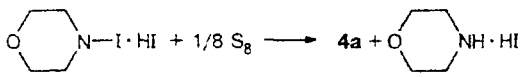
probably, higher sulfides of amines are also formed.

When the reaction was carried out in an excess of amine **2** (3) or in pyridine, the yield of compounds **4a** and **5a** was 60—70%, and in DMF the yield was ~30% ($Me_2N)_2S$ was additionally formed). Resinification of the reaction mixture was observed in nitromethane, benzene, and toluene.

In the presence of an excess of morpholine the reaction proceeded through the intermediate formation of *N*-iodoamines, which was confirmed by the experiment with the independently prepared *N*-iodomorpholine hydroiodide (the adduct of iodine with morpholine)[3] (Scheme 3).

Scheme 3



Thus, we developed a laboratory procedure for the synthesis of *N,N'*-thiobisamines without recourse to sulfur dichloride, which is inconvenient to use.[4]

Experimental

Melting points were determined on a Koffler heating stage. ^1H NMR spectra were obtained of a Bruker WM-250 instrument (250 MHz).

***N,N'*-Thiobisamines (4a and 5a).** A mixture of sulfur (0.32 g, 1.25 mmol), amine **2** (3) (80 mmol) and pyridine (5 mL) was heated in a reflux condenser until the dissolution of the components. A solution of iodine (2.54 g, 10 mmol) in pyridine (10—15 mL) was added over 1 min to the reaction mixture with stirring. After several minutes of heating, the solution decolorized. The reaction mixture was concentrated *in vacuo*, the residue was mixed with water (50—70 mL), and the crystals formed were filtered off, washed three times with water, and dried to afford compound **4a** or **5a**.

***N,N'*-Thiobismorpholine (4a).** The yield was 63%, m.p. 125—126 °C (from MeOH) (*cf.* Ref. 1: m.p. 125 °C), R_f 0.44 (EtO_2, Silufol). Found (%): C, 47.51; H, 7.66; N, 13.78; S, 14.89. $C_8H_{16}N_2O_2S$. Calculated (%): C, 47.03; H, 7.89; N, 13.71; S, 15.69. ^1H NMR ($CDCl_3$,), δ: 3.25 (t, CH_2); 3.65 (t, CH_2).

***N,N'*-Thiobispiperidine (5a).** The yield was 71%, m.p. 74—75 °C (from MeOH—H_2O) (*cf.* Ref. 1: m.p. 74 °C), R_f 0.76 (Et_2O, Silufol).

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Resonance capture of electrons by molecules of substituted pyrans

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Negative-ion mass spectrometry in the mode of resonance capture of electrons and photoelectron spectroscopy in combination with quantum-chemical calculations showed that the formation of the resonance states of negative molecular ions in the reaction of electrons with molecules of substituted pyrans in the ultraviolet optical excitation energy region occurs according to the mechanism of intershell Feshbach resonance with the consecutive excitation of an electron from several higher occupied MO to one vacant MO. In a low-energy region, the resonance at 1.4 eV is a resonance of form and the resonance at 3—4 eV is the usual electron exciting Feshbach resonance with a parent triplet state $(\pi,\pi^*)^3$. The one and the same vacant π^*_{CC} MO is "active" in all the resonances mentioned.

Key words: molecular orbital, resonance state; resonance capture of electrons; photoelectron spectroscopy.

The efficiency of the earlier proposed method[1] of interpretation of resonance states (RS) of negative molecular ions (NMI) that involves the combined application of negative ions (NI) mass spectrometry in the

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Table 1. REC mass spectra of NI of dihydropyran molecules

Ions	1		2		3	
	m/z	*I* (%)	*m/z*	*I* (%)	*m/z*	*I* (%)
$[M-H]^-$	83	38.3 (8.0)	97	2.6 (1.5) 0.5 (4.0) 3.1 (6.4)	97	57.7 (1.3) 2.0 (4.1) 7.7 (7.3)
$[M-H-H_2]^-$	81	75.0 (8.4)				
$[M-H-H_2O]^-$	65	15.5 (8.5)				
$[M-H-C_2H_2]^-$	57	11.0 (8.8)				
$[M-H-C_2H_4]^-$	55	40.0 (8.3)			69	0.8 (1.4) 1.2 (4.4) 20.8 (6.4) 2.8 (9.0)
$[M-H-H_2CO]^-$	53	73.3 (8.8)	67	15.9 (6.0) 100 (8.5)	67	100 (8.0)
$[M-H-H_3COH]^-$					65	7.7 (7.5)
$[M-H-H_2CCCH_2]^-$					57	7.1 (8.0)
$[M-H-H_3CCHCH_2]^-$					55	43.8 (8.0)
$[M-H-C_2H_4O]^-$					53	4.9 (8.0)
$C_2H_3O^-$	43	9.0 (8.6) 2.0 (6.4)	43	1.0 (6.5) 2.9 (9.0)	43	36.9 (8.0)
C_2HO^-	41	28.3 (8.1) 18.3 (10.1)			41	4.6 (6.2) 4.6 (8.8)
$C_3H_3^-$					39	7.7 (8.7)
CHC^-	29	53.3 (8.1)	29	0.2 (6.6) 1.4 (9.0)	29	2.3 (8.0)
$C_2H_3^-$	27	30.0 (8.6)			27	3.8 (8.0) 3.1 (9.3)
C_2H^-	25	3.0 (3.0) 16.0 (8.5)			25	7.7 (8.0)
OH^-	17	33.3 (8.2)				
O^-	16	16.0 (7.2) 100 (9.2)				
CH_3^-	15	3.5 (9.3)				

