accord with a delocalization which involves only the internal cyclopropane bond.

The bond distances and angles we observe here for **4** are in remarkably good agreement with those calculated by Haddon using MINDO/3 for the parent homotropylium cation **3**.[14] This is shown by the compilation of data in Table V. The cation **4** is a little more bent than the calculations indicated for **3** while the agreement between calculated and observed bond lengths is excellent. This agreement is all the more remarkable in as much as a substantial part of the positive charge of **4** would be on the hydroxy group and the importance of cyclic delocalization reduced.

It is possible to estimate a bond order for the C_1,C_7 bond of **4** using the distance found here (1.626 (8) Å) and the empirical bond valence method developed by Brown.[26] With use of this method, which for C,C bonds essentially consists of establishing a relationship beween the lengths and bond orders of single, double and triple bonds, a bond order of 0.76 is found. This compares to a value of 0.56 estimated by Winstein from UV spectra for the bond order of the C_1,C_7 bond of the parent homotropylium.[4a]

The packing is shown in Figure 4. The structure comprises of alternate layers of anions (at $z = 0, {}^1/_2$) and cations (at roughly $z = {}^1/_4, {}^3/_4$) parallel to the *ab* planes. Within the cation layer, disordered cations are arranged in paired chains. Thus a cation, which resembles a half-closed hand, is related to another in the adjacent chain as though the hands were interlinked fingertips to finger tips but displaced along *b* because of the 2_1 operation. The cation is hydrogen bonded to the $SbCl_6^-$ ions through either O(2)···Cl(22) or the bifurcated system O(2)···Cl(11), Cl(12).

The anions form a regular array, but there is no regular close packing of halogen ions within the layer. The perturbation appears to be caused by the interactions of the cation and anion layers. These are Cl(21) alternating with the C(2)C(3)C(5)C(6)O(2) portion of the cation along the *b* direction and a similar alternation of Cl(22) and Cl(22)^f pairs with C(8) along the *b* direction. All interactions appear to be weak ionic or van der Waals forces, and thus packing considerations do not appear to be important in determining the conformation of the cation. This is in accord with the conclusions reached previously from a comparison of the solution and solid-state ^{13}C NMR spectra.

Conclusion

The results we have described above show that protonated 2,3-homotropone, **5**, has the same structure in both the solid state and solution. Moreover, the bond lengths of this cation as determined by X-ray diffraction are fully in accord with it having a homotropylium structure. These results fully substantiate the concept of homoaromaticity as it was originally developed by Winstein some 20 years ago.

Further structural work on related systems will be reported shortly.

Registry No. 4, 80976-39-2; **5**, 3818-97-1.

Supplementary Material Available: A listing of structure factor amplitudes for $[C_8H_8OH^+][SbCl_6^-]$ (9 pages). Ordering information is given on any current masthead page.

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Singlet–Triplet Reactivity of a β,γ-Unsaturated Ketone: Mechanistic Studies in Photochemistry[1]

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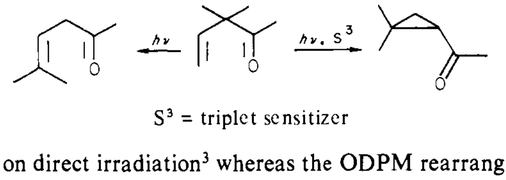
Abstract: The photochemistry of bicyclo[3.2.1]oct-2-en-7-one (**1**) and four halogen-substituted derivatives is reported. The parent ketone **1** undergoes a 1,3-acyl shift (1,3-AS) with an efficiency of 0.42 on direct irradiation. Introduction of a chlorine atom at the bridgehead (ketone **9**) or on the double bond (ketone **5**) reduces the 1,3-AS efficiency to 0.11 and 0.14, respectively. Bromine atom substituents (ketones **8** and **4**) lower the 1,3-AS efficiencies even farther to 0.088 and 0.062. However, this loss in singlet reactivity does not result in successively more efficient intersystem crossing to the ketone triplet state, for no oxadi-π-methane (ODPM) products, the triplet rearrangement products, are found on direct irradiation for any of the ketones examined. The oxadi-π-methane products are formed upon sensitized irradiations with the triplet sensitizers acetone and acetophenone. As with the direct irradiations, the efficiencies of the sensitized ODPM reactions decrease monotonically with heavy-atom introduction, i.e., ODPM: 0.08 (H); 0.0062 and 0.03 (Cl); 0.0033 and 0.007 (Br); triplet sensitized 1,3-AS: 0.048 (H); 0.0041 and 0.009 (Cl); 0.0036 and 0.0029 (Br). The disappearance efficiencies reflect the same trend for heavy-atom substitution. It is concluded that introduction of the heavy atom increases the radiationless decay rate for the triplet state. Acetophenone and benzophenone phosphorescence quenching studies indicated that energy transfer from bromo ketone **4** was slower than the diffusion-controlled rate, indicating excited state complex formation between the sensitizer and **4**. Furthermore, a combined acetophenone sensitization–piperylene quenched reaction gave a nonlinear Stern–Volmer plot from which was derived a 6-ns lifetime for the complex. It was concluded that the heavy-atom effect was to increase the importance of the radiationless decay processes for the triplet complex.

The photochemistry of β,γ-unsaturated ketones has received extensive attention.[2] Particular interest has been directed toward the nature of the two major rearrangement reactions, the 1,3-acyl shift (1,3-AS) and the oxadi-π-methane (ODPM) rearrangement (eq 1). With a few notable exceptions, the 1,3-AS rearrangement occurs on direct irradiation[3] whereas the ODPM rearrangement



(1)

S³ = triplet sensitizer

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(2) Reviews: (a) Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (b) Houk, K. N. *Ibid.* **1976**, *76*, 1–74. Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73–114. Recent leading references: (c) Henne, A.; Siew, N. P. Y.; Schaffner, K. *Helv. Chim. Acta* **1979**, *62*, 1952–1965; *J. Am. Chem. Soc.* **1979**, *101*, 3671–3673. (d) Schaffner, K. *Tetrahedron* **1976**, *32*, 641–653.

(3) Sensitized 1,3-AS reaction have been noted: (a) Schexnayder, M. A.; Engel, P. S. *Tetrahedron Lett.* **1975**, 1153–1156. (b) Engel, P. S.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 145–153. (c) See ref 1.

0002-7863/82/1504-2456$01.25/0

is the predominant reaction[4] on triplet sensitization of constrained β,γ-unsaturated ketones.[5] The conclusion[2] from earlier studies was that the 1,3-AS reaction occurred primarily from the n,π* singlet, whereas the ODPM reaction occurred exclusively from the π,π* triplet state of β,γ-unsaturated ketones.

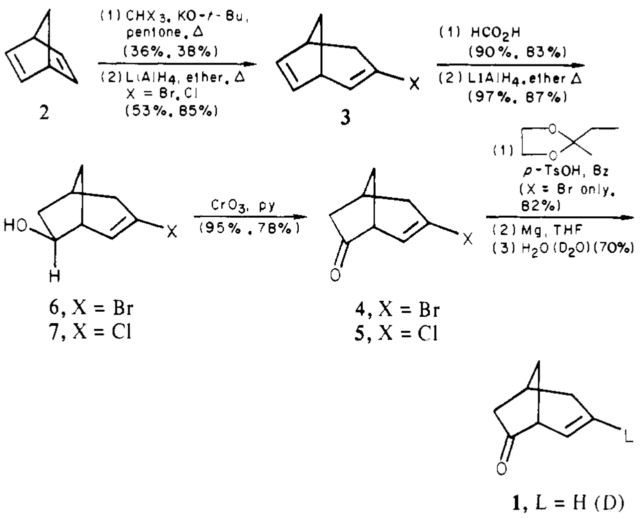
More recent CIDNP studies by Schaffner[2b,6a] and Cerfontain[6b,c] have demonstrated that for certain β,γ-unsaturated ketones in which the carbonyl is not part of a ring at least a portion of the 1,3-AS rearrangement occurs from a triplet excited state *on direct irradiation*. Dalton[7] has further suggested that in some cases a major fraction of the 1,3-AS reaction may originate from a short-lived, upper triplet state (T_2) of largely n,π* character.

While much attention has been concentrated on the 1,3-AS rearrangement, less success has been realized in determining the nature of the ODPM reaction. Efforts to study both reactions have been severely limited because of the absence of ODPM products on direct irradiation and of phosphorescence from β,γ-unsaturated ketones in general. Thus direct measurements of triplet state behavior are difficult. Yet, in order to arrive at a firm mechanistic picture for β,γ-unsaturated ketone photochemistry, it will be necessary to determine the photochemical and photophysical properties of the triplet excited state(s). For attainment of this, a molecular design which will encourage S–T intersystem crossing would be desirable. It is toward this goal that the current status of our studies is reported.

Factors which are known[8-11] to affect S–T intersystem crossing include the following: (1) heavy-atom effects;[8,9] (2) the magnitude of the singlet–triplet energy difference between the two states;[8] (3) the configuration of the initial and of the final states;[8,9] and (4) vibronic or Franck–Condon factors.[8,10,11] Theoretical and experimental studies have established the importance of a number of these factors for photophysical processes.[8-12] The actual effect on the photochemical processes for any particular molecular system will depend on the competitive rates of all of the processes emanating from a particular excited state. Thus, the difficulty in assessing the nature of an individual effect on photochemical reactions is compounded by the fact that both the population and depopulation rates of the state will be altered when a molecular change is imposed. Further complicating an analysis of the structure–reactivity effects occurs when biradical intermediates are formed, for their multiplicity, and thus reactivity, may also be influenced.[12a] Extensive studies on heavy-atom effects on photodimerization of acenaphthalenes[12b] and coumarins[12c] as well as type II reactions[12a] have pointed to the importance of other intersystem-crossing processes in competition with the excited-state S^1–T conversion. Therefore, estimates from photophysical studies should be applied to photochemical reactions with caution.

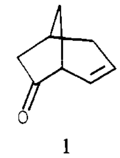
Our approach to exploring the structural modification which would enhance k_{ST} has been to systematically examine the effects of heavy atoms, of energy gap alteration, of state configuration manipulation, and of vibronic effects on the spectroscopy and photochemical behavior of a series of β,γ-unsaturated ketones of a common carbon framework. The design of the carbon framework was predicated on (1) maximization of the possibility of observing a vanishingly small ODPM reaction amidst a continuous 1,3-AS process, (2) assurance of a significantly large carbonyl–olefin interaction, and (3) synthetic availability. Of these, 1 was considered most important. The molecular design chosen required that the 1,3-AS be reversible and, ideally, a degenerate rearrangement. Bicyclic ketones have proven exceptionally useful in this way for other studies of reactive intermediates.[13] Thus, it was decided that bicyclic ketones would meet the above criteria best.

Scheme I. General Route to Bicyclic Ketones **1**, **4**, and **5**[a]



[a] Yields are given in the order X = Br, X = Cl for each step.

In analyzing desirable bicyclic derivatives, bicyclo[3.2.1]oct-2-en-7-one (**1**) was chosen because it met all three criteria listed above as well as a rigid olefin framework which has been found ncessary for general ODPM reactivity[14-16] and is available through a variety of synthetic approaches.[17]



1

This paper reports the influence of halogen substitution on the photochemistry of **1** and is the first in the series of substituted bicyclo[3.2.1]oct-2-en-7-one photochemistry.[1]

Results

Ketone Synthesis. The synthesis of the bicyclo[3.2.1]octenone framework was achieved by the general method of Moore, Moser, and LaPrade[17a] and is outlined in Scheme I. 3-Bromo- and

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(4) The ODPM rearrangement on direct irradiation has been noted: (a) Williams, J. R.; Ziffer, H. *Chem. Commun.* **1967**, 194–195; 469–470. (b) Eckersley, T.; Parker, S. D.; Rogers, N. A. J. *Tetrahedron Lett.* **1976**, 4393–4394.

