Tetrahedron Letters No.41, pp. 4355-4358, 1968. Pergamon Press. Printed in Great Britain.

SKELETAL REARRANGEMENTS OF ORGANIC COMPOUNDS ON ELECTRON IMPACT.
3-METHYL-4-ARYLIDENEISOXAZOLONES-5

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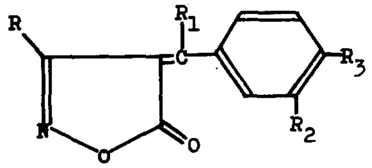
(Received in Japan 4 May 1968; received in UK for publication 8 July 1968)

The studies on electron impact induced skeletal rearrangements of organic compounds are at present an important and interesting area of mass spectrometry[1] because of their mechanistic implications and their limitations to the computerized element mapping technique.[2] During the study on the Michael addition reaction of 3-methyl-4-benzylideneisoxazolone-5 (I)[3] it was observed that its mass spectrum has interesting ions and a detailed study was started. High energy (80 eV) impact induced cleavage of the title compounds appears to proceed in several ways, hydrocarbon ions being invariably intense, even becoming the base peak (m/e 128: $C_{10}H_8$) for some compounds. However, the low energy (15 eV) spectra were featured only with five peaks: M^+, $(M-1)^+$, $(M-69)^+$, $(M-70)^+$, and m/e 43, two of which are concerned with the migration of an exocyclic arylidene portion of the molecule (or it may be the accepting site of a migrating group), a process unrecorded in the literature.

m/e 43 ($MeC{\equiv}O^+$) and $(M-69)^+$ (arylidene + CO)

Exact mass measurements of the ion at m/e 43 of the low energy spectra of I (R.I. 22 %) and III (R.I. 2 %) could reveal this to be solely C_2H_3O (Found: 43.018 for I; 43.018 for III. Calc.: 43.018) (plus a weak C_3H_7 (Found: 43.053 for I; 43.055 for III. Calc.: 43.055) if the energy is higher than nominal 16 eV). Shift to m/e 44 was seen in the spectrum of 3-monodeuteriomethyl analogue[4] (II) of I. This species can be observed in the low energy spectrum of VI (R.I. 16 %), but not in the spectra of IV and VIII. This trend roughly holds for high energy spectra (Table)



I R=Me $R_1=R_2=R_3=H$
II R=CH_2D $R_1=R_2=R_3=H$
III R=R_2=Me $R_1=R_3=H$
IV R=R_3=Me $R_1=R_2=H$
V R=CH_2D $R_1=R_2=H$ R_3=Me
VI R=Me $R_1=R_2=H$ R_3=Cl
VII R=Me R_1=D $R_2=R_3=H$
VIII R=Me $R_1=R_2=H$ R_3=OMe
IX R=Ph $R_1=R_2=R_3=H$
X R=Ph R_1=D $R_2=R_3=H$
XI R=Ph $R_1=R_2=H$ R_3=Me

TABLE Partial Mass Spectra (80 eV) of I, III, IV, VI, VII, and VIII ($\%\Sigma_{43}$)

	m/e 43	$(M-70)^+$		$(M-69)^+$	
I	1.8	m/e 117	3.2	m/e 118	2.6
III	5.4	m/e 131	6.2	m/e 132	1.7
IV	1.1	m/e 131	2.4	m/e 132	3.3
VI*	7.1	m/e 151	1.2	m/e 152	1.7
		m/e 153	0.4	m/e 154	0.6
VII	6.3	m/e 118	3.0	m/e 119	2.4
VIII	1.3	m/e 147	1.0	m/e 148	3.2

* Chlorine-containing peaks were corrected for ^{13}C isotope peaks.

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and a partial mass shift to m/e 44 was again seen for 3-monodeuteriomethyl analogue (V) of IV. These results can be rationalized if one considers that a C_3-methyl migrates yielding an acylium ion. This type of migration again operates for 3-phenyl-4-arylideneisoxazolones-5 (IX XI) affording an m/e 105 (benzoyl ion) ($\%\Sigma_{43}$ $4\sim5$) and one may say that a C_3-group easily migrates for isoxazolones-5.

