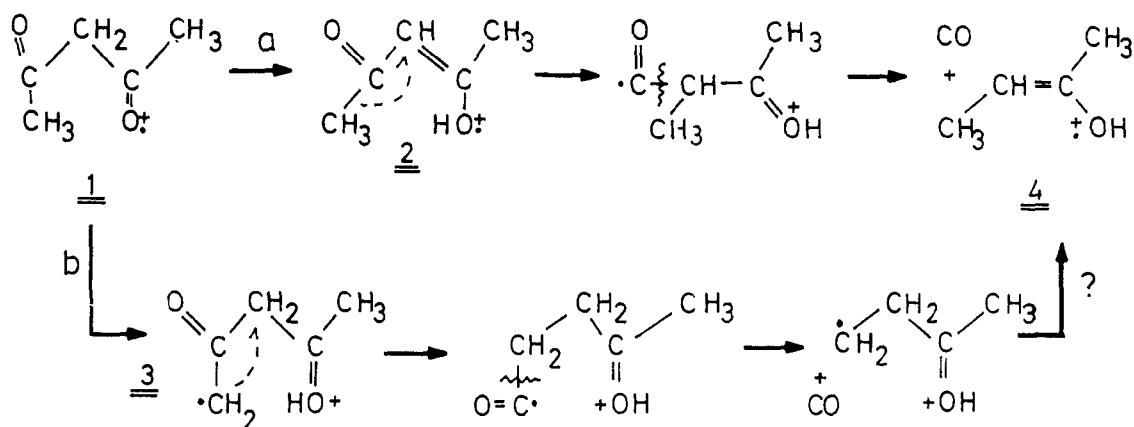# OMS Letters

LOSS OF CO FROM THE MOLECULAR IONS OF 2,2-DIMETHYL-3,5-HEXANDIONE.

The mechanism of CO loss from the molecular ions of 1,3-dicarbonyl compounds has been in the focus of interest for many years [1]. Recently, S.Tajima, K.Ogino and S.Tobita [2] have suggested two possible mechanisms (Scheme 1) for the elimination of CO from the molecular ions of 2,4-pentanedione.

Scheme 1: Proposed mechanisms for CO loss from acetylacetone ions 1 [2].

These authors proposed that the CO elimination starts from the molecular ions of the diketo tautomer 1 either by a 1,3-hydrogen migration to give the molecular ion 2 of the enol tautomer or by a 1,4-hydrogen shift resulting in a distonic ion 3. However, these proposals can not account for the loss of CO from the molecular ions of 2,2-dimethyl-3,5-hexandione (pivaloyl-acetone), which we will present in this letter.

