BASE CATALYZED CONDENSATION OF THIOBARBITURIC ACID WITH SOME AROMATIC ALDEHYDES

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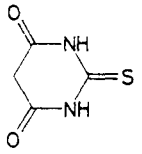
The 2-thiobarbituric acid (*I*) represents an attractive compound due to its possibility to react in a different way with the formation of interesting derivatives with potential biological activity. The condensation reaction between 2-thiobarbituric acid (*I*) and carbonyl compounds is treated only in a few papers and the named reaction is acid catalyzed[1-5] or the used catalyst is not given[6]. The acid catalyzed condensation of 2-thiobarbituric acid with carbonyl compounds is also used as a spot reaction in the aromatic aldehydes test[7].



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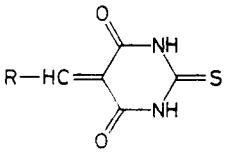

II, R = 4-$CH_3OC_6H_4$
III, R = 4-$C_2H_5OC_6H_4$
IV, R = 4-$C_5H_5CH_2OC_6H_4$
V, R = 1-naphthyl

In this paper the base catalyzed condensation reaction of 2-thiobarbituric acid with some aromatic aldehydes resulting in the formation of 5-arylidene-2-thiobarbituric acids is described. The condensation reaction of 2-thiobarbituric acid was carried out with 4-methoxybenzaldehyde, 4-ethoxybenzaldehyde, 4-benzyloxybenzaldehyde, and 1-naphthaldehyde using morpholine[8] as a catalyst. The yields are very high, with exception of 4-ethoxybenzaldehyde.

It could be supposed that the lower yield is caused due to the presence of ethyl group which have higher negative influence through resonance and inductive effects on the polarization of the aldehyde group with the respect to the fact, that all condensation reaction were carried out in the same conditions and the solubility of all synthesized derivatives in the reaction medium is practically the same.

EXPERIMENTAL

Melting points were not corrected. IR spectra were recorded on a Perkin–Elmer 437 spectrophotometer as a KBr discs (wave numbers in cm^{-1}). Mass spectra were recorded on a Shimadzu QP 1000 EX spectrometer.

General Procedure for the Condensation of 2-Thiobarbituric Acid (*I*) with Aldehydes

In the apparatus provided with the Dean–Stark device the benzene solution of 2-thiobarbituric acid (*I*; 720 mg, 5 mmol), aldehyde (5 mmol), morpholine (0·2 ml), and glacial acetic acid (0·1 ml) is heated 15 h. In the course of reaction from the solution crystals of the product were separated, which are filtered off, recrystalized from mixture dioxane–water and dried on air.

5-(4-*Methoxybenzylidene*)-2-*thiobarbituric acid* (II): yield 1 272 mg, (97%), m.p. >280°C (decomp.). For $C_{12}H_{10}N_2O_3S$ (262·3) calculated: 54·95% C, 3·84% H, 10·68% N, 12·22% S; found 54·70% C, 4·06% H, 10·49% N, 12·03% S. IR spectrum: 3 630—3 300, 3 270—2 980, 2 970—2 400, 1 700, 1 680—1 620, 1 605, 1 560—1 480, 1 435, 1 415, 1 395, 1 350, 1 315, 1 275, 1 215, 1 180, 1 150, 1 005, 840, 790, 525, 500, 460. Mass spectrum, *m/z* (%): 262 (100, M^+), 247 (55), 231 (31), 188 (15), 150 (33), 118 (26), 103 (26), 64 (12).

5-(4-*Ethoxybenzylidene*)-2-*thiobarbituric acid* (III): yield 1 030 mg (75%), m.p. 300°C (decomp.). For $C_{19}H_{12}N_2O_3S$ (276·3) calculated: 56·51% C, 4·38% H, 10·14% N, 11·60% S; found: 56·38% C, 4·16% H, 10·31% N, 11·39% S. IR spectrum: 3 650—3 320, 3 280—3 100, 3 080, 2 980, 2 920, 1 700, 1 690—1 630, 1 610, 1 590—1 485, 1 475, 1 450, 1 435, 1 395, 1 355, 1 315, 1 270, 1 220, 1 190—1 140, 1 110, 1 045, 980, 925, 860, 840, 790, 580, 530, 435. Mass spectrum, *m/z* (%): 276 (100, M^+), 247 (55), 231 (31), 188 (15), 150 (33), 118 (25), 89 (26), 64 (18), 42 (12).

5-(4-*Benzyloxybenzylidene*)-2-*thiobarbituric acid* (IV): yield 1 680 mg (99%), m.p. 271°C (decomp.). For $C_{18}H_{14}N_2O_3S$ (338·3) calculated: 63·88% C, 4·17% H, 8·28% N, 9·48% S; found: 63·60% C, 3·97% H, 8·01% N, 9·16% S. IR spectrum: 3 640—3 300, 3 260—2 995, 2 980—2 800, 1 700, 1 690—1 620, 1 605, 1 570, 1 560—1 490, 1 435, 1 400, 1 390, 1 315, 1 270, 1 220, 1 180, 1 120, 1 050—960, 840, 790, 745, 700, 610, 525, 510, 480. Mass spectrum, *m/z* (%): 338 (89, M^+), 247 (55), 188 (33), 144 (16), 101 (22), 91 (100), 43 (19).

5-(1-*Naphthylidene*)-2-*thiobarbituric acid* (V): yield 1 400 mg (99%), m.p. 262°C (decomp.). For $C_{15}H_{10}N_2O_2S$ (282·3) calculated: 63·82% C, 3·57% H, 9·92% N, 11·36% S; found: 63·66% C, 3·42% H, 9·89% N, 11·15% S. IR spectrum: 3 700—3 300, 3 280—2 980, 2 960—2 840, 1 695, 1 690—1 660, 1 595, 1 580—1 500, 1 440, 1 410, 1 380, 1 330—1 300, 1 275, 1 245, 1 230—1 195, 1 180, 1 145, 1 070—1 040, 870, 810, 795, 775, 710, 530, 505, 485. Mass spectrum, *m/z* (%): 282 (100, M^+), 222 (37), 180 (35), 152 (45), 127 (6), 111 (10), 76 (18), 59 (92).

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