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Mass Spectra of Substituted Butenolides

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The mass spectra of a series of substituted butenolides were studied. Their fragmentations in the mass spectrometer strongly depend upon the nature of the substitutents. The fragment's ions include the lactone skeletons, substituents, and resultant derived from the loss of a carbon dioxide from lactone.

INTRODUCTION

5-Alkoxyfuran-2(5H)-ones (butenolides) are the important synthons owing to their multi-functional nature for transformation reactions, e.g. cycloadditions, enolate and acetal chemistry and conjugate addition reactions.¹ This series of compounds is also found highly bioactive.² The multifunctional characters are worth studying in the gas phase condition. The mass spectra of the butenolides containing a variety of substituents are determined in this work.

RESULTS

None of fragmentation of the butenolides has been reported, except for fused butenolides, which have heen studied for the characterization of the natural products.³ The fragmentation of the non-fused series is strongly dependent on the nature of the substituents. In general, the molecular ions are weak or absent from the spectra, and the spectra are relatively simple due to the stable lactone sketetones. The observed fragment ions include the butenolide skeletone, substituents and resultant from the loss of a carbon dioxide from lactone. Therefore, the results were discussed according to their substituents.

5-Alkoxybutenolides (1-7)-Unusual protonated molecular ions were observed instead of the molecular ions except for methoxy-(1) and ethoxyl-(2) derivatives. The latter yielded [M-1]⁺ ions. Formation of quasi-molecular ions might be due to the higher oxygen content that enhances their ability to abstract a proton from the matrix. Competitive fragmentation yields butenolide cation A as a base peak (loss of alkoxide radical or loss of a alcohol from quasi-molecular ion), methyleneoxybutenolide cation B (cleavage of a bond next to oxygen atom of alkoxyl group), and ion C (from loss of carbon dioxide from the ring) (Scheme I).

Scheme I



5-Alkylcarbonyoxylbutenolides (8-13)-Quasi-molecular ions were also observed for this series of compounds. Formation of ion A and ion D were competed with the formation of alkylcarbonyl cation and their daughter ions. While the alkylcarbonyl cations are the base peaks in this class except for compound 10, which forms propylcarbonyl in 91% relative intensity. This fact is due to the low ionization potential of the alkylcarbonyl as well as phenylcarbonyl radicals (Table 2) leading to corresponding cations. Ions B, C are absent from this class.

5-Disubstituted butenolides (14-21)-For this series of compounds, loss of a substitutent (R_2) resulted in either a stable cation or stable radical because the fragmentation