First of all, it is necessary to determine unequivocally the tautomeric form of the molecular ions of the 1,3-diketones which is responsible for the loss of CO, and the structure of the product ions [M-CO]$^{+\cdot}$ Therefore, the 70 eV mass spectra of the pure diketo and ketoenol tautomers of 1,3-diketones have been obtained by GC/MS [3], and the resulting spectra of the tautomeric pivaloylacetones 5 and 6 are shown in figure 1. Obviously, only the diketo molecular ions 5 fragment by loss of CO as indicated by the presence of a peak at m/z 114 only in the spectrum of this tautomer. The loss of CO from the diketo ion has also been suggested by L.Zamir et al. [1c]. Furthermore, we have investigated all possible product ions by comparison of their CA spectra with those of reference compounds. In contrast to acetylacetone, pivaloylacetone is an unsymmetrical 1,3-diketone. Therefore each of the two CO groups may be
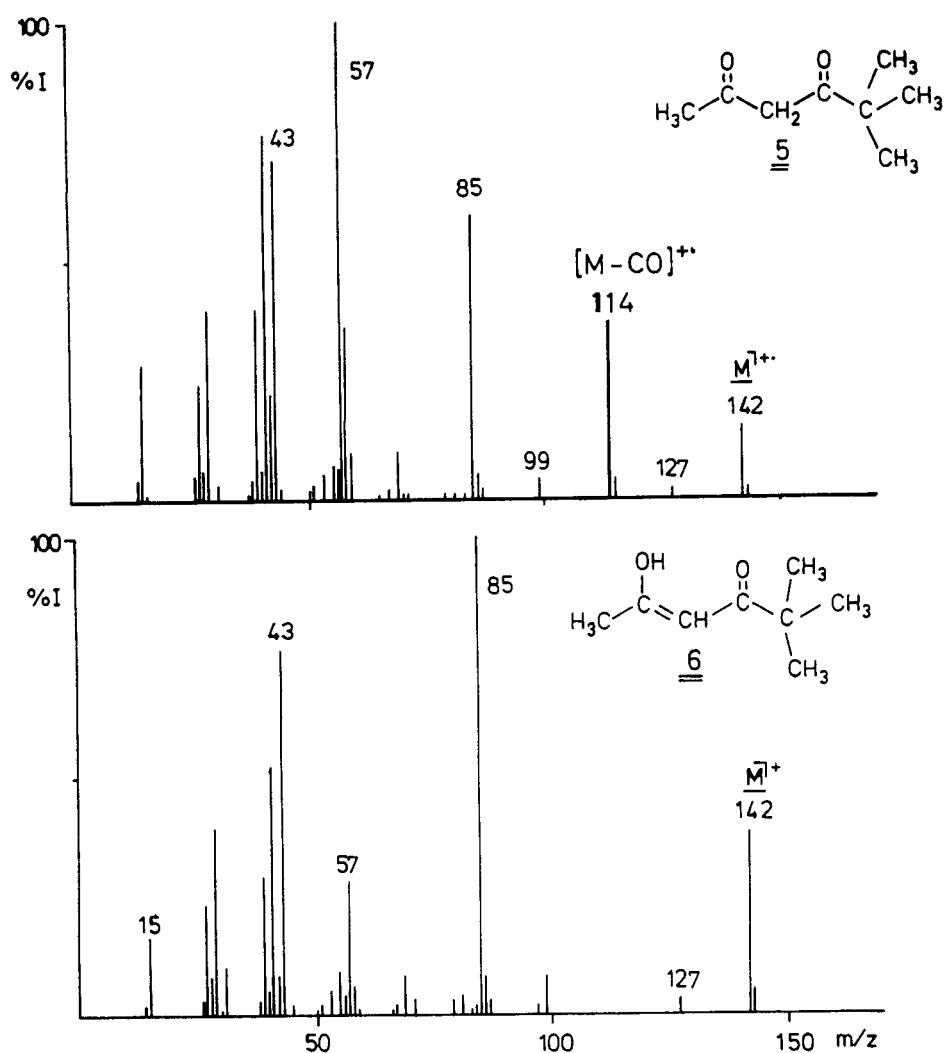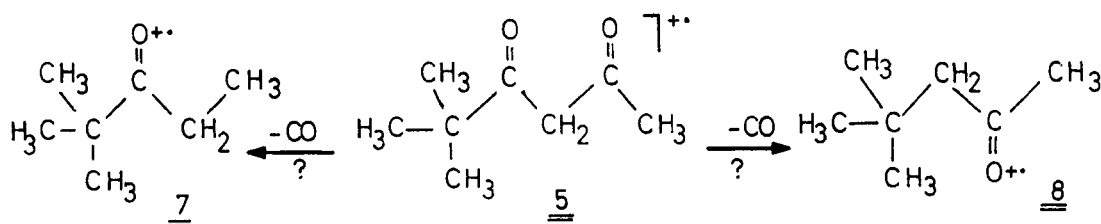
Figure 1: 70eV mass spectra of the tautomers **5** and **6** of pivaloylacetone.

eliminated by a shift of theneighbouring alkyl group. Migration of the methyl group leads to t-butylethylketone ions **7**, while migration of the larger t-butyl group leads to the isomeric neopentylmethylketone ions **8** (Scheme 2).

Scheme 2: Product ions of the CO elimination from **5**.

The CA spectra of the reference ketones **7** and **8** (Figure 2) are quite different and can be correlated to the structure of the isomeric ketones. The CA spectra of the $[M\text{-}CO]^{+\cdot}$-ions from **5** (spectrum in the middle of Figure 2) is quite similar to the CA spectrum of **8** indicating a migration of the t-butyl group exclusively. This selectivity is further corroborated by the MIKE spectrum of (^{13}C)-pivaloylacetone labelled at the CO group of the acetone moiety. This MIKE spectrum shows that only unlabelled CO is eliminated as indicated by the complete   shift of the signal m/z 114 to m/z 116. Therefore, the $[M\text{-}CO]^{+\cdot}$ product ions of pivaloylacetone have the structure of neopentylmethylketone ions or of its enolic tautomers.
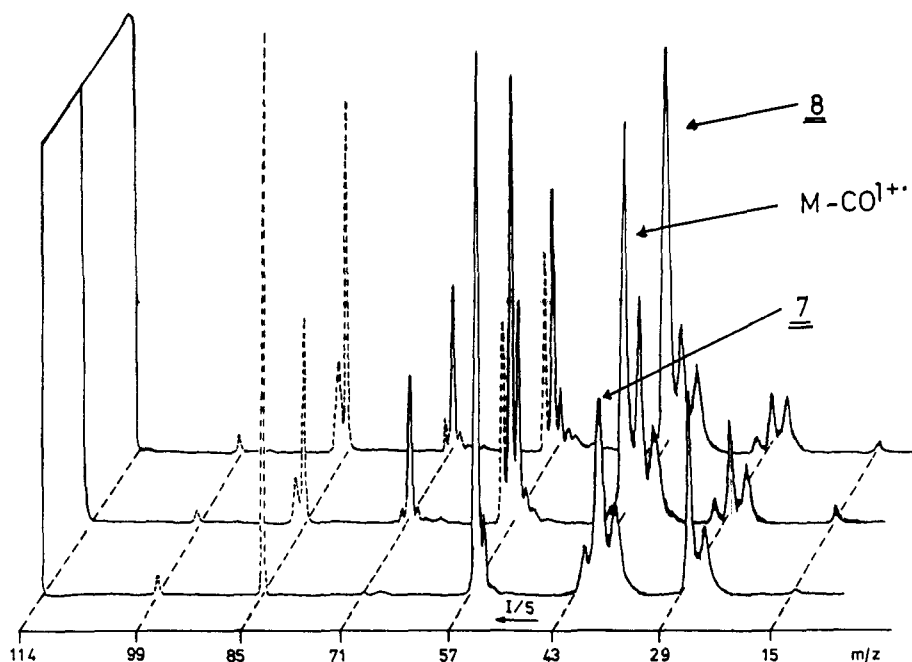
Figure 2: CA spectra of $[M\text{-}CO]^{+\cdot}$ from **5** and of molecular ions of **7** and **8**.

