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# ORGANIC MASS SPECTROMETRY II. THE ELECTRON IMPACT FRAGMENTATION OF DIMEDONE AND 2-ETHYLDIMEDONE

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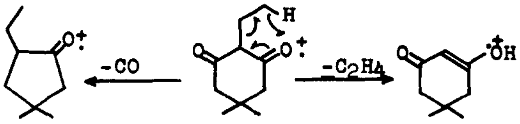
SIMILARITY between the mass spectrum of 2-ethyldimedone (I) and that of dimedon (II) below m/e 140 (Fig. 1) would suggest that the first step of the electron impact fragmentation of I is the formation of dimedone cation (as the enol form II') by transfer of a γ-hydrogen from the ethyl group to oxygen with simultaneous β-cleavage. Such a process has been observed in the fragmentation of aliphatic ketones having a suitably oriented γ-hydrogen atom (1).



b I II'

An alternate route involving elimination of carbon monoxide from I to form the m/e 140 ion b would deserve little consid-

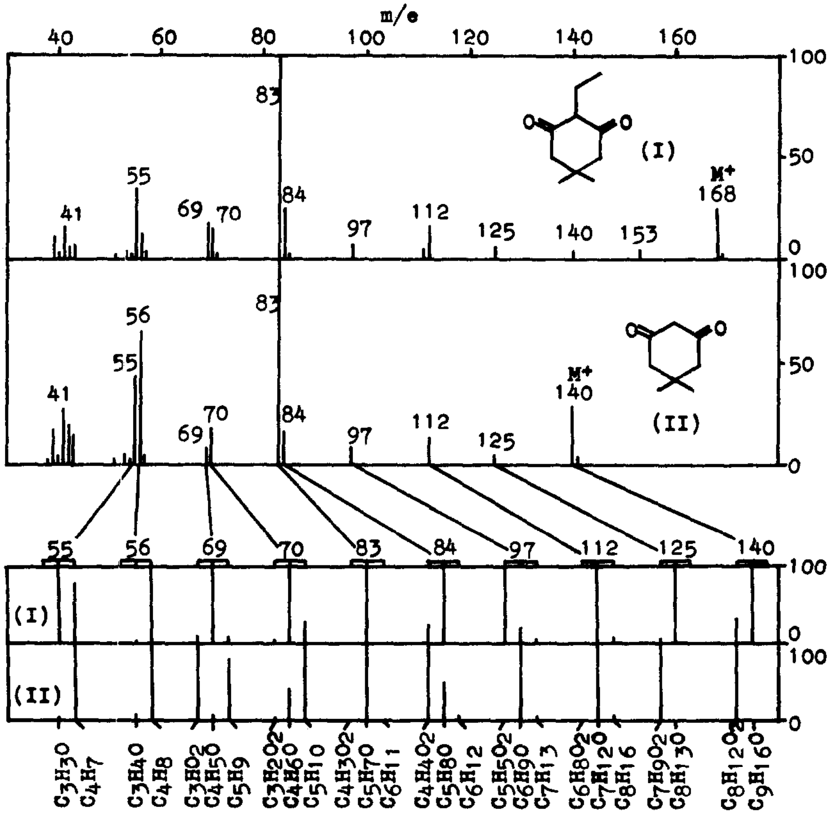


FIG. 1

**Mass spectra of 2-ethyldimedone (I) and dimedone (II)**

**Upper part: mass spectra recorded by a single focussing mass spectrometer. Lower part: mass spectra recorded by a double focussing mass spectrometer and the most intense peak in each mass number is taken as a standard (100%).(5).**

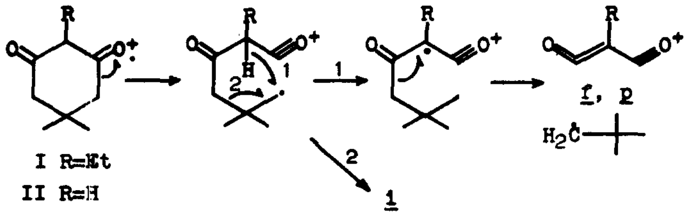
eration since expulsion of carbon monoxide from a molecular ion of cyclic ketones is not usually important.

Contrary to this expectation, however, the high-resolution mass spectrum of I shows that the peak at m/e 140 consists mainly in the ion b (77%) produced by the loss of carbon monoxide, and only 23% of the peak corresponds to the ion II' due to loss of an ethylene molecule. It is obvious that the ethylene molecule comes from the $C_2$-side chain, since dimedone (II) loses only carbon monoxide from the molecular ion to form the M-28 ion e' and no ethylene molecule is eliminated from the ring.

Examination of the other fragment peaks by the high-resolution mass spectrometer indicates that some of the peaks in the spectrum of I show very different compositions from that at the same m/e in the spectrum of II (Fig.1). Thus, for example, at m/e 97 the fragment from I corresponds to the ion f and is different from the ion g produced from II, though the low-resolution mass spectra of both I and II exhibit a quite similar peak at m/e 97.

