An Electron-impact Mass Spectral (EIMS) Study of N-1 and C-6 Carboxyalkyl- and Alkoxycarbonyl-alkyl-substituted Derivatives of Uracil

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The electron impact (EI) induced mass spectral fragmentation of seventeen, including seven newly synthesized, N-1 and C-6 carboxyalkyl- and alkoxycarbonylalkyl-substituted derivatives of uracil and thymine was investigated. Fragmentation pathways are proposed on the basis of accurate mass and metastable transition measurements. The correlation between the intensities of the $M^{+\bullet}$ and selected fragment ions of these compounds is discussed. The data obtained provide the basis for distinguishing isomers and metamers.

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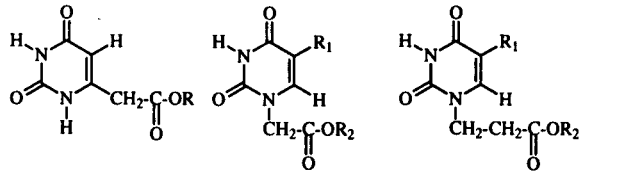
Carboxyalkyl- and alkoxycarbonylalkyl-substituted derivatives of uracil and thymine are well known compounds having multiple biological activities [1-8]. Because of the biological importance of these compounds, there is considerable interest in their spectral analysis. Mass spectrometry continues to be the most convenient and effective method for the determination of the nature of covalent modifications to N- and C-substituted analogs of nucleobases [7-10].

The correlation of the abundances of the $M^{+\bullet}$ and selected fragment ions of 2-alkylthiouracils [11], *o*-, *m*- and *p*-substituted benzylthiouracils [12] and benzylthio-6-methyluracils [13] as well as 2-substituted benzylthioorotic acids [14] have been previously studied using electron impact ionization in our laboratory. Our studies have now been extended to the elucidation of mass spectral fragmentation of seventeen N-1 and C-6 carboxyalkyl- and alkoxycarbonylalkyl-substituted derivatives of uracil and thymine **1-17**, (see Figure 1), including seven newly synthesized compounds, namely **3**, **4**, **9**, **11**, **14**, **16** and **17**. We propose to determine the positions of carboxyalkyl or alkoxycarbonylalkyl groups linked to the uracil skeleton on the basis of differences in the respective μ values, *i.e.*, in the ratio of the intensity of the selected fragment ion peaks to that of the parent ion peak.



1 R = H
2 R = CH_3
3 R = *i*-C_3H_7
4 R = *n*-C_4H_9

5 R_1 = H R_2 = H
6 R_1 = CH_3 R_2 = H
7 R_1 = H R_2 = CH_3
8 R_1 = CH_3 R_2 = CH_3
9 R_1 = H R_2 = *i*-C_3H_7
10 R_1 = H R_2 = *n*-C_4H_9
11 R_1 = CH_3 R_2 = *n*-C_4H_9

12 R_1 = H R_2 = H
13 R_1 = CH_3 R_2 = H
14 R_1 = H R_2 = CH_3
15 R_1 = CH_3 R_2 = CH_3
16 R_1 = H R_2 = *n*-C_4H_5
17 R_1 = CH_3 R_2 = *n*-C_4H_5

Figure 1. Structures of C-6 and N-1 carboxyalkyl and alkoxycarbonylalkyl substituted uracil and thymine derivatives **1-17**.

Results and Discussion.

Based on metastable transitions and exact mass determinations (Tables 1 and 2), the principal mass fragmentation routes of compounds **1-4**, **5-11** and **12-17** are interpreted as shown in Scheme 1, Scheme 2 and Scheme 3, respectively. As can be seen from Schemes 1 and 2, and the data presented in Table 1, the principal mass fragmentation pathways of 6-carboxymethyluracils **1**, **2** and 6-alkoxycarbonylmethyluracils **3**, **4** are similar to those of the isomeric 1-carboxymethyluracils **5**, **6** and 1-alkoxycarbonylmethyluracils **7-11**, but show differences in the abundances of analytically important fragment ions. The electron impact induced mass fragmentation of **1-17** begins with the cleavage of C_{sp2}-O, C_{sp3}-C_{sp2} and C_{sp3}-C_{sp3} bonds of either the carboxyalkyl or alkoxycarbonylalkyl substituent. The retro Diels-Alder type reaction, which is typical of the mass decomposition processes of the molecular ions of uracil derivatives [15], occurs only in the second step of the mass fragmentation. The common feature of the fragmentation of the molecular ions of **1-4** and **5-11** is the unimolecular decomposition reaction giving [M-•OR] *b* and [M-•COOR] *e* even-electron fragment ions. The first of these ions is produced by radical-site-initiated α-cleavage of the C_{sp2}-O bond, and the other one is formed by charge-site-initiated inductive cleavage of the C_{sp3}-C_{sp2} bond.

