SYNTHESIS OF THIENO[2,3-d]THIA[1]PYRANO[4,3-b]PYRROLE DERIVATIVES

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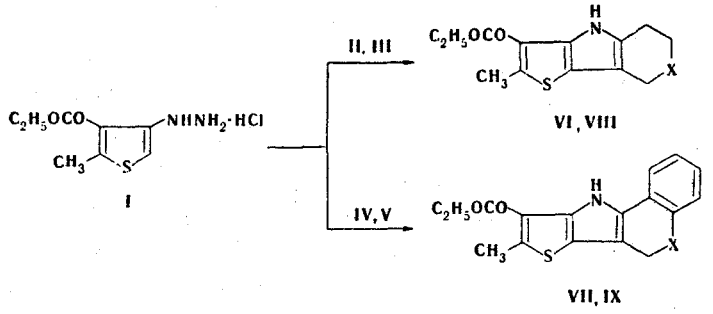
It is shown that 2-methyl-3-carbethoxy-4H,8H,5,6-dihydrothieno[2,3-d]thia[1]pyrano [4,3-b]pyrrole and 8-methyl-9-carbethoxy-10H,5,6-dihydrothieno[2,3-d]thia[1]chromeno[4,3-b]pyrrole and their S,S-dioxides, respectively, are obtained in the reaction of 2-methyl-3-carbethoxy-4-thienylhydrazine with tetrahydro-4-thiopyrone, tetrahydro-4-thiopyrone S,S-dioxide, 4-thiochromanone, and 4-thiochromanone S,S-dioxide in the presence of an acid catalyst.

In addition to arylhydrazines, hydrazines of the heteroaromatic series such as pyridyl- and quinolylhydrazines [1], hydrazinouracils, hydrazinopyrimidines (see [2-4]), etc. are used for the preparation of condensed pyrrole systems under the conditions of the Fischer reaction. A communication [5] regarding the use of 2-methyl-3-carbethoxy-4-thienylhydrazine (I) or its N-acyl derivative [6] in the synthesis of substituted thieno[3,2-b]pyrroles recently appeared.

In the present paper we report the reaction of hydrazine I with tetrahydro-4-thiopyrone (II), tetrahydro-4-thiopyrone S,S-dioxide (III), 4-thiochromanone (IV), and 4-thiochromanone, S,S-dioxide (V) in the presence of an acid catalyst.



VI, VII X = S; VIII, IX X = SO_2

As a result we obtained 2-methyl-3-carbethoxy-4H,8H,5,6-dihydrothieno[2,3-d]thia[1]pyrano[4, 3-b]pyrrole (VI) and 8-methyl-9-carbethoxy-10H,5,