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Benzocyclobutenylidene—Cycloadditions, Reactivity, and Multiplicity[1]

Heinz Dürr* and Helmut Nickels

Fachbereich 14-Organische Chemie, Universität des Saarlandes, D 6600 Saarbrücken, West Germany

Luba A. Pacala and Maitland Jones, Jr.

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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EHT and CNDO/2 calculations on benzocyclobutenylidene (**6**) are described. Flash pyrolysis of the tosylhydrazone salt **7** affords benzocyclobutene and *o*-xylene in low yield, along with the formal syn and anti carbene dimers **13** and **14**. Condensed-phase reactions were achieved by photolysis of the salt **15**. Benzocyclobutenylidene (**6**) gave rise to the formal carbene dimers **17** and **18**. Insertion of carbene **6** into the carbon–hydrogen bonds of 2,3-dimethylbutane produced the benzocyclobutenes **20** and **21** (insertion ratio tertiary:primary = 9:1). Cycloaddition of **6** to olefins gave only spiro[3.2]hexene derivatives **22**. Multiplicity studies of **6** with cis or trans olefins indicated that **6** undergoes [1 + 2] cycloaddition in a stereospecific manner. Competition experiments using dienes and monoolefins implicate an equilibrium between singlet and triplet **6**. Further competition experiments with styrene/para-substituted styrene pairs demonstrated that **6** reacts faster with electron-poor styrenes. Possible explanations for this apparent anomaly are discussed.

This paper reports some reactions of benzocyclobutenylidenes. In such carbenes the constraints introduced by confining the carbene in a small rigid system may perturb the electronic properties of the divalent carbene and thus alter reactivity from that expected from simple phenylcarbenes.

Previous work is meager. Unsubstituted cyclobutenylidene (**1**) has been generated only once previously from the carbon-atom-mediated deoxygenation of cyclobutanone.[2] Vinylacetylene was found as the product. Perchlorocyclobutene and pentachlorocyclobutene have been subjected to halogen metal exchange and adducts noted.[3] Finally, Gaspar and co-workers have used the Bamford–Stevens reaction to generate 2-fluoro-3-phenyl-2-cyclobutenylidene and noted stereospecific addition to olefins.[4] These workers further found "normal" singlet behavior.

By analogy with the saturated carbene cyclobutanylidene (**2**), which is known to undergo both intramolecular insertion and ring contraction,[5] one might have hoped for methylenecyclopropene (**3**) or cyclobutadiene (**4**) formation from **1**. Such reactions have not been observed. The difficulty of these intramolecular processes apparently allows intermolecular reactions to compete favorably with the intramolecular ones.[2]

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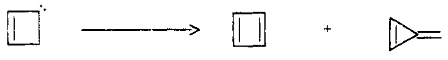

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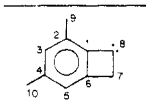
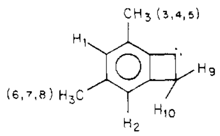
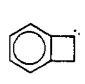
Table I. Charge Density Distribution in 6

	atom	EHT	CNDO for singlet 6	CNDO for triplet 6
 **6**	C_1	−0.0972	−0.0551	0.0390
	C_2	0.2135	0.0855	0.0298
	C_3	−0.2450	−0.0583	−0.0262
	C_4	0.2085	0.0882	0.0438
	C_5	−0.2031	−0.0606	−0.0189
	C_6	0.0985	0.0631	0.0241
	C_7	−0.0692	−0.0193	−0.0878
	C_8	−0.4990	−0.0888	−0.1365
	C_9	−0.3615	−0.0256	−0.0139
	C_{10}	−0.3622	−0.0228	−0.0142
 **6**	H_1	0.1061	−0.0081	−0.0068
	H_2	0.1024	−0.0203	−0.0135
	H_3	0.1240	0.0015	−0.0008
	H_4	0.1405	0.0119	0.0071
	H_5	0.1405	0.0119	0.0071
	H_6	0.1247	0.0003	−0.0014
	H_7	0.1490	0.0148	0.0086
	H_8	0.1409	0.0148	0.0086
	H_9	0.1484	0.0142	−0.0119
	H_{10}	0.1484	0.0142	−0.0119

The benzoannulated system of **1** (**5** and **6**) should have properties similar to those of the basic system. This fact, as well as the easier experimental access to **5** and **6**, has stimulated us to study these benzo derivatives of **1**. Only the early work of Blomquist and Heins[6] and the recent report by O'Leary and Wege[7] on an addition reaction to benzene exist to illuminate the properties of such species.



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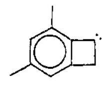

6

We describe here EHT and CNDO/2 calculations on **6**, flash pyrolytic generation of **5**, intermolecular reactions with olefins of the photochemically generated carbene **6**, and studies of reactivity, multiplicity, and electrophilicity/nucleophilicity of **6**.

Calculations. We have carried out semiempirical calculations (EHT, CNDO/2) for **6** to obtain information

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[1] Portions of this work have been previously communicated: Dürr, H.; Nickels, H.; Philippi, W. *Tetrahedron Lett.* **1978**, 4387. See also: Dürr, H.; Werndorf, F. *Angew. Chem., Int. Ed. Engl.* **1974**, *86*, 413. Dürr, H.; Fröhlich, S.; Kausch, M. *Tetrahedron Lett.* **1977**, 1767. For reviews see: Dürr, H. *Top. Curr. Chem.* **1973**, *40*, 103. Dürr, H. "Photochemie"; Houben-Weyl: Stuttgart, 1975; Vol. IV/5b, p 1158. Dürr, H. *Top. Curr. Chem.* **1975**, *55*, 87.

[2] Dyer, S. F.; Kammula, S.; Shevlin, P. B. *J. Am. Chem. Soc.* **1977**, *99*, 8104.

[3] Semmelhack, M. F.; DeFranco, R. J. *Tetrahedron Lett.* **1971**, 1061; *J. Am. Chem. Soc.* **1972**, *94*, 8838.

[4] Yue, V. T.; Courson, C. J.; Brinkman, M. R.; Gaspar, P. P. *J. Org. Chem.* **1978**, *43*, 4873.

[5] Rey, M.; Huber, U. A.; Dreiding, A. S. *Tetrahedron Lett.* **1968**, 3583.

[6] Blomquist, A. T.; Heins, C. F. *J. Org. Chem.* **1969**, *34*, 2906.

[7] O'Leary, M. A.; Wege, D. *Tetrahedron Lett.* **1978**, 2811.

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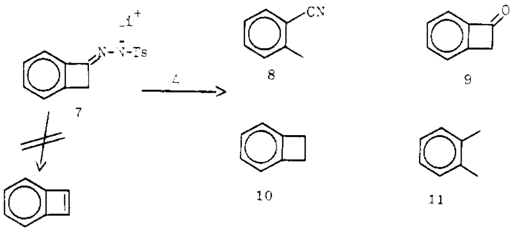
about the charge density at the carbene center and the σ/p splitting. The σ/p splitting allows conclusions to be made as to the most probable ground state of the carbene, and the calculated charge density at the divalent center can be used for predictions of nucleophilic or electrophilic behavior.[8]

The calculations demonstrate a slight excess of negative charge on C-8: EHT, −0.499; CNDO/2, −0.088 (singlet), −0.136 (triplet). This indicates a weakly nucleophilic character for **6** (Table I).