Table 1

Elemental Composition and Relative Intensities of the Ion Peaks in the Spectra of **1-11**

Ion	m/z	Elemental Composition	Relative Intensities (%) **1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
$M^{+\bullet}$	170	$C_6H_6N_2O_4$	1	-	-	-	25	-	-	-	-	-	-
a	184	$C_7H_8N_2O_4$	-	100	-	-	-	48	86	-	-	-	-
	198	$C_8H_{10}N_2O_4$	-	-	-	-	-	-	-	98	-	-	-
	212	$C_9H_{12}N_2O_4$	-	-	100	-	-	-	-	-	74	-	-
	226	$C_{10}H_{14}N_2O_4$	-	-	-	100	-	-	-	-	-	79	-
	240	$C_{11}H_{16}N_2O_4$	-	-	-	-	-	-	-	-	-	-	88
b	153	$C_6H_5N_2O_3$	1	5	48	44	1	-	18	-	64	21	-
[M-•OR]	167	$C_7H_7N_2O_3$	-	-	-	-	-	1	-	40	-	-	15
c	152	$C_6H_4N_2O_3$	1	6	17	24	1	-	31	-	1	7	-
	166	$C_7H_6N_2O_3$	-	-	-	-	-	1	-	33	-	-	14
d	126	$C_5H_6N_2O_2$	9	6	47	89	57	-	6	-	90	90	-
	140	$C_6H_8N_2O_2$	-	-	-	-	-	72	-	1	-	-	86
e	125	$C_5H_5N_2O_2$	4	8	30	22	13	-	72	-	82	79	-
[M-•COOR]	139	$C_6H_7N_2O_2$	-	-	-	-	-	15	-	87	-	-	90
f	83	C_4H_5NO	28	3	3	7	22	-	9	-	23	46	-
	97	C_5H_7NO	-	-	-	-	-	13	-	18	-	-	23
g	82	C_4H_4NO	1	3	2	8	100	-	100	-	92	100	-
	96	C_5H_6NO	-	-	-	-	-	100	-	100	-	-	100
h	68	C_3H_2NO	100	17	13	22	4	-	1	-	2	3	-
	82	C_4H_4NO	-	-	-	-	-	5	-	6	-	-	2
i	57	C_4H_9	-	-	-	74	-	-	-	-	-	82	51
j	55	C_3H_5N	6	7	12	30	13	-	8	-	10	20	-
	69	C_4H_7N	-	-	-	-	-	15	-	3	-	-	14
k	44	CO_2	61	-	-	-	10	12	-	-	-	-	-
l	43	C_3H_7	-	-	91	-	-	-	-	-	100	-	-
m	42	C_2H_2O	22	12	13	19	10	15	5	17	11	13	16
n	41	C_2HO	3	7	24	86	5	35	4	52	30	69	82
o	29	C_2H_5	-	-	-	87	-	-	-	-	-	70	38

Table 2

Elemental Composition and Relative Intensities of the Ion Peaks in the Spectra of **12-17**

