trans isomer, also strongly suggest that **4** is not an intermediate in the formation of *both* β-methoxy ester and diester products. Although SN2 displacement of palladium by nucleophile has been demonstrated in acetic acid systems[10] and postulated for alcoholic systems,[17] it is clear that β-methoxy ester and diester products are best explained by two distinctly different intermediates arising from the rate-determining step (formation of the Pd–C σ-bonded complex).

The effect of added acetate to this system is quite remarkable in that it can change the course of the reaction completely, and either β-methoxy ester or diester can be obtained at will. Several explanations are possible. If paths a and b each are exclusively responsible for the formation of β-methoxy ester and diester, respectively, sodium acetate may enhance the formation of intermediate **2** by base catalysis. Also, acetate ion may influence the rates of the reactions occurring by the different pathways by coordination to palladium, thereby changing the structures of the intermediate complexes and thus their activity.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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Evidence for Structurally Different $C_7H_7^+$ Ions. An Electron Impact Study of Benzyl Phenylacetate

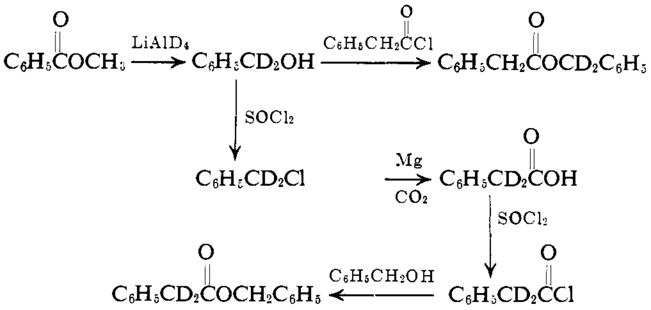
Sir:

The structure of the $C_7H_7^+$ ion formed from various precursors has interested mass spectrometrists for over 15 years.[1-6] Indeed the ring expansion of the ion when formed from benzyl-type derivatives and the subsequent decomposition routes are among the more interesting examples of bond migrations in organic chemistry.

In most systems studied, usually by isotopic labeling, the $C_7H_7^+$ ion has ring expanded to form a tropylium ion, and those ions with sufficient energy to further decompose are both completely H–D and carbon scrambled. As a contrast to the usual simple losses of hydroxyl or halogen to form $C_7H_7^+$, Meyerson[7] has examined the mass spectra of diphenylmethane and bibenzyl. Deuterium labeling studies seem to indicate that the symmetrical bibenzyl forms $C_7H_7^+$ ions with an energy distribution similar to that of other simple benzyl derivatives: the C_7 species is best described as a tropylium ion formed by random insertion of hydrogen into the carbon skeleton.[8] Diphenylmethane, on the other hand, apparently forms a tropylium ion *via* a different energetic pathway—1,2 insertion [*i.e.*, the hydrogen (deuterium) atoms on the methylene group insert onto adjacent carbon atoms].

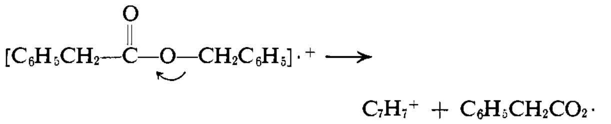
In an effort to further elucidate this structural problem, and to explore the possibility of generating two structurally and energetically different $C_7H_7^+$ ions from different parts and by different pathways within the same molecule, we have examined the mass spectrum of benzyl phenylacetate and its d_2 and d_4 isomers. The synthetic route is outlined in Scheme I.

Scheme I

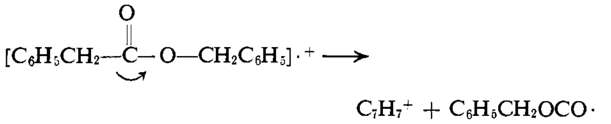


The low-temperature mass spectra of benzyl phenylacetate (I), benzyl-α-d_2 phenylacetate-d_2 (II), benzyl-α-d_2 phenylacetate (III), and benzyl phenylacetate-α-d_2 (IV) were obtained at 70 eV.[9] The relative intensities of selected ions are shown in Table I.

