Structure and Decomposition of the $C_7H_8\cdot^+$ Ion Formed by γ-Hydrogen Rearrangement[1]

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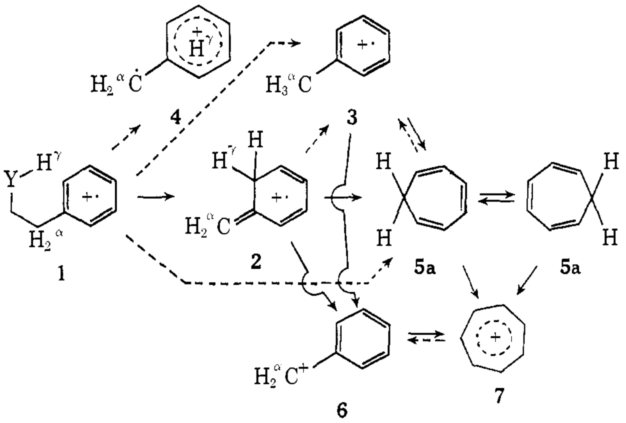
Abstract: The abundant $C_7H_8\cdot^+$ ions (**2**) found in the mass spectra of $C_6H_5CH_2CH_2YH$ (**1**) compounds have been studied by examination of the behavior of deuterium-labeled ions of different internal energies. The positional identity of the hydrogen atoms in **2** ions undergoing metastable decomposition is completely lost; the isotope effect is identical with that found for the metastable decomposition of toluene (**3**) and cycloheptatriene (**5**) ions, consistent with isomerization of **2**, **3**, and **5** to a common structure before decomposition. That structure appears to resemble **5** more closely than **2** or **3**. However, **2** ions of higher internal energies undergo direct cleavage loss of hydrogen before isomerization more readily than do **3** and, especially, **5** ions; the labeling results are only consistent with rearrangement of the γ-H to yield the methylenecyclohexadiene structure, **1** → **2**.

One of the first mass spectral rearrangements found useful for structure determination was that producing $C_7H_8\cdot^+$ and homologous odd-electron ions from alkyl benzenes.[3] Deuterium labeling studies have shown that compounds of the general type C_6H_5-CH_2CH_2YH produce $C_7H_8\cdot^+$ by specific transfer of the γ-hydrogen atom with negligible scrambling of other H atoms.[3b,4] An early proposal[5] that this rearrangement proceeds through a six-membered ring intermediate, **1** → **2**, has met with fairly general acceptance,[6-8] although the formation of toluene (**3**)[3b] and π-bonded (**4**)[4b] structures has also been considered (Scheme I). Consistent with the pathway **1** → **2**, ortho substituents reduce the tendency for this rearrangement.[6] Also, the abundances of $C_7H_8\cdot^+$ in the spectra of meta-substituted *n*-butylbenzenes obtained with 12 eV electrons correlate with the Hammett σ values of the substituents, although there is no correlation for abundances found using 70 eV electrons or those for para substituents.[7a] Ion cyclotron resonance (icr) studies show that $C_7H_8\cdot^+$ ions formed from *n*-butylbenzene do not undergo a reaction characteristic of the toluene structure **3** after lifetimes of $\sim 10^{-2}$ sec.[7b] However, the hydrogen atoms of the $C_7H_8\cdot^+$ ions from **1** are completely scrambled in those low energy ions which undergo metastable decomposition,[4b] and collisional activation (CA) spectra indicate[9] that nondecomposing $C_7H_8\cdot^+$ ions from a variety of sources, including **1** and **5**, and **3** of higher energies, isomerize to a common structure such as **5**. Thus the icr evidence only rules out the formation from **1** of low energy **3** ions.[10]

Scheme I



A more critical study of this rearrangement appeared to be feasible utilizing the technique in which the behavior of precursor ions of several ranges of internal energies is examined.[11] Such a study of $C_7H_8\cdot^+$ ions from toluene and cycloheptatriene showed that ions of higher internal energies could undergo the direct decompositions **3** → **6** and **5** → **7**, respectively, in competition with isomerization reactions.[11b] Earlier work indicated that **3** can isomerize to a common structure such as **5**.[3,12] This ion may then scramble by the reverse reaction **5** ⇄ **3**,[13] or further by **5a** ⇄ **5b**

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(1) Metastable Ion Characteristics. XXVI. Part XXV: F. W. McLafferty and I. Sakai, *Org. Mass Spectrom.*, in press.

