emphasized that our estimation of isocyanide isomerization energies does not require knowledge of any heats of formation.

The core binding energies of *tert*-butyl isocyanide, *tert*-butyl cyanide,[33] phenyl isocyanide, and benzonitrile[33] can be used to predict values for the corresponding isocyanide-to-cyanide isomerization enthalpies. The isomerization enthalpy is calculated to be -27 kcal mol^{-1} for *tert*-butyl isocyanide and -28 kcal mol^{-1} for phenyl isocyanide. Given the uncertainty in the core replacement energies ($\sim$5 kcal mol^{-1}), our results indicate that $\Delta E_{\rm iso}$ for the isocyanide RNC is essentially independent of the R group.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-A003-76SF00098.

Registry No. CH_2CCH_2, 463-49-0; CH_2CO, 463-51-4; BH_3CO, 13205-44-2; HNCO, 75-13-8; CH_3CN, 75-05-8; NH_2CN, 420-04-2; CH_3NC, 593-75-9; *t*-BuNC, 7188-38-7; C_6H_5NC, 931-54-4; N_2O, 10024-97-2; CO_2, 124-38-9; HCCF, 2713-09-9; NCF, 1495-50-7; CH_2N_2, 334-88-3; HN_3, 7782-79-8.

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(33) To be consistent with our assignment of the CH_3CN spectrum, we assume that the carbon 1s binding energy of the CN carbon atom of a nitrile is always lower than that of the carbon atom directly bonded to the CN group. Thus we take 291.8 and 291.85 eV for the CN carbon atoms of $(CH_3)_3CN$[23] and C_6H_5CN,[34] respectively.

(34) Lindberg, B.; Svensson, S.; Malmquist, P. A.; Basilier, E.; Gelius, U.; Siegbahn, K., Uppsala University, Institute of Physics Report UUIP-910, December 1975.

Structure of the Intermediate Formed in the Reaction of the Styrene Radical Cation and Neutral Styrene

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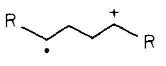
Abstract: The structure of the ion–molecule adduct produced in the gas-phase reaction of the styrene radical cation with neutral styrene has been probed by collisionally stabilizing the adduct and then acquiring its collision-activated decomposition (CAD) spectrum with a tandem mass spectrometer. The CAD spectrum of the adduct is nearly identical with the CAD spectra of the *cis*- and *trans*-diphenylcyclobutane radical cations and with the product ion resulting from a 1,4-regiospecific water elimination from the 1,4-diphenylbutan-1-ol radical cation; therefore the radical cations from all four precursors possess the same structure. The ΔH_f of this radical cation is shown to be $\leq$239 kcal/mol; therefore it cannot have the *trans*-1,2-diphenylcyclobutane structure (ΔH_f = 247 kcal/mol). The results support a two-step mechanism for the [1 + 2] cycloaddition reaction.

Radical cations are thought to play important roles as intermediates in organic cycloaddition reactions.[1-11] The mechanism of the [2 + 1] cycloaddition reactions[12] occurring in solution has not been firmly established, but likely possibilities have been proposed, and they include a concerted process[9] and a two-step process involving an acyclic 1,4-radical cation[13] as an intermediate[6,7] (structure a). A long-bond cyclobutane radical cation



a

has been postulated in a recent theoretical study, and it represents a third possible intermediate.[8] Evidence is presented in this report that points to formation of a stable 1,4-radical cation intermediate in the reaction of styrene radical cation and neutral styrene. Although similar structures have been proposed in the literature,[6-8,14] the experiments described herein constitute the first direct evidence of a 1,4-radical cation intermediate in the [2 + 1] cycloaddition of alkene radical cations and alkene neutrals.

Aryl-substituted ethylene radical cations, which are structurally similar to styrene, have been demonstrated to undergo reaction with their corresponding neutrals to produce diaryl-substituted cyclobutane products.[6-9] The gas-phase ion–molecule chemistry of styrene itself has been investigated by ICR spectrometry, and the C_6H_6 elimination mechanism observed for decomposing [styrene radical cation + styrene] adducts was interpreted to involve a 1-phenyltetralin radical cation intermediate.[4] However, this result only applies to an energized intermediate in a collision-free environment and may not pertain to adducts that have been collisionally stabilized.

Accordingly, the structures of the nondecomposing styrene ion–molecule adducts were examined in the present work. Ion–molecule adducts can be stabilized with a high-pressure chemical ionization source and then analyzed with a tandem mass spectrometer (MS/MS). The $C_{16}H_{16}$ radical cation adduct was separated from other ion products by using the first stage of mass analysis of a high-resolution tandem mass sepctrometer[15] and then collisionally activated prior to fragment ion mass analysis by the second stage. The structure of the adduct radical cation was

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(1) Chess, E. K.; Lin, P. -H.; Gross, M. L *J. Org. Chem.* **1983**, *48*, 1522.