Low voltage spectra of each of the compounds exhibit the (M-69) with the relative intensity of $5\sim10$ %. Mass spectrum of α-deuteriated derivative[5] (VII) displayed the (M-69) at m/e 119 while the spectrum of II had this peak at m/e 118 disclosing that methyl hydrogens do not participate at all in the m/e 118 of I. Appropriate mass shift was seen for other analogues (Table). Exact mass determinations of the

(M-69) of I (m/e 118: C_8H_6O. Found: 118.040. Calc.: 118.042) and III (m/e 132: C_9H_8O. Found: 132.060. Calc.: 132.057) show that this is homogeneous and an oxygen is included. A metastable ion (80 eV) in the spectra of I, II, and VII reveals that the m/e 118 of I decomposes into an m/e 90 (C_7H_6) suggesting that C-O group is probably at a terminal position. This species may be represented as (substituted)-phenyl ketene radical ion, the formation of which is unusual but apparently demands the migration of an exocyclic arylidene portion probably with the retention of an intact carbon skeleton. The formation of this (M-69) is not considered to be random in spite of its uncertain identity, since the participated hydrogen appears to be site-specific and, further, this type of cleavage seems to be a general behaviour for 3-phenyl-4-arylideneisoxazolones-5 (IX, X, XI), the spectra (80 eV) of which have an $(M-131)^+$, a counterpart of the $(M-69)^+$ of the 3-methyl series, in moderate intensity.

Very unfortunately, ^{18}O-labelling experiments have not yet succeeded, thus leaving one moot point as to the origin of the incorporated oxygen atom of the $(M-69)^+$ as well as the m/e 43 species. Therefore, discussion on the mechanistic implications is reserved.

$(M-70)^+$ (arylidene + HCN)

The results of repeated mass measurements (I, C_8H_7N (Found: 117.059. Calc.: 117.058); III, C_9H_9N (Found: 131.075. Calc.: 131.074)), an increase in intensity of the m/e 118 for II and m/e 132 for V, and a complete shift to m/e 118 for VII reveal that a benzylidene hydrogen and at least one of the methyl hydrogens are included in the $(M-70)^+$. Appropriate mass shift was seen for IV, VI, and VIII (Table). A metastable ion (15 eV: m/e 73 for I) indicates that this species is most probably a daughter ion of M^+ and (substituted)-benzyl cyanide radical ion (or its ring expanded one) is one of possible structures, which again demands the migration of an exocyclic portion of the molecule. Whatever the true structure may be, the fact that a nitrogen is included can only be accomodated on the premise that a skeletal rearrangement operates. This (M-70) was observed in the low energy spectra with the relative intensity of 5~20 %.

5-Alkoxyisoxazoles have an ion (C_3-substituent (Me or Ph) + CO) as the base peak[6] and factors governing such rearrangements for isoxazoles and isoxazolones-5 are to be studied in future. It is of interest to note that the fragmentations of 4-substituted-3,5-dimethylisoxazoles appear to be preceded by the cleavage of an N-O linkage[7] in line with the chemical reactions.[8]

All of the low resolution spectra were obtained with a Hitachi RMU 6D mass spectrometer (total ion currents, 80 μA: ion source, 200°: inlet system, 200° or 250°). High resolution spectra were through a CEC-110-B type spectrometer at 12.5, 15, 16, and 70 eV, which were recorded on a photographic plate.

Acknowledgement. I thank Kao Sekken Co. and Mr. N. Wasada, the Government Institute of Technology (Tokyo), for making available the facilities there.

References.

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2. K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1725 (1964).
3. T. Nishiwaki, to be published. Among the undeuteriated compounds III, IV, VI, and VIII were unknown. They were obtained by the condensation of 3-methylisoxazolone-5[9] and appropriate aldehyde. Purity and structures were checked by elemental analyses, exact mass measurements of M^+, and other methods.
4. Due to the presence of an intense $(M-1)^+$ the isotopic purity (ca. 45∼50 %) of II and V was assumed from that of 3-monodeuteriomethyl-4-isopropylideneisoxazolone-5 and from an intense (M-15) of V, since these three compounds were secured from the same source of 3-monodeuteriomethylisoxazolone-5, a reaction product of ketene dimer, hydroxylamine hydrochloride, potassium carbonate, and deuterium oxide,[9] in an almost similar reaction condition.
5. The isotopic purity of VII (ca. 90 %) was assumed from benzaldehyde-α-d.
6. T. Nishiwaki, to be published. This was proved by extensive deuterium labellings.
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