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FRAGMENTATION AND REARRANGEMENT OF PHENYLCYCLOPROPYLCARBINOL INDUCED BY ELECTRON IMPACT

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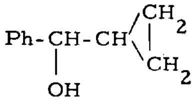
Parallel correlation between the mechanisms of mass spectral fragmentations and those of reactions in solution (1) in connection with the recent progress in the related rearrangements (2) promted us to study the mass spectral behavior of cyclopropylcarbinyl cation. The fragmentation of cyclopropane derivatives was reported to be the cleavage of two carbon-carbon single bonds with or without migration of atom or functional group attached to cyclopropylcarbinyl carbon (3-6). It was conceivable that when certain suitable group was attached to the cyclopropylcarbinyl carbon, cyclopropylcarbinyl cation was formed by electron impact.

Phenylcyclopropylcarbinol [1] was chosen because of the facility of cyclopropylcarbinyl cation formation. The possibility to examine the migratory apptitude of phenyl and hydroxyl groups was also expected. The deuterated isomers [2-6] were synthesized: reduction of benzoylcyclopropane by lithium aluminiumdeuteride gave 2; treatment of benzylidenecyclopropane with diborane-d_6 gave 3 (7); treatment of 1 with deuterium oxide gave 4, and reduction of benzoylcyclopropane-d_4 [7] (8) by lithium aluminiumhydride or lithium aluminiumdeuteride gave 5 or 6, respectively.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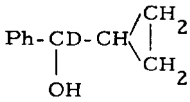
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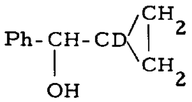
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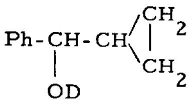
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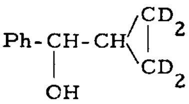
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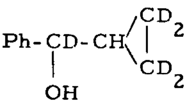
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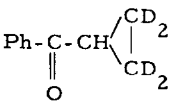
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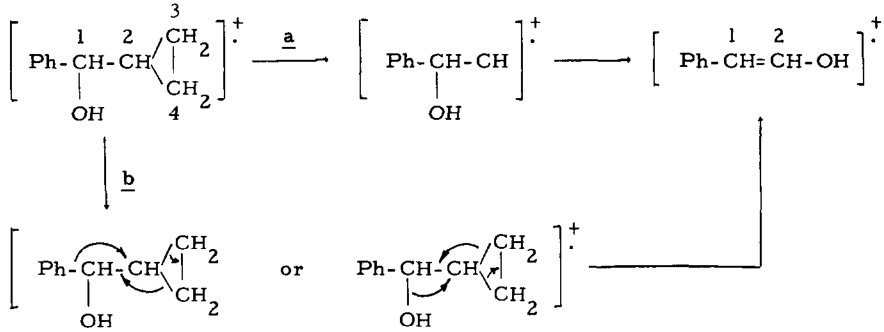
The fragmentations carried out on Hitachi RMS-4 at 70 eV gave following ions: m/e (relative %), 148 (M^+) (2), 147 (2), 120 (100, base peak), 107 (14), 105 (30), 104 (35), 91 (52), 79 (28), 78 (19), 77 (38), and 51 (22); metastable ions: m/e (calcd. as $m_1 \rightarrow m_2$), 97.5 (97.30, 148 → 120), 77.4 (77.36, 148 → 107), 69.0 (69.01, 120 → 91), 58.4 (58.33, 107 → 79), 56.5 (56.47, 105 → 77), 75.0 (75.05, 79 → 77), and 33.8 (33.77, 77 → 51).

Among these fragment ions, relatively abundant ions of m/e 120, 105, 104 and 91 were difficult to explain by simple cleavage mechanism.