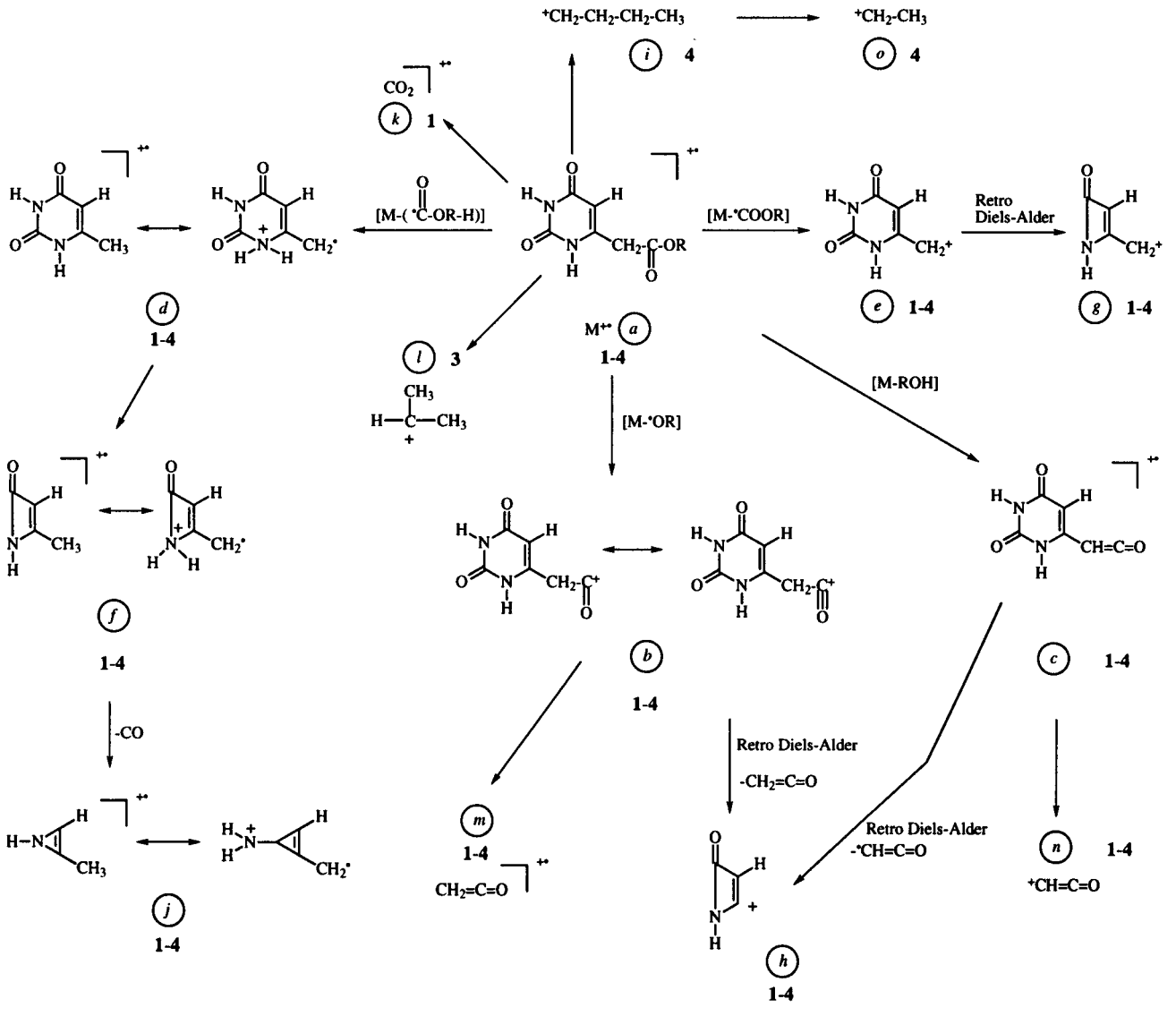
Ion	m/z	Elemental Composition	Relative Intensities % **12**	**13**	**14**	**15**	**16**	**17**
$M^{+\bullet}$	184	$C_7H_8N_2O_4$	7	-	-	-	-	-
a	198	$C_8H_{10}N_2O_4$	-	100	95	-	-	-
	212	$C_9H_{12}N_2O_4$	-	-	-	100	-	-
	240	$C_{11}H_{16}N_2O_4$	-	-	-	-	52	-
	254	$C_{12}H_{18}N_2O_4$	-	-	-	-	-	89
b	167	$C_7H_7N_2O_3$	3	-	54	-	30	-
[M-•COOR]	181	$C_8H_9N_2O_3$	-	2	-	30	-	40
c	166	$C_7H_6N_2O_3$	6	-	4	-	29	-
	180	$C_8H_8N_2O_3$	-	1	-	4	-	15
d	139	$C_6H_7N_2O_2$	14	-	24	-	27	-
[M-•COOR]	153	$C_7H_9N_2O_2$	-	13	-	72	-	51
e	138	$C_6H_6N_2O_2$	85	-	100	-	100	-
	152	$C_7H_8N_2O_2$	-	43	-	22	-	100
f	125	$C_5H_5N_2O_2$	12	-	6	0	9	-
	139	$C_6H_7N_2O_2$	-	15	-	21	-	30
g	126	$C_5H_6N_2O_2$	2	-	1	-	2	-
	140	$C_6H_8N_2O_2$	-	7	-	2	-	4
h	112	$C_4H_4N_2O_2$	25	-	10	-	20	-
	126	$C_5H_6N_2O_2$	-	39	-	46	-	84
i	96	C_5H_6NO	48	-	15	-	34	-
	110	C_6H_8NO	-	29	-	51	-	53
j	95	C_5H_5NO	25	-	12	-	29	-
	109	C_6H_7NO	-	16	-	25	-	30