(2) (a) Postdoctoral Fellow, 1971–1972; (b) John Simon Guggenheim Memorial Foundation Fellow, 1972. (c) We are grateful to the National Institutes of Health (GM 16575 and GM 16609) for generous support of this work.

(3) (a) S. Meyerson, *Appl. Spectrosc.*, **9**, 120 (1955); (b) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963; (c) S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, 90, 3419 (1968).

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(5) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(6) H. Budzikiewicz, C. Djerassi, and D. H. Williams in "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 82.

(7) (a) R. Nicoletti and D. A. Lightner, *J. Amer. Chem. Soc.*, **90**, 2997 (1968); (b) M. M. Bursey, M. K. Hoffman, and S. A. Benezra, *Chem. Commun.*, 1417 (1971).

(8) In a private communication J. Occolowitz, Eli Lilly and Co., points out that, based on appearance potentials, the calculated heats of formation of $C_7H_8\cdot^+$ from *n*-butylbenzene and 2-phenylethanol are 213 and 211 kcal/mol, respectively. Thus the rearranged $C_7H_8\cdot^+$ ions formed at threshold energies cannot have structure **5** ($\Delta H_f = 240$ kcal/mol) but must have a structure of similar or lower enthalpy to that of **3** ($\Delta H_f = 215$ kcal/mol).

(9) F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente III, S.-C. Tsai, and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, **95**, 3886 (1973).

(10) The isomerization of **2** is not consistent, however, with the conclusion[7b] that these $C_7H_8\cdot^+$ ions should be of lower average internal energy than those from toluene; it is possible that the CA spectra of **2** and **5** are the same coincidentally.

(11) (a) I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, **92**, 3937 (1970); (b) I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

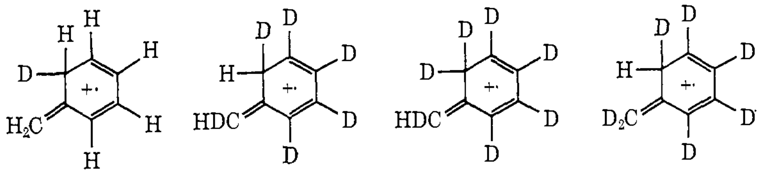
(12) F. Meyer and A. G. Harrison, *ibid.*, **86**, 4757 (1964).

(13) A. Venema, N. M. M. Nibbering, and Th. de Boer, *Tetrahedron Lett.*, 2141 (1971).

Scheme II

Precursor	$C_6H_5C_2H_4OD$	$C_6D_5CHDCH_2OH$	$C_6D_5CHDCH_2OD$	$C_6D_5C_2D_4OH$

2



3	$(CH_2DC_6H_5\cdot^+)$	$(CH_2DC_6D_5\cdot^+)$	$(CHD_2C_6D_5\cdot^+)$	$(CHD_2C_6D_5\cdot^+)$
	8, *m/e* 93	**9**, *m/e* 98	**10**, *m/e* 99	**11**, *m/e* 99
H loss:	*m/e* 92	*m/e* 97	*m/e* 98	*m/e* 98
D loss:	*m/e* 91	*m/e* 96	*m/e* 97	*m/e* 97
α-Cleavage of **1**:	*m/e* 91	*m/e* 97	*m/e* 97	*m/e* 98

(hydrogen migration around the ring and random methylene insertion between ring carbon atoms).[12] Direct comparison of the behavior of $C_7H_8\cdot^+$ from **1** with the behavior of **3** and **5** might shed further light on the latter processes also.

