chloride (**13**). The methanol solution of the phosphonium salt **15** was added at the same time as a solution of potassium hydroxide (0.80 g, 0.0143 mol) and methanol (5 mL) to a methanol–ether (4 mL) solution of aldehyde **8** (6.23 g, 0.035 mol) at 0 °C under an argon atmosphere. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was diluted with water and the aqueous mixture extracted several times with diethyl ether. The combined extracts were washed once with water and then dried over magnesium sulfate. Following filtration, the solvent was removed under reduced pressure. The residue was mixed with hexane and loaded onto a basic alumina column (Brockman grade I, 150g). The product was eluted with hexane. The first few fractions of **4** contained a retro-type polyene. These fractions were discarded without any further purification. A 35% yield of pure **4** was obtained. HPLC showed two major isomers at 14.48- and 16.24-mL retention volumes: ^{1}H NMR ($CDCl_3$) 1.04 (s, 12 H, *gem*-dimethyls), 1.4–1.70 (8 H, CH_2), 1.71 (6 H, C2′ and C2″ CH_3), 1.9–2.1 (br m, CH_2—C=C, 4 H), 6.05–6.80 ppm (6 H, alkene protons); IR (neat) 2840–3150 (CH), 970 (*trans*-alkene), 1363, 1387 (*gem*-dimethyls), 1380 (methyl); UV (methanol) 312 nm (16.24-mL HPLC peak) 308 (14.48-mL HPLC peak). The shorter wavelength of the 14.48-mL peak indicates cis stereochemistry. A cis peak was also noted fo the 14.48-mL peak. Each collected HPLC peak gave identical mass spectra for the saturated and unsaturated analogues: MS, *m/e* 324 (molecular ion, base peak), 322, 309, 105; calcd for $C_{24}H_{36}$ *m/e* 324.2817, found *m/e* 324.2810.

Preparation of 1,6-Bis(2,6,6-trimethylcyclohex-1-enyl)-3-methylhexa-1,3,5-triene. β-Ionyltriphenylphosphonium salt **13** (20.784 g, 0.044 mol) in methanol (7 mL) was added at the same time as a solution of potassium hydroxide (0.80 g, 0.014 mol) and methanol (5 mL) to a methanol (4 mL) solution of **8** (6.23 g, 0.035 mol) at 0 °C under an argon atmosphere. The reaction mixture was worked up as previously described. A 75% yield of pure **5** was obtained. Some retro product was removed by chromatography. HPLC showed two peaks (isomers) at 17.36- and 18.24-mL retention volumes: ^{1}H NMR ($CDCl_3$) 1.06 (s, 12 H, *gem*-dimethyls), 1.4–1.70 (8 H, CH_2), 1.71 (6 H, C2′ and C2″ CH_3), 1.9–2.1 (7 H, in-chain methyl and CH_2—C=C), 6.08–6.82 ppm (5 H, alkenyl protons); UV (methanol) 314 nm (18.24-mL peak) 309 (17.36-mL peak); MS, *m/e* 338, 336, 323, 105; calcd for $C_{25}H_{38}$ *m/e* 338.2974, found *m/e* 338.2964.

Hydrogenation of Polyene Intermediates 2–5. Each polyene intermediate (1 mg) was dissolved in ethyl acetate (5 mL) at room temperature. Palladium on activated carbon (100 mg) was added, and the hydrogenation carried out for 8 h at room temperature with stirring under a hydrogen gas pressure of 50 psi. The catalyst was removed by filtration and the sample concentrated in vacuo. No UV maxima in hexane were noted after hydrogenation: IR (neat) 2830–2950 (CH), 1458 (CH_2), 1362, 1380 (*gem*-dimethyl), 1370 (methyl); MS (saturated analogue of **3** – *m/e* 446) *m/e* 431, 390, 291, 249, 221, 179, 138, 125 (base peak), 111. MS (saturated analogue of **2** – *m/e* 460) *m/e* 445, 404, 305, 249, 235, 179, 138, 125 (base peak), 111. MS (saturated analogue of **4** – *m/e* 334) 319, 278, 125 (base peak), 111. MS of (saturated analogue of **5** – *m/e* 348) *m/e* 333, 292, 179, 193, 125 (base peak), 111.

Acknowledgment. I thank Dr. S. Richardson for his GC/MS work on identifying possible structures of hydrocarbons from the thermal degradation of β,β-carotene. I also thank Dr. W. H. Starnes, Jr., for reprints and useful discussions about the nature of polyene degradations. Finally, I thank Professor W. H. Okamura of the University of California at Riverside for preprints of his manuscripts on the thermal rearrangements of retinal-type products.