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(8) Bauld, N. L. Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(9) Bauld, N. L.; Pabon, R. *J. Am. Chem. Soc.* **1983**, *105*, 633.

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(12) This notation refers to the number of electrons involved in the cycloaddition reaction. Thus, [2 + 1] is the number of electrons involved in a [2 + 2] carbon cycloaddition.

(13) The "1,4-radical cation" terminology refers to a structure in which the charge and radical sites are separated. The concept is similar to that of an "ion dipole" proposed recently by Holmes and Radom (see ref 18).

(14) (a) Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 3783. (b) Collins, J. R.; Gallup, G. A. *Ibid.* **1982**, *104*, 1530.

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0002-7863/84/1506-0539$01.50/0

Table I. Collision-Activated Decomposition (CAD) Spectra of $C_{16}H_{16}$ Radical Cations

		carbon units eliminated from $C_{16}H_{16}$												
	$C_{16}H_{16}$ radical cation source	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
I.	styrene ion–molecule adduct	10.3	15.9	8.2	4.6	1.8	11.7	6.7	31.9	4.2	2.1	1.1	1.0	0.4
II.	*cis*-1,2-diphenylcyclobutane	7.8	11.9	8.5	4.0	1.6	10.9	5.3	38.6	5.6	3.3	1.2	1.0	0.5
III.	*trans*-1,2-diphenylcyclobutane	7.9	12.0	9.1	4.2	1.6	11.2	5.4	37.3	5.1	3.4	1.4	1.1	0.4
IV.	[1,4-diphenylbutan-1-ol radical cation $-H_2O$]	7.1	11.4	7.9	3.7	1.5	11.3	6.4	38.7	5.1	3.7	1.6	1.2	0.6
V.	[2.2]paracyclophane	17.2	6.7	4.2	2.7	1.1	1.6	4.7	45.7	4.5	6.3	2.5	2.0	0.7
VI.	2-phenyltetralin	18.9	9.9	4.8	3.1	1.4	18.7	8.5	21.3	7.2	3.6	1.3	0.9	0.3
VII.	1-phenyltetralin	8.8	40.6	10.8	4.2	1.6	18.6	4.7	2.5	5.0	1.6	0.8	0.6	0.2
VIII.	1,4-diphenylbut-1-ene	9.0	40.6	10.7	4.4	1.6	18.0	4.6	2.5	5.1	1.7	0.9	0.6	0.3
IX.	1,3-diphenylbut-1-ene	43.1	12.5	8.7	3.6	1.7	14.0	6.8	2.3	3.6	1.7	0.8	0.6	0.2
X.	*cis*-2,3-diphenylbut-2-ene	46.8	15.3	7.6	4.4	2.0	6.9	6.2	3.4	3.4	2.3	0.9	0.7	0.2

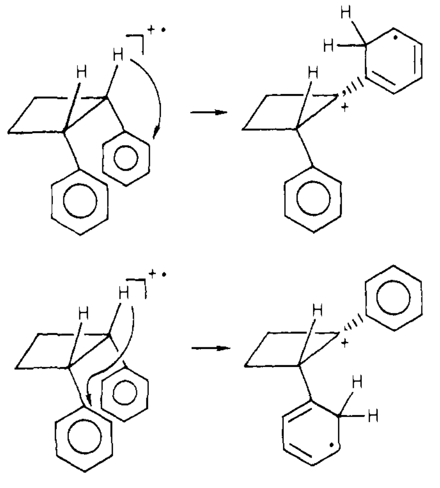
assigned by comparing its CAD spectrum to spectra of reference $C_{16}H_{16}$ radical cations.[16] The reference compounds were chosen to mimic $C_{16}H_{16}$ structures anticipated from a variety of possible mechanisms: [2 + 1] and [7 + 2] cycloadditions and head-to-head, head-to-tail, and tail-to-tail condensations of two styrene species. The rate constant for the reaction was also measured by using pulsed ion cyclotron resonance (ICR) spectrometry, and the thermochemistry of the $C_{16}H_{16}$ radical cation system has been estimated on the basis of ionization and appearance potential measurements. These experiments are all consistent with a 1,4-ion dipole intermediate and are not in accord with a concerted [2 + 1] cycloaddition mechanism.[9]

