## **New Mass Spectra**

## Electron Impact Mass Spectra of Substituted 2-OTMS-acetophenones

The electron impact mass spectrum of 2-OTMS-acetophenone shows a significant ortho effect (Fig. 1). Whereas in the case of the 3- and 4-isomers the relative abundance of the molecular ion is about 30%, it is 0.7% for the ortho isomer, the  $[M-CH_3]^+$ ion being the base peak. This can be explained by formation of a cyclic ion (Scheme 1), which is supported by the difference in ionization energy and appearance energy of this ion (120 kJ mol<sup>-1</sup>), compared with 280 kJ mol<sup>-1</sup> for the 3- and 4-isomers.<sup>1</sup>





In this paper we wish to report the mass spectra of the substituted 2-OTMS-aceto-phenones 1-16.



All spectra were recorded on a CH-7 instrument (Varian MAT) with a data system SS 100, operating at 70 eV ionizing energy, 100  $\mu$ A ionizing current, and 200 °C ion source temperature. The mass spectrometer was equipped with a gas chromatograph F 20 FE (Bodenseewerk Perkin-Elmer), using a 4 m packed glass column with 0.5% OV-17 on Chromosorb G-AW-DMCS (60/80 mesh) as stationary phase and helium as carrier gas. The GC/MS interface was a two-stage Biemann-Watson separator (200 °C).

The TMS ethers were prepared from the corresponding 2-hydroxyacetophenones by silylation with bis(trimethylsilyl)acetamide (BSA) at 70 °C using pyridine as solvent. The reaction mixtures were directly analysed by GC/MS after 15 min.

The preparation of the substituted 2hydroxyacetophenones is described elsewhere:  $5-NO_2$ ,  $^24-NO_2$ ,  $^33-NO_2$ ,  $^25-I$ ,  $^45-Br$ ,  $^5$  4-Br,  $^6$  5-Cl,  $^7$  4-Cl,  $^6$  4-CH<sub>3</sub>,  $^{8.9}$  5-OCH<sub>3</sub>,  $^{10}$  5-NHCOCH<sub>3</sub>,  $^{11}$  4-NHCOCH<sub>3</sub>,  $^{12}$ 

## Table 1. Relative abundances (%) of important ions (m/z)

- 1: R = H 208 (0.7), 193 (100), 175 (6), 163 (3), 151 (7), 135 (3), 91 (5), 89 (8), 75 (8), 73 (9), 45 (9), 43 (11)
- 2: R = 5-NO<sub>2</sub> 253 (—), 238 (100), 208 (3), 192 (60), 181 (8), 180 (7), 166 (13), 149 (6), 75 (20), 73 (37), 45 (17), 43 (23)
- **3**: R = 4-NO<sub>2</sub> 253 (0.3), 238 (100), 208 (4), 192 (69), 181 (6), 180 (27), 166 (4), 149 (10), 75 (21), 73 (45), 45 (17), 43 (25)
- 4:  $R = 3-NO_2$
- 1 1 5 (102)
  253 (--), 238 (100), 220 (4), 192 (85), 177 (12), 166 (8), 164 (12), 149 (20), 75 (23), 73 (32), 45 (21), 43 (32)
  5: R = 5-1
- 334 (7), 319 (100), 301 (3), 262 (10), 247 (6), 192 (51), 177 (5), 149 (5), 75 (12), 73 (32), 45 (10), 43 (15)
- 6: R = 5-Br 288 (1.4), 286 (1.4), 273 (100), 271 (98), 255 (15), 253 (15), 192 (11), 177 (11), 174 (6), 149 (7), 75 (20), 73 (37), 45 (20), 43 (32)
- 7: R = 4-Br
  - 288 (0.6), 286 (0.6), 273 (100), 271 (98), 255 (10), 253 (10), 192 (8), 177 (11), 149 (7), 128 (13), 75 (18), 73 (29), 45 (18), 43 (25)
- 8: R = 5-CI
  - 244 (0.4), 242 (1.1), 229 (39), 227 (100), 211 (5), 209 (13), 187 (4), 185 (9), 75 (13), 73 (23), 45 (13), 43 (22)
- 9: R = 4-Cl 244 (0.2), 242 (0.6), 229 (40), 227 (100), 211 (7), 209 (15), 187 (4), 185 (8), 75 (11), 73 (29), 45 (12), 43 (18)
- 10: R = 5-CH<sub>3</sub>
  - 222 (2.0), 207 (100), 189 (4), 177 (2.8), 165 (4), 149 (3), 75 (7), 73 (14), 45 (9), 43 (12)
- 11: R = 4-CH<sub>3</sub>
  - 222 (0.8), 207 (100), 189 (10), 177 (4), 165 (9), 149 (5), 75 (7), 73 (8), 45 (7), 43 (8)
- 12: R = 5-OCH<sub>3</sub>
  - 238 (8), 223 (100), 208 (7), 205 (5), 180 (28), 165 (4), 151 (3), 150 (4), 75 (8), 73 (18), 45 (10), 43 (8)
- 13: R = 4-0CH<sub>3</sub>
- 238 (5), 223 (100), 205 (1.3), 180 (12), 165 (3), 151 (5), 150 (2), 104 (8), 75 (6), 73 (12), 45 (8), 43 (10) 14: R = 5-NHCOCH<sub>2</sub>
  - 265 (5), 250 (100), 208 (32), 180 (10), 166 (8), 151 (6), 75 (15), 73 (30), 45 (11), 43 (19)
- 15: R = 4-NHCOCH<sub>3</sub>
   265 (8), 250 (100), 208 (95), 193 (9), 180 (7), 166 (5),
- 151 (7), 136 (18), 75 (15), 73 (44), 45 (10), 43 (28) **16:** R = 5-NH<sub>2</sub>
  - 223 (15), 208 (100), 190 (7), 166 (14), 150 (5), 106 (6), 75 (10), 73 (17), 45 (8), 43 (6)

 $5-NH_2$ .<sup>11</sup> 2-Hydroxyacetophenone, 5methyl-2-hydroxyacetophenone and 4methoxy-2-hydroxyacetophenone were obtained from EGA-Chemie, 7924 Steinheim, FRG.

Fragmentations were identified by the presence of metastable ions and the spectra of the corresponding ethers with a  $d_9$ -labelled TMS group.

Relative abundances of important ions

are given in Table 1. According to the inductive effect of the substituent group the relative intensities of the molecular ions differ from <1 up to 15% except for the iodine compound showing an intensity of 7%.

Loss of a methyl group from  $[M]^+$  leads to the base peak for all compounds investigated. The methyl groups on the silicon are mainly involved in this reaction, whereas



Figure 1. El mass spectrum of 1.

fission at the acetyl group is of much lower abundance, as shown by the spectra of the labelled compounds.

The elimination of water from the [M-15]<sup>+</sup> ion, present in all spectra, predominates in the case of the halides. This reaction seems to proceed by complicated rearrangements, because the spectra of the labelled compounds show the loss of H<sub>2</sub>O as well as HDO and D<sub>2</sub>O.

For nitro, iodo and bromo derivatives cleavage of the substituent from the [M- $CH_3$ ]<sup>+</sup> ion is an outstanding reaction (Fig. 2), though it results in a 'odd-electron' fragment ion. On the contrary, loss of the substituent from [M]<sup>+</sup> is not observed.

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