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# SYNTHESIS OF SOME 4-THIAZOLIDONE DERIVATIVES FROM 4-(CYCLO-3-ALKENYL)THIOSEMICARBAZONES

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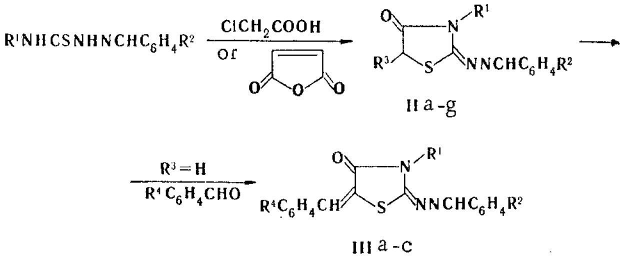
The reaction of 4-(cyclo-3-pentenyl)- and 4-(cyclo-3-hexenyl)thiosemicarbazones with chloroacetic acid gave 2-hydrazono derivatives of 3-cyclo-pentenyl(cyclohexenyl)thioazolid-4-one, the condensation of which with aromatic aldehydes gave 5-benzylidene derivatives. Representatives of 4-thiazolidone with a carboxy group in the 5 position were synthesized by condensation of the same thiosemicarbazones with maleic anhydride. Some of the substances obtained have bactericidal activity.

Pseudothiohydantoin derivatives that have a broad range of antimicrobial and pharmacological activity because of their structural similarity to a number of the most important antibiotics have been obtained by condensation of thiosemicarbazones with α-halo carboxylic acids [1-4]. 4-Thiazolidine derivatives that contain a carboxymethyl group in the 5 position have been obtained by the reaction of thiosemicarbazones with maleic anhydride [5, 6]. It is also known [2, 7] that the introduction of alkyl or aryl substituents in molecules of medicinals is often accompanied by a significant increase in their physiological effect.

In this connection, we synthesized pseudothiohydantoin derivatives (IIa-g) that contain a cycloalkenyl grouping by condensation of 4-(cyclo-3-pentenyl)- and 4-(cyclo-3-hexenyl)-thiosemicarbazones (I) with chloroacetic acid and maleic anhydride.

5-Benzylidene derivatives (IIIa-c), which were also obtained in one step by condensation of thiosemicarbazone Ia with chloroacetic acid and aromatic aldehydes, were synthesized by condensation of derivatives II with aromatic aldehydes, respectively.



IIa-g

IIIa-c

I $R^1$=cyclo-3-pentenyl or cyclo-3-hexenyl; ; II a $R^1$=cyclo-3-pentenyl,$R^2=R^3$=H; b $R^1$=cyclo-3-pentenyl $R^2$=OH-2, $R^3$=H; c $R^1$=cyclo-3-pentenyl $R^2$=H, $R^3=CH_2COOH$; d $R^1$=cyclo-3-pentenyl,$R^2$=OH-2, $R^3=CH_2COOH$; e $R^1$=cyclo-3-pentenyl,$R^2=NO_2$-3, $R^3=CH_2COOH$; f $R^1$=cyclo-3-pentenyl,$R^2$=OH-2, $R^3$=H; g $R^1$=cyclo-3-hexenyl $R^2=N(CH_3)_2$-4, $R^3$=H; III $R^1$= cyclo-3-pentenyl, a $R^2=R^4$=H; b $R^2$=H, $R^4$=OH-2; c $R^2$=OH-2, $R^4$=H

The identical character of III obtained by the different variants is confirmed by data from their IR spectra. Thus absorption bands at 670 ($\delta_{C-H}$ in the benzene ring), 760 ($\gamma_{C-S-C}$), 990 ($\delta_{C-H}$ in C=CH), 1330 and 1340 ($\delta_{C-OH}$), 1400 ($\delta_H$ in C=CH), 1500 (aromatic ring), 1550 ($\gamma_{C=N}$), and 1580 cm$^{-1}$ (conjugated $\gamma_{C=C}$).

Compounds I have bactericidal activity. The preparations had a selective effect on microbes that use molecular oxygen for oxidative processes.