continued

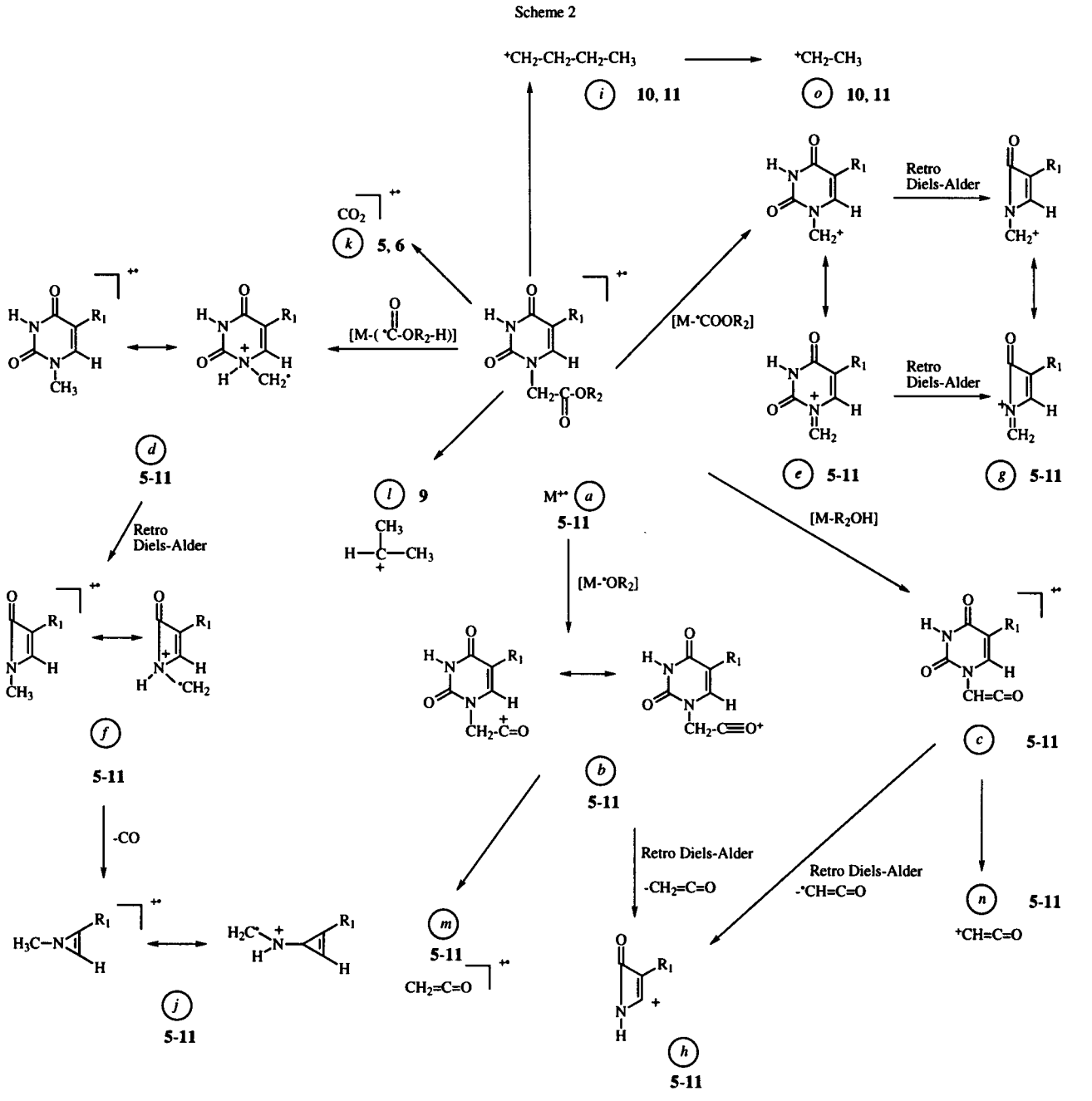
Table 2 (continued)

Ion	m/z	Elemental Composition	Relative Intensities % 12	13	14	15	16	17
k	82	C_4H_4NO	100	-	13	-	40	-
	96	C_5H_6NO	-	63	-	63	-	79
l	83	C_4H_5NO	6	-	1	-	3	-
	97	C_5H_7NO	-	5	-	5	-	6
m	69	C_3H_3NO	17	-	5	-	12	-
	83	C_4H_5NO	-	9	-	19	-	10
n	68	C_3H_2NO	13	-	4	-	11	-
	82	C_4H_4NO	-	23	-	19	-	21
o	55	C_3H_5N	20	-	35	-	46	-
	69	C_4H_7N	-	3	-	3	-	4
p	41	C_2H_3N	14	-	7	-	31	-
	55	C_3H_5N	-	24	-	55	-	68
r	57	C_4H_9	-	-	-	-	11	13
s	29	C_2H_5	-	-	-	-	38	22

