

*cis*-1 is pyrolyzed under the same conditions **8** and **9** are formed again, the former in nearly quantitative yield (95% and 2.5% yield, respectively), vinylacetylene (**2**), however, cannot be detected in the pyrolysate by glpc. At higher isomerization temperatures styrene is formed in increasing amounts and becomes the main product at 710° (72% from *trans*-, 95% from *cis*-1).

The following mechanism is proposed for this new entry to the  $C_8H_8$  energy surface. In the first step the diradical **4** is formed from *trans*-1. This species may either dissociate to **2** or ring-close to the *cis* isomer, which subsequently rearranges to 1,2,4,5-cyclooctatetraene (**5**) by a [3,3] sigmatropic shift. Disrotatory cyclization of **5** leads to **9** and 1,5-carbon bridging to diradical **6**. Formation of **8** by an insertion reaction of the "carbene resonance form" of **6** (**7**) concludes the process. This mechanism is supported by the analogous conversion of 1,5-hexadiyne to 3,4-bismethylenecyclobutene,<sup>9</sup> for which 1,2,4,5-hexatetraene has been postulated as an intermediate,<sup>10</sup> as well as the thermal rearrangement of 3,4-bismethylenecyclobutene to benzene and fulvene which presumably proceeds *via* the same bisallenic intermediate.<sup>11</sup> More direct mechanistic evidence was obtained when the dimethyl derivatives of *trans*- and *cis*-1 were pyrolyzed; at 480° *trans*- and *cis*-10<sup>12</sup> rearrange to **11** and **12**, hydrocarbons that lack the characteristic  $H_4$ ,  $H_5$  and  $H_7$ ,  $H_8$  resonance signals of **8** and **9**.

Finally, pyrolysis experiments in the 0.5–1 Torr pressure region hint that intermediate **5** may be a vibrationally excited species.<sup>13,14</sup> Under these conditions the concentration of **9** is increased to nearly 20% while that of **8** is reduced by the corresponding amount.

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(12) These compounds<sup>6</sup> were prepared from the sodium salts of *cis*- and *trans*-1 with methyl iodide in liquid ammonia and characterized by spectroscopic methods.

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### Long-Lived $\beta$ -Phenylethyl and Ethylenebenzenium Cations in the Gas Phase<sup>1</sup>

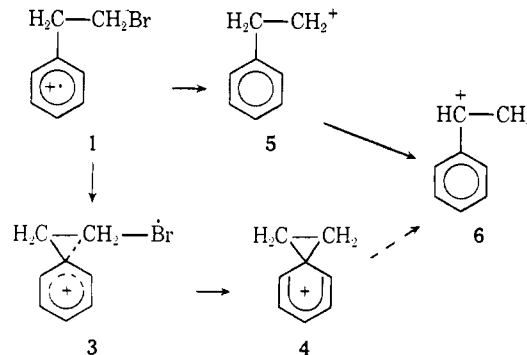
Sir:

The  $C_8H_8^+$  ion generated by unimolecular expulsion of  $Br\cdot$  from  $C_6H_5CH_2CH_2Br\cdot^+$  (**1**) is very abundant in comparison to  $C_8H_{11}^+$  generated from  $C_6H_5CH_2CH_2CH_2\cdot$

(1) Metastable Ion Characteristics. XXXIII. For paper XXXII see P. F. Bente, III, F. W. McLafferty, D. J. McAdoo, and C. Lifshitz, *J. Phys. Chem.*, submitted for publication.

$Br\cdot$  + (**2**).<sup>2</sup> Based on a variety of evidence, Shapiro<sup>3</sup> has proposed that this is due to aryl participation (**3**), possibly to form the ethylenebenzenium ion (**4**) instead of the classical  $\beta$ -phenylethyl cation (**5**) (Scheme I).