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(15) (a) Engel, P. S.; Schexnayder, M. *J. Am. Chem. Soc.* **1972**, *94*, 9252–9255. (b) Neywick, C. V. Ph.D. Thesis, University of Kansas, 1976. (c) Gonzenbach, H.-U.; Tegmo-Larsson, I.-M.; Grosclaude, J.-P.; Schaffner, K. *Helv. Chim. Acta* **1977**, *60*, 1091–1123 (see ref 28).

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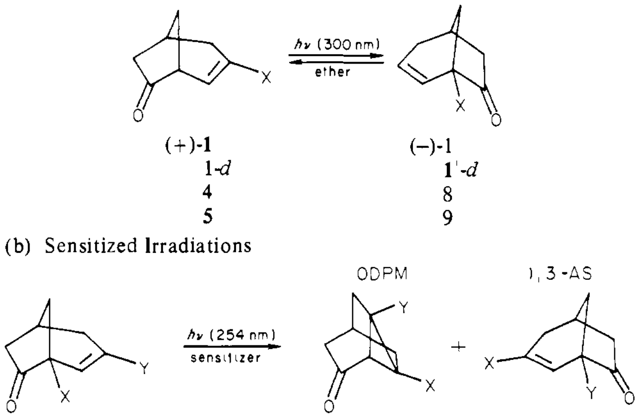
Scheme II. Photochemical Reactions of Ketones **1**, **4**, **5**, **8**, and **9**

(a) Direct Irradiations

(b) Sensitized Irradiations



(a):

(+)-**1**	(−)-1
1-*d*	**1**′-*d*
4	8
5	9

(b):

		ODPM	1,3-AS
(+)-**1**	acetone[a]	10	(−)-1
4	acetone,[a] acetophenone[b]	**11**	8
5	acetone[a]	**12**	9
8	acetone[a,b]	**11**	4
9	acetone[a]	**12**	5

[a] As the solvent. [b] Conditions were benzene (solvent) and 350-nm irradiation.

3-chlorobicyclo[3.2.1]oct-2-en-7-one (**4** and **5**, respectively) were obtained in good yield by treatment of the 3-halodienes[18] with formic acid followed by reduction with lithium aluminum hydride and then oxidation with chromium trioxide in pyridine.[19] The bromo ketone **4** was converted to bicyclo[3.2.1]oct-2-en-7-one (**1**) by hydrolysis of the vinyl Grignard derived from the bromo ketal of **4** (Scheme I). Both the 3-protio and 3-deuterio ketones **1** (L = H or D) were obtained by this method. Optically active **1** was obtained by resolution of *exo*-bromobicyclo[3.2.1]oct-2-en-7-ol (**6**) as the brucine salt of the phthalate half ester followed by hydrolysis and Grignard reduction. Finally, the bridgehead-substituted bicyclic ketones **8** and **9** were obtained by large scale irradiations of the corresponding 3-substituted derivatives **4** and **5** (Scheme II).

Exploratory Photochemistry. Each of the ketones was irradiated in ether at 300 nm (direct irradiation) and in acetone at 254 nm (sensitized irradiation). Isolation procedures which would detect even small amounts of ODPM products did not reveal any of the tricyclic ketone from the direct irradiations. Both the 1,3-AS and ODPM products were isolated in sensitized runs of **4** and **5**. In addition, bromo ketones **4** and **8** were subjected to benzophenone sensitization in benzene at 350 nm; **4** was also examined for acetophenone sensitization at 350 nm. The results of these studies are outlined in Scheme II and are detailed in the Experimental Section.

Quantitative Photochemical Studies. Quantum efficiency determinations for each ketone under direct irradiation and acetone-sensitization conditions were performed and are given in Table I. As noted in Table I under the acetone sensitization results, both 1,3-AS and ODPM product formation were monitored. The fact that the 1,3-AS quantum yields are approximately 4–8% of the values obtained on direct irradiation may indicate that the sensitized 1,3-AS is arising from direct light absorption or by singlet sensitization from acetone rather than by triplet sensitization. While we cannot rigorously rule out the singlet sensitization by acetone, the direct absorption of 4–8% of the incident light by these ketones is unlikely. The relative absorptivities of acetone and the ketones were measured with acetone absorbing greater than 98% of the light.

Table I. Quantum Efficiencies[a] for [1,3] Acyl Shift (1,3-AS) and Oxadi-π-methane (ODPM) Rearrangements

Direct

ketone	ϕ_{dis}	$\phi_{1,3\text{-AS}}$	$\Sigma\phi_{1,3}$(forward and reverse)[b]
1(−)[c]	0.42 ± 0.04	0.42[d] ± 0.04	0.84 (1(−) + 1(+))
4	0.16 ± 0.02	0.088 ± 0.009	0.15 (4 + 8)
5	0.211 ± 0.02	0.14 ± 0.02	0.25 (5 + 9)
8	0.095 ± 0.01	0.062 ± 0.007	
9	0.16 ± 0.02	0.11 ± 0.01	

Acetone Sensitization

ketone	ϕ_{dis}	$\phi_{1,3\text{-AS}}$	ϕ_{ODPM}
1	0.22 ± 0.02	0.048 ± 0.008	0.080 ± 0.008
4	0.015 ± 0.004	0.0036 ± 0.0005	0.0033 ± 0.0003
5	0.030 ± 0.004	0.0041 ± 0.0005	0.0062 ± 0.001
8	0.021 ± 0.002	0.0029 ± 0.0004	0.007 ± 0.0009
9	0.046 ± 0.005	0.009 ± 0.001	0.030 ± 0.003

[a] Ketones were irradiated at 300 (direct) and 254 nm (sensitized). Solutions of ~10^{-2} M were degassed with purified N_2 and irradiated in a merry-go-round apparatus (Southern New England, RPR-100) and were run in duplicate. Analysis was by GLC, employing an internal standard. Actinometry was by potassium ferrioxalate.[20] A 10% error in light output was used to calculate the standard deviation. Values reported were those extrapolated to zero conversion. [b] The sum of the forward and reverse appearance quantum efficiencies for the reversible 1,3-AS migration. [c] Racemization of the active ketone 1 was followed polarimetrically at 578, 546, 436, and 365 nm. The mechanism for the racemization was assumed to be a concerted [1,3] acyl migration.[21] [d] The racemization quantum efficiency was assumed equal to ϕ_{dis} and ϕ_{app} for 1 (see text). GLC analysis showed no new products in high conversion runs (~66%).

Table II. Quantum Efficiencies for the Sensitized 1,3-AS and ODPM Rearrangements of Bromo Ketones 4 and 8 as a Function of the Sensitizer

ketone	sensitizer (E_{T}, kcal/mol)[22]	10^2-$\phi_{1,3\text{-AS}}$	10^2-ϕ_{ODPM}
4	acetone (79–82)[a]	0.36	0.33
	acetophenone (74.1)[b]	0.13	0.36
	benzophenone (69.2)[b]	*c*	0.0
8	acetone (79–82)[a]	0.3	0.7
	acetophenone (74.1)[b]	0.7	2.0
	benzophenone (69.2)[b]	*c*	0.0

[a] Sensitizer was also the solvent; 254-nm excitation. [b] Benzene solvent; 350-nm excitation. [c] A small peak on the GLC trace appeared at approximately the retention time of the 1,3-AS product. This low yield product was not identified.

In addition to acetone-sensitization experiments, other sensitizers were also conducted. Since the triplet energies of β,γ-unsaturated ketones have been estimated to be about 74 kcal/mol[3a,23] and, furthermore, the direct measurement of these triplet energies from phosphorescence emission has not been possible, the use of sensitizers of decreasing triplet energies was employed in order to estimate the triplet energy. With bicyclic ketones **4** and **8**, the ODPM reaction could be sensitized with acetone (E_{T} = 79-82 kcal/mol)[22] and acetophenone (E_{T} = 74.1 kcal/mol)[22] but not with benzophenone (E_{T} = 69.2 kcal/mol).[22] The quantum yields for both the 1,3-AS and ODPM reactions as a function of sensitizer are given in Table II.

For acetophenone and benzophenone, the contribution toward the 1,3-AS product formation from singlet sensitization must be negligible due to the extremely short lifetime of the singlet state

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(21) The conclusions are not altered if a mechanism invoking an acyl–allyl diradical is employed in this analysis. The quantum yield for diradical formation would be twice that given in Table I (i.e., ϕ = 0.82) which is unusually large. Stereochemical investigations also indicated stereospecific reaction consistent with a concerted [1,3] acyl migration.[5]

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Table III. Piperylene Quenching Studies on the Direct Irradiation of 4[a]

run	piperylene quencher concn, M	$\phi_0/\phi_{q(\mathrm{dis})}$	$\phi_0/\phi_{q(1,3\text{-AS})}$
1	0.5	1.00	1.02
2	1.0[b]	1.01	0.99
3	1.5	0.95	0.88
4	10.0	1.00	0.94

[a] Irradiation at 300 nm for 41 min (31% conversion of 4). [b] No trans to cis isomerization observed for *trans*-piperylene as the quencher.

Table IV. *cis*-Piperylene Quenching of the Acetophenone-Sensitized Rearrangement of Bromo Ketone 4[a]

cis-piperylene, M	$[8]_0/[8]_q$[b]	$[11]_0/[11]_q$[c]	(trans/cis)$_k$[d]	(trans/cis)$_0$[e]
0.000	1.00	1.00[f]	0	0
0.001	1.00	1.17 1.13 1.09	g	g
0.003	0.88	3.05 2.76	g	g
0.005	0.92	4.91 5.89 5.35	1.64	1.38
0.007	0.85	6.54 6.40	1.27	1.19
0.010	0.81	11.33 10.16 11.55	1.27	1.25

[a] Irradiation of a 0.073 M solution of 4 at 350 nm for 330 min. [b] The ratio of 1-bromo ketone 8 without quencher present to 8 with quencher present. These are average values. With addition of piperylene the yield of 8 measured by GLC actually increased slightly. [c] The ratio of ODPM product 11 without quencher present to 11 with quencher present. [d] The ratio of *trans*- to *cis*-piperylene in the reaction mixture as a function of piperylene concentration. [e] The ratio of *trans*- to *cis*-piperylene from acetophenone sensitization (no bromo ketone present) as a function of piperylene concentration. [f] Five determinations of $[11]_0$ were performed. [g] Product formation was too small for VPC analysis.

of these aryl ketone sensitizers. However, the contribution from direct absorption for **4** (~1.7%) is appreciable and may account for the 1,3-AS product formation in this experiment. This is not the case for acetophenone sensitization of the 11% 1,3-AS reaction observed from **8**.

A quenching experiment employing various concentrations of *trans*-piperylene in a 0.026 M solution of bromo ketone **4** was examined next. Table III reveals that no quenching could be detected even when piperylene was used as the solvent. When bromo ketone **4** was irradiated at 300 nm in benzene with 1.5 M cis-piperylene to 70% conversion, only a small diminution in the disappearance efficiency ($\phi_0/\phi_q = 1.06$) and 1,3-AS appearance efficiency ($\phi_0/\phi_q = 1.13$) was noted. The benzene solution was also examined for HBr as a possible byproduct by titrametric determination. No acid was detected.

Finally, a combined acetophenone sensitization–piperylene quenching study was carried out on **4**. The acetophenone concentration was 0.15 M in benzene, sufficiently large to assure that greater than 98% of the incident radiation (RPR-350 lamps) was absorbed by the sensitizer. The concentration of **4** was 0.073 M, also sufficiently large to assure that energy transfer from triplet acetophenone to **4** was complete. The effect of varying the concentration of *cis*-piperylene (0–0.1 M) on the extent of cis to trans isomerization of piperylene and on the photorearrangements of **4** are given in Table IV. An independent control experiment in which the acetophenone-sensitized isomerization of piperylene was determined indicated that the ratio of the *trans*- to *cis*-piperylene was the same as that obtained by the indirect sensitization in the presence of bromo ketone **4**. The results of these studies are also given in Table IV.