Scheme 1

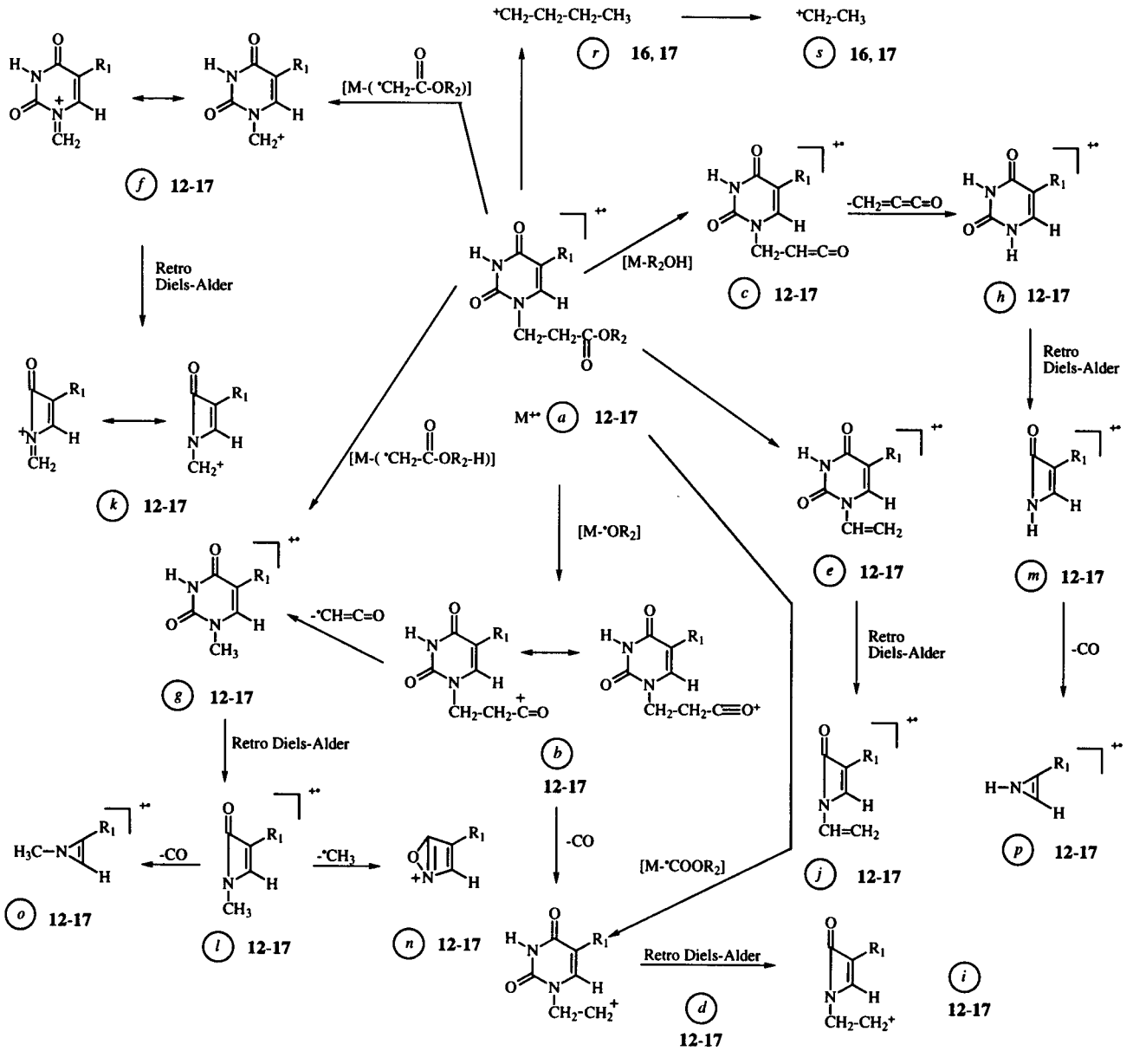


Scheme 2



It should be mentioned that during the cleavage of C_{sp2}-C_{sp3} bond of the carboxymethyl and alkoxycarbonylmethyl substituent in the derivatives **1-11**, the positive charge is stabilized more effectively on the uracil skeleton substituted at the N-1 annular nitrogen atom for **5-11** than on that substituted at the C-6 carbon atom for **1-4**. The peaks corresponding to the *e* ions of **5-11** are therefore two to three times more intense than those of the *e* ions of **1-4**. It was also found that the molecular ions of **2-4** were the base peaks of the respective fragmentation spectra. In the mass spectra of **5-8**, **10** and **11**, the base peaks were those corresponding to the even-electron fragment ions *g*. These ions were formed by the elimination of neutral H-N=C=O molecules from the even-electron fragment ions *e* during the second step of the mass fragmentation of the molecular ions of **5-8**, **10** and **11**, *i.e.*, during the retro Diels-Alder mass fragmentation reaction. Similarly, the base ion of the mass spectrum of **1**, *i.e.*, the even-electron fragment ion *h*, was formed in the retro Diels-Alder reaction. In the mass spectrum of 1-isopropoxycarbonylmethyluracil **9**, the base peak was that corresponding to the even-electron fragment ion *l* (m/z 43),

Scheme 3



which was formed by the inductive cleavage of C_{sp3}-O bond of alkoxycarbonylalkyl substituent of the molecular ion of **9**. The presence of the odd-electron fragment ions *d* could be explained in terms of elimination of neutral a CO_2 (or [COOR-H]) molecule with simultaneous transfer of hydrogen to either carbon atom (Scheme 1) or an annular nitrogen atom (Scheme 2). In the latter case, the odd-electron ion *d* would have the structure of a distonic ion. This structure would also be possible in the case of *c* ions (Schemes 1 and 2) which were formed from the molecular ions *a* by elimination of the neutral alcohol (or water) molecules (Figure 2).

As can be deduced from Scheme 3 and the data presented in Table 2, the main fragmentation pathways of 1-carboxyethyluracils **12** and **13** and 1-alkoxycarbonylethyluracils **14-17** are similar to those of the molecular ions of **5-11**. However, the base peaks (100% relative intensity) in the mass spectra of **13** and **15** are the respective molecular ions, while the base peaks of the mass spectra of **12**, **14**, **16** and **17** are those corresponding to the odd-electron fragment ions *e* [M-•R_2OH] with m/z of 138 for **12**, **14** and **16** and 152 for **17**, respectively.

