Tetrahedron Letters No.42, pp. 4101-4103, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE STRUCTURE OF THE M-CO ION FROM 2-PYRONES UPON ELECTRON IMPACT

Hisao Nakata
Department of Chemistry, Aichi Kyoiku University, Higashi-ku, Nagoya
and
Akira Tatematsu
Faculty of Pharmacy, Meijo University, Showa-ku, Nagoya, Japan

(Received in Japan 8 July 1967)

Since our first report on the mass spectral fragmentation of several 2-pyrones (1), Pirkle has questioned (2) our proposal of the intermediacy of a furan radical ion as an M - CO fragment from 2-pyrones. Their argument is based on the fact that specific deuteration at C_3 and C_6 of the pyrone nucleus did not lead to the same isotopic distribution in an m/e 39 peak derived from an assumed symmetrical furan intermediate. Recently, Brown and Green (3) have invalidated the Pirkle's conclusion by pointing out that the differences in these isotopic distributions (2) can equally well be explained by observed multiple pathways to the m/e 39 ion.

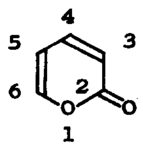
The discussion of the intermediacy of the furan ion is possibly related to the experimental demonstration as to whether or not the bond formation between C_3 and O_1 takes place after carbon monoxide expulsion from the molecular ion. We now wish to present supporting, though not conclusive, evidence that the fragmentation occurs, at least in part, through an intermediate with a $C_3 - O_1$ bond in some 2-pyrones.

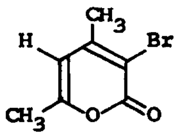
Fig. 1. Mass Spectrum of 3-Bromo-4,6-dimethyl-2-pyrone (I).

The mass spectrum of 3-bromo-4,6-dimethyl-2-pyrone (I) is reproduced in Fig. 1. The appearance of appropriate meta-stable ion peaks (m*) suggested one of the major fragmentation sequences as the following.

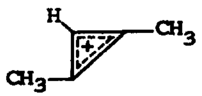
$$\boxed{m/e\ 204,\ 202} \xrightarrow[-\ \mathrm{CO}]{m^*\ 151.0} \boxed{m/e\ 176,\ 174} \xrightarrow[-\ \mathrm{Br}\cdot]{m^*\ 51.6} \boxed{m/e\ 95} \xrightarrow[-\ \mathrm{CO}]{m^*\ 47.3} \boxed{m/e\ 67}$$

The accurate mass measurement established the elemental composition of the m/e 67 ion as a hydrocarbon fragment, $C_5H_7^+$. This ion carries all hydrogen atoms in I, and, therefore, includes C_4, C_5, and C_6, as well as two methyl groups. As assigned previously (1), its structure may be formulated as II. Since the carbonyl carbon atom of I (C_2) was already removed directly from the molecular ion, the third step of the above fragmentation is the loss of C_3 as carbon monoxide. Existence of a prominent meta-stable ion peak at m/e 47.3





(I)



(II)

indicates a simultaneous elimination of one carbon (C_3) and one oxygen atom (O_1) from the m/e 95 ion, and this requires prior formation of a C - O bond between C_3 and O_1 at an earlier stage of the fragmentation.

Although we do not as yet know the exact structure of each fragment ion, the present result clearly shows that an intermediate having the $C_3 - O_1$ bond is involved in the fragmentation of bromodimethylpyrone (I). One of the most attractive and plausible representations of this ion seems to be the corresponding furan structure, but other alternative formulations cannot be excluded. On the other hand, it is also conceivable that the M - CO peak originates from several, structurally different fragment ions of the same composition including the furan radical ion. The extent of its contribution to the M - CO peak may probably depend on the structure of a given 2-pyrone.

References

1. H. Nakata, Y. Hirata, and A. Tatematsu, Tetrahedron Letters, **1965**, 123.
2. W. H. Pirkle, J. Am. Chem. Soc., **87**, 3022 (1965).
3. P. Brown and M. M. Green, J. Org. Chem., **32**, 1681 (1967).