Table V. Change in Specific Rotation of 1 (L = H) as a Function of Irradiation Time[a]

time,[b] min	specific rotation at λ, nm			
	578	546	436	365
0	−44.3	−51.9	−109.6	−253.9
15	−36.1	−42.2	−88.3	−202.8
30	−31.5	−36.6	−76.9	−171.9
45	−26.0	−30.4	−63.9	−116.7
61	−19.7	−23.0	−50.2	−78.3

[a] Irradiation at 300 nm in ether ($c = 1.03$). [b] The actinometer[20] reading for this run was 0.77 mEinsteins/h.

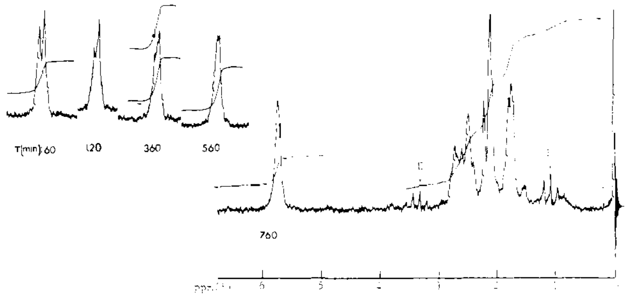

Figure 1. ^{1}H NMR of 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1**, L = D) in CCl_4 after irradiation for up to 760 min (full spectrum). Insets are in the 5–6-ppm region. E indicates ether impurity from incomplete solvent removal before ^{1}H NMR analysis.

For determination of the quantum efficiency for the 1,3-AS photorearrangements of the parent ketone, bicyclo[3.2.1]oct-2-en-7-one (**1**), the change in optical rotation of the partially resolved ketone was followed as a function of the absorbed radiation. Table V presents the experimental rotations monitored at four different wavelengths. The quantum efficiency for the 1,3-AS was obtained from expression 2, employing the integrated rate expression for

$$\phi_{\mathrm{rac}} = (K_0/A_{\mathrm{T}})\tfrac{1}{2} \ln (\alpha_0/\alpha) \tag{2}$$

a unimolecular racemization first employed by Smith[24] for the thermolysis of (+)-α-pinene. To express the efficiency of the degenerate rearrangement as a quantum efficiency for racemization (ϕ_{rac}), we must convert the first-order rate constant to the reaction efficiency, i.e., eq 2, where K_0 is the total number of moles of ketone present; A_{T} is the total number of einsteins absorbed by the ketone and α_0 and α are the initial and final rotations, respectively. With use of this equation and the data in Table V, a value of 0.42 ± 0.04 was obtained for the racemization quantum efficiency.

An assumption employed in the derivation of eq 2 was the constancy of the total ketone concentration during a kinetic run. For a test of this, a sample of 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1**, L = D) was irradiated for a period of 12 h. Figure 1 shows the changes in the vinyl region of the ^{1}H NMR spectrum of this sample as well as a comparison of the final spectrum from irradiation at 300 nm in ether. This length of an irradiation is equivalent to approximately four turnover periods for complete reaction of the ketone (light output = 0.72 mEinsteins/h for 0.87 mmol of **1**). During this period, no evidence of new products was obtained either from GLC analysis (on several columns) or by NMR. It is particularly noteworthy that there was no evidence for the formation of the ODPM product, 1-deuteriotricyclo[3.2.1.0^{2,7}]octan-3-one (**10**, L = D), which is easily separable from the β,γ-unsaturated ketone **1** on a 10% UCON GLC column and can also be detected by the distinctive broad singlet at δ 1.85 in the ^{1}H NMR.

Emission Studies. Ether solutions of ketones **1** (L = D), **4**, and **5** (0.1 M) were examined for fluorescence emission. A broad structureless emission centered at ca. 410 nm was noted for all three. The two halogen-containing ketones emitted a considerably

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(24) Smith, D. F. *J. Am. Chem. Soc.* 1927, *49*, 43–50.

Table VI. Stern-Volmer Quenching of Acetone Phosphorescence in 1:2 (v:v) Ether:Ethanol Glass at 77 K

run	added 1 (L = D), ×10³ M	P_0/P (acetone)
1	0	1
2	4.2	1.67
3	8.4	2.0
4	17.0	2.5
5	34	3.8
6	84	7.3

least-squares slope 72.5 M^{-1} and intercept 1.26

weaker fluorescence and were slightly red-shifted (~5 nm) relative to the unsubstituted ketone **1**. Phosphorescence emission was not observed for any of these ketones, employing a number of glasses and with maximum slit openings in the spectrophosphorimeter.

Low temperature quenching studies were also conducted on the phosphorescence emission of acetone, acetophenone, and benzophenone by ketones **1**, **4**, and **5**. The Stern-Volmer quenching of acetone by each of the ketones was determined in order to establish the relative efficiency of energy transfer from the sensitizer to the substrate. The data obtained for **1** (L = D) is shown in Table VI. The slopes obtained for **1**, the chloro ketone **5**, and bromo ketone **4** were 73, 47, and 108 M^{-1}, respectively. With use of these values, the relative efficiency of energy transfer from acetone were determined to be 1.00, 0.64, and 1.48 for ketones **1**, **4**, and **5**, respectively, and the quantum efficiencies for the ODPM reaction were adjusted for energy-transfer efficiencies.

Room-temperature quenching studies were conducted on the phosphorescence of acetophenone and benzophenone in carbon tetrachloride.[25] The results for the quenchers naphthalene, *trans*-1,3-pentadiene, and bromo ketone **4** are given in Table VII. Both naphthalene and *trans*-1,3-pentadiene quenched the emission of each of the sensitizers with approximately the same efficiency (i.e., $k_{ET}\tau \approx$ constant) and were assumed to occur by diffusion-controlled, energy-transfer processes. The lifetime of benzophenone's phosphorescent state obtained from this study (6.2 (±0.3) × 10^{-5} s^{-1}) is in excellent agreement with the results reported by Schuster[26] and by Saltiel[27] for a 0.01–0.005 M benzophenone in CCl_4 ((6.8 ± 0.1) × 10^{-5} s^{-1}).

Bromo ketone **4** quenched the phosphorescence of acetophenone 40 times less efficiently than either of the two hydrocarbons. With benzophenone, the calculated rate constant for energy transfer to **4** was only $^1/_{300}$th as fast as either hydrocarbon quencher. The calculated rate constant for acetophenone quenching by **4** was 2.6 (±0.8) × 10^8 M^{-1} s^{-1}, in reasonable agreement with the values for dichloroethylene quenching of butyrophenone triplets ((1.6–4.0) × 10^8 M^{-1} s^{-1}).[25] Likewise, the rate constant for bimolecular quenching by benzophenone with **4** was 3.4 × 10^7 M^{-1} s^{-1}, in agreement with those values found for monoolefins quenching of benzophenone phosphorescence at room temperature ((4–5.7) × 10^7 M^{-1} s^{-1}).[25] This latter rate constant is too small to be diffusion controlled and probably is occurring by some other mechanism, perhaps by a charge-transfer complex or exciplex.[3a,23,25]

Discussion

Bicyclo[3.2.1]oct-2-en-7-one (**1**) has proven to be a good model for exploring the photochemistry of β,γ-unsaturated ketones. The 1,3-acyl shift (1,3-AS) reaction was monitored by the photoracemization of optically active **1** and proceeds in high efficiency (ϕ = 0.42 ± 0.04) without appreciable decomposition of the ketone by competing pathways, even for long irradiation times. The apparent photostability of this β,γ-unsaturated ketone, however, does establish that the oxadi-π-methane (ODPM) rearrangement is not a competitive process under direct irradiation conditions.

Scheme III. Mechanism for Substituted Bicyclo[3.2.1]oct-2-en-7-one Photochemistry

A. Direct Irradiations

$$K^0 \xrightarrow[\text{or 300 nm}]{\text{254 nm}} K^1$$

$$K^1 \xrightarrow{k_{1r}} \text{1,3-AS rearrangement}$$

$$K^1 \xrightarrow{k_f} K^0 + h\nu$$

$$K^1 \xrightarrow{k_{ic}} K^0$$

$$K^1 \xrightarrow{k_{isc}} K^3 \rightarrow K^0\ (?)$$

B. Sensitized Irradiations

$$S^0 \rightarrow \xrightarrow{\phi_{TS}} S^3$$

$$S^3 + K^0 \xrightarrow{k_{ET}} K^3 + S^0$$

$$S^3 \xrightarrow{k_{Sd}} S^0$$

$$K^3 \xrightarrow{k_{2r}} \text{ODPM rearrangement}$$

$$K^3 \xrightarrow{k_{1d}} K^0$$

$$K^3 \xrightarrow{k_{3r}} \text{1,3-AS rearrangement}$$

where K = ketone, S = sensitizer, k_i's are the rate constants for reaction (1r, 2r, or 3r), fluorescence (f), energy transfer (ET), intersystem crossing (isc), internal conversion (ic), and decay (1d or Sd), and ϕ_{TS} is the efficiency for triplet production by the sensitizer.

However, this ketone does undergo an efficient ODPM rearrangement upon acetone sensitization (ϕ = 0.22 ± 0.02), and this is accompanied by some 1,3-AS reaction. Thus, the triplet reactivity is primarily by way of the ODPM rearrangement. This dichotomy of excited state reactivity for a β,γ-unsaturated ketone has been frequently observed and is now established for the parent ketone (**1**) in this series.

The exploration of substituent effects on the photochemistry of **1** was begun with the halogens, chlorine and bromine, as heavy-atom (HA) perturbers of the excited-state processes. Both bridgehead (**8** and **9**) and olefinic substitutions (**4** and **5**) were examined. In each case, the photorearrangements were shown to consist of 1,3-AS reactions on direct irradiation and a combination of ODPM and 1,3-AS reactions on acetone sensitization. Thus, the qualitative aspects of the photochemical processes remain unchanged upon heavy-atom substitution. The principal interest here was the demonstration that ODPM reactions did not occur on direct irradiation which precludes any significant intersystem crossing to the triplet state responsible for tricyclic ketone formation. This point will be dealt with again later.

A quantitative evaluation of the substituent effects on the photochemistry of **1** is revealed in Tables I and II. It is clear for *both* the 1,3-AS and the ODPM reactions that the introduction of a halogen on the olefinic (C-3) carbon or at the bridgehead carbon (C-1) produces a dramatic reduction in the reaction efficiency.

An examination of the possible avenues available to these β,γ-unsaturated ketones suggests a number of tests for the origin of the heavy-atom effect. The mechanism outlined in Scheme III presents the elementary processes.

A. Direct Irradiations. Introduction of a halogen at the bridgehead or on the double bond should facilitate α-bond cleavage for ketones **4**, **5**, **8** and **9**. Thus, the lower 1,3-AS rearrangement efficiencies observed must be due to increased rates of the competing processes such as fluorescence, internal conversion, or, possibly, intersystem crossing. The decrease in the fluorescence yield mitigates against the first of these, however. Furthermore, several investigators including Dalton et al.[7] and Schuster, Engel,

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(25) (a) Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859–3865. We thank Professor Wagner for suggesting this experiment. (b) Clark, W. D. R.; Litt, A. D.; Steel, C. *Ibid.* **1969**, *91*, 5413–5414.

(26) Schuster, D. I.; Weil, T. M. *Mol. Photochem.* **1974**, *6*, 69–80.

(27) Saltiel, J.; Curtis, H. C.; Metts, L.; Miley, J.; Winterle, J.; Wrighton, M. *J. Am. Chem. Soc.* **1970**, *92*, 410–411.

