

Thirteen Stable Isomers of Gaseous  $C_8H_9^+$  Cations<sup>1</sup>Claus Köppel,<sup>2a</sup> C. C. Van de Sande,<sup>2b</sup> N. M. M. Nibbering,<sup>2c</sup>  
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**Abstract:** Collisional activation mass spectra show that the following  $C_8H_9^+$  carbocations are stable for  $\geq 10^{-5}$  s: *o*-, *m*-, and *p*-methylbenzyl, methyltropylium,  $\alpha$ -phenylethyl, homotropylium, 2,4- and 2,5-dimethylphenyl, *o*- and *p*-ethylphenyl, ethylenebenzenium, and protonated benzocyclobutene. The  $\beta$ -phenylethyl cation was the only isomer for which no evidence of stability could be found. Molecular ion isomerization for xylenes and ethylbenzene lead mainly to methyltropylium ion formation, but dimethyl- and ethylphenyl halides isomerize to the corresponding methylbenzyl structures. In sharp contrast to its behavior in superacid medium,  $\beta$ -phenylethyl chloride yields protonated benzocyclobutene and an unique isomer, as yet unidentified.

Despite extensive studies over many years of gaseous cations derived from aromatic compounds,<sup>3,4</sup> it has been established only recently that such simple carbocations as benzyl,<sup>4,5</sup> tolyl,<sup>4</sup> and benzenium<sup>6</sup> are reasonably stable (lifetimes  $> 10^{-5}$  s) in the gas phase. This study of  $C_8H_9^+$  isomers was undertaken to compare the behavior of homologous ions, as previous reports have given little evidence for stable  $C_8H_9^+$  structures. Isotopic labeling shows that the decomposition of  $C_8H_9^+$  ions generated from *p*-xylene,<sup>7</sup> ethylbenzene,<sup>8</sup> *p*-ethyltoluene,<sup>9</sup>  $\beta$ -phenylethyl chloride,<sup>8</sup>  $\alpha$ - and  $\beta$ -phenylethyl bromide,<sup>10</sup> and 7-methylcycloheptatriene<sup>11</sup> is accompanied by extensive loss of the original positional identity of both the hydrogen and carbon atoms. Appearance potential (AP) values for the methylbenzyl radicals are similar (*o*-,  $7.61 \pm 0.05$ ; *m*-,  $7.65 \pm 0.03$ ; and *p*-,  $7.46 \pm 0.03$ ),<sup>12</sup> and AP of  $C_8H_9^+$  ions from *m*- and *p*-xylene, and from  $\alpha$ -bromo-*m*- and *p*-xylene, are the same within experimental error.<sup>13</sup> The decompositions of metastable  $C_8H_9^+$  ions from a variety of sources appear to occur from a common structure or mixture of structures.<sup>14</sup> In contrast, we now find that at least 13  $C_8H_9^+$  isomers are stable, utilizing data from "collisional activation" (CA) mass spectra. Such spectra have been found uniquely useful for ion structural characterization because their abundances are essentially independent of the internal energy of the precursor ion.<sup>15</sup> In preliminary communications<sup>1,16</sup> we have reported particular CA data on ions **4**, **5**, and **10–12**; this further study finds no evidence that **14** is stable, contrary to previous indications.<sup>16a</sup>

## Results and Discussion

The most characteristic peaks in the  $C_8H_9^+$  CA spectra (*m/e* 51, 89, 90, and 91) are given in Table I; for higher accuracy the abundance of the first was measured against that of *m/e* 39, and the latter three relative to each other. Two types of peaks were found at *m/e* 91; one is shifted to lower mass units by  $\sim 0.25$  units, indicating that an activation energy of  $\sim 20$  eV is required for its formation. Also the methyltropylium ions (**4**) are unique in that a unimolecular decomposition occurring in the mass spectrometer drift region produces  $C_7H_6^+$ , *m/e* 90. The differences in the CA spectra found for 13 isomers are not sufficient, however, to allow unequivocal distinction to be made for all isomers, especially those differing only by the position of substitution on the aromatic ring; the CA spectra of isotopically labeled compounds (Table II) were used to investigate the stability of such isomers.

**Methylbenzyl Ions (1, 2, 3).** The CA spectrum of  $C_8H_9^+$  ions from each of the three isomeric  $\alpha$ -bromoxylenes was found to be independent of electron energy, consistent with formation of only methylbenzyl ions from each. Although the spectra are closely similar, the meta isomer is distinguishable from the other two on the basis of  $[51^+]/[39^+]$ . The CA spectra of labeled derivatives of **3** indicate a substantial degree of isotopic scrambling, but the lack of dependence of the spectra on electron energy indicates that most of this isomerization takes place *after* collision. For the  $\alpha'$ -*d*<sub>1</sub> derivative, which should give  $CH_2DC_6H_4CH_2^+$  ions, the majority of the CA loss of C(H, D)<sub>3</sub> involves the original methyl group, as does the loss of methane. Similarly, the  $\alpha$ -labeled derivatives show that CA loss of  $CH_2$  originates largely from the methylene group. Thus the isomerization of **3** to **1** or **2** is not extensive before collision, and the major proportion of ions cannot have the methyltropylium structure **4**, in contrast to previous conclusions based on appearance potential data.<sup>13</sup> The similarities in the CA spectra of **1**, **2**, and **3** thus appear to arise more from their similar behavior after collisional activation than from prior isomerization.

From isotopic labeling and mechanistic evidence, Shen, Dunbar, and Olah<sup>5a</sup> concluded that the reaction of toluene and benzyl ions yields methylbenzyl ions. The CA spectrum of  $C_8H_9^+$  ions produced from a 1:1 mixture of toluene and benzyl bromide at 0.1 Torr completely confirms their conclusion.