Interestingly, the even-electron fragment ions *f* [M-•CH_2COOR] of **12-17** (Scheme 3) have the same ele-

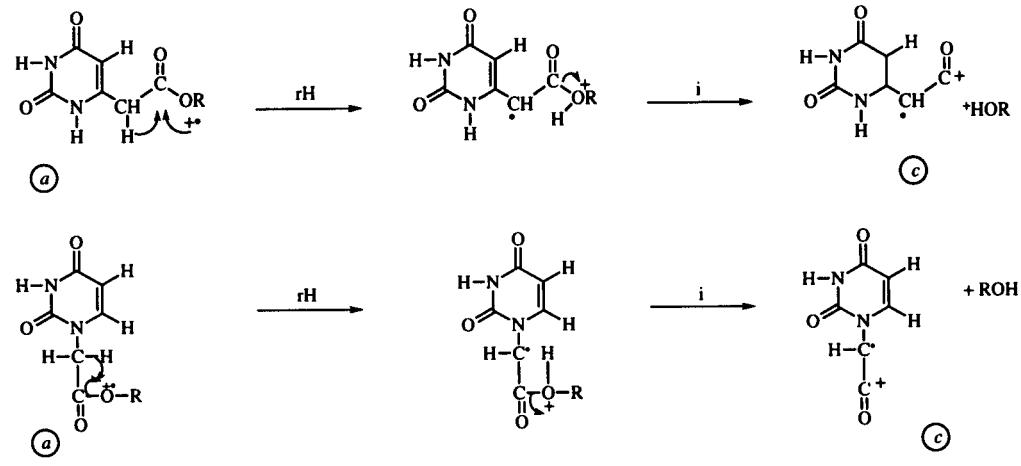
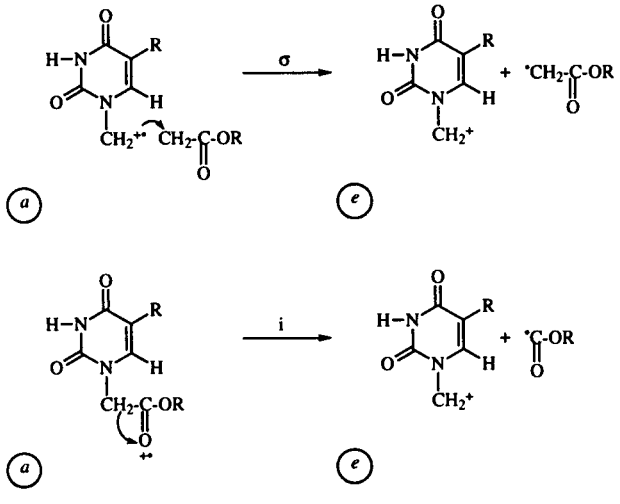


Figure 2. The formation pathways of *c* ions [M$^{+\bullet}$-ROH].

mental composition as the even-electron fragment ions *e* [M-•COOR] of **1-11**. However, the origin of the *e* and *f* ions is different. The *f* ions [M-•CH_2COOR] of **12-17** were obtained from the molecular ions *a* by simple σ cleavage of the C_{sp3}-C_{sp3} bond. Ions *e*, in contrast, were obtained by simple inductive cleavage of the C_{sp3}-C_{sp3} bond as shown below:



The differences in the abundances of characteristic analytical even-electron fragment ions [M-•OR] and [M-•COOR] of compounds **1-17** allow for differentiation between isomers, as well as metamers, formed from the above N-1 and C-6 substituted uracil and thymine derivatives. The intensity ratios of the [M-•OR] ion peak to that of the parent ion peak (μ_1 = int. (M$^{+\bullet}$-•OR)$^+$/int. M$^{+\bullet}$) as well as the [M-•COOR] ion peak to that of the corresponding parent ion peak (μ_2 = int. (M$^{+\bullet}$-•COOR)$^+$/int. M$^{+\bullet}$) for these compounds are presented in Table 3. The correlation between the relative intensities of the analytical ions and M$^{+\bullet}$, *i.e.*, the values of μ_1, and μ_2, and the structure of N-1 and C-6 substituted carboxyalkyluracils and alkoxycarbonylalkyluracils is considered below; this problem apparently has not been previously studied. The data presented in Table 3 can be summarized as follows:

[a] The C-6 carboxymethyl-substituted uracil **1** can be distinguished from isomeric N-1 carboxymethyl-substituted uracil **5** on the basis of higher μ_1 value. [b] The C-6 alkoxycarbonylmethyl-substituted uracils **2**, **3** and **4** can be distinguished from isomeric N-1 alkoxycarbonylmethyl-substituted uracils **7**, **9** and **10** on the basis of higher μ_2 value. [c] The series of metameric 6-methoxycarbonylmethyluracil **2**, 1-carboxymethylthymine **6**, 1-methoxycarbonylmethyluracil **7** and 1-carboxyethyluracil **12** having elemental composition $C_7H_8N_2O_4$ can be differentiated on the basis of the respective μ_2 values:

$$\mu_2\ 2.00 > \mu_2\ 0.83 > \mu_2\ 0.31 > \mu_2\ 0.08$$

12 **7** **6** **2**

[d] The series of metameric 1-methoxycarbonylmethylthymine **8**, 1-carboxyethylthymine **13**, and 1-methoxycarbonylethyluracil **14** having elemental composition $C_8H_{10}N_2O_4$ can be differentiated on the basis of μ_1 and μ_2 values:

$$\mu_1\ 0.54 > \mu_1\ 0.40 > \mu_1\ 0.02$$

14 **8** **13**

$$\mu_2\ 0.88 > \mu_2\ 0.25 > \mu_2\ 0.13$$

8 **14** **13**

[e] The series of metameric 6-isopropoxycarbonylmethyluracil **3**, 1-isopropoxycarbonylmethyluracil **9** and 1-methoxycarbonylethylthymine **15** having elemental composition $C_9H_{12}N_2O_4$ can be differentiated on the basis of μ_1 and μ_2 values:

$$\mu_1\ 0.86 > \mu_1\ 0.48 > \mu_1\ 0.30$$

9 **3** **15**

$$\mu_2\ 1.70 > \mu_2\ 0.72 > \mu_2\ 0.30$$

9 **15** **3**

[f] *n*-Butoxycarbonylmethylthymine **11** can be distinguished from metameric *n*-butoxycarbonylethyluracil **16** on the basis of higher μ_2 value, and lower μ_1 value.

[g] In the series of metamers investigated the derivatives of thymine **6**, **8**, **11**, **13** and **15** have lower μ_1 values than the corresponding N-1 and C-6 substituted uracil derivatives.

Table 3

The μ_1 and μ_2 Values Calculated from the Electron Impact Mass Spectra Recorded at 70 eV of Isomers and Metamers from the Series of Compounds of **1-16**

μ_1 = int. $(M^{+\bullet}\text{-}{}^{\bullet}OR)^+$/int. $M^{+\bullet}$
μ_2 = int. $(M^{+\bullet}\text{-}{}^{\bullet}COOR)^+$/int. $M^{+\bullet}$

Compound	Elemental Composition	$M^{+\bullet}$ m/z	μ_1	μ_2
1	$C_6H_6N_2O_4$	170	1.00	4.00
5	$C_6H_6N_2O_4$	170	0.04	0.52
2	$C_7H_8N_2O_4$	184	0.05	0.08
6	$C_7H_8N_2O_4$	184	0.02	0.31
7	$C_7H_8N_2O_4$	184	0.20	0.83
12	$C_7H_8N_2O_4$	184	0.42	2.00
8	$C_8H_{10}N_2O_4$	198	0.40	0.88
13	$C_8H_{10}N_2O_4$	198	0.02	0.13
14	$C_8H_{10}N_2O_4$	198	0.54	0.25
3	$C_9H_{12}N_2O_4$	212	0.48	0.30
9	$C_9H_{12}N_2O_4$	212	0.86	1.70
15	$C_9H_{12}N_2O_4$	212	0.30	0.72
4	$C_{10}H_{14}N_2O_4$	226	0.44	0.22
10	$C_{10}H_{14}N_2O_4$	226	0.26	1.00
11	$C_{11}H_{16}N_2O_4$	240	0.17	1.02
16	$C_{11}H_{16}N_2O_4$	240	0.57	0.51

Conclusions.

1. The primary mass fragmentation of compounds **1-17** is due to the cleavage of C_{sp2}-O, C_{sp2}-C_{sp3} and C_{sp3}-C_{sp3} bonds of the alkoxycarbonylalkyl or carboxyalkyl substituent.

2. The position of the carboxyalkyl and alkoxycarbonylalkyl substituent at the uracil ring may be deduced on the basis of the intensity of the respective molecular and analytical fragment ions [M-•OR] and [M-•COOR] shown in Tables 1 and 2.

3. The values of μ_1 and μ_2 *i.e.*, the ratio of the intensities of the selected fragment ions to that of the molecular ions $M^{+\bullet}$, depend on the structure of the carboxyalkyl and alkoxycarbonylalkyl substituent.

4. The N-1 substituted thymine derivatives **6**, **8**, **11**, **13** and **15** can be distinguished from the corresponding metameric N-1 and C-6 substituted derivatives of uracil on the basis of lower μ_1 values.

EXPERIMENTAL

The purity of all described compounds was monitored by melting points and thin layer chromatography (tlc). The uncorrected melting points were determined on a Böetius microscope hot stage and R_f values refer to silica gel F_{254} tlc plates (Merck) developed with chloroform/methanol (9:1) and observed under uv light, λ = 254 and 366 nm. The uv/visible spectra were recorded on a Kontron Uvikon 940 spectrophotometer. The ^1H nmr spectra were recorded on a Varian Unity plus 500 MHz spectrometer in dimethyl-d_6 sulfoxide solution with tetramethylsilane as the internal standard. All chemical shifts are given in δ values. Elemental analyses were performed on a Perkin-Elmer analyser. Low- and high-resolution spectra were recorded on a Model AMD 402 two-sector mass spectrometer with ionizing voltage 70 eV, accelerating voltage 8 kV, and resolution 20000. Samples were introduced by direct insertion probe at the source temperature of ~150°. The elemental compositions of the ions were determined relative to perfluorokerosene. All measured masses agreed with those of the elemental compositions listed in Tables 1 and 2 to within ±2 ppm. The B/E linked scan mass spectra were obtained on the same instrument. The values of μ_1 and μ_2 were calculated as means of two to four measurements.