Scheme I



Similar "phenonium" ion structures have been postulated to explain analogous mass spectral data.<sup>4</sup> However, Grützmacher<sup>5</sup> has argued against aryl participation, presenting evidence that losses of  $Br\cdot$  from **1** and **2** have equal energy requirements (identity of ionization and appearance potential values).<sup>6</sup> From solution studies Olah<sup>7</sup> has given strong evidence for the formation from  $C_6H_5CH_2CH_2Cl$  of **4** and the rearranged  $\alpha$ -phenylethyl ion (**6**), but not of **5**; isotopic labeling is consistent with the formation of **6** from **5**, but not from **4**. Recently the homologous  $C_7H_7^+$  ions, such as tropylium, benzyl, and tolyl, have been shown<sup>8</sup> to be stable in the gas phase utilizing collisional activation (CA) spectra.<sup>9,10</sup> We report here evidence from CA spectra for the formation of stable **4**, **5**, and **6** cations from **1**.

The  $C_7(H,D)_5$ - $C_7(H,D)_7$  region of the CA spectra<sup>11</sup> of **1**,  $C_6H_5CH_2CD_2Br$  (**1b**),  $C_6H_5CD_2CH_2Br$  (**1c**), and  $C_6H_5CD_2CD_2Br$  (**1d**) (Table I) show dramatic changes with ionizing electron energy below 15 eV, indicating that a mixture of isomers is formed whose composition is sensitive to electron energy.<sup>9</sup> In contrast,  $C_6H_5CH(CH_3)Br$  appears to give a single isomeric product, presumably **6**.<sup>11</sup> At the lowest electron energy at which measurements could be made ( $\sim 11$  eV), the spectra of the  $d_2$  isomers **1b** and **1c** became identical within experimental error and consistent with that

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(11) Lower mass peaks are much less characteristic; complete CA spectra of these and other  $C_8H_8^+$  isomers will be discussed in the full paper.

Table I. Partial CA Spectra of C<sub>6</sub>H<sub>9</sub><sup>+</sup> Ions

Compound	Electron energy	Relative abundance <sup>a</sup>						
		<i>m/e</i>						
		89	90	91	92	93	94	95
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br	70	43	36	21				
	15	33	36	31				
	12	<2	45	55				
	11.5		30	70				
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CD <sub>2</sub> Br	70	16	26	26	19	13		
	15	16	25	27	16	16		
	12		20	50	30			
	11.5		10	45	45			
C <sub>6</sub> H <sub>5</sub> CD <sub>2</sub> CH <sub>2</sub> Br	70	16	24	26	20	14		
	15	13	21	27	21	18		
	12		10	40	50			
	11.5		15	45	40			
C <sub>6</sub> H <sub>5</sub> CD <sub>2</sub> CD <sub>2</sub> Br	70	5	15	17	16	30	12	5
	15	8	15	21	12	33	9	3
	12			40	60			
	11.5			20	80			
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )Br <sup>b</sup>	70	47	53					

<sup>a</sup> Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer of reversed geometry,<sup>10</sup> ion accelerating potential 3.8 kV. Unimolecular metastable decompositions of the precursor ion selected by the magnetic field occurring in the field-free drift region between the magnetic and electrostatic (ESA) analyzers were measured by scanning the ESA potential; no peaks were found in the region *m/e* 89–94. The pressure in the field-free region is then increased with helium until the precursor ion intensity is reduced to 10% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan. The data are the computer averaged composites of at least 25 separate scans. Precision was poor at the lowest electron energies because of low sensitivity and rapid change of relative intensities with electron energy; these data are generally based on several composite scans. <sup>b</sup> The values are not changed appreciably by lowering the ionizing electron energy.

predicted for the spectrum of the ethylenebenzenium ion **4** from those using **1** and **1d** as precursors. The dominant loss of CH<sub>2</sub> in the CA spectrum of **1** at this energy is reflected for **1b** and **1c** in the major peaks at *m/e* 91 and 93, C<sub>7</sub>H<sub>7</sub><sup>+</sup> and C<sub>7</sub>H<sub>5</sub>D<sub>2</sub><sup>+</sup>. The α- and β-carbon atoms must have become equivalent, while the lack of C<sub>7</sub>H<sub>6</sub>D<sup>+</sup> (*m/e* 92) indicates that the α- and β-hydrogen atoms have not been scrambled in the process. This strongly implies that the lowest energy pathway for Br· loss from **1** involves anchimeric assistance,<sup>3,4</sup> in contrast to the conclusions from appearance potential evidence.<sup>5</sup> Possibly anchimeric assistance is also effective in Br· loss from **2**.

