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A NOVEL REARRANGEMENT IN THIOESTERS UPON ELECTRON IMPACT

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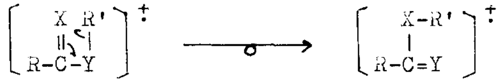
In contrast to carboxylic acid esters, little is known on mass spectrometry of thioesters.[1-3] Especially no literature has been publihsed on aromatic thioesters. In the course of our studies on mass spectroscopy of thioesters, we have found a novel skeletal rearrangement shown below;

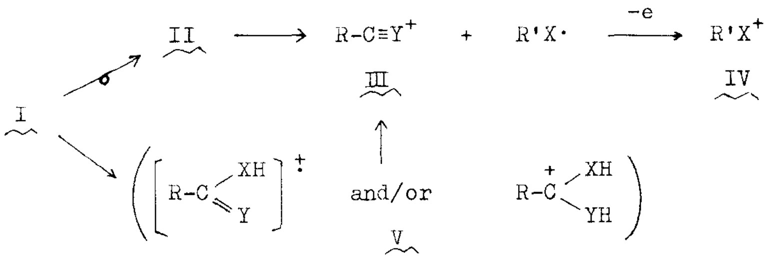


I(**a** - **h**) **II**(**a** - **h**) (1)

in which R, R', X and Y are those listed in Table I with percentage of Σ_{30} of each parent peak at the ionizing voltage of 70eV.

Mass spectra were obtained on a Hitachi RMU-6E mass spectrometer with inlet system and ion source temperatures of 200°C. The ionizing voltages were 70, 20, 15, and 12eV. The purity of materials were confirmed by vpc with a Parkin-Elmer F6 instrument with FID. Carbowax-20M column maintained at 200°C was used for benzoates, while XF-1150 column was used at 100°C for acetates. Patterns which concern in this article, calculated from the corrected spectral data, are presented in Tables II and III, in which parent peaks are set to 100%. This procedure may be more convenient for comparison of fragmentations of various compounds than usual manner, where the largest peak is set to 100%.

(A) Benzoates. Mass spectrum of O-ethyl thiobenzoate, **Ia**, has peaks at M/e 105 and 61 that correspond to **III** and **IV**, respectively. Although the presence of **III** does not directly mean the rearrangement process 1 because it might be produced through **V**, an appropriate metastable peak at M/e 66.42 (105^2/166), which clearly exists even at 20eV of ionizing voltage, and the presence of **IV** strongly support the reaction. That this reaction is induced by electron impact was



(2)

confirmed by a control experiment; heating Ia for 10 minutes at 200°C under an atmosphere of air[4] followed by analyses with vpc and ir showed no change of the material. The mass spectrum of the corresponding methyl ester, **Ic**, is similar to that of **Ia** with peaks at M/e 105, 47, and 72.53 ($105^2/152$).

S-ethyl thiobenzoate, **Ib**, and its methyl analog, **Id**, also undergo the rearrangement, to a less extent, which is suggested by peaks at M/e 121 and 61, and 121 and 31, respectively. Especially, in **Ib**, M/e 121 ion exists (2.8% of the parent ion) even at 15eV of ionizing voltage, where M/e 139 and 138 ions, corresponding to **V**, cannot be detected. However no metastable peaks corresponding to the rearrangement were observed. Neither thermal rearrangement nor hydrolysis was detected by a control experiment.

On the other hand, no evidence for the rearrangement was obtained with ethyl benzoate-carbonyl-^{18}O.

(B) Acetates. Peaks at M/e 61 and 43, respectively corresponding to **III** and **IV**, also exsist in mass spectrum of O-ethyl thioacetate, **Ie**. Interestingly, a metastable peak appears at M/e 35.78 ($61^2/104$), which is observable even at 20eV of ionizing voltage, instead of M/e 17.78 ($43^2/104$). This supports the reaction 3

$$\mathbf{Ie} \xrightarrow{\sigma} \mathbf{IIe} \longrightarrow C_2H_5S^+ + CH_3\dot{C}{=}O \qquad (3)$$

instead of 2, although relative importance is not known. Similar spectrum was obtained with O-methyl thioacetate, **Ig**, with peaks at M/e 47 and 43. However the appropriate metastable peak was not observed. As is in the case of benzoates, this rearrangement is less important in S-alkyl thioacetates than in their O-alkyl analogs but fairly significant as shown in Table II.

The same type of rearrangement is known to proceed in thioncarbonates (Schönberg rearrangement) both thermally[5-8] and electron-impactively[9] However, in contrast to Schönberg rearrangement, where thiocarbonyl function is necessary,

Table I

Compd	R	R'	X	Y	Σ_{30},%
a	C_6H_5-	C_2H_5-	S	O	6.1
b	C_6H_5-	C_2H_5-	O	S	3.4
c	C_6H_5-	CH_3-	S	O	14.9
d	C_6H_5-	CH_3-	O	S	3.5
e	CH_3-	C_2H_5-	S	O	13.1
f	CH_3-	C_2H_5-	O	S	12.2
g	CH_3-	CH_3-	S	O	23.5
h	CH_3-	CH_3-	O	S	11.9

Table III

Compd	M/e	Ion	Abundance, % 70eV	 20eV	 15eV	 12eV
Ia	122	VI	56	53	42	25
	121	VII[a]	209	95	32	0
Ic	122	VI	20	79	12	3.5
	121	VII[a]	165	91	27	1.5
Ie	60	VI	41	28	19	11
	59	VII[a]	110	40	10	1.5
Ig	60	VI	25	20	15	7
	59	VII[a]	110	57	23	3

a. The ordinal acyl cation, R-C≡X$^+$.

Table II

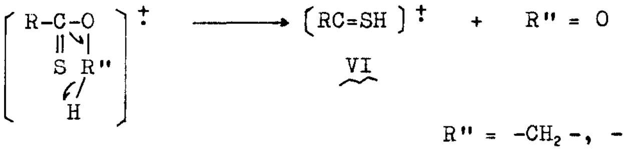
Compd	M/e	Ion	Abundance,%
Ia	105	III	152
	61	IV	3.5
	66.42[a]	—	—
Ib	121	III	4.5
	45	IV	26
Ic	105	III	27
	47	IV	4
	72.53[a]	—	—
Id	121	III	2.5
	31	IV	0.5
Ie	61	IV	39
	43	III	231
	35.78[a]	—	—
If	59	III	12
	45	IV	23
Ig	47	IV	20
	43	III	48
Ih	59	III	2.5
	31	IV	1.5

a. Metastable peak.

the present reaction takes place in an organic ester that has a carbonyl group.

Another interesting observation is that, in O-alkyl thioesters, peaks at M/e 122 (for Ia and Ic) and 60 (for Ie and Ig) become more dominant than those at M/e 121 (for Ia and Ic) and 59 (for Ie and Ig), respectively, when the ionizing voltage is decreased (Table III). Appropriate metastable peaks at M/e 89.66

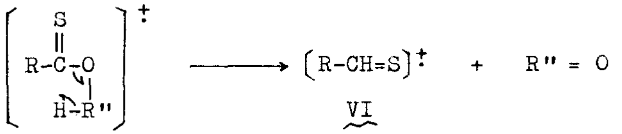
($122^2/166$ for **a**), 97.92 ($122^2/152$ for **c**), 34.62 ($60^2/104$ for **e**), and 40.00 ($60^2/90$ for **g**) support the rearrangement(s):



(4)

R" = $-CH_2-$, $-C_2H_4-$

and/or



(5)

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