SYNTHESIS OF DERIVATIVES OF A NEW HETEROCYCLIC SYSTEM – 1,2,4-DITHIAZEPINE

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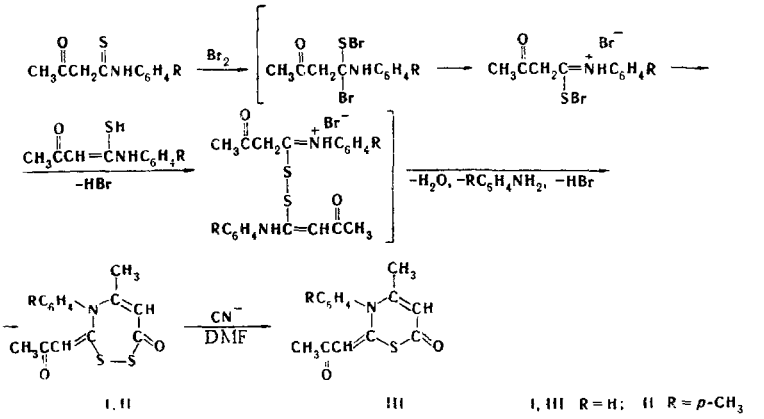
Prior to our research 1,2,4-dithiazepine and its substituted derivatives were unknown. We have shown that compounds of this series (I and II) can be obtained by the action of half-molar amounts of bromine on solutions of acetylthioacetic acid arylamides in chloroform at low temperature. The reaction evidently proceeds via the following scheme:



I, II III I, III R = H; II R = *p*-CH_3

EXPERIMENTAL

3-Acetonylidene-4-phenyl-5-methyl-1,2,4-dithiazepin-7-one (I). This compound, with mp 197-198° (two recrystallizations from absolute alcohol; it began to decompose at 199-201° with the evolution of gas bubbles) and M 309.8 (cryoscopically in dioxane) at 280 (ebullioscopically in dichloroethane) (calculated M 291.39), was obtained in 84% yield. PMR spectrum (in CF_3COOH), δ, ppm: 8.15, 7.15 (5H, m, phenyl ring); 5.65 (2H, s, =CH); 2.15 (6H, s, CH_3). IR spectrum (in KBr): 3060, 3030, and 3010 (phenyl ring); 2930 (CH_3); 1615 cm^{-1} (C=O). UV spectrum (in ethanol): λ_{max} 343 nm (log ε 4.80).

3-Acetonylidene-4-(p-tolyl)-5-methyl-1,2,4-dithiazepin-7-one. This compound, with mp 222-224° (dec., twice from absolute ethanol), was obtained in 67% yield.

The presence of a disulfide bond in I was confirmed by its conversion by means of cyanide ion in dimethylformamide to a cyclic monosulfite – 2-acetonylidene-3-phenyl-4-methyl-1,3-thiazin-6-one (III) – with mp 181-182° (recrystallized twice from ethanol) and M 259 (mass spectroscopically) (M calculated 259), in 74% yield. IR spectrum (KBr): 1665, 1610 (C=O); 1590 cm^{-1} (C=C). UV spectrum (in ethanol), λ_{max}, nm (log ε): 223 (4.26), 240 (4.04), 288 (3.93), 351 (4.65), 356 (4.64).

The results of elementary analysis of I, II, and III were in agreement with the calculated values.

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