REACTION OF 2,3-DIHYDRO-4-PHENYL-1H-1,5-BENZODIAZEPINETHIONE-2 WITH ACETYLHYDRAZINE

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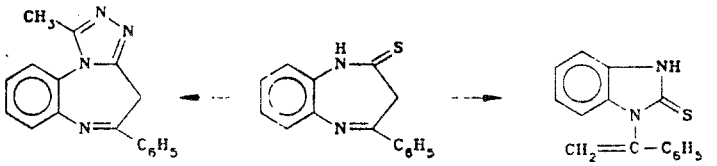
2,3-Dihydro-4-phenyl-1H-1,5-benzodiazepinethione-2 (I) on heating in DMF both with acetylhydrazine and in its absence undergoes a [1, 3]-sigmatropic rearrangement into 1-(1-phenylvinyl)benzimidazole-2-thione (II). A similar thermal rearrangement has been noted previously for the oxygen analog of compound I [1, 2].



III I II

If the starting materials are heated in chloroform the chief reaction product is 1-methyl-5-phenyl-4H-1,2,4-triazolo[4,2-*a*][1,5]benzodiazepine (III). The formation of similar tricyclic systems has been reported for 1,4-benzodiazepinethiones [3, 4].

The results of elemental analyses corresponded to the calculated compositions.

1-Phenylvinylbenzimidazole-2-thione (II). A solution of 2.52 g (10 mmoles) compound I in 20 ml DMF was heated at bp for 4 h. The solvent was distilled off and the residue recrystallized from 2-propanol, mp 187-188°C. IR spectrum (KBr) (cm^{-1}): 3240 (NH), 1192 (C=S), 900 (=CH_2). PMR spectrum (DMSO-D_6) (δ, ppm): 5.57 and 6.40 (each 1H, s, =CH_2), 6.85-7.65 (9H, m, H_{Ar}), 13.09 (1H, m, NH). Mass spectrum, m/z (I_{rel}, %: here and below the 10 most intense peaks are listed): 252 (M^+, 100), 251 (78), 220 (32), 219 (29), 150 (88), 103 (70), 91 (25), 90 (20), 77 (82), 51 (38).

1-Methyl-5-phenyl-4H-1,2,4-triazolo[4,3-*a*][1,5]benzodiazepine (III). A mixture of 1.26 g (5 mmoles) compound I and 1.11 g (15 mmoles) acetylhydrazine in 20 ml chloroform was heated at bp for 24 h. The solvent was distilled off and the residue washed with water and dried. A mixture of compounds II and III was obtained which was separated by column chromatography (Al_2O_3, 4:1 $CHCl_3$-hexane). Two substances were separated.

Compound I. Yield 0.11 g (9%).

Compound II. Mp 104°C (from ethanol). IR spectrum (KBr) (cm^{-1}): 1450-1550 (C=N). PMR spectrum ($CDCl_3$, δ, ppm): 210 (3H, s, CH_3), 5.58 and 6.20 (each 1H, d, J = 12.0 Hz, CH_2), 6.84-7.38 (9H, m, H_{Ar}). Mass spectrum, m/z (I_{rel}, %): 274 (M^+, 100), 246 (59), 245 (20), 149 (18), 144 (18), 132 (22), 131 (28), 116 (23), 102 (18), 77 (31). Yield 0.93 g (68%).

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