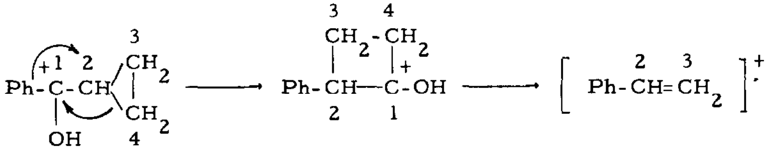
The Ion of m/e 120. The ion was assigned as $[\mathrm{Ph\text{-}CH{=}CH\text{-}OH}]^{\cdot +}$, the formation of which was considered as eq. I. The reported mechanism (3-6) of the cleavage of the two carbon-carbon bonds of cyclopropane was proved (a) by the determination of the composition (C_8H_8O) by high resolution mass spectrometry (9); (b) by no shift of m/e 120 in the case of 5, and (c) by the one mass unit shift to m/e 121 in the cases of 2, 3, 4, and 6. There was no evidence to differenciate the two route a or b.

(I)



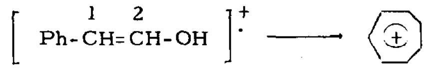
The Ion of m/e 104. High resoltion mass spectrometry indicated the composition of the ion to be C_8H_8. The peak of m/e 104 shifted to 106 in the cases of 5 and 6, and partly to 105 in the case of 3, but did not shift in the cases of 2 and 4. In the case of 3, metastable peak (m/e 74. 5) indicated the fragmentation from M - 1 (m/e 148) to m/e 105. The composition of m/e 105 ion in the case of 3 was determined to be the mixture of C_8H_7D and C_7H_5O. The above mentioned data showed that the formation mechanism of the ion could be explained by eq. II, that is, rearrangement of cyclopropylcarbinyl cation to cyclobutyl cation.

(II)



The Ion of m/e 91. The composition of the ion of m/e 91 was determined by high resolution mass spectrometry to be C_7H_7. Detection of metastable ion (m/e 69. 0) indicated that this ion was formed from C_8H_8O ion (m/e 120). The fact that the peak of m/e 91 shifted partly to m/e 92 in the case of 2, 3, 4, and 6 but not in the case of 5 also indicated the fragmentation mechanism as eq. III (10).

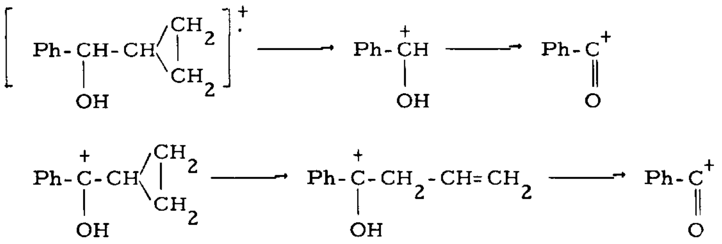
(III)



The ratic of peak height of m/e 91 to 92 was 2 in the case of 2 and 0. 5 in the case of 3.

These data were considered to indicate that the ratio of the migratory aptitude of phenyl to that of hydroxyl was approximately 2. This datum showed that this rearrangement was ionic.

The Ion of m/e 105. Exact mass measurement indicated the composition of this ion was C_7H_5O. From the fact that the peak of m/e 105 did not shift in all the cases of 1 through 6, two mechanisms were conceivable. Under the mass-spectrometric conditions (Hitachi-RMS-4, 70 eV, standard condition for measurement less than m/e 300), however, no metastable ion was observed to support any mechanism.



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7. The detailed description of this reduction: K. Sisido, M. Tamura, M. Tanouti, and K. Utimoto, to be published.
8. Benzoylcyclopropane-d_4 [7] was prepared from ethyl benzoylacetate and 1, 2-dibromoethane-d_4.
9. We thank Hitachi Co. for the high resolution mass spectrometry.
10. Fragmentation via carbonyl type ion [8] was not conceivable, because it was reasonable that keto-enol tautomerism did not occur during the mass spectrometric fragmentation (11).

$$[\mathrm{Ph\text{-}CH_2\text{-}CHO}]^{+\cdot} \qquad 8$$

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