Organic Ions in the Gas Phase. XI. Phenylated Cyclopropane Ion in the Decomposition of 3-Phenylpentane

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3-Phenylpentane breaks down under electron impact in the mass spectrometer by reaction path 1. The spectra of 3-phenylpentane-1-d and -3-d reveal further details of this path. The C_2H_5 radical lost in step 1 consists solely of one of the original ethyl groups; thus no rearrangement of the parent ion precedes the primary cleavage. Step 2 apparently encompasses two separate reactions: I, β-cleavage and γ-hydrogen migration in the phenylpropyl ion; II, rearrangement to a phenylated cyclopropane ion, followed by shift of two electron pairs to give the observed products. Reaction II is the lower-energy process and accounts for 90% of the $C_7H_7^+$ ion yield obtained with 70-v. electrons.

Evidence has been reported for cationated cyclopropanes as intermediates in gas-phase ionic decompositions in the mass spectrometer.[2] Such species in which the coordinating cation is phenyl can account for the formation of $C_7H_7^+$ from t-butylbenzene, of $C_8H_9^+$ and $C_7H_7^+$ from 3-ethyl-3-phenylpentane, and for the label retentions observed in these ions when formed from labeled molecules.[2]
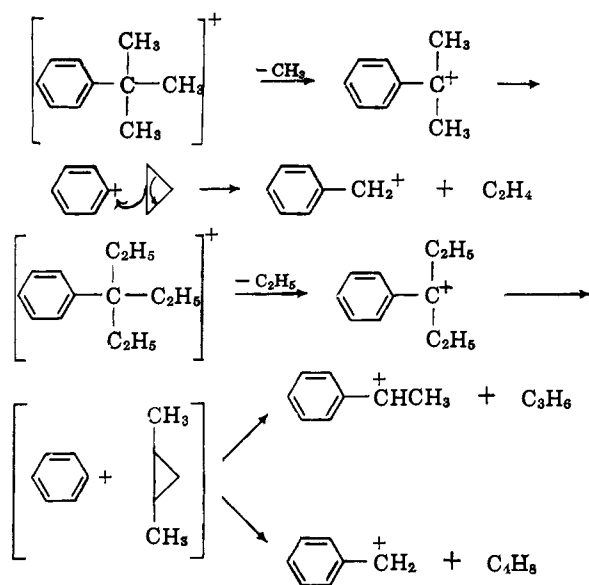
The products can be formed simply by the shift of two electron pairs,[2,3] as shown in the first equation. Further evidence for such intermediates has been uncovered in a study of mass spectra of 3-phenylpentane unlabeled, -1-d, and -3-d.

Experimental

Unlabeled 3-phenylpentane was prepared by sodium-catalyzed ethylation of 1-phenylpropane.[4,5] The 1-d species was isolated by fractional distillation from the synthesis of 3-ethyl-3-phenylpentane-1-d^{2a}; the 3-d species was available from another investigation.[6] Both labeled species were purified by gas chro-

TABLE I
PARTIAL SPECTRA OF 3-PHENYLPENTANES

| m/e	Unlabeled	-1-d^a	-3-d
150	0.0	4.6 ⎫	0.0
149	0.0	95.4 ⎬ 100.0	100.0
148	100.0	b ⎭	b
147	0.1	0.0	0.1
121	.0	7.1	0.0
120	.2	149	297
119	287	140	14.9
93	0.4	3.7	1.2
92	0.0	101	222
91	533	408	303
67	0.6	0.7	0.7
66	0.6	4.3	11.9
65	26.0	23.6	16.9

^{a} Contains 4.6% 3-phenylpentane-d_2. ^{b} Assumed zero in calculating isotopic composition.

matography. Isotopic composition of the labeled species was determined from the parent peaks in the 70-v. spectra.
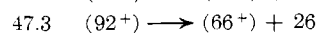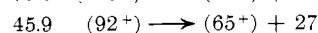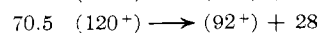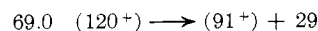
	1-d	3-d
Unlabeled, %	12.0	45.9
d_1, %	84.0	54.1
d_2, %	4.0	0.0

The d_2-material in the 3-phenylpentane-1-d suggests that the temperature during alkylation rose high enough to effect some dehydrogenation.[4]