Results

This study of the $C_7H_8\cdot^+$ ions from **1** utilizes the general approach employed in the investigation of $C_7H_8\cdot^+$ ions from **3** and **5**.[14,15] Three internal energy regions of these ions are examined: (I) $C_7H_8\cdot^+$ ions undergoing unimolecular metastable (MI) decomposition in the field-free drift region to yield $C_7H_7^+$; (II) $C_7H_8\cdot^+$ ions decomposing to yield $C_7H_7^+$ after collisional activation in the drift region; and (IV) $C_7H_8\cdot^+$ ions which have decomposed in the ion source to yield $C_7H_7^+$ ions having sufficient internal energy to undergo metastable decomposition in the drift region. Energy region III utilized in the previous study[11b] involves $C_7H_8\cdot^+$ decomposing in the ion source to give $C_7H_7^+$ ions of lifetimes $>10^{-5}$ sec; this region could not be used in this study because the bulk of $C_7H_7^+$ ions are formed directly from the molecular ion.

The $C_7H_8\cdot^+$ ions studied were generated from the following 2-phenylethanols: $C_6H_5C_2H_4OH$, $C_6H_5C_2H_4OD$, $C_6D_5CHDCH_2OH$, $C_6D_5CHDCH_2OD$, $C_6D_5C_2D_4OH$, and $C_6D_5C_2D_4OD$. The partially deuteriated molecules should yield (Scheme II) ions **8–11** if structure **2** is formed (products for structure **3** are given in parentheses). Note that the last two isomers of Scheme II will give identical product ion structures for mechanism **1** → **3** but not for **1** → **2**.

Unimolecular Metastable and Collisionally Activated Decompositions (Energy Regions I and II). The MI and CA data are shown in Table I for ions **8–11** generated with 70 eV electrons. The value of $[C_7(H,D)_8\cdot^+ - H]/[C_7(H,D)_8\cdot^+ - D]$ corrected to reflect an equal number of H and D atoms is given as "observed/statistical;" *e.g.*, for ion **8**, $C_7H_7D\cdot^+$, the value is divided by 7. For both the MI and CA data, the observed/statistical values are found to be independent of the original positions of the isotopic labels, so that H/D scrambling must be complete, and the observed/statistical value represents the isotope effect (*i*).[15] These values are entered in Table II and compared with the corresponding values for toluene determined from $C_6H_5CD_3$ and $C_6D_5CH_3$ under the same experimental conditions. Values reported previously[11b] for *i* and α (proportion of the decomposing $C_7H_8\cdot^+$ ions which are scrambled) for toluene and cycloheptatriene are given for comparison; the previous *i* values for regions I and II are high due to measurement error.[14]

Table I. $[C_7(H,D)_8\cdot^+ - H]/[C_7(H,D)_8\cdot^+ - D]$ for Metastable (MI) and Collisionally Activated (CA) Decompositions of $C_7(H,D)_8\cdot^+$

	MI (region I)		CA (region II)	
Ion	$[C_7(H,D)_8\cdot^+ - H]/[C_7(H,D)_8\cdot^+ - D]$	Obsd/statistical	$[C_7(H,D)_8\cdot^+ - H]/[C_7(H,D)_8\cdot^+ - D]$	Obsd/statistical
8	17.8 ± 0.2	2.54 ± 0.02	13.2 ± 1.0	1.88 ± 0.15
9	0.85 ± 0.03	2.54 ± 0.09	0.61 ± 0.02	1.82 ± 0.06
10	0.371 ± 0.007	2.60 ± 0.05	0.25 ± 0.01	1.78 ± 0.06
11	0.366 ± 0.003	2.56 ± 0.02	0.26 ± 0.01	1.80 ± 0.10