Results and Discussion

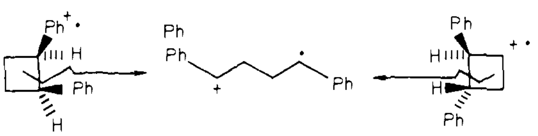
Stabilized Adducts. A $C_{16}H_{16}$ radical cation adduct can be observed in the high-pressure source as the collisionally stabilized product of the styrene ion-molecule reaction. The collision-activated decomposition (CAD) spectrum of the adduct is dominated by dissociation back to the starting materials $C_8H_8^{+\cdot}$ (m/z 104) and neutral C_8H_8 (see Table I). Because the resolution of the second stage of mass analysis was not sufficiently high to allow unit resolution of the individual masses, the CAD data are presented in terms of percent of total ionization for peak clusters (e.g., the intensities of the C_2H_4, C_2H_5 and C_2H_6 losses are combined). The spectrum of the $C_{16}H_{16}$ ion-molecule adduct matches closely the spectra of II–IV, which are in turn identical with each other within the error of these experiments. In addition, other general characteristics of the styrene ion–molecule adduct (I) spectrum are identical with those of the spectra of II–IV. For example, sharp profiles of the C8 and C9 loss clusters are common to I and II–IV, and these spectral traits are unique among the reference compounds studied. These observations are strong evidence that the majority of the styrene ion-molecule adducts have the same structure as radical cations II–IV. In contrast to the earlier ICR study,[4] the structure of the collisionally stabilized adduct is clearly *not* that of 1-phenyltetralin (VII). However, it is emphasized here that the conclusions of the earlier study were based on observations of ion–molecule adducts with sufficient energy for decomposition. By comparison, the ion–molecule adducts that are analyzed in the present report have been extensively stabilized.

When contrasted with the spectra of II–IV, the spectrum of I exhibits slightly more intense envelops for peaks representing loss of Cl (CH_2, CH_3, etc.) and C2 fragments and a slightly less abundant C8 loss. These differences are either due to the ion–molecule adduct possessing a different amount of internal energy than the reference compound ions or due to a small fraction of other ion–molecule adducts possessing different structures. For example, the presence of a small amount of 1-phenyltetralin would serve to enhance the peak corresponding to the loss of C_2H_4, which is more abundant in the spectrum of the adduct than in the spectra of II–IV. The presence of a small amount of 1-phenyltetralin would be consistent with the previous study[4] and with the behavior observed for the decomposing adducts.

Scheme I



Scheme II



The structure of the styrene ion–molecule adduct is revealed by a consideration of the possible structures of the radical cations II–IV. The observation that the CAD spectra of *cis*- and *trans*-1,2-diphenylcyclobutane (II and III) are identical may be interpreted to indicate that one or both of the structures are isomerizing to the same structure, because it is unlikely that the two isomers would give identical CAD spectra. The cis and the trans isomers have significantly different structures, and it is reasonable to expect that their CAD spectra would be different if structure is maintained upon ionization because two similar compounds, *cis*- and *trans*-divinylcyclobutane, are easily distinguishing on the basis of their CAD spectra.[3]

A possible explanation for the identical spectra of II and III is an intramolecular epimerization in which the cyclobutane ring remains intact. This possibility requires the formation of a benzylic carbonium or radical site, which could be accomplished either by a 1,3-hydrogen shift from the benzylic carbon to the ortho position of the 1-phenyl group or by a 1,4-hydrogen transfer to the ortho position of the 2-phenyl group (see Scheme I). A hydrogen atom may be subsequently transferred from the phenyl group to either side of the carbonium ion, thereby effecting epimerization. The 1,4 shift is not likely because it would require significant isotopic label reorganization in *cis*-1,2-diphenylcyclobutane-*1,2*-d_2, but this was not observed. The m/z 104 (C_8H_8) signal of the unlabled *cis*-1,2-diphenylcyclobutane (II) is shifted cleanly to m/z 105 (C_8H_7D) in the CAD spectrum of *cis*-1,2-diphenylcyclobutane-*1,2*-d_2. Significant losses of C_8H_8 (m/z 104) and $C_8H_6D_2$ (m/z 106) from *cis*-1,2-diphenylcyclobutane-*1,2*-d_2 would be expected as a result of an epimerization via the 1,4-hydrogen-transfer

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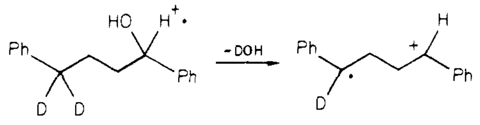
Table II. Thermochemistry[a]

trans-1,2-diphenylcyclobutane	$\Delta H_f = +58.4$ kcal/mol IP = 8.2 ± 0.1 eV $AP_{104} = 9.0 \pm 0.1$ eV
1,4-diphenylbutan-1-ol	$\Delta H_f = -13.7$ kcal/mol IP = 8.5 ± 0.1 eV $AP_{208} = 8.5 \pm 0.1$ eV

[a] Reference 20.