Mass spectra were measured on a modified[7] Consolidated model 21–103c instrument with 70-v. electrons. Table I shows partial spectra, corrected for the contributions of naturally occurring C^{13} and D^8 and of unlabeled 3-phenylpentane in the deuterated materials. That the fragment ions included arise in a common reaction sequence is shown by the metastable peaks[2b]

$$69.6 \; (119^+) \longrightarrow (91^+) + 28$$
$$46.4 \quad (91^+) \longrightarrow (65^+) + 26$$
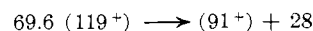
in the spectrum of the unlabeled species. More diffuse metastable peaks at about the same masses in the spectra of the labeled species doubtless include unresolved components for metastable transitions of labeled ions.

$$69.0 \quad (120^+) \longrightarrow (91^+) + 29$$
$$70.5 \quad (120^+) \longrightarrow (92^+) + 28$$
$$45.9 \quad (92^+) \longrightarrow (65^+) + 27$$
$$47.3 \quad (92^+) \longrightarrow (66^+) + 26$$

Measurements to determine dependence of label retention on ionizing voltage[9,10] were made with the repeller plates at an average potential of 3 v.; actual settings, adjusted for maximum ion current, were 3.55 v. on the inner repeller and 2.45 v. on the outer one.

(1) (a) American Oil Co.; (b) Michigan State Univ.

(2) (a) P. N. Rylander and S. Meyerson, J. Am. Chem. Soc., **78**, 5799 (1956); (b) H. M. Grubb and S. Meyerson, in "The Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 453.

(3) The $C_7H_7^-$ ion is shown here as having the nominal benzyl structure. It might be better represented, however, as the symmetrical tropylium ion (see ref. 2b; also, P. N. Rylander, S. Meyerson, and H. M. Grubb, J. Am. Chem. Soc. **79**, 842 (1957); S. Meyerson and P. N. Rylander, J. Chem. Phys., **27**, 901 (1957)). The phenylethyl structure written for the $C_8H_9^+$ ion is also to be regarded as nominal only.

(4) H. Pines, J. A. Vesely, and V. N. Ipatieff, J. Am. Chem. Soc., **77**, 554 (1955).

(5) We are indebted to D. L. Esmay for this synthesis.

(6) H. Hart and R. E. Crocker, J. Am. Chem. Soc., **82**, 418 (1960).

(7) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, presented before 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.
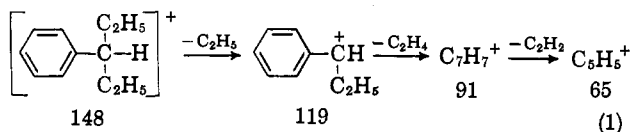
(8) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1960.

(9) S. Meyerson, J. Chem. Phys., **34**, 2046 (1961).

(10) S. Meyerson, T. D. Nevitt, and P. N. Rylander, in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliott, Ed., Pergamon Press, New York, N. Y., 1963, p. 313.

Discussion

The observed metastable peaks define reaction path 1.

(1)

The ionic structure shown for $C_9H_{11}^+$ is nominal only. Label retentions in fragment ions from labeled species must reflect the nature of the decomposition steps and hence the structures of the reaction intermediates.

Retentions calculated[2b] from the spectra are

	1-d	3-d
$C_9H_{11}^+$, %	50.5 to 52.0	100
$C_7H_7^+$, %	16.3 to 19.8	41.5
$C_5H_5^+$, %	12 to 16	46

The uncertainties in the case of the ions from the 1-d species arise because of the unknown contributions of the d_2 impurity. The lower limits shown were arrived at by assuming that the ions derived from 3-phenylpentane-d_2 all contain at least one deuterium atom. The upper limits were arrived at by ignoring contributions of the d_2 species.

Retentions in the $C_9H_{11}^+$ ions establish unequivocally that the C_2H_5 radical lost in the first step is one of the original ethyl groups. Thus no rearrangement of the parent ion precedes the primary decomposition.

