Sulfur ylides
9.* Resonance electron capture by molecules of keto-stabilized sulfur ylides containing a phthalimide fragment

V. K. Mavrodiev, I. I. Furlei, S. N. Lakeev, F. Z. Galin, and G. A. Tolstikov*

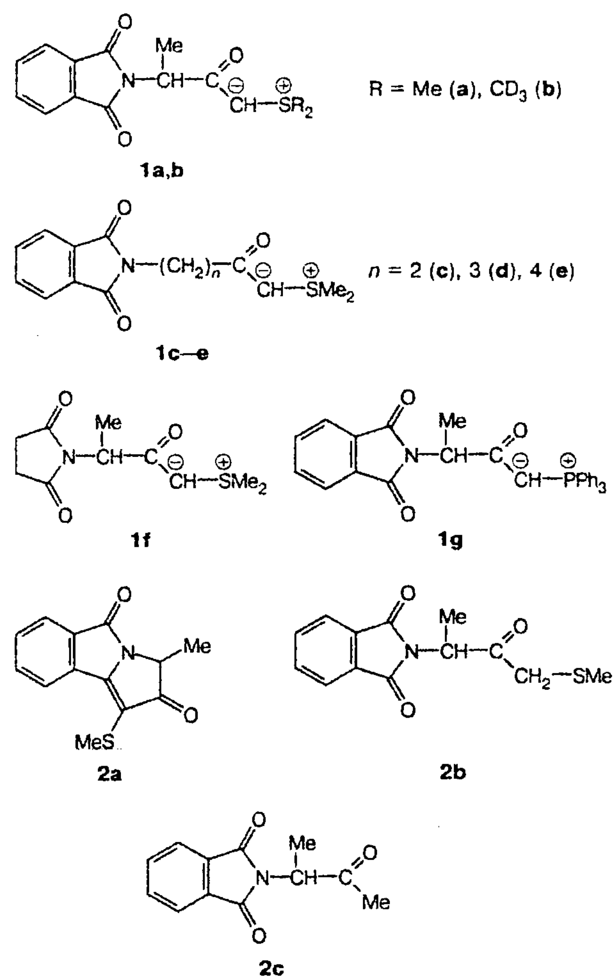
Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: galin@bash.ac.ru

The mass spectra of negative ions of keto-stabilized sulfur and phosphorus ylides (obtained from amino acids) and products of their thermal conversion are studied. The most characteristic peaks in the mass spectra of ylides belong to negative molecular ions and to $[M - H]^-$ ions. Peaks of fragment ions in the mass spectra of ylides and products of their thermal conversion coincide both in mass numbers and resonance energies.

Key words: mass spectrometry of negative ions, resonance electron capture, keto-stabilized sulfur and phosphorus ylides, thermal conversion.

In studies of the formation of negative ions (NI) *via* resonance electron capture (REC) by 1-dimethylsulfuranylidene-3-phthalimidobutan-2-one molecules we found that a peak of the $[M - 14]^-$ ion appears in the range of thermal electron energies (0.3 eV)[2] and that the relative intensities of ion peaks in the mass spectrum are changed because of thermal decomposition of the ylide as the temperature of the inlet system increases. To determine the contributions of thermal decomposition products, we recorded the mass spectra of NI of sulfur and phosphorus ylides (**1a—g**) at different temperatures of the inlet system (60—120 °C) and those of the main products (**2a—c**) of the thermolysis of compound **1a** (at 145 °C (1 Torr)), which were isolated as individual substances (Scheme 1).

Scheme 1



Experimental

Mass spectra and ionization efficiency curves were obtained on an MI-1201 instrument adapted for detecting NI under conditions of resonance electron capture.[3] The electron energy scale was calibrated against the maximum efficiency of C_6H_6 ionization to generate $C_6H_5^-$ ions and of SF_6 ionization to generate SF_6^- ions.

The synthesis of sulfur ylides **1a—g** was reported previously.[4,5] Phosphorus ylide **1f** was synthesized according to the known procedure.[6] Compound **2a** was obtained as a result of thermolysis of **1a** by intramolecular cyclization accompanied by elimination of the methanol molecule.[7,8]

Results and Discussion

The mass spectrum of compound **2a** contains a peak of molecular NI whose fragmentation proceeds by the sulfide mechanism[9] with the formation of $[M - Me]^-$ and $[M - SMe]^-$ ions in the electron energy range from 1 to 4 eV (Table 1).