Registry No. **1**, 7235-40-7; **2**, 82848-18-8; **3**, 85098-47-1; **4**, 85098-48-2; **5**, 85098-49-3; **7**, 40244-29-9; **8**, 53018-97-6; **10**, 3991-53-5; **11**, 79-77-6; **12**, 53319-91-8; **13**, 77837-61-7.

Gas-Phase Diels–Alder Reaction of the *o*-Quinodimethane Radical Cation and Neutral Styrene

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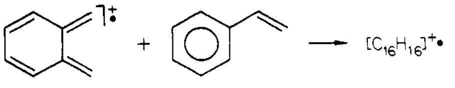
The collision complex formed in the ion–molecule reaction of *o*-quinodimethane radical cation and neutral styrene was investigated by using mass spectrometry/mass spectrometry (MS/MS) techniques. The reaction was conducted in a high-presure chemical-ionization source, where the reagents were ionized by low-energy charge exchange and the reaction products were collisionally stabilized. The collision complex was shown to have the structure of 2-phenyltetralin through the use of deuterium labeling and direct comparison with the properties of reference radical cations. These results establish the structural integrity of low-energy *o*-quinodimethane radical ions and are evidence for a Diels–Alder reaction mechanism.

Cycloaddition reactions, particularly the Diels–Alder reaction, are of considerable interest in both theoretical and experimental organic chemistry. However, there have been few reports of cycloadditions which involve radical cations reacting in either the gas phase[1] or in solution.[2] Furthermore, in the studies conducted of gas-phase reactions, no cycloadduct has been isolated and directly examined usually because the exothermicity of the reaction drives the adduct to dissociate to other products. Thus, indirect methods such as isotope labeling and product analysis have been employed to infer the structure of the intermediate.[1]

This is a report of the structure determination of the intermediate formed in the gas-phase reaction involving the *o*-quinodimethane radical cation (I) and styrene neutral (II) as depicted in eq 1. The approach makes use of the



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technique mass spectrometry/mass spectrometry (MS/MS). The reactant ion was formed by a low-energy charge exchange and reacted with neutral styrene in a high-pressure chemical-ionization (CI) source. The resulting intermediate, which was stabilized by collision with an inert background gas, was isolated by mass selection using the first-stage mass spectrometer and submitted to collisional activation. Its structure was determined by comparing its collision-induced dissociation (CID) spectrum with spectra of reference $C_{16}H_{16}$ ions. The spectra were obtained by the second-stage spectrometer.

The efficacy of CID spectra in structure determinations of gas-phase ions is now well established.[3,4] Here we describe the extension of the methodology to the determination of the structures of radical ion–molecule reaction intermediates which proves to be a useful complement to the technique of ion cyclotron resonance spectrometry. In an ICR cell, the excess internal energy in the collision complex determines the relative abundances of fragments and may prohibit observation of the intermediate because of the relatively long time between collisions. On the other hand, if the reaction is carried out at the higher pressures of a chemical-ionization (CI) source, the intermediate may be stabilized by collisions with buffer gas. Its structure may then be probed by separating it from other mass ions, reactivating it by using high-energy collisions, and observing the CID spectrum independent of internal energy effects. This aproach to studying ion–molecule reactions has been advocated for identifying *products* of proton-transfer reactions.[5] It has also been applied to determining the structures of *products* of reactions of metal ions and organic molecules[6] and to the *products* of the reaction of ionized butadiene and methyl vinyl ether.[7] However, this is the *first* reported determination of the structure of the *intermediate* formed in a condensation reaction of a radical cation and a neutral molecule in the gas phase.

The reactant *o*-quinodimethane radical cation has been characterized in part. Its heat of formation has been estimated to be 240[8] and 255 kcal mol^{-1},[9] both of which are close to the accepted values for the isomeric styrene (232 kcal mol^{-1}) and cyclooctatetraene (COT) ions (257 kcal mol^{-1}).[10] Levsen, Borchers, Stolze, and Budzikiewicz[9] have reported recently that styrene and *o*-quinodimethane ions can be distinguished by their CID spectra; however, the differences in spectra are not large.

Much more is known about the isomeric styrene and COT radical cations.[8-22] At internal energies of 0.9–1.2 eV above the ground state of ionic COT, isomerization takes place. At lower energies, the two ions have distinctive structures. It is likely, therefore, that the *o*-quinodimethane radical cation structure is also a stable form of $[C_8H_8]^{+\cdot}$.

