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.

Acknowledgment. Financial support from the National Institutes of Health (Grant GM 16611) and the University of Kansas Research Fund and the National Science Foundation (Grants CHE 77-07826 and 78-03307) for equipment grants toward the purchases of the Bruker WP80 FT-NMR and the PE 555 UV spectrometers is gratefully acknowledged. B.M. acknowledges the leave granted by the Institute of Chemistry, A. Mickiewicz University, Poznan, Poland.

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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† Osaka University.
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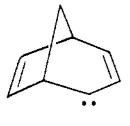
action of carbenes are of interest in view of the recent argument that the stabilization due to homoaromaticity is possible in cationic species but not in neutral or anionic hydrocarbon.[9,10] Homoconjugated interaction between the vacant p orbital of the divalent carbon and the π orbital of the carbon–carbon double bond or the Walsh orbital of a cyclopropane ring has been demonstrated in foiled methylenes[6] such as 7-norbornenylidene,[11,12] bicyclo[3.2.1]oct-2-en-8-ylidene,[13] bicyclo[3.3.1]non-2-en-9-ylidene,[14] *endo*-tricyclo[3.2.1.0^{2,4}]oct-8-ylidene,[12,15] bicyclo[4.1.1]oct-2-en-7-ylidene,[16] bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene,[17] 9-barbaralylidene,[18] and tetracyclo[3.2.1.0^{2,7}.0^{4,6}]oct-3-ylidene.[19] Quantitative assessment of homoconjugative interaction has been made on the intramolecular rearrangement of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-ylidene[20] and bicyclo[3.2.1]octa-2,6-dien-8-ylidene.[20]

This paper describes a general quantitative treatment of homoconjugative interaction with respect to bicyclo[3.2.1]octa-2,6-dien-4-ylidene (**1**). As a reference, bicyclo[3.2.1]oct-2-en-4-ylidene (**2**), vinylcarbene, and others have been examined. Ab initio SCF calculations were carried out for closed-shell singlets within the framework of the restricted Hartree-Fock approximation. All geometries were fully optimized with the minimal STO-3G basis set,[21] using the energy gradient method.[22] Frontier orbital energies were calculated with the split-valence 4-31G basis set[23] at the STO-3G optimized geometries.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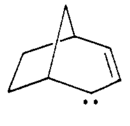
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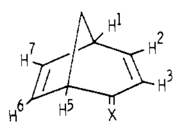
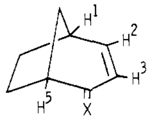
Results

Preparation of Diazo Compounds. The bicyclo[3.2.1]octa-2,6-dien-4-ylidene (**1**) was generated by either thermolysis of the sodium salt (**5**) of bicyclo[3.2.1]octa-2,6-dien-4-one tosylhydrazone (**4**) or photolysis of 4-diazobicyclo[3.2.1]octa-2,6-diene (**6**). The synthesis of tosylhydrazone **4** could not be accomplished by the usual acid-catalyzed condensation since facile structural rearrangement took place under the reaction conditions. With use of pyridine as a solvent (0 °C), however, the ketone **3** was readily converted into **4**, which consisted of syn and anti isomers (**4a** and **4b**), in 96% yield. Pyrolysis of the sodium salt **5**, prepared upon treatment of **4** with sodium hydride in THF, in a previously degassed system at 1×10^{-6} mmHg at 97 °C, followed by washing and distillation, gave unstable wine red diazo compound **6** in 23% yield. The NMR spectrum of **6** was highly characteristic and in conjunction with spin-decoupling experiments allowed the proton resonances to be unequivocally assigned. The coupling constants of the four doublet–doublet protons at δ 5.43 (H^2, $J_{H^2H^3}$ = 9.3 Hz, $J_{H^1H^2}$ = 6.3 Hz), 5.94 (H^7, $J_{H^6H^7}$ = 5.5 Hz, $J_{H^1H^7}$ = 3.0 Hz), 5.75 (H^3, $J_{H^3H^5}$ = 2.0 Hz), and 5.63 (H^6, $J_{H^5H^6}$ = 2.9 Hz) confirmed that **6** contained the bicyclo[3.2.1]octadienyl structure.



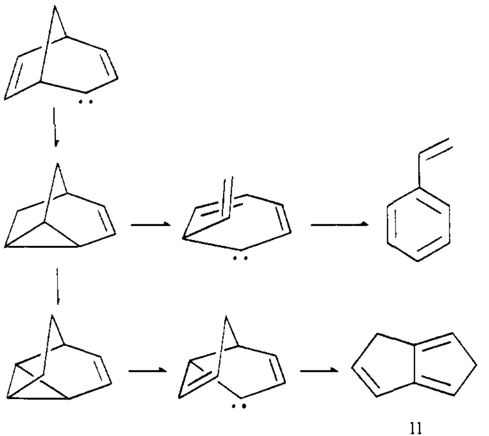
3, X = O
4, X = NNHTs
5, X = NNNaTs
6, X = N_2



7, X = O
8, X = NNHTs
9, X = NNNaTs
10, X = N_2

Similarly, were prepared tosylhydrazone **8** of bicyclo[3.2.1]oct-2-en-4-one (**7**) and 4-diazobicyclo[3.2.1]oct-2-ene (**10**). The NMR spectrum of **10** shows two vinyl protons as doublet–doublets at δ 5.69 (H^3, $J_{H^2H^3}$ = 9.8 Hz, $J_{H^3H^5}$ = 1.5 Hz), and 5.28 (H^2, $J_{H^1H^2}$ = 7.0 Hz, $J_{H^2H^3}$ = 9.8 Hz), while the IR spectrum shows an absorption of C=N_2 at 2030 cm^{-1}.

Scheme I



Carbenic Rearrangements of Carbenes 1 and 2. Pyrolysis of the sodium salt **5** at 200 °C gave styrene (56%) along with 4.7% of unstable dihydropentalene **11**, whose structural assignment was carried out by comparison with the sample formed from *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-ylidene[15] and bicyclo[3.2.1]octa-2,6-dien-8-ylidene.[20] Although a number of processes can be drawn, a probable pathway is the carbene–carbene rearrangement shown in Scheme I. The homoconjugative interaction between the p orbital of the divalent carbon and those of C_2–C_3 and C_6–C_7 bonds would induce the rearrangement, as indicated in the corresponding carbonium ion.[24] It is of interest to compare the

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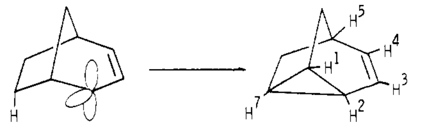
rearrangement of tetracyclo[3.2.1.$0^{2,7}$.$0^{4,6}$]oct-3-ylidene into *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene.[19] The rigidity of the structure apparently enforces the stabilizing C_2–C_7 and C_4–C_6 interactions.[19]

Thermolysis (300 °C) of diazo compound **10** gave tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**12**)[25] exclusively. The alkene **12** is formed by direct insertion of the divalent carbon into the endo-C–H bond. This is the first example of the insertion of vinylcarbenes into a C–H bond[26] since vinylcarbenes undergo facile 1,2-hydrogen migration to dienes[27,28] or intramolecular addition to cyclopropene derivatives.[27,29] Bredt's rule retards the 1,2-hydrogen migration in **2**, and hence the p orbital of the divalent carbon interacts with the s orbital of endo-C–H bond. Carbene **2** seems to react in a singlet state, since hydrogen abstraction products could not be detected among the products.



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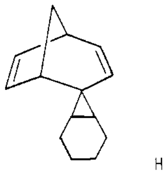
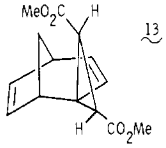
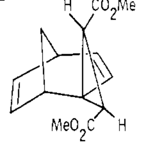
Addition Reaction of Carbenes 1 and 2 to Alkenes. Thermal decomposition of the sodium salt **5** in cyclohexene and in dimethyl fumarate at 180 °C gave the adduct of **13** and two trans adducts (**14a** and **14b**) in 3.5% and in 13% yields, respectively.



13

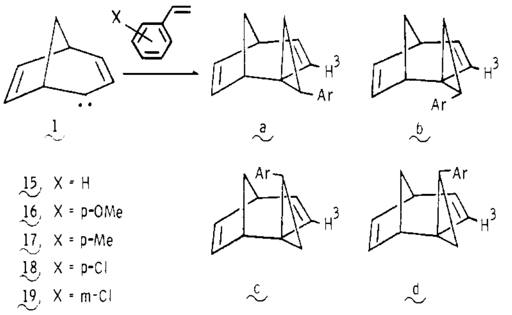


14a



14b

The formation of the cyclopropanes with an electron-withdrawing group is faster than that with an electron-donating group. The reactivity of carbenes toward an olefin with an electron-withdrawing substituent should be argued carefully because 1,3-dipolar cycloaddition of parent diazo compounds takes place easily. Consequently, photochemical decomposition of **6** has been carried out at low temperature. The authentic samples of the cyclopropane derivatives (**15–19**) were prepared in 33–40% yields by thermal decomposition of the corresponding sodium salt in styrene derivatives. The adducts, which consist of four stereoisomers (**a–d**), were separated and purified by repeated silica gel thin-layer chromatography. The structure of the adducts was established by ^1H NMR and mass spectroscopies. Typically, the NMR spectrum of conformationally stable adduct **19a** showed a doublet absorption of H^3 at δ 4.35 ($J_{H^2H^3}$ = 9.6 Hz), a doublet–doublet absorption of H^2 at δ 5.91 ($J_{H^2H^3}$ = 9.6 Hz, $J_{H^1H^2}$ = 6.3 Hz), and absorptions of H^6 and H^7 at δ 5.84 ($J_{H^5H^6}$ = 2.7, $J_{H^6H^7}$ = 5.1 Hz) and 6.26 ($J_{H^1H^7}$ = 2.7 Hz), respectively. The absorptions of the cyclopropane protons, H^a, H^b, and H^c appear at δ 2.25, 1.12, and 1.05 with coupling constants of $J_{H^aH^b}$ = 6.0, $J_{H^aH^c}$ = 8.4, and $J_{H^bH^c}$ = 5.0 Hz, respectively. The total yields of the adducts to styrene and substituted styrenes and the chemical shifts of H^3 of four stereoisomers are summarized in Table I. The similar photochemical treatment of **10** in substituted styrene gave the corresponding cyclopropane adducts (**26–30**).

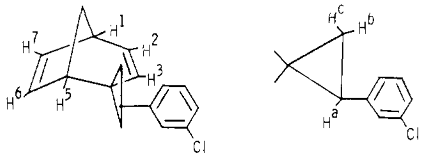


15, X = H
16, X = p-OMe
17, X = p-Me
18, X = p-Cl
19, X = m-Cl

Table I. The Yield of Cyclopropanes[a] and the Chemical Shift of H^3 Protons[b]

substituent on styrene	total yield, %	chemical shift of the H^3 proton of the stereoisomers, δ			
p-MeO	62	4.87	4.77	4.42	4.42
p-Me	25	4.89	4.68	4.33	4.31
H	55	4.93	4.74	4.37	4.37
p-Cl	45	4.99	4.75	4.37	4.37
m-Cl	45	4.99	4.74	4.35	4.35

[a] The sodium salt 5 was thermolyzed in styrenes. [b] NMR spectra were taken in CCl_4 solution.