Scheme III



mechanism. Epimerization via the 1,3-hydrogen-transfer mechanism cannot be unequivocally ruled out, but it would be sterically difficult. Therefore, it is unlikely that the 1,2-diphenylcyclobutanes are epimerizing via a mechanism in which the cyclobutane ring remains intact.

An alternative reaction leading to identical structures starting with *cis*- and *trans*-1,2-diphenylcyclobutane radical cations is a ring opening of the cyclobutane (Scheme II). This reaction would yield a 1,4-radical cation (structure b) and would be analogous to reactions of aromatic substituted cyclobutane and cyclopropane radical cations that have been observed in solution.[17] Stable gas-phase ions with the radical and charge sites cleanly separated (called "ion dipoles") have also been observed as product ions formed from rearrangement elimination reactions.[18]

Another method of generating the 1,4-radical cation was sought in order to provide additional structure confirmation. Certain alcohols have been demonstrated to eliminate H_2O via a regiospecific 1,4 mechanism involving only benzylic hydrogens;[19] thus if 1,4-diphenylbutan-1-ol undergoes such an elimination, the 1,4-radical cation (structure b) is generated. In fact 1,4-diphenylbutan-1-ol does eliminate H_2O via a 1,4 mechanism. This conclusion was verified by the observation that at least 92% and probably >99% of the water eliminated (see Experimental Section) as determined from the mass spectrum of 1,4-diphenylbutan-1-ol-*4,4-d*$_2$ occurred as DOH (Scheme III). We again emphasize that the CAD spectrum of the $C_{16}H_{16}$ radical cation produced as the product of water elimination from 1,4-diphenylbutan-1-ol (IV) is identical with the spectra of the styrene ion-molecule adduct and both of the 1,2-diphenylcyclobutane radical cations. These identities constitute proof that the three radical cations possess identical structures.

The formation of a 1,2-diphenylcyclobutane structure from the 1,4-water elimination seems unlikely because it would require the addition of approximately 26 kcal/mol of ring strain[20] to the ion. Therefore, a more probable structure resulting from the 1,4-water elimination is the 1,4-ion radical b. One test of this conclusion is a comparison of the ΔH_f of *trans*-1,2-diphenylcyclobutane radical cation and the ΔH_f of the $C_{16}H_{16}$ radical cation from the 1,4-water elimination. Accordingly, ΔH_f values were calculated for these two ions. These calculations were accomplished by estimating neutral ΔH_f values[20] and determining ionization and appearance energies for *trans*-1,2-diphenylcyclobutane and 1,4-diphenylbutan-1-ol (Table II, Figure 1). The ΔH_f of the $C_{16}H_{16}$ radical cation product of the 1,4-water elimination (≤239 kcal/mol) is calculated to be at least 8 kcal/mol lower than the ΔH_f of the *trans*-1,2-diphenylcyclobutane radical cation (247 kcal/mol). The *cis*-1,2-diphenylcyclobutane is expected to have an even higher ΔH_f than the *trans*-1,2-diphenylcyclobutane because of the unfavorable interaction of the two phenyl groups. The 8 kcal/mol represents a minimum energy difference between the two structures because the appearance energy for $C_{16}H_{16}^{+\cdot}$ is equal to the ionization energy of the alcohol precursor. This 8 kcal/mol difference is too large to be ascribed to experimental error; hence the structure of the 1,4-water elimination radical cation IV, and of I, II, and III also, cannot be a classical cyclobutane radical cation.