6-Carboxymethyluracil **1** [2], 6-carboxymethylthymine **2** [2], 1-carboxymethyluracil **5** [1], 1-carboxymethylthymine **6** [3], 1-carboxyethyluracil **12** [5], 1-carboxyethylthymine **13** [6], as well as the esters of 1-carboxymethyluracil **7** and **10** [1,2] and 1-carboxyethylthymine **8** and **15** [4,6] were prepared as described in the literature.

Esterification Procedure of 1-(or 6-)Carboxyalkyluracils and 1-(or 6-)Carboxyalkylthymine Leading, Respectively, to 1-(or 6-)Alkoxycarbonylalkyluracils **3**, **4**, **9**, **14**, **16** and 1-(or 6-)Alkoxycarbonylalkylthymine **11** and **17**.

To 30 ml of the appropriate alcohol three drops of acetyl chloride were added, and the solution was stirred at room temperature for 15 minutes. Next, 2 mmoles of either 1-(or 6-)carboxyalkyluracil or 1-(or 6-)carboxyalkylthymine was added and the stirring was continued for 3 hours at 80°. The reaction mixture was then cooled to room temperature, neutralized with triethylamine and evaporated to dryness. The crude solids of **9**, **11**, **14**, **16** and **17** were crystallized from 50% ethanol. Derivatives **3** and **4** were isolated by preparative tlc on silica gel plates (Merck) in chloroform-methanol (9:1) as developing solvent system. The experimental data of the newly synthesized derivatives are shown in Tables 4a and 4b.

Table 4a

Analytical Data of Compounds **3**, **4**, **9**, **11**, **14**, **16**, **17**

Compound	Formula Molecular Mass	Yield (%)	mp (°C)	TLC-R_f $CHCl_3$/MeOH 9:1	Elemental analysis Found/(Calcd.)		
					C	H	N
3	$C_9H_{12}N_2O_4$ 212.2	44	232	0.49	50.86 (50.94)	4.68 (4.71)	13.25 (13 20)
4	$C_{10}H_{14}N_2O_4$ 226.2	40	180-182	0.47	53.00 (53.09)	6.21 (6.23)	12.47 (12.38)
9	$C_9H_{12}N_2O_4$ 212.2	62	137-139	0.43	50.90 (50.94)	4.75 (4.71)	13.26 (13.20)
11	$C_{11}H_{16}N_2O_4$ 240.3	73	124-125	0.57	55.06 (55.99)	6.67 (6.71)	11.76 (11.66)
14	$C_8H_{10}N_2O_4$ 198.2	75	135-137	0.52	48.78 (48.89)	5.02 (5.09)	14.05 (14.14)
16	$C_{11}H_{16}N_2O_4$ 240.3	71	79-81	0.55	54.91 (54.99)	6.76 (6.77)	11.76 (11.66)
17	$C_{12}H_{18}N_2O_4$ 254.3	70	94-95	0.66	56.61 (56.68)	7.11 (7.14)	10.90 (11.02)

Table 4b

Spectral Data of Compounds **3**, **4**, **9**, **11**, **14**, **16**, **17**

Compound	UV/VIS	λ max-nm (ε)	^{1}H NMR DMSO-d_6 δ (ppm)	
3	*p*H 1 and 7	262 (10 000)	1.20 s CH_3	4.93 m O-CH
	*p*H 12	284 (8 500)	1.21 s CH_3	5.44 s 5-H
			3.44 s 6-CH_2	
4	*p*H 1 and 7	262 (9900)	0.87 t CH_3	4.08 t O-CH_2
	*p*H 12	283 (8300)	1.34 m CH_2-CH_2	superimposed on DMSO-d_6
			1.56 m CH_2-CH_2	O-CH_2
				5.46 s 5-H
9	*p*H 1 and 7	262 (10200)	1.21 s CH_3	4.94 m O-CH
	*p*H 12	261 (7600)	1.24 s CH_3	5.00 d 5-H
			4.45 s O-CH_2	7.62 d 6-H
11	*p*H 1 and 7	268 (10200)	0.93 t CH_3	1.74 s 5-CH_3
	*p*H 12	270 (8400)	1.33 m -CH_2-CH_2	4.12 t O-CH_2
			1.52 m -CH_2-CH_2	4.56 s N-CH_2
				7.49 s 6-H
14	*p*H 1 and 7	265 (9800)	2.71 t CH_2-CO	5.54 d 5-H
	*p*H 12	264 (7000)	3.60 s O-CH_3	7.63 d 6-H
			3.89 t N-CH_2	
16	*p*H 1 and 7	265 (9800)	0.88 t CH_3	3.90 t N-CH_2
	*p*H 12	264 (7400)	1.28 m -CH_2-CH_2	4.01 t O-CH_2
			1.55 m-CH_2-CH_2	5.52 d 5-H
			2.70 t -CH_2-CO	7.62 d 6-H
17	*p*H 1 and 7	270 (800)	0.85 t CH_3	3.87 t N-CH_2
	*p*H 12	270 (7800)	1.30 m -CH_2-CH_2	4.03 t O-CH_2
			1.51 m -CH_2-CH_2	1.74 s 5-CH_3
			2.58 t CH_2-CO	7.51 s 6-H

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