In addition to investigating the nature of the ion–molecule reaction intermediate, we hoped to shed light on the nature of the reactant $[C_8H_8]^{+\cdot}$. For example, we can infer that the reactant structure is that of *o*-quinodimethane and, additionally, that the reaction proceeds as an ionic analogue of a [4 + 2] cycloaddition if we can show that the collision complex formed in eq 1 is 2-phenyltetralin radical cation. Moreover, we expect that this reactant ion should be a reactive diene in a Diels–Alder type reaction because of its expected rigid planar structure, cisoid configuration, and propensity to rearomatize.

Experimental Section

Ion cyclotron resonance spectra were obtained with a Varian ICR-9 spectrometer operated with a conventional drift cell.[1] An ionizing energy of 12.5 eV was used as measured with a digital voltmeter. Single resonance spectra were obtained while operating in the field modulation mode with a marginal oscillator frequency of 153 or 97 kHz. Additionally, double resonance experiments were performed in both the field and pulsed modes. All sample were prepared on a vacuum manifold and degassed thoroughly prior to use. The *o*-quinodimethane precursors were admitted to the cell from one of the inlets to a pressure of 2 × 10^{-6} torr (pressure was read on the ion pump monitor) and allowed to equilibrate for a few minutes. The styrene or deuterated styrene was then admitted via the second inlet.

All collisionally induced dissociation (CID) and unimolecular metastable data were acquired by using a Kratos MS-50 Triple Analyzer mass spectrometer.[23] A Kratos EI/CI high-pressure source was operated at 0.1–0.5 torr in the CI mode at 200 °C with nitric oxide or at 100 °C with carbon disulfide as low-energy charge-exchange reagent ions. The reagent gases were ionized by electron impact with 280-eV electrons. Samples of the reference compounds and *o*-quinodimethane precursors were admitted to the source by the direct-insertion CI probe (which also served as the inlet for the reagent gas), and the styrenes were admitted through a heated (80 °C) inlet in a stream of helium to aid in mass transfer and eliminate electrical breakdown. The helium flow rate was adjusted such that the ratio of helium to charge-exchange reagent gas in the source was always less than 1:4.

The various ions to be investigated were separated by the double-focussing first-stage mass spectrometer (MS-I) at an accelerating potential of 6 kV and a mass resolution of 2000–5000 (10% valley definition). Their unimolecular or CID spectra were acquired by scanning an electrostatic analyzer functioning as the second-stage mass spectrometer (MS-II) by the mass-analyzed ion kinetic energy (MIKE) technique.[24] All CID spectra were recorded with a helium gas pressure sufficient to reduce the intensity of the main-beam ion current by 50%. This attenuation corresponded to a pressure of 9 × 10^{-7} to 2 × 10^{-6} torr as measured in the guard-vacuum housing.[23] All spectra were recorded by signal averaging 9–35 scans at a repetition rate of 20 s with a Data General Nova 4X computer and software that has been developed in our laboratory. The data were plotted by using a Calcomp 1012 drum plotter. The CID spectra shown here have not been corrected for the unimolecular metastable contributions.

Deuterium-labeled styrenes were synthesized by reducing appropriately labeled acetophenones to labeled 1-phenylethanols

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with $LiAlH_4$ and dehydrating the alcohols by distilation from H_3PO_4. The acetophenone-*2,3,4,5,6*-d_5 was prepared through a Friedel–Crafts acylation reaction by using benzene-d_6 (Merck Sharpe and Dohme) and acetyl chloride with aluminum trichloride. The acetophenone-α,α,α-d_3 was made by exchanging the active hydrogen for deuterium by the action of $NaOD/D_2O$, with tetrahydrofuran as the solvent.

o-Methylbenzyl acetates (d_0 and β,β-d_2) were prepared by acetylating the corresponding alcohols with acetic anhydride in pyridine. The alcohols were synthesized by reduction of o-toluic acid (Aldrich Chemical Co.) with $LiAlH_4$ and $LiAlD_4$, respectively.

