AZINES AND AZOLES.

64.* MASS SPECTRA AND TAUTOMERISM OF 2-ARYL-4,6-DIOXO-1,3-THIAZINES

A. I. Krylov, V. N. Kuklin, and B. A. Ivin

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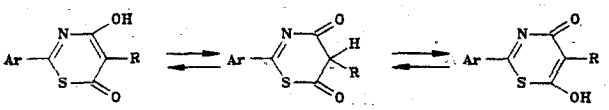
Mass spectra of 2-aryl-4,6-dioxo-1,3-thiazines were studied and the general fragmentation paths of these compounds determined. Based on mass spectra of compounds with fixed structures, 2-aryl-5,5-dialkyl-4,6-dioxo-1,3-thiazines, 4-alkoxy- and 4-acyloxy-2-aryl-6-oxo-1,3-thiazines, the decomposition paths of the dicarbonyl and hydroxycarbonyl forms were determined. It was concluded on the basis of the obtained data that 2-aryl-4,6-dioxo-1,3-thiazines exist in the gas phase predominantly in the hydroxycarbonyl form.

Mass spectrometry is being effectively used to investigate tautomeric transformations. Thus, for example, the structure and the amino-imide tautomerism of sulfanilamides [2, 3], the keto-enolic transformations of aliphatic β-dicarbonyl compounds [4, 5], and the keto-enolic transformations of aromatic and heterocyclic, 1,3-diketones [6-8] have been investigated in detail. This approach is of special interest because the substances are investigated in the gas phase under high vacuum, circumstance which allow the exclusion of solvation and association effects taking place in solutions. In addition, mass spectrometry is widely used as a determination method for physiologically active substances in biological media. In this connection, mass spectra of 2-aryl-4,6-dioxo-1,3-thiazines and their tautomerism in the gas phase have been investigated.

The following tautomeric transformations are possible in the 2-aryl-4,6-dioxo-1,3-thiazine series obtained by us:

Scheme 1



A comparison of mass spectra of 2-aryl-4,6-dioxo-1,3-thiazines (I-VI) (see Table 1) showed that the main decomposition paths are the same for all compounds of the series. The presence of a molecular ion peak is typical of all the investigated compounds. In addition, the spectra of compounds I-VIII exhibit a series of common, intense peaks (see Table 1) which can be used for the identification of arylthiazindiones. One of the most intense peaks belongs to the fragment ($M-CO^{+\cdot}$). An analogous fragmentation is also observed in 1,3-thiazine-4-ones [9]. The high intensity of the $M-CO^{+\cdot}$ ion peaks agrees with data in [10] about the high stability of molecular ions of thiazoles; the intensity of their corresponding peaks is close to 100%.

To corroborate the correctness of attributing the structure of ion $M-CO^{+\cdot}$ and to confirm the influence of the substituent at the $C_{(5)}$ atom of the β-dicarbonyl fragment, we investigated the mass spectra of 5-bromo- and 5-ethyl-2-phenyl-1,3-thiazindiones (VII and VIII). It was established that the fragmentation paths of the indicated compounds are analogous to those of compounds not substituted at $C_{(5)}$. At the same time, one of the essentially important decomposition paths of compound VII is the elimination of bromine accompanied by the generation of quite intense ion peaks ($M-Br^+$, 41.6%; $M-CO-Br^+$, 17.7%). The most intense peak in compound VIII belongs to the ion [$M-CO-CH_3^+$, m/z 190 (100%)].

*For Communication 63, see [1].

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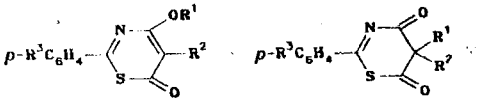
TABLE 1. Intensity (in % based on the maximum value) of the Fundamental Characteristic Ion Peaks in Mass Spectra of 2-Aryl-4,6-dioxo-1,3-thiazines and 4- and 5-Substituted 2-Phenyl-6-oxo-1,3-thiazines



