REPLACEMENT OF BROMINE BY HYDROGEN IN BROMO DERIVATIVES OF TETRAHYDROPYRIMIDO[4,5-b][1,4]BENZTHIAZINE UNDER CONDITIONS OF ELECTRON-IMPACT IONIZATION

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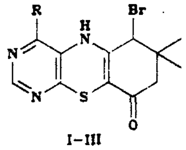
In a study of the electron-impact mass spectra* of 6-Br derivatives I-III of 6,7,8,9-tetrahydropyrimidio[4,5-b][1,4]benzthiazine we observed the presence of intense peaks of $[M-78]^+$ ions (A), which do not contain a Br atom. The intensities (I_{rel}) of the A ion peak in the spectra of I-III are 100% and exceed the intensities of the molecular-ion peaks by factors of 3.2, 2.8, and 3.2, respectively. The subsequent fragmentation of the A ions via the principal fragmentation pathway resembles the fragmentation of the molecular ions of I-III.



I-III

I R=Cl; II R=$N(CH_3)_2$; III R=OCH_3

Since, according to data from the NMR spectra and the results of elementary analysis, the presence of an admixed debrominated compound in samples of I-III was completely excluded, we studied the mass spectra of I-III at various ionization-chamber temperatures. We found that peaks of A ions and products of their fragmentation are completely absent in the spectra at ~50-60°C. These peaks appear only at ionization-chamber temperatures above 70°C, and their intensities increase as the source temperature is increased.

An analysis of the mass spectra of I-III recorded with the instrument after prior introduction of D_2O into the ion source revealed a marked decrease in the intensities of the A ions, which is accompanied by the appearance of $[A + 1]^+$ ion peaks and an increase in their intensities. Changes in the intensities of the isotope peaks in the molecular-ion group were not observed in the spectra; this indicated the absence of replacement of the labile proton of the NH group of I-III by deuterium under these conditions.

The data obtained demonstrate unequivocally that the appearance of A ions is due to an ion-molecular debromination reaction, viz., replacement of the Br atom by hydrogen (or deuterium) in the ion source. The possibility of the realization of such reactions, together with the already well-known protonation and methylation reactions, should be taken into account in conducting mass-spectrometric analyses.

Compounds I-III were obtained by bromination of the corresponding 9-oxotetrahydropyrimido[4,5-b][1,4]benzthiazines [1] with bromine in acetic acid.

Compound I had mp 228°C (from benzene) and was obtained in 76% yield; II had mp 202-204°C (from ethanol) and was obtained in 45% yield; III had mp 208-209°C (from ethanol) and was obtained in 62% yield. The results of elementary analysis of I-III were in agreement with the calculated values, and the IR and PMR spectra confirmed the proposed structures.

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*The mass spectra were obtained with a Varian MAT-112 mass spectrometer (USA) with direct introduction of the samples into the ion source. The temperature of the ionization chamber was 190°C, and the ionizing-electron energy was 70 eV.

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1-TELLURACHROMYLIUM PERCHLORATE

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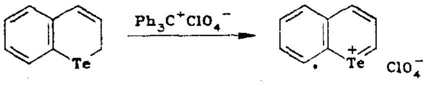
Derivatives of tellurapyrylium [1] and 1-tellurachromylium [2] cations were obtained relatively recently from the corresponding tellurapyrones and tellurachromones. We have synthesized the parent representative of 1-tellurachromylium salts, viz., 1-tellurachromylium perchlorate (I), by treatment of tellurachromene with trityl perchlorate in CF_3COOH:



A mixture of 2.44 g (10 mmole) of tellurachromene and 3.43 g (10 mmole) of trityl perchlorate in 50 ml of anhydrous trifluoroacetic acid was refluxed for 30 min. The triphenylmethane that precipitated when the mixture was cooled was removed by filtration, and the filtrate was evaporated on a water bath to a volume of 10 ml. The solution was cooled, and the crystals of I were removed by filtration, washed successively with 5 ml of cold trifluoroacetic acid and three times with 10 ml portions of absolute ether, and dried to give 1.2 g (35%) of fine dark-violet crystals with mp 160-162°C (dec.). IR spectrum (in mineral oil): 1670, 1640, 1580, 1530, 1320, 1260, 1150, 1100, and 760 cm^{-1}. UV spectrum (in CF_3COOH), λ_{max}, nm (log ε): 327 (3.99), 410 (3.31), and 560 (2.58). Found, %: C 31.6, H 2.2. $C_9H_7ClO_4Te$. Calculated, %: C 31.5, H 2.0.

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