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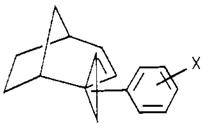
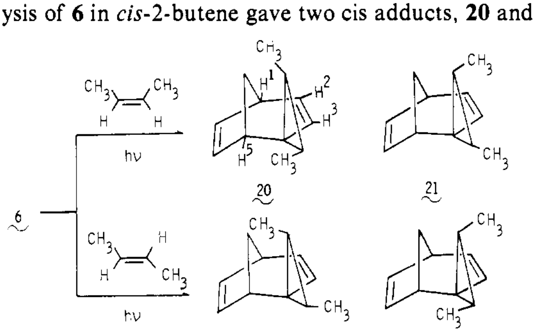


26, X = H
27, X = p-OMe
28, X = p-Me
29, X = p-Cl
30, X = m-Cl

To know the spin multiplicity of a carbene at the stage of the addition is particularly important for mechanistic consideration. The addition reactions of carbenes **1** and **2** proceeded stereospecifically with respect to *cis*- and *trans*-2-butenes. Thus, photolysis of **6** in *cis*-2-butene gave two cis adducts, **20** and **21**, in the 3:2 ratio. On the other hand, two trans adducts **22** and **23** were obtained from *trans*-2-butene in the 1:1 ratio. The structures of **20–23** were confirmed by NMR spectra. The absorptions of the olefinic protons of H^2, H^3, H^6, and H^7 indicated the bicyclo[3.2.1]octadiene structure. The stereochemistry of these adducts was mainly assigned by the chemical shift of the absorption of the H^5 protons, which appeared at δ 1.69 for **20**, 2.33 for **21**, 2.09 for **22**, and 2.11 for **23**. The H^5 absorption of **20** is



20 21 22 23

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(26) (a) Franck-Neumann, M.; Buchecker, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 526. (b) Hartzler, H. D. *J. Am. Chem. Soc.* **1970**, *92*, 1412.

(27) Closs, G. L.; Closs, L. E.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796.

(28) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680.

(29) Bunnell, C. A.; Fuchs, P. L. *J. Org. Chem.* **1977**, *42*, 2614.

Table II. Relative Rate Constants for Additions of 1 and 2 to Substituted Styrenes, $XC_6H_4CH{=}CH_2$ [a]

X in $XC_6H_4CH{=}CH_2$	σ value	k_X/k_H	
		carbene 1	carbene 2
p-OCH_3	−0.268	1.02	0.78
p-CH_3	−0.170	0.92	0.90
H	0.00	1.00	1.00
p-Cl	0.227	1.13	1.56
m-Cl	0.373	1.26	2.18

[a] The standard deviations (σ) were within 0.07, and satisfactory cross checkes were obtained (ref 1a, Vol. 1, p 153 ff).

shifted to 0.6 ppm higher than that of **21** by the shielding effect of two methyl groups on the cyclopropane ring. On the other hand, the H^5 protons of **22** and **23** shifted 0.2 ppm by the shielding effect of one methyl group. The similar pattern is seen to the absorptions of the H^3 proton. Thus, the H^3 proton of **21** appears 0.47 ppm higher than **20** and those of **22** and **23** are shielded by 0.20 ppm with one methyl group. The stereospecific addition observed seems to confirm that the carbene **1** reacts in a singlet state.

The similar photolysis of diazo compound **10** in *cis*-2-butene at −42 °C gave *cis*-cyclopropanes (**24a** and **24b**) (99%), while that in *trans*-2-butene gave *trans*-cyclopropanes (**25a** and **25b**) (98%) in a stereospecific manner.

Relative Reactivities of Carbenes 1 and 2 to Substituted Styrenes. In order to avoid the contamination of the cyclopropane formation via pyrrazoline intermediates, we carried out photolysis of diazo compound **6** in over tenfold excess of a mixture of two styrenes at 0 °C with high-pressure mercury lamp through a Pyrex filter solution (>310 nm) for 10 min. Analysis of the cyclopropane products were carefully carried out by using the samples prepared separately. The rate-constant ratios were determined by a competitive method in which two olefins were allowed to compete for a limited amount of carbene **1**. The rate-constant ratio (K_{rel}) is given by the equation, where P_X and P_H are the moles of product derived from styrene X and H, respectively, and I_X and I_H are the initial moles of substituted and unsubstituted styrenes.

$$K_{rel} = \frac{K_X}{K_H} = \frac{P_X I_H}{P_H I_X}$$

The results of the reactivity study of **1** with substituted styrenes are summarized in Table II. The rate of addition of **1** to a styrene is accelerated by electron-withdrawing substituents and retarded by electron-donating ones. The data correlate with Hammett linear free energy relationship using σ values. The ρ was calculated by a least-square analysis to be +0.25 ± 0.01 with a correlation coefficient of 0.996 as shown in Figure 1. Diazo compound **6** reacts with styrenes in dark to give cyclopropanes in 45–65% yields. When a solution of **6** in a mixture of two styrenes was allowed to stand at 0 °C for 9 h in dark, the wine red color of **6** faded. The analysis of the reaction mixture gave the relative rate constants as shown in Table III. The rate data correlate with a Hammett linear free energy relationship using σ values as shown in Figure 2. The ρ for the reaction is +1.26 ± 0.02 (γ = 0.999).

Similar competitive reactions of **6** with substituted styrenes at 170 °C gave the linear free energy relationship. The ρ value is 0.82 and rather close to the calculated value of 0.78 obtained with the assumption that ρ values should decrease with increase in temperature.[30] The cyclopropane formation under the reaction condition is due to either the 1,3-dipolar cycloaddition of **6**, followed by thermal decomposition of a pyrazoline intermediate[30,31] or direct addition of carbene **1** which is formed thermally.

The relative reactivity of carbene **2** toward substituted styrenes was also determined by the similar competitive method. The relative rate constant data shown in Table II correlate well with the Hammett σ constants. The ρ value was calculated to be +0.68 ± 0.05. Similar treatment of diazo compounds **10** in substituted styrenes gave the relative rate constants as shown in Table III. A good linear relationship (correlation coefficient, γ = 0.992) was again obtained, leading to a value for ρ of 1.35 ± 0.06 (0 °C).

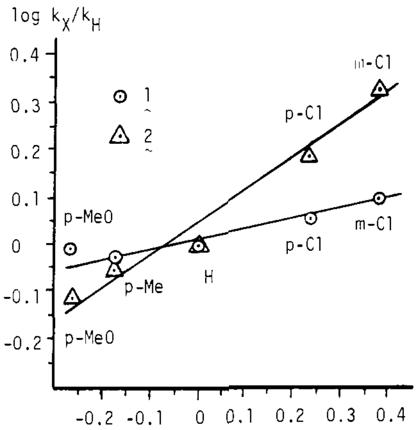

Figure 1. Plot of log k_{rel} vs. σ values for the reactions of bicyclo[3.2.1]octa-2,6-dien-4-ylidene (**1**) and bicyclo[3.2.1]oct-2-en-4-ylidene (**2**) with substituted styrenes.

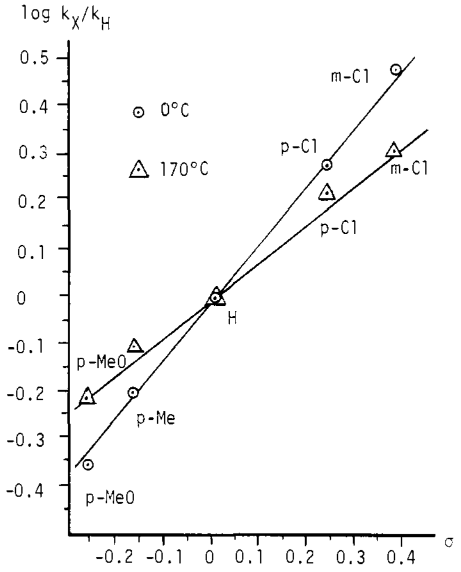

Figure 2. Plot of log k_{rel} vs. σ values for the reactions of 4-diazobicyclo[3.2.1]octa-2,6-diene (**6**) with substituted styrenes.

Table III. Relative Rate Constants of the Reactions of Substituted Styrenes with Diazo Compounds 6 and 10 in the Dark[a]

	k_X/k_H			
	diazo 6		diazo 10	
substituent	0 °C	170 °C	0 °C	180 °C
p-OCH_3	0.44	0.61	0.40	0.62
p-CH_3	0.63	0.78	0.71	0.76
H	1.00	1.00	1.00	1.00
p-Cl	1.88	1.66	2.11	1.57
m-Cl	2.99	2.03	3.19	1.80

[a] The standard deviations (σ) were within 0.2, and satisfactory cross checks were obtained (ref 1a, Vol. 1, p 153 ff).

Geometries and Electronic Structures. In Figure 3 are given the optimized geometrical parameters of carbenes **1** and **2** obtained by the STO-3G calculations.[21] As for the $C_3C_4C_5$ angle associated with the carbene center, **1** and **2** possess essentially the same values (109.0 and 109.6°), these being significantly larger than 100.5° for CH_2, 101.2° for $C(OMe)_2$, 101.8° for $C(OH)_2$, 102.8° for CF_2, 104.6° (cis), and 103.3° (trans) for $CHCH{=}CH_2$, and 106.9° for CCl_2.

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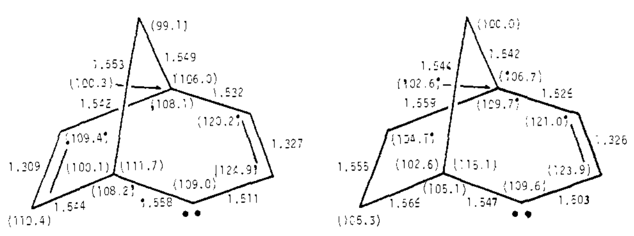


1 **2**

Figure 3. STO-3G geometries of carbenes **1** and **2**. Bond angles given in parentheses are in degrees and bond lengths in angstroms.

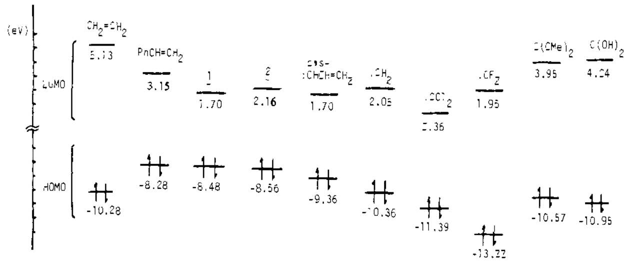
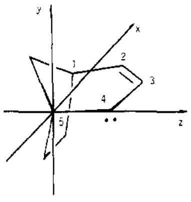


Figure 4. 4-31G frontier orbital energies calculated at the STO-3G optimized geometries. The geometrical parameters of singlet carbenes are as follows: $:CH_2$ ($\angle HCH = 100.5°$, $r_{C-H} = 1.122$ Å); $:CF_2$ ($\angle FCF = 102.8°$, $r_{C-F} = 1.323$ Å); $:CCl_2$ ($\angle ClCCl = 106.9°$, $r_{C-Cl} = 1.803$ Å); $:C(OMe)_2$ ($\angle OCO = 101.2°$, $r_{C-O} = 1.360$ Å, $\angle COC = 112.2°$, $r_{O-C(methyl)} = 1.441$ Å); $:C(OH)_2$ ($\angle OCO = 101.8°$, $r_{C-O} = 1.357$ Å, $\angle COH = 106.1°$, $r_{O-H} = 0.987$ Å).