The fragmentation patterns of I and II are summerized in Fig. 2. The well-known $\alpha$-cleavage (2) of I with simultaneous loss of a methyl radical leads to the ion a which decomposes further to the ion c by elimination of carbon monoxide. Dimedone (II) can fragment in the same way to produce the ions d and g. Loss of carbon monoxide from I affords the monoketone cation b which then eliminates an ethylene molecule by the cyclic mechanism discussed above to form the enol cation e. The latter process has been established in the case of

2-ethylcyclopentanone (3). Dimedone loses also carbon monoxide to form the same five-membered ketone e' (keto form). The fragments f and p can be delived from I and II, respectively, by the following process:



I R=Et
II R=H

The ion i may also be produced by the similar way and no explanation would be necessary for the formation of other small fragments.

The enol form II' of dimedone would be expected to show a different fragmentation pattern from that of the keto form II, since the mass spectrum of dimedone isopropyl ether shows no peak at M-28. However, since II' is a minor component of the peak at m/e 140 of I and since m/e 112 corresponding to II'-CO can also be afforded from the ion b, evidence leading to differenciation between II and II' was not obtained (4).

The mass spectra were recorded by Hitachi Mass Spectrometer Model RMU-6C (single focussing) and RMU-6D with an attachment Model ME-1010A (double focussing), using an all-glass inlet system. The ionizing energy was kept at 80 eV.

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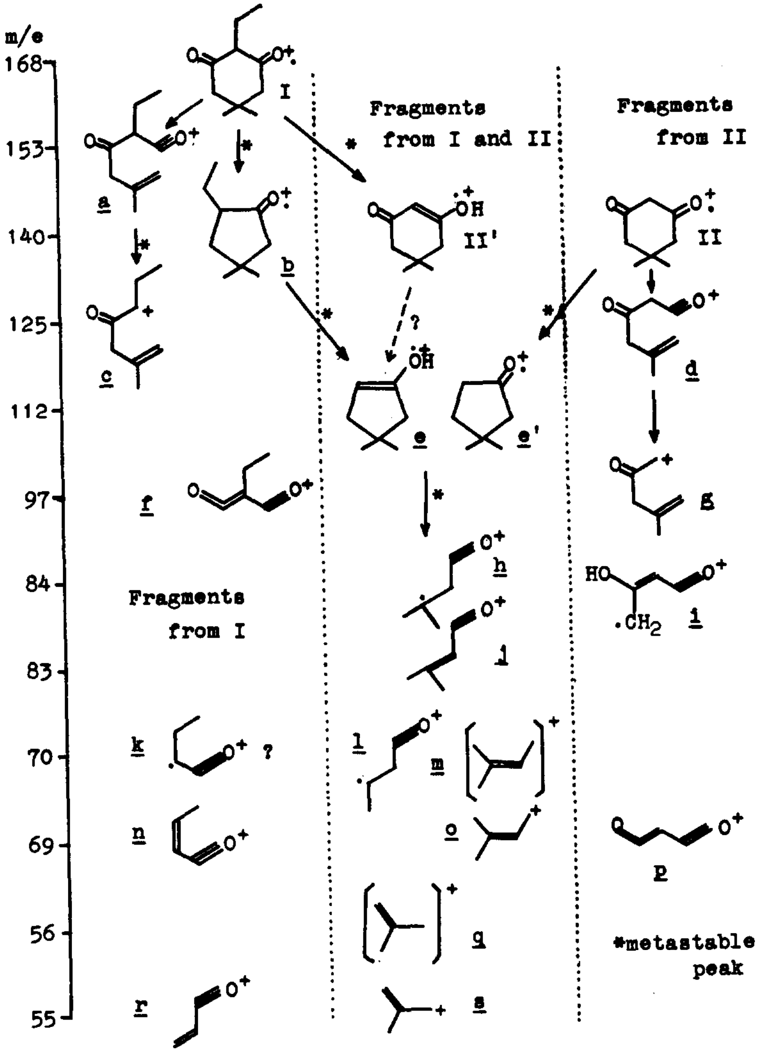
m/e
168
153
140
125
112
97
84
83
70
69
56
55
I
Fragments from I and II
Fragments from II
II'
II
a
b
c
d
e
e'
f
g
h
i
j
Fragments from I
k
l
m
n
o
p
q
r
s
*metastable peak

FIG. 2

## REFERENCES AND FOOTNOTES

1. H. Budzikiewicz, C. Djerassi and D. H. Williams, Interpretation of Mass Spectra of Organic Compounds p. 22. Holden-Day, Inc., San Francisco (1964).
2. Reference 1, p. 1.
3. J. Seibl and T. Gäumann, Z. Anal. Chem. **197**, 33 (1963).
4. Dimedone and 2-ethyldimedone exist in a dimeric enol-form in a solid state, but in a dilute chloroform solution monomeric diketo-form is predominant. K. Nakanishi, Infrared Absorption Spectroscopy p. 65. Holden-Day, Inc., San Francisco (1962).
5. Exact masses were not measured but, when three peaks could be observed in a mass number, the peak at the lowest mass was assigned as a fragment containing two oxygen atoms, one at the middle as that having one oxygen and one at the highest mass as a hydrocarbon fragment.