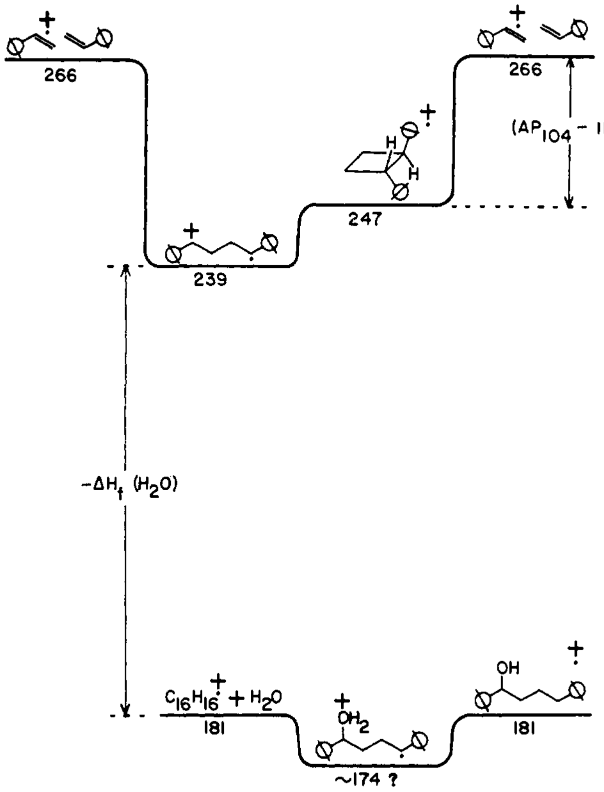


Figure 1. Schematic potential energy surface for the styrene ion-molecule reaction.

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(20) ΔH_f values were calculated according to the group additivity scheme of Benson: Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968. In the calculation of ΔH_f of 1,4-diphenylbutan-1-ol, we assumed that C-(O)(C_B)(C)(H) is 1.9 kcal more positive than C-(O)(C_2)(H).

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(22) Gioumousis, G.; Stevenson, D. P. *J. Phys. Chem.* **1958**, *29*, 294.

(23) Groenewold, G. S.; Gross, M. L. *Angew. Chem., Int. Ed. Engl.*, submitted for publication.

(24) Experiments performed in this laboratory involving the reactions of [1,3-butadiene radical cation + 1,3-butadiene] and [1,3-butadiene + vinyl methyl ether] radical cation have been interpreted in terms of a mechanism in which an acyclic intermediate is initially formed. The acyclic structure subsequently ring closes or can be collisionally stabilized prior to cyclization. The results of these experiments will be submitted to this journal for publication.

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Calculation of the appearance energy of the *m/z* 104 ion originating from *trans*-1,2-diphenylcyclobutane radical cation resulted in a ΔH_f of 266 kcal/mol. This value corresponds precisely with the ΔH_f of styrene radical cation plus neutral styrene. Thus, if the *m/z* 104 ion from *trans*-1,4-diphenylcyclobutane has the styrene radical cation structure and the expelled neutral is styrene, then we may conclude that the styrene ion–molecule reaction occurs with little or no activation energy, because the ionized *trans*-1,2-diphenylcyclobutane has in fact ring opened to the 1,4-radical cation (structure b). This conclusion is in accord with the very small activation energy recently predicted for the [2 + 1] ethylene ion–molecule reaction.[8,9]

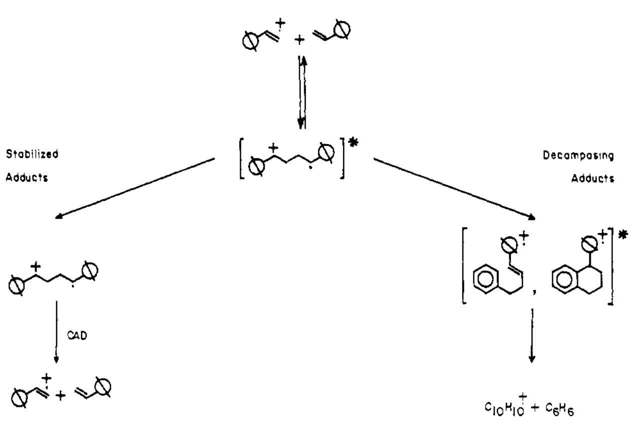
Another facet of the thermochemical measurements that requires comment is the observation that the ionization potential of 1,4-diphenylbutan-1-ol is identical with the appearance potential of the *m/z* 208 ion (loss of H_2O). The molecular ion is probably observable only because it isomerizes to a more stable benzyloxonium radical cation.[18,34] Accordingly, we have placed this species 7 kcal lower in energy than the corresponding alcohol radical cation (Figure 1), because the methyleneoxonium ion dipole has been determined to be 7 kcal/mol more stable than the corresponding methanol radical cation.[18d] In fact, the benzyloxonium radical cation may be even more stable because of the resonance stabilization of the phenyl substituents.

Proposed Mechanism. Collisional stabilization of the styrene ion–molecule adduct results in a structure which has been identified by CAD spectroscopy as a 1,4-radical cation. The distinguishing fragmentation of the 1,4-radical cation is a reversion to the C_8H_8 radical cation and neutral C_8H_8, and the C_8H_8 ion accounts for the base peak in the CAD spectra of I–IV and in the 70-eV mass spectra of *cis*- and *trans*-1-2-diphenylcyclobutane[21] and 1,4-diphenylbutan-1-ol. The 1,4-radical cation eliminates very little C_6H_6.

