

DECOMPOSITION OF DIAZOKETONES UNDER ELECTRON IMPACT CONDITIONS

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The thermal and photolytic behavior of diazoketones has received much attention because of the variety of reactions they undergo.² Correlation between thermal and photolytic reactions and reactions induced by electron impact³ made a study of the mass spectral fragmentation of diazoketones of great interest. Since no report of the mass spectrum of a diazoketone exists, we undertook an examination of the electron impact induced decompositions of 9-diazo-10-ketophenanthrene (I) and 9-diazo-10-keto-4,5-methylenephenanthrene (II).^{4,5} The latter compound is particularly intriguing since fragmentation may lead to the theoretically important antiaromatic [1.7.6.3.8.4]-dibenzopentalene (XI).

Table I and Scheme 1 summarize the major fragmentation patterns for the diazoketones I and II. No other peaks account for more than 10% of the base peak

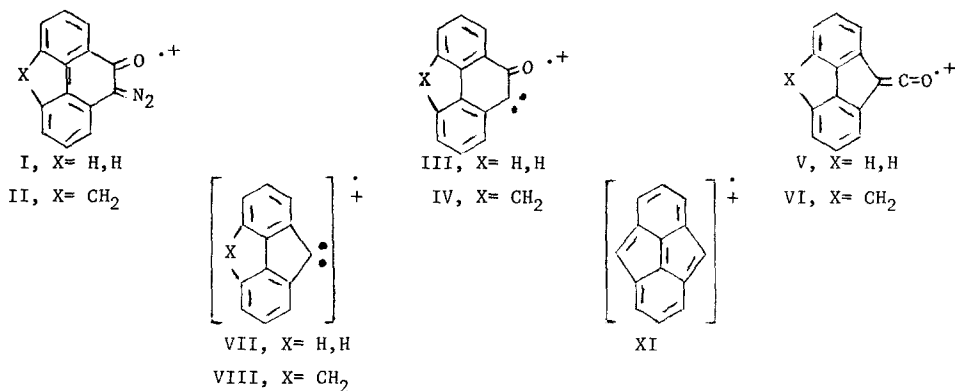
TABLE I. Relative abundance of important ions from diazoketones^a

Compound	M^{\ddagger}	$M-N_2^{\ddagger}$	$M-N_2-CO^{\ddagger}$	$M-N_2-CO-H^{\ddagger}$	$M-N_2-CO-HC\equiv CH^{\ddagger}$
I	5.0	21.5	100.0 [22.1] ^b	56.4	5.0
II	23.0	87.9	100.0 [38.5] ^b	18.5	16.7

a) All spectra were recorded at 70 ev ionizing voltage.

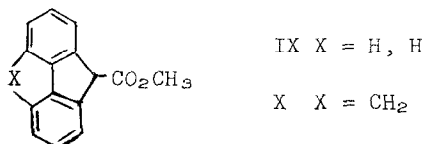
b) Relative abundance of doubly charged ion.

SCHEME I. Structures of major ions



which in both cases represents the loss of 56 from the molecular ion, ie CO + N₂. The structure of the M-N₂ ion is of some interest as to whether the Wolff rearrangement occurs under electron impact condition.

To investigate the structure of the M-N₂ ions from I and II, we generated the corresponding ketene ion molecules independently from esters IX and X.



These molecules show strong peaks for loss of CH₃OH directly from the molecular ion characterized by metastables at m/e 164.6 and 176.3 respectively to generate the ketene ion molecules V and VI. These also undergo loss of carbon monoxide accompanied by metastables at m/e 140.1 and 151.8. McLafferty has shown that metastable peak characteristics serve as a fingerprint for ions of identical structure and energy.⁶ Table II compares the metastable peak characteristics for the C₁₄H₈O⁺ → C₁₃H₈⁺ and C₁₅H₈O⁺ → C₁₄H₈⁺ generated from both the esters and diazoketones. The identity within each ester diazoketone pair

TABLE II. Metastable Peak Characteristics for CO Elimination

Starting Compound	$\frac{[m^*] \times 10}{[\text{parent}]^{\dagger a}}$	$m^*_{w_{1/2}}^b$
I	14.3 \pm 2.5	1.0 \pm 0.3
IX	12.2 \pm 2.8	1.2 \pm 0.3
II	9.5 \pm 1.5	1.6 \pm 0.3
X	8.0 \pm 2.0	1.8 \pm 0.3

- a) Parent ion is the $C_{14}H_8O^{\dagger}$ from I and IX and $C_{15}H_{20}^{\dagger}$ from II and X.
 b) This value represents the width at half height of the metastable peak expressed in a.m.u.

of the relative height and width strongly indicate that the ions derived from the diazo ketones have the same structure as the corresponding ions derived from the esters, i.e. structures V and VI and not III and IV. Furthermore, high relative abundances of the metastable peaks for the transitions involving loss of nitrogen from the molecular ion are suggestive that this nitrogen elimination and rearrangement leading to ketenes are concerted under electron impact conditions.⁷

The structure of the $C_{14}H_8^{\dagger}$ ion derived from II poses an important question since both VIII and XI can be written. Compound XI is an isomer of the recently synthesized pyracylene whose properties are best described in terms of a perturbed 12-annulene.⁸ If structure VIII best represented the ion, its appearance potential should closely approximate that of ion VII. The fact that the appearance potential of $C_{14}H_8^{\dagger}$ ion is almost 1 ev lower than that for VII (see Table III) suggests it is considerably more stable. This observation

TABLE III. Appearance Potentials^a

Compound	$[M-N_2]^{\dagger}$	$[M-N_2-CO]^{\dagger}$
I	8.6 ev	14.7 ev
II	8.6 ev	13.8 ev

- a) All values are \pm 0.2 ev.

is anticipated if structure XI represents this ion. Furthermore, the unusually strong doubly charged ion at m/e 88 supports the assignment, the latter representing an aromatic dication. Current work is in progress to convert ester X into [1.7.6.3.8.4]-dibenzopentalene.

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