Table 1. Mass Parameter of Substituted Butenolides 1-21

Compo	bund $m/z(\%)$
1	113(M-1, 6), 99(2), 88(4), 86(5), 85(22), 84(3), 83(100)3
-	$82(5), 75(4), 72(2), 71(4), 70(47)^{\circ}, 69(7), 59(6), 58(20), 71(4), 70(47)^{\circ}, 69(7), 70(47)^{\circ}, 70(47)^{\circ$
	55(82), 54(30), 53(6), 45(4), 43(6), 42(32), 41(15),
2	$127(M-1, 2), 113(2)^{c}, 100(15), 99(20), 85(2), 84(36)^{d},$
	83(100) ^a , 71(4), 69(4), 56(9), 55(65), 54(11), 53(3).
3	143(M+1, 10), 126(2), 113(12) ^c , 101(8), 100(11), 99(4),
	$98(24)^{d}$, $84(14)$, $83(100)^{a}$, $71(2)$, $69(10)$, $57(7)$, $56(7)$,
	55(37), 54(10), 53(4), 43(26), 42(8), 41(22).
4	$172(5)$, $171(M+1, 50)$, $143(3)$, $141(3)$, $126(2)^{d}$, $117(7)$,
	113(6) ^c , 101(18), 97(7), 87(6), 84(34), 83(100) ^a , 71(30),
	70(12), 69(51), 57(9), 56(7), 55(35), 54(8), 43(43),
	42(11), 41(32).
5	185(M+1, 3), 125(2), 113(4)°, 101(7), 97(2), 85(7),
	84(31), 83(100) ^a , 71(3), 69(5), 57(7), 56(11), 55(44),
	54(6), 53(4), 43(42), 42(9), 41(29).
6	213(M+1, 2), 169(2), 155(2), 113(3) ^c , 112(3), 111(10),
	102(5), 101(7), 97(5), 85(5), 84(4), 83(100) ^a , 71(10),
	70(16), 69(71), 68(6), 67(5), 57(30), 56(22), 55(65),
	54(8), 53(4), 43(47), 42(16), 41(53).
7	153(35), 138(3) ^d , 110(2), 84(21), 83(100) ^a , 82(10), 56(2),
	55(22), 54(9), 53(3).
8	143(M+1, 2), 100(4), 84(5), 83(100) ^a , 82(35), 71(4),
	57(4), 55(33), 54(21), 53(7), 45(4), 44(3), 43(95), 42(7),
	41(4).
9	157(M+1, 2), 127(5), 97(11), 96(7), 85(13), 84(9),
	83(85) ^a , 71(16), 70(7), 69(14), 58(4), 57(100), 56(4),
	55(44), 54(8), 53(9), 45(9), 44(5), 43(44), 42(19), 41(22).
10	$171(M+1, 2), 141(15), 84(7), 83(100)^{a}, 82(7), 71(91),$
	55(11), 54(5), 43(17), 42(3), 41(9).
11	185(M+1, 2), 155(4), 103(8), 93(2), 87(4), 85(100), 84(3),
	83(29)°, 74(4), 73(44), 61(6), 60(16), 57(8), 56(7), 55(16),
	45(13), 43(13), 42(11), 41(21).
12	199(M+1, 16), 169(5), 144(6), 100(6), 99(100), 97(8),
	$8/(20), 84(4), 83(30)^{\circ}, 74(4), 73(44), 71(8), 70(7), 69(8),$
	61(9), 60(82), 57(10), 56(12), 55(25), 45(22), 43(21),
11	42(17), 41(33).
15	205(5), 204(NI, 21), 170(5), 175(59), 147(2), 151(2), 152(2)
	100(0), 103(100), 03(30), 02(10), 78(3), 77(33), 33(13), 54(7), 51(20), 50(7)
14	JH(1), J1(20), J0(1). 101(34) 100(\$4) 80(4) 73(4) 58(4) 57(100) ⁶ 54(4)
14	101(24), 100(30), 99(4), 72(0), 38(0), 37(100) , 30(4), 55(10) 73(10)
15	33(10), 43(10). 126(4) 114(3) 00(13) 83(14) 46(3) 45(100) ^b
15	120(4), 114(3), 99(13), 02(14), 40(3), 43(100) . 100(M 7) 108(100) 80(7) \$7(10)
17	103(M, 7), 108(100), 80(7), 54(10). 123(M, 5), 108(6), 108(100), 81(3), 80(15), 70(5), 60(01).
1,	55(3) 54(35) 52(10) 43(15)
18	137(M 1) 110(7) 109(100) 108(26) 84(3) 83(36)
	82(46) 57(4) 56(4) 55(3) 43(5)
19	$153(M, 1), 110(6), 101(9), 73(3), 71(3), 57(3), 45(100)^{b}$
	43(22).
20	109(5), 81(7), 74(3), 73(98), 70(5), 66(5), 61(9), 54(10).
	45(10), 44(29), 43(100), 41(8).
21	243(M, 4), 106(8), 105(100), 77(7).

^d [M-CO₂]⁺.

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Table 2. Ionization Potentials of Some Possible Radicals

		_
radical	IP/eV	
CH₃O	10.83 (9.8)4	
C ₂ H ₅ O	10.80	
n-C3H7O	10.75	
n-C₄H₀O	10.73	
CH3CO	8.90 (7.9) ⁴	
C ₂ H ₅ CO	8.87 (7.7)4	
n-C3H7CO	8.86	
n-C₄H₀CO	8.86	
n-C5H11CO	8.86	
C6H5CO	8.96	
CH3OCH2	8.48 (6.9) ⁴	
В	9.44	
с	9.88	
Е	8.55	

center is a tertiary carbon as well as the carbon next to the double bond and oxygen. The signals of the ion from substituent (R_2) seem to be competed with ion E as a base peak. While the ions resulted from R_2 are base peaks (14, 15, 19) and ions E are the base peaks (16, 17), the possible resultant R_2 cation (i.e. H, Me, Et) is too small a substituent to be detected under normal mass spectral experiment. Ethyl group in compound 18 undergoes a proton transfer to the oxygen atom on the ring followed by the loss of an ethylene molecule with the formation of ion at 109 u as the base peak. The acetate (20) and phenylcarbonyl (21) derivatives afford acetyl and phenylcarbonyl cations as the base peaks, respectively.