**$\alpha$ -Phenylethyl Ion (5).** Formation of a single stable  $C_8H_9^+$  isomer from  $\alpha$ -phenylethyl bromide is indicated from the CA spectrum, which is independent of ionizing electron energy. Although the abundances of *m/e* 89, 90, and 91 are similar to those of the spectra of **1**, **2**, and **3**, the *m/e* 91 is unusual in being distinctly closer to *m/e* 90, consistent with the formation of *m/e* 91 from  $C_8H_9^+$  ions which have gained an unusually high amount ( $\sim 20$  eV) of internal energy on collision. Again data from isotopically labeled precursors (Table II) are consistent

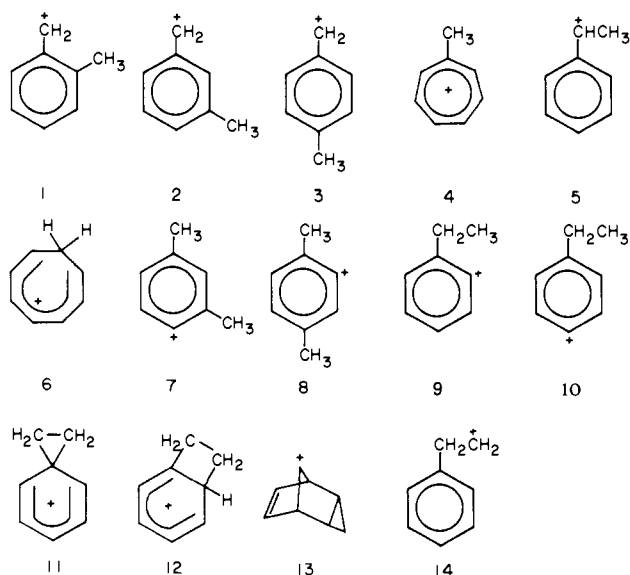


Table I. Partial Collisional Activation Spectra of C<sub>8</sub>H<sub>9</sub><sup>+</sup> Ions

| Compd,<br>electron energy, eV <sup>a</sup>  | Rel abundance, <sup>b</sup> <i>m/e</i> |                 |                    |                 |
|---|--|-----------------|--------------------|-----------------|
|   | 51/39                                  | 89              | 90                 | 91              |
| α-Bromo- <i>o</i> -xylene <sup>c</sup>  | 1.8                                    | 49              | 28                 | 23              |
| α-Bromo- <i>m</i> -xylene <sup>c</sup>  | 1.5                                    | 51              | 26                 | 24              |
| α-Bromo- <i>p</i> -xylene <sup>c,d</sup>  | 1.7                                    | 48              | 27                 | 24              |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br + C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> <sup>e</sup> | 1.7                                    | 48              | 26                 | 26              |
| α-Phenylethyl bromide <sup>c,f</sup>  | 2.6                                    | 51              | 29                 | 20 <sup>g</sup> |
| Styrene + H <sup>+</sup> <sup>e</sup>   | 2.6                                    | 51              | 31                 | 18 <sup>g</sup> |
| Methylcycloheptatriene <sup>j</sup>   | 1.8                                    | 60              | (165) <sup>j</sup> | 11              |
| 19  | 1.6                                    | 72              | (590)              | <1.5            |
| <i>o</i> -Xylene <sup>j</sup>   | 1.8                                    | 61              | (175)              | 11              |
| 19  | 1.5                                    | 60              | (550)              | <1.5            |
| <i>m</i> -Xylene <sup>j</sup>   | 1.6                                    | 59              | (175)              | 11              |
| 19  | 1.5                                    | 65              | (560)              | <1.5            |
| <i>p</i> -Xylene <sup>j</sup>   | 1.7                                    | 58              | (170)              | <1              |
| 19  | 1.6                                    | 61              | (460)              | <1              |
| Ethylbenzene <sup>j</sup>   | 2.1                                    | 61              | (410)              | 6 <sup>g</sup>  |
| 19  | 1.8                                    | 75              | (570)              | 5 <sup>g</sup>  |
| Cyclooctatetraene + H <sup>+</sup> <sup>e,h</sup>   | 2.6                                    | 57              | 26                 | 17 <sup>g</sup> |
| <i>o</i> -Bromoethylbenzene   | 2.3                                    | 57 <sup>j</sup> | 28                 | 15 <sup>g</sup> |
| 11.5  | 2.5                                    | 57              | 27                 | 16 <sup>g</sup> |
| <i>p</i> -Bromoethylbenzene   | 2.3                                    | 57 <sup>i</sup> | 28                 | 16 <sup>g</sup> |
| 12  | 2.4                                    | 48              | 32                 | 20 <sup>g</sup> |
| 4-Iodo- <i>m</i> -xylene <sup>c</sup>   | 1.4                                    | 64              | 22                 | 15              |
| 2-Bromo- <i>p</i> -xylene   | 1.7                                    | 59              | 25                 | 16              |
| 12  | 1.5                                    | 51              | 26                 | 23              |
| β-Phenylethyl iodide  |  | 51              | 16                 | 33              |
| 10.7  |  | 31              | 11                 | 58              |
| β-Phenylethyl bromide   | 2.4                                    | 53              | 16                 | 31              |
| 17.7  |  | 48              | 15                 | 38              |
| 14.7  | 2.6                                    | 42              | 14                 | 44              |
| 12.0  |  | 37              | 10                 | 52              |
| 10.7  | 2.7                                    | 35              | 10                 | 55              |
| β-Phenylethyl chloride  | 2.3                                    | 58              | 21                 | 22              |
| 18  |  | 54              | 30                 | 16              |
| <i>n</i> -Propylbenzene   |  | 59              | 23                 | 18              |
| 19  |  | 55              | 28                 | 18              |
| Benzocyclobutene + H <sup>+</sup> <sup>e</sup>  | 2.9                                    | 54              | 29                 | 17              |
| Isomer "X"  | 2.2                                    | 59              | 19                 | 22              |
| 6-Methylene-2-norbornene <sup>j</sup>   | 1.8                                    | 54              | (140) <sup>j</sup> | 6               |