The HOMO and LUMO LCAO coefficients concerning a divalent carbon for **1** and **2** as well as CH_2, CF_2, and $C(OMe)_2$ are collected in Table IV. For easy visualization the divalent carbon atom (C_4) and two atoms (C_3 and C_5) are placed on the *xz* plane as shown in **31**. Thus, the $2p_y$ AO corresponds to the p orbital of the divalent carbon. As Table IV reveals, all HOMO's are of σ character while all LUMO's of p character, though they are delocalized to some extent over a molecule except for methylene. An important point is that **1** as well as **2** takes the σ^2 electronic configuration (**32**) for a singlet ground state rather than the p^2 configuration (**33**) where the filled p orbital is incorporated into a homoaromatic ring in such a way to make an integral part of the 6π electron system. In Figure 4 are summarized the 4-31G frontier orbital energies calculated at the STO-3G optimized geometries, which are to be discussed below.



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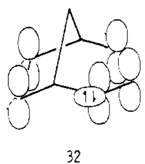

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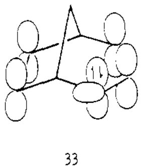

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Discussion

The relative rate constant data which were obtained by the photolysis of **6** in substituted styrenes correlate well with the Hammett equation, giving a ρ value of +0.25 (0 °C). The cyclopropane formation is ascribed to the addition of carbene **1** to styrenes. The possibility that the cyclopropanes are produced via pyrazolines by nitrogen expulsion is excluded by the following two facts: (a) the thermal decomposition of diazo **6** in styrenes gave a ρ value of +1.26 at the same temperature (0 °C); (b) the photolysis was completed within shorter time (10 min) than the thermal decomposition (9 h). The ρ value obtained may be the minimum value for **1**. The slight deviation of *p*-methoxystyrene in Figure 1 may be ascribed to the partial contamination of the cyclopropane formation via either pyrazoline[32] or biradical intermediates.[30]

Table IV. Coefficients of LCAO for Singlet Carbenes[a,b]

	carbene 1	carbene 2	CH_2	CF_2	$C(OMe)_2$
HOMO					
1s	−0.1126	−0.1217	−0.1415	0.1466	−0.1243
2s	0.5263	0.5656	0.6440	−0.6306	0.5667
$2p_x$	−0.5445	−0.5879	−0.6961	0.4634	0.4770
$2p_y$	−0.0080	−0.0428	0.0	0.0	0.0
$2p_z$	0.4537	0.4337	−0.2638	0.3713	−0.4039
LUMO					
1s	−0.0053	−0.0038	0.0	0.0	0.0
2s	0.0255	0.0240	0.0	0.0	0.0
$2p_x$	−0.0117	−0.0628	0.0	0.0	0.0
$2p_y$	0.6896	0.7068	1.0000	0.9535	0.9464
$2p_z$	−0.0166	0.0481	0.0	0.0	0.0

[a] Calculations were performed with the STO-3G minimal basis set at the STO-3G optimized geometries. [b] The values are described only on the divalent carbons. In each carbene, the divalent carbon and their neighboring atoms were placed on the *xz* plane in the Cartesian coordinate, as shown in 31.

Although nucleophilic nature has been demonstrated for some carbenes,[7,33-35] pyrazoline intermediacy is not necessarily excluded. In this sence, the present positive ρ value of +0.25 provides clear quantitative demonstration of the nucleophilicity of a carbocyclic carbene. The stereospecific addition of carbene **1** toward *cis*- and *trans*-2-butenes indicates that **1** reacts with substituted styrenes in a singlet state. It is noteworthy that the absorptions of the triplet state could not be detected in the ESR spectra which were taken at 77 and 4 K under controlled conditions.[36]

As a reference of carbene **1**, the carbene **2** has been generated photochemically. The similar competitive experiment showed that correlation of k_{rel} with Hammett σ constant yielded a reaction constant of ρ +0.68. This positive value confirms clearly that carbene **2** is nucleophilic. In this case, the possible cyclopropane formation via pyrazoline intermediate is also excluded by the comparison of the ρ value (+1.35) obtained from the corresponding thermal decomposition of diazo **10**.

As described in Table IV, the homoconjugative interaction is not strong enough to place the p^2 configuration lower in energy than the σ^2 one. The energy for the promotion of two electrons from the σ orbital to the p orbital would not be compensated with such homoconjugated stabilization.

The base-catalyzed hydrogen–deuterium exchange of the allylic

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(32) Overberger, C. G.; Weinshenker, N.; Anselme, J.-P. *J. Am. Chem. Soc.* **1965**, *87*, 4119.

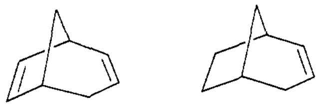
(33) Diphenylcyclopropenylidene: Jones, W. M.; Stowe, M. E.; Wells, E. E.; Lester, E. W. *J. Am. Chem. Soc.* **1968**, *90*, 1849. Thioxanthenylidene: Patrick, T. B.; Dorton, M. A.; Dolan, J. G. *J. Org. Chem.* **1978**, *43*, 3303. Arylhetarylcarbenes: Mayor, C.; Wentrup, C. *J. Am. Chem. Soc.* **1975**, *97*, 7467.

(34) $C(OMe)_2$: (a) Hoffmann, R. W.; Lillenblum, W.; Dittrich, B. *Chem. Ber.* **1974**, *107*, 3395. (b) Hoffmann, R. W.; Reiffen, M. *Ibid.* **1976**, *109*, 2565. (c) Lemal, D. M.; Gosselink, E. P.; Mcgregor, S. D. *J. Am. Chem. Soc.* **1966**, *88*, 582.

(35) Dürr et al. showed the ρ value of benzocyclobutenylidene to be +1.57. Dürr, H.; Nickels, H.; Pacala, L. A.; Jones, M., Jr. *J. Org. Chem.* **1980**, *45*, 973.

(36) (a) Moritani, I.; Murahashi, S.-I.; Nishino, M.; Yamamoto, Y.; Itoh, K.; Mataga, N. *J. Am. Chem. Soc.* **1967**, *89*, 1259. Murahashi, S.-I.; Moritani, I.; Nagai, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1655. (b) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

hydrogens of bicyclo[3.2.1]octa-2,6-diene is $10^{4.5}$ times faster than that of the corresponding saturated bicyclo[3.2.1]oct-2-ene. The energy difference is calculated to be 6.8 kcal/mol.[9b] On the contrary, the solvolysis rate of *p*-nitrobenzoate of bicyclo[3.2.1]octadien-4-ol is 4×10^3 times slower than the saturated



= ⊖ $10^{4.5}$: 1

= ⊕ 1 : 4×10^3

analogue under compatible condition.[37] The energetic destabilization is about 4 kcal/mol. Therefore, one can argue that 7 + 4 = 11 kcal/mol is not enough to promote electrons from the σ orbital to the higher p orbital. As shown in Figure 4, the HOMO–LUMO energy gap of **1** (ΔE_1 = 10.18 eV) is smaller by 12.5 kcal/mol than that of **2** (ΔE_2 = 10.72 eV). The difference between ΔE_1 and ΔE_2 is in harmony with the above experimental stabilization energy (11.0 kcal, 0.47 eV). The fact that cyclic carbenes **1** and **2** show weak nucleophilicity in the addition to olefins can be confirmed by comparing their frontier orbital energy levels with those of the well-known carbenes. Generally, in the reaction of carbenes with olefins, for given alkenes the higher lying the HOMO of carbenes, the more nucleophilic the carbene.[3] For example, the energy level of the HOMO of nucleophilic $C(OMe)_2$ (−10.57 eV) is higher than that of electrophilic CF_2 (−13.33 eV). The energy level of the HOMO of **1** (−8.48 eV) is even higher than that of $C(OMe)_2$, suggesting nucleophilic character of **1**.

One may argue that **1** and **2** with lower LUMO energies should show the electrophilic activity, too. As expected simply from the perturbational theoretical criterion,[39] however, the proximity of HOMO and LUMO energy levels leads to the fact that the electronic state of carbene is not described well just with a single configuration but at least with two configurations; $\Phi = C_1|(\text{HOMO})(\overline{\text{HOMO}})| + C_2|(\text{LUMO})(\overline{\text{LUMO}})|$, where a bar over MO stands for the β spin. It is to be noted that the quantity, $2C_2^2$, corresponds with the occupation number of LUMO and increases with the decrease in the HOMO–LUMO energy gap.[39] In other words, the LUMO's of **1** and **2**, already interacting with their HOMO's, do not seem to be particularly concerned to accept extra electrons from alkene. It is apparent from Table IV that the magnitude of the $2p_y$ coefficient of LUMO decreases in the order of $CH_2 > CF_2 > C(OMe)_2 > \mathbf{2} > \mathbf{1}$. This order seems to be related to the efficiency of the electrophilic interaction between the carbene's LUMO and the olefin's HOMO [CH_2(electrophilic) > CF_2(weak electrophilic)[38] > $C(OMe)_2$(nucleophilic)[34]]. It is of interest to note that the $2p_y$ coefficient of the LUMO of **1** is smaller than that of $C(OMe)_2$, probably resulting in a less effective overlap with the HOMO of olefin.

It would be of interest to compare **1** and **2** with vinylcarbene. Vinylcarbene[40] is highly reactive, and hence its reactivity has not been determined. In carbenes **1** and **2** the Bred't rule retards the 1,2-hydrogen migration.[41] Even if the intramolecular addition takes place, the resultant cyclopropanes would undergo rearrangement to **1** and **2**.[28,40,42] Therefore, one can assume that **1** and **2** are a model of trans vinylcarbene. The STO-3G equilibrium geometries of *cis*- and *trans*-vinylmethylenes in a singlet state are shown in Figure 5.[43] As Figure 4 shows, the 4-31G frontier orbital energy of vinylcarbene is similar to that of **1**, indicating the nucleophilic character. This result shows a good coincidence with the previous EHT calculations.[6,44]

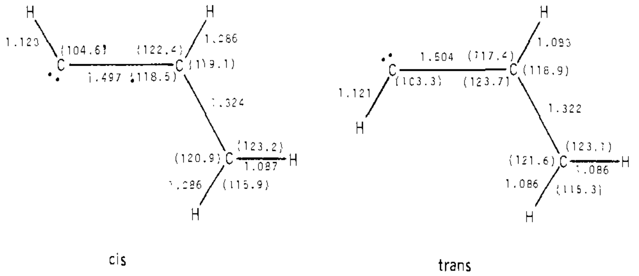


Figure 5. STO-3G geometries of cis and trans vinylmethylenes. **Bond** angles given in parentheses are in degrees and bond lengths in angstroms.