In addition, the energy difference ΔE between the carbene orbitals σ and p was calculated by EHT to be 0.56 eV. Thus **6** should have a triplet ground state σp.[8] By way of comparison, phenylcarbene itself is calculated to have an excess charge of −0.56 and a σ/p difference of 0.5 eV.[8] An MO diagram of **6** will be published elsewhere.[9]

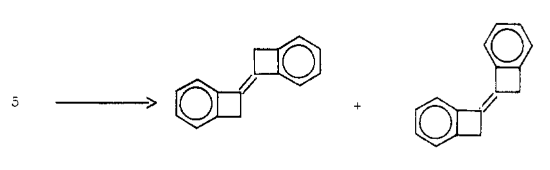
Flash Pyrolyses. In the hope of uncovering evidence for the elusive 1,2-insertion reaction in carbene **5**, we undertook a study of the flash pyrolysis of the lithium salt of benzocyclobutenone tosylhydrazone (**7**). We hoped that the insertion reaction would be favored by the gas phase, in which competing intermolecular reactions should be minimized.

Salt **7** was prepared according to standard procedures from the readily accessible benzocyclobutenone. Pyrolysis at 350 °C led to two isolable low-boiling products, **8** and **9**, in about 5% yield each. Gas chromatographic analysis on a 2 m 15% SE 30 on Chromosorb W column at 130 °C revealed additional traces (less than 1%) of benzocyclobutene (**10**) and *o*-xylene (**11**). Compounds **8** and **9** were shown by comparison of spectra with those of known samples to be *o*-toluonitrile (**8**) and benzocyclobutenone (**9**), respectively.



Nitrile **8** may be formed through pyrolysis of benzocyclobutenone azine (**12**), which could easily be produced by reaction of **5** with diazo compound made by pyrolysis of the tosylhydrazone salt. Although ketazines are known[10] to form nitriles on pyrolysis and reasonable mechanisms can be written for this case, flash pyrolysis of authentic azine does not give **8** or **9** under our conditions. However, in the carbene reaction **12** would be formed in an exothermic reaction of **5** with its precursor, and we cannot be certain that a simple pyrolysis of **12** is a sufficiently close model. We tentatively attribute the formation of ketone **9** to the reaction between the carbene and the tosyl group in either an inter- or an intramolecular fashion.

When the reaction mixture was first fractionated on a neutral alumina column (activity grade I, hexane eluent) and then examined by gas chromatography at higher temperature (4 m, 10% PMPE on Chromosorb W column at 230 °C), two new products, **13** and **14**, were obtained in equal amounts. Although the retention times of **13** and **14** approximated that of authentic benzocyclobutadiene dimer prepared by the method of Cava and Napier[11] from a sample of dibromobenzocyclobutene, examination of spectra revealed that neither **13** nor **14** was in fact the sought-after dimer. The two compounds are instead the formal dimers of carbene **5**. No trace of benzocyclobutadiene dimer could be detected. The formation of the dimers can be reasonably attributed either to reaction of **5** with the diazo compound formed from pyrolysis of the tosylhydrazone salt **7** or even to dimerization of the carbene **5**.



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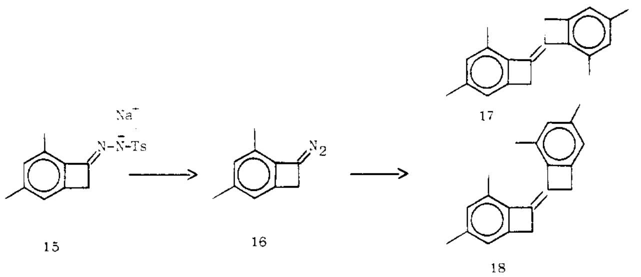
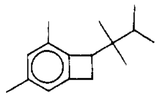
Condensed-Phase Reactions. In the condensed phase one expects inter- rather than intramolecular reactions. The generation of **6** was achieved by irradiating suspensions of sodium salt **15** in the presence of suitable substrates (alkanes, alkenes). Salt **15** was prepared according to the procedure of Blomquist and Heins.[6] In the photolysis of **15** in benzene an intermediate (UV λ_{max} 333, 320 nm, red solution; IR 2100 cm^{-1}) can be detected. It is likely to be 4,6-dimethyldiazobenzocyclobutene (**16**) since the compounds derived from **6** do not show UV absorptions above 300 nm. After removal of the solvent and chromatography of the photolysate on silica gel, **17** and **18** were isolated in an overall yield of 32%. The isomer ratio was determined by high pressure LC (Al_2O_3, dry *n*-heptane) to be **17**:**18** = 7:3. Catalytic hydrogenation (Pd/C) of **17** and **18** to the dihydroproduct **19** (88% yield) excluded the formation of a dimerization product of dimethylbenzocyclobutadiene.



Reactivity. In order to study the reactivity of carbene **6**, the relative tertiary:primary carbon–hydrogen insertion ratio was determined.[12] Photolysis of **15** in 2,3-dimethylbutane afforded the expected insertion products **20** and **21** in an overall yield of 4.2% (**17** and **18**, 45%). The structural assignment of **20** and **21** was based on elemental analysis and infrared and NMR spectroscopy (see Experimental Section).



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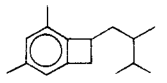

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The ratio **20**/**21** was determined by high pressure LC (reversed phase, acetonitrile). Corrected for statistical factors, insertion occurred 9.0 times more often at the tertiary than the primary carbon–hydrogen bonds of 2,3-dimethylbutane. This insertion selectivity shows **6** to be somewhat more discriminating than cyclopentadienylidene

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[8] Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

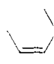
[9] Kausch, M.; Dürr, H., in preparation. Kausch, M. Ph.D. Dissertation, University of Saarbrücken, 1977.

[10] Buu-Hoi, N. P.; Sanit, G. *Bull. Soc. Chim. Fr.* **1967**, 955.

[11] Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1956**, *78*, 500; **1957**, *79*, 1701. We thank D. W. Brown for a sample of the dibromo compound.

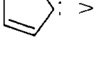
[12] Moss, R. A. *J. Org. Chem.* **1966**, *31*, 3296.

Table II. Addition of 6 to Olefins

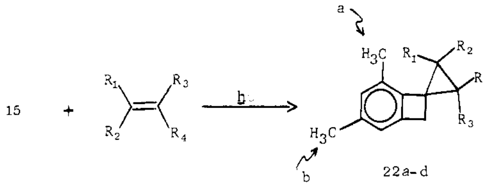
	reaction partner	yield, %	
		17 + 18	22
22a		trace	55[a]
22b		trace	58[a]
22c		7-8	61[a]
22d		10-11	38-40[a]

[a] bp 70 °C (10^{-3} torr).

(7.32). Further, carbon-hydrogen insertion is not observed when 6 reacts with olefins. These data allow us to place 6 between cyclopentadienylidene and phenylcarbene in a reactivity sequence.

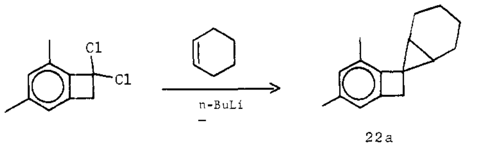
$:CH_2 > :CHCO_2R >$  $> 6 >$ phenylcarbene[1,13]

[1 + 2] Cycloaddition of 6. Carbene 6 was generated photochemically in various olefins in order to study intermolecular reactions in more detail. After chromatography on silica gel using petroleum ether as eluent (Table II), the crude reaction mixtures were carefully analyzed by NMR in order to detect insertion products (vinylic region). However, no signals in the olefinic range were detected. All addition products were characterized by elemental analysis and spectroscopy and found to be stable under the conditions of formation.