$C_7H_8\cdot^+$ Ions Yielding $C_7H_7^+ \rightarrow C_5H_5^+$ Metastable (Energy Region IV). The $C_7(H,D)_7^+$ ion formed by α cleavage of **1** will have the same composition as either the $(C_7(H,D)_8\cdot^+ - H)$ or the $(C_7(H,D)_8\cdot^+ - D)$ ion (Scheme II), so that only the metastables corresponding to decomposition of the interference-free $C_7(H,D)_7^+$ ion can be used. Table III summarizes the sum of the abundances for the metastable decompositions involving the loss of $C_2(H,D)_2$ from $(C_7(H,D)_8\cdot^+ - H)$ for ions **8** and **10** and from $(C_7(H,D)_8\cdot^+ - D)$ for ions **9** and **11** for two series of measurements. Summing the metastable abundances for the possible $C_2(H,D)_2$ losses obviates any effect of scrambling in the $C_7(H,D)_7^+$ ions on this determination;[15] our data on their metastable decomposition to form $C_5(H,D)_5^+$ indicate that in this process scrambling is nearly complete. The overall sum of the metastable abundances (Σ) for both $(C_7(H,D)_8\cdot^+ - H) \rightarrow C_5(H,D)_5^+$ and $(C_7(H,D)_8\cdot^+ - D) \rightarrow C_5(H,D)_5^+$ should be almost independent of the isotopic distribution in **2**.[16] This is expected because the small increase in the appearance potential for the D-loss reaction over that for the H-loss reaction should have a very small effect on the range of internal energies of $C_7(H,D)_8\cdot^+$ ions undergoing hydrogen loss, and the relative abundance of precursor ions having this range of internal energies should be little affected by the isotopic identity. In support of this, the sum of the abundances for the metastable decompositions $[C_7(H,D)_8\cdot^+ - H]$ and $[C_7(H,D)_8\cdot^+ - D]$ showed a standard deviation of ±5% for the mean value of the six labeled **1** isomers.

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(14) M. A. Baldwin and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, in press.

(15) Further details of the method are given in ref 12b.

(16) F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfeld, *J. Amer. Chem. Soc.*, 93, 3720 (1971).

Table II. Isotope Effect (i) and Degree of Scrambling (α) for $C_7H_8\cdot^+$ Ions from Phenylethanol, Toluene, and Cycloheptatriene for Energy Regions I–IV

Energy region	Av energy, eV, for toluene[a]	2-Phenylethanol i	2-Phenylethanol α	Toluene i	Toluene α	Toluene[b] i	Toluene[b] α	Cycloheptatriene[b] i	Cycloheptatriene[b] α
I	11.8	2.56 ± 0.06[c]	1.00 ± 0.01	2.63 ± 0.06	1.00 ± 0.01	2.80 ± 0.06	1.00	2.6 ± 0.1	0.99 ± 0.01
II	12.4	1.82 ± 0.10	1.00 ± 0.02	2.06 ± 0.10	0.98 ± 0.01	2.33 ± 0.08	0.98 ± 0.01	2.1 ± 0.2	0.95 ± 0.03
III	14.0			1.66 ± 0.05	0.90 ± 0.02	1.51 ± 0.04	0.89 ± 0.01	1.49 ± 0.04	0.92 ± 0.01
IV	15.7	1.53 ± 0.12	0.56 ± 0.13	1.45 ± 0.12	0.78 ± 0.03	1.40 ± 0.04	0.72 ± 0.01	1.22 ± 0.03	0.88 ± 0.01

[a] Taken from ref 11b. [b] Values obtained in a previous study[11b] under somewhat different experimental conditions. Values for energy regions I and II are higher than the true values because peak heights were measured instead of peak areas.[14] [c] Errors shown represent the observed standard deviation plus estimate of possible errors from isotopic impurities.