Table VII. Energy-Transfer Rate Constants from Acetophenone and Benzophenone Triplets to Naphthalene, *trans*-1,3-Pentadiene, and Bromo Ketone 4 in CCl_4 at 20 °C

donor (E_T, kcal/mol)[22]	acceptor (E_T, kcal/mol)[22]	$k_{ET}\tau$,[a] M^{-1}	τ, s^{-1}	k_{ET}, $M^{-1}\ s^{-1}$
acetophenone[b] (74.1)	naphthalene (60.9)	1.8 (±0.3) × 10^5	1.8 (±0.3) × 10^{-5}	(1 × 10^{10})[c]
	trans-1,3-pentadiene (59.2)	2.4 (±0.5) × 10^5	2.4 (±0.5) × 10^{-5} av 2.1 (±0.4) × 10^{-5}	*c*
	bromo ketone 4	5.4 (±0.3) × 10^3	(2.1 (±0.4) × 10^{-5})[d]	2.6 (±0.8) × 10^8
benzophenone[e] (69.2)	naphthalene	6.3 (±0.1) × 10^5	6.3 (±0.1) × 10^5	*c*
	trans-1,3-pentadiene	6.0 (±0.3) × 10^5	6.0 (±0.3) × 10^{-5} av 6.2 (±0.2) × 10^{-5}	*c*
	bromo ketone 4	2.1 (±0.2) × 10^3	(6.2 (±0.2) × 10^{-5})[d]	3.4 (±0.6) × 10^7

[a] Slope of the Stern–Volmer relationship. [b] Argon deaerated solutions (0.002 M) irradiated at either 330 or 345 nm. [c] Assumed rate constant for k_{ET} was 1 × 10^{10} $M^{-1}\ s^{-1}$, the rate of diffusion in CCl_4 at 20 °C.[22] [d] The average value for the naphthalene and *trans*-1,3-pentadiene value was used. [e] Argon deaerated solutions (0.01 M) irradiated at 385 nm.

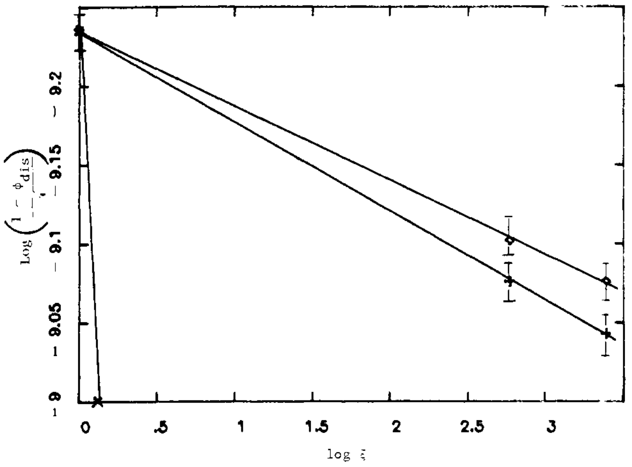

Figure 2. Direct irradiation: correlation of ζ with decay: ◇, for ketones **1**, **4**, and **5**; +, for ketones **8** and **9**; x, predicted value for a slope of 2.

et al.[28] have reported only small variations in the singlet lifetimes and fluorescence rate constants for a wide variety of structurally different β,γ-unsaturated ketones.[29] Of the remaining two possibilities, enhanced rates of internal conversion and intersystem crossing, the latter pathway has often been cited as the mechanism responsible for the reduction in fluorescence yields upon halogen substitution.[30,31]

In the case of ketones **4** and **5**, if it is assumed that intersystem crossing is the major decay pathway for the singlet excited state, a correlation between k_{isc} and the heavy-atom spin–orbit coupling parameter, ζ, should be possible.[30] To obtain k_{isc}, we assumed the "decay efficiency" $(1 - \phi_{dis})$ to be the efficiency for intersystem crossing (ϕ_{isc}) as indicated in eq 3. By rearranging this expression

$$\phi_{isc} = (1 - \phi_{dis}) = k_{isc}\tau_S \qquad (3)$$

$$k_{isc} = \alpha\zeta^n \quad \text{(ref 30)}$$

$$\log (1 - \phi_{dis})/\tau_S = n \log \zeta + \text{const} \qquad (4)$$

and substituting for k_{isc}, we obtain eq 4 which relates the disappearance quantum efficiencies and the singlet lifetime to ζ, where τ_S is the singlet lifetime and ζ is the spin–orbit coupling parameter.

Since Dalton[7] and Engel and Schuster[28] have shown that τ_S is relatively constant ($\tau_S \simeq$ 1–5 ns) for a number of β,γ-unsaturated ketones, a value $\tau_S = 10^{-9}$ s was employed for the five bicyclic ketones in this study. Using the efficiencies given in Table I, we obtained a correlation between log $((1 - \phi_{dis})/\tau_S)$ and log ζ (Figure 2) for ketones **1**, **4**, and **5**, giving a value of 0.048 for *n*. A similar correlation was also obtained for the bridgehead-substituted ketones **1**, **8**, and **9** where, again, the slope was very small. If heavy-atom induced spin–orbit coupling were the major pathway for decay, a slope of ca. 2 would be expected.[30,32] It appears, then, that enhanced rates of internal conversion rather than intersystem crossing is the most probable mode for singlet decay.

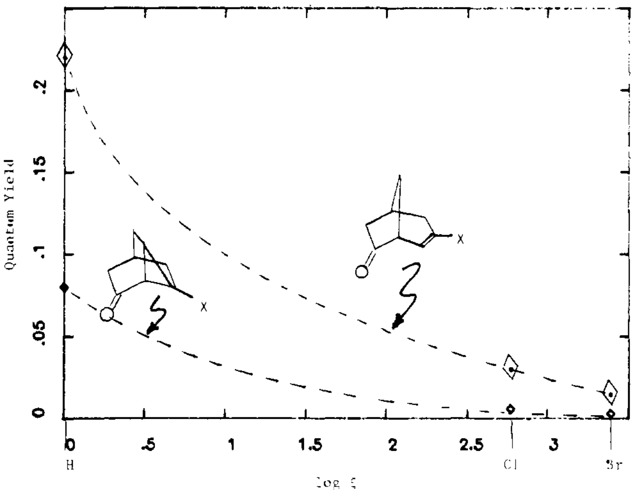

Figure 3. Quantum efficiency vs. halogen substituent for the sensitized reactions of ketones **1**, **4**, and **5**.

B. Sensitized Irradiations. The effect of halogen substitution on the photosensitized reactions of bicyclo[3.2.1]oct-2-en-7-one is reflected in Figure 3. Again, a dramatic drop in the efficiencies for reactant disappearance and product appearance is observed for both bridgehead and olefin substitution. Examination of Scheme III suggests three mechanisms which could contribute to these reduced reaction efficiencies: (1) a reduction in the rate for energy transfer from the sensitizer to the halo ketones, (2) a reduction in the reaction rate (k_{2r}), and (3) an increase in k_{1d}, the decay or intersystem crossing rate constant.

The first of these factors was examined by two methods: (1) the relative rate of acetone phosphorescence quenching in EPA glasses at 77 K and (2) the relative rate of acetophenone and benzophenone phosphorescence quenching in carbon tetrachloride solution at ambient temperature. In the first of these studies, ketones **1**, **4**, and **5** showed little difference in relative quenching efficiencies, ranging from 0.6 to 1.5.

From Table VII it is seen that ambient-temperature studies of energy transfer from acetophenone and benzophenone are not diffusion controlled. Energy transfer from acetophenone to **4** was shown to be 40 times slower than the diffusion-controlled bimolecular rate as determined with naphthalene or piperylene as the triplet energy acceptors. Benzophenone was even less efficiently quenched: the bimolecular rate constant, k_{ET} = 3.4 (±0.6) × 10^7

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(28) Schuster, D. I.; Eriksen, J.; Engel, P. S.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 5025–5027.

(29) Preliminary results with bromoketone **5** indicate that its singlet lifetime is ~10^{-9} s. We thank Professor D. I. Schuster for this determination.

(30) McGlynn, S. P.; Azumi, T.; Kinoshita, M. "Molecular Spectroscopy of the Triplet State"; Prentice-Hall: Englewood Cliffs, N.J., 1969, Chapters 6 and 7. See also ref 31 and 32.

(31) Ermolaev, U. L.; Svitashev, K. K. *Opt. Spectrosc.* **1959**, *7*, 399.

(32) See also: Koziar, J. C.; Cowan, D. O. *Acc. Chem. Res.* **1978**, *11*, 334–341 and references therein for an example of a spin–orbit coupling parameter correlation with photochemical reactivity.

Scheme IV. Acetophenone-Sensitized Rearrangements of Bromo Ketone

B′. Acetophenone-Sensitized Irradiations

$$S^0 \xrightarrow{\phi_{TS}} S^3$$

$$S^3 \xrightarrow{k_{Sd}} S^0$$

$$S^3 + Q \xrightarrow{k_{Sq}} Q^3 + S^0$$

$$S^3 + K^0 \xrightarrow{k_{ET}} (S\cdots K)^3$$

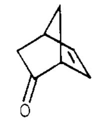
$$(S\cdots K)^3 \xrightarrow{k_{2r}'} \text{ODPM product}$$

$$(S\cdots K)^3 + Q^0 \xrightarrow{k_{Cq}} S^0 + K^0 + Q^3$$

$$(S\cdots K)^3 \xrightarrow{k_{Cd}} S^0 + K^0$$

where the individual rate constants (k_i's) are for sensitizer decay (Sd) or quenching (Sq) and for sensitizer–ketone triplet complex ($(S\cdots K)^3$), reaction (2r), quenching (Cq), or decay (Cd)

M^{-1} s^{-1}, was about 300 times less than the bimolecular rate for diffusion. These rate constants are in the range that suggest an excited-state complex is formed between the sensitizer and bromo ketone which would account for the photochemical reactivity with acetophenone sensitization and also the quenching of benzophenone phosphorescence. Regardless of the nature of the energy-transfer process, the magnitude of the two rate constants are very close to that reported for **13** which quenched acetophenone and benzophenone phosphorescence with relative rates of 14 and 538 times slower than diffusion-controlled quenching by dienes.[3a] Thus, halogen substitution does not observably alter the rate of energy transfer from the series of sensitizers employed in this study.



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Photosensitization as sensitizers with acetophenone was accomplished for both **4** and **8** although the relative formation efficiencies of the ODPM and the 1,3-AS products differed. Benzophenone (E_T = 69.2 kcal/mol), on the other hand, gave no ODPM product. This places the triplet energies for **4** and **8** between 74 and 78 kcal/mol, a result which is in excellent agreement with the values estimated by the same technique for other bicyclic ketones, notably bicyclo[2.2.1]hept-2-en-7-one (**13**).[3a] Thus, the introduction of the bromine atom substituent has little effect on the triplet energy of this β,γ-unsaturated ketone.