Note. Electron energy (in eV) in maxima of the corresponding curves of effective output is given in brackets.

mode of resonance capture of electrons (REC) and photoelectron spectroscopy (PES), has been demonstrated by numerous examples.[2–4] We have also shown,[3] and later found a theoretical basis,[5] that in the ultraviolet optical excitation energy region, the main resonance is an intershell one and the REC mass spectra of practically all studied compounds are described by one or two series of these resonances that result from the consecutive excitation of an electron from several higher occupied MO (HOMO) to the corresponding lower and higher vacant MO. Thus, the number of "active" vacant MO is limited mainly by two of them with the lowest energy. To explain such a "severe" selection of vacant MO it is necessary to increase the number of classes of organic compounds investigated. For this purpose, the derivatives of dihydropyrans **1**—**3** were studied in this work by means of REC mass spectrometry, PES, and quantum-mechanical calculations using the MNDO method in sp-basis.

The studied compounds form NI mainly in the high-energy region of electron energies (Table 1). In this case the majority of fragment NI's appears as the result of decomposition of $[M-H]^-$ ions with the separation of stable neutral fragments (see Table 1). Along with the stability of a neutral fragment, the driving force of these fragmentation processes is also stabilization of NI by the formation of double bond.[2]

The energy of the first singlet transition for the substituted pyrans with similar electron structure is 6.0—6.5 eV,[6] therefore, the resonance at 6.4 eV (compounds **1** and **3**) and 6.0 eV (compound **2**) is, probably, the first intershell Feshbach resonance that results from the excitation of an electron with π_{CC}-HOMO to one of the lower vacant MO. We used the PES data to determine the nature of higher energy resonances. The ionization energies (IE) and RS in Fig. 1 are presented in one scale and superposed for each of the compounds in such a way that the energy of the first intershell resonance

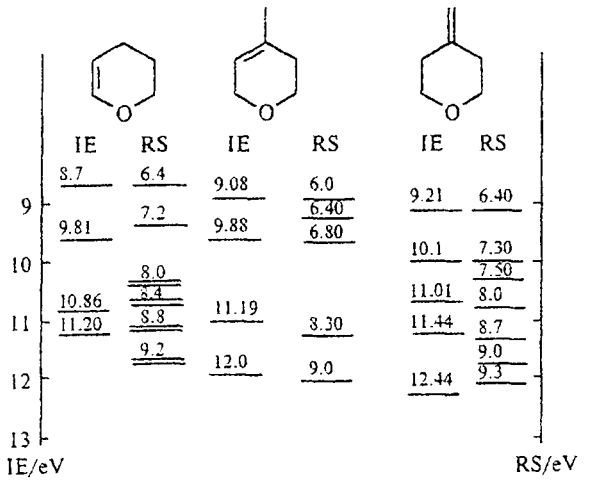

Fig. 1. Ionization energies (IE) and resonance states (RS) of negative molecular ions of dihydropyrans.

coincides with the first IE. As can be seen, the energy distances between the RS and IE coincide within 0.1—0.3 eV limits. This means that the other high-energy resonances are also intershell and result from the excitation of an electron from a deeper OMO to one and the same vacant MO. The closeness of the energies of the first IE, the singlet transitions, and the first high-energy RS of the compounds under study and cyclenes of different structure[6,7] allows one to conclude that the MO responsible for the formation of RS in substituted pyrans is the vacant π^*_{CC}-MO, which, probably, determines also the form of the REC mass spectra in the low-energy region of electron energies (1—4 eV). In fact, the resonance at 1.4 eV coincides within 0.3—0.5 eV with the position of the form resonance at π^*_{CC} in cyclenes[8] and the resonance at 3—4 eV (See Table 1) differs by only 0.5 eV from the energy of the first triplet electron transition in the same molecules.[6] The latter allows one to attribute it to the usual electron excited feshbach resonance with two coupled electrons on the vacant π^*_{CC}-MO.

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A new method for the synthesis of diorganylvinylphosphine oxides

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Diorganylvinylphosphine oxides were synthesized in 31—38% yields on heating (50 °C) diorganylphosphine oxides with vinyl sulfoxides or divinyl sulfone in the presence of KOH.

Key words: diorganylphosphine oxides, ethyl vinyl sulfoxide, divinyl sulfone, reaction; diorganylvinylphosphine oxides.

Among the known methods for the synthesis of diorganylvinylphosphine oxides, which are reactive intermediates and semi-products,[1] the reaction of chlorodiorganylphosphine with oxirane followed by dehydrochlorination of the intermediate 2-chloroethyldiorganylphosphine oxides,[2] as well as oxidation of diorganyl-

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