Mass spectra and elemental analysis showed that the products were 1:1 carbene-olefin adducts. The IR spectra exhibit the cyclopropane ring stretching at 1000 and 1030 cm^{-1}. The NMR spectra are summarized in Table III.

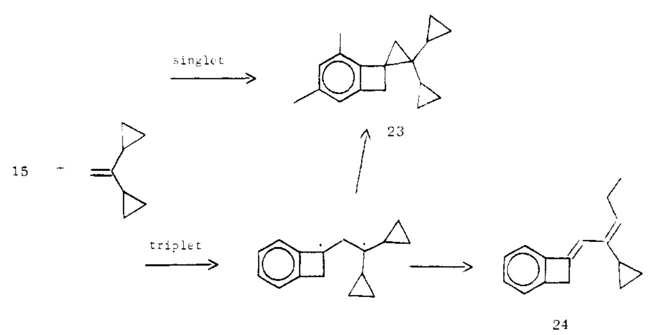
Adduct 22a is also accessible via a carbenoid intermediate. Treatment of the dichlorobenzocyclobutene with *n*-butyllithium at −40 °C in ether/cyclohexene led to a fraction obtained from the reaction mixture by short-path distillation (98 °C (10^{-1} torr)) containing 22a (25%).



Stereospecificity Studies. The stereochemistry of the addition of 6 to olefins was investigated in order to gain information regarding the spin state of the reacting carbene 6 at ambient temperature. According to the hypothesis of Skell[14] and the calculations of Hoffmann[8] and Dewar,[15] a singlet carbene should yield a cyclopropane retaining the stereochemistry of the olefin, whereas the triplet should add with loss of the original stereochemical relationship.

The [1 + 2] cycloaddition of 6 to *cis*-4-methyl-2-pentene (see Table IV) afforded only *cis*-**22c**, and *trans*-4-methyl-2-pentene gave only *trans*-**22d**. A mixture of **22c** and **22d** could be separated by high pressure LC (Al_2O_3, dry *n*-heptane), and the NMR spectra of **22c** and **22d** show characteristic differences. In addition to chemical shift differences in the case of the trans addition products, **22d**, the cyclobutene CH_2 group gives rise to a pair of AB systems in the ratio of 2:1. In the cis product, **22c**, the NMR spectrum exhibits a broadened singlet. Thus the addition of 6 to cis and trans olefins was shown to proceed stereospecifically within the limits of detection, which were ca. 3% of the "wrong" stereoisomer.

In order to probe the stereospecificity of the cycloaddition of 6 with another technique,[16] 1,1-dicyclopropylethylene was used as olefinic substrate. A triplet species can be expected to generate a biradical intermeidate, which may either cyclize to 23 or rearrange to 24.



Since this kind of rearrangement has been shown to be a very fast process (10^8 s^{-1} at 30 °C),[16] it can often compete with radical recombination processes. The singlet carbene should, however, add in a direct fashion, leading to 23 as the only product.

A suspension of 15 in 1,1-dicyclopropylethylene was therefore irradiated under the usual conditions. After careful workup (column chromatography) only 23 (and no trace of 24 or other olefinic compound) was isolated. The crude reaction mixture was studied by NMR spectroscopy, and no olefinic protons could be detected. High pressure LC (Al_2O_3, dry *n*-heptane) showed the formation of but a single product. Yet it is known from the reaction of 1,1-dicyclopropylethylene with diphenylcarbene that this test is less sensitive than the studies of stereochemistry with cis or trans olefins. Therefore, the results of these experiments do not absolutely allow the conclusion that the singlet carbene is the only reacting species. Further, there could be a singlet-triplet equilibrium, which has been postulated for arylcarbenes such as phenylcarbene, methylphenylcarbene, and diphenylcarbene, with the singlet being more reactive in these cases.[17,18]

Photolysis of 15 in the presence of sensitizers (xanthone and *m*-methoxyacetophenone) gave no unambiguous result. The same products as in the direct irradiation were isolated. It may be possible that the sensitization—triplet energy transfer—was not effective under the conditions employed or that the two spin states are in equilibrium.

Competition experiments were carried out to probe further the question of the multiplicity of the reacting intermediate. Thus 15 was photolyzed in equimolar mixtures of 2-methyl-1-butene with diphenylethylene or

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(13) Closs, G. L.; Coyle, J. J. *J. Am. Chem. Soc.* **1965**, *87*, 4270.

(14) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496, 6427.

(15) Dewar, M. J. S.; Hadden, R. C.; Weiner, P. K. *J. Am. Chem. Soc.* **1974**, *96*, 253.

(16) Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6451.

(17) Gaspar, P. P. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. 2, Chapter 6.

(18) Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193.

Table III. NMR Spectra (δ) of 22a-d[a]

	H_a, H_b	H_c, H_d	CH_3 (a)	CH_3 (b)[b]	R_1, R_2, R_3, R_4
22a	6.82 (2) [s]	3.08 (2) [s]	2.00 (3) [s]	2.31 (3) [s]	1.0-2.3 (10) [m]
22b	6.82 (2) [s]	2.9 (2) [s]	2.18 (3) [s]	2.31 (3) [s]	1.08-1.35 (10) [m]
22c[c]	6.73 (2) [s]	2.99 (2) [s]	2.01, 2.28 (3) [s]	2.28 (3) [s]	0.80-1.60 (12) [m]
22d[c]	6.72 (2) [s]	3.02-3.08 (2) [2AB, 6]	2.15, 2.13, 2.11 (3) [s]	2.28 (3) [s]	0.80-1.80 (12) [m]

[a] Number of protons in parentheses, multiplicity and coupling constants in brackets. [b] The relatively constant position of the lower field methyl signal identifies it as that belonging to CH_3 (b). Two cis adducts and two trans adducts are apparently found as indicated by the multiple signals observed. [c] Formed as a mixture of syn and anti isomers.

Table IV. Stereochemistry of the Addition of 6 to *cis*- and *trans*-4-Methyl-2-pentenes

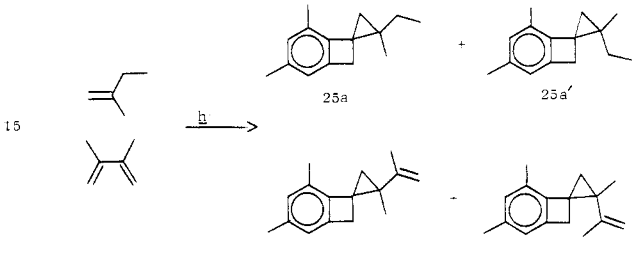
olefin	yield, %	% cis adducts	% trans adducts
cis-4-methyl-2-pentene	61	≥97	≤3
	60		
trans-4-methyl-2-pentene	38	≤3	≥97
	40		

Table V. Yield and Syn/Anti Ratio of Adducts 22e-i

	X	yield, %	syn[a]/anti[b]	mp[c]
22e	H	57.7	0.20	65-66
22f	*m*-Br	8.0	0.37	
22g	*p*-Cl	27.0	0.74	80-82
22h	*p*-CH_3	45.5	0.20	71-72
22i	*p*-OCH_3	10.9	0.29	84-84

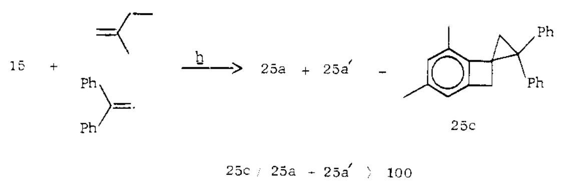
[a] Only syn 22h could be isolated by preparative TLC. [b] Anti isomers 22e,g,i were isolated by TLC; 22f could only be identified in the reaction mixture. [c] Of anti isomers.