1- and 2-Phenyltetralins were prepared by addition of phenyllithium or phenylmagnesium bromide to 1- and 2-tetralones (Aldrich), respectively, followed by a Birch reduction (Li/NH_3) of the resulting phenyl-substituted tetralols.[25] 2-Phenyl-1-tetralone was reduced to 2-phenyltetralin-*1,1*-d_2 through the use of a 3:1 mixture of $AlCl_3/LiAlD_4$ according to the method of Brewster and Bayer.[26] The 2-phenyl-1-tetralone was prepared by method of Johnson and Glenn[27] from 2,4-diphenylbutanoic acid.[28] 3-Phenyl-1-tetralone was reduced with $AlCl_3/LiAlD_4$[26] to yield 3-phenyltetralin-*1,1*-d_2. 3-Phenyl-1-tetralone-*2,2*-d^2, prepared by exchanging the active hydrogen of 3-phenyl-1-tetralone by the action of $NaOD/D_2O$ in dry THF, was reduced to 3-phenyltetralin-*2,2*-d_2 with $AlCl_3/LiAlH_4$. 3-Phenyl-1-tetralone was prepared by the method of Springer[29] from ethyl 3,4-diphenyl-3-hydroxybutanoate, with minor modifications (polyphosphoric acid was used to cyclize the 3,4-diphenylbutanoic acid, instead of H_2SO_4). The ethyl 3,4-diphenyl-3-hydroxybutanoate was prepared through the Reformatsky reaction of ethyl α-bromoacetate and benzyl phenyl ketone (both Pfaltz and Bauer) by using an activated "molecular" zinc reagent first described by Rieke and Uhm.[30]

2-Phenyl-1-o-tolylpropene was prepared by adding the Wittig ylide, derived from (o-methylbenzyl)triphenylphosphonium bromide, to acetophenone, and using t-BuOK/DMF as the base and solvent system. 1,2-Di-o-tolylethene was fortuitously isolated as a minor side product in the previous reaction.

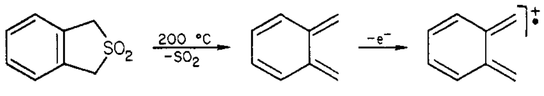
1-Phenyl-3-o-tolylpropene was synthesized by using the previously mentioned Wittig procedure with (2-o-tolylethyl)triphenylphosphonium bromide and acetaldehyde.

1,3-Dihydrobenzo[c]thiophene S,S-dioxide was generously donated by J. R. Hass and L. A. Levy[31] (NIEHS, Research Triangle Park, NC).

All compounds have ^1H NMR and mass spectra consistent with the structures. Mass spectrometric analysis of the deuterated compounds gave the following isotopic labeling purities: styrene-β,β-d_2, 90% d_2, 9% d_1, 1% d_0; styrene-*2,3,4,5,6*-d_5, 84% d_5, 12% d_4, 2% d_3, 2% d_2; o-methylbenzyl acetate-α,α-d_2, 98% d_2, 1.5% d_1, 0.5% d_0; 2-phenyl-d_5-tetralin, 96% d_5, 2% d_4, 2% d_3; 2-phenyltetralin-*1,1*-d_2, 98% d_2, 2% d_1; 3-phenyltetralin-*1,1*-d_2, 95% d_2, 3% d_1, 2% d_0; 3-phenyltetralin-*2,2*-d_2, 97% d_2, 2% d_1, 1% d_0. These analyses were conducted at sufficiently low ionizing energy that the $(M - H)^+$ was not a significant contribution to the spectra.

Results and Discussion

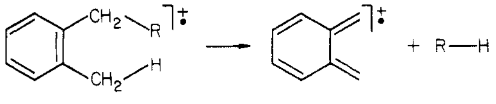
Neutral o-quinodimethane is formed in the pyrolysis at 200 °C of the sulfone III. Generation of this specific neutral was established by trapping the reactive diene in a Diels–Alder reaction with N-phenylmaleimide to give the N-phenyl imide of tetralin-*cis*-2,3-dicarboxylic acid.[32] Low-energy charge exchange of this diene in the source of a mass spectrometer should afford I, initially at least (eq 2). Additionally, a $C_8H_8^{+\cdot}$ species, presumably of the



(2)

III I

o-quinodimethane structure, can be generated from the loss of acetic acid or water from ionized o-methylbenzyl acetate (IV) or o-methylbenzyl alcohol (V), respectively (eq 3). All



(3)

IV, R = OAc
V, R = OH

of these general methods of preparation of $C_8H_8^{+\cdot}$ were used in the high-pressure experiments; however, only IV and V were used as sources for $C_8H_8^{+\cdot}$ in the ICR studies.

ICR Results. The $C_8H_8^{+\cdot}$ ion generated in the ICR reacted with neutral styrene to produce an ion–molecule collision complex at m/z 208 ($C_{16}H_{16}^{+\cdot}$), which subsequently lost the elements of benzene to form $C_{10}H_{10}^{+\cdot}$, m/z 130 (eq 4).[33] Double-resonance experiments were performed to confirm this reaction sequence.

$$C_8H_8^{+\cdot} + C_8H_8 \rightarrow [C_{16}H_{16}]^{+\cdot} \rightarrow C_{10}H_{10}^{+\cdot} + C_6H_6 \quad (4)$$

The measured rate constant for this reaction is approximately 10 times greater than that for the styrene radical cation reacting with neutral styrene.[20] The difference in rate constants may be due to the differences in the ion structures of the two $C_8H_8^{+\cdot}$'s or to internal energy effects. Therefore a careful study of the structure of the products of the two ion–molecule reactions in question should provide a means to resolve these two possibilities. If the products are the same, it is likely that the difference in rates is due to variations of internal energy. However, if the products are different, then the reactant ions should have different structures.