Table III. Abundances of the Metastables $C_7(H,D)_7^+ \xrightarrow{m^*} C_5(H,D)_5^+$ Arising only from $C_7(H,D)_8\cdot^+$

Ion	$[C_7(H,D)_7^+ \xrightarrow{m^*} C_5(H,D)_5^+]/[C_7(H,D)_8\cdot^+] \times 10^3$ [a] Run 1[b]	Run 2[b]
8	8.35 ± 0.23	6.83 ± 0.31
9	5.78 ± 0.15	4.84 ± 0.27
10	1.72 ± 0.42	1.29 ± 0.23
11	6.80 ± 0.33	5.56 ± 0.15

[a] Using $(C_7(H,D)_8.^+ - H)$ for **8** and **10**, $(C_7(H,D)_8\cdot^+ - D)$ for **9** and **11** (Scheme II). For example, the values for **8** represent the sum of the relative abundances for the metastable decompositions $C_7H_6D^+ \rightarrow C_5H_4D^+$ and $C_7H_6D^+ \rightarrow C_5H_5^+$.[15] [b] Runs made 1 week apart.

If the $C_7(H,D)_8\cdot^+$ ions formed by rearrangement have structure **2**, and if the further loss of hydrogen from **2** that occurs before it isomerizes involves the H atoms of the ring methylene group, the relative abundances for the metastable decompositions from $[C_7(H,D)_8\cdot^+ - (H,D)]$ for isomers **8–11** should be given by eq 1–4, respectively.[15] Using eq 1, 2, and 4 with

$$\frac{[m^*(C_7H_6D^+ \rightarrow)]}{\sum - [m^*(C_7H_6D^+ \rightarrow)]} = \frac{7i\alpha/(7i + 1) + i(1 - \alpha)/(i + 1)}{\alpha(7i + 1) + (1 - \alpha)(i + 1)} \qquad (1)$$

$$\frac{\sum - [m^*(C_7H_2D_5^+ \rightarrow)]}{[m^*(C_7H_2D_5^+ \rightarrow)]} = \frac{2i\alpha/(2i + 6) + i(1 - \alpha)/(i + 1)}{6\alpha/(2i + 6) + (1 - \alpha)/(i + 1)} \qquad (2)$$

$$\frac{[m^*(C_7D_7^+ \rightarrow)]}{\sum - [m^*(C_7D_7^+ \rightarrow\ )]} = \frac{i\alpha/(i + 7)}{7\alpha/(i + 7) + (1 - \alpha)} \qquad (3)$$

$$\frac{\sum - [m^*(C_7HD_6^+ \rightarrow)]}{[m^*(C_7HD_6^+ \rightarrow)]} = \frac{i\alpha/(i + 7) + i(1 - \alpha)/(i + 1)}{7\alpha/(i + 7) + (1 - \alpha)/i + 1} \qquad (4)$$

the data of runs 1 and 2 (Table III) gives $i = 1.57$ and 1.49 and $\alpha = 0.60$ and 0.51, respectively; substituting these values in eq 3 for **10** predicts $(m^*(C_7(H,D)_8\cdot^+ - H)]/[C_7(H,D)_8\cdot^+]$ values of 0.00145 and 0.00106 for runs 1 and 2, respectively, which are within the standard deviations found for the experimental values. The average values for i and α are compared in Table II with those for toluene taken under the same experimental conditions and with those for toluene and cycloheptatriene reported previously.[11b]

Similar calculations were made under the assumptions that the $C_7(H,D)_8\cdot^+$ rearrangement ions have the structure **3**, and that the further loss of hydrogen from **3** occurs only from the methyl group. No solution could be found using equations analogous to 1, 2, and 4 for labeled ions **8**, **9**, and **11** of structure **3**; a value of $i = 1.5$ leads to α values of 0.34, 0.87, and 1.09, respectively, while $i = 1.3$ gives a negative value, 0.70 and 1.03.