2,3-dimethyl-1,3-butadiene. These dienes are known to be efficient scavengers for triplet species.[17]



Adducts **25b** and **25b′** could be separated by column chromatography on silica gel by using petroleum ether. Careful analysis of the reaction mixture by NMR and high pressure LC provided the following data [conditions, (**25b** + **25b′**)/(**25a** + **25a′**)]: direct photolysis, 17.0; photolysis in the presence of *m*-methoxyacetophenone, 19.0; photolysis in O_2 atmosphere, 10.0.

The analogous competition using diphenylethylene led to ratios in excess of 100. This is typical triplet behavior,



and the combination of stereospecific addition to olefins and highly preferred addition to dienes is most suggestive of a singlet/triplet equilibrium in which the products are determined by the relative magnitudes of the singlet and triplet rates.

Nucleophilicity or Electrophilicity of 6. In order to probe the question of nucleophilicity or electrophilicity, a study of the relative rates of addition of **6** to substituted styrenes was carried out. Only if the addition reaction is stereospecific does this study allow firm conclusions as to the nucleophilicity or electrophilicity of **6**. Photolysis of **15** in styrenes was carried out as described above, and after workup the syn and anti isomers of **22e–i** were isolated in the ratios given in Table V. The ratios were determined by NMR and high pressure LC (SiO_2, *n*-heptane).

Table VI. Relative Rate Constants for the Addition of 6 to Styrenes

substituent	k_{rel} (k_X/k_H)	σ
m-Br	3.96	0.39
p-Cl	2.41	0.23
H	1.00	0.00
p-CH_3	0.73	−0.17
p-OCH_3	0.30	−0.27

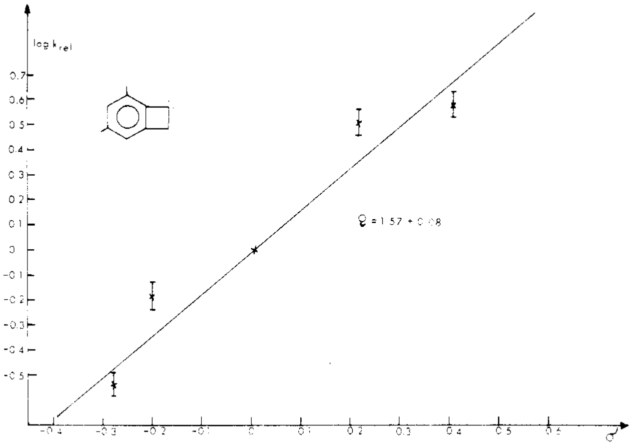
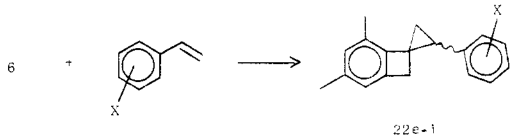


Figure 1.



Structural assignments of **22e–i** are based mainly on spectroscopy. The CH_2 group of the four-membered ring appears as an AB system in the NMR spectrum, and the cyclopropyl protons appear as an ABX system. Chemical shifts and coupling constants of the ABX systems were calculated with the aid of the program LAOCOON/3[19] and are as indicated for *anti*-**22e**: ν_A = 1.53 ppm, J_{AB} = 6.00 Hz; ν_B = 1.76 ppm, J_{AX} = 7.73 Hz; ν_X = 2.65 ppm, J_{BX} = 7.16 Hz. Because of the anisotropic effect of the phenyl group, the CH_3 (a) resonance is shifted upfield in the case of the syn isomers (~1 ppm).

Competition experiments were carried out to determine the relative reactivities (k_{rel}) by irradiating suspensions of **15** at 16 °C in equimolar amounts of styrene and substi-

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(19) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

tuted styrenes (Table VI) in a tenfold excess. The relative ratio of styrenes and products (**22**) was shown to be constant during the course of the photolysis. The k_{rel} values were then calculated by

$$k_{\text{rel}} = \frac{k_X}{k_H} = \frac{p_X}{p_H}$$

where p_X and p_H are the mole fractions of adducts derived from styrene (H) and substituted styrene (X). The product ratio was determined by high pressure LC (SiO_2, *n*-heptane, <5-ppm H_2O). The relative rate constants were correlated with σ parameters according to Hammett. The ρ value of this Hammett plot was calculated by a least-squares analysis to be $\rho = 1.57 \pm 0.08$ (Figure 1). The correlation coefficient is 0.965. If the stereospecificity of the addition to styrenes were complete (which is the case with *cis*- or *trans*-4-methyl-2-pentene), **6** would be expected to be highly nucleophilic. On the other hand, it is known that styrenes are efficient scavengers for triplet species,[17,21] a fact which complicates the interpretation of the highly positive ρ value.

Indeed, we ourselves have shown that it is very likely that triplets are involved in the reactions of **6** with dienes and styrenes. How then can one account for the large positive ρ value? There seem to be only two possibilities. Either **6** is one of the most nucleophilic carbenes known or another intermediate is involved. Perhaps the diazo compound formed on irradiation of the sodium salt is adding with loss of nitrogen to form the cyclopropanes. As there is no evidence that simple phenylcarbenes are nucleophilic, and as **6** shows no tendency to add to electron-deficient olefins such as cyanoethylene or diethyl maleate, it is difficult to credit the first possibility. Additions of diazo compounds to styrenes do yield positive ρ values. For instance, 9-diazoxanthene gives a ρ of 0.97 ± 0.05.[22]

Discussion and Summary

The reactions of benzocyclobutenylidenes **5** and **6** show that these carbenes undergo predominant dimerization in the gas phase and intermolecular reactions in solution. Our investigations have demonstrated that benzocyclobutenylidene does not produce insertion product very easily, or, in other words, it prefers to undergo addition reactions if possible. That means that **6** (as well as **5**) is a carbene with rather high selectivity.

The cycloaddition of **6** with cis or trans olefins demonstrates that addition is stereospecific and implicates the singlet carbene as the reactive species.

Thus benzocyclobutenylidene (**6**) resembles cyclopentadienylidenes,[23] cyclohexadienylidene,[24] and cycloheptatrienylidene,[25] which also add in a stereospecific manner. An experiment to generate triplet **6** by sensitization did not change the stereospecificity of the reaction. It is probable that a singlet/triplet equilibrium exists (see also ref 26).

Another point which should be mentioned here is the stereoselectivity of the [1 + 2] cycloadditions observed for **6**. Table V gives the syn/anti ratios derived from cycloaddition reactions of **6** with different styrenes. Of course these ratios are different from **1**. From Table V it appears that steric factors are responsible for the different syn/anti ratios in the cycloadditions of **6**.

