STRUCTURE OF THE CONDENSATION PRODUCT OF BENZAMIDRAZONIUM IODIDE WITH ACETYLACETONE

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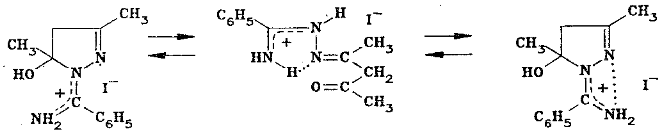
Attempts to synthesize the little studied 1,2,4-triazepine derivatives from β-dicarbonyl compounds and amidrazones or their salts have been unsuccessful [1-3], and the primary condensation products were assigned a hydrazone structure. In any case, such compounds can exist in theory in not only two linear forms (hydrazone and ene hydrazine), but also three cyclic forms, viz., 5-hydroxypyrazoline, 1,2,4-triazoline, and 7-hydroxy-1,3,4-triazepine.

We have studied the structure of such a product (I) from the reaction of benzamidrazonium iodide with acetylacetone. I was isolated in quantitative yield, mp 123-125° (from 2:1 ethyl acetate—acetonitrile).



Ia (E) Ib(E,Z) Ia (Z)

According to the PMR data, the product salt exists in solution as a tautomeric mixture of the 5-hydroxypyrazoline form Ia (which is present as two stereoisomers, Z and E, due to hindered rotation around the $C{-}N_{(1)}$ bond) and the hydrazone form Ib (E,Z) in the proportions Ib:Ia(Z):Ia(E) = 9:61:30. PMR spectrum ($DMSO{-}D_6$): Ib(E,Z) — 2.13 ($CH_3C{=}N$), 2.25 (CH_3CO), 3.77 ($\alpha{-}CH_2$), NH signals of low intensity and not localized; Ia(Z) — 1.02 ($5{-}CH_3$), 2.19 ($3{-}CH_3$), 3.12 and 3.35 (diastereotopic methylene protons, J_{AB} = 19.0 Hz), 9.45, 9.63 (NH_2) Ia(E) — 1.85 ($5{-}CH_3$), 1.96 ($3{-}CH_3$), 3.29 (CH_2), 8.69, 9.75 (NH_2). The aromatic ring protons give a multiplet in the 7.5-7.8 ppm region the OH protons of both Ia forms give a general broad signal at 7.40 ppm that disappears upon dilution with D_2O. Increase of temperature causes a broadening and consolidation of the signals of the E- and Z-isomers of the 5-hydroxypyrazoline form ($\Delta G^{\neq}$ = 85 kJ/mole). ^{13}C NMR spectrum ($DMSO{-}D_6$): Ib — 19.8 (CH_3CN), 30.7 (CH_3CO), 53.2 (CH_2), 161.3, 165.0 ($C{=}N_{(1)}$), 194.2 ($C{=}O$); Ia(Z) — 16.4 ($5{-}CH_3$), 24.0 ($3{-}CH_3$), 53.5 (CH_2), 95.0 ($C_{(5)}$), 160.4, 166.1 ($C_{(3)}$, $C{-}N^+$); Ia(E) — 16.7 ($5{-}CH_3$), 26.5 ($3{-}CH_3$), 52.1 (CH_2), 94.7 ($C_{(5)}$), 159.5, 164.2 ($C_{(3)}$, $C{-}N^+$); aromatic ring signals lie in 126-133 ppm region.

The free base, which is obtained by alkaline treatment of the salt (mp 91-93°, from acetonitrile) exists in $DMSO{-}D_6$ solution as a 39:61 tautomeric mixture of hydrazone and ene hydrazine forms. From the temperature dependence of the equilibrium constant the thermodynamic parameters of the ene hydrazine—hydrazone transition can be determined: ΔH° = 12.0 kJ/mole, ΔS° = 43.8 J/mole•deg.

The effect of structural factors on the position of the tautomeric equilibrium in solutions of the salts and free bases is being studied.

LITERATURE CITED

1. H. Neuenhoffer and F. Weischedel, Ann. Chem., 761, 34 (1972).
2. A. Spassov, E. Golovinsky, and G. Russev, Chem. Ber., 99, 3728 (1966).
3. S. K. Robev, Dokl. Bolg. Akad. Nauk, 36, 1315 (1983).

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