IX–XI

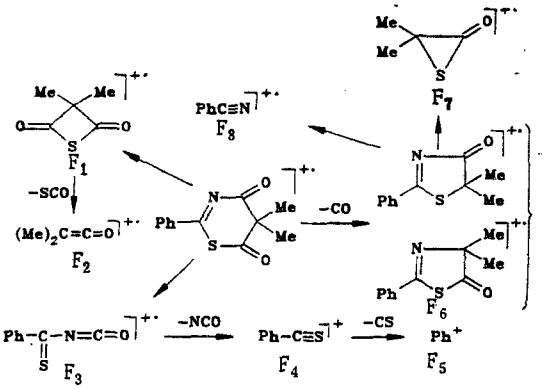
I–VI, XII

Compound	R^2	R^3	M*	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}
I	H	H	205 (12,3)	102	42 (2,9)	163 (6,6)	121 (9,9)	77 (22,9)	177 (100)	74 (8,5)	103 (8,1)	69 (22,5)	104 (56,4)
II	H	$N(CH_3)_2$	248 (15,6)	102 (5,8)	42 (0,8)	206 (10,5)	164 (19,2)	120 (5,4)	220 (40,5)	74 (2,0)	146 (43,8)	69 (8,2)	147 (100)
III	H	CH_3O	235 (7,4)	102 (2,2)	42 (4,0)	193 (9,2)	151 (12,4)	107 (2,0)	207 (89,7)	74 (6,3)	133 (10,7)	69 (24,3)	134 (100)
IV	H	Cl	239 (10,9), 241 (42)	102 (15,9)	42 (3,5)	197 (4,7), 199 (9,1)	155 (16,9), 157 (6,3)	111 (17,8), 113 (6,1)	211 (86,9), 213 (37,1)	74 (19,1)	137 (13,9), 139 (16,1)	69 (35,2)	138 (100), 140 (31,0)
V	H	Br	283 (8,9), 285 (8,9)	102 (23,4)	42 (5,6)	241 (6,5), 243 (6,8)	199 (13,1), 201 (13,4)	155 (11,0), 157 (10,6)	255 (81,4), 257 (100)	74 (21,4)	181 (11,3), 183 (22,0)	69 (35,7)	182 (81,0), 184 (79,2)
VI	H	NO_2	250 (3,3)	102 (4,9)	42 (3,2)	208 (5,3)	166 (1,7)	122 (1,5)	222 (100)	74 (24,3)	148 (0,8)	69 (38,7)	149 (25,4)
VII	C_2H_5	H	233 (8,0)	130 (2,9)	70 (4,0)	163 (1,5)	121 (32,1)	77 (62,0)	205 (64,8)	102 (8,4)	103 (20,5)	97 (45,3)	104 (57,2)
VIII	Br	H	283 (39,4), 285 (40,9)	—	120 (3,1), 122 (4,7)	163 (2,1)	121 (28,9)	77 (40,8)	255 (56,9), 257 (60,9)	152 (4,0), 154 (4,0)	103 (14,7)	147 (24,2), 149 (24,1)	104 (100)
IX	H	H	219 (3,6)	—	—	—	121 (22,5)	77 (18,0)	191 (100)	88 (19,1)	103 (3,2)	69 (16,2)	118 (7,3)
X	C_2H_5	H	247 (6,4)	—	—	—	121 (36,0)	77 (8,3)	219 (52,9)	116 (1,0)	103 (2,3)	97 (1,5)	118 (29,2)
XI	H	H	301 (18,0)	—	—	—	121 (32,1)	77 (21,9)	273 (100)	172 (71,5)	—	69 (68,5)	200 (94,5)
XII	CH_3	H	233 (0,2)	130 (12,2)	70 (100)	163 (8,9)	121 (32,1)	77 (20,5)	205 (64,8)	—	103 (19,0)	—	—

* I–VIII R^1=H; IX, X, XII R^1=CH_3; XI R^1=$COCF_3$.

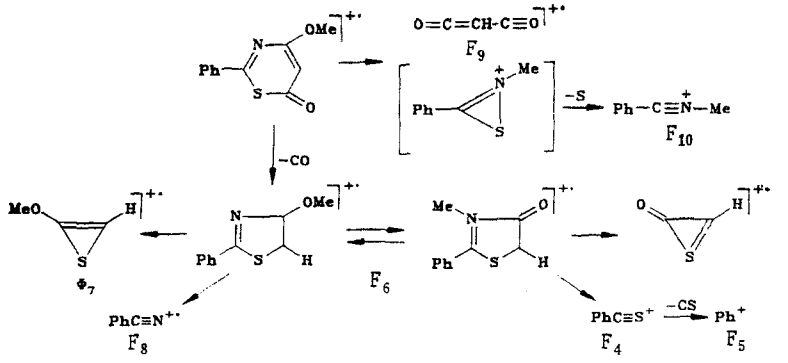
In order to detect the presence in the gas phase of either of the tautomeric forms of the investigated compounds, we investigated the paths of decomposition during electron impact of compounds IX-XII, which served as models for the dicarbonyl and hydroxycarbonyl forms. The decomposition of 5,5-dimethyl-2-phenyl-4,6-dioxo-1,3-thiazine (XII), model of the dioxo form, follows several, clearly observed at 70 eV, paths (Scheme 2). According to the overall ionic flow, the path $M^{+\cdot} \rightarrow F_2F_3 \rightarrow F_4 \rightarrow F_5$ is of a higher preference. The ion A [m/z 70, $(CH_3)_2C{=}C{=}O^{+\cdot}$], formed directly from the molecular ion, has the maximal intensity. The path $M^{+\cdot} \rightarrow F_6 \rightarrow F_7F_8$ is also of interest because these ions are typical only of the diketone form. We must particularly point out the absence of rearrangement processes during the decomposition of ions $M^{+\cdot}$ and $M{-}CO^{+\cdot}$ in the case of diketone XII.

