in 20-mL fractions gave fractions 1-38, hexane, nil; 39-87, 0.25% ether in hexane, 109 mg (0.641 mmol, 99.1%) of 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene; 88-121, nil; 122–200, 1% ether in hexane, 11.0 mg (0.030 mmol) of benzopinacol, mp 193–194 °C; 201–250, 2.47 g (13.5 mmol, 98.2%) of benzophenone, mp 47–48 °C; 251–301, 2% ether in hexane, nil; 302–337, 6% ether in hexane, 0.980 g (5.32 mmol, 98.0%) of benzhydrol, mp 80–81 °C; 338–450, 10% ether in hexane, nil. Φ(benzopinacol) = 2.00 × 10^{-3}.

Energy-Transfer Test. Quenching of Benzophenone Triplets by 1,1-Dimethyl-2-methylene-1,2-dihydronaphthalene. A solution of 110 mg (0.646 mmol) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene, 2.73 g (15.0 mmol) of benzophenone, and 1.16 g (6.30 mmol) of benzhydrol in 750 mL of anhydrous *tert*-butyl alcohol was irradiated for 20 h through filter B on the Black Box apparatus. The photolysate was concentrated in vacuo to yield 4.17 g of a white, crystalline residue. The light absorbed was 16.3 mEinsteins. The residue was chromatographed on a 3 × 100 cm silica gel column slurry packed in hexane. Elution in 20-mL fractions gave fractions 1–65, hexane, nil; 66–100, 0.25% ether in hexane, 107 mg (0.629 mmol, 97.3%) of 1,1-dimethyl-2-methylene-1,2-dihydronaphthalene; 101–150, nil; 151–160, 1% ether in hexane, 2.68 g (14.7 mmol, 98.2%) of benzophenone, mp 47–48 °C; 161–220, 2% ether in hexane, nil; 221–270, 6% ether in hexane, 1.09 g (5.92 mmol, 94%) of benzhydrol, mp 80–81 °C; 271–370, 10% ether in hexane, nil. No benzopinacol was observed.

Emission Studies Magic Multipliers.[8] The fluorescence spectrum of each compound was measured in a 4:1 methylcyclohexane–isopentane solution at 77 and 295 K using an Aminco-Keirs spectrofluorometer equipped with a Hanovia 901C-1 150-W xenon arc lamp. Concentrations of solutions were adjusted to give optical densities of 0.8–0.9. All solutions were thoroughly degassed immediately before the spectra were obtained. Emission wavelength maxima were found to be independent of excitation wavelength over a 50-nm range. Magic multipliers were calculated by dividing the integrated intensity of fluorescence at 77 K by the integrated intensity of fluorescence at 295 K. The average value obtained for each compound: 2,2-dimethyl-1-methylene-1,2-dihydronaphthalene, M = 10.8 (three runs); 4,4-dimethyl-1-methylene-1,4-dihydronaphthalene, M = 10.1 (three runs); 3,4-benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene, M = 10.2 (three runs).

Single Photon Counting. The apparatus and procedure have been described previously.[8,9] Individual samples were prepared in a 4:1 methylcyclohexane–isopentane solution to give an optical density in the range of 0.8–0.9, thoroughly degassed immediately before counting, and counted at 77 K until a minimum of 2000 counts in the maximum channel was obtained. Data was collected at less than 5% lamp flash frequency to ensure exclusion of double photon counting. Excitation wavelength was varied over the range 275–310 nm and emission was monitored over the range 305–360 nm with an RCA 8850 photomultiplier. The decay range was found to be independent of excitation wavelength, emission wavelength, and optical density to within 5% using the "A value" as a measure of the comparative fit of computer-calibrated decay rate to experimentally observed decay rate. The data are reported as follows: compound, average lifetime, average decay rate, number of runs, A value.

(1) 2,2-Dimethyl-1-methylene-1,2-dihydronaphthalene, 7.136 ns, 0.140 × 10^9 s^{-1}, 6, 0.047.

(2) 1-Methylene-4,4-dimethyl-1,4-dihydronaphthalene, 4,636 ns, 0.216 × 10^9 s^{-1}, 6, 0.027.

(3) 3,4-Benzo-2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene, 83.8 ps, 0.132 × 10^{11} s^{-1}, 6, 0.040.

