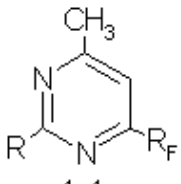
Main directions of fragmentation of molecular ions of perfluorosubstituted 1,3-diazines and 1,2,4-triazoles.

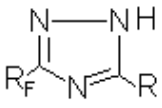
L.M.Popova, S.V.Vershilov

Investigation of mass-spectra of heteroaromatic compounds has shown that pyrimidines, 1,2,4-triazoles and most of their haloido-, alkyl- and amino- derivatives as conjugated systems possess quite a high (Wm over 10%) stability with regard to electron impact [1-3] , which allows to accurately determine the molecular mass of the compounds. Thus, the relative intensity of molecular ion M^+ of unsubstituted pyrimidine is 42% and at its dissociation two molecules of hydrogen cyanide are split off consequently resulting in formation of fission ions $[C_3H_3N]^+$ and $[C_2H_2]^+$ with the intensity of 15 and 16% respectively. [4]. The mass spectrum of 1H-1,2,4-triazole is similar to that of 1,2,3-triazole. On the basis of data on mass-spectra of deutero analogues of 1,2,4-triazole and some its derivatives it has been concluded[4] that in gas phase M^+ of these compounds exists in two asymmetric tautomeric forms. Decomposition of derivatives of 1,2,4-triazole runs mainly by elimination of HCN or RCN according to different mechanisms [4], elimination of the molecule N2[2] is slight (peak intensity is less then 1%) in the presence of perfluorosubstitutes in the azole molecule.

The technique of chromato-mass-spectroscopy (electron impact, 70eV) was used for confirmation of the structure and composition of 6-perfluorosubstituted 2-amino- (1), 2-hydroxy- (2), 2-mercapto- (3) and 2-methylthio- (4) 4-methylpyrimidines and 3-perfluorosubstituted 5-amino (5-7) and 5-mercapto- (8) 1,2,4-triazoles.



1-4



5-8

R_F = C_6F_{13} R = NH_2 (5), SH (8), SCH_3 (4); $CF(CF_3)OC_3F_7$ R = NH_2 (1, 6),

OH (2), SH (3); $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ R = NH_2 (7).

In the mass-spectra of the substances investigated, the peaks of molecular ions $[M^+]$, typical for halogen-containing heterocyclic compounds [3], are present along with peaks of isotope ions $[M+1]^+$, as well as $[M+2]^+$ (less 1then %) in spectra of 2-mercapto- (3), 2-methylthio- (4) 4-methylpyrimidine and 5-mercapto-1,2,4-triazole (8).

A high intensity of the peaks of molecular ions (39-78%) is an evidence of considerable resistance of 3-perfluorosubstituted triazoles to electron impact.

The analysis of the mass-spectra (Table) allows to assume that primary fragmentation of molecular ions takes place mainly as a result of simple break as well as benzyl one of perfluorosubstituent of the side chain. The peaks of ions $[M-F]^+$ are present in the spectra of investigated pyrimidines (1-4) and 1,2,4-triazoles. The ions $[M-CF_3]^+$, $[M-C_2F_5]^+$ $[M-C_3F_7-O]^+$ are typical for fragmentation of compounds containing perfluorinated substituents as well as the presence of peaks of ions with m/z 31 $[CF]^+$, 69 $[CF_3]^+$, 76 $[C_2NF_2]^+$, 77 $[HC_2NF_2]]^+$, 78 $[H_2C_2NF_2]^+$, 100 $[C_2F_4]^+$, 119 $[C_2F_5]^+$ and 169 $[C_3F_7]^+$ in the spectra of compounds (1-4)[3]. The fragments with m/z 164 and 133 (5), 183 and 133 (6,7) and 150 (80 are of great interest, they obviously are formed as a result of perfluorosubstituent decomposition. The intensive peaks of fragments with m/z 183 (to which a gross-formula $C_2F_4C_2N_4H_3$ may be assigned) in the spectra of 5-amino-1,2,4-triazoles is bound up with break of the ether bond C-O in the perfluorinated substituent, elimination of high stable difluorocarbene followed by skeleton rearrangement [3]. But in contrast to perfluoroalkanes [3], the peaks of $[M-F]^+$ ions are not the maximal.

The peaks of fission ions with m/z 51,44,29,28 and some others are typical for fragmentation of pyrimidine derivatives [6,7]. The peaks with m/z 45 (CHS) [7,8] are typical for mass-spectra of S-containing compounds(3,4). The presence of peaks of characteristic ions with m/z 150 in the spectrum of 5-mercapto-1,2,4-triazole (8) and with m/z 164 and 133 (5) , 183 and 133 (6,7) in the spectra of 5-amino-1,2,4-triazoles as well as peaks of ions with m/z 57, 42,41,28, 27 is typical for fragmentation of triazole derivatives [9-11]. This allows to use this method for identification of such compounds.

Thus, we have analyzed the mass-spectra of some 6-perfluorosubstituted 1,3-diazines (1-4) and 3-perfluorosubstituted 1,2,4-triazoles (5-8), determined the molecular masses of the compounds, determined the main regularities of fragmentation of molecular ions under electron impact.