Scheme 2



An analysis of the mass spectra of 4-methoxy-2-phenyl-1,3-thiazine-6-one (IX), model of the hydroxycarbonyl form, showed that its inherent fragmentation paths are different from the dicarbonyl form XII. The main decomposition direction of methoxythiazine IX should be considered the path $M^{+\cdot} \rightarrow F_6 \rightarrow F_7F_8$ (Scheme 3). The difference is that the maximal intensity belongs to the peak of ion D^1, formed when a molecule of CO (100%) is eliminated from the molecular ion. Another path, $M^{+\cdot} \rightarrow F_9 \rightarrow F_{10}$, is also of interest because in this case ion m/z 69 ($O{=}C{=}CH{-}C{\equiv}O^{+}$), absent in the spectrum of the dioxo form XII, and the rearrangement ion m/z 118, typical only of compound IX, are formed. The decomposition paths of 4-methoxy-5-ethyl-2-phenyl-1,3-thiazine-6-one (X) and of 4-trifluoroacetoxy-2-phenyl-1,3-thiazine-6-one (XI) are identical to those observed in the case of 4-methoxythiazine IX.

Scheme 3



Thus, a comparison of the fragmentation paths of compounds with fixed dicarbonyl and hydroxycarbonyl forms allowed us to consider the ions m/z $40 + R^1 + R^2$ and M^+: $-(40 + R^1 + R^2)$ as typical of the dicarbonyl form, and ions m/z $68 + R^1$ and $Ar{-}C{\equiv}\overset{+}{N}R^1$ as typical of the hydroxycarbonyl form. Analogous ions (m/z 42 and 69) were selected earlier for the potentially tautomeric aliphatic 1,3-diketones [4].

Mass spectra of potentially tautomeric 2-aryl-4,6-dioxo-1,3-thiazines (I-VIII) exhibits peaks of both tautomeric forms (see Table 1), however, when their intensities are compared, it is possible to speak of a significant preponderance of the hydroxycarbonyl group.

EXPERIMENTAL

Compounds I-XII were prepared according to known methods [11, 12]. Their constants agreed with published data.

The mass spectra were obtained with a Hewlett-Packard 5985 instrument at an ionization tension of 70 eV. The temperature of the ionic source was 200°C in a direct input regime. The temperature of the setting system was 150-220°C. A thermogravimetric investigation of compounds I-XII by the material evaporation curves in the mass spectrometer and according to DTA curves, taken with a derivatograph manufactured by MOM (Hungary), showed that in the conditions used for recording the mass spectra the investigated substances did not pyrolyze.

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Z,E-ISOMERS OF 10,10-DIMETHYL-9-BENZYLIDENE-9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE AND REACTIONS OF 10,10-DIMETHYL-9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE UNDER CONDITIONS OF BASIC CATALYSIS

N. S. Prostatkov, A. V. Varlamov, Kossuo Kozm, A. E. Aliev, and A. A. Fomichev

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The synthesis of 9-benzylidenesilaazaanthracenes has been achieved, and the configurations of their Z- and E-isomers have been established. The reactions of silaazaanthracene in the presence of aromatic aldehydes and bases have been studied; these result in dimerization, oxidation, cleavage of the Si—C bond, and desilylation of the heterocyclic system.

We have previously synthesized various examples of dihydrosilaazaanthracenes and have studied their conformational states [1-3]. Based on the feasibility of the existence of their 9-benzylidene derivatives in the form of geometric isomers, differing from one another in the position of the phenyl group of the benzylidene fragment relative to the pyridine ring,

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Patrice Lumumba Peoples' Friendship University, Moscow 117923.

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