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Note

A Novel Rearrangement Reaction of Benzophenone Oxime upon Electron Impact

D. Stefanović

Institute »Ruđer Bošković«, 41000 Zagreb, Croatia, Yugoslavia

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A »hidden« rearrangement reaction in benzophenone oxime was found by examination of a noncharacteristic, low abundance fragment ion.

A large number of rearrangement reactions occurring in a mass spectrometer are subject to intensive study. The importance of such reactions in the determination of ion structure and fragmentation mechanism is well documented. Many of these rearrangement reactions represent a very favourable pathway for the molecule to fragment and often give rise to prominent peaks in its mass spectrum. It must be noted, however, that even a study of some low intensity, noncharacteristic peaks may reveal some interesting and unexpected fragmentation reactions and supply new information about the behaviour of the molecule under electron impact.

In the course of our study on the mass spectra of some oximes of diarylketones, a fragment peak of low intensity, whose existence seems unlikely on the basis of the original structure, has drawn our attention. The same peak can also be found in the spectra of benzophenone oxime run on different instruments and applying various sample introduction techniques¹.

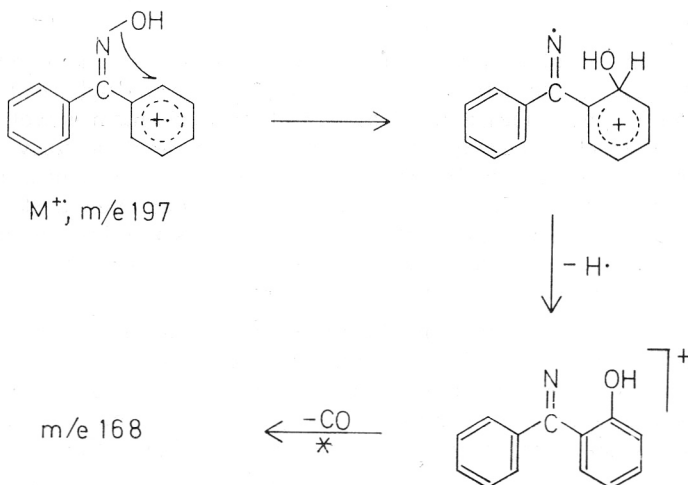
The peak in question appears at m/e 168 (relative abundance 6%, Σ_{20} 0.017%). The elemental composition of the corresponding ion was shown by high resolution measurement to be $C_{12}H_{10}N$. A second field metastable peak is centered at m/e 144, indicating a formation of this ion from the $[M - 1]^+$ by loss of 28 mass units, *i. e.* by expulsion of a molecule of carbon monoxide. A direct insertion probe was used for the introduction of the sample and no thermal decomposition was observed in the sample temperature range from 20 to 50 °C.

Deuterium labelling indicates that either OH or H migrate to the ring, *i. e.* that the first reaction step is not a loss of a hydroxyl hydrogen from the unrearranged molecular ion. Replacement of the hydroxyl hydrogen by deuterium (90%) results in a shift of m/e 168 to 169. The ratio m/e 169/168 increases from 0.5 in undeuterated compound to 1.5 in the deuterated analogue, indicating a considerable retention of deuterium in the $[C_{12}H_{10}N]^+$ ion. A cluster of peaks between m/e 166 and 169 of similar intensities prevents a precise calculation to be made on the distribution of deuterium in this ion. A possible shift of m/e 167 to 168 and, on the other hand, scrambling between

the hydrogen of the hydroxyl group already attached to the ring and other hydrogens in the ring², may contribute to the intensity of the m/e 168 peak.

Two mechanisms seem reasonable to account for the formation of $[C_{12}H_{10}N]^+$. The first one involves a hydroxyl group migration to the ring, followed by the loss of a hydrogen radical from the same ring. A molecule of carbon monoxide is subsequently lost from this ion. An alternative mechanism would be a migration of the hydroxyl hydrogen to the ring, followed by the loss of a hydrogen radical, a migration of the oxygen to the ring and finally a loss of the CO molecule.

On the basis of deuterium labelling no difference between the two proposed mechanisms could be made because of scrambling and/or random loss of hydrogens in the formation of $[M-H]^+$ ion. However, a hydroxyl group migration, which has been shown to occur in the course of formation of m/e 94, $[C_6H_5OH]^+$ in a one-step process from the molecular ion, speaks in favour of the mechanism shown bellow.



This example points to the existence of a number of »hidden« degradation reactions which, although not always of a diagnostic value, are certainly of mechanistic interest. Tremendous work would be required in order to approach the detailed knowledge of the electron impact behaviour even for the simple molecules.

EXPERIMENTAL

Mass spectra were obtained on a Varian MAT CH-7 mass spectrometer at 70 eV, 60 μ A and 3600 V. The temperature of the ion source was about 130 °C. The samples were introduced by the direct insertion method, the rod temperature being 20 °C. Exact mass determination was performed on a CEC 21-110 C instrument at the »J. Stefan« Institute, Ljubljana, Yugoslavia.

Benzophenone oxime was prepared by reaction of benzophenone with hydroxylamine hydrochloride. It was recrystallized from methyl alcohol and purified by liquid column chromatography. Introduction of benzophenone oxime directly into the source with D_2O^3 produced the O- d_1 derivative ($d_1 = 90\%$).

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SAŽETAK

Nova reakcija pregrađivanja benzofenonoksima u spektrometru masa*D. Stefanović*

Mehanizam nastajanja fragment-iona $[C_{12}H_{10}N]^+$ uključuje migraciju hidroksilne skupine na aromatsku jezgru u molekularnom ionu benzofenonoksima. To pregrađivanje, uočeno ispitivanjem signala niskog intenziteta, upućuje na obilje neotkrivenih putova raspada iona u spektrometru masa.

INSTITUT »RUĐER BOŠKOVIĆ«
41000 ZAGREB

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