In an attempt to obtain additional information on the nature of the excited-state complex between acetophenone and bromo ketone **4**, a combined sensitization-quenching experiment was performed. The results in Table IV show that the ODPM reaction is quenched while the 1,3-AS reaction remains unaffected with added piperylene. This may be due to competing absorption by the bromo ketone. The complex processes involved in the energy-transfer steps in the acetophenone-sensitized reaction require modification of the acetone-sensitization mechanism in Scheme III. Competitive energy transfer from acetophenone to **4** and to piperylene is included as well as the indication that energy transfer from acetophenone to **4** occurs by formation of an excited-state complex and not by direct triplet energy transfer (Scheme IV). This latter point derives from the lower rate obtained for the energy-transfer process in the phosphorescence quenching of acetophenone (vide supra) and has analogy with the lower rates of bimolecular quenching of butyrophenone by alkenes and halo olefins reported by Kochevar and Wagner[25a] and acetophenone quenching by β,γ-unsaturated ketones reported by Engel.[3a]

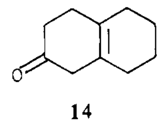
The Stern–Volmer expression for the ODPM reaction derived from Scheme IV yields a quadratic expression (eq 5), where $\tau_{complex}$

$$(\phi_0/\phi)_{ODPM} = \{(1 + k_{Sq}[Q])/(k_{Sd} + k_{ET}[K])\}\{1 + k_{Cq}\tau_{complex}[Q]\} \quad (5)$$

$= (k_{2r}' + k_{Cd})^{-1}$. The data given in Table IV were analyzed by the nonlinear, least-squares regression BMDPAR program by Dixon and Brown[33] which gave as a best fit (99% confidence level) the quadratic expression shown in eq 6 and is shown in Figure 4.

$$(\phi_0/\phi)_{ODPM} = (1 + 437[Q])(1 + 104[Q]) \quad (6)$$

The first coefficient (437 M^{-1} s^{-1}) is in reasonably good agreement with the value of 840 M^{-1} s^{-1} obtained from eq 5, employing values of k_{ET} (2.6 × 10^8 M^{-1} s^{-1}, Table VII), k_{Sq} ($\equiv k_{diffusion}$ = 1.6 × 10^{10} M^{-1} s^{-1} for benzene at 25 °C),[22] k_{Sd} (1 × 10^5 s^{-1}),[34] and a ketone concentration of 0.073 M. The difference between these two values can be attributed to the small variations in the rate constants (k_{ET} and k_{Sd}) due to the different solvents employed. If the triplet is quenched at a diffusion-controlled rate, then the $k_{Cq}\tau_{complex}$ value (104 M^{-1} s^{-1}) obtained from the nonlinear, least-squares analysis translates into a lifetime of 6 ns. This is in remarkably good agreement with the value of 4 ns determined by Engel[23] for 3,4,5,6,7,8-hexahydronaphthalene-2(1*H*)-one (**14**) by a competitive quenching method.



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It appears, then, that the bromine substituent has little effect on the lifetime of the triplet or the energy-transfer process. The most likely effect of halogen substitution is to reduce the ratio k_{2r}'/k_{Cd} by lowering k_{2r}' while increasing k_{Cd}, thus keeping the lifetime relatively constant.

Experimental Section[35]

A. Synthesis. *exo*-3-Bromobicyclo[3.2.1]oct-2-en-7-ol (6). A solution of 10 g (0.043 mol) of *exo*-3-bromobicyclo[3.2.1]oct-2-en-7-yl formate[17a,18] in a small amount of ether was added dropwise to a suspension of 3.7 g of lithium aluminum hydride in 800 mL of ether and refluxed for 17 h. The reaction was quenched by 200 mL of 5% hydrochloric acid and the water layer extracted three times with 75 mL of ether. The combined ether solution was dried over magnesium sulfate, and the ether was removed in vacuo to give 8.7 g (0.042 mol, 97%) of crude *exo*-3-bromobicyclo[3.2.1]oct-2-en-7-ol (**6**). A small amount of the crude bromo alcohol was purified by column chromatography followed by micro distillation in vacuo for spectral data. The spectral data were as follows: NMR (CCl_4) δ 1.5–3.0 (m, 8 H), 3.7 (s, 1 H, alcoholic), 4.2 (d, 1 H, J = 5 Hz, –OCH), 6.1 (d, 1 H, J = 6 Hz, olefinic); IR (CCl_4) 3610 (OH), 3350 (OH), 3040 (–C=CH), 2950 (CH), 1660 cm^{-1} (–C=C–); mass spectrum (145 °C), *m/e* (relative intensity) 77 (62%), 78 (26), 79 (100), 105 (39), 123 (16), 156 (15), 157 (9), 158 (61), 159 (12), 160 (46), 202 (9), 203 (7), 204 (9).

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(33) Dixon, W. J.; Brown, M. B., Eds., BMDP-79, Biomedical Computer programs, B-Series, University of California Press: Berkeley, Los Angeles, Calif., 1979.

(34) Cohen, S. G.; Laufer, D. A.; Sherman, W. *J. Am. Chem. Soc.* **1964**, *86*, 3060.

(35) Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Vapor-phase chromatography (VPC) was performed on a Varian Aerograph Model 1200 attached to a Varian CDS 111 computing data analyzer using $^1/_8$ in. × 6 ft or $^1/_2$ in. × 12 ft columns (injector temperature, 260 °C). Mass spectra were obtained at 70 eV on a Varian MAT CH-5 instrument. Microanalyses were performed on a 185B Hewlett-Packard in the Department of Medicinal Chemistry, The University of Kansas. The following spectrophotometers were used: NMR, Varian EM 360, A60-A, HA-100; IR, Beckman AccuLab 3; UV, Cary 14; fluorescence and phosphorescence, Aminco-Bowman. The irradiations were performed on a Rayonet photochemical reactor equipped with a merry-go-round sample holder using RPR-3500 Å, RPR-3000 Å, or RPR-2537 Å lamps. All irradiations were analyzed by VPC using heptadecane or pentadecane as an internal standard. Sensitized irradiations were carried out with sufficient sensitizer to capture 95% of the incident light. The column chromatographic separations were carried out with a silica gel column, slurry packed in 1% ether in hexane. The eluting solvents were 4 or 5% ether–hexane, 150 mL fractions. A Hewlett-Packard 2100A computer was used for the linear least-squares analysis for the calculation of quantum yields. The optical rotations were obtained from a Perkin-Elmer 141 polarimeter in the Department of Medicinal Chemistry, The University of Kansas.

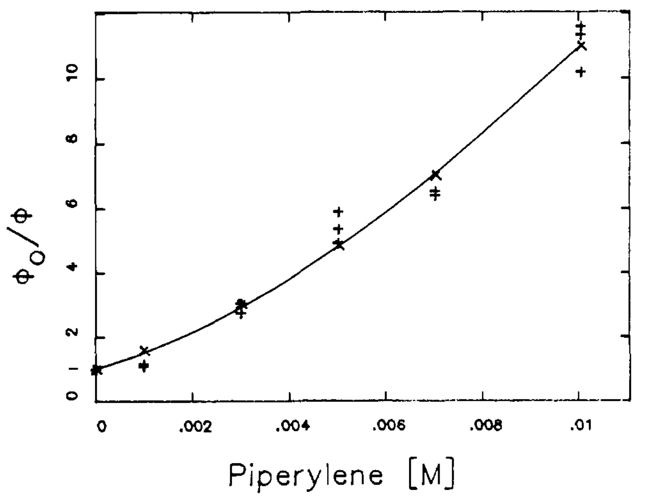

Figure 4. *cis*-Piperylene quenching of the acetophenone-sensitized rearrangement of **5**. The +'s are the experimentally determined values; the ×'s are obtained from eq 6.

Anal. Calcd for $C_8H_{11}OBr$: C, 47.31; H, 5.46. Found: C, 47.62; H, 5.55.

3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). To a magnetically stirred solution of 9.5 g of pyridine in 150 mL of methylene chloride was added 6 g of chromium trioxide.[36] The resulting deep burgundy solution was stirred for an additional 15 min at room temperature. At the end of this period, 2.12 g (0.01 mol) of the bromo alcohol **6** in a small volume of methylene chloride was added in one portion. After being stirred for 4 h at room temperature, the solution was decanted and the residue was washed with three 100-mL portions of 5% sodium hydroxide, 100 mL of 5% hydrochloric acid, and 100 mL of saturated sodium chloride and was dried over magnesium sulfate. After evaporation of the solvent in vacuo, the residue was distilled to give 1.62 g (0.008 mol, 80%) of pure 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) as a colorless liquid, bp 77–82 °C (0.5 mmHg). The spectral data were as follows: NMR (CCl_4) δ 1.6–3.2 (m, 8 H), 6.1 (d, 1 H, J = 8 Hz, olefinic); IR (CCl_4) 3045 (–C=CH), 2830–2950 (CH), 1750 (C=O), 1650 cm^{-1} (–C=C–); UV λ_{max} (hexane) 315 (ϵ 161), 303 (316), 293 (348), 285 nm (284); mass spectrum (96 °C), m/e (relative intensity) 77 (100%), 78 (49), 79 (55), 156 (50), 157 (16), 158 (50), 200 (12), 201 (1), 202 (12).

Anal. Calcd for C_8H_9OBr: C, 47.80; H, 4.51. Found: C, 47.96; H, 4.52.

***exo*-3-Chlorobicyclo[3.2.1]oct-2-en-7-yl Formate.** The same procedure of Moore, Moser, and LaPrade[17a] was employed for the addition of the dihalocarbene to norbornadiene (**2**) substituting chloroform for bromoform but otherwise without modification. Starting with 204 g (1.71 mol) of chloroform in 136 mL of pentane, 55 g (0.6 mol) of norbornadiene (**2**), and 59 g (0.76 mol) of potassium *tert*-butoxide in 40 mL of pentane, 40 g (0.23 mol, 38%) of a mixture of *exo*- and *endo*-3,4-dichlorobicyclo-[3.2.1]octa-2,6-diene was obtained. The product distilled at 65–68 °C (3 mmHg). Reduction of the dichloride with lithium aluminum hydride was accomplished as outlined above except that 125 h of reflux in ether was required. Starting with 40 g (0.23 mol) of the dichloride, 28 g (0.20 mol, 85%) of 3-chlorobicyclo[3.2.1]octa-2,6-diene (**3b**) was obtained.

***exo*-3-Chlorobicyclo[3.2.1]oct-2-en-7-yl Formate.** Following the method of Sauers, Beisler, and Feilich,[18] 28 g (0.15 mol, 83%) of *exo*-3-chlorobicyclo[3.2.1]oct-2-en-7-yl formate was obtained from 28 g (0.18 mol) of 3-chlorobicyclo[3.2.1]octadiene (**3b**) as a liquid. The spectral data for 3-chlorobicyclo[3.2.1]oct-2-en-7-yl formate were as follows: NMR (CCl_4) δ 1.5–3.0 (m, 8 H), 5.1 (doublet of doublets, 1 H, J = 6 Hz, J = 2 Hz, O=COCH), 5.9 (d, 1 H, J = 6 Hz, olefinic), 7.9 (s, 1 H, HCOO–); IR (CCl_4) 3050 (–C=CH), 2950 (CH), 1715 (C=O) 1660 cm^{-1} (–C=C–); mass spectrum (164 °C), m/e (relative intensity) 77 (98%), 78 (29), 79 (91), 103 (34), 105 (100), 112 (29), 113 (77), 114 (1), 115 (24), 139 (24), 140 (27), 186 (5), 187 (2), 188 (2).

Anal. Calcd for $C_9H_{11}O_2Cl$: C, 57.92; H, 5.94. Found: C, 57.91; H, 5.96.

***exo*-3-Chlorobicyclo[3.2.1]oct-2-en-7-ol (7).** With use of the procedure for the bromo alcohol **6**, 22 g (0.14 mol, 87%) of **7** was obtained from 30 g (0.15 mol) of 3-chlorobicyclo[3.2.1]oct-2-en-7-yl formate as a colorless liquid, bp 70 °C (0.9 mmHg). The spectral data for *exo*-3-chlorobicyclo[3.2.1]oct-2-en-7-ol (**7**) were as follows: NMR (CCl_4) δ 1.2–2.8 (m, 8 H), 3.8 (s, 1 H, alcoholic), 4.2 (d, 1 H, J = 5 Hz, -OCH), 5.8 (d, 1 H, J = 6 Hz, olefinic); IR (CCl_4) 3610 (-OH), 3360, 3060 (HC=C–), 2940 (CH), 1670 cm^{-1} (–C=C–); mass spectrum (218 °C), m/e (relative intensity) 77 (78%), 79 (100), 80 (19), 105 (55), 112 (24), 113 (49), 114 (45), 115 (19), 158 (8), 160 (2).

Anal. Calcd for $C_8H_{11}OCl$: C, 60.57; H, 6.99. Found: C, 60.42; H, 7.22.