This very specific migration of the tert. butyl group of **5** is in opposition to the mechanism b of Scheme 1. The proposed initial 1,4-H-shift can occur only from the methyl group of **6** and should eventually lead to **7** by a specific rearrangement of the original methyl group.

To establish the structure of the product ions $[M\text{-}CO]^{+\cdot}$ more in detail the isomeric enolic ions **9** and **10** have been prepared by a McLafferty rearrangement from suitable precursor ions. The CA spectra of the central enol and the terminal enol tautomer ions (Figure 3) can be easily distinguished and correlated with the structures of ions **9** and **10**. The CA spectrum of the central enol ion **9** exhibits only a small peak m/z 57 of the t-butylcation which can be explained by an energetically unfavorable vinylic cleavage.
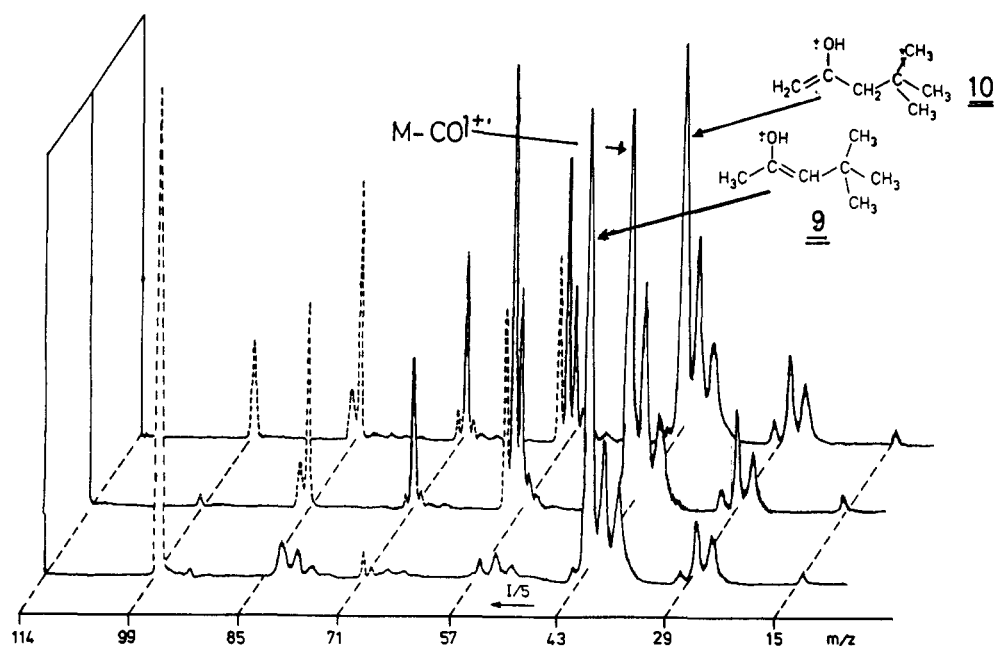
Figure 3: CA spectra of [M-CO]⁺˙ from 5 and the tautomeric ions 9 and 10.

Comparison of the CA spectrum of the [M-CO]$^{+\cdot}$ ions with those of 9 and 10 shows that the product ions are probably terminal enol ions 10 but not at all central enol ions 9. One should note that the CA spectra of the enol ions 10 and the ketone molecular ions 8 (Figure 2) are quite similar indicating an isomerization of these ions by two successive 1,5-H-shifts .