Calculations. The Pople semiempirical SCF method[24a,36] (complete neglect of differential overlap) was used for closed-shell SCF ground-state calculations. A CI treatment was applied to the SCF MOs including both single and double excitations. For single excitations, the highest six occupied and lowest six unoccupied MOs were used to give 36 configurations; double excitations were selected by a first-order perturbation approach[37,38] from the 325 possible configurations obtained by promoting from the highest five occupied to the lowest five vacant MOs. Configurations were represented as a linear combination of Slater determinants such that each configuration was an eigenfunction of the spin operator S^2 as described by Murrell and McEwen.[39] Matrix elements between configurations were calculated from general formulas obtained by the standard methods for reduction of many-electron integrals.[24a,36b,39]

Valence state ionization potentials were those described by Hinze and Jaffe.[40] Two-electron repulsion integrals were calculated by the Pariser–Parr approach.[41] Resonance integrals were calculated by the expression $\beta_{ij} = (S_{ij}/1 + S_{ij})(I_i + I_j)K$, where S_{ij} is the overlap integral[42] and I_i and I_j are the valence state ionization potentials for orbitals i and j, respectively. Nearest-neighbor and selected 1,3 resonance integrals were used. The constant K was obtained by fitting β to the spectral transition of ethylene using a configuration interaction calculation that included single and double excitations.[37]

Standard geometry for the bicyclo[3.1.0]hexenyl system and dihydronaphthalene systems was assumed, based on reported model compounds.[43] The geometry for the spiroindene system was based on the reported MINDO/2 calculation for the ground-state optimized geometry of spiro[2.4]hepta-4,6-diene.[44] Geometries for intermediate species were assumed.

Calculations were performed with Fortran IV programs[37] on a PDP-11/T55 computer having 32K words of memory. Direct access to and from two disks of 1.2 × 10^6 words per disk allowed storage and use of the large matrices encountered in configuration-interaction calculations.

Acknowledgments. Support of this research by the National Science Foundation, by NIH Grant GM07487, and by the U.S. Army Research Office is gratefully acknowledged.

References and Notes

(1) (a) This is part 121 of our photochemical series. (b) Also this is part 5 of our series on the bicycle rearrangement.

(2) (a) For part 120 see: Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.*, **1979,** *101,* 6367–6383. (b) For part 4 on bicycle photochemistry see: Zimmerman, H. E.; Cutler, T. P. *J. Org. Chem.* **1978,** *43,* 3283–3303.

(3) (a) Zimmerman, H. E.; Hackett, P.; Juers, D. F.; Schröder, B. *J. Am. Chem. Soc.* **1967,** *89,* 5973–5974. (b) Zimmerman, H. E.; Juers, D. F.; McCall, J. M.; Schröder, B. *Ibid.* **1971,** *93,* 3653–3662. (c) Zimmerman, H. E.; Cutler, T. P. *J. Chem. Soc., Chem. Commun.* **1978,** 232–234. (d) See ref 2b. (e) Also note Hamer, N. K.; Stubbs, M. *Chem. Commun.* **1970,** 1013–1014. (f) For pioneering descriptive work contemporary with ours note Tabata, T.; Hart, H. *Tetrahedron Lett.* **1969,** 4929–4936. (g) A number of other reactions involve bicycling as part of their mechanisms.[4]

(4) (a) Zimmerman, H. E.; Döpp, D.; Huyffer, P. S. *J. Am. Chem. Soc.* **1966,** *88,* 5352–5353. (b) Zimmerman, H. E.; Crumrine, D. S. *Ibid.* **1968,** *90,* 5612–5614. (c) Zimmerman, H. E.; Huyffer, P. S. *Ibid.* **1969,** *91,* 434–445. (d) Berson, J. A.; Willcott, M. R. *Ibid.* **1966,** *88,* 2494–2502. (e) Berson, J. A.; Grubb, P. W.; Clark, R. A.; Hartter, O. R.; Willcott, M. R. *Ibid.* **1967,** *89,* 4076–4081. (f) Hart, H.; Rogers, T. R.; Griffiths, J. *Ibid.* **1969,** *91,* 754–756. (g) Childs, R. F.; Winstein, S. *Ibid.* **1968,** *90,* 7146–7147. (h) Zimmerman, H. E.; Schuster, D. I. *Ibid.* **1961,** *83,* 4486–4488; **1962,** *84,* 5427–4540. (i) Zimmerman, H. E.; Eberbach, W. *Ibid.* **1973,** *95,* 3970–3976. (j) Madigan, M. D.; Swenton, J. S. *Ibid.* **1971,** *93,* 6316–6318. (k) Swenton, J. S.; Burdett, K. A.; Madigan, D. M.; Johnson, T.; Rosso, P. D. *Ibid.* **1975,** *97,* 3428–3435. (l) Kato, M.; Tsuji, M.; Miwa, T. *Bull. Chem. Soc. Jpn.* **1978,** *51,* 1450–1455.