In contrast to these observations, the styrene ion–molecule adducts which have enough internal energy to decompose unimolecularly (detected by observation of metastable ions) have enhanced signals corresponding to the loss of C_6H_6, a finding that is in accord with the earlier ICR data.[4] To account for the dichotomous behavior of the stabilized and the decomposing ions, the rate constant for the reaction of styrene radical cation and neutral styrene was determined by pulsed ICR spectrometry. The disappearance of the styrene radical styrene cation (C_8H_8, *m/z* 104) was measured as a function of time, and this experiment yielded a rate constant value of 6.0×10^{-11} cm^3 s^{-1} molecule^{-1}. The rate constant was then compared to the Langevin collision constant[22] of 1.23×10^{-9} cm^3 s^{-1} molecule^{-1} to determine that the reaction is about 5% efficient at producing products that are *observable* by using ICR spectrometry. This low efficiency is consistent with the property of the styrene ion–molecule intermediate to decompose to $C_8H_8^{+\cdot}$, i.e., back to starting material. In addition, the ICR time-dependence data for *m/z* 104, when plotted as log (I/I_0) vs. time, are linear for >96% of the reaction. This observation is in accord with an interpretation that the reacting species has a single structure, although two or more structures would not be detected if their reactions with neutral styrene have the same rate constant. This possibility is regarded as remote, because the radical cations of two other C_8H_8 isomers (benzocyclobutene and *o*-xylylene) have rate constants for the reaction with neutral styrene that are much greater than the rate constant of styrene radical cation,[23] and a third isomer (1,3,5,7-cyclooctatetraene) does not react at all with neutral styrene.[4]

A mechanism that consolidates all of the data discussed above employs an initially formed 1,4-radical cation whose major decomposition channel is to revert to starting material (Scheme IV). A facile, reversible condensation of styrene radical cation with neutral styrene is in accord with the absence of any activation barrier for the reaction. Furthermore, a rate constant for the disappearance of *m/z* 104 that is only 5% of the theoretical maximum is consistent with the observation that the major decomposition pathway of the styrene ion–molecule adduct is a reversion to *m/z* 104. The reversion of the 1,4-ion radical to starting material can be intercepted by collisional stabilization of the adduct, but the characteristic reversion to *m/z* 104 reappears in the CAD spectrum.

Scheme IV



Barely in competition with the reversion to starting material is a rearrangement to a second intermediate, which is characterized by its elimination of C_6H_6. The elimination of C_6H_6 is a property of the 1-phenyltetralin structure,[4] which can be formed from the 1,4-radical cation with no carbon skeleton rearrangement. However 1-phenyltetralin and 1,4-diphenylbut-1-ene give identical CAD spectra (VII and VIII in Table I); therefore, they are either interconverting or isomerizing to a third structure. For this reason, there exists more than one possibility for the rearranged structure.

The results of these experiments are interpreted to indicate that the reaction of an alkene radical cation with a neutral alkene does *not* initially produce a classical cyclic intermediate but rather an acyclic 1,4-radical cation.[24] Under low-pressure (collision free) conditions and in solution, the acyclic intermediates are likely to be short-lived and, therefore, difficult to observe before they cyclize. In contrast, the acyclic intermediate in the styrene ion–molecule reaction can be observed in the gas phase by stabilizing it in a relatively high pressure of an inert bath gas. If this is generally true, it will provide experimental justification for the recent theoretical prediction that [2 + 1] cyclodimerizations are stepwise.[8]

We must point out, however, that the evidence obtained to date does not permit us to distinguish the acyclic 1,4-radical cation and a cyclic long-bond form in which the ionic and radical sites are interacting (structure c). A long-bond cyclic structure may

c

actually exist at an energy minimum as has been shown by the theoretical calculations of Bellville and Bauld[8,34] and Collins and Gallup.[35] Experimental studies of Bauld and Pabon[9] and Roth and Manion Schilling[36] point to a similar conclusion. On the other hand, the ring-opened form, which may be more stable for the system reported here because of the delocalization of the positive charge and the unpaired electron over the phenyl rings, serves as an entirely adequate explanation for the results we have obtained thus far.

Experimental Section

Mass Spectrometry. All CAD spectra were acquired with a Kratos MS-50 triple-analyzer mass spectrometer[15] equipped with a standard Kratos EI/CI source and operated in the CI mode. The styrene and the $C_{16}H_{16}$ reference compounds were ionized by NO[25] and CS_2[26] charge exchange at pressures of approximately 0.6 torr. These reagent gases were used because they undergo low-energy charge exchange (IP(NO)

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[34] Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 5700.