Most remarkable is the large positive ρ value determined by our competition studies. Benzocyclobutenylidene (**6**) shows the largest positive ρ ever determined in a simple addition reaction, surpassing even that of cycloheptatrienylidene (1.05).[27] A number of considerations reduce our ability to interpret this value. First, **6**, both by calculation and experiment, has been shown to be similar to simple phenylcarbenes. Although it does not undergo intramolecular 1,2 carbon–hydrogen insertion as does methylphenylcarbene, the nature of the expected product makes this not surprising. There is no indication in the chemistry of phenylcarbenes of nucleophilic behavior, but the crucial determination of a ρ value seems not to have been made. Second, styrene is an excellent triplet trap, and even though we have shown that the reacting species with simple olefins is the singlet, it is probable that with styrenes the triplet would be more reactive than the singlet. Finally, it is quite possible that we are observing an addition of diazo compound.

Experimental Section

General Procedures. Melting points are uncorrected. The NMR spectra were recorded on Varian A-60, XO-100, and Bruker HX 90 spectrometers in $CDCl_3$ with tetramethylsilane as internal standard. IR spectra were determined on a Beckman IR 4230 or Perkin-Elmer 237B or 283 instrument. Chemical ionization mass spectra were recorded at the Cornell mass spectrometry facility (Ithaca, NY) on an AEI-MS-902 spectrometer with an SRI chemical ionization source. GC mass spectra were obtained on a Varian Aerograph series 1400 gas chromatograph combined with a Du Pont Instruments 21-490 mass spectrometer. The high pressure LC measurements were carried out on a self-made apparatus using a UV detector (254 nm) and a refractometer. The eluant was *n*-heptane, distilled and dried over Al_2O_3 (<5-ppm H_2O) and acetonitrile. As stationary phases, Al_2O_3 (Woelm 5 μm), Spherisorb Alumina 5 μm, and reversed phase were used. The column dimensions were 30, 20, and 15 cm × 4 mm. The pressure was varied between 30 and 120 atm. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. UV spectra were recorded on a Cary 14 spectrophotometer. Photolyses were carried out in an immersion irradiation apparatus using nitrogen as protecting gas. The irradiations were carried out with a mercury high pressure lamp (Hanovia 450 W) using a Pyrex filter ($\lambda \geq$ 290 nm) or a $CuSO_4$ solution ($\lambda \geq 360$ nm). Before the irradiation, solutions were flushed for 20 min with dry, oxygen-free nitrogen. The progress of the reaction was followed by measuring the nitrogen evolution. After evaporation of solvent, products were separated on silica gel columns (Merck: 0.02–0.05 m) with an automatic fraction collector.

Benzenediazoniumcarboxylate Hydrochloride. Anthranilic acid (27.5 g, 0.201 mol) (Matheson, practical grade) was dissolved in 300 mL of absolute ethanol in a 1-L beaker. The magnetically stirred solution was cooled to 4 °C in an ice bath. To this cold solution was added 20 mL of concentrated HCl, followed by 50 mL of cold isoamyl nitrite (Aldrich) (0.374 mol). The dark solution was stirred for 10 min in an ice bath. Ether (300 mL) was added and the stirring continued for an additional 5 min. The yellow crystals were isolated by suction filtration and were washed with 100 mL of ether: yield, 33.5 g (0.182 mol), 90.6%. The pale yellow crystals turn pink on exposure to moisture.

1,1-Dichlorobenzocyclobutene. A 1-L flask was charged with benzenediazoniumcarboxylate hydrochloride (33.54 g, 0.18 mol),

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(20) Doering, W. von E.; Henderson, W. A. *J. Am. Chem. Soc.* **1958**, *80*, 5274.

(21) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4015.

(22) Jones, G. W.; Chang, K. T.; Munjal, R.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 2922.

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(24) Jones, M., Jr.; Harrison, A. M.; Rettig, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 7462.

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(26) Dürr, H.; Bujnoch, W. *Tetrahedron Lett.* **1973**, 1433.

(27) Christensen, L. W.; Waali, E. E.; Jones, W. M. *J. Am. Chem. Soc.* **1972**, *94*, 2118.

1,2-dichloroethane (400 mL), propylene oxide (25 mL), and freshly distilled 1,1-dichloroethylene (118 mL, 143 g, 1.47 mol). The flask was fitted with a water-cooled reflux condenser and a gas bubbler, and the mixture was refluxed overnight. The reaction mixture was cooled to room temperature, and the tan precipitate was removed by suction filtration, leaving a dark brown solution. The solvents were removed under reduced pressure to give a crude dark brown product used directly in the next step: NMR (CCl_4/Me_4Si) δ 7.45–7.26 (m, 3.8 H), 3.65 (s, 2.0 H); IR (neat) 2932, 1448, 1457, 993, 911 cm^{-1}.

Benzocyclobutenone. The crude 1,1-dichlorobenzocyclobutene was refluxed for 24 h with 100 mL of 3% aqueous sulfuric acid. The brown mixture was cooled to room temperature, and the organic phase was removed. The dark aqueous layer was extracted with ether (4 × 50 mL). The ether extracts were added to the organic layer, and the combined ether layers were washed with 50 mL of saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate. The ether was removed on the rotary evaporator. Distillation under reduced pressure yielded 9.90 g (0.075 mol) of a colorless liquid: yield, 41.5% from the salt; bp 50 °C (0.1 mm); NMR (CCl_4/Me_4Si) δ 7.25–7.77 (m, 4 H), 3.89 (s, 2 H); IR (neat) 1775, 1755, 760, 955, 1140, 1460, 1580, 2340 cm^{-1}.

Benzocyclobutenone Tosylhydrazone. Benzocyclobutenone (1.02 g, 0.0086 mol) was dissolved in 15 mL of methanol. To this was added an equivalent amount (1.61 g, 0.0086 mol) of *p*-toluenesulfonylhydrazine. The mixture was stirred until the tosylhydrazine dissolved to give a pale yellow solution. After the mixture stood undisturbed at room temperature for approximately 10 min, precipitation of white crystals began. The crystals were collected by suction filtration and air-dried (1.68 g, 0.0059 mol): yield, 68.0%; mp 152 °C dec. Discoloration began at 148 °C.

The mother liquor was concentrated on the rotary evaporator, and a second crop of white crystals was collected (0.37 g): mp 152 °C dec; total yield 83.4%. Third crop, 0.17 g; total yield 89.8%. NMR ($CDCl_3/Me_4Si$) δ 8.05–7.22 (m, 8 H), 3.78 (dd, 2 H), 2.41 (s, 3 H).

Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.94; N, 9.78. Found: C, 62.93; H, 4.95; N, 9.77.

Sodium Salt of Benzocyclobutenone Tosylhydrazone.[28] Benzocyclobutenone tosylhydrazone (1.00 g, 0.0035 mol) was placed in a 100-mL round-bottomed flask. Ether was added (25 mL) and the mixture was stirred at room temperature. The tosylhydrazone did not dissolve completely. Sodium hydride (57% in mineral oil) (0.1567 g of suspension = 0.0898 g of sodium hydride, 0.0037 mol) was added. The mixture was stirred under nitrogen for 11 h. The white precipitate was isolated by filtration under a nitrogen atmosphere and dried overnight in a vacuum desiccator.

Lithium Salt of Benzocyclobutenone Tosylhydrazone. The tosylhydrazone (1.00 g, 0.0035 mol) was dissolved in THF (30 mL) and cooled to dry ice/acetone temperature. The solution was stirred under nitrogen for 30 min at this temperature. Butyllithium (0.00349 mol, 2.18 mL) was added dropwise with stirring over a period of 15 min. Addition of each drop of butyllithium resulted in localized purple color which disappeared after stirring. After the addition of butyllithium was complete, the mixture was stirred at −78 °C for 30 min. The mixture was then warmed to room temperature, still under a nitrogen atmosphere. The solvents were removed on the rotary evaporator, and drying was completed on a vacuum line. The resulting product was a yellow powder (1.157 g (0.00395 mol) > 100%). Extensive pumping on the vacuum line did not remove all the THF, accounting for the unusually high yield.