High-Pressure Results. The o-quinodimethane radical cation reacted with neutral styrene in the chemical ionization source to produce the intermediate $C_{16}H_{16}^{+\cdot}$, which was accelerated from the source, mass analyzed, and then characterized by its unimolecular metastable or collision-induced dissociations. The spectra obtained were identical no matter what source was used for the o-quinodimethane ion.

The excess internal energy contents of the reactant ion and of the collision complex were removed through multiple collisions with the buffer or bath gas molecules present in the source at a pressure of 0.1–0.5 torr. Thus, a collision complex generated in a source operated at 0.5 torr and having a residence time of 10^5 s should undergo approximately 150 collisions, on the average. The high-pressure-source technique requires that we use a more complicated ionizing medium and lower partial pressures of reactants to minimize ionic polymerization to give $C_{24}H_{24}^{+\cdot}$, etc. For that reason, we chose to ionize the C_8H_8 neutral or its precursor by charge exchange with CS_2 (IP $\simeq$ 10 eV,[34] eq 5). The excess CS_2 also served as the bath gas, permitting collisional stabilization.

$$CS_2^{+\cdot} + C_8H_8 \rightarrow CS_2 + C_8H_8^{+\cdot} \quad (5)$$

The disadvantage of this high-pressure method is that we cannot be certain how the $C_{16}H_{16}^{+\cdot}$ is formed. Its

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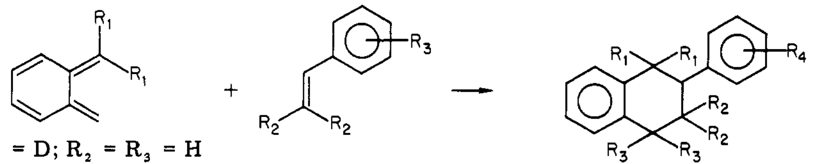
Table I. Unimolecular Metastable Losses for Collision Complexes[a] and Model 2-Phenyltetralins[b]



C1, R_1 = D; R_2 = R_3 = H
C2, R_1 = R_3 = H; R_2 = D
C3, R_1 = R_2 = H; R_3 = D

M1, R_1 = R_2 = R_3 = R_4 = H
M2, R_1 = D; R_2 = R_3 = R_4 = H
M3, R_1 = R_3 = R_4 = H; R_2 = D
M4, R_1 = R_2 = R_4 = H; R_3 = D
M5, R_1 = R_2 = R_3 = H; R_4 = D

model compd or collision complex	unimolecular metastable losses, rel abundance[c]					
	M − H	M − CH_3	M − CH_2D	M − CHD_2	M − C_6H_6	M − C_8H_8
C1[d]	23	16	<3	12	19	3.4
C2	*f*	5.7	<0.2	<0.2	14	1.5
C3	5.2	5.2	<0.2	<0.2	8.5	1.2
M1	9.0	16			34	4.2
M1a[e]	48	107			38	7.7
M2	8.5	4.5	<0.2	15	25	3.9
M3	7.5	0.4	12	<0.2	37	3.6
M4	9.3	22	<0.2	<0.2	23	2.5
M5	7.0	19	<0.2	<0.2	21	2.4

[a] Collision complexes are denoted as C1-C3, refering to the reactants used (shown above). [b] 2-Phenyltetralins are denoted as M1-M5, refering to the compound legend shown above. [c] Units for abundances are relative to a main-beam intensity normalized to 100 000 units. [d] Ionized with CS_2 as the reagent ion; all other complexes were formed with NO as a reagent gas. [e] Ionized by electron impact (50 eV). [f] Peak was not resolved from the main beam.

formation could involve styrene ion + styrene, styrene ion + *o*-quinodimethane, or *o*-quinodimethane ion + styrene. The first possibility can be ruled out by using isotopically labeled reagents. Since both styrene and *o*-quinodimethane have the same mass, *m*/*z* 104, and since both styrene ion and *o*-quinodimethane ions react with their respective neutrals to give *m*/*z* 208, it was necessary to label one of the reactants with deuterium so as to uniquely define the cross products. Moreover, since a molecule containing 16 carbons has a significant mono-^{13}C-containing isotope peak, one compound was labeled with two or more deuteriums so as to shift the mass of the intermediate formed in the cross-reactions 2 amu or more apart, which also removed the ^{13}C contribution from an ion one mass unit lower.