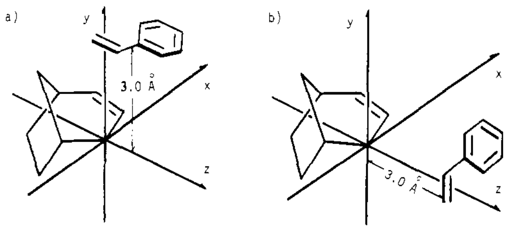


Figure 6. Two extreme approach models for the reaction of **2** with styrene: (a) p approach; (b) σ approach.

Table V. Energy Component Analysis for Two Geometries of Approach in the Reaction of 2 with Styrene[a]

	energy, kcal/mol	
	p approach	σ approach
electrostatic	−3.2	0.9
exchange repulsion	16.2	4.1
polarization	−0.1	−0.2
charge transfer	−3.0	−0.2
total	9.9	4.6

[a] Interaction energies were calculated with STO-3G, where STO-3G optimized geometries of 2 and styrene were arranged as shown in Figure 6. The positive value corresponds to destabilization and the negative one to stabilization.

Usually, a carbene with a σ^2 configuration is electrophilic, and the vacant p orbital is used for the interaction with the HOMO of alkenes. For **1** and **2**, however, the electrophilic interaction is prevented for a sterical reason and, instead, the paired σ electrons interact with the LUMO of alkenes. To demonstrate this, model calculations were carried out with the STO-3G basis set for the reaction of **2** with styrene, and the interaction energy was decomposed into chemically interpretable components: the electrostatic, exchange repulsion, polarization, and charge-transfer terms.[45] As is shown in Figure 6, two extreme approach models were considered. Carbene **2** was placed so that C_3, C_4, and C_5 atoms could be on the *xz* plane, where C_4 was placed on the origin, and so that *z* axis could pass through a center of the angle of

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(37) Diaz, A. F.; Sakai, M.; Winstein, S. *J. Am. Chem. Soc.* **1970**, *92*, 7477.

(38) (a) Moss, R. A.; Mallon, C. B. *J. Am. Chem. Soc.* **1975**, *97*, 344. (b) Jefford, C. W.; Mareda, J.; Gehret, J.-C.; Kabengele, T.; Graham, W. D.; Burger, U. *Ibid.* **1976**, *98*, 2585.

(39) $C_2 \propto (S_{\text{HOMO,LUMO}})/(\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})$, where S is the overlap integral between HOMO and LUMO and $(\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})$ is the energy difference between HOMO and LUMO.

(40) ESR studies at low temperature: (a) Arnold, D. R.; Humphreys, R. W.; Leigh, W. J.; Palmer, G. E. *J. Am. Chem. Soc.* **1976**, *98*, 6225. (b) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wasserman, E. *Ibid.* **1974**, *96*, 4680. (c) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511.

(41) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516.

(42) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481.

(43) The geometry is consistent with that obtained by MINDO/3. Chung, C. S. C. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 456.

(44) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

(45) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294.

$C_3C_4C_5$. Styrene was placed to be horizontal to the *xz* (p) and the *xy* (σ) plane, respectively, where the axis passed through the center of the olefin moiety of styrene. The distance between C_4 and the center of the olefin moiety of styrene was set to be 3.0 Å. The calculated results are given in Table V. The contribution of the exchange repulsion term, which represents the steric hindrance between **2** and styrene, is greater for p approach (16.2 kcal/mol), the net interaction becoming more repulsive for p approach (9.9 kcal/mol) than for σ approach (4.6 kcal/mol). This result is in contrast to the case of CH_2 and CF_2 additions to olefins where p approach is more favorable due to a smaller exchange repulsion.[46] Although the exchange repulsion may be relaxed to some extent with a proper choice of reaction pathways or by use of molecular distortion, it is apparent that steric hindrance plays a significant role in the addition of carbenes **1** and **2**. This is considered to be another reason why carbenes **1** and **2** prefer the nucleophilic addition in spite of their low-lying LUMO's.

As a carbene is stabilized with conjugative interaction, its energy of HOMO becomes higher and that of LUMO becomes lower. The increase of selectivities for carbenes is correlated to the abilities of the neighboring groups to supply electrons to the electron-deficient carbene carbon atom, thus stabilizing the carbene.[47] The degree of electrophilicity of a carbene is correlated inversely with the selectivity. Consequently, with highly conjugated carbenes, the philicity would be influenced sterically by the molecular structures of carbenes and alkenes.

Experimental Section

General Remarks. All melting points are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. The NMR spectra were obtained on JNM-MH-60 and HNM-4H-100 spectrometers, and chemical shifts are reported in δ values downfield from the internal standard tetramethylsilane. Mass spectra were taken on a Hitachi RSM-4 mass spectrometer. GLC was carried out with a JEOL 20K by using a 1-m column packed with Carbowax 20 M on Celite or a 1-m column packed with Apieson L.

Bicyclo[3.2.1]octa-2,6-dien-4-one (3). The ketone **3** was prepared by the method of Freeman.[48] To an ethereal solution of diazomethane (0.3 N, 2 L, 0.6 mol) was added bicyclo[3.1.0]hex-2-ene-6-*endo*-carbonyl chloride (31.4 g, 0.22 mol) at 0 °C for 30 min. After additional stirring at 0 °C for 5 h, ether was removed under reduced pressure. Crude *endo*-6-(diazomethyl)ketobicyclo[3.1.0]hex-2-ene was dissolved in THF (1.3 L) and was irradiated under nitrogen with a high-pressure mercury lamp using a filter (200 mg of $BiCl_3$, 150 mL of 10% HCl solution, 1-cm filter width). Evolution of 3.3 L of nitrogen gas was observed. To the THF solution was added 4-*tert*-butyl-1,2-dihydroxybenzene (0.5 g). Evaporation of the solvent, followed by distillation (bp 74 °C (8mmHg)) gave **3** (11.9 g, 45%): NMR (CCl_4) δ 7.18 (d–d, $J_{H^2H^3}$ = 9.9 Hz, $J_{H^1H^2}$ = 6.2 Hz, H^2), 6.58 (d–d, $J_{H^6H^7}$ = 5.2 Hz, $J_{H^1H^7}$ = 3.0 Hz, H^7), 6.11 (d–d, $J_{H^6H^7}$ = 5.2 Hz, $J_{H^5H^6}$ = 3.4 Hz, H^6), 5.28 (d–d, $J_{H^2H^3}$ = 9.9 Hz, $J_{H^3H^5}$ = 2.0 Hz, H^3), 3.3–3.0 (m, H^1, H^5), 2.49 (m, 2 H^8).

Bicyclo[3.2.1]octa-2,6-dien-4-one *p*-Toluenesulfonylhydrazone (4). To a solution of *p*-toluenesulfonylhydrazine (6.62 g, 35.9 mmol) in dry pyridine (60 mL), was added bicyclo[3.2.1]octa-2,6-dien-4-one (4.32 g, 35.9 mmol) at 0 °C. The resulting solution was allowed to stand for 5 days at 0 °C. Removal of pyridine under reduced pressure gave white solid, which was then dissolved in CH_2Cl_2 and subjected to a short silica-gel chromatography. The tosylhydrazone **4** (9.9 g) was obtained in 96% yield; mp 169–174 °C dec; IR (Nujol mull) 3210 cm^{-1} (N–H). Anal. ($C_{15}H_{16}N_2O_2S$) C, H, N, S. The NMR spectrum showed that the tosylhydrazone consisted of two stereoisomers (**4a** and **4b**). **4a**: NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 6.83 (d–d, $J_{H^2H^3}$ = 9.5 Hz, $J_{H^1H^2}$ = 6.5 Hz, H^2), 6.38 (d–d, $J_{H^6H^7}$ = 5.5 Hz, $J_{H^1H^7}$ = 3.0 Hz, H^7), 5.95 (d–d, $J_{H^6H^7}$ = 5.5 Hz, $J_{H^5H^6}$ = 3.1 Hz, H^6), 5.91 (d–d, $J_{H^2H^3}$ = 9.5 Hz, $J_{H^3H^5}$ = 2.0 Hz, H^3), 3.37 (m, H^5), 3.04 (m, H^1), 2.42 (s, 3 H), 2.1 (m, H^8). **4b**: NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 6.57 (d–d, $J_{H^2H^3}$ = 9.4 Hz, $J_{H^1H^2}$ = 6.4 Hz, H^2), 6.40 (d–d, $J_{H^1H^7}$ = 3.0 Hz, $J_{H^6H^7}$ = 5.3 Hz,H^7), 5.86 (d–d, $J_{H^6H^7}$ = 5.3 Hz, $J_{H^5H^6}$ = 3.0, H^6), 5.65 (d–d, $J_{H^2H^3}$ = 9.4 Hz, $J_{H^3H^5}$ = 1.9 Hz, H^3), 3.72 (m, H^1), 3.03 (m, H^5), 2.43 (s, 3 H), 2.1 (m, H^8).

Sodium Salt (5) of Bicyclo[3.2.1]octa-2,6-dien-4-one *p*-Toluenesulfonylhydrazone. To a suspension of sodium hydride (0.40 g of NaH in oil (50%) was washed with pentane, 8.3 mmol) in dry THF (10 mL) was added a solution of tosylhydrazone **4** (1.2 g, 4.2 mmol) in dry THF (50 mL). The mixture was stirred for 12 h. Evaporation of the solvent under reduced pressure gave the sodium salt **5**.

4-Diazobicyclo[3.2.1]octa-2,6-diene (6). The sodium salt **5** of bicyclo[3.2.1]octa-2,6-dien-4-one tosylhydrazone (232 mg, 0.75 mmol) was placed in Pyrex tube fitted with a short tube connected to a trap which is cooled to 77 K. The Pyrex tube was slowly heated at 97 °C in a Kugelrohr heating apparatus under highly reduced pressure (1.0 × 10^{-6}mmHg). The red-yellow oil collected in the trap contained THF and 4-diazobicyclo[3.2.1]octa-2,6-diene (48 mg). Chilled pentane (3 mL) was added, and the pentane solution was washed with cold water (0 °C) and dried. Distillation at –30 °C under the pressure of 1.0 × 10^{-6}mmHg gave 4-diazobicyclo[3.2.1]octa-2,6-diene (20 mg, 23%): IR (liquid film) 2040 cm^{-1} ($C{=}N_2$); NMR (100 MHz, CCl_4) δ 5.94 (d–d, $J_{H^6H^7}$ = 5.5 Hz, $J_{H^1H^7}$ = 3.0 Hz, H^7), 5.75 (d–d, $J_{H^2H^3}$ = 9.3 Hz, $J_{H^3H^5}$ = 2.0 Hz, H^3), 5.63 (d–d, $J_{H^6H^7}$ = 5.5 Hz, $J_{H^5H^6}$ = 2.9 Hz, H^6), 5.43 (d–d, $J_{H^2H^3}$ = 9.3 Hz, $J_{H^1H^2}$ = 6.3 Hz, H^2), 3.27 (m, H^5), 2.79 (m, H^1), 1.8 (m, 2 H^8); UV ($\lambda_{max}^{CCl_4}$) 535 nm.