<sup>a</sup> 70 eV if not given. <sup>b</sup> Abundance of the mass 51 relative to that of 39, and of the 89, 90, and 91 relative to the total of these three peaks. Reproducibility on separate determinations ± 10% relative. <sup>c</sup> CA spectrum of ions produced at low electron energies is identical within experimental error. <sup>d</sup> Data for the chloride and for *p,p'*-dimethyl-1,2-diphenylethane are identical within ± 20% (earlier runs). <sup>e</sup> Obtained with H<sub>2</sub>O at high (~0.1 Torr) ion source pressures. <sup>f</sup> Data for the iodide are identical within ± 20% (earlier runs). <sup>g</sup> Unusually high activation energy required for formation; peak shifted to lower mass by ~0.25 units. <sup>h</sup> [89<sup>+</sup> + 90<sup>+</sup> + 91<sup>+</sup>]/[39<sup>+</sup>] ~ 70% that for **5**. <sup>i</sup> [89<sup>+</sup>]/[39<sup>+</sup>] = 0.6 for ortho, 0.9 for para isomer. <sup>j</sup> Abundances of *m/e* 89, 90, and 91 based on the sum of all CA peaks = 500; on this basis [89<sup>+</sup> + 90<sup>+</sup> + 91<sup>+</sup>] = 55-110 for CA spectra of other C<sub>8</sub>H<sub>9</sub><sup>+</sup> isomers. Values in parenthesis include ions formed by decomposition of metastable C<sub>8</sub>H<sub>9</sub><sup>+</sup> ions.<sup>20</sup>

with the α-phenylethyl ion structure, the loss of methyl (and methane) mainly involving the β-carbon atom.<sup>17</sup> For the CH<sub>2</sub> loss 0 and ≤17% arise from the β and α carbons, respectively, the latter value being a maximum in that it includes H/D scrambling. Thus the CH<sub>2</sub> loss after collisional activation mainly involves opening of the aromatic ring, consistent with its unusually high energy requirement. Note also that the labeling results preclude any appreciable equilibration between **5** and the ethylenebenzenium ion **11**.

As expected, protonation of styrene yields mainly **5**; use of D<sub>2</sub>O (Table II) for this shows that isotopic scrambling accompanying protonation is relatively minor.

**Methyltropylium Ion (4).** In contrast to the other molecular ions studied, those of methylcycloheptatriene (**15**), xylene (**16**), and ethylbenzene (**17**) yield C<sub>8</sub>H<sub>9</sub><sup>+</sup> metastable ions which decompose by loss of CH<sub>3</sub> to give *m/e* 90. This fragmentation is consistent with the methyltropylium structure (**4**) for the decomposing C<sub>8</sub>H<sub>9</sub><sup>+</sup> ions (at least CH<sub>3</sub> loss seems less likely for **1-3** and **5-14**), and the formation of **4** is analogous to the predominant formation of tropylium ions from cycloheptatriene and toluene ions.<sup>4</sup> The very low abundance of *m/e* 91 in

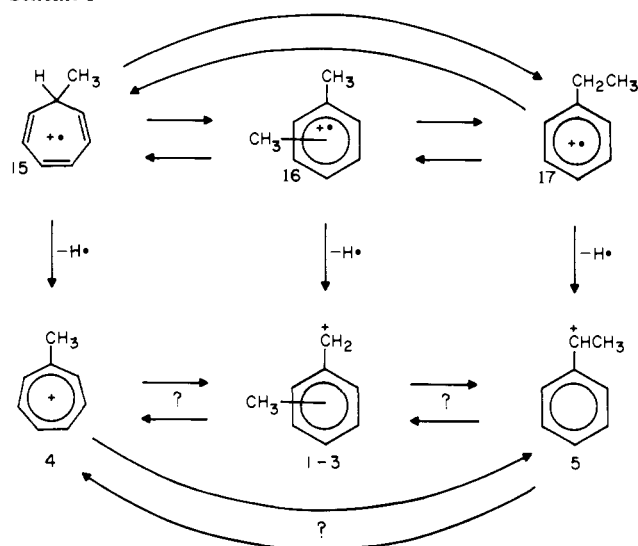
the CA spectra of these C<sub>8</sub>H<sub>9</sub><sup>+</sup> ions formed at low electron energies from **15** and **16** indicates that there is little (<10%) of any other C<sub>8</sub>H<sub>9</sub><sup>+</sup> isomer present, and presumably these C<sub>8</sub>H<sub>9</sub><sup>+</sup> ions are mainly **4**.<sup>20</sup> The CA peak ratio [51<sup>+</sup>]/[39<sup>+</sup>] shows that roughly 40% of the C<sub>8</sub>H<sub>9</sub><sup>+</sup> ions formed at 70 eV from **17**, and possibly some from **15** and *o*-xylene, have structure **5**. The ratio [89<sup>+</sup>]/[91<sup>+</sup>], although in this case a less accurate measurement,<sup>20</sup> indicates that an appreciable amount of **5** is formed from **17** even at low electron energies, and that substantial amounts of the methylbenzyl isomers **1-3** are formed from **15**, as well as from the **16** isomers, using 70-eV electrons. The expected C<sub>8</sub>H<sub>9</sub><sup>+</sup> products **1-3** and **5** (Scheme I) were shown (vide supra) to have relatively high stabilities; in view of this, it would seem surprising that **4**, which corresponds to the most stable ion (tropylium) of the homologous C<sub>7</sub>H<sub>7</sub><sup>+</sup> ions,<sup>4,21,22</sup> would not also be quite stable. Thus, at least at low electron energies, equilibration of the C<sub>8</sub>H<sub>9</sub><sup>+</sup> isomers **1-3** ⇌ **4** ⇌ **5** should be negligible. Cycloheptatriene and toluene ions formed at low electron energies undergo nearly complete equilibration before hydrogen loss; by analogy, the formation of **4** from **16** and **17**, which increases with lowered

