

LETTERS TO THE EDITOR

LOW ENERGY RESONANCE STATES OF NEGATIVE MOLECULAR IONS. FIVE-MEMBERED RING HETEROCYCLES AND CYCLOPENTADIENE

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A previous study of electron capture processes by heterocyclic compounds XC_4H_4 ($X = O, S, Se, NH$) revealed (cf. [1]) that negative molecular ions (NMI) of furan, thiophene, and selenophene, which are formed in two electron energy regions ($E_{e1} = 5$ and 8-9 eV), undergo extensive fragmentation, leading to a single type of ion composition. In the case of $X = NH, CH_2$, in contrast, the yield of fragment ions at high E_{e1} is low, and peak maxima for $(M-H)^-$ are observed at 2.05 and 1.65 eV, respectively.

In the present paper we have studied the formation of negative ions by the above compounds and by cyclopentadiene, using a modified mass spectrometer [2], which has greater sensitivity than that used in earlier studies. (Experimental conditions: electron current 1 mA at a distribution or resolution half-width of 0.3 eV; electron energy scan range 0-15 eV; accelerating voltage 3.6 kV.) New resonance states of NMI were observed at 2.2 eV ($X = S$) and 1.65 eV ($X = Se$), which correlate with the energies for the first $(M-H)^-$ ion peaks for pyrrole and cyclopentadiene and which are represented by the ions HX^- and X^- . These resonances can only be resonance forms of the molecular ground state, since bond rearrangement accompanied by the formation of ions such as HS^- and HSe^- requires a time frame equal to one C-H bending vibration, which is commensurate with or comparable to the resonance lifetime of the form relative to electron loss or discharge ($\sim 10^{-14}$ sec). The ion composition is determined by energetics, primarily by the electron affinity, which is large in the case of S, Se, SH, and SeH, and small in the case of NH, NH_2 , CH_2 , and CH_3 .

Another series of resonances was also observed at low E_{e1} (HNC_2H^- ions for pyrrole, $(M-H)^-$ ions for the other heterocycles); a feature of these resonances is that their position on the E_{e1} scale is 0.5-0.6 eV lower than the first triplet excited states (T_1) for these molecules [3] (3.5 and 4.0 eV; 3.3 and 3.8 eV; 3.5 and 4.1 eV for $X = O, S, NH$, respectively; T_1 for $X = Se$ is not known). We assume, therefore, that for XC_4H_4 heterocycles in this case electronically excited Feshbach resonance is observed, of the type $(\sigma_g 1s) (\sigma_u 1s)^2 {}^2\Sigma_g^+ H^-$ from H_2 at $E_{e1} \approx 10$ eV, and $(1s) (2s)^2 {}^2S$ at 19.34 eV for He, in which the mother state is the first excited mixed T_1 state [1].

The existence of no more than two NMI dissociation channels from these resonance states, and the relative low ion yield can be explained in terms of the symmetry of the NMI states and the dissociation products. Since the HOMO levels of these compounds are of the π -type, corresponding with the irreducible representation a_2 for the symmetry group C_{2v} , the NMI (resonance) states for all of these heterocycles must be the same, namely, A_2 . Fragmentation ions in these resonances are formed in the ground state, corresponding therefore with the full-symmetry spectroscopic state (A_1 in C_{2v}). For this reason, dissociation of the NMI is forbidden, and the formation of fragment ions in low yields (peak intensities 0.1-1.0% of maximum) is indicative of only a slight disruption or lifting (of the symmetry interdiction), associated with atomic vibrations within the ring, which distort the NMI geometry.

With respect to the previously discovered resonances in the range E_{e1} 5.1-6.7 eV, they probably consist of Feshbach resonance with simultaneous excitation and electron transfer from the HOMO to one of the low-lying unoccupied orbitals. For example, the NMI resonance state for furan at $E_{e1} = 5.55$ eV occurs via excitation of the S_1 state (6.06 eV [3]) of the molecule, since this process is allowed by the symmetry of the NMI state and that of the fragmentation products.