Vacuum Pyrolysis of the Sodium Salt 5 of *p*-Toluenesulfonylhydrazone of Bicyclo[3.2.1]octa-2,6-dien-4-one. The sodium salt **5** prepared from *p*-toluenesulfonylhydrazone (2.0 g, 6.9 mmol) was pyrolyzed at 200 °C under reduced pressure (5mmHg). The hydrocarbon products (460 mg, 64%) were collected in a trap cooled at 77 K. The GLC analysis showed that the products consisted of 88% of styrene, 7.4% of bicyclo[3.3.0]octa-1,4,6-triene (**11**), and 4.5% of an unidentified mixture of eight products. The structure of bicyclo[3.3.0]octa-1,4,6-triene was identified by comparison of the IR and NMR spectra with those of an authentic sample.

The Adduct of 1 to Cyclohexene (13). A mixture of the sodium salt **5** of tosylhydrazone of bicyclo[3.2.1]octa-2,6-dien-4-one (237 mg, 0.764 mmol) and dry cyclohexene (1 mL) in a sealed tube was heated at 175–245 °C for 40 min. The reaction mixture was subjected to a short silica-gel chromatography. The eluent was concentrated and subjected to the preparative TLC. Elution with CCl_4 gave the adduct (5 mg, 3.5%): mass spectrum, *m/e* 186; IR (liquid film) 3040, 1610, 1580, 1020 cm^{-1}; NMR (CCl_4) δ 6.31 (d–d, $J_{H^6H^7}$ = 5.5 Hz, $J_{H^1H^7}$ = 3.0 Hz, H^7), 6.23 (d–d, $J_{H^2H^3}$ = 10.0 Hz, $J_{H^1H^2}$ = 6.0 Hz, H^2), 5.74 (d–d, $J_{H^6H^7}$ = 5.5 Hz, $J_{H^5H^6}$ = 3.0 Hz, H^6), 5.17 (br d–d, $J_{H^2H^3}$ = 10.0 Hz, $J_{H^3H^5}$ = 2.2 Hz, H^3) 2.74 (m, H^1, H^5), 2.1–0.8 (m, 12 H).

Spiro[2,3-bis(carbomethoxy)cyclopropane-1,4′-bicyclo[3.2.1]octa-2′,6′-diene] (14). A suspension of the sodium salt **5** of the tosylhydrazone (284 mg, 0.92 mmol) and dimethyl fumarate (648 mg, 4.48 mmol) in dry benzene (3 mL) was heated at 190 °C for 25 min in a sealed tube. The reaction mixture was dissolved in ether (10 mL) and washed with water (5 mL). Evaporation of the solvent, followed by sublimation (at 180 °C, removal of excess dimethyl fumalate), gave an oily residue which then was distilled by Kugelrohr distillation (160 °C (2 mmHg)). The distillate was subjected to TLC (silica gel). Elution with benzene (R_f 0.52–0.65) gave the adduct (30 mg, 13%). The NMR spectrum shows the ratio of **14a**/**14b** = 2:3. **14a**: mass spectrum, *m/e* 238; IR (liquid film) 3045, 1720, 1020 cm^{-1}; NMR (CCl_4) δ 6.33 (d–d, $J_{H^6H^7}$ = 5.8 Hz, $J_{H^1H^7}$ = 3.5 Hz, H^7), 6.20 (d–d, $J_{H^2H^3}$ = 10.0 Hz, $J_{H^1H^2}$ = 6.4 Hz, H^2), 5.79 (d–d, $J_{H^6H^7}$ = 5.8 Hz, $J_{H^5H^6}$ = 3.3 Hz, H^6), 5.10 (br d–d, $J_{H^2H^3}$ = 10.0 Hz, $J_{H^3H^5}$ = 2.5 Hz, H^3), 3.68 (s, 3 H), 3.60 (s, 3 H), 2.73 (m, 2 H), 2.43 (s, 2 H), 1.90 (m, 2 H). Anal. ($C_{14}H_{16}O_4$) C, H. **14b**: mass spectrum, *m/e* 238; IR (liquid film) 3045, 1720, 1020 cm^{-1}; NMR (CCl_4) δ 6.24 (d–d, $J_{H^6H^7}$ = 5.8 Hz, $J_{H^1H^7}$ = 3.2 Hz, H^7), 6.19 (d–d, $J_{H^2H^3}$ = 9.5 Hz, $J_{H^1H^2}$ = 6.7 Hz, H^2), 5.37 (d–d, $J_{H^6H^7}$ = 5.8 Hz, $J_{H^5H^6}$ = 3.2 Hz, H^6), 5.14 (br d–d, $J_{H^2H^3}$ = 9.5 Hz, $J_{H^3H^5}$ = 2.2 Hz, H^3), 3.53 (s, 3 H), 3.50 (s, 3 H), 2.78 (m, 2 H), 2.42 (d, *J* = 6.0 Hz, 1 H), 2.33 (d, *J* = 6.0 Hz, 1 H), 2.03 (m, 2 H).

Preparation and Characterization of Spiro[2-arylcyclopropane-1,4′-bicyclo[3.2.1]octa-2′,6′-diene] (15–19). A mixture of the sodium salt **5** (315 mg, 1.02 mmol) and freshly distilled styrene or a substituted styrene (12.2 mmol) was placed in a Pyrex tube and dissolved in dry benzene (1.5 mL) with stirring. The resulting viscous solution was heated at 180 °C for 30 min in a sealed tube. The reaction mixture was dissolved in ether and subjected to short silica-gel chromatography. Evaporation of the solvents of the eluent, followed by Kulgerohr distillation (bp 180 °C (4mmHg)) gave a mixture of the adducts. The stereoisomers of the adducts were separated by careful TLC (silica gel, CCl_4) repeatedly. The complete assignment of the four isomers could not be done because the amount of the fourth component was too small to be isolated. The spectral data of the typical cyclopropane adducts toward styrene and unsubstituted styrenes are described below.

Spiro[phenylcyclopropane-1,4′-bicyclo[3.2.1]octa-2′,6′-diene] (15): mass spectrum, *m/e* 208; NMR (CCl_4) δ 7.04 (s, 5 H), 6.23 (d–d, $J_{H^6H^7}$ = 5.3 Hz, $J_{H^1H^7}$ = 2.8 Hz, H^7), 5.89 (d–d, $J_{H^6H^7}$ = 5.3 Hz, $J_{H^5H^6}$ = 4.0 Hz, H^6), 5.77 (d–d, $J_{H^1H^2}$ = 6.1 Hz, $J_{H^2H^3}$ = 9.5 Hz, H^2), 4.37 (d, $J_{H^2H^3}$

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= 9.5 Hz, H^3), 2.67 (m, H^1, H^5), 2.30 (d–d, $J_{H^aH^c}$ = 5.0 Hz, $J_{H^aH^b}$ = 8.6 Hz, H^a), 2.00 (m, 2 H^8), 1.15 (d–d, $J_{H^aH^b}$ = 8.6 Hz, $J_{H^bH^c}$ = 7.0 Hz, H^b), 0.99 (d–d, $J_{H^aH^c}$ = 5.0 Hz, $J_{H^bH^c}$ = 7.0 Hz, H^c).

Spiro[2-(*p*-methoxyphenyl)cyclopropane-1,4′-bicyclo[3.2.1]octa-2′,6′-diene] (16): mass spectrum, *m/e* 238; NMR (CCl_4) δ 7.13 (d, *J* = 9.1 Hz, 2 H), 6.75 (d, *J* = 9.1 Hz, 2 H), 6.26 (d–d, $J_{H^6H^7}$ = 5.9 Hz, $J_{H^1H^7}$ = 3.0 Hz, H^7), 6.21 (d–d, $J_{H^6H^7}$ = 5.9 Hz, $J_{H^5H^6}$ = 2.0 Hz, H^6), 5.86 (d–d, $J_{H^2H^3}$ = 10.3 Hz, $J_{H^1H^2}$ = 6.1 Hz, H^2), 4.87 (d, $J_{H^2H^3}$ = 10.3 Hz, H^3), 3.76 (s, CH_3), 2.7 (m, H^1, H^5), 2.28 (br t, H^a), 2.05 (m, 2 H^8), 1.3–0.8 (m, H^b, H^c).

Spiro[2-(*p*-methylphenyl)cyclopropane-1,4′-bicyclo[3.2.1]octa-2′,6′-diene] (17): mass spectrum, *m/e* 222; NMR (CCl_4) δ 6.92 (s, 4 H), 6.21 (d–d, $J_{H^6H^7}$ = 5.7 Hz, $J_{H^1H^7}$ = 2.7 Hz, H^7), 5.84 (d–d, $J_{H^6H^7}$ = 5.7 Hz, $J_{H^5H^6}$ = 2.7 Hz, H^6), 5.83 (d–d, $J_{H^1H^2}$ = 6.0 Hz, $J_{H^2H^3}$ = 9.8 Hz, H^2), 4.33 (d, $J_{H^2H^3}$ = 9.8 Hz, H^3), 2.67 (m, H^1, H^5), 2.28 (s, CH_3) 2.24 (d–d, $J_{H^aH^b}$ = 6.6 Hz, $J_{H^aH^c}$ = 8.5 Hz, H^a), 1.98 (m, 2 H^8), 1.09 (d–d, $J_{H^aH^b}$ = 6.6 Hz, $J_{H^bH^c}$ = 4.6 Hz, H^b), 0.98 (d–d, $J_{H^aH^c}$ = 8.5 Hz, $J_{H^bH^c}$ = 4.6 Hz H^c).

Spiro[2-(*p*-chlorophenyl)cyclopropane-1,4′-bicyclo[3.2.1]octa-2′,6′-diene] (18): mass spectrum, *m/e* 242, 244; NMR (CCl_4) δ 7.3–6.9 (m, 4 H), 6.23 (d–d, $J_{H^6H^7}$ = 5.3 Hz, $J_{H^1H^7}$ = 3.0 Hz, H^7), 5.87 (d–d, $J_{H^1H^2}$ = 6.8 Hz, $J_{H^2H^3}$ = 9.1 Hz, H^2), 5.84 (d–d, $J_{H^6H^7}$ = 5.3 Hz, $J_{H^5H^6}$ = 3.0 Hz, H^6), 4.37 (d, $J_{H^2H^3}$ = 9.1 Hz, H^3), 2.71 (m, H^1, H^5), 2.24 (d–d, $J_{H^aH^b}$ = 6.3 Hz, $J_{H^aH^c}$ = 8.2 Hz, H^a), 1.99 (m, 2 H^8), 1.12 (d–d, $J_{H^aH^b}$ = 6.3 Hz, $J_{H^bH^c}$ = 5.0 Hz, H^b), 1.06 (d–d, $J_{H^aH^c}$ = 8.2 Hz, $J_{H^bH^c}$ = 5.0 Hz, H^c).