(5) (a) Corey, E. J.; Jautelat, M. *J. Am. Chem. Soc.* **1967,** *89,* 3912–3914. (b) See ref 3a. (c) Zimmerman, H. E.; Baum, A. A. *Ibid.* **1971,** *93,* 3646–3653. (d) Tang, C. S. F.; Rapoport, H. *J. Org. Chem.* **1973,** *38,* 2806–2809.

(6) (a) Zimmerman, H. E. *Mol. Photochem.* **1971,** *3,* 281–292.

(7) (a) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977,** *8,* 379–385. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956,** *235,* 518.

(8) (a) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1974,** *96,* 439–449.

(9) (a) For a general review, note Birks, J. B.; Muro, I. H. *Prog. React. Kinet.* **1967,** *4,* 239–303. (b) Ware, W. R.; Doemeny, L. J.; Nemzek, T. L. *J. Phys. Chem.* **1973,** *77,* 2038–2048. (c) Hu, M. H.; Ware, W. R. *J. Am. Chem. Soc.* **1976,** *98,* 4718–4727.

(10) (a) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975,** *97,* 3718–3725. (b) Zimmerman, H. E.; Albrecht, F. X.; Haire, M. J. *Ibid.* **1975,** *97,* 3726–3740. (c) Zimmerman, H. E.; Tolbert, L. M. *Ibid.* **1975,** *97,* 5497–5507. (d) Zimmerman, H. E. *Pure Appl. Chem.* **1977,** *49,* 389–398. (e) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978,** *34,* 1775–1803. (f) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *J. Am. Chem. Soc.* **1978,** *100,* 4146–4162. (g) Zimmerman, H. E.; Welter, T. R. *Ibid.* **1978,** *100,* 4131–4145. (h) See ref 2a,b. (i) Zimmerman, H. E.; Diehl, D. R. *J. Am. Chem. Soc.* **1979,** *101,* 1841–1857.

(11) (a) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976,** *98,* 7680–7689. (b) See ref 10d. (c) See also ref 12. (d) This point has been noted ubiquitously in papers on our di-π-methane rearrangement.

(12) Previously we had termed this a Grob fragmentation. However, this term seems now to be operationally defined as fragmentations occurring from heterolytic mechanisms with a departing anion and attacking nucleophile or base.[12b] Referees have previously argued against our earlier terminology. Hence, we recently[2a] termed this type of process a 1,4 diradical 2,3 fragmentation. (b) Grob, C. A.; Schiess, P. W. *Angew Chem.* **1967,** *79,* 1–14. (c) As noted in ref 2a and 11a, the fragmentation—derived from photochemical precursors, from azo precursors by loss of nitrogen, and from heterolytic processes—involves species which are different in extent of bonding with leaving groups and, in cases, in electronic configuration.

(13) Note footnote 21 of ref 2b.

(14) See ref 10f.