 $R_1 = H$ $R_2 = OMe$ 1; OEt 2; OPr-n 3; O-Pentyl-n 4;

O-Hex-n 5; O-Oct-n 6. OAc 8; OC(O)Et 9;

OC(O)Pr-n 10; OC(O)Bu-n 11; OC(O)pentyl-n 12;

OC(O)Ph 13.

 $R_1 = OH R_2 = Bu-n 14$; $CH_2OMe 15$.

 $R_1 = CN R_2 = H 16$; Me 17; Et 18; CH₂OMe 19; CH₂OAc 20;

CH2OC(O)Ph 21.

DISCUSSION

The ionization potentials (IP) for some possible ions resulting from this series were obtained by means of theoretical calculation using the PM3 method⁵ under an AM-PAC/MOPAC environment.⁶ From the table, we find that the radicals of acyl, methyl methylene ether, and butenolidc skeletons have lower IP values and are suggested to be formed as a cations according to Stevenson's Rule.⁷ Indeed, those ions are observed in most cases as the base peaks.

The formation of ion \mathbf{F} is an unfavorable process. Once it is formed, it can undergo ring expansion, as in the case of the methylenepyrrole system, to form ion \mathbf{G} , which undergoes a tautomerization to form an enol form \mathbf{H} and then resonance to a six electrons system I (Scheme II).⁸ The heat formation for those ions obtained from calculation using the PM3 method are 218.95, 185.24, 168.65 and 168.65 kcal/mol for ions \mathbf{F} , \mathbf{G} , \mathbf{H} , and \mathbf{I} , respectively. Lower heat of formation for the possible ions \mathbf{H} , \mathbf{I} , and \mathbf{G} support the possible isomerization mechanism.

Scheme II



EXPERIMENTAL

The electron impact mass spectra were obtained on a JEOL model JMX-DX 300 double-focusing mass spectrometer. Samples were introduced via a direct insertion probe; the source temperature was kept at 150 °C. The trap current for the 70 eV mass spectra was maintained at 300 μ A and the accelerating voltage was maintained at 3 kV. All mass spectra were obtained at resolution 5000 (10% valley definition). The reported relative intensities of peaks are averaged from two runs. The semiempirical calculations PM3 were performed using the AMPAC/MOPAC program⁶ on a Silicon Graphics Workstation.

Preparation of Compounds 1-21

Sensitized photooxidation of furfuryl alcohol in acetone solution would give 5-hydroxybutenoid⁹ which was reacted with *p*-toluenesulfonic acid in methanol, ethanol, butanol, hexanol, heptanol, and octanol solution at room temperature for one day. After the usual work-up, compounds 1^{10} , 2^{11} , 3, 4, 5, 6, 18, or 19 were obtained, respectively. Compound 7 was obtained from 5-hydroxybutenolide reacting with *p*-toluenesulfonic acid in dry benzene under reflux for 6 h. 5-Hydroxybutenolide dissolved in dry pyridine was treated with acetyl chloride, propanoyl chloride, butanoyl chloride, pentanoyl chloride, hexanoyl chloride, or benzoyl chloride at 5-10 °C for 10 min. After purification, the products obtained were compounds 8, 9, 10, 11, 12, or 13, respectively. Photooxygenation of 2,5-di-tert-butylfuran and 2,5-dimethoxymethylfuran in methylcne chloride at -30 °C for 3 h yielded compounds 14¹² and 15, respectively. Low temperature singlet oxygenation of 2-substituted furans followed by reduction with dimethyl sulfide led to cis-enediones, which on subsequent treatment with TMSCN produced 2-cyano-2-alky1-5-hydroxy-2,5-dihydrofurans. Those compounds were oxidized with PCC afforded compounds 16, 17, 18, 19, 20, and 21,13 respectively.

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Key Words

Mass spectra; Butenolides; 5-Alkoxyfuran-2(5H)ones; Quasi-molecular ions; PM3 method.

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