Spiro[2-(*m*-chlorophenyl)cyclopropane-1,4′-bicyclo[3.2.1]octa-2′,6′-diene] (19): mass spectrum, *m/e* 242, 244; NMR (CCl_4) δ 7.2–6.9 (m, 4 H), 6.26 (d–d, $J_{H^6H^7}$ = 5.1 Hz, $J_{H^1H^7}$ = 2.7 Hz, H^7), 5.91 (d–d, $J_{H^1H^2}$ = 6.3 Hz, $J_{H^2H^3}$ = 9.6 Hz, H^2), 4.35 (d, $J_{H^2H^3}$ = 9.6 Hz, H^3), 2.73 (m, H^1, H^5), 2.25 (d–d, $J_{H^aH^b}$ = 6.0 Hz, $J_{H^aH^c}$ = 8.4 Hz, H^a), 2.01 (m, 2 H^8), 1.12 (d–d, $J_{H^aH^b}$ = 6.0 Hz, $J_{H^bH^c}$ = 5.0 Hz, H^b), 1.05 (d–d, $J_{H^aH^c}$ = 8.4 Hz, $J_{H^bH^c}$ = 5.0 Hz, H^c).

Photochemical Reaction of 4-Diazobicyclo[3.2.1]octa-2,6-diene (6) in Substituted Styrene. Typically, a solution of **6** (40 mg) in *m*-chlorostyrene (6 mL) was irradiated at 0 °C for 20 min with a high-pressure mercury lamp (Eikosha—1 kW) using a filter solution of benzene–naphthalene, which cut the light shorter than 310 nm. Evaporation of *m*-chlorostyrene, followed by short distillation, gave the cyclopropane adduct (55 mg) in 60% yield. Careful GLC analysis showed that the products consisted of two stereoisomers. The spectral data were consistent with those which were obtained by the thermal reaction of the sodium salt **5** in *m*-chlorostyrene, although the product ratio is different.

Competitive Carbenic Reactivities of Substituted Styrenes in the Photochemical Decomposition of 6. To an equivalent molar mixture of styrene and substituted styrenes (*p*-MeO, *p*-Me, *p*-Cl, and *m*-Cl styrenes, 0.5–1.3 mmol) was added a pentane solution (0.5 mL) of 4-diazobicyclo[3.2.1]octa-2,6-diene **6** (2 mg, 0.015 mmol) at 0 °C. The solution was irradiated at 0 °C for 10 min by a high-pressure mercury lamp (Eikosha, 1 kW) using a filter solution of benzene–naphthalene. The cyclopropane fraction was analyzed by GLC. With use of standard solutions of the cyclopropane compounds, the relative ratios of the cyclopropane products were determined. The ratio of *p*-MeO/H formed was 1.02. The other ratios were as follows: *p*-Me/H = 0.92; *p*-Cl/H = 1.13; *m*-Cl/H = 1.26. The rate data correlate well (Figure 1) with a Hammett linear free energy relationship using σ values. The ρ for reactions is +0.25 with γ = 0.996.

Competitive Reactivities in Thermal Reactions (at 0 °C) of 6 with Substituted Styrenes. To an equimolar mixture of styrene and substituted styrenes (*p*-MeO, *p*-Me, *p*-Cl, and *m*-Cl styrenes, 0.35–0.40 mmol) was added a pentane solution of 4-diazobicyclo[3.2.1]octa-2,6-diene (**6**) (2 mg, 0.015 mmol) at 0 °C. The mixture was allowed to stand in dark until the color of red-violet disappeared (9 h). The reaction mixture was directly subjected to GLC analysis (FID, Gaule column Q-45, Apieson-L, 45 m, column temperature 160 °C). The relative ratios were determined by using internal standard. The ratios obtained are *p*-MeO/H = 0.44, *p*-Me/H = 0.63, *p*-Cl/H = 1.88, and *m*-Cl/H = 2.99. The Hammett treatment gave ρ = 1.26 (γ = 0.999).

Competitive Reactivities in Thermal Reaction (at 170 °C) of 6 with Substituted Styrenes. To a mixture of styrene and a substituted styrene (*p*-OMe, *p*-Me, and *m*-Cl styrenes, 0.25-mmol each) was added a pentane solution of 4-diazobicyclo[3.2.1]octa-2,6-diene (**6**) (2 mg, 0.015 mmol) at −78 °C. The mixture was immersed in an oil bath (170 °C). When red-violet color disappeared (within 5–10 s), the reaction mixture was immediately cooled to −78 °C. The reaction product was subjected to GLC analysis (column KF-96, 10% 4 m, column temperature 220 °C). The ratios obtained are *p*-MeO/H = 0.61, *p*-Me/H = 0.78, *p*-Cl/H = 1.66, and *m*-Cl/H = 2.03. The Hammett treatment gave ρ = 0.82 (γ = 0.997).

Photolysis of 6 in *cis*-2-Butene. A solution of 4-diazobicyclo[3.2.1]-octa-2,6-diene (**6**) (50 mg, 0.37 mmol) in *cis*-2-butene (6 mL) which contained 2.4% of *trans*-2-butene was photolyzed with high-pressure mercury lamp using a filter solution of potassium salt of phthalic acid (0.027 mol/L, 1 cm, 310 nm) at −45 °C. The GLC analysis showed that **20** (57.5%), **21** (38.5%), **22** (2.0%), and **23** (2.0%) were contained in the cyclopropane fraction. The structures of four isomers were determined by the following spectral data. **20**: mass spectrum, *m/e* 160; IR (liquid film) 3050, 1621, 1592, 1019 cm^{-1}; NMR (60 MHz, CCl_4) δ 6.11 (d–d, $J_{H^6H^7}$ = 5.7 Hz, $J_{H^1H^7}$ = 2.5 Hz, H^7), 6.05 (d–d, $J_{H^2H^3}$ = 10.0 Hz, $J_{H^1H^2}$ = 6.3 Hz, H^2), 5.58 (d–d, $J_{H^6H^7}$ = 5.7 Hz, $J_{H^5H^6}$ = 2.6 Hz, H^6), 4.88 (d–d, $J_{H^2H^3}$ = 10.0 Hz, $J_{H^3H^5}$ = 2.1 Hz, H^3), 2.64 (m, H^1), 1.95–1.85 (m, H^{8a}, H^{8b}), 1.69 (m, H^5), 1.01 (d, *J* = 4.8 Hz, 3 H^{CH_3}), 0.97 (d, *J* = 4.1 Hz, 3 H^{CH_3}), 1.1–0.7 (m, H^{11}, H^{12}). **21**: mass spectrum, *m/e* 160; IR (liquid film) 3055, 1621, 1590, 1017 cm^{-1}; NMR (60 MHz CCl_4) δ 6.12 (d–d, $J_{H^6H^7}$ = 5.4 Hz, $J_{H^1H^7}$ = 2.7 Hz, H^7), 5.81 (d–d, $J_{H^2H^3}$ = 9.9 Hz, $J_{H^1H^2}$ = 6.2 Hz, H^2), 5.50 (d–d, $J_{H^6H^7}$ = 5.4 Hz, $J_{H^5H^6}$ = 2.8 Hz, H^6), 4.41 (d–d, $J_{H^2H^3}$ = 9.9 Hz, $J_{H^3H^5}$ = 2.3 Hz, H^3), 2.61 (m, H^1), 2.33 (m, H^5), 1.93 (d–t, $J_{H^{8a}H^{8b}}$ = 8.7 Hz, $J_{H^{8b}H^1}$ = $J_{H^{8b}H^5}$ = 4.5 Hz, H^{8b}), 1.73 (d, $J_{H^{8a}H^{8b}}$ = 8.7 Hz, H^{8a}), 1.07 (d, *J* = 4.4 Hz, 3 H^{CH_3}), 1.05 (d, *J* = 5.7 Hz, 3 H^{CH_3}), 0.91 (d–d, *J* = 7.0, 4.4 Hz, H^9 or H^{10}), 0.72 (d–d, *J* = 7.0, 5.7 Hz, H^9 or H^{10}). **22**: mass spectrum, *m/e* 160; IR (liquid film) 3060, 3045, 1620, 1590, 1018 cm^{-1}; NMR (60 MHz, CCl_4) δ 6.11 (d–d, $J_{H^6H^7}$ = 5.4 Hz, $J_{H^1H^7}$ = 2.9 Hz, H^7), 5.91 (d–d, $J_{H^2H^3}$ = 9.5 Hz, $J_{H^1H^2}$ = 6.1 Hz, H^2), 5.55 (d–d, $J_{H^6H^7}$ = 5.4 Hz, $J_{H^5H^6}$ = 2.9 Hz, H^6), 4.70 (d–d, $J_{H^2H^3}$ = 9.5 Hz, $J_{H^3H^5}$ = 2.1 Hz, H^3), 2.62 (m, H^1), 2.09 (m, H^5), 1.87 (d–t, $J_{H^{8a}H^{8b}}$ = 9.3 Hz, $J_{H^{8b}H^1}$ = $J_{H^{8b}H^5}$ = 4.7 Hz, H^{8b}), 1.74 (d, $J_{H^{8a}H^{8b}}$ = 9.3 Hz, H^{8a}), 1.13 (d, *J* = 5.9 Hz, 3 H^{CH_3}), 1.00 (d, *J* = 5.2 Hz, 3 H^{CH_3}), 0.73 (m, H^9, H^{12}). **23**: mass spectrum, *m/e* 160; IR (liquid film) 3060, 3045, 1621, 1593, 1018 cm^{-1}; NMR (60 MHz, CCl_4) δ 6.12 (d–d, $J_{H^6H^7}$ = 4.8 Hz, $J_{H^1H^7}$ = 2.8 Hz, H^7), 5.95 (d–d, $J_{H^2H^3}$ = 9.2 Hz, $J_{H^1H^2}$ = 6.0 Hz, H^2), 5.62 (d–d, $J_{H^6H^7}$ = 4.8 Hz, $J_{H^5H^6}$ = 2.8 Hz, H^6), 4.68 (d–d, $J_{H^2H^3}$ = 9.2 Hz, $J_{H^3H^5}$ = 2.0 Hz, H^3), 2.65 (m, H^1), 2.11 (m, H^5), 2.0–1.6 (m, H^{8a}, H^{8b}), 1.18 (d, *J* = 5.8 Hz, 3 H^{CH_3}), 1.09 (d, *J* = 5.8 Hz, 3 H^{CH_3}), 0.65–0.25 (m, H^{10}, H^{11}). Under the photoreaction condition, the isomerizations of *cis*-2-butene and the cyclopropane products were not detected.

Photolysis of 6 in *trans*-2-Butene. A solution of **6** (50 mg, 0.37 mmol) in *trans*-2-butene (6 mL) of which purity is 99.9% was irradiated as described in the photolysis of **6** in *cis*-2-butene. The GLC analysis of the products showed that **22** (47.6%), **23** (48.1%), **20** (2.6%), and **21** (1.7%) were obtained.