(15) (a) Zimmerman, H. E. *Acc. Chem. Res.* **1972,** *5,* 393–401. (b) For discussion

of avoided crossings and degeneracy or splitting note same reference.
(16) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966,** *88,* 1564–1564, 1566–1567.
(17) (a) Michl, J. *Mol. Photochem.* **1972,** 243–255, 257–286, 287–314. (b) Note ref 15.
(18) (a) Zimmerman, H. E.; Steinmetz, M. G. *J. Chem. Soc., Chem Commun.* **1978,** 230–232. (b) See ref 10a. (c) See ref 15a.
(19) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969,** *91,* 3316–3323.
(20) (a) Zimmerman, H. E. *Angew, Chem., Int. Ed. Engl.* **1969,** *8,* 1–11. (b) See ref 4.
(21) (a) Zimmerman, H. E. In "Pericyclic Reactions", Marchand, A. L., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, pp 53–107. (b) See ref 11a. (c) Zimmerman, H. E. *Acc. Chem. Res.* **1971,** *4,* 272–280.
(22) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967,** *89,* 3932–3933. (b) Zimmerman, H. E.; Elser, W. R. *Ibid.* **1969,** *91,* 887–896. (c) See ref 19.
(23) (a) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972,** *94,* 8749–8761. (b) See ref 2b, 3b, 10i, and 15a.
(24) (a) Zimmerman, H. E. "Quantum Mechanics for Organic Chemists"; Academic Press: New York, 1975. (b) Zimmerman, H. E.; Hancock, K. G.; Licke, G. C. *J. Am. Chem. Soc.* **1968,** *90,* 4892–4911.
(25) Teller, E. *J. Phys. Chem.* **1937,** *41,* 109–116.
(26) All melting points were determined using a calibrated hot-stage apparatus. Mass spectra were obtained using an AEI MS-902 mass spectrometer at 70 eV. Proton nuclear magnetic resonance spectra were obtained using a JEOL MH-100 spectrometer. Vapor phase chromatography was performed on a Varian Aerograph Series 2100 instrument employing a flame ionization detector which was calibrated for the relative responses of the detected compound and standard. Column chromatography was performed on silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) packings mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored by a hand-held UV lamp.
(27) (a) House, H. O.; Paragamian, V.; Ro, R. S.; Wluka, D. J. *J. Am. Chem. Soc.* **1960,** *82,* 1452–1457. (b) Floyd, M. B.; Allen, G. R., Jr. *J. Org. Chem.* **1970,** *35,* 2647–2653. (c) Marvell, C. S.; Hinman, C. W. *J. Am. Chem. Soc.* **1954,** *76,* 5435–5437. (d) Stoermer, R.; Asbrand, E. *Chem. Ber.* **1931,** *64,* 2796–2804.
(28) (a) Hattersley, P. J.; Lockhart, I. M.; Wright, J. *J. Chem. Soc. C* **1969,** 217–222. (b) Klemm, L. H.; Shabtai, J.; Taylor, D. R. *J. Org. Chem.* **1968,** *33,* 1480–1488. (c) Marvell, E. N.; Geiszler, A. O. *J. Am. Chem. Soc.* **1952,** *74,* 1259–1263. (d) Clemo, G. R.; Dickenson, H. G. *J. Chem. Soc.* **1937,** 255–257. (e) Arnold, R. T.; Buckley, J. S. Jr.; Richter, J. *J. Am. Chem. Soc.* **1947,** *69,* 2322–2325.
(29) Witting, G.; Reppe, H. G.; Eicher, T. *Justus Liebigs Ann. Chem.* **1961,** *643,* 47–67.
(30) (a) Corey, E. J.; Chaykowsky, M. *J. Am. Chem. Soc.* **1965,** *87,* 1353–1364. (b) Thiele, J.; Merck, K. *Justus Liebigs Ann. Chem.* **1918,** *415,* 257–273. (c) Staley, W. W.; Fox, M. A.; Hirzel, T. K. *J. Am. Chem. Soc.* **1976,** *98,* 3910–3916.
(31) (a) Marvell, E. N.; Stephenson, J. L. *J. Am. Chem. Soc.* **1955,** *77,* 5177–5179. (b) Soffer, M. O.; Stewart, R. A.; Cavagnol, J. C.; Getterson, H. E.; Bowler, E. A. *Ibid.* **1950,** *72,* 3704–3709. (c) Cromwell, N. H.; Campbell, R. D. *J. Org. Chem.* **1957,** *22,* 520–523. (d) Christol, H.; Jacquier, R.; Mousseron, M. *Bull. Soc. Chim. Fr.* **1959,** 11–15. (e) Klemm, L. H.; Klopfenstein, C. E.; Shabtai, J. *J. Org. Chem.* **1970,** *35,* 1069–1075.
(32) Dannenberg, H.; Keller, H. H. *Justus Liebigs Ann. Chem.* **1967,** *702,* 149–162.
(33) Heimgartner, H.; Ulrich, L.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1971,** *54,* 2313–2354.
(34) Meites, L.; Meites, T. *Anal. Chem.* **1948,** *20,* 984–985.
(35) Pople, J. A. *Trans. Faraday Soc.* **1953,** *49,* 1375–1385.
(36) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Molecules"; McGraw-Hill: New York, 1949.
(37) Zimmerman, H. E.; Steinmetz, M. G., unpublished results.
(38) Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1974,** *35,* 33–58.
(39) Murrell, J. N.; McEwen, K. L. *J. Chem. Phys.* **1956,** *25,* 1143–1149.
(40) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962,** *84,* 540–546.
(41) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953,** *21,* 767–776.
(42) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949,** *17,* 1248–1267.
(43) (a) Kennard, O.; Ed. "Molecular Structures and Dimensions", Vol. A1; Unwin Brothers: Cambridge, England, 1972. (b) Favinni, G.; Zuccarello, F.; Buimi, G. *J. Mol. Struct.* **1969,** *3,* 385–394. (c) Lambert, J. E.; Carhart, R. E.; Corfield, P. W. R. *Chem. Commun.* **1969,** 999–1000. (d) Hehre, W. J. *J. Am. Chem. Soc.* **1974,** *96,* 5207–5217.
(44) Schoeller, W. W.; Dahm, J. *Tetrahedron* **1973,** *29,* 3237–3239.