* For Part 8, see Ref. 1.

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Table 1. Mass spectra of negative ions of compounds **1a—g** and **2a—c**[a]

Compound	*M*	*m/z*	*I* (%)[b]	E_m/eV[c]
1a	277	277	13	0.1
		276	<0.1	6.8
		263	100	0.3
		262	0.1	6.7
		248	<0.1	1.2
			<0.1	3.0
		245	16	0.1
		244	0.1	6.8
		230	3.6	1.0
			3.2	1.7
			2.0	3.0
		216	0.1	1.2
			0.1	2.8
		198	<0.1	3.7
		172	<0.1	3.6
		146	2.6	1.0
			5.5	1.7
			4.1	5.0
			2.8	6.0
		47	<0.1	1.1
			<0.1	3.8
			<0.1	8.9
1b	283	283	15	0.1
		282	<0.1	6.6
		266	100	0.3
		265	<0.1	6.8
		248	10	0.2
		247	<0.1	7.0
		230	11	1.0
			9.1	1.7
			8.0	3.0
		216	0.1	1.2
			0.1	2.8
		198	<0	3.7
		172	0.2	3.7
		146	3.0	1.0
			3.0	1.7
1c	277	277	16	0.1
		276	<0.1	6.8
		263	100	0.3
		262	0.1	6.8
		248	<0.1	1.3
			<0.1	2.8
		245	20	0.1
		244	<0.1	6.8
		230	4.6	1.0
			3.5	6.8
		216	0.1	1.2
			0.1	2.8
		198	<0.1	3.8
		172	<0.1	3.6
		146	3.0	1.0
			5.8	1.8
			3.8	5.0
			3.1	6.2
		47	<0.1	1.2
			<0.1	4.0
			<0.1	8.2
1d	291	291	21	0.1
		290	<0.1	6.5
		277	100	0.3
		276	0.1	6.5
		262	<0.1	1.2
		230	<0.1	1.2
		146	0.5	1.0
			1.1	2.0
			1.5	4.8
		47	0.2	1.2
			1.5	3.6
			0.8	6.0
			0.9	8.0
1e	305	305	46.7	0.1
		304	0.1	6.2
		302	4.2	0.4
		291	100	0.2
		290	0.1	6.6
		276	<0.1	1.1
		244	<0.1	1.2
			<0.1	2.9
		146	0.7	1.0
			1.4	1.9
			1.6	4.8
		47	0.7	1.2
			2.1	3.7
			1.2	6.1
			0.3	8.0
1f	225	98	9.0	1.6
			100	4.5
			63	6.2
			2.5	8.5
1g	477	199	100	0
		198	0.2	0.8
			1.5	7.0
		185	0.3	3.0
			0.2	4.0
2a	245	245	100	0.1
		244	0.5	6.8
		230	22	1.0
			19	1.7
			13	3.0
		198	0.1	3.9
2b	263	263	100	0.3
		262	0.1	6.7
		248	<0.1	1.2
			<0.1	3.0
		216	0.1	1.2
			0.1	2.8
		198	0.1	3.7
		172	<0.1	3.6
		146	2.0	5.1
			5.1	1.7
			3.5	5.0
			2.5	6.0
		47	<0.1	1.1
			<0.1	3.8
			<0.1	8.9
2c	217	217	100	0.1
		216	0.9	6.1
		174	2.7	2.8
		146	15	0.3
			30	1.7
			65	2.7

[a] Spectra were obtained at an inlet system temperature of 60 °C.
[b] Peak intensities at the maxima of ionization efficiency curves (IEC) relative to the peak with maximum intensity.
[c] E_m is the electron energy at the IEC maximum.