Table II. Partial Collisional Activation Spectra of Isotopically Labeled Ions

| Compound<br>electron energy, eV <sup>a</sup>  | Relative abundance, <sup>b</sup> <i>m/e</i> |    |     |     |     |     |     | Label retention <sup>e</sup> |                  |                  |
|---|---|----|-----|-----|-----|-----|-----|------------------------------|------------------|------------------|
|   | 89  | 90 | 91  | 92  | 93  | 94  | 95  | -CH <sub>4</sub>             | -CH <sub>3</sub> | -CH <sub>2</sub> |
| $\alpha$ -Bromo- <i>p</i> -xylene- $\alpha'$ - <i>d</i> <sub>1</sub> <sup>c</sup>       | 36  | 32 | 7.7 | 25  |     |     |     | 25 (56)                      | 28 (67)          | 100 (78)         |
| $\alpha$ -Bromo- <i>p</i> -xylene- $\alpha$ - <i>d</i> <sub>1</sub>                     | 17  | 39 | 35  | 9.3 |     |     |     | 65 (56)                      | 73 (67)          | 38 (78)          |
| $\alpha$ -Bromo- <i>p</i> -xylene- $\alpha$ - <sup>13</sup> C                           | 9.0   | 46 | 36  | 9.0 |     |     |     | 81 (88)                      | 76 (88)          | 37 (88)          |
| $\alpha$ -Bromo- <i>p</i> -xylene- $\alpha,\alpha$ - <i>d</i> <sub>2</sub> <sup>c</sup> | 5.9   | 18 | 43  | 26  | 5.2 |     |     | 88 (28)                      |                  | 22 (58)          |
| $\alpha$ -Phenylethyl- $\beta$ - <sup>13</sup> C  | 34  | 39 | 6.9 | 20  |     |     |     | 34 (88)                      | 24 (88)          | 100 (88)         |
| $\alpha$ -Phenylethyl- $\alpha$ - <i>d</i> <sub>1</sub> bromide                         | 18  | 37 | 28  | 16  |     |     |     | 64 (56)                      | 84 (67)          | 83 (78)          |
| Styrene + D <sup>+</sup> (- $\beta$ - <i>d</i> <sub>1</sub> ) <sup>d</sup>              | 35  | 36 | 15  | 14  |     |     |     | 31 (56)                      | 38 (67)          | 86 (78)          |
| $\beta$ -Phenylethyl- $\alpha,\alpha$ - <i>d</i> <sub>2</sub> bromide                   | 16  | 26 | 27  | 9.9 | 21  |     |     |                              |                  | 68 (58)          |
| 17.7  | 17  | 22 | 25  | 7.8 | 27  |     |     |                              |                  | 72               |
| 14.7  | 15  | 21 | 28  | 7.7 | 29  |     |     |                              |                  | 67               |
| 12.0  | 16  | 19 | 28  | 8.8 | 28  |     |     |                              |                  | 53               |
| 10.7  | 14  | 21 | 27  | 7.0 | 30  |     |     |                              |                  | 54               |
| $\beta$ -Phenylethyl- $\beta,\beta$ - <i>d</i> <sub>2</sub> bromide                     | 15  | 27 | 28  | 9.4 | 21  |     |     |                              |                  | 67               |
| 17.7  | 16  | 24 | 27  | 8.1 | 28  |     |     |                              |                  | 73               |
| 14.7  | 16  | 20 | 28  | 8.7 | 28  |     |     |                              |                  | 65               |
| 12.0  | 17  | 21 | 27  | 6.9 | 28  |     |     |                              |                  | 54               |
| 10.7  | 16  | 19 | 28  | 8.4 | 31  |     |     |                              |                  | 57               |
| $\beta$ -Phenylethyl- $\alpha,\alpha,\beta,\beta$ - <i>d</i> <sub>4</sub> bromide       | 2.8   | 19 | 23  | 16  | 29  | 8.3 | 1.8 |                              |                  |                  |
| 17.7  | 3.1   | 15 | 21  | 14  | 32  | 9.3 | 5.1 |                              |                  |                  |
| 14.7  | 5.1   | 17 | 17  | 12  | 34  | 12  | 3.1 |                              |                  |                  |
| 12.0  | 3.8   | 15 | 18  | 10  | 40  | 10  | 3.8 |                              |                  |                  |
| 10.7  | 3.9   | 18 | 19  | 9.2 | 39  | 6.6 | 3.9 |                              |                  |                  |
| $\beta$ -Phenylethyl- $\alpha$ - <sup>13</sup> C bromide                                | 24  | 39 | 21  | 17  |     |     |     | 55                           | 60               | 55 (88)          |
| 17.7  | 19  | 33 | 23  | 25  |     |     |     | 59                           | 69               | 65               |
| 14.7  | 17  | 29 | 27  | 27  |     |     |     | 61                           | 72               | 63               |
| 12.0  | 14  | 27 | 30  | 29  |     |     |     | 59                           | 66               | 56               |
| 10.7  | 12  | 26 | 32  | 31  |     |     |     | 54                           | 71               | 56               |
| $\beta$ -Phenylethyl- $\beta$ - <sup>13</sup> C bromide                                 | 22  | 40 | 21  | 17  |     |     |     | 58                           | 55               | 56               |
| 17.7  | 19  | 33 | 25  | 24  |     |     |     | 60                           | 73               | 64               |
| 14.7  | 18  | 30 | 26  | 27  |     |     |     | 58                           | 62               | 61               |
| 12.0  | 14  | 26 | 30  | 30  |     |     |     | 58                           | 69               | 58               |
| 10.7  | 14  | 26 | 30  | 30  |     |     |     | 61                           | 51               | 55               |

<sup>a</sup> 70 eV if not given. <sup>b</sup> Reproducibility on separate determinations  $\pm < 10\%$  relative. <sup>c</sup> CA spectrum of ions produced at low electron energies is identical within experimental error. <sup>d</sup> Obtained at high ion source pressures of D<sub>2</sub>O. <sup>e</sup> Percent of ions, formed by loss of CH<sub>2</sub>, CH<sub>3</sub>, or CH<sub>4</sub>, which completely retain the isotopic label(s); values calculated for complete isotopic scrambling are given in parentheses.

