ISOMERIZATION OF TRIALKYLIDENE(ARYLIDINE) TRIAMINOGUANIDINES TO 4,5-DIHYDRO-1,2,4-TRIAZOLE DERIVATIVES

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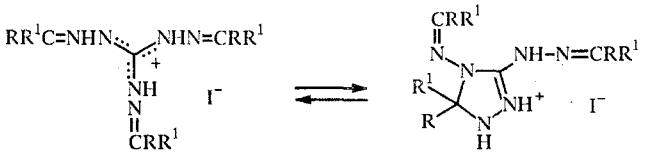
Some products of the condensation of triaminoguanidine with carbonyl compounds have found application as agents to combat coccidioses [1]; however, the structure of this class of substances has not been studied. We synthesized Ia-c by the action of the corresponding oxo compound on triaminoguanidinium iodide and investigated their structure in solutions by means of NMR spectroscopy.

Compound Ia in solution in d_6-DMSO has linear structure A, as does derivative Ib, if it is synthesized by brief heating in DMSO. Quantitative cyclization to isomer B is observed when it is refluxed for a long time in acetonitrile; this is confirmed by, in addition to other spectral details, the presence of the $C_{(5)}$ signal of the 1,2,4-triazoline ring at 70.2 ppm [2]. Immediately after dissolving in $CDCl_3$ or in d_6-DMSO, derivative Ic exists in the form of linear tautomer A; however, the A $\rightleftarrows$ B equilibrium is established after 24 h (the percentage of tautomer B is 20%).



A B

I a R = H, R^1 = $C_6H_4OCH_3$-*p*; b R = CH_3, R^1 = C_6H_5; c R = R^1 = CH_3

Compound Ia ($C_{25}H_{26}N_6O_3 \cdot HI$). This compound had mp 154-155°C (from DMF). ^1H NMR spectrum (d_6-DMSO): 3.78 (9H, s, $3CH_3$), 7.06-7.94 (15H, m, $12H_{arom}$ + 3NH), 8.70 ppm (3H, s, 3CH).

Compound Ib ($C_{25}H_{26}N_6 \cdot HI$). Form A has mp 190-192°C (from ethanol). ^1H NMR spectrum (d_6-DMSO): 2.64 (9H, s, $3CH_3$), 7.70 (9H, m, m- and p-H), 8.20 ppm (6H, m, o-H). Form B had mp 164-165°C (from acetonitrile). ^1H NMR spectrum (d_6-DMSO): 1.68 (3H, s, 5-CH_3), 2.38 and 2.64 (6H, s, $2CH_3$), 6.12 [1H, s, $N_{(1)}H$], 7.36-8.36 ($15H_{arom}$, m), 10.08 and 10.22 ppm [2H, s, $N_{(2)}H$ and NH_{exo}]. ^{13}C NMR spectrum (d_6-DMSO): 150.6; 152.4 and 153.2 (3C=N); 125.4-141.1 ($12C_{arom}$); 70.2 [$C_{(5)}$]; 26.3, 14.5, and 14.3 ppm ($3CH_3$).

Compound Ic ($C_{10}H_{20}N_6 \cdot HI$). This compound had mp 136-137°C (from acetone). ^1H NMR spectrum of form A ($CDCl_3$): 2.16 (18H, s, $6CH_3$); 12.53 ppm (3H, br, 3NH, in d_6-DMSO). Form B: 1.27 (6H, s, two 5-CH_3); 1.96, 2.03, 2.05, and 2.12 (12H, s, $4CH_3$), 5.50 ppm [1H, s, $N_{(1)}H$].

Satisfactory results of elementary analysis for the C, H, and N content were obtained for Ia-c.

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