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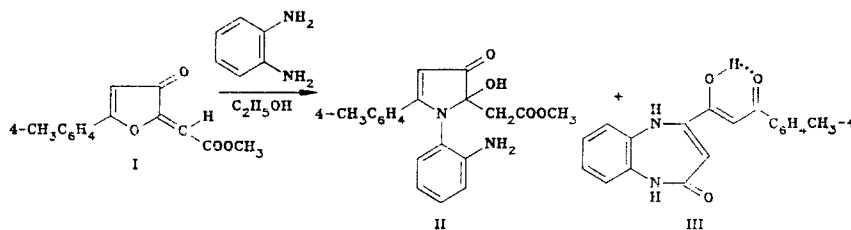
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UNUSUAL RECYCLIZATION OF 2-METHOXYCARBONYLMETHYLENE-5-p-TOLYL-2,3-DIHYDROFURAN-3-ONE UPON TREATMENT WITH o-PHENYLENEDIAMINE

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It has previously been shown that the reaction of 2-alkoxycarbonylmethylene-5-aryl-2,3-dihydrofuran-3-ones with o-phenylenediamine in benzene leads to the formation of addition products at the 2-exo-ethylene bond, therefore, to derivatives of 1,2,3,4-tetrahydro-2-quinoxalone [1]. In an unexpected result, for the reaction of 2-methoxycarbonylmethylene-5-p-tolyl-2,3-dihydrofuran-3-one (I) with o-phenylenediamine in benzene solution, we isolated 1-o-aminophenyl-2-hydroxy-2-methoxycarbonylmethyl-5-p-tolyl-2,3-dihydropyrrol-3-one (II) in 48% yield, along with a small amount of 4-p-toluoylacetyl-2,5-dihydro-1H-benzo-1,5-diazepin-2-one (III).



The formation of compounds II and III is probably the result of nucleophilic attack by the diamine at the electrophilic site of the C(2) atom in furanone I, and subsequent recyclization, which can occur via two pathways.

To a solution of 2.44 g (0.01 mole) 2-methoxycarbonylmethylene-5-p-tolyl-2,3-dihydrofuran-3-one [2] in 100 ml ethanol was added a solution of 1.08 g (0.01 mole) o-phenylenediamine in 50 ml ethanol, and the mixture was refluxed for 20 min. The solvent was evaporated and the residue crystallized from ethanol (compound II) and acetone (compound III).

Compound II. Orange substance, yield 1.7 g (48%), mp 162-163°C (dec). IR spectrum: (in KBr): 3457 (NH₂_{as}), 3385 (NH₂_s), 3240-3180 (OH), 1738 (CO ester), 1660 cm⁻¹ (C(3) = O). PMR spectrum (DMSO-D₆): 2.23 (3H, s, CH₃); 2.72 (2H, d.d, CH₂, J_{gem} = 17.0 Hz); 3.42 (3H, s, OCH₃); 5.37-5.50 (3H, broadened singlet, NH₂, OH); 5.56 (1H, s, 4-H); 6.45-7.38 ppm (8H, m, 2C₆H₄). The spectral data are consistent with published data [3].

Compound III. Brick red substance, yield 0.1 g (3%), mp 247-248°C (dec). IR spectrum (in KBr): 3180-3150 (NH), 1693 (CO amide), 1608-1587 cm⁻¹ (CO chelate, C=C). PMR spectrum (DMSO-D₆): 2.34 (3H, s, CH₃); 6.08 (1H, s, 3-H); 6.52 (1H, s, CH chelate); 7.12-7.47 (8H, m, 2C₆H₄); 11.91 ppm (1H, broadened singlet, NH amide). The spectral data are consistent with the results of [4, 5]. Mass spectrum, m/z (% of maximum peak): 320 (34.0) M⁺, 160 (34.2) [p-CH₃C₆H₄COCH=C=O]⁺ 132 (28.5)