Monitoring of Photoreactions and Thermal Reactions of 6 in Styrene. A solution of diazo **6** in a mixture of styrene and pentane (1 × 10^{-2} mol/L) was placed in two NMR tubes. One of the sample was irradiated at 0 °C through a Pyrex filter, and its NMR spectra were taken periodically. The absorption of **6** faded after 10 min. The NMR spectrum showed that the product obtained after evaporation of styrene and pentane, followed by addition of CCl_4 consists of the cyclopropane adducts. The second sample was allowed to stand in dark at 0 °C, and the NMR spectra were taken at 5, 10, 20, and 240 min. The absorption of **6** disappeared within 240 min. Careful analysis of the cyclopropane fraction with GLC showed that the relative product ratio of the stereoisomers obtained from the irradiation was different from that of the thermal reaction.

Bicyclo[3.2.1]oct-3-en-2-one (7). To a solution of 3-chlorobicyclo-[3.2.1]oct-3-en-2-ol[49] (42.5 g, 0.268 mol) in THF (1 L) was added sodium, which was cut in small pieces (12 g, 0.52 mol), gradually for 12 h with stirring under nitrogen atmosphere. Water (20 mL) was added very slowly. Then, sodium (20 g, 0.87 mol), cut in small pieces, was added carefully. After additional stirring for 24 h, water was added slowly until water and THF layers were separated. The THF layer was removed and combined to the ether solution obtained by the extraction of the water layer with ether. The combined solution was washed with saturated NaCl solution and dried over Na_2SO_4. Evaporation of the solvent followed by distillation using a modified von Braun flask (bp 100 °C (20mmHg)) gave *exo*-bicyclo[3.2.1]oct-3-en-2-ol (26.7 g, 80%): mp 83–85 °C (micro melting point apparatus) (lit.[50] 88–89 °C); IR (CCl_4) 3300 (OH), 3040, 1720, 1640 cm^{-1}; NMR (60 MHz, CCl_4) δ 6.01 (d–d–m, $J_{H^3H^4}$ = 9.5 Hz, $J_{H^4H^5}$ = 6.5 Hz, H^4), 5.43 (d–d–d, $J_{H^3H^4}$ = 9.5 Hz, $J_{H^2H^3}$ = 3.9 Hz, $J_{H^1H^3}$ = 1.9 Hz, H^3), 3.66 (m, H^2), 3.17 (br s, OH), 2.63–2.1 (m, H^1, H^5), 2.2–0.95 (m, methylene proton 2 H^6, 2 H^7, 2 H^8). To the chromic anhydride–pyridine complex, prepared by the addition of chromic anhydride (153 g, 1.53 mol) to pyridine (500 mL) at 0–5 °C, was added a solution of bicyclo[3.2.1]oct-3-en-2-ol (70.9 g, 0.57 mol) in pyridine (50 mL) in one portion, and the mixture was stirred for 48 h. Ether (300 mL) was added, and the precipitates were washed with ether

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(500 mL). The combined ether solution was washed with a cold 2 N HCl solution. Evaporation of ether, followed by distillation (bp 94–99 °C (17 mmHg)) gave bicyclo[3.2.1]oct-3-en-2-one (32.5 g, 47%):[50,51] IR (liquid film) 1675 (C═O), 1605 (C═O) cm^{-1}; NMR (60 MHz, CCl_4) δ 7.19 (d–d–d, $J_{H^3H^4}$ = 10.0 Hz, $J_{H^4H^5}$ = 7.2 Hz, J = 1.6 Hz, H^4), 5.67 (d–d, $J_{H^3H^4}$ = 10.0 Hz, $J_{H^1H^3}$ = 1.4 Hz, H^3), 3.05–2.63 (m, H^1, H^5), 2.4–1.1 (m, 2 H^6, 2 H^7, 2 H^8). Anal. ($C_8H_{10}O$) C, H.

Bicyclo[3.2.1]oct-3-en-2-one *p*-Toluenesulfonylhydrazone (8). To a solution of *p*-toluenesulfonylhydrazine (24.4 g, 0.13 mol) in dry pyridine (100 mL) was added a solution of bicyclo[3.2.1]oct-3-en-2-one (**7**) (16 g, 0.13 mol) at 0 °C, and the mixture was allowed to stand for 12 days. Pyridine was removed by distillation under reduced pressure. The filtrate was subjected to silica-gel chromatography. Elution with CH_2Cl_2 and evaporation of CH_2Cl_2 gave the tosylhydrazone of bicyclo[3.2.1]oct-3-en-2-one (11.3 g, 29%).

The Sodium Salt 9 of *p*-Toluenesulfonylhydrazone of Bicyclo[3.2.1]-oct-3-en-2-one. To a suspension of NaH (50% NaH in oil was washed with pentane, 44 mmol) in THF (10 mL) was added a solution of tosylhydrazone (**8**) (9.2 g, 32 mmol) in THF (60 mL). The mixture was evaporated under reduced pressure.

4-Diazobicyclo[3.2.1]oct-2-ene (10). Sodium salt **9** was heated carefully at 90–107 °C under high vacuum (1.0 × 10^{-6}mmHg) for 6 h. The volatile red-violet product was collected in a trap cooled to 77 K. The products were dissolved in pentane (1 mL). The pentane solution was washed with cold water (0 °C). Evaporation of pentane under reduced pressure (4mmHg), followed by distillation of the residue, gave **10** (33 mg, 7%): IR (liquid film) 3040, 2030 cm^{-1} ($C{=}N_2$); NMR (60 MHz, CCl_4) δ 5.69 (d–d, $J_{H^2H^3}$ = 9.8 Hz, $J_{H^3H^5}$ = 1.5 Hz, H^3), 5.28 (d–d, $J_{H^2H^3}$ = 9.8 Hz, $J_{H^1H^2}$ = 7.0 Hz, H^2), 2.84 (m, H^5), 2.45 (m, H^1), 2.2–1.1 (m, 6 H).

Thermal Decomposition of 10. When a pentane solution of **10** was subjected to GLC (injection temperature 300 °C, KF-96, 2 m, 10%), a single peak was appeared. The product was identified to be tricyclo-[3.2.1.0^{2,7}]oct-3-ene (**12**) by comparison of its spectral data with those of an authentic sample:[25] mass spectrum, *m/e* 106; IR (liquid film) 3050, 1620, 1022 cm^{-1}; NMR (60 MHz, CCl_4) δ 5.84 (t, J = 3.0 Hz, 2 H), 2.50 (b t, J = 3.0 Hz, 1 H), 1.7–1.3 (m, 5 H), 0.73 (d, J = 9.0 Hz, 2 H).

Photolysis of 10 in *cis*-2-Butene. A solution of diazo **10** (40 mg, 0.30 mmol) in *cis*-2-butene (6 mL) which contains 2.4 mol % of *trans*-2-butene was irradiated at −42 °C with a high-pressure mercury lamp using a filter solution (>310 nm) (potassium hydrogen phthalate, 5.5 g/1 L of H_2O, 1 cm) for 100 min. GLC analysis (KF-96, 4 m, 20%, column temperature 130 °C) shows that *cis*-cyclopropane (**24a**) (67%), *cis*-cyclopropane (**24b**) (33%), and *trans*-cyclopropane (**25a** + **25b**) (0.5%) were obtained. The structural assignment of these four isomers was confirmed by the NMR spectral data of the samples collected by preparative GLC. **24a**: NMR (60 MHz, CCl_4) δ 5.90 (d–d, $J_{H^2H^3}$ = 10.0 Hz, $J_{H^1H^2}$ = 6.0 Hz, H^2), 5.00 (d, $J_{H^2H^3}$ = 10.0 Hz, H^3), 2.40 (m, H^1, H^5), 2.0–1.1 (m, 8 H), 1.1–0.7 (m, 6 H^{CH_3}). **24b**: NMR (60 MHz, CCl_4), δ 5.60 (d–d, $J_{H^2H^3}$ = 9.1 Hz, $J_{H^1H^2}$ = 6.3 Hz, H^2), 4.51 (d, $J_{H^2H^3}$ = 9.1 Hz, H^3), 2.35 (m, H^1), 1.90 (m, H^5), 1.8–1.2 (m, 8 H), 1.0–0.7 (m, CH_3, 6 H). Under the photoreaction condition, isomerization of *cis*-2-butene and the cyclopropane products was not detected.

Photolysis of 10 in *trans*-2-Butene. Diazo compound **10** was photolyzed in *trans*-2-butene (99.9%) under the similar condition employed for the photoreaction in *cis*-2-butene. The cyclopropane products consist of **25a** + **25b** (98%), **24a** (1.3%), and **24b** (0.9%).

Preparation and Characterization of Spiro[2-arylcyclopropane-1,4′-bicyclo[3.2.1]oct-2′-ene] (26–30). A mixture of the sodium salt of tosylhydrazone of bicyclo[3.2.1]oct-2-en-4-one (**9**) (400 mg, 1.3 mmol) and freshly distilled styrene or substituted styrene (1 mL) was placed in a Pyrex tube. Dry benzene (1 mL) was added with stirring. The resulting viscous mixture was heated at 200 °C for 30 min in a sealed tube. To the reaction mixture was added ether (10 mL), and the ether solution was filtered over a short silica-gel column. The eluent was condensed and distilled by using a Kugelrohr (180 °C (4 mmHg)) apparatus. The distillate was subjected to TLC (silica gel). The elution with CCl_4 gave a mixture of stereoisomers, spiro[2-arylcyclopropane-1,4′-bicyclo-[3.2.1]oct-2′-ene]. The structural assignment was performed by the following spectral data.

Spiro[2-phenylcyclopropane-1,4′-bicyclo[3.2.1]oct-2′-ene] (26) (yield 33%): mass spectrum, *m/e* 210; IR (liquid film) 3040, 1608, 1030 cm^{-1}; NMR (60 MHz, CCl_4) δ 7.08 (s, 5 H), 5.9–5.6 (d–d, J = 10, 6.0 Hz, 1 H), 4.9–4.35 (doublet signals of H^3 protons of the stereoisomers appear at δ 4.81, 4.52, and 4.43, J = 10 Hz, total protons 1 H), 2.38 (m, 1 H), 2.2–1.2 (m, 8 H), 1.2–0.8 (m, 2 H).

Spiro[2-(*p*-methoxyphenyl)cyclopropane-1,4′-bicyclo[3.2.1]oct-2′-ene] (27) (yield 35%): mass spectrum, *m/e* 240. IR (liquid film) 3045, 1618, 1040 cm^{-1}; NMR (60 MHz, CCl_4) δ 6.95 (d, J = 9 Hz, 2 H), 6.63 (d, J = 9 Hz, 2 H), 5.9–5.6 (d–d, J = 10 and 6 Hz, 1 H), 4.9–4.3 (doublet signals of H^3 protons of the stereoisomers appear at δ 4.77, 4.51, and 4.40, J = 10 Hz, total protons 1 H), 3.69 (s, 3 H), 2.36 (m, 1 H), 2.2–1.2 (m, 8 H), 1.1–0.8 (m, 2 H).

