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A NEW HETEROCYCLIC SYSTEM 4-THIA-1,3,7a, 9-TETRAAZACYCLOPENTA[*def*]PHENANTHRENE

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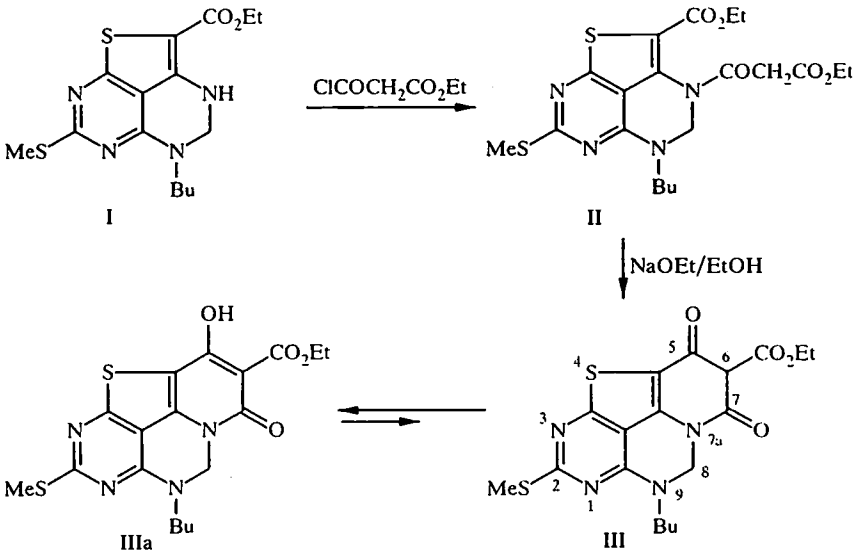
Studies directed toward the creation of methods and routes for the synthesis of condensed heterocyclic pyrimidines, which are of interest in the plan for the discovery of biologically active substances [1-4], have led to the synthesis of the first example of a new heterocyclic system – ethyl 9-butyl-2-methylthio-5,7-dioxo-6,7,8,9-tetrahydro-5H-4-thia-1,3,7a,9-tetraazacyclopenta[*def*]phenanthren-6-carboxylate (III).



Synthesis of the desired compound III was achieved by acylation of ethyl 5-butyl-7-methylthio-3,4-dihydro-5H-1-thia-3,5,6,8-tetraazaacenaphthylen-2-carboxylate (I), which we had prepared previously [4], ethoxycarbonylacetyl chloride in boiling benzene with subsequent Diekmann cyclocondensation of the acyl derivative II.

It was established by ^{1}H NMR spectroscopy that compound III in chloroform solution is transformed into the enol form III a, which is evidently stabilized by an intramolecular hydrogen bond between the proton of the enol OH group and the carbonyl oxygen of the ester group. The signal of the proton at $C_{(6)}$ in the ^{1}H NMR spectrum of compound III is observed at 7.79 ppm. The intensity of this signal decreases with time and the signal of an OH group appears at 14.26 ppm. A broad OH absorption band appears in the IR spectrum at 3424 cm^{-1}.

Ethyl 5-Butyl-7-methylthio-3-(ethoxycarbonylacetyl)-3,4-dihydro-5H-1-thia-3,5,6,8-tetraazaacenapthylen-2-carboxylate (II). A mixture of compound I [4] (0.5 g, 1.4 mmol), anhydrous benzene (20 ml), and ethoxycarbonylacetyl chloride (0.36 ml, 0.42 g, 2.8 mmol) was boiled for 2 h. The solvent was evaporated to dryness, and the residue recrystallized to give compound II (0.31 g, 47%), m.p. 129-130°C (from ethyl acetate). ^{1}H NMR spectrum ($CDCl_3$):

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0.95 (3 H, t, CH_3), 1.37 (7 H, m, CH_3, CH_2CH_2), 2.57 (3 H, s, SCH_3), 3.73 (4 H, NCH_2, OCH_2), 3.92 (2 H, q, OCH_2), 4.35 (2 H, q, OCH_2), 5.2 ppm (2 H, s, CH_2). IR spectrum: 1744, 1705, 1688 cm^{-1} (CO). Found, %: C 51.40, H, 5.48, N 11.78. Calc. for $C_{20}H_{26}N_4O_5S_2$, %: C 51.49, H 5.62, N 12.01.

Ethyl 9-Butyl-2-methylthio-5,7-dioxo-6,7,8,9-tetrahydro-5H-4-thia-1,3,7a,9-tetraazacyclopenta[*def*]phenanthren-6-carboxylate (III). Sodium ethoxide in ethanol, prepared from sodium (0.005 g, 0.2 mmol) and anhydrous ethanol (5 ml) was added dropwise at 5-10°C to a suspension of compound II (0.1 g, 2 mmol) in ethanol (3 ml). The reaction mixture was stirred for 2 h at 10°C, acidified to pH 2.0 with hydrochloric acid, and the precipitate filtered off to give compound III (0.06 g, 55%), m.p. 185-187°C (from ethanol). ^1H NMR spectrum ($CDCl_3$): 0.87 (3 H, t, CH_3), 1.36 (7 H, m, CH_3, CH_2CH_2), 2.49 (3 H, s, SCH_3), 3.62 (2 H, t, NCH_2), 4.36 (2 H, q, OCH_2), 5.38 (2 H, s, CH_2), 7.79 (1 H, s, CH), 14.26 ppm (1 H, s, OH). IR Spectrum: 3424 (OH), 1675, 1612 cm^{-1} (CO). Found, %: C 51.25, H 5.33, N 12.94. Calc. for $C_{18}H_{22}N_4O_4S_2$, %: C 51.17, H 5.25, N 13.26.

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