The second possibility (styrene ion + *o*-quinodimethane) could not be examined independently in the high-pressure CI source when the sulfone was used as the source of *o*-quinodimethane because neutral *o*-quinodimethane was also present. However, this possibility is removed when *o*-methylbenzyl acetate is used as the C_8H_8 ion precursor as no neutral *o*-quinodimethane was part of the mixture. As discussed above, the experimental results were identical regardless of the source of the *o*-quinodimethane ion (see Figure 1). Thus, if styrene ion reacted with *o*-quinodimethane, the product must have the same structure as that for *o*-quinodimethane ion + neutral styrene. Furthermore, the ICR double-resonance experiments establish that the *o*-quinodimethane is the reactant ion under the low-pressure conditions of that experiment.

The high-pressure experiment provided us the opportunity, lacking in the ICR experiments, to ionize a reference or model compound under essentially the same conditions as the collision complex so that direct comparisons can be made. The charge exchange with $CS_2^{+\cdot}$ is a low-energy or "soft" ionization technique, minimizing fragmentation and rearrangements. Thus, the structures of the reference ions should be maintained under these ionizing conditions. In addition, the multiple collisions should thermalize the ionized reference ions and the reaction intermediates to produce species that have approximately the same internal energies.

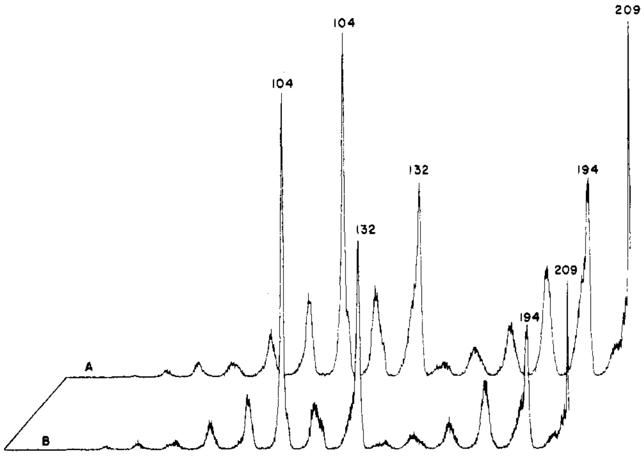


Figure 1. CID spectra of (a) the product of the ion–molecule reaction of *o*-quinodimethane radical cation and neutral styrene-*β*,*β*-d_2 and (b) the molecular ion of 3-phenyltetralin-2,2-d_2.

Unimolecular Metastable Decompositions. A very small fraction of the ions representing the collision complex still had sufficient energy to spontaneously decompose after the two-stage mass analysis. The unimolecular or metastable dissociations of the collision complexes and of the isotopically labeled 2-phenyltetralins are presented in Table I. Due to the rather poor resolution of the MS-II, ion clusters were not often resolved, and only the maximum intensity corresponding to the cluster is given for most cases. As can be seen, the metastable spectra of the various labeled 2-phenyltetralins ionized by charge exchange are approximately the same. This is not true for the spectra of the complexes, for which fluctuations in relative intensities were seen for losses of H and CH_3, depending on the experimental conditions. These dissociations, however, are by far the most sensitive to internal energy. This can be seen even for 2-phenyltetralin by comparing the spectra of the ion produced by NO charge

Table II. CID Spectral Data of Other $C_{16}H_{16}$ Isomeric Radical Cations

	fragment *m/z*							
compd	91	103–104[a]	115	125–130[a]	151	165	175–180[a]	189–193[a]
2-phenyl-1-*o*-tolylpropene (VI)	5	6	15	9	8	14	32	100
3-*o*-tolyl-1-phenylpropene (VII)	16	26	31	13	5	10	22	100
1-phenyltetralin	18	7	8	36	8	25	100	17

[a] Unresolved multiplet.

exchange (M1) and by 50-eV electron impact (M1a). The losses of H and CH_3 increased relative to the main beam by factors of 5.3 and 6.7, respectively, due to the ionizing energy increasing from about 8.3 eV in the charge exchange[33] to 50 eV. Thus, we see differences in metastable spectra of collision complexes which we ascribe to varying amounts of collisional stabilization resulting from pressure differences from one experiment to another. Therefore, we turned to CID spectra of the ions to minimize internal energy effects.