Retention in the $C_7H_7^+$ ion from the 1-d species is about one-third that of $C_9H_{11}^+$. This value can be accounted for equally well by either of two mechanisms: I, cleavage of the β-carbon–carbon bond with concomitant hydrogen migration from the β-carbon to the aryl moiety, as has been shown to occur in formation of $C_7H_8^+$ from 1-phenylbutane[11]; II, rearrangement of $C_9H_{11}^+$ to a phenylated cyclopropane ion either concerted with or following the primary loss of C_2H_5, followed by shift of two electron pairs, as in decomposition of t-butylbenzene, to give $C_7H_7^+$ and C_2H_4

(I)

(II)
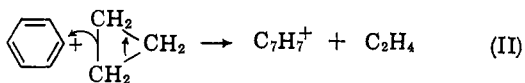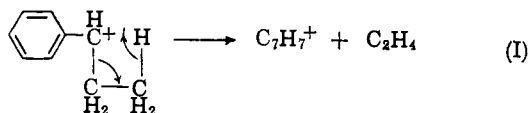
The 3-phenylpentane-3-d data furnish a basis for distinguishing between these mechanisms. Deuterium retention in $C_7H_7^+$ formed from this species by I should be 100%; by II, 33%. The experimental value is 41.5%, intermediate between the two predicted values.

The possibility that more than one path might be involved was explored by measuring the C_7 spectral region at ionizing voltages varying from the appearance potential of $C_7H_7^+$ to 70 e.v. and examining the voltage dependence of label retention in the $C_7H_7^+$ ion.[9,10] In the ion derived from 3-phenylpentane-1-d, retention was found to be independent of ionizing voltage over the entire range studied. In that derived from the 3-d species, retention is constant at about 35% over a range of some 3 v. immediately above the appearance potential; it then increases smoothly to a maximum of

(11) J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **81**, 4116 (1959).

41.2%, attained at about 40 v., above which it is independent of ionizing voltage. The appearance potential apparently corresponds to the onset of II. The dependence of label retention on ionizing voltage implies that $C_7H_7^+$ arises by more than one reaction and can be accounted for by contributions from the two mechanisms II and I in appropriate proportions: about 90:10 at ionizing voltages greater than 40 v.

Neither the precise structure of the intermediate in path II nor the way in which it is formed is clear. The present data, coupled with those on t-butylbenzene-α-C^{13}, require that the three carbon atoms and the six hydrogen atoms in the side chain become indistinguishable as viewed from the phenyl group. A phenylated cyclopropane ion most simply represents $C_9H_{11}^+$ with the required symmetry.

The likelihood that $C_7H_7^+$ is formed from both 3-phenylpentane and t-butylbenzene mainly via a common intermediate poses an interesting problem. In the spectrum of the former compound, the ratio of intensities $C_7H_7^+:C_9H_{11}^+$ is about 2:1; in that of the latter, it is about 1:2. The probability of losing C_2H_4 following primary β-cleavage is grossly different in the two compounds. Moreover, the difference in behavior is not limited to this specific pair of compounds, but is characteristic of the two classes of alkylbenzenes to which they belong[2b] —secondary alkylbenzenes in which both substituents on the α-carbon are larger than methyl, and 2-methyl-2-phenylalkanes.

The difference can be accounted for if the phenylated cyclopropane structure is assumed to arise largely by rearrangement of $C_9H_{11}^+$ ions formed intially in the less stable classical structures.[12]

The energy released by rearrangement of the secondary carbonium ion derived from 3-phenylpentane should be greater than that released by rearrangement of the initially more-stable tertiary ion derived from t-butylbenzene. The excess energy furnishes proportionately greater driving force for further decomposition.

The $C_7H_7^+$ ion derived from 3-phenylpentane decomposes further to $C_5H_5^+$ to only a small extent, as indicated by the low intensity of the latter ion. In the spectrum of the 3-d species, label retention in $C_5H_5^+$ is greater than that in $C_7H_7^+$. This finding implies—if contributions from other, unknown precursors are not involved—that $C_7H_7^+$ ions differing in label retention differ also with respect to further decomposition to $C_5H_5^+$ and C_2H_2. Specifically, the data can be accommodated by a population of $C_7H_7^+$ ions all having the symmetrical tropylium configuration[2b,3] if the probability of further decomposition—as measured by the intensity ratio $C_5H_5^+:C_7H_7^+$—is assumed to be twice as great for ions arising by mechanism I as for those arising by mechanism II.

Thus, differences in energy content of molecule-ions, even those that decompose by nominally the same path, can be propagated through sequential reaction steps. Rearrangements, including particularly those to nonclassical structures, may well perform a critical function in the internal energy conversions responsible for the rich detail found in mass spectra of organic molecules.

(12) N. Muller and R. S. Mulliken, *ibid.*, **80**, 3489 (1958).