Pyrolysis of the Tosylhydrazone Salts of Benzocyclobutenone. Pyrolyses of the dry tosylhydrazone salts (sodium or lithium) were carried out at 350–370 °C over the course of 1–2 h at a reduced pressure of 0.05–0.1 torr. No more than 1.5 g of a salt could be pyrolyzed during any one run since the residue which accumulates at the bottom of the pyrolysis flask serves as an insulator and subsequent additions are not "flash" pyrolyzed but only heated slowly. Immediately after each addition the pressure in the system rose. The next addition was not made until the system had been pumped down to its original pressure. The products, usually yellow or tan in color, were trapped on a cold finger maintained at −196 °C. They were isolated by washing the cold finger with diethyl ether or carbon tetrachloride. Insoluble solids were removed by filtration through glass wool. Injection of the mixture of pyrolysis products onto a 15-ft 20% SE-30 (Chromosorb W) column (column temperature 130 °C, detector temperature 225 °C) permitted isolation of the volatile products.

Elution of the crude product through a column of aluminum oxide (eluent, 90:10 hexane/ether) yielded an unidentified yellow oil and a yellowish solid. Dissolution of this yellowish solid in ether and injection into the gas chromatograph (4-ft 10% PMPE-5 ring column at 232 °C) separated the sample into two components. Both samples were cream-colored solids which showed a parent ion of 204 in the CI mass spectrum. A ^1H NMR spectrum of the first peak was very similar to that obtained for the second. First peak: NMR (CCl_4/Me_4Si) δ 3.75 (s), 7.08–7.17 (m); IR (CCl_4) 2950, 1585, 1474, 1421, 1285, 1249, 1211, 870, 770, 690 cm^{-1}. Second peak: NMR (CCl_4/Me_4Si) δ 3.95 (s), 7.10–7.27 (m); IR (CCl_4) 2956, 1588, 1478, 1448, 1251, 1215, 1141, 866, 770, 694 cm^{-1}. The results were similar to those obtained by Blomquist and Heins.[6] On the basis of the NMR spectra and the mass spectra, the two fractions were identified as the syn and anti isomers of the carbene dimer. Infrared data were of no use in distinguishing the two isomers.

Benzocyclobutenone Azine. Benzocyclobutenone (1.00 g, 0.0085 mol) was dissolved in 5 mL of butanol, and a solution of hydrazine (0.1428 g, 0.0042 mol) (95%) in 5 mL of butanol was added. The solution was heated to reflux and then stirred at room temperature for 3 h. Only a small amount of solid formed. The mixture was then refluxed for an additional hour and stirred at room temperature overnight. The yellow crystals were isolated by suction filtration. The product was recrystallized from ethanol: yield, 0.6323 g (64.4%); mp 154–156 °C.

Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.72; H, 5.22; N, 12.11. Found: C, 82.51; H, 5.23; N, 12.00.

Pyrolysis of Benzocyclobutenone Azine. Ketazine (0.537 g, 0.00231 mol) was pyrolyzed at 350 °C at 0.5 torr. No pressure change was observed during the course of the pyrolysis. The small amount of solid collected on the cold finger was washed off with ether. The ether was removed under reduced pressure to yield 0.0750 g of a pale yellow powder. A considerable amount of yellow solid was found in the bottom of the pyrolysis flask. The IR spectrum of the residue in the pyrolysis flask was identical with that of azine.

1,1′-Bis(4,6-dimethylbenzocyclobutenylidene) (17 and 18). Compound **15** (3.37 g, 0.01 mol) prepared from the corresponding tosylhydrazone and NaH in THF was suspended in benzene (300 mL) and irradiated for 2 h by using a Hanovia 450-W medium-pressure Hg lamp (Pyrex filter). After filtration the solvent was evaporated. The crude crystals thus formed were recrystallized from $CHCl_3$/acetone to yield **17** and **18** as colorless plates (410 mg, 32%): mp 187–189 °C (lit.[6] mp 189 °C); NMR δ 2.32 (s, 12 H), 3.73 (s, 4 H), 6.77 (s, 4 H); IR (film) 1705 cm^{-1} (w) (C=C stretching band); mass spectrum, *m/e* 260 (M^+, 100%), 245 ($M^+ - CH^3$, 80%), 230 (245 − CH_3, 80%).

Anal. Calcd for $C_{20}H_{20}$: C, 92.27; H, 7.74. Found: C, 92.60; H, 7.72.

Separation of **17** and **18** was achieved by high pressure LC (Spherisorb Alumina 5 μm, *n*-heptane): retention time, 7.80 min (**17**); 7.10 min (**18**); column, 20 × 0.4 cm; 100-atm pressure.

4,4′,6,6′-Tetramethyl-1,1′-bis(benzocyclobutenyl) (19). Compounds **17** and **18** (70 mg, 0.65 mmol) were dissolved in benzene (50 mL). Concentrated $HClO_4$ (1 mL) and 300 mg of Pd/C were added. After 5 h of hydrogenation and filtration the benzene was evaporated. Recrystallization of the residue from pentane gave **19** as colorless needles (150 mg, 88%): mp 126–128 °C; NMR δ 2.18 (s, 6 H), 2.28 (s, 6 H), 2.40–3.20 (m, 6 H), 6.74 (s, 2 H), 6.83 (s, 2 H); IR (film) 1380 cm^{-1} (m, CH_3).

Anal. Calcd for $C_{20}H_{22}$: C, 91.54; H, 8.45. Found: C, 91.50; H, 8.58.

1-(1,1,2-Trimethylpropyl)-4,6-dimethylbenzocyclobutene (20) and 1-(2,3-Dimethylbutyl)-4,6-dimethylbenzocyclobutene (21). Photolysis of 2.670 g (7.7 mmol) of **15** in 2,3-dimethylbutane afforded, after chromatography on silica gel with petroleum ether, 70 mg (4.2%) of **20** and **21** as a high-boiling liquid

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[28] Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* 1972, *94*, 1655.

Table VII. Preparation and Analytical Data of Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′-phenylcyclopropanes] (22e–i)

	% N_2 evolution	irradiation time, h	formula	elemental analysis calcd C	calcd H	found C	found H	mass spectrum [M^+ (%)]
22e	86	3.5	$C_{18}H_{18}$	92.26	7.74	92.00	7.80	(22)
22f	32	6	$C_{18}H_{17}Br$	69.00	5.43	69.00	5.52	(100)
22g	69	7.5	$C_{18}H_{17}Cl$	80.59	6.33	80.10	6.31	
22h	78	7.5	$C_{19}H_{20}$	91.88	8.12	92.20	8.06	(65)
22i	40	8	$C_{19}H_{20}O$	86.32	7.63	86.60	7.55	(4)

which could be separated with high pressure LC (reversed phase, acetonitrile): retention time (column; 15 × 0.4 cm; 80 atm), 5.8 min (**20**), 5.1 min (**21**); ratio of isomers, **20**/**21** = 3/2; NMR δ 0.70–1.00 (m, 13 H), 2.22 (s, 3 H), 2.28 (s, 3 H), 2.90 (d, 2 H, J = 6 Hz), 3.58 (m, 1 H), 6.70 (s, 1 H), 6.78 (s, 1 H); IR (film) 2280 (s), 2940 (s), 2980 (s), 1370, 1380, and 1390 cm^{-1} (m, CH_3).