Collisionally Activated Decompositions. Internal energy effects have been demonstrated to be far less influential on the intensity ratios of fragment ions produced by collisional activation than on unimolecular metastable ion intensities.[1,2,34] Thus, CID spectra should provide a more reliable probe of ion structure than unimolecular metastable spectra.

The CID spectra of the collision complex for the ion–molecule reaction between the *o*-quinodimethane radical cation and neutral styrene-*β,β*-d_2 and of the corresponding reference compound, 3-phenyltetralin-*2,2*-d_2, are nearly identical (see Figure 1). Small differences occur for the losses of H, CH_3, and C_6H_6, but these intensities may vary slightly with the internal energy of the precursor because the dissociations represent the three processes with the lowest activation energies. Both spectra are characterized by the dominant loss of C_6H_6 (*m/z* 132), which is also a major peak in the 70-eV mass spectrum of 3-phenyltetralin-*2,2*-d_2, and the loss of $C_8H_6D_2$ (*m/z* 104), which represents the retro-Diels–Alder (RDA) reaction. The RDA reactions of the intermediate and reference proceeded with very little hydrogen scrambling, eliminating mostly carbons 2 and 3 of the tetralin structure as the vinyl group of the departing styrene molecule.

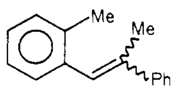
It should also be noted that $C_{16}H_{16}^{+\cdot}$ complexes were also formed when pure styrene or *o*-quinodimethane were introduced alone into the source. The unimolecular metastable and CID spectra of these collision complexes do not resemble the spectra in Figure 1. The CID spectrum for the styrene–styrene collision complex is reported elsewhere[37] and consists primarily of a single narrow peak at *m/z* 104, which splits cleanly into doublets at *m/z* 104 and 106 and at *m/z* 104 and 109 when styrene is reacted with styrene-*β,β*-d_2 and styrene-*2,3,4,5,6*-d_5, respectively. The losses of C_6H_6, CH_3, and H were all minor processes as compared to the return to starting materials. On the other hand, the CID spectrum of the intermediate from the reaction of *o*-quinodimethane ion with *o*-quinodimethane is characterized by the losses of CH_3, C_2H_5, and C_7H_8 in the ratio 5.5:2.2:1.0, clearly different from the ratio of intensities shown in Figure 1. These intermediates did not contribute to the spectra in Figure 1, however, as the deuterium labeling shifted the intermediate for the desired cross-chemistry to *m/z* 210 and that for the styrene intermediate to *m/z* 212, while the *o*-quinodimethane intermediate occurred at *m/z* 208.

Equally good correspondence exists for the CID spectrum of 2-phenyl-d_5-tetralin and that of the intermediate involving *o*-quinodimethane radical cation and styrene-*2,3,4,5,6*-d_5. The CID spectrum of the collision complex for styrene and *o*-quinodimethane-*α,α*-d_2 radical cation corresponds to that resulting from a one-to-one combination of 2-phenyltetralin-*1,1*-d_2 and 3-phenyltetralin-*1,1*-d_2, which is exactly what one would predict on the assumption that both methylene groups of the *o*-quinodimethane ion are equivalent.

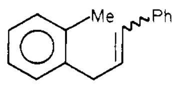
A detailed analysis of the isotopic label distribution for a given loss, such as that of C_6H_6, could provide further confirmation that the chemical properties of the intermediate are identical with those of the reference compound, 2-phenyltetralin. However, the CID spectra cannot be taken at unit resolution for these compounds; therefore, the peak shapes were mathematically deconvoluted. For the intermediate formed from styrene-d_5, the label distribution for losses of $C_6HD_5/C_6H_2D_4/C_6H_3D_3/C_6H_4D_2$ was found to be in the ratio 18:42:30:10. The 2-phenyltetralin ionized under identical charge-exchange conditions gave 26:43:25:6 as the corresponding ratio of losses. The ratio of losses appeared to depend slightly on the internal energy. For example, the corresponding ratio of losses from 2-phenyl-d_5-tetralin ionized by 15-eV electrons was 17:41:30:10, along with 2% loss of C_6H_5D, which is nearly identical with that of the labeled complex.

Thus, CID spectra of the deuterium-labeled collision complexes all correspond to the CID spectra of those deuterium-labeled 2-phenyltetralins which one would predict assuming that (1) the structure of the $C_8H_8^{+\cdot}$ ion is that of *o*-quinodimethane and (2) that the reaction proceeds through an ionic analogue of a [4 + 2]cycloaddition.