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TABLE 1. Characteristics of the Synthesized II and III

| Compound | mp, °C | $R_f$[a] | UV spectrum, $\lambda_{max}$, (log ε) | Found, % | | | Empirical formula | Calc., % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | N | S | | C | N | S | |
| IIa | 178 | 0,78[b] | 235 (3,93), 285 (4,30), 315 (4,28) | 62,5 | — | 11,2 | $C_{15}H_{15}N_3OS$ | 63,1 | — | 11,2 | 62 |
| IIb | 200—201 | 0,82[c] | 245 (3,98), 290 (4,41), 363 (4,48) | 58,9 | 13,7 | — | $C_{15}H_{15}N_3O_2S$ | 59,8 | 13,9 | — | 70 |
| IIc | 96—98 | 0,86[d] | 245 (4,20), 312 (4,35) | 60,5 | — | 9,2 | $C_{17}H_{17}N_3O_3S$ | 59,5 | — | 9,3 | 52 |
| IId | 143—144 | 0,62[c] | 237 (4,17), 295 (4,30), 332 (4,22) | 56,3 | — | 9,4 | $C_{17}H_{17}N_3O_4S$ | 56,8 | — | 8,9 | 61 |
| IIe | 175—176 | 0,59[e] | 265 (4,25), 285 (4,77), 305 (4,28) | — | 14,8 | 8,3 | $C_{17}H_{16}N_4O_5S$ | | 14,4 | 8,2 | 51 |
| IIf | 167—169 | 0,72[f] | 245 (4,78), 290 (4,37), 330 (4,31) | 61,1 | 12,9 | — | $C_{16}H_{17}N_3O_2S$ | 60,9 | 13,0 | — | 69 |
| IIg | 152—153 | 0,90[d] | 238 (4,00), 310 (3,98), 350 (4,48), 390 (4,02) | 63,1 | — | 9,4 | $C_{18}H_{22}N_4OS$ | 62,97 | — | 9,3 | 48 |
| IIIa | 181—182 | 0,61[f] | 245 (4,26), 360 (4,44), 370 (4,46) | 70,7 | — | 8,6 | $C_{22}H_{19}N_3OS$ | 70,8 | — | 8,6 | 53 |
| IIIb | 178 | 0,66[f] | 245 (4,10), 295 (4,54), 350 (4,40) | 68,8 | 10,6 | — | $C_{22}H_{19}N_3O_2S$ | 67,9 | 10,8 | — | 64 |
| IIIc | 195—196 | 0,83[b] | 230 (4,36), 300 (4,52), 365 (4,56), 420 (3,00) | 68,2 | 10,5 | — | $C_{22}H_{19}N_3O_2S$ | 67,9 | 10,8 | — | 54 |

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[a] Thin-layer chromatography in ethanol—benzene. [b] 1:1. [c] 1:3. [d] 1:4. [e] 1:2. [f] 4:1.

## EXPERIMENTAL

The IR absorption spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer. The UV spectra of solutions in ethanol were recorded with an SF-4 spectrophotometer. Compounds I were obtained by the method in [8]. The characteristics of the compounds obtained are presented in Table 1.

4-Thiazolidones (IIa,b,f,g). An equimolar mixture (11 mmole) of the corresponding thiosemicarbazide I, chloroacetic acid, and anhydrous sodium acetate in glacial acetic acid was refluxed for 1 h, after which the precipitate was removed by filtration, washed with hot water, and recrystallized from aqueous pyridine.

5-Carboxymethyl-4-thiazolidones (IIc-e). An equimolar mixture (12 mmole) of the corresponding thiosemicarbazide I and maleic anhydride in 15 ml of glacial acetic acid was refluxed for 1 h, and the precipitate was removed by filtration and recrystallized from ethanol.

5-Benzylidene-4-thiazolidones (IIIa-c). An equimolar mixture 5 mmole), of II, benzaldehyde or salicylaldehyde, chloroacetic acid, and anhydrous sodium acetate in glacial acetic acid was heated for 1 h, after which the precipitate was removed by filtration and recrystallized from aqueous pyridine.

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