3-Chlorobicyclo[3.2.1]oct-2-en-7-one (5). The product, 5.4 g (0.035 mol, 78%) of 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**), was obtained from 7.1 g (0.045 mol) of *exo*-3-chlorobicyclo[3.2.1]oct-2-en-7-ol (**7**), vide infra, as a colorless liquid, bp 79–82 °C (1.4 mmHg). The spectral data for the chloro ketone **5** were as follows: NMR (CCl_4) δ 1.5–3.1 (m, 8 H), 5.8 (d, 1 H, J = 8 Hz, olefinic); IR (CCl_4) 3060 (HC=C–), 2840–2060 (CH), 1745 (C=O), 1640 cm^{-1} (–C=C–); UV λ_{max} (ether) 313 (ϵ 138), 302 (261), 293 (281), 285 (237); mass spectrum (210 °C), m/e (relative intensity) 77 (76%), 79 (34), 91 (45), 93 (46), 112 (100), 113 (29), 114 (35), 156 (30), 158 (11).

Anal. Calcd for C_8H_9OCl: C, 61.36; H, 5.79. Found: C, 61.38; H, 5.93.

3-Bromobicyclo[3.2.1]oct-2-en-7-one Ketal. A solution of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) (4.43 g, 0.022 mol), *p*-toluenesulfonic acid monohydrate (260 mg), 2-methyl-2-ethyl-1,3-dioxolane (80 mL), and benzene (80 mL) was distilled with a total condensation, partial takeoff head for 5 h. The cooled reaction mixture was diluted with benzene, washed with 5% aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated in vacuo. After several recrystallizations from methanol, 4.46 g (0.018 mol, 82%) of white crystals were obtained (mp 57–59 °C). The spectral data were as follows: NMR (CCl_4) δ 1.5–3.0 (m, 8 H), 3.8 (s, 4 H, ketal), 6.0 (d, 1 H, J = 8 Hz, olefinic); IR (CCl_4) 3060 (HC=C–), 2840–2950 (CH), 1660 cm^{-1} (–C=C–); mass spectrum (23 °C), m/e (relative intensity) 60 (58%), 77 (34), 112 (100), 165 (96), 244 (15), 246 (15).

Anal. Calcd for $C_{10}H_{13}O_2Br$: C, 49.00; H, 5.35. Found: C, 49.48; H, 5.49.

3-Deuteriobicyclo[3.2.1]oct-2-en-7-one (1-*d*). A solution of bromo ketal (1.05 g, 4.28 mmol) in 3 mL of tetrahydrofuran was added dropwise to the solution of 20 mL THF and 0.2 g (8.2 mmol) of magnesium. After a 3-h reflux, 5 mL of D_2O was added followed by 10 mL of 10% hydrochloric acid. The resulting solution was stirred for 1 h, washed with saturated sodium bicarbonate solution, and extracted with chloroform. After evaporation of the solvent in vacuo, the residue was distilled to give 0.36 g (3 mmol, 70%) of pure 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1-*d***) as a colorless liquid. The spectral data were as follows: NMR (CCl_4) δ 1.5–2.8 (m, 8 H), 5.6 (d, 1 H, J = 5 Hz, olefinic); IR (CCl_4) 3050 (HC=C–), 2840–2980 (HC), 2270 (–C=CD), 1740 cm^{-1} (C=O); mass spectrum (214 °C), m/e (relative intensity) 77 (17%), 78 (39), 79 (100), 80 (55), 122 (5), 123 (21), 124 (2); UV λ_{max} (isooctane) 312 (ϵ 90), 302 (167), 290 (193), 283 nm (154). NMR and MS indicated 90 ± 5% d_1.

Anal. Calcd for C_8H_9OD: C, 78.01; H, 9.00. Found: C, 78.20; H, 8.66.

Phthalate Half-Ester of 3-Bromobicyclo[3.2.1]oct-2-en-7-ol. A mixture of 4.4 g (0.022 mol) of bromo alcohol **6**, 15 mL of pyridine, and 3.24 g (0.022 mol) of acid-free phthalic anhydride was heated at 90 °C for 3 h.[34] After being cooled, the mixture was poured into a slurry of ice and 10% hydrochloric acid and the resulting mixture extracted four times with methylene chloride. The extracts were washed with 10% hydrochloric acid and twice with water and dried over magnesium sulfate. After removal of the solvent, 6.9 g (0.02 mol, 90%) of the half-ester was obtained (mp 127–128 °C). The spectral data were as follows: NMR ($CDCl_3$) 1.5–3.0 (m, 8 H), 5.3 (t, 1 H, O=COCH), 6.2 (d, 1 H, J = 7 Hz, olefinic), 7.5–8.1 (m, 4 H, aromatic), 12.3 (s, 1 H, carboxylic).

Anal. Calcd for $C_{16}H_{15}OBr$: C, 54.41; H, 4.24. Found: C, 54.65; H, 4.32.

Resolution of Phthalate Half-Ester of 3-Bromobicyclo[3.2.1]oct-2-en-7-ol. The half-ester of Bromo alcohol **6**, 10.06 g (0.029 mol), was thoroughly mixed with 11.4 g (0.029 mol) of (–)-brucine, and the mixture was heated in 50 mL of refluxing acetone for 1 h and left overnight at room temperature.[37] The solvent was evaporated to give pale brown crystals (mp 85–150 °C) which were dissolved in a minimum amount of methanol and placed in a refrigerator. After 24 h, 11.4 g (53%) of white crystals (mp 126–128 °C) were obtained from the methanol solution. From the mother liquor 9 g (42%) of pale brown crystals was obtained (mp 117–120 °C). After several recrystallizations in methanol, 11.22 g of the resolved brucine salt was decomposed with 10% aqueous hydrochloric acid and extracted with chloroform. The extracts were washed with 5% aqueous sodium bicarbonate solution, the carbonate solution was

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(36) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000–4002.

(37) Goering, H. L.; Humski, K.; Fickes, G. N. *J. Org. Chem.* **1969**, *34*, 624–627. This general procedure was followed by the resolution of bromo alcohol **6**.

acidified with 10% aqueous hydrochloric acid and extracted with chloroform which was dried over magnesium sulfate to give 5.24 g (99%) of resolved half-ester (mp 148–149 °C), $[\alpha]^{25}_{D}$ −16.8° (*l* 1; *c* 0.953, ethanol). Decomposition of 6.9 g of diasteriomeric crude brucine salt gave 2 g (5.7 mmol, 62%) of the enantiomeric half-ester (mp 136–137 °C), $[\alpha]^{25}_{D}$ +10.5° (*l* 1; *c* 0.781, ethanol).

Resolved 3-Bromobicyclo[3.2.1]oct-2-en-7-ol (6). The levorotatory (−) half-ester, 8.88 g (0.025 mol), was dissolved in a solution of 69 mL of methanol, 60 mL of water, and 2.84 g (0.05 mol) of potassium hydroxide. After 2-h reflux, the solution was extracted with chloroform to give 4.9 g (0.024 mol, 96%) of (−)-3-bromobicyclo[3.2.1]oct-2-en-7-ol ((−)-**6**), $[\alpha]^{25}_{D}$ −11.5° (*l* 1; *c* 1.25, ethanol). (+)-3-Bromobicyclo[3.2.1]oct-2-en-7-ol, 1.79 g (0.009 mol, 45%), $[\alpha]^{25}_{D}$ +24.7° (*l* 1; *c* 0.914, ethanol), was obtained from 6.9 g (0.02 mol) of (+) half-ester by the same procedure.

Resolved 3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). The levorotatory (−)-3-bromobicyclo[3.2.1]oct-2-en-7-ol ((−)-**6**), 5.5 g (0.027 mol), was oxidized by the same procedure as given previously to give 4.43 g (0.022 mol, 81%) of (−)-3-bromobicyclo[3.2.1]oct-2-en-7-one, $[\alpha]^{25}_{D}$ −119° (*l* 1; *c* 1.077, ethanol). (+)-3-Bromobicyclo[3.2.1]oct-2-en-7-one ((+)-**4**), 1.45 g (7.2 mmol, 82%), $[\alpha]^{25}_{D}$ +274.8° (*l* 1; *c* 0.856, ethanol), was obtained from 1.79 g (8.8 mmol) of (+)-bromo alcohol **6**.

(−)-Bicyclo[3.2.1]oct-2-en-7-one ((−)-1). The synthetic procedures for the 3-deuteriobicyclic ketone **1-*d*** were employed. The Grignard reagent was hydrolyzed with H_2O instead of D_2O. A solution of 4 g (16 mmol) of the (−)-bromo ketal in 10 mL of THF afforded 0.7 g (5.7 mmol, 36%) of (−)-bicyclo[3.2.1]oct-2-en-7-one, $[\alpha]^{25}_{D}$ −41.35° (*l* 1; *c* 0.844, ethanol). The spectral data for (−)-bicyclo[3.2.1]oct-2-en-7-one (**1**) were as follows: NMR (CCl_4) δ 1.5–2.9 (m, 8 H), 5.6 (d, 2 H, *J* = 5 Hz, olefinic); IR (CCl_4) 3040 (−C=CH), 2860–2970 (CH), 1740 (C=O), 1625 cm^{-1} (−C=C−); UV λ_{max} (isooctane) 312 (ϵ 127), 300 (223), 290 (237), 285 nm (217); mass spectrum (178 °C), *m/e* (relative intensity) 77 (36%), 78 (91), 79 (100), 80 (19), 91 (18), 122 (29), 123 (4).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.20; H, 8.66.

3-Bromobicyclo[3.2.1]oct-2-en-7-yl α-Methoxy-α-((trifluoromethyl)phenyl)acetate. Determination of Optical Purity. A solution of (−)-2-methyl-2-((trifluoromethyl)phenyl)acetic acid (MTPA, Aldrich), $[\alpha]^{25}_{D}$ −69° (*l* 1; *c* 1.131, methanol; lit.[38] −71.8°), 448 mg, 1 mL of distilled thionyl chloride, and sodium chloride (5 mg) were refluxed for 50 h. After excess thionyl chloride was removed in vacuo, the residue was distilled to give 0.3 g (61%) of MTPA chloride. (+)-Bromo alcohol (+)-**6**, 225 mg (1.11 mmol), was treated with 227 mg (1.10 mmol) of MTPA chloride in 1 mL of pyridine. The resulting solution was allowed to stand overnight, and then 2 mL of water was added. The mixture was extracted with ether, and the extracts were washed with 5% aqueous hydrochloric acid and 5% sodium carbonate solution and dried over magnesium sulfate to give 380 mg (80%) of (+,−)-MTPA ester. The crude MTPA ester was purified by silica gel chromatography using ether–hexane as solvents. 10% Ether–hexane eluate gave 279 mg (59%) of pure MTPA ester, $[\alpha]^{25}_{D}$ −35° (*l* 1; *c* 0.81, ethanol).

The same procedure was repeated with (−)-bromo alcohol (−)-**6** to give (−,−)-MTPA ester, $[\alpha]^{25}_{D}$ −50° (*l* 1; *c* 1.36, ethanol). The spectral data for 3-bromobicyclo[3.2.1]oct-2-en-7-yl α-methoxy-α-((trifluoromethyl)phenyl)acetate were as follows: NMR ($CDCl_3$) δ 1.0–3.0 (m, 8 H), 3.5 (q, 3 H, *J* = 0.1 Hz), 5.4 (dd, *J* = 6, 3 Hz), 6.2 (d, 1 H, *J* = 7 Hz, olefinic), 7.5 (m, 5 H, aromatic); IR (CCl_4) 3060 (−C=CH), 2940 (CH), 1740 (O=CO−), 1660 cm^{-1} (−C=C−); F NMR[39] showed two diastereomeric CF_3 peaks at δ 88.349 for (−,−)-MTPA ester and 88.413 ppm for (+,−)-MTPA ester in a ratio of 1:1. The resolved (−,−)-MTPA ester also showed two diastereomeric CF_3 peaks at 88.413 and 88.349 ppm in a ratio of 0.62:1. On the basis of the ratio of two diastereomers, the optical purity of (−,−)-MTPA ester was determined to be 20%.