As expected, the $C_7H_7^+$ ion dominates the spectra of benzyl phenylacetate. In the d_4 species, this peak shifts cleanly to $C_7H_5D_2^+$. The two dideuterated esters, III and IV, show that the C_7 ion is formed by two different pathways.



$$[C_6H_5CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2C_6H_5]\cdot^+ \longrightarrow C_7H_7^+ + C_6H_5CH_2CO_2\cdot \quad (1)$$



$$[C_6H_5CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2C_6H_5]\cdot^+ \longrightarrow C_7H_7^+ + C_6H_5CH_2OCO\cdot \quad (2)$$

The presence of metastable peaks at 36.3 and 37.9 amu in the mass spectra of III and IV confirms these processes. The C_7 moiety appears to be formed more easily by cleavage of the benzyl–oxy bond (eq 1) than by cleavage within the phenylacetate portion of the molecule, if one assumes equal decomposition rates for the reactive C_7 ions (*vide infra*).

As expected, the total ion current within the C_7 ions from III and IV is the same, relative to that carried by the molecular ions, and the amounts of ion current carried by $C_7H_7^+$ and $C_7H_5D_2^+$ ions are reversed in these two esters.

The distributions of the deuterium label found within the C_5 ions from II are quite similar to those found by

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(1) P. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).

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(4) K. L. Rinehart, A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *ibid.*, **90**, 2983 (1968).

(5) A. S. Siegel, *ibid.*, **92**, 5277 (1970).

(6) M. K. Hoffman, manuscript submitted for publication.

(7) S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, **90**, 3419 (1968).

(8) The data are not nearly as conclusive as one might have expected, and the actual situation may perhaps be more complicated than the interpretation implies. See ref 7; also see below.

(9) The data here reported were obtained from direct probe samples at a source temperature of 100° using an AEI MS9 mass spectrometer. Spectra obtained at higher temperatures differed primarily in that they exhibited less intense molecular ions. The relative ratios of the C_7 and C_5 species remained essentially unchanged.

Table I. Relative Intensities of Selected Ions[a]

	$C_6H_5CH_2CO_2CH_2C_6H_5$ (I)	$C_6H_5CD_2CO_2CD_2C_6H_5$[b] (II)	$C_6H_5CH_2CO_2CD_2C_6H_5$[b] (III)	$C_6H_5CD_2CO_2CH_2C_6H_5$[b] (IV)
$M\cdot^+$	100[c]	100[c]	100[c]	100[c]
$C_7H_5D_2$		324	196	102
$C_7H_6D_1$		21.7	8.4	14.6
C_7H_7	319	13.0	110	191
$C_5H_3D_2$		18.7	9.12	6.99
$C_5H_4D_1$		20.1	9.98	8.25
C_5H_5	41.4	8.1	21.1	21.2

[a] Corrected for ^{13}C contributions. [b] II was found to be 88.8 atom % d_4, 9.5 atom % d_3, and 1.7 atom % d_2; III was found to be 97.7 atom % d_2 and 2.3 atom % d_1; IV was found to be 95.4 atom % d_2 and 4.6 atom % d_1 by low-voltage mass spectrometry. [c] Total ion intensity for all molecular ions, including partially deuterated molecular ions.

Meyerson[7] for bibenzyl-α,β-d_4 ($d_2 = 0.40$; $d_1 = 0.43$; $d_0 = 0.165$), which is thought to experience complete H–D randomization in the decomposition of the tropylium ion. However, a tropylium ion formed by random insertion should produce the $C_5H_5^+$, $C_5H_4D^+$, and $C_5H_3D_2^+$ ions in the ratio 0.47:0.47:.047 for II, values substantially different from those found (0.40:0.43:0.17).