Spiro[2-(*p*-methylphenyl)cyclopropane-1,4′-bicyclo[3.2.1]oct-2′-ene] (28) (yield 39%): mass spectrum, *m/e* 224; IR (liquid film) 3040, 1630, 1040 cm^{-1}; NMR (60 MHz, CCl_4) δ 6.95 (s, 4 H), 5.9–5.6 (d–d, J = 9, 6 Hz, 1 H), 4.9–4.35 (doublet signals of H^3 protons of the stereoisomers appear at δ 4.80, 4.52, and 4.41, J = 9 Hz, total protons 1 H), 2.35 (m, 1 H), 2.28 (s, 3 H), 2.2–1.2 (m, 8 H), 1.2–0.8 (m, 2 H).

Spiro[2-(*p*-chlorophenyl)cyclopropane-1,4′-bicyclo[3.2.1]oct-2′-ene] (29): (yield 37%): mass spectrum, *m/e* 244, 246; IR (liquid film) 3040, 1630, 1018 cm^{-1}; NMR (60 MHz, CCl_4) δ 7.2–6.9 (m, 4 H), 5.9–5.6 (d–d, J = 10, 7 Hz, 1 H), 4.9–4.3 (doublet signals of H^3 protons of the stereoisomers appear at δ 4.78, 4.46, and 4.38, J = 10 Hz, totally 1 H), 2.40 (m, 1 H), 2.2–1.2 (m, 8 H), 1.2–0.8 (m, 2 H).

Spiro[2-(*m*-chlorophenyl)cyclopropane-1,4′-bicyclo[3.2.1]oct-2′-ene] (30) (yield 40%): mass spectrum, *m/e* 244, 246; IR (liquid film) 3040, 1600, 1038 cm^{-1}; NMR (60 MHz, CCl_4) δ 7.2–6.8 (m, 4 H), 5.9–5.8 (d–d, J = 11, 7 Hz, 1 H), 4.9–4.35 (doublet signals of H^3 protons of the stereoisomers at δ 4.78, 4.50, and 4.41, J = 11 Hz, totally 1 H), 2.40 (m, 1 H), 2.2–1.2 (m, 8 H), 1.2–0.8 (m, 2 H).

Carbenic Reactivity of Substituted Styrenes in the Photochemical Decomposition of 10. To an equivalent molar mixture of styrene and a substituted styrene (*p*-MeO, *p*-Me, *p*-Cl, and *m*-Cl styrenes) (0.5-mmol each) was added a pentane solution of diazo compound **10** at −78 °C. The solution was irradiated by a high-pressure mercury lamp (1 kW) using a filter solution (100 g of naphthalene in 500 mL of benzene, 3-cm width) at 0 °C until the color of **10** disappeared (10 min). The products were analyzed by GLC using internal standards. The relative ratios of the cyclopropane products were determined as follows: *p*-MeO/H = 0.78, *p*-Me/H = 0.90, *p*-Cl/H = 1.56, and *m*-Cl/H = 2.18. The rate data correlate with a Hammett linear free energy relationship. The ρ for reactions is +0.68 with γ = 0.98.

Competitive Reactivities in Thermal Reaction (at 0 °C) of 10 with Substituted Styrenes. To an equimolar mixture of styrene and a substituted styrene (*p*-OMe, *p*-Me, *p*-Cl, and *m*-Cl) was added a pentane solution of **10** at −78 °C. The mixture was stirred at 0 °C until the red-violet color of the diazo compounds was disappeared (90 min). The products were analyzed by GLC, and the relative ratio of the cyclopropane products was determined by using internal standards. The ratios are as follows: *p*-MeO/H = 0.40, *p*-Me/H = 0.71, *p*-Cl/H = 2.11, and *m*-Cl/H = 3.19. The Hammett treatment gives ρ = +1.35 with γ = 0.992.

Competitive Reactivities in Thermal Reaction (at 170 °C) of 10 with Substituted Styrenes. To a mixture of styrene and a substituted styrene (*p*-OMe, *p*-Me, *p*-Cl, and *m*-Cl styrenes) (0.25-mmol each) was added a pentane solution of **10** at −78°. The mixture was immediately immersed into an oil bath (170 °C) with vigorous stirring. When the wine red color disappeared (within 10 s), the mixture was cooled to −78 °C. The GLC analysis showed that the ratios obtained are *p*-MeO/H = 0.62, *p*-Me/H = 0.76, *p*-Cl/H = 1.57, and *m*-Cl/H = 1.80. The rate data correlate with a Hammett linear free energy relationship. The ρ value is 0.74 with γ = 0.996.

Acknowledgment. All calculations were carried out at the Computer Center of the Institute for Molecular Science, using the IMSPAK program.[52]

Registry No. 1, 80976-43-8; **2**, 80976-44-9; **3**, 1122-53-8; **4a**, 80976-45-0; **4b**, 80997-16-6; **5**, 80976-46-1; **6**, 80976-47-2; **7**, 3212-77-9; **8**, 80976-48-3; **9**, 80976-49-4; **10**, 80976-50-7; **11**, 33284-11-6; **12**, 3725-23-3; **13**, 80976-51-8; **14a**, 80976-52-9; **14b**, 81025-24-3; **15a**, 80976-53-0; **15b**, 81025-25-4; **15c**, 81025-26-5; **15d**, 81025-27-6; **16a**, 80976-54-1; **16b**, 81025-28-7; **16c**, 81025-29-8; **16d**, 81025-30-1; **17a**, 80976-55-2; **17b**, 81025-31-2; **17c**, 81025-32-3; **17d**, 81025-33-4; **18a**, 80976-56-3; **18b**, 81025-34-5; **18c**, 81025-35-6; **18d**, 81025-36-7; **19a**, 80976-57-4; **19b**, 81025-37-8; **19c**, 81025-38-9; **19d**, 81025-39-0; **20**, 80976-58-5; **21**, 81025-40-3; **22**, 81025-41-4; **23**, 81025-42-5; **24**, isomer 1, 80976-59-6; **24**, isomer 2, 81025-43-6; **25**, isomer 1, 81025-44-7; **25**, isomer 2, 81025-45-8; **26a**, 80976-60-9; **26b**, 81025-46-9; **26c**, 81025-47-0; **26d**, 81025-48-1; **27a**, 80976-61-0; **27b**, 81025-49-2; **27c**, 81025-50-5; **27d**, 81025-51-6; **28a**, 80976-62-1; **28b**, 81025-52-7; **28c**, 81025-53-8; **28d**, 81025-54-9; **29a**, 80976-63-2; **29b**, 81025-55-0; **29c**, 81025-

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56-1; **29d**, 81025-57-2; **30a**, 80976-64-3; **30b**, 81025-58-3; **30c**, 81025-59-4; **30d**, 81025-60-7; bicyclo[3.1.0]hex-2-ene-6-*endo*-carbonyl chloride, 58846-09-6; *endo*-6-(diazomethyl)ketobicyclo[3.1.0]hex-2-ene, 80976-65-4; styrene, 100-42-5; *p*-methoxystyrene, 637-69-4; *p*-methylstyrene, 622-97-9; *p*-chlorostyrene, 1073-67-2; *m*-chlorostyrene, 2039-85-2; dimethyl fumarate, 624-49-7; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *exo*-3-chlorobicyclo[3.2.1]oct-2-en-2-ol, 80976-66-5; *exo*-bicyclo[3.2.1]oct-3-en-2-ol, 4802-43-1.

Super-Charged Polycyclic π Systems: Pyrene and Perylene Tetraanions

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Abstract: Fused benzenoid systems pyrene, perylene, and their alkyl and phenyl derivatives were reduced with sodium and potassium to the doubly and quadruply charged species. The dianions revealed paratropicity, while the tetraanions acquired diatropic, aromatic ring current. Some of the quadruply charged systems revealed a high degree of asymmetry which can be rationalized as a result of an asymmetrical location of the metal cations. This phenomenon, as well as ring current effects, is discussed in terms of ^{1}H, ^{13}C, and ^{23}Na NMR spectroscopies and theoretical calculations.

The problem of the contributions of various kinds of cyclic conjugations to the nature of polycyclic π-conjugated systems presents a subject of interest.[1] A comprehensive study of the species which are formed in the course of the reduction process of π-conjugated polycyclic hydrocarbons should give an insight into this challenging subject. The reasoning behind this allegation is that different stages in the reduction process are assumed to give rise to different, or even opposite, types of cyclic conjugation. The resulting carbanions can be classified by the number of negative charges taken up by the π system; this basic classification can be further subdivided by making reference to the diatropicity and paratropicity which are caused by the charging and are quite straightforwardly detected by NMR methods.

Singly charged polycyclic species such as indenyl[2] and fluorenyl[2,3] anions exhibit a considerably diatropic ring current, in line with their Hückeloid number of peripheral π electrons. In contrast, the cycloocta[*def*]fluorenyl anion[4] contains a periphery of 16 π electrons and was shown to be a paratropic, antiaromatic system. A large group of doubly charged carbanions is known, some of which are classified as aromatic, such as the *sym*-dibenzcyclooctatetraene,[5] dibenzpentalene derivatives,[6] heptalene,[7] etc. Other doubly charged species, examplified by phenanthrene,[8] anthracene,[8,9] and pyrene[10] dianions, reveal an enhanced paratropic character. Recently, the class of polycyclic anionic systems was extended to include triply charged species—the triindene trianion[11] and even quadruply charged molecules such as the octalene[12] and the acepleiadylene[13] tetraanions.

Table I. ^{1}H NMR Chemical Shifts (ppm)[a] of 1, 1^{2-}, 2S, and 2A

system	δ	assignment[b]
1	8.31 (d, $J = 7.6$ Hz)	1, 3; 8, 10
	8.11 (t, $J = 7.6$ Hz)	2; 9
	8.20 (s)	5, 6, 12, 13
1^{2-}[c]	0.01 (d)	1, 3; 8, 10
	2.22 (t)	2; 9
	2.94 (s)	5, 6, 12, 13
2S	5.20 (m,[d] $J = 7.8$ Hz)	1, 2; 9, 10
	5.99 (m,[d] $J = 7.8$ Hz)	3; 8
	4.17 (d,[e] $J = 1.9$ Hz)	12, 13
	5.64[f]	5, 6
2A	5.42 (m,[d] $J = 7.5$ Hz)	1, 2; 8, 9
	5.82 (m,[d] $J = 7.5$ Hz)	3; 10
	5.64 (AB, $J = 5.4$ Hz)	5, 6; 12, 13

[a] Chemical shifts are recorded with respect to the solvent signals and then referred to SiMe$_4$. [b] The numbering[18a] is as shown in Scheme I. [c] Reference 10. [d] Parts of an ABK pattern assigned to protons 1, 2, 3 (8, 9, 10). [e] The doublet is due to coupling with protons 1, 10. [f] This absorption is assumed to be hidden under the signals of protons 5, 6, 12, 13.

We have shown previously[14] that a four-electron reduction of benzenoid hydrocarbon such as pyrene (**1**) and perylene (**7a**) is feasible. The two neutral hydrocarbons **1** and **7a** exhibit low-field ^{1}H NMR absorptions (Tables I and VII) rationalized by the existence of an enhanced peripheral diatropic ring current. These systems afford a nice example of the two approaches which were suggested to account for the aromaticity of polyfused conjugated

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