B. Exploratory Photochemistry. Direct Irradiation of 3-Deuteriobicyclo[3.2.1]oct-2-en-7-one (1-*d*). A solution of 107.1 mg of 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1-*d***) in 10 mL of anhydrous ether was degassed with purified nitrogen and irradiated with 16 RPR-3000 Å lamps for 3 h, in Pyrex tubes, affording a mixture of 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1-*d***) and 1-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1′-*d***) as determined by NMR. GLC analysis indicated no ODPM product (**10-*d***).

Direct Irradiation of 3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). A solution of 200 mg (1 mmol) of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) in 15 mL of anhydrous ether was degassed for 15 min with purified nitrogen. The sample was irradiated in a Pyrex tube using 15 RPR-3000 Å lamps for 8 h. The solvent was then evaporated in vacuo to give 197 mg of pale yellow liquid. Silica gel chromatography gave 90 mg (61%) of 1-bromobicyclo[3.2.1]oct-2-en-7-one (mp 45–48 °C) in 4% ether–hexane eluate and 50 mg of recovered **4**. The spectral data for 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) were as follows: NMR (CCl_4) δ 1.8–2.8 (m, 7 H), 5.7 (m, 2 H, olefinic); IR (CCl_4) 3050 (−C=CH), 2900 (CH), 1760 (C=O), 1640 cm^{-1} (−C=C−); UV λ_{max} (ether) 303 (ϵ 125), 290 (225), 280 (242), 272 nm (215); mass spectrum (120 °C), *m/e* (relative intensity) 41 (27%), 50 (33), 65 (23), 77 (100), 91 (40), 93 (43), 156 (80), 158 (72), 200 (13), 201 (2), 202 (14).

Anal. Calcd for C_8H_9OBr: C, 47.80; H, 4.51. Found: C, 47.91; H, 4.52.

Direct Irradiation of 3-Chlorobicyclo[3.2.1]oct-2-en-7-one (5). A solution of 965 mg (4.8 mmol) of 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) in 100 mL of anhydrous ether was divided among five Pyrex tubes and degassed with nitrogen. The samples were irradiated with 16 RPR-3000 Å lamps for 20 h. The solvent was then evaporated in vacuo to give a pale yellow liquid. Silica gel chromatography gave 320 mg (44%) of 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) (3% ether–hexane eluate, first two fractions) and 239 mg of recovered **5** (3% ether–hexane eluate, last two fractions). The spectral data for 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) were as follows: NMR (CCl_4) δ 1.8–2.9 (m, 7 H), 5.7 (m, 2 H, olefinic); IR (CCl_4) 3040 (C=CH), 2900 (CH), 1760 (C=O), 1630 cm^{-1} (−C=C−); UV λ_{max} (isooctane) 313 (ϵ 119), 300 (209), 292 (221), 285 nm (184); mass spectrum (210 °C), *m/e* (relative intensity) 51 (15%), 65 (13), 77 (73), 91 (44), 93 (39), 112 (100), 156 (20), 158 (6).

Anal. Calcd for C_8H_9OCl: C, 61.36; H, 5.79. Found: C, 61.39; H, 5.89.

Direct Irradiation of (−)-Bicyclo[3.2.1]oct-2-en-7-one ((−)-1). A solution of 103 mg of (−)-bicyclo[3.2.1]oct-2-en-7-one ((−)-**1**) in 10 mL of anhydrous ether was degassed with nitrogen and irradiated with 15 RPR-3000 Å lamps. The change in the optical rotation during the photoracemization was determined at 15 min intervals during the irradiation (Table V). After 76-min irradiation, the solvent was removed in vacuo to give 100 mg (97%) of pale yellow oil which was a mixture of (+)- and (−)-bicyclo[3.2.1]oct-2-en-7-one.

Direct Irradiation of 1-Bromobicyclo[3.2.1]oct-2-en-7-one (8). A solution of 122.9 mg of 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) in 10 mL of anhydrous ether was degassed with purified nitrogen and irradiated with 15 RPR-3000 Å lamps for 2 h. NMR and GLC analyses showed that the irradiated solution was a mixture of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) in a ratio of 1:2.7 and indicated a 34% conversion of **8** (by VPC 1% DEGS at 120 °C). The NMR spectrum for the photolyzed mixture showed a doublet at δ 6.1 and a singlet at δ 5.7 which are consistent with the olefinic hydrogens of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**), respectively.

Direct Irradiation of 1-Chlorobicyclo[3.2.1]oct-2-en-7-one (9). A solution of 58.7 mg of 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) in 10 mL of anhydrous ether was degassed with purified nitrogen and irradiated with 15-RPR-3000 Å lamps for 25 h. NMR and GLC analyses showed that the irradiated solution was a mixture of 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) and 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) in a ratio of 1:1.8 and indicated a 46% conversion of **9** (by VPC 10% UCON polar at 100 °C). The NMR spectrum for the photolyzed mixture showed a doublet at δ 5.7 and a singlet at δ 5.6 which are consistent with the olefinic hydrogens of 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) and 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**), respectively.

Acetone-Sensitized Irradiation of 3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). A solution of 352 mg of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) in 90 mL of reagent acetone was divided among six quartz tubes and degassed with purified nitrogen. The samples were irradiated with 15 RPR-2537 Å lamps for 12 h, affording a crude yellow oil after removal of the solvent in vacuo. The product mixture was chromatographed on a silica gel column. Elution with 4% ether–hexane gave 39 mg (26% based on recovered **4**) of 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**). This was followed by elution with 20% ether–hexane, which gave 50 mg (33% based on recovered **4**) of 1-bromotricyclo[3.2.1.0^{2,7}]octan-3-one (**11**) as a clear oil. The starting material, 202 mg of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**), was obtained in the second fraction of 4% ether–hexane eluate. The spectral data for 1-bromotricyclo[3.2.1.0^{2,7}]octan-3-one (**11**) were as follows: NMR (CCl_4) δ 1.3–2.5 (m, 9 H); IR (CCl_4) 3050 (cyclopropyl), 2850–2950 (−CH), 1700 cm^{-1} (cyclopropyl ketone); mass spectrum (150 °C), *m/e* (relative intensity) 77 (100%), 78 (32), 79 (30), 80 (40), 91 (50), 93 (55), 156 (50), 158 (45), 200 (6), 202 (6).

Anal. Calcd for C_8H_9OBr: C, 47.80; H, 4.51. Found: C, 48.40; H, 4.57.

Acetone-Sensitized Irradiation of 3-Chlorobicyclo[3.2.1]oct-2-en-7-one (5). A solution of 442 mg of 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) in 120 mL of acetone was divided among eight quartz tubes and degassed

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[38] Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

[39] We thank Professor J. S. Swenton, The Ohio State University, for obtaining the F NMR spectra on the MTPA esters.

with nitrogen. The samples were irradiated with 15 RPR-2537 Å lamps for 14 h, affording a crude yellow oil after removal of the solvent in vacuo. The product mixture was chromatographed on a silica gel column. Elution with 4% ether-hexane which gave 40 mg (13% based on recovered **5**) of 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) was followed by the recovered starting material, 132 mg of 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) in the second fraction of 4% ether-hexane eluate. Elution with 20% ether-hexane gave 106 mg (34% based on recovered **5**) of 1-chlorotricyclo[3.2.1.0^{2,7}]octan-3-one (**12**) as a clear oil. The spectral data for 1-chlorotricyclo[3.2.1.0^{2,7}]octan-3-one (**12**) were as follows: NMR (CCl_4) δ 0.7–2.4 (m, 9 H); IR (CCl_4) 3060 (cyclopropyl), 2860–2940 (CH), 1700 cm^{-1} (cyclopropyl ketone); mass spectrum (190 °C) *m/e* (relative intensity). 77 (73%), 79 (28), 91 (41), 93 (38), 112 (100), 113 (23), 114 (34), 156 (6), 158 (2).

Anal. Calcd for C_8H_9OCl: C, 61.36; H, 5.79. Found: C, 61.32; H, 5.47.

Acetone-Sensitized Irradiation of 3-Deuteriobicyclo[3.2.1]oct-2-en-7-one (1-*d*). A solution of 350 mg of 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1**-*d*) in 105 mL of reagent acetone was divided among seven quartz tubes and degassed with nitrogen. The samples were irradiated with 15 RPR-2537 Å lamps for 12 h, affording a yellow crude oil after removal of the solvent in vacuo. The product mixture was chromatographed on a silica gel column. Elution with 4% ether-hexane gave 238 mg of a mixture of starting ketone **1**-*d* and 1-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1′**-*d*), followed by elution with 30% ether-hexane which gave 80 mg (71%) of 1-deuteriotricyclo[3.2.1.0^{2,7}]octan-3-one (**10**-*d*) as a clear oil. The spectral data for compound **10**-*d* were as follows: NMR (CCl_4) δ 1.0–2.4 (m, 9 H); IR (CCl_4) 3050 (cyclopropyl), 2870–2950 (CH), 2300 (CD), 1690 cm^{-1} (cyclopropyl ketone); mass spectrum (218 °C), *m/e* (relative intensity) 77 (17%), 78 (58), 79 (100), 80 (47), 122 (8), 123 (19), 124 (2).

Anal. Calcd for C_8H_9OD: C, 78.01; H, 9.00. Found: C, 78.65; H, 8.65.

Acetone-Sensitized Irradiation of 1-Bromobicyclo[3.2.1]oct-2-en-7-one (8). A solution of 60.6 mg of 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) in 10 mL of reagent acetone in a quartz tube was degassed with nitrogen. The sample was irradiated with 15 RPR-2537 Å lamps for 3 h. NMR and VPC analyses showed that the photoproducts were 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and 1-bromotricyclo[3.2.1.0^{2,7}]octan-3-one (**11**) in a ratio of 1:1.7 and indicated a 27% conversion of **8** (VPC using a $^1/_8$ in. × 6 ft 1% DEGS column at 125 °C: retention time, 25 min for 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**), 27.5 min for 1-bromotricyclo[3.2.1.0^{2,7}]octan-3-one (**8**), and 29.5 min for 1-bromobicyclo[3.2.1]oct-2-en-7-one (**11**)).

Acetone-Sensitized Irradiation of 1-Chlorobicyclo[3.2.1]oct-2-en-7-one (9). A solution of 30.1 mg of 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) in 10 mL of reagent acetone in a quartz tube was degassed with nitrogen. The sample was irradiated with 15 RPR-2537 Å lamps for 2 h. NMR and VPC analyses showed that the photoproducts were 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) and 1-chlorotricyclo[3.2.1.0^{2,7}]octan-3-one (**12**) in a ratio of 1:2.5 and indicated a 52% conversion of **9** (GLC using a $^1/_8$ × 6 ft 15% FFAP column at 175° C: retention time, 29.5 min for 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**), 33.5 min for 1-chlorotricyclo[3.2.1.0^{2,7}]octan-3-one (**9**), and 40.5 min for 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**12**).

Benzophenone-Sensitized Irradiation of 3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). A solution of 114.3 mg of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and 74.7 mg of benzophenone in 10 mL of reagent benzene in a Pyrex tube was degassed with purified nitrogen and irradiated with 16 RPR-3500 Å lamps for 2.5 h. VPC analysis indicated that the irradiated solution was a mixture of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and less than 8% of 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) at a 32% conversion of **4**. No evidence of 1-bromotricyclo[3.2.1.0^{2,7}]octan-3-one (**11**) was obtained.

Acetophenone-Sensitized Irradiation of 3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). 3-Bromobicyclo[3.2.1]oct-2-en-7-one (**4**), 108 mg, and 115 mg of acetophenone were dissolved in 10 mL of reagent benzene and placed in a Pyrex tube. The sample was degassed with purified nitrogen and irradiated with 16 RPR-3500 Å lamps for 5 h. VPC analysis showed that the photoproducts were 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) and 1-bromotricyclo[3.2.1.0^{2,7}]octan-3-one (**11**) in a ratio of 1:3 and indicated a 39% conversion of **4**.