To better visualize what the data may mean, the isotopic distributions of $C_5H_5^+$ ions from $C_7H_7^+$ ions were calculated assuming that the $C_7H_7^+$ ions from eq 1 and 2 are similar in structure and have completely randomized H–D prior to loss of acetylene. The results of these calculations, expressed as observed/calculated ratios, are given in Table II.

Table II. Observed/Calculated Ratios for Distribution of Deuterium in C_5 Ions[a]

	II	III	IV
d_2	0.93	0.76	1.22
d_1	0.91	0.78	1.18
d_0	1.79	1.36	0.90

[a] A referee has suggested this form for presentation of data.

The data are clearly inconsistent with complete randomization of H–D within the decomposing "C_7H_7" ions. Indeed, the scrambling results are not consistent with C_7 models of benzyl-α-d_2, tropylium-*1,2*-d_2, or norcaradienyl-d_2, if equal rates of decomposition and similar structure of the two C_7 moieties are assumed.

The ratios in Table II likewise indicate that the C_7 ions derived from the benzyloxy grouping decompose less readily than those formed from the phenylacetate benzyl portion. This result, in part, may account for the greater intensity of the C_7 ion formed by benzyl–oxygen bond cleavage.

The apparent difference in the rate of decomposition of the C_7 ions is most readily explainable if the reactive C_7 ions formed by the two processes are structurally different. The labeled benzyl phenylacetates thus represent the first case in which decomposing $C_7H_7^+$ ions have not attained an equilibrated energy manifold on the normal ion time scale.[10] Further studies to elucidate the exact structure of the two C_7H_7 ions include ion kinetic energy measurements and low-voltage spectra will be presented in the full paper.

Acknowledgment. Acknowledgment of financial support of this work is made to the Kansas State University Bureau of General Research and (by J. C. W.) to the National Science Foundation Undergraduate Research Participation Program, Kansas State University, summer, 1972.

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(10) An ion kinetic energy study of isomeric C_7H_7 methyl ethers indicates equilibrium to a common structure occurs in the formation of the $C_7H_7^+$ ion. $C_7H_7^+$ ions which react further, however, may do so from structurally different forms on the metastable time scale: R. G. Cooks, M. Bertrand, and M. K. Hoffman, manuscript in preparation.

Geometrical Reaction Coordinates.[1] II. Nucleophilic Addition to a Carbonyl Group

Sir:

In the course of a survey of crystal-structure analyses of compounds containing nucleophilic groups and electrophilic centers we have discovered some structural regularities which, we believe, provide an experimental basis for mapping the reaction coordinate (minimum energy pathway) for the addition reaction of a nucleophile to a carbonyl group. The observed distance between nucleophile (N:) and carbonyl carbon ranges, in the examples studied, from about 1.5 Å (covalent bonding) to 3 Å; the longer distances have sometimes been interpreted as evidence for nonbonded interactions of donor–acceptor or dipole–dipole type. We take the view that each example can be regarded as a case where the addition reaction has proceeded to a greater or lesser extent but has been frozen in at a certain stage by the intra- or intermolecular constraints imposed by the crystal environment. Each case then provides a sample point on or close to the reaction coordinate, and a sufficiently large number of points should map out the reaction coordinate, provided that the perturbations from the different crystal and molecular environments can be averaged out. Similar arguments[1,2] have been used to derive the minimum energy pathway for the nucleophilic substitution reactions $I^- + I\text{–}I \rightarrow [I\cdots I\cdots I]^- \rightarrow I\text{–}I + I^-$ and $X + CdS_3Y \rightarrow [X\cdots CdS_3\cdots Y] \rightarrow XCdS_3 + Y$. In this communication we present results for the addition of an amino group to a carbonyl or, equivalently, for the reverse elimination process.

Structural parameters for intramolecular $N\cdots C{=}O$

(1) Part I: H. B. Bürgi, *Inorg. Chem.*, in press.

(2) H. Bent, *Chem. Rev.*, **68**, 587 (1968).