Table

Mass spectra of 6-fluorosubstituted 4-methylpyrimidines (1-40 and 3-perfluorosubstituted 5-amino- (4-7) and 5-mercapto- (8) 1,2,4-triazoles (EI, 70eV)

Compound N	M	m/z ($I_{rel.}$,%)[a]
1	393, 16	394(9), 393(35), 274(11), 324(9), 266(60), 169(50), 150(16), 147(12), 145(43), 119(21), 117(16), 100(97), 97(56), 78(16), 71(7), 69(100), 67(19), 51(6), 50(16), 45(31), 31(13),20(19)
2	39,14	394(7), 394(18), 325(11), 266(11), 169(100), 144(61), 119(14), 117(30), 100(46), 97(100), 78(6), 69(59), 67(8), 51(15), 45(50), 44(7), 31(9), 28(26)
4	458,23	459 (6), 458 (29), 447 (7), 446 (18), 445 (100), 223 (6), 183 (5), 168 (9), 155 (6), 141 (12), 140 (6), 139 (6), 131 (41), 119 (5), 116 (5), 115 (10), 92 (6), 77 (50), 74 (6), 69 (9), 51 (7), 45 (7), 44 (6)
5	402.12	403(9), 402(78), 283(37), 213(5), 169(7), 164(15), 134(9), 133(100), 131(24), 119(23), 108(5), 105(6), 100(17), 93(6), 91(20), 70(7), 69(53), 57(17), 56(5), 55(11), 53(6), 43(27), 42(5), 41(12), 29(8), 28(13), 27(5)
6	368.11	368(7), 299(19), 251(5), 183(58), 169(40), 154(19), 133(31), 130(18), 127(22), 126(5), 119(24), 112(5), 111(92), 108(13), 100(29), 91(9), 82(6), 76(10), 70(8), 69(100), 57(30), 55(6), 54(7), 53(18), 50(8), 47(9), 43(70), 42(12), 41(12), 31(20), 29(31), 28(85), 27(11)
7	534,13	535 (5), 534 (39), 515 (9), 465 (38), 445 (5), 415 (9), 349 (17),
		184 (9), 183 (100), 169 (99), 154 (42), 150 (8), 135 (6), 133 (49), 131 (18), 130 (20), 127 (25), 126 (6), 119 (33), 112 (5),
		111 (59), 108 (13), 100 (41), 93 (5), 91 (7), 76 (6), 70 (7),
		69 (97), 57 (17), 55 (11), 53 (8), 50 (5), 43 (32), 42 (7), 41 (16), 39 (7), 31 (9), 29 (12), 28 (20), 27 (7)
8	419,16	420 (6), 419 (55), 400 (21), 169 (7), 150 (100), 131 (24), 125 (10), 119 (22), 113 (5), 108 (12), 100 (17), 94 (15), 93 (5), 91 (24), 74 (8), 69 (48), 55 (6), 43 (5), 42 (7), 41 (8), 31 (5), 29 (5), 28 (9), 27 (5)

Note.[a] Peaks of ions with relative intensity of less then 5% are not given

References

1. Poliakova A.A., Khmelnitsky R.A. Mass-spectrometry in organic chemistry .// L.: Khimiya, 1972.-367p.
2. Jonson R. Guide on mass-spectrometry for chemists-organics.// M.: Mir, 1975.-242p.
3. Vulfson M.S., Zaikin V.G., Mikaya A.I. Mass-spectrometry of organic compounds.//M.:Khimiya, 1986. 312p.
4. Maquestiau A., Van Herbeke Y. et Flammang R. Tragmentation du 1,2,4-triazole sous L'Impact Electronique.//Org. Mass.Spectrom.-1972.-v.6.-P.1139-1144
5. Cotter G.L. Mass spectra of some azoles// Org.Mass.Spectrom.-1972.-v.6N10.-p.1071-1075
6. Nishiwaki T. Electron impact study on simple pyrimidines//Tetrahedron.-1966.-v.22.-P.3117-3129
7. Strecowski L. Electron impact ionization mass spectrometry of fimethylamino-, metoxy-, and methylthiopyrimidines. Rearrangement in molecular ions.//Rocz.Chem.-1976.-v.50-P377-379
8. New physical and chemicals methods for studying organic compounds/Ioffe B.V., Zenkevitch I.G., Kuznetsov M.A., Bershtein I.Ya.// L.: Izd. Leningradskogo un-ta,1984.-240p., p.150
9. Hoggarth E. Compounds related to Thiosemicarbazide. Part 1. 3-Pehyl-1,2,4-triazole Derivatives //J.Chem.Soc.-1949.-P.1160-1163
0. Blackman A.J., Bowie J.H. Mass Spectra of 1,2,4-triazoles. II. Alkyl 1,2,4-triazoles //Org. mass. Spectrum.-1973.-v.7.-P.57-64
1. Fragmentation D'Azoles sous L'Impact Electronique/ A. Maquestiau, Y.Van Haverbeke, R.Flammang, R.G.Cooks// Org. Mass.Spectrom.-1975.-V.10-P 946-957

Journal content