Scheme I



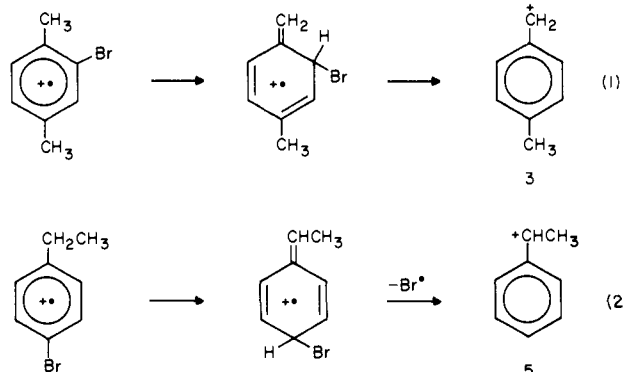
electron energy, is probably due to interconversions of these C<sub>8</sub>H<sub>10</sub><sup>+</sup> isomers. This favored formation of **4** indicates, not surprisingly, that **15** has a lower activation energy for H• loss than **16** or **17**. Ionization of either cycloheptatriene or toluene with 70-eV electrons gives a 4:1 mixture of tropylium and benzyl ions, suggesting rapid interconversion of these C<sub>7</sub>H<sub>7</sub><sup>+</sup> ions at high energies. In contrast, interconversion of the C<sub>8</sub>H<sub>9</sub><sup>+</sup> isomers **1-3**  $\rightleftharpoons$  **4**  $\rightleftharpoons$  **5** is far from complete under high-energy conditions; in fact it is possible that much of the isomeric

product formation arises from the competitive interconversion **15**  $\rightleftharpoons$  **16**  $\rightleftharpoons$  **17**. To the extent that the stabilities of the product ions reflect the density of states of activated complexes of the reactions important in forming the C<sub>8</sub>H<sub>9</sub><sup>+</sup> isomers, these results indicate that the ion stabilities are in the order **4** > **5** > **1-3**.

**Homotropylium Ion (6).** Protonation of cyclooctatetraene produces C<sub>8</sub>H<sub>9</sub><sup>+</sup> ions whose CA spectrum is similar to that of  $\alpha$ -phenylethyl ions (**5**), but the differences in [89<sup>+</sup>]/[91<sup>+</sup>] and in [89<sup>+</sup> + 90<sup>+</sup> + 91<sup>+</sup>]/[39<sup>+</sup>] are substantially greater than the experimental error. Although the data could arise from a mixture of isomers such as protonated benzocyclobutene (**12**) and **5**, they could also be due to a substantial proportion of the ions retaining the original homotropylium structure **6** for 10<sup>-5</sup> s.

**Dimethylphenyl and Ethylphenyl Ions (7-10).** The CA spectrum of the C<sub>8</sub>H<sub>9</sub><sup>+</sup> ions from 4-iodo-*m*-xylene is insensitive to ionizing electron energy and substantially different than that of any logical more stable ion product, such as **2**, and so these appear to be mainly 2,4-dimethylphenyl ions, **7** or its ring isomers. The C<sub>8</sub>H<sub>9</sub><sup>+</sup> CA spectra from *o*- and *p*-bromoethylbenzene, as well as from 2-bromo-*p*-xylene, are similar to that of **7** in showing a relatively low loss of CH<sub>2</sub> and high loss of CH<sub>4</sub>; these were distinctive features of the CA spectra of the methylphenyl ions,<sup>4</sup> homologues of **7-10**. Because the *o*-, *m*-, and *p*-methylphenyl ions formed at 70 eV largely maintain their isomeric identity,<sup>4,19</sup> it is possible that **7** and **8** also have not isomerized to a mixture of xylyl ions, although we did not investigate this possibility. At lower electron energies the CA C<sub>8</sub>H<sub>9</sub><sup>+</sup> spectrum from 2-bromo-*p*-xylene changes substan-

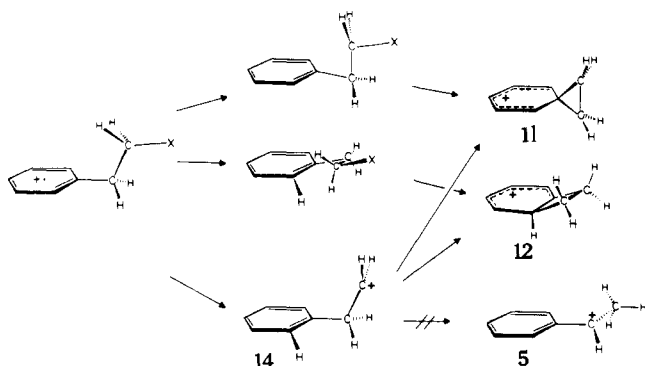
tially, indicating major formation of methylbenzyl ions, presumably **3**. This appears to arise from isomerization of the molecular ions competitive with bromine loss, for which the activation energy should be substantially higher than that of the corresponding loss from the iodo compound. A methylenecyclohexadiene structure is a logical intermediate (eq 1); an analogous mechanism was used to explain benzyl ion formation from the molecular ions of tolyl derivatives.<sup>4</sup>



