SYNTHESIS OF SUBSTITUTED 4H-1,3-BENZOTHIAZINES

V. A. Zagorevskii, K. I. Lopatina,
T. V. Sokolova, and S. M. Klyuev

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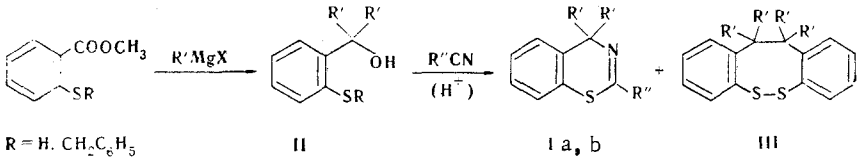
We have accomplished the synthesis of previously unknown 4,4-dialkyl-4H-1,3-benzothiazines (I) by reaction of 2-mercapto-α,α-dialkylbenzyl alcohols with nitriles under the influence of acidic agents (H_2SO_4, $HClO_4$) via the scheme



R = H, $CH_2C_6H_5$ II I a, b III

I a R″ = CH_3; b R″ = C_6H_5; III R′ = C_2H_5

The IR, UV, and PMR spectral data are in agreement with assigned structure I. Spontaneous debenzylation occurs under the conditions of condensation of alcohol II (R = $CH_2C_6H_5$) with nitriles. In addition to benzothiazine I, 7,7,8,8-tetraethyl-7,8-dihydrodibenzo[c,g]thiathiocine (III) is formed. The structure of III was confirmed by its IR spectrum (absence of OH and SH groups) and mass spectum (symmetrical disintegration of the molecular ion with m/e 356 to a fragment ion with m/e 178, which is accompanied by a metastable transition). Nonequivalence of the CH_2 (and CH_3) protons is observed in the PMR spectrum of III; this seems of interest for the conformational analysis of this sort of eight-membered sulfur-containing ring.

EXPERIMENTAL

2-Methyl-4,4-diethyl-4H-1,3-benzothiazine (Ia). This compound had bp 94-95° (2 mm) and n_D^{20} 1.5652. Found: C 71.2; H 7.8; N 6.2; S 14.7%. $C_{13}H_{17}NS$. Calculated: C 71.2; H 7.8; N 6.4; S 14.6%. The individuality of the compound was monitored by this thin layer-chromatography and gas–liquid chromatography. The picrate of Ia had mp 161-162°. Found: C 51.0; H 4.4; N 12.5; S 7.5%. $C_{13}H_{17}NS \cdot C_6H_3N_3O_7$. Calculated: C 50.9; H 4.5; N 12.5; S 7.2%. The picrate of Ib had mp 176.5-.77° (from alcohol). Found: C 56.3; H 4.4; N 11.1; S 6.2%. $C_{18}H_{19}NS \cdot C_6H_3N_3O_7$. Calculated: C 56.4; H 4.3; N 11.0; S 6.2%.

Compound III had mp 88-89°. Found: C 74.1; H 8.0; S 17.7%. $C_{22}H_{28}S_2$. Calculated: C 74.1; H 7.9; S 17.9%.

Institute of Pharmacology, Academy of Medical Sciences of the USSR, Moscow.
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