Anal. Calcd for $C_{16}H_{24}$: C, 88.50; H, 11.18. Found: C, 89.05; H, 11.23.

In addition, 0.450 g (45%) of a mixture of **17** and **18** was eluted.

Photolysis of 4,6-Dimethylbenzocyclobutenone Tosylhydrazone Sodium Salt (15) in Olefins. General Procedure. Compound **15** (3.370 g, 0.01 mol) was dissolved in 350 mL of olefin and photolyzed under N_2. The excess olefin was evaporated (after filtration) and the residue subjected to chromatography on silica gel.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′,3′-tetramethylenecyclopropane] (22a). Photolysis of **15** in cyclohexane (94% N_2) gave after workup 1.10 g (55%) of **22a** as a colorless liquid. Purification by distillation at 70 °C (10^{-3} torr): IR (film) 1000 (w), 1040 (w) cm^{-1}; mass spectrum (room temperature), m/e 212 (M^+, 44%), 198 [$(M - CH_2)^+$, 20%], 183 [$(M - C_2H_5)^+$, 10%], 169 [$(198 - C_2H_5)^+$, 100].

Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.60; H, 9.43.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′,2′,3′-trimethylcyclopropane] (22b). Irradiation of **15** in 2-methyl-2-butene (92% N_2) afforded after workup 1.15 g (58%) of **22b** as a colorless liquid (purified by distillation): IR (film) 1000 (m), 1030 (m) cm^{-1}; mass spectrum (room temperature), m/e 200 (M^+, 80%); 185 ($M^+ - CH_3$, 100).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.10; H, 10.03.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-*cis*-2′-methyl-3′-isopropylcyclopropane] (22c). Irradiation of **15** in *cis*-4-methyl-2-pentene (96% N_2) gave 1.35 g (61%) of **22c** as a colorless liquid (distillation): IR (film) 1040 (w), 1360, 1380 (s) cm^{-1}; mass spectrum (room temperature), m/e 199 ($M^+ - CH_3$, 14).

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.60; H, 10.43.

syn- and *anti*-**22d** were separated by high pressure LC. In addition, **17** and **18** were obtained in 8% yield (0.10 g).

Spiro[4,6-dimethylbenzocyclobutene-1,1′-*trans*-2′-methyl-3′-isopropylcyclopropane] (22d). Photolysis of **15** in *trans*-4-methyl-2-pentene afforded after workup 0.800 g (38%) of **22d** as a colorless oil: IR (film) 1010, 1035 (w), 1360, 1380 cm^{-1}.

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.40; H, 10.30.

In addition to **22d**, crystals of **17** and **18** (0.14 g, 11%) were isolated.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′,2′-dicyclopropylcyclopropane] (23). Photolysis of **15** in dicyclopropylethylene (prepared from dicyclopropyl ketone and methylenetriphenylphosphine) gave 320 mg (21%) of **23** (oil): NMR δ 0.2–1.3 (m, 10 H), 2.2 (s, 3 H), 2.3 (s, 3 H), 3.15 (AB, 2 H, J = 14 Hz), 6.8 (s, 1 H); mass spectrum, m/e (rel intensity) 238 (100).

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 89.90; H, 9.27.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′-phenylcyclopropanes] (22e–i). General Procedure. Compound **15** (2.00 g, 6.4 mmol) was irradiated in 350 mL of styrene or para-substituted styrenes until the end of N_2 evolution. After removal of styrenes under vacuum, the residue was subjected to chromatography on silica gel. The addition products **22e–i** were eluted with petroleum ether (40–80 °C). Purification of the adducts **22e–i** was achieved by preparative TLC (see also Tables V, VI, and VII).

Photolysis in Dimethyl Maleate. Irradiation of **15** in dimethyl maleate afforded, after removal of the solvent and chromatography on silica gel (petroleum ether), 200 mg of **17** and **18** (24%). Elution with a mixture of petroleum ether/ethyl acetate (1:1) gave 150 mg of 4,6-dimethylbenzocyclobutenone azine (18%): mp 166–168 °C; IR (KBr) 1680 (m) cm^{-1} (C=N); mass spectrum, m/e 288 (M^+, 100); ^{1}H NMR ($CDCl_3$) δ 2.73 (s, 6 H), 2.43 (s, 6 H), 3.93 (s, 4 H), 6.93 (s, 4 H).

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.20; H, 6.99; N, 9.60.

Reaction of 1,1-Dichloro-4,6-dimethylbenzocyclobutene with *n*-Butyllithium. To a mixture of 50 mL of cyclohexene in 150 mL of ether was added 5 g of 1,1-dichloro-4,6-dimethylbenzocyclobutene. The suspension was cooled to −40 °C and purged with nitrogen. An equimolar amount of *n*-butyllithium in hexane was added dropwise during 1 h. The mixture was stirred for an additional hour at −40 °C. The resulting suspension was extracted with water, and the organic layer dried and concentrated under vacuum. The resulting yellow oil was submitted to short-path distillation; 2 g of a colorless liquid was obtained. According to NMR analysis, the amount of **22a** was 19%. An attempted separation by distillation and column chromatography was not successful.

Competition Experiments in Equimolar Mixtures of 2,3-Dimethyl-1,3-butadiene and 2-Methyl-1-butene. Compound **15** (15 g) was suspended in a mixture of 17.5 g (250 mmol) of 2-methyl-1-butene and 20.5 g (250 mmol) of 2,3-dimethyl-1,3-butadiene. The suspension was purged with N_2 (O_2) and then irradiated. After evaporation of the solvent, the hydrocarbon fraction was isolated by column chromatography (silica gel/petroleum ether) and analyzed by NMR and high pressure LC.

A similar experiment was run in an equimolar mixture of diphenylethylene and 2-methyl-1-butene. After evaporation of the solvent and chromatography, the product mixture was analyzed by NMR and high pressure LC.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′,2′-diphenylcyclopropane] (25c). Photolysis of **15** in diphenylethylene afforded 500 mg (60%) of **25c** as colorless rhombs: mp 63 °C; ^{1}H NMR δ 10.5 (s, 3 H), 2.0 (s, 2 H), 2.3 (s, 3 H), 3.1 (AB, 2 H), 6.65 (s, 1 H), 6.73 (s, 1 H), 7.1–7.5 (m, 10 H); mass spectrum, m/e 310 (M^+, 70).

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.50; H, 7.18.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′-ethyl-2′-methylcyclopropane] (25a and 25a′). Photolysis in 2-methyl-1-butene (73% N_2 in 4.5 h) afforded, besides traces of **17** and **18**, 300 mg (31%) of **25a** and **25a′** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.7–2.1 (m, 10 H), 2.16 (s, 3 H), 2.28 (s, 3 H), 3.04 (AB, 2 H), 6.72 (s, 2 H); mass spectrum, m/e 200 (M^+, 100).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.00; H, 10.01.

Spiro[4,6-dimethylbenzocyclobutene-1,1′-2′-isopropenyl-2′-methylcyclopropane] (25b and 25b′). Irradiation in 2,3-dimethyl-1,3-butadiene gave 64 mg (12.5%) of **25b′** as a colorless oil. The second fraction from column chromatography (silica gel/petroleum ether) contained 140 mg (27.5%) of **25b**.