[35] Collins, J. R.; Gallup, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1530.

[36] Roth, H. D.; Manion Schilling, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 7210.

= 9.3 eV, IP(CS_2) = 10 eV) and they serve as a nonreactive background for collisional stabilization. Samples were admitted to the mass spectrometer either by using a direct-insertion CI probe or through a custom-built heated inlet that was continually flushed with helium gas to aid in mass transfer and to eliminate electrical breakdown. Collision-induced dissociation was observed by admitting helium to the collision cell until a 50% reduction of the main beam was observed. The CAD spectra reported have not been corrected for unimolecular metastable contributions because these contribute less than 5% to any CAD signal, with the following exceptions: loss of C_6H_6 from 1-phenyltetralin, 12%; loss of C_6H_6 from 1,4-diphenylbut-1-ene, 17%; loss of CH_3 from *cis*-2,3-diphenylbut-2-ene, 8%.

Ionization and appearance energies were determined with a Kratos MS-50 mass spectrometer operated with the repeller voltage = 0 V and with a trap current of 36 μA. The IP and AP values were obtained by plotting log (I/I_0) vs. the ionizing voltage both for the unknown ion and for two reference ions. The reference ions that were used were C_6D_6, m/z 84 from deuterated benzene (IP = 9.25 eV) and 1,2,3,4-tetrahydronaphthalene, m/z 132 (IP = 8.44 eV).[27] The voltage corresponding to the onset of the unknown ion is calculated on the basis of the position of its curve relative to the curves of the reference ions (semilog method).

The rate constant was measured with a Varian ICR-9 spectrometer modified to operate in a trapped mode. An elongated cell similar to the type introduced by McIver was employed.[28] The spectrometer was operated at a magnetic field strength of 10.4 kG, 153.7-kHz excitation frequency, and an ionizing energy of 15 eV, as measured with a digital voltmeter. Styrene disappearance curves were recorded by monitoring m/z 104 intensity as ion detection delay time was increased from 0 to 500 ms under the control of a pulse programmer. Styrene pressure in the spectrometer was measured with an ion gauge. The ion gauge pressure values were corrected by calibrating the ion gauge against a Datametrics Model 1173 Barocel electronic manometer.

Materials. [2.2]Paracyclophane and stryene were purchased from Aldrich Chemical Co. The 1- and 2-phenyltetralins were synthesized by adding phenyllithium to 1- to 2-tetralone (Aldrich), respectively, and submitting the benzylic alcohols thus formed to a Birch reduction (Li/NH_3).[29] The *cis*-1,3-diphenylbut-1-ene was generously donated by C. A. Kingsbury and G. M. Underwood. The 1,4-diphenylbut-1-ene was synthesized by adding phenyllithium to 4-phenylbutanal and dehydrating the resulting alcohol by distillation in the presence of a catalytic amount of H_2SO_4. The 2,3-diphenyl-2-butene was made in a similar fashion from acetophenone and 1-phenylethyllithium.

cis- and *trans*-1,2-diphenylcyclobutane were synthesized according to the method of Dodson and Zielski.[30] cis-1,2-Diphenylcyclobutane-*1,2*-d_2 was obtained by hydrogenating 1,2-diphenylcyclobutene with D_2; the d_2 product was shown to be 10.5% d_0, 30.4% d_1, 51.9% d_2, and 7.2% d_3 by using mass spectrometry and low ionizing energy (10 eV).

1,4-Diphenylbutan-1-ol was obtained by reducing 4-phenylbutyrophenone (Aldrich) with lithium aluminum hydride in refluxing tetrahydrofuran. NMR 90 MHz ($CDCl_3$): δ 7.28–6.88 (complex, 10, aromatic), 4.60–4.41 (br t, 1, –CH), 2.66–2.38 (complex t, 2, –CH_2), 2.23 (br s, 1, –OH), 1.78–1.56 (complex, 4, –CH_2). Mass spectrum 70 eV (m/z, relative intensity): 226, 0.3%, 225, 0.2%; 224, 0.2%; 210, 0.9%; 209, 1.4%, 208, 4.6%; 133, 0.6%; 131, 0.7%; 130, 0.5%; 129, 0.8%; 121, 1.3%; 120, 10.2%; 118, 2.0%; 117, 12.1%; 116, 1.3%; 115, 5.1%; 108, 5.2%; 107, 67.1% 106, 1.5%; 105, 19.7%, 104, 100%; 103, 3.4%; 92, 5.4%; 91, 7.3%; 89, 1.5%; 80, 3.1%; 79, 43.3%; 78, 8.0%; 77, 23.8%; 65, 7.4%; 63, 1.6%; 53, 1.0%; 52, 1.6%; 51, 6.3%.