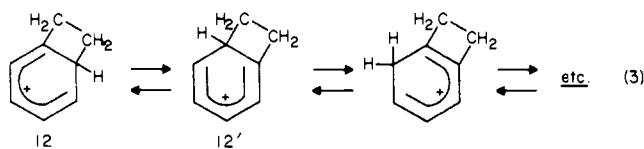
The  $C_8H_9^+$  ions produced from *o*- and *p*-bromoethylbenzene yield CA spectra that are sufficiently different from those of such expected isomerization products **4**<sup>18</sup> or **5** to provide evidence for the stability of ethylphenyl ions (**9**, **10**). The CA spectra of **9** and **10** ions formed with 70-eV electrons show distinctive differences in  $[89^+]/[39^+]$ , indicating isomeric stability analogous to that of the homologous *o*-, *m*-, and *p*-methylphenyl ions.<sup>4,19</sup> Other  $C_8H_9^+$  isomers such as **5** may be formed in addition to **9** and **10**; at low electron energies the CA spectrum from the para isomer is quite similar to that of **5**, again consistent with a competing isomerization of the molecular ion (eq 2). Note, however, that the proportion of methyltropylium ions (**4**) formed even at low electron energies must be small, in contrast to previous assumptions from isotope effect studies.<sup>18</sup> The CA spectrum was also recorded for  $C_8H_9^+$  ions formed by decomposition of metastable *p*-bromoethylbenzene ions in the field-free drift region before the magnetic field; under these conditions the isotope effect conclusions<sup>18</sup> are borne out, the CA spectrum indicating that half of these ions are **4**, the remainder being **5** and/or **8**.<sup>16b</sup> Rearrangement to cycloheptatriene molecular ions apparently involves a much tighter activated complex than does eq 2.

**Ethylenebenzenium, Protonated Benzocyclobutene, Isomer "X", and  $\beta$ -Phenylethyl Ions (**11**–**14**).** The  $C_6H_5CH_2CH_2X$  derivatives studied ( $X = I, Br, Cl,$  and  $CH_3$ , **18**–**21**) all gave  $C_8H_9^+$  ions whose CA spectra change dramatically with change in the ionizing electron energy. Plots of the peak abundances<sup>1</sup> (Table I) vs. component proportions show that the spectral data for each compound can be rationalized as arising from binary mixtures of isomeric  $C_8H_9^+$  ions whose composition changes with electron energy. Further, for each of the molecules **18**–**21** the CA spectrum of the component

Scheme II



formed at higher energy corresponds to  $[89^+]/[90^+]/[91^+] = 59:19:22$ , indicating the common formation of an unknown isomer "X"; the proportion of X formed at 70 eV is 70, 75, 80, and  $\sim 60\%$  for **18**–**21**, respectively.<sup>1</sup> At low energies **18** and **19** give  $C_8H_9^+$  ions of the same CA spectrum (not of "X"), and so these ions probably represent a relatively pure  $C_8H_9^+$  isomer; evidence will be presented below that this is the ethylenebenzenium ion, **11** (Scheme II). At low electron energies **20** and **21** appear to yield **12**; their CA  $C_8H_9^+$  spectra not only agree closely with each other but also with that obtained by the ion source protonation of benzocyclobutene. In the latter process protonation probably occurs at other ring positions, but isomerizations such as eq 3 should be rapid.



Initial formation of the  $\beta$ -phenylethyl ion **14** is a logical possibility (Scheme II), although ab initio molecular orbital calculations indicate that **14** should collapse without activation to structure **11**.<sup>23</sup> In a preliminary communication we reported evidence for the formation of **14**, based on a slightly greater loss of  $CH_2$  than  $CD_2$  in the CA spectrum of  $C_8H_7D_2^+$  ions from the ionization of  $C_6H_5CD_2CH_2Br$  at 12 eV; the effect was not observed with 11.5 or 15-eV ionizing electrons. These measurements have been repeated on our revised instrumentation of substantially higher resolution, sensitivity, and precision,<sup>24</sup> and this effect cannot be substantiated; the CA spectra of the  $\alpha,\alpha$ - $d_2$  and  $\beta,\beta$ - $d_2$  derivatives are identical within experimental error over the full range of ionizing electron energies. Some H/D scrambling does take place as shown by the  $\alpha,\alpha,\beta,\beta$ - $d_4$  derivative, so as a further check the CA spectra of  $C_7^{13}CH_9^+$  ions from the  $\alpha$ - $^{13}C$  and  $\beta$ - $^{13}C$  derivatives were also examined. Again, these spectra were identical using ionizing electrons over the range 10.7–70 eV. Thus this more detailed study finds no evidence for  $\beta$ -phenylethyl ions (**14**) of  $\geq 10^{-5}$ -s lifetimes, in agreement with theoretical predictions.<sup>23</sup>

From the labeling data both of the  $C_8H_9^+$  isomers formed from  $C_6H_5CH_2CH_2Br$  must have a structure in which the original  $\alpha$ - and  $\beta$ -carbon atoms have become identical in their CA behavior, or the isomer must at least be formed through such an intermediate. Further, the original  $\alpha$  and  $\beta$  carbons of **19** must have become situated in these two  $C_8H_9^+$  isomers so that these atoms are preferentially involved in the loss of  $CH_2$ ,  $CH_3$ , and  $CH_4$  in the CA spectra. A logical choice for one of these  $C_8H_9^+$  isomers is the ethylenebenzenium ion **11**. Such ions have been the subject of numerous solution studies since they were proposed by Cram;<sup>25</sup> conclusive NMR evidence has been presented for formation of **11** by the ionization of **20** in superacid medium.<sup>26</sup> The  $C_8H_9^+$  ion formed at low electron energies from **18** and **19** appears to be the more logical candidate for structure **11**. Its CA spectrum is unique (Table I) in showing the highest loss of  $CH_2$  and lowest loss of  $CH_3$  of any of the isomers studied; collisional activation of **11** could logically lead to opening of the three-membered ring producing excited **14**, for which  $CH_2$  loss to produce the stable benzyl ion would appear to be favored over the rearrangement necessary for  $CH_3$  loss. A relatively high tendency for  $CH_2$  loss is also found in the CA spectra of three-membered ring isomers of  $C_2H_4O^+$ ,  $C_2H_5O^+$ ,  $C_3H_6O^+$ ,  $C_2H_5S^+$ , and  $C_3H_7S^+$ .<sup>27</sup> Although the abundance of  $C_8H_9^+$  in the normal mass spectra of **19** and **20** is only a few percent of that of  $C_7H_7^+$ , the appearance potentials of  $C_7H_7^+$  and  $C_8H_9^+$ <sup>28</sup> are similar, consistent with the formation of **11** and **12** at low energies involving anchimeric assistance;<sup>29</sup> such tight activated-complex reactions should not be favorable at higher energies relative