25b: ^{1}H NMR ($CDCl_3$) δ 1.2 (s, 2 H), 1.46 (s, 3 H), 1.76 (s, 3 H), 2.2 (s, 3 H), 2.3 (s, 3 H), 2.9 (s, 2 H), 4.75 (s, 2 H), 6.76 (s, 2 H); mass spectrum, m/e 212 (M^+, 5).

Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.00; H, 9.30.

25b′: ^{1}H NMR ($CDCl_3$) δ 1.26 (AB, 2 H), 1.90 (s, 3 H), 1.73 (s, 3 H), 2.0 (s, 3 H), 2.3 (s, 3 H), 3.1 (AB, 2 H), 4.90 (AB, 2 H), 6.70 (s, 2 H); mass spectrum, m/e 212 (M^+, 80).

Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.00; H, 9.50.

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Registry No. 6, 70080-30-7; **7**, 72610-89-0; **15**, 72610-67-4; **17**, 70080-31-8; **18**, 70087-70-6; **19**, 70080-39-6; **20**, 70244-22-3; **21**, 70080-37-4; **22a**, 72610-68-5; **22b**, 70080-33-0; **22c**, isomer 1, 72610-69-6; **22c**, isomer 2, 72657-60-4; **22d**, isomer 1, 72657-61-5; **22d**, isomer 2, 72657-62-6; *cis*-**22e**, 72610-70-9; *trans*-**22e**, 72610-71-0; *cis*-**22f**, 72610-72-1; *trans*-**22f**, 72610-73-2; *cis*-**22g**, 72610-74-3; *trans*-**22g**, 72610-75-4; *cis*-**22h**, 72610-76-5; *trans*-**22h**, 72610-77-6; *cis*-**22i**, 72610-78-7; *trans*-**22i**, 72610-79-8; **23**, 70080-38-5; **25a**, 72610-80-1; **25a′**, 72610-81-2; **25b**, 72610-82-3; **25b′**, 72610-83-4; **25c**, 72610-84-5; benzenediazoniumcarboxylate hydrochloride, 4661-46-5; anthranilic acid, 118-92-3; 1,1-dichlorobenzocyclobutene, 68913-13-3; 1,1-dichloroethylene, 75-35-4; benzocyclobutenone, 3469-06-5; benzocyclobutenone tosylhydrazone, 72610-85-6; benzocyclobutenone azine, 19164-69-3; benzocyclobutenone tosylhydrazone sodium salt, 72610-86-7; (*E*)-benzocyclobutenone dimer, 72610-87-8; (*Z*)-benzocyclobutenone dimer, 72610-88-9; 4,6-dimethylbenzocyclobutenone tosylhydrazone, 20643-23-6; dicyclopropylethylene, 822-93-5; 4,6-dimethylbenzocyclobutenone azine, 20643-22-5; 1,1-dichloro-4,6-dimethylbenzocyclobutene, 6590-38-1; cyclohexene, 110-83-8; 2-methyl-2-butene, 513-35-9; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; *m*-bromostyrene, 2039-86-3; *p*-chlorostyrene, 1073-67-2; styrene, 100-42-5; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4.

Preparation and Acetolysis of β-[7-[π-(Norbornadienyl)iron tricarbonyl]]ethyl Methanesulfonate. Inhibition of Delocalization by Complexation[1]

Robert S. Bly* and Thomas L. Maier

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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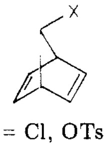
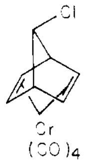
In the absence of oxygen the acetolysis of β-[7-[π-(norbornadienyl)iron tricarbonyl]]ethyl methanesulfonate at 98 °C is about 5×10^{-5} times as rapid as that of β-(7-norbornadienyl)ethyl methanesulfonate and produces β-[7-[π-(norbornadienyl)iron tricarbonyl]]ethyl acetate as the only product. π complexation with tricarbonyliron completely inhibits double bond participation in both the rate- and product-determining steps of the reaction.

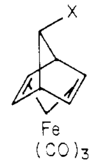
We have long been interested in π-electron delocalization during solvolysis[2] and in the possible inhibition of such delocalization by π complexation to a transition metal.[3] In this latter connection we once attempted to compare the relative solvolysis rates of 7-chloronorbornadiene (1-Cl) and its tetracarbonylchromium π complex 2-Cl[4] but found that in 80% ethanol the complex dissociates about as rapidly as it solvolyzes.[5] The first clear demonstration of such inhibition was provided by Hunt, Lillya, and Rausch, who estimate that 7-[π-(norbornadienyl)iron tricarbonyl] tosylate (**3**-OTs) hydrolyzes in 80% acetone at least 10^6 times more slowly than would 7-norbornadienyl tosylate (**1**-OTs) itself.[6]



1-X, X = Cl, OTs, OMs

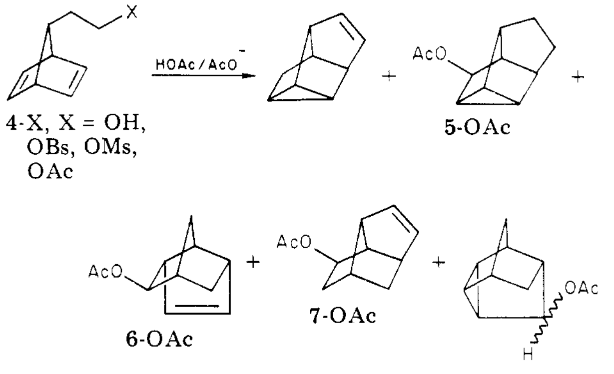


2-Cl



3-X, X = OTs, H

More recently we observed that β-(7-norbornadienyl)ethyl brosylate (**4**-OBs) acetolyzes with extensive π-electron delocalization in both the rate- and product-determining steps.[7] At 98 °C it is about $10^{4.5}$ times as reactive as either β-(*anti*-7-norbornenyl)ethyl or β-(7-norbornyl)ethyl brosylate, **9**- and **10**-OBs, respectively.[2c] It produces no products of direct solvolytic displacement, viz., **4**-OAc; only tri- and tetracyclic products, eq 1, are formed.[7]



4-X, X = OH, OBs, OMs, OAc

5-OAc

6-OAc

7-OAc

8-OAc

(1)

In contrast, neither **9**- nor **10**-OBs shows any evidence of σ- or π-electron delocalization during acetolysis; each yields only the unrearranged acetate; cf. eq 2 and 3.[2c]

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(3) (a) R. S. Bly and R. L. Veazey, *J. Am. Chem. Soc.*, **91**, 4221 (1969); (b) R. S. Bly, R. C. Strickland, R. T. Swindell, and R. L. Veazey, *ibid.*, **92**, 3722 (1970); (c) R. S. Bly, R. A. Mateer, K. K. Tse, and R. L. Veazey, *J. Org. Chem.*, **38**, 1518 (1973); (d) R. S. Bly and T. L. Maier, *ibid.*, **43**, 614 (1978).

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(5) D. F. Hunt, C. P. Lillya, and M. D. Rausch, *Inorg. Chem.*, **8**, 446 (1969); cf. footnote 16.

(6) D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Am. Chem. Soc.*, **90**, 2561 (1968).

(7) R. S. Bly, R. K. Bly, G. B. Konizer, and S. P. Jindal, *J. Am. Chem. Soc.*, **98**, 2953 (1976).

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