Increasing the electron energy to 12 eV substantially decreases [C<sub>7</sub>H<sub>5</sub>D<sub>2</sub><sup>+</sup>] in the CA spectrum of **1b**, and slightly increases [C<sub>7</sub>H<sub>5</sub>D<sub>2</sub><sup>+</sup>] in that of **1c**, consistent with methylene loss by benzylic cleavage from the β-phenylethyl cation **5**. The 12-eV data can be fit within experimental error by assuming that [90<sup>+</sup>]/[91<sup>+</sup>] = 1 in the CA spectrum of pure C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub><sup>+</sup> ions and that [5]/[4] = 1:3; note that [6] < [5]. The stability of gaseous **5** ions (half-life >10<sup>-5</sup> sec)<sup>9</sup> is in contrast to the rearrangement proclivity in solution<sup>7</sup> and to that for somewhat analogous ions such as ROCH<sub>2</sub>CH<sub>2</sub><sup>+</sup> → RO<sup>+</sup>=CHCH<sub>3</sub> and RNHCH<sub>2</sub>CH<sub>2</sub><sup>+</sup> → RN<sup>+</sup>H=CHCH<sub>3</sub>.<sup>12</sup>

This is not true at higher ionizing energies, however; the CA spectra are consistent with the formation of the α-phenylethyl cation, **6**, as the dominant isomer.

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However, the similarity of the CA spectra of C<sub>8</sub>H<sub>9</sub><sup>+</sup> from **1b** and **1c** suggests that **6** is not formed mainly by isomerization from **5**, as indicated in solution.<sup>7,11,13a</sup>

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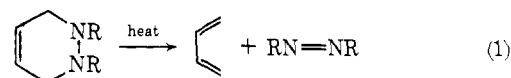
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### Formation of *cis*-Azomethane by a Retro-Diels–Alder Reaction

Sir:

The retro-Diels–Alder reaction of 1,2,3,6-tetrahydropyridazine derivatives (eq 1) has been little exploited,



although the thermal cleavage of the dialkylazodicarboxylate adducts<sup>1</sup> of anthracene<sup>2</sup> has been known for decades. Cohen and coworkers<sup>3</sup> found that hydrolysis of the azodicarboxylate–cyclopentadiene adduct generated a reducing agent, postulated to be diimide formed by cleavage of the expected hydrolysis product. Corey and Mock<sup>4</sup> used hydrolysis of the anthracene adduct for generation of diimide at 50–90°, reducing several unsaturated compounds and detecting diimide by mass spectroscopy.

We became interested in the stereochemistry of the elimination reaction (eq 1), which should be capable of giving either *cis* or *trans* azo compounds, depending upon the geometry at the nitrogens in the tetrahydropyridazine. We postulated that electronic interaction of the lone pair electrons on the nitrogens with the olefinic π electrons (n,π mixing) might lead to significant differences in the energy barrier for cleavage of conformations leading to *cis* and *trans* azo compounds.

We selected tetrahydropyridazines with *N*-methyl substituents for our initial studies for several reasons. They are easily prepared from dialkyl azodicarboxylate adducts by lithium aluminum hydride reduction, and the products, *cis*- and *trans*-azomethane, are both known and fairly thermally stable. The *cis* form of azomethane is not readily available, since the only published preparation is by photolysis of the *trans* form, and the equilibrium fraction of *cis* azomethane is small, 0.09 ± 0.01 in water.<sup>5</sup> Methyl groups are small enough so that the *cis* form should not be greatly

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