Sulfur as a Regiochemical Control Element. Synthesis of 2-Alkoxy(acyloxy)-3-alkyl(aryl)thiobuta-1,3-dienes

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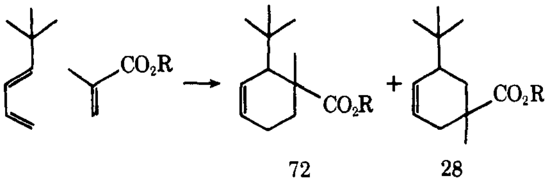
Abstract: The internal competition between substituents in the 2,3 positions of a diene—one being a sulfur and the other an oxygen substituent—is discussed. To examine this question, a general approach to 2-alkoxy(acyloxy)-3-alkyl(aryl)thiobuta-1,3-dienes has been developed. Bromocyclobutanone undergoes displacement with sulfur nucleophiles without competing rearrangements of the benzylic acid type. These compounds have been O-alkylated and O-acylated to give 1-alkoxy(acyloxy)-2-alkyl(aryl)thiocyclobutenes. Thermal opening of the cyclobutenes, preferably by the technique of flash vacuum pyrolysis, gave the desired dienes normally in overall yields of 35–67%.

While the generalization of the reaction between a conjugated diene and an olefin to form a substituted cyclohexene adduct was formulated in 1928,[1,2] this fundamental and broad reaction continues to mystify chemists. Many features such as those dealing with stereochemistry are well understood, but many aspects still remain aloof. For example, the observation of endo addition has been rationalized by (1) inductive (van der Waals or dipolar) forces,[3] (2) charge transfer,[4] (3) secondary bonding forces,[5] (4) favorable geometry for overlap,[6] and (5) secondary orbital interactions.[7]

Even more unsettled is the question of regiochemistry, which has been claimed to be "the biggest unsolved problem in the field".[8] Simple electronic effects do not greatly affect regioselectivity. Thus, both an electron-donating (e.g., 2-ethoxy-1,3-butadiene)[2d] and an electron-withdrawing substituent (e.g., 2-cyano-1,3-butadiene)[9] on the diene lead to the same orientation with a dienophile such as acrylic ester. Steric factors do not overwhelm the reaction as illustrated in eq 1.[2d]



(1)

A frontier orbital PMO approach has been highly successful in explaining many features of the Diels-Alder reaction including regioselectivity.[10,11] Various levels of sophistication have been used and a very large number of reactions are correctly "predicted" by this approach. In its simplest version, only the HOMO-LUMO pair of frontier orbitals is considered and the regiochemistry evolves from consideration of the terminal

0002-7863/80/1502-3548$01.00/0