1,4-Diphenylbutan-1-ol-*4,4*-d_2 was synthesized starting from 4-phenylbutyric-*4,4*-d_2 acid,[19a] which was reduced to 4-phenylbutan-1-ol-*4,4*-d_2 with lithium aluminum hydride. The alcohol was then oxidized to 4-phenylbutanal-*4,4*-d_2 with pyridinium chlorochromate.[31] The 4-phenylbutanal-*4,4*-d_2 was reacted with a 10% molar excess of phenylmagnesium bromide according to standard procedures.[32] The crude product was chromatographed on silica gel with a 10% ethyl acetate/petroleum ether eluant solution. The product was purified by sublimation at 10 mtorr, 55 °C. The NMR and mass spectral analysis were consistent with 1,4-diphenyl-butan-1-ol-*4,4*-d_2. Elemental composition was determined by mass spectrometry at low ionizing energy (10 eV) to be 85.4% d_2, 15.6% d_1.

Water Elimination from 1,4-Diphenylbutan-1-ol-*4,4*-d_2. Mass spectrometry was used to measure the D/H distribution in the products of ionic water elimination, and the following products were obtained: –H_2O, 15.1%; –DOH, 77.0%; –D_2O, 7.9%. The combination of unknown isotope effects and possible competing mechanisms makes the exact assignment of mechanism and k_H/k_D value impossible. However, a regiospecificity of 99.3% was calculated by using a k_H/k_D of 2.20.[33] The most mechanistically mixed possibility would be calculated for k_H/k_D = 1.0, which yields 92.2% regiospecificity. Therefore, contributions from elimination mechanisms other than 1,4 account for at most 7.8% of the total water loss and are likely <1% of the total.

Registry No. Styrene radical cation, 34504-74-0; styrene, 100-42-5; styrene ion–molecule adduct, 74168-41-5; *cis*-1,2-diphenylcyclobutane radical cation, 88243-92-9; *trans*-1,2-diphenylcyclobutane radical cation, 88243-93-0; [1,4-diphenylbutan-1-ol-H_2O] radical cation, 71364-17-5; [2.2]paracyclophane radical cation, 88243-94-1; 2-phenyltetralin radical cation, 88181-24-2; 1-phenyltetralin radical cation, 88181-25-3; 1,4-diphenylbut-1-ene radical cation, 88243-95-2; 1,3-diphenylbut-1-ene radical cation, 88243-96-3; *cis*-2,3-diphenylbut-2-ene radical cation, 85549-56-0; *cis*-1,2-diphenylcyclobutane-*1,2*-d_2 radical cation, 88181-26-4; 1,4-diphenylbutan-1-ol-*4,4*-d_2, 88181-27-5.

Singlet and Triplet Dimesitylcarbene[1]

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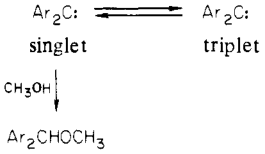
Abstract: The triplet states of essentially all diarylcarbenes react with substrates such as methanol or their parent diazo compounds both of which are thought to be specific quenchers for the singlet state. To rationalize these results, investigators have proposed that the singlet and triplet states of these carbenes are linked by efficient equilibria. In this kinetic study we have found that the singlet and triplet states of dimesitylcarbene exhibit quite distinct chemistries. The singlet state alone reacts with methanol, 1-propanol, and 1,3-cyclohexadiene, while the triplet carbene dimerizes to give olefin or, for example, reacts with oxygen. No evidence was found for reaction of the triplet carbene via the singlet manifold. Arguments are presented to explain the enhanced free energy difference between the spin states of this carbene and the relative persistence of its triplet.

The relationship between singlet and triplet states in diarylcarbenes has attracted the interest of many investigators.[2-14] Spectroscopic studies have shown that essentially all such carbenes have triplet ground states.[15-18] Chemical evidence has led to the

Scheme I



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[1] Issued as NRCC publication No. 22629.

[2] (a) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1964. Jones, M., Jr.; Moss, R. A. "Carbenes"; Wiley: New York, 1973. (b) Etter, R. M.; Skovronek, H. S.; Skell, P. S. *J. Am. Chem. Soc.* **1959**, *81*, 1008. For further examples see ref 3–14.

[3] Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013, 4015.

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