In addition to intramolecular cyclization resulting in compound **2a**, thermolysis of compound **1a** also follows a mechanism involving the loss of a methyl radical and addition of a hydrogen atom from another molecule to form compound **2b**. Such a mechanism is confirmed by the presence of peaks of $[M - CD_3 + H]^-$ ions (*m/z* 266) in the mass spectrum of NI of compound **1b**. (The intensities of the peaks of ions with *m/z* 267 and 268 in the mass spectrum of NI of compound **1b** correspond to the natural abundance of C, N, H, and S isotopes constituting the ion with *m/z* 266.) Thus, ylides **1a,c—e** in the ionization chamber of the mass spectrometer undergo thermolysis with the formation of sulfides of type **2b**, whose molecular weight formally corresponds to the $[M - 14]^-$ ion peak. Fragmentation of this ion resembles that of organic sulfides[5]: the REC mass spectrum of NI contains peaks of $[M - Me]^-$ ions with *m/z* 248 (for compounds **1a,c**) and with *m/z* 262 and 276 (for **1d,e**, respectively), as well as peaks of $[M - SMe]^-$ ions with *m/z* 216 (for compounds **1a,c**) and with *m/z* 230 and 244 (for **1d** and **1e**, respectively), and of SMe^- ions (*m/z* 47) (see Table 1).

It should be noted that cyclization with the formation of a compound of type **2b** is observed for sulfur ylides whose molecules contain a phthalimide fragment and one or two methylene groups (compounds **1a—c**). If the molecules contain three or more methylene groups (compounds **1d,e**), no compounds of type **2a** are formed as a result of thermolysis (no peaks of $[M - MeOH]^-$ ions are detected in the mass spectra of NI of these compounds in the range of thermal electron energies; only peaks of $[M - CH_2]^-$ ions are observed in this case, which corresponds to molecular NI of compounds of type **2b**).

This conclusion is confirmed by the mass spectra of sulfur ylides (the temperature of the inlet system was 60 °C) and products of thermal decomposition of compound **1a** listed in Table 1. Comparison of the mass spectra of NI of compound **1a** with those of **2a** and **2b** shows that, except for the ions with *m/z* 277, 276, and, partly, with *m/z* 146, all the remaining ions are formed from compounds **2a** and **2b**. For the intensities of ion peaks and the energies of the resonance maxima of compound **2b** this can be clearly seen in Table 1. The contribution of ion peaks of compound **2a** to the mass spectrum of **1a** can be easily reproduced if the intensity of the line with *m/z* 245 is taken to be 100%. Then, the intensities of peaks of fragment ions (with *m/z* 244, 230, and 198) in the mass spectrum of compound **1a**, for which *m/z* values coincide with those of peaks of the ions of compound **2a**, will coincide with those of compound **2a** within the limits of experimental error.

Thus, the peaks of molecular NI (*m/z* 277, 291, 305), $[M - H]^-$ ions, and the phthalimide fragment with *m/z* 146 in the mass spectra of NI correspond to sulfur ylides **1a—e**. The remaining peaks in the spectra of these compounds belong to sulfide compounds (similar to **2a,b** formed from ylide **1a**) produced upon thermal decomposition in the course of bleeding with ylides. However, it cannot be ruled out that the mass spectrum of sulfur ylide can also contain other ion peaks with low intensity, masked with ion peaks of compounds of types **2a** and **2b**, whose fragmentation under conditions of REC is accompanied by rearrangements. For instance, splitting of H_2O and CO molecules from ions with *m/z* 216 is observed in the mass spectrum of compound **2b** (the ions with *m/z* 198 and 172, respectively); this is indicated by metastable peaks with *m/z* 181.5 and 136.7, respectively, in the range of electron energies from 2.2 to 2.5 eV.

Thermal decomposition of compound **1a** results in compound **2c** as the temperature of the inlet system increases to 120 °C. This is indicated by the appearance of both a peak of an ion with *m/z* 174 in the mass spectrum of **1a** and a new resonance on the ionization efficiency curve near the peak with *m/z* 216 (at an electron energy of 6.1 eV), characteristic only of the REC mass spectra of NI of compound **2c**.

Common to the mass spectra of compounds **1a—e,g** with conjugated π-bonds is the presence of intense peaks of molecular NI in the range of thermal electron energies. The absence of such a peak in the mass spectrum of compound **1f** indicates that the formation of molecular NI is due to the presence of the phthalimide fragment in the molecular structure.

The ion peaks observed in the mass spectrum of NI of phosphorus ylide **1g** (at 60 °C) only correspond to the products of its thermal decomposition, namely, to $OPPh_3$ (*m/z* 185 PPh_2^-) and a cyclic compound of type **2a** (*m/z* 199, 198).

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