Discussion

Initial Structure of the $C_7H_8\cdot^+$ Ion from 1. Analogous to the behavior of $C_7H_8\cdot^+$ ions from toluene and cycloheptatriene,[13] $C_7H_8\cdot^+$ ions formed by γ-H rearrangement from **1** with higher internal energies (region IV) are only partially scrambled before they lose a hydrogen atom. Within experimental error, the data fit the postulate that the hydrogen atom lost from the unscrambled $C_7H_8\cdot^+$ comes equally from hydrogens originally in the γ position and a ring position and not in the α position. The methylenecyclohexadiene structure **2** appears to be the only possibility which is consistent with these data; certainly structures **3** and **4** are ruled out. Thus the favored mechanism **1** → **2** must be important for higher energy decompositions; most, if not all, of the remaining decompositions probably also involve **1** → **2**, followed by isomerization.

Relative Rates of Isomerization and Decomposition of $C_7H_8\cdot^+$. The **2**, **3**, and **5** ions of low energy undergoing metastable decomposition have all been completely scrambled (Table II). The isotope effects exhibited by the reactions of **2** and **3**, and thus the internal energies of these decomposing ions, are nearly equal.[17] Meyerson has used thermochemical calculations[3b] to show that the transition states for H loss from **3** and **5** are of equal energy; following his arguments, our data are consistent with (but do not require) the isomerization of **2** and **3** to a common ion structure before H loss. Isotope effects can thus be a sensitive probe to compare the internal energies of activated complexes.

Unfortunately, for the data derived from the CA spectra of $C_7H_8\cdot^+$ (energy region II) it was not possible to determine with complete certainty that the values for **2** are different from those for **3** and **5**. These α values represent the scrambling occurring before as well as after the ions undergo collision.[18] Although

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[17] Utilizing the relationship found previously between the i and internal energy (Figure 1, ref 11b), the values differ by <0.1 Ve from the mean.

[18] F. W. McLafferty, P. F. Bente III, R. Kornfeld, S.-C. Tsai, and I. Howe, *J. Amer. Chem. Soc.*, **95**, 2120 (1973).

the isotope effects indicate that the decomposing **2** ions are probably of higher energy than the decomposing **3** or **5** ions, the **2** ions are at least as completely scrambled. This supports the previous conclusions that the identity of the CA spectra of **2** and **5** is not a coincidence, and that isomerization of these ions to a common structure (or mixture of structures) is extensive before collision.[9,10]

In energy region IV the proportion of **2** ions undergoing hydrogen loss before isomerization[19] is much higher than for **3** or **5**. The rate of direct H loss from **2** is nearly as high as the isomerization rate. It seems reasonable that hydrogen loss from the cross-conjugated allylic system of **2** should occur no more readily than hydrogen loss from the linear conjugated system of **5** or the benzylic system of **3**. This suggests that **2** isomerizes much less readily than **3** or **5**, and that the mechanism for the scrambling of the hydrogen atoms in **3** and in **5** does not involve initial conversion to **2**.

Experimental Section

All data were obtained with a Hitachi RMU-7 double-focusing mass spectrometer with an accelerating potential of 3.9 kV, ionizing electrons of 70 eV and 100 μA, and inlet and ion source temperatures of 200°. The geometry of the instrument was reversed so that the magnetic sector precedes the electrostatic sector.[20] The products from the decomposition of a mass-analyzed beam of precursor ions occurring in the field-free region after the magnetic field are determined by scanning the potential of the electrostatic sector. Collisional activation spectra are obtained by increasing the pressure in this field-free region with helium until the precursor ion intensity is reduced to 10% of its original value. The abundance ratios reported in Table I are mean values of at least six measurements. The $C_7(H,D)_8\cdot^+$ abundances have been corrected for isobaric contributions from $C_6{}^{13}C(H,D)_7{}^+$ and from $C_7(H,D]_7{}^+$ due to isotopic impurities. CA data for loss of D have been corrected for loss of H_2, but not for the MI contributions. The kinetic energy released during the cleavage of the C–H or C–D bond shows an isotope effect (energies of 0.107 ± 0.008 eV and 0.136 ± 0.008 eV, respectively) leading to different peak widths, so that it was necessary to use peak areas for relative abundance values.[14] Each of the data in Table III represents the mean value of four measurements.