The above conclusions require that other $C_{16}H_{16}$ structures give spectra which are not identical with that of 2-phenyltetralin. Therefore, the CID spectra of 2-phenyl-1-o-tolylpropene (VI) and 3-*o*-tolyl-1-phenylpropene (VII) were measured along with the CID spectrum of 1-phenyltetralin (see Table II). The two acyclic $C_{16}H_{16}$ isomers are the carbon-skeletal structures for acyclic combination of the *o*-quinodimethane and styrene moities. However, VI and VII do differ from a directly formed intermediate by a hydrogen atom rearrangement. The spectra, however, are clearly unlike that of 2-phenyltetralin. The CID spectra of [2.2]paracyclophane, 1,3- and 1,4-diphenyl-1-butene, and 2,3-diphenyl-2-butene, which have



VI



VII

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been reported elsewhere,[37] are also vastly different from that of 2-phenyltetralin.

We feel that the evidence presented here indicates that the CID spectrum for 2-phenyltetralin is almost certainly unique, even though we have not investigated all possible $C_{16}H_{16}$ isomers. The similarity in the spectra of the collision complex and 2-phenyltetralin coupled with the evidence gleaned from the deuterium-labeling experiments allows us to conclude that the structure of the collision complex for the ion–molecule reaction between the *o*-quinodimethane radical cation and neutral styrene is that of 2-phenyltetralin. On the basis of this conclusion, we infer that the reaction is an ionic analogue of a [4 + 2] cycloaddition, and that the structure of the $C_8H_8^{+\cdot}$ is that of *o*-quinodimethane. However, we cannot rule out partial ring closing of the *o*-quinodimethane to give benzocyclobutane radical cation although it seems unlikely that the ring-closed form would be reactive with neutral olefins such as styrene. It is noteworthy that the gas-phase reaction involves the reaction of an ionized diene, whereas solution Diels–Alder reactions are preferred if the reactant dienophile is ionized.[2]

We can envision two applications of this experimental approach. First, the identification of isomeric ions (or their neutral precursors) which give nearly identical EI or collision-induced decomposition spectra (such as C_8H_8 isomers) can be accomplished by "derivatizing" the ion or neutral in a high-pressure source followed by analysis using MS/MS.[38] For example, we anticipate that of the isomeric C_8H_8 compounds only neutral styrene will give 2-phenyltetralin by reaction with the *o*-quinodimethane "reagent ion". Second, it may be possible to execute the synthesis of reference compounds and obtain their mass spectra in a matter of minutes by using these methods. The actual synthesis yields the gas-phase radical cation as a product and is conducted on the microsecond time scale. By use of the strategy developed here, reference CID spectra of 2-phenyltetralin and its specifically deuterium-labeled forms could be obtained without resorting to preparative procedures in a synthesis laboratory followed by conventional mass spectrometric analysis.

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Registry No. I, 84985-65-9; II, 100-42-5; III, 2471-91-2; IV, 17373-93-2; V, 89-95-2; VI, 14019-65-9; VII, 612-14-6; 1-phenyltetralin, 3018-20-0; 3-phenyltetralin-*2,2*-d_2, 85049-24-7; 3-phenyltetralin-*2,2*-d_2 radical cation, 85049-25-8; 2-phenyltetralin, 29422-13-7.

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Notes

Inversion of Reactivity (Umpolung) of α,β-Ethylenic Ketones and Aldehydes. Electrochemical Deprotection of γ-Thioacetalated Phosphonium Salts

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Organophosphorus compounds have been exploited for reversible inversion of reactivity (umpolung) of α,β-ethylenic ketones and aldehydes by heteroatom exchange.[1] Except for a special case,[1d] a Wittig or a Wittig–Horner reaction was used to remove the phosphorus group in such a way that the carbonyl compound was the only electrophilic counterpart to be used as the β-acylvinyl anion equivalent.

We are developing a synthetic route (Scheme I) for reversible d^3 inversion of reactivity[2] of α,β-ethylenic ketones and aldehydes **1** in which the ylides **3**, obtained[3] from phosphonium salts **2**, are synthetic equivalents of β-acylvinyl anions. As a part of this program[4] we have devised and wish to report an efficient electrochemical deprotection of γ-thioacetalated phosphonium salts **4** followed by base elimination of the phosphorus group with subsequent generation of β-branched α,β-ethylenic ketones or aldehydes **6**.

Several chemical methods have been developed for the hydrolysis of the thioacetal group;[5] their usefulness depends essentially on their selectivity toward other functional group in the molecule. Although it has never been optimized for preparative scale, the electrochemical method has been shown to be effective for the hydrolysis of simple dithianes, and the fixed-potential electrolysis can produce the desired selectivity.[6] Moreover, the phos-

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