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AROMATIZATION OF 2,3-DIHYDRO-3-HYDROXYPYRAZINE 1,4-DIOXIDES IN HSO_3F-SbF_5 SUPERACID: A NEW PATHWAY TO PYRAZINE 1,4-DIOXIDES

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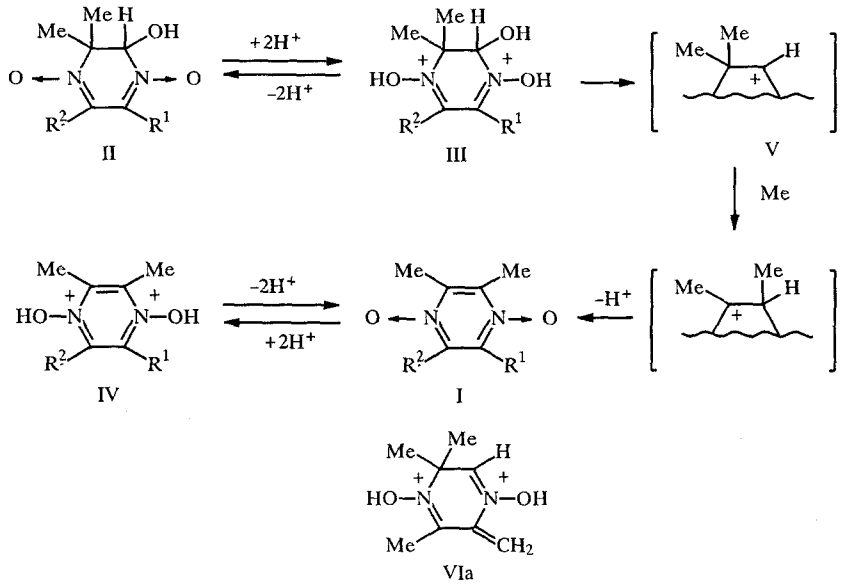
Pyrazine 1,4-dioxides hold interest as biologically active compounds, but methods for their synthesis are rather limited.

We propose a new approach for the preparation of pyrazine 1,4-dioxides I involving the rearrangement of 2,3-dihydropyrazine 1,4-dioxides II by the action of HSO_3F-SbF_5 superacid. In studying the behavior of IIa-IIc in acids by PMR spectroscopy, we found that upon maintenance of solutions of these compounds (c = 0.3 mole/liter) in HSO_3F-SbF_5 (1:1 mole ratio) at 140°C for 30 min, the PMR spectra of the protonated starting compounds (dications IIIa-IIIc) are entirely transformed into the spectra corresponding to protonated 2,3-dimethylpyrazine 1,4-dioxides Ia-Ic, namely, dications IVa-IVc. Neutralization of these solutions with sodium bicarbonate led to pyrazine 1,4-dioxides Ia-Ic, which were identified according to their melting points and PMR spectra [1-3]. The yields of Ia-Ic were 78, 57, and 87%, respectively.

The PMR spectra of dications IIIa and IVa* are given below as an example. IIIa (−20°C):† 1.85 and 2.12 (3H, s, 3H, s, 2,2-CH_3), 3.13 (6H, s, 5,6-CH_3), 6.30 (1H, s, 3-H), 9.67 (1H, s, N^+-OH), 11.10 ppm (1H, s, N^+-OH). IVa (40°C): 3.27 ppm (12H, s, 2,3,5,6-CH_3).

The key step in the aromatization is apparently the 1,2-shift of the methyl groups in intermediate carbocations V. Since such shifts are also characteristic for other substituents, this method may prove rather general.



I—V a $R^1 = R^2 = CH_3$, b $R^1 = CH_3$, $R^2 = H$, c $R^1 = R^2 = H$

*Some of the OH group signals were not observed, probably due to rapid proton exchange with the acid.

†SO_2ClF was added to reduce the viscosity.

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The required use of HSO_3F-SbF_5 superacid for this aromatization is probably a consequence of the need to provide conditions for formation of relatively unstable secondary ions V and suppress reactions involving external nucleophiles, which compete with the 1,2-methyl shift. Thus, in HSO_3F, in contrast to the more acidic HSO_3F-SbF_5 system, dication VIa rather than the protonated form of Ia is formed from dication IIIa. PMR spectrum of VIa (40°C): 2.22 (6H, s, 2,2-CH_3), 3.07 (3H, s, 6-CH_3), 7.43 (1H, d.d, J = 6 and 1.5 Hz, =CH), 7.68 (1H, d, J = 6 Hz, =CH), 8.83 ppm (1H, d, J = 1.5 Hz, 3-H).

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