2-Phenyl-d_5-ethan-1,1,2,2-d_4-ol. Toluene-d_8 (Aldrich, 99% ^{2}H) was refluxed with 1 equiv of Br_2. The resulting benzyl-d_7 bromide was distilled *in vacuo*, converted to the Grignard reagent, and carbonated to produce labeled phenylacetic acid. This was exchanged with basic ^2H_2O for 2 hr at 90° to ensure a high deuterium content at the benzylic position.[21] Reduction with $LiAl^2H_4$ in ether followed by hydrolysis with H_2O, yielded the named compound, isotopic composition d_9, 89.2%; d_8, 10.1%; d_7, 0.7%.

2-Phenyl-d_5-ethan-2-d-1-ol. The labeled phenylacetic acid was exchanged at the hydroxyl group with methanol-*O-d* and converted to the α-bromo acid chloride by refluxing with $SOCl_2$ followed by addition of bromine. This was converted to the methyl ester by addition of methanol-*O-d* at 0°, reduced with $LiAlH_4$ in ether and decomposed with H_2O to yield the named compound, isotopic composition d_6, 90.6%; d_5, 8.5%; d_4, 0.9%. Treatment of the unlabeled bromoester under identical conditions gave a product which contained no more than 1% 1-phenylethanol by nmr analysis.

The *O*-d_1 compounds were prepared by D_2O exchange in the mass spectrometer inlet system. Average isotopic purity values $C_6H_5CH_2CH_2OD$, d_1, 91%; $C_6D_5CHDCH_2OD$, d_7, 84%.

Acknowledgments. We are indebted to Dr. T. Wachs and P. F. Bente III for improvements to the mass spectrometer.

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[19] As much as 6% of the approximately 44% unscrambled **2** ions (Table II) could be due to **2** ions which had isomerized so that the endomethylene group is retained as the methylene group of **5**; about 10% of the H atoms of the methylene group of **5** are lost specifically (Table II). However, this correction reduces the value for H loss before scrambling of **3** to ~14%.[11b]

[20] T. Wachs, P. F. Bente III, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 333 (1972).

[21] J. G. Atkinson, J. J. Csakvary, G. T. Herbert, and R. S. Stuart, *J. Amer. Chem. Soc.*, **90**, 498 (1968).

Crystal and Molecular Structure of a Caged Polycyclic Tetraoxyazaphosphorane, $(PO_4N)(C_6H_5CN)(C_6H_5)(C_6H_9)$

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Abstract: The reaction of *N*-phenyl-*N′*-benzoyldiimide with 1-phospha-2,8,9-trioxaadamantane gives a caged adamantanoid tetraoxyazaphosphorane. X-Ray crystallographic analysis shows that the molecule has the geometry of a distorted trigonal bipyramid with a five-membered ring in an apico–equatorial skeletal position, the ring oxygen apical and the ring nitrogen equatorial. The main distortions from the ideal D_{3h} skeletal symmetry are: a bending of the C_3–skeletal axis (169.8° angle), a contraction of the diequatorial angle of the adamantanoid moiety (106.2° angle), and a contraction of the apico–equatorial angle of the five-membered ring (83.8° angle).

Certain α,β-unsaturated ketones react with esters of three-coordinate phosphorus to give relatively stable cyclic oxyphosphoranes,[2] **1**. By analogy with a related cyclic pentaoxyphosphorane[3] whose structure is known from X-ray crystallography,[4] the oxyphos-

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