Benzophenone-Sensitized Irradiation of 1-Bromobicyclo[3.2.1]oct-2-en-7-one (8). 1-Bromobicyclo[3.2.1]oct-2-en-7-one (**8**), 49.5 mg, and 57.9 mg of benzophenone were dissolved in 10 mL of reagent benzene and placed in a Pyrex tube. The solution was degassed with nitrogen and irradiated with 16 RPR-3500 Å lamps for 2 h. VPC analysis showed that the irradiated solution was a mixture of 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) and approximately 2% of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and indicated a 70% conversion of **8**.

C. Quantitative Investigations. Quantum Yield Determinations. General Procedures. Quantum yield determinations were performed by the following general procedure. A solution of between 40 and 100 mg of the β,γ-unsaturated ketone in 10 mL of solvent was placed in a Pyrex or a quartz tube and degassed with purified nitrogen. Irradiation was carried out with 15 or 16 RPR-2537, RPR-3000, and RPR-3500 Å lamps. Light output was monitored by potassium ferrioxalate[20] actinometry according to the method of Hatchard and Parker. After irradiation, the samples were removed from the photoreactor and the contents determined by one of the following methods. The results are given in Tables I, II, and V.

Method A. The solution of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) was analyzed directly by VPC using pentadecane as an internal standard. A $^1/_8$ in. × 6 ft 1% DEGS column at 125 °C in a Varian Aerograph 1200 was used and carrier gas (N_2) flow rate was 15 cm^3/min.

Method B. The ether solution of 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) and 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) was analyzed by VPC using a $^1/_8$ in. × 6 ft 10% UCON polar column at 100 °C.

Method C. The acetone solution of 1-chlorobicyclo[3.2.1]oct-2-en-7-one (**9**) and 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**) was analyzed by VPC using a $^1/_8$ in. × 6 ft 15% FFAP column at 175 °C.

Method D. The acetone solution of 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**2**-*d*) was analyzed by VPC using a $^1/_8$ in. × 6 ft 10% UCON polar column at 105 °C.

Method E. Benzophenone and acetophenone-sensitized reactions of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) and 1-bromobicyclo[3.2.1]oct-2-en-7-one (**8**) were analyzed by VPC using a $^1/_8$ in. × 6 ft 12% DEGS column at various temperatures (110–150 °C).

Method F. The quantum yield for the photoracemization of (−)-bicyclo[3.2.1]oct-2-en-7-one ((−)-**1**) was determined as follows: a solution of the ketone (−)-**1** in 10 mL of ether was degassed with nitrogen and irradiated with 15 RPR-3000 Å lamps. The optical rotation was determined at 15-min intervals during the progress of the irradiation (Table V).

Piperylene Quenching Experiments. Quenching of Direct Irradiation of 3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). A 0.26-mmol solution of the bromo ketone **4** and various concentrations of piperylene (Table III) in 10 mL of benzene (or ether) was degassed with nitrogen and irradiated with 16 RPR-3000 Å lamps. The irradiated samples were analyzed directly by VPC using a $^1/_8$ in. × 6 ft 12% DEGS column. The cis-trans isomerization of piperylene was monitored by a $^1/_2$ in. × 9 ft 20% β′,β-oxydipropionitrile column.

Simultaneous Sensitization and Quenching of 3-Bromobicyclo[3.2.1]oct-2-en-7-one (4). A mixture of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**), 147 mg (0.73 mmol), acetophenone, 180 mg (1.5 mmol), and various concentrations of *cis*-piperylene in 10 mL of benzene in Pyrex tubes was carefully degassed with nitrogen gas in an ice bath for 15 min. The resulting solutions were irradiated for 330 min using 15 RPR-3500 Å lamps. The photolyzed mixtures were analyzed by VPC using a $^1/_8$ in. × 9 ft 15% DEGS column at 165 °C. Acetophenone-sensitized cis-trans isomerization for piperylene was also examined independently by VPC using a $^1/_2$ in. × 9 ft 20% β,β′-dioxypropionitrile column at 75 °C. The results are given in Table IV and analyzed by the BMDPAR nonlinear, least-squares regression program[33] (see Discussion).

D. Emission Spectroscopy. Quenching of Acetone Phosphorescence. A 0.399 M glass of acetone in anhydrous ether-absolute ethanol (1/2, v/v) at 77 K was prepared, and the phosphorescence spectrum was determined ($\lambda_{\text{excitation}}$ = 254 nm, 5.0-nm entrance slit, 2.0-mm exit slit, 0.5-mm photomultiplier slit). The observed emission ($\lambda_{\max}$ = 445 nm) was in agreement with the literature[40] ($\lambda_{\max}$ = 455 ± 10 mm). The phosphorescence spectrum of the solution was then determined with increasing concentrations of the β,γ-unsaturated ketones in the acetone solution. The solutions were prepared by adding a ketone solution to 1.0 mL of the stock acetone solution and diluting to 2.0 mL with a solution of ether:ethanol (1:2, v:v). The resulting phosphorescence bands for acetone solutions were recorded (Table VI), and a linear Stern-Volmer relationship was observed in all cases. The data are reported as follows (quencher, slope of the Stern-Volmer plot ($k_q\tau$), *x* intercept, maximum quencher concentration): **run 1**, 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**), slope = 108 M^{-1}, 0.91, 0.1 M; **run 2**, 3-chlorobicyclo[3.2.1]oct-2-en-7-one (**5**), slope = 47 M^{-1}, 1.02, 0.04 M; run 3, 3-deuteriobicyclo[3.2.1]oct-2-en-7-one (**1**-*d*), slope = 73 M^{-1}, 1.26, 0.08 M.

Quenching of Acetophenone and Benzophenone Phosphorescence. (a) Low-Temperature Studies. The phosphorescence intensities of ca. 0.1 M solutions of both acetophenone and benzophenone in ether-ethanol glasses at 77 K were significantly reduced in the presence of 0.03 M concentrations of 3-bromobicyclo[3.2.1]oct-2-en-7-one (**4**) (λ_{ex} = 350

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[40] Borkman, R. F.; Kearns, D. R. *J. Chem. Phys.* **1966**, *44*, 945–949.

nm). *cis*-Piperylene, 0.025 M, also reduced the phosphorescence intensity of acetophenone.

(b) Room-Temperature Studies. Argon-deaerated carbon tetrachloride or benzene (spectrograde) solutions of acetophenone or benzophenone were analyzed at room temperature (20 °C) for phosphorescence emission. The deaeration was continued until the phosphorescence reached a constant intensity. For acetophenone, 0.002 M solutions were excited at 330 or 345 nm and the full emission monitored; in the ratio mode of the spectrophosphorimeter for benzophenone, 0.01 M solutions were excited at 385 nm. The spectra obtained were in good agreement with those reported by Saltiel et al.[27] and by Steel.[25b]

The emission was then quenched with measured concentrations of either piperylene, naphthalene, or bromo ketone **4** and the Stern–Volmer relationships determined for each quencher. The average value obtained from duplicate experiments and their standard deviations are presented in Table VII.

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Registry No. (+)-**1**, 68520-09-2; (−)-**1**, 68520-06-9; **1**-*d*, 65109-19-5; **1′**-*d*, 65109-21-9; **2**, 121-46-0; **3a**, 51788-41-1; **3b**, 61097-60-7; **4**, 81095-66-1; (+)-**4**, 68520-11-6; (−)-**4**, 81132-01-6; **5**, 81095-67-2; **6**, 81095-68-3; (+)-**6**, 81132-02-7; (−)-**6**, 81132-03-8; **6** phthalate half ester, 81095-69-4; (+)-**6** phthalate half ester, 81132-04-9; (−)-**6** phthalate half ester, 81132-05-0; (+)-**6** phthalate half ester (−)-brucine salt, 81176-42-3; **7**, 81095-70-7; **8**, 81095-71-8; **9**, 81095-72-9; **10**-*d*, 81095-73-0; **11**, 81095-74-1; **12**, 81095-75-2; *cis*-piperylene, 1574-41-0; *trans*-piperylene, 2004-70-8; acetophenone, 98-86-2; benzophenone, 119-61-9; naphthalene, 91-20-3; (−)-2-methyl-2-((trifluoromethyl)phenyl)acetic acid, 17257-71-5; (+)-3-bromobicycyl[3.2.1]oct-2-en-7-yl α-methyl-α-((trifluoromethyl)phenyl)acetate, 81095-76-3; (−)-3-bromobicyclo[3.2.1]oct-2-en-7-yl α-methyl-α-((trifluoromethyl)phenyl)acetate, 81132-06-1; *exo*-3-bromobicyclo[3.2.1]oct-2-en-7-yl formate, 10027-55-1; *exo*-3,4-dichlorobicyclo[3.2.1]octa-2,6-diene, 35501-78-1; *endo*-3,4-dichlorobicyclo[3.2.1]octa-2,6-diene, 59531-01-0; *exo*-3-chlorobicyclo[3.2.1]oct-2-en-7-yl formate, 81095-77-4; 3-bromobicyclo[3.2.1]oct-2-en-7-one ketal, 81095-78-5.

Structure and Reactivity of Bicyclo[3.2.1]octa-2,6-dien-4-ylidene and Bicyclo[3.2.1]oct-2-en-4-ylidene. Nucleophilicity of Vinylcarbenes

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Abstract: Carbocyclic carbenes, bicyclo[3.2.1]octa-2,6-dien-4-ylidene (**1**) and bicyclo[3.2.1]oct-2-en-4-ylidene (**2**), were generated by photolysis of the corresponding diazo compounds, **6** and **10**, which were prepared by careful vacuum pyrolysis of the sodium salts of the corresponding tosylhydrazones. The addition reactions of **1** and **2** toward substituted styrenes indicate that the styrene with an electron-withdrawing group is a better acceptor of **1** and **2**. For a quantitative treatment of the substituent effect, rate-constant ratios were determined by a competitive method. The data (at 0 °C) correlate well ($\gamma > 0.98$) with the Hammett σ constants. The ρ values were computed to be +0.25 for carbene **1** and +0.68 for carbene **2**, indicating nucleophilic character. Diazo compounds **6** and **10** undergo nucleophilic dipolar addition toward substituted styrenes, giving spiro[2-arylcyclopropane-1,4′-bicyclo[3.2.1]oct-2′,6′-diene] (**15–19**), where their ρ values were +1.26 and +1.35, respectively. The equilibrium geometries of singlet carbenes **1** and **2** were determined by means of the STO-3G SCF energy gradient method. The 4-31G frontier orbital energies for **1** and **2** were compared with those for several typical carbenes. The energy levels of HOMO of carbene **1** and carbene **2** are found to be close to that of vinylmethylene and even higher than that of nucleophilic dimethoxycarbene, indicating nucleophilic character. The model calculation with STO-3G basis set for the reaction of carbene **2** with styrene shows that steric effect also plays a role in the nucleophilic approach of **2**.

Considerable understanding of the relationship between spin states of carbenes and their reactivity toward alkene has been accumulated.[1,2] For singlet carbenes, Moss et al. have shown that carbene reactivities form a continuous spectrum from electrophilic through nucleophilic in accord with calculated values.[3,4] The electrophilic nature can be attenuated by overlap of its vacant p orbital with electron-donating substituents or by incorporation of the vacant p orbital into an aromatic system. The carbene can behave as a nucleophile if extensive destabilization of its filled σ orbital (HOMO) is achieved.[5] The variation of carbenic "philicity" with the structure of carbocyclic carbenes has been demonstrated by the Hammett treatment of the addition reaction toward substituted styrenes, in accord with the EHT calculation.[6] Cycloheptatrienylidene shows a positive ρ of +1.05 (nucleophilic),[7] while cyclopentadienylidene shows a negative ρ of −0.78 (electrophilic).[8] Quantitative evaluation of homoconjugative inter-

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