to formation of  $C_7H_7^+$  by benzylic cleavage, in keeping with the low relative  $C_8H_9^+$  abundance found using 70-eV electrons. At this energy for **18**  $[C_8H_9^+]/[C_7H_7^+] = 5$ , consistent with the much lower bond dissociation energy of C–I than of C–Br and initial formation of **14** at higher energies for **18–21**.

The structure of isomer “X” has not been elucidated. Stable structures such as **13** are possibilities, and formation through isomerization of initial high energy **11**, **12**, or **14** ions is indicated by the labeling data (Table II). The CA spectrum of  $C_8H_9^+$  ions from 6-methylene-2-norbornene, a possible precursor of **13**, is consistent with that of a 1:2 mixture of X/**4**, but other isomeric compositions would also agree within the large experimental error.<sup>20</sup> Further identification efforts are in progress.

This gas-phase behavior of **20** is in sharp contrast to that in superacid medium,<sup>26</sup> in which solvent effects should be minimized; Olah and Porter report detailed NMR evidence for the formation of **5** and **11** (Scheme II), with no indication of the two isomers **12** and X found here. Formation of **5** from **14** involves migration of the  $\alpha$ -hydrogen atom; the similar isomerization  $isobutyl^+ \rightarrow tert\text{-}butyl^+$ , favored in solution, was also found to be less competitive in the gas phase than methyl migration to give  $sec\text{-}butyl^+$ .<sup>30</sup> In comparing the gas-phase behavior of **18–21**, both enthalpy and entropy effects appear to be critical.<sup>1</sup> Four-membered ring formation of gaseous **12** occurs only by loss of the smaller Cl and  $CH_3$  groups, consistent with the high steric interference of the ortho hydrogen atom. In solution perhaps solvation increases steric crowding for the loss of chlorine from **20**, causing **11** to be formed instead of **12**. Formation from **20** and **21** of **12** instead of the sterically-favorable **11** suggests that this selection is based on energetic favorability. The bond dissociation energies of the C–X bonds in **20** and **21** are substantially higher than those in **18** and **19**, so that the higher energy required for C–X cleavage could be offset by a lower energy requirement for four- vs. three-membered ring closure. This suggests that the heat of formation of **12** is actually less than that of **11**; experimental or theoretical<sup>23</sup> studies on this point could be helpful here.

**Stabilities of  $C_8H_9^+$  Ions.** The mass spectra of hydrocarbons have been extensively studied over many years, with the general conclusion that the spectra of this class give among the least specific spectra–structure correlations and exhibit a high tendency for “random” rearrangements.<sup>3,31</sup> Evidence for the stability of benzyl and tolyl ions<sup>4</sup> contrasted sharply with long-held conclusions concerning their facile isomerizations to tropylium ions.<sup>3</sup> Thus the wide variety of  $C_8H_9^+$  isomers found in this study to be stable for  $\geq 10^{-5}$  s clearly indicates that many types of gaseous carbocations can be long-lived. Here these included substituted phenyl ions (**7–10**), plus many in which the positive charge would be expected to be well stabilized. No evidence could be found for the primary carbenium ion **14**, consistent with its low expected stability,<sup>23</sup> and most of the observed isomerizations appeared to occur in the odd-electron molecular ions. Less rearrangement was observed for even-electron  $C_8H_9^+$  isomers such as **1–5** than found for their homologues benzyl and tropylium<sup>4</sup> at higher energy. This could be due in part to the stabilizing effect of the extra methyl group in **1–5**, and also to the lower energy required for their further decomposition, making isomerization less competitive. Isomeric characterization of fragment carbocations such as these  $C_8H_9^+$  ions could thus be a valuable aid in structure determination of unknown molecules, as long as rearrangements accompanying the formation of the fragment ions can be minimized or understood.

### Experimental Section

Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer of reversed geometry.<sup>24</sup> A 100- $\mu$ A ionizing electron

beam of 70-eV energy (lower where noted) and an accelerating potential of 7.8 kV were used; sample reservoir and ion source temperatures were 150 °C. The magnetic field is set to select the  $C_8H_9^+$  precursor ions; ionic products of metastable  $C_8H_9^+$  ion decompositions (the MI spectrum) occurring in the field-free drift region between the magnetic and electrostatic (ESA) analyzers are measured by scanning the ESA potential repeatedly under computer control. The pressure in a special collision chamber near the  $\beta$ -focal point<sup>24b</sup> is increased with helium until the precursor ion intensity is reduced to 25% of its original value, and the CA product abundances are determined in a second ESA scan. The resulting CA spectra are the computer-averaged composites of at least 16 scans. The  $m/e$  89, 90, and 91 peaks are not completely resolved; correcting the abundances for neighboring peak contributions for the data of  $\beta$ -phenylethyl bromide changed this from 50:20:30 to 53:16:31. For the isotopically labeled compounds the data of several independent runs were averaged.

The CA peaks of abundance most sensitive to isomeric structure are those at  $m/e$  51, 89, 90, and 91, while the  $m/e$  39 peak abundance is nearly independent ( $\pm 1.5\%$ ) of isomeric identity. Major CA peaks occur at the following masses (approximate abundances in parentheses): 27 (5), 39 (10), 41 (1), 51 (15–30), 53 (5), 63 (11), 65 (8), 74 (4), 75 (5), 101 (2), 102 (10–25), and 89, 90, and 91 (11–22). The abundance of  $m/e$  88 is  $< 1\%$  of the sum of those of  $m/e$  89, 90, and 91. In some CA spectra the  $m/e$  91 is shifted to lower masses by  $0.25 \pm 0.05$  units, consistent with the conversion of  $\sim 20$  eV of kinetic energy to internal energy in  $C_8H_9^+$  ions undergoing this decomposition. In the earlier work<sup>16a</sup> utilizing an ion accelerating potential of 3.9 kV (and thus poorer resolution) this mass shift was doubled, making  $m/e$  91 not distinguishable from  $m/e$  90. Most  $C_8H_9^+$  isomers show metastable ion decompositions producing peaks at  $m/e$  77, 79, 103, and 104; the abundances of these peaks are generally in the range 35–100, 30–80, 40–140, and 10–100%, respectively, based on the total abundances of the unique CA spectrum.

**Isotopically Labeled Compounds.** Benzocyclobutene was made by heating  $\alpha,\alpha'$ -dibromo-*o*-xylene with excess Ag powder under vacuum, with purification by preparative GC. Synthesis of other compounds have been described previously<sup>10,11,16</sup> or employed similar standard procedures. <sup>13</sup>C-labeled compounds were made using  $Ca^{13}CO_3$  and <sup>13</sup>CH<sub>3</sub>I of 90% isotopic purity.

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## Steric Effects in the Singlet-Triplet Transitions of Methyl- and Chlorobiphenyls<sup>1</sup>

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**Abstract:** A potential energy diagram has been constructed which explains semiquantitatively the effects of ortho and para methyl and chloro substitution on  $S \leftrightarrow T$  transitions of biphenyl. Triplet EPR spectra indicate that the ortho-substituted biphenyls maintain planar triplets. Both ortho-substituted biphenyls display maximum phosphorescence intensities at the same energy as does biphenyl itself. However, rate constants for reversible energy transfer from triplet benzophenone to the ortho-substituted biphenyls are only 1–5% as large as those for transfer to biphenyl itself. The greater twist in the ground states of the ortho-substituted biphenyls necessitates a greater change in geometry during these nonvertical energy transfers. The lower rate constants probably reflect the involvement of rotationally excited ground states.

A few years ago, it was reported that the lowest triplet state of biphenyl is planar and thus possesses a markedly different conformation from the twisted ground state.<sup>2</sup> This conclusion was based on the observation of a 10 kcal difference between the "0-0" bands for phosphorescence and  $S \rightarrow T$  absorption of biphenyl and on the efficiency with which biphenyl quenches triplet ketones. Subsequent spectroscopic<sup>3-5</sup> and theoretical<sup>6</sup> investigations have also concluded that triplet biphenyl is planar.

Ortho substituents increase the barrier to planarity in the ground state of biphenyl<sup>7</sup> and ought to similarly destabilize the planar conformation of the triplet state. The original report noted that several ortho-substituted biphenyls were worse quenchers than biphenyl itself,<sup>2</sup> but it could not be determined whether the triplets had become nonplanar. Lewis and Kasha's classic paper on phosphorescence<sup>8</sup> indicated that 2,2'-dihalo-biphenyls phosphoresce at appreciably higher energies than biphenyl itself; they suggested nonplanar triplets. In contrast, Marchetti and Kearns have reported that ortho bromo and iodo substituents lower the 0-0 phosphorescence energy of biphenyl.<sup>9</sup> Since so little is known about steric effects in excited states and since interest in the consequences of geometric differences between ground and excited states remains high, it seemed worthwhile to determine how large a substituent can be in the ortho position without forcing triplet biphenyl out of planarity and how much rates of nonvertical energy transfer<sup>10</sup> vary with geometric differences between ground and excited state. This paper reports our investigations of the spectroscopic and triplet quenching behavior of the methyl- and chlorobiphenyls.

### Results

**Quenching of Triplet Benzophenone.** The efficiencies with

which naphthalene, biphenyl, and 2-, 3-, and 4-chlorobiphenyl quench the photoreduction of benzophenone in benzene containing 0.5 M isopropyl alcohol<sup>11</sup> were determined. In a given run, degassed solutions containing a fixed concentration of ketone and varying concentrations of quencher were irradiated in parallel at 25 °C with the 365-nm region of a mercury arc. Disappearance of ketone was monitored by UV analysis. After irradiation, each tube was opened and poured into a vial which was kept tightly stoppered in the dark overnight. This preanalysis procedure was employed since the absorbance of samples immediately after irradiation was high and decreased slowly to steady values, a phenomenon which is probably related to the formation of thermally unstable radical-coupling products.<sup>13,14</sup> Stern-Volmer plots of  $\Phi^0/\Phi$  vs. quencher concentration were linear and yielded the slopes ( $K_q$ ) listed in Table I. Naphthalene, biphenyl, 2-chlorobiphenyl, 2-methylbiphenyl, and 4-methylbiphenyl were also used to quench the phosphorescence of benzophenone in degassed benzene solution, for which  $K_q$  values are also listed in Table I.

Quenching constants increase with decreasing ketone concentration for biphenyl and its 3-chloro and 4-methyl derivatives, but not for the ortho-substituted derivatives. Such concentration dependence indicates reversible energy transfer.<sup>2,15,16</sup> Figures 1 and 2 display the dependence of  $K_q^{-1}$  on ketone concentration and Table II lists actual  $k_t\tau_B$  values (1/interpret). With  $k_t$  known to equal  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for naphthalene,<sup>17</sup>  $\tau_B$  values for triplet benzophenone and therefore  $k_q$  values for the biphenyls could be calculated.

$$K_q = \frac{k_t\tau_B}{1 + k_{-1}[B]\tau_Q} \quad (1)$$