This result is in contrast to the mechanism a proposed by S.Tobita et al [2] (Scheme 1), which yields the central enol ion 9 as the product ion. Thus, both mechanisms of Scheme 1 are disproved at least in the case of the CO loss from the diketo ion 6 of pivaloylacetone. We propose an other mechanism for the CO loss including an ion/molecule complex as the crucial intermediate (Scheme 4). By this mechanism, the loss of CO starts with an α-cleavage into a pivaloyl cation, which gives rise to a large peak at m/z 85 in the 70 eV EI-mass spectrum of 6 , and an acetonyl radical. The incipient pivaloyl cation is captured by the neutral fragment during the decomposition of metastable ions 6 to form an ion/neutral complex. The stabilization energy (144 kJ mol⁻¹, calculated by the classical formula for the ion/induced dipole and ion/dipole interaction [4]) allows for internal ion/molecule reactions. The loss of CO from the pivaloyl cation, which corresponds to the well known spontaneous fragmentation of acylium cations [5], gives rise to a new ion/neutral complex of the remaining t-butyl cation and the acetonyl radical. A recombination of the electrophilic t-butyl cation and the nucleophilic acetonyl radical yields the molecular ion of neopentylmethylketone 8. The selectivity of the migration of the t-butyl group can be explained by the lower energy of the complex

$[(CH_3)_3CCO^+/\cdot CH_2COCH_3]$ (ΔH_f = 308 kJmol^{-1}), compared to the complex $[CH_3CO^+/\cdot CH_2COC(CH_3)_3]$ (ΔH_f = 343 kJmol^{-1}) arising from the rearrangement of $\dot{C}H_3$. Similar results have been obtained for the CO loss of 6 other unsymmetrically substituted 1,3-diketones. In each case a specific migration of the larger alkyl group has been observed during the loss of CO, in agreement with the greater stabilization energy calculated for the resulting ion/neutral complexes. These results will discussed in detail in the full paper.
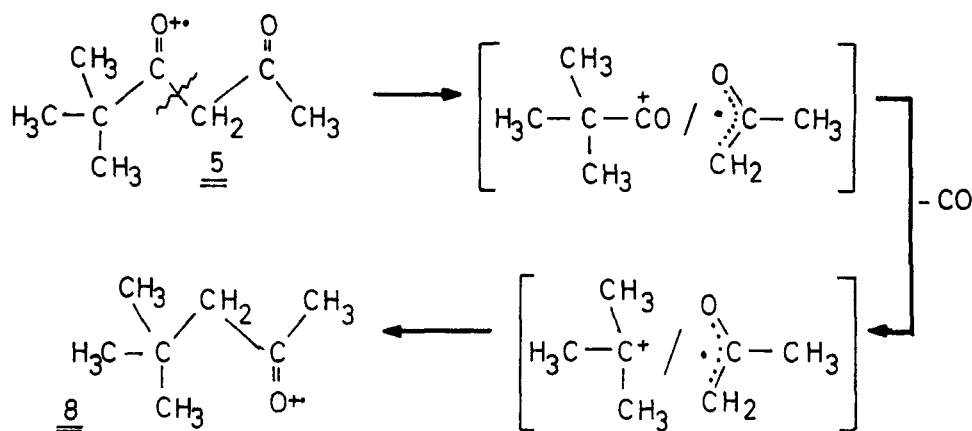
Scheme 4: Intermediary ion/neutral complex during CO loss from **5**.

Yours

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References:

1. N.Schamp, and M.Vandewalle; Bull.Soc.Chim.Belges **75** , 539 (1966). b) J.H.Bowie and D.H.Williams; J.Org.Chem. **31** , 1384 (1966). c) I.Howe and D.H.Williams; J.Chem.Soc.(C) 202 (1968). d) L.Zamir, B.Skytte Jansen and E.Laresen; Org.Mass Spectrom. **2** , 49 (1969). e) S.Tajima, A.Negeshi, S.Tobita and T.Tsuchiya; Adv.in Mass Spectrometry 1985 (Proceeding of the 10th IMSC, Ed. by J.F.J.Todd),Part B, 745, John Wiley & Sons, Chichester ,1986.

2. S.Tajima, Kazuo Ogino and S.Tobita; Org.Mass Spectrom. **22** , 379 (1987).

3. M.Masur, H.-Fr.Grützmacher,H.Münster and H.Budzikiewicz; Org.Mass Spectrom. **22**, 493 (1987).

4. T.Su and M.T.Bowers; Gas Phase Ion Chemistry (Ed. M.T.Bowers), Vol.1, 83, Academic Press, New York,1979.

5. D.H.Williams, B.J.Stapleton and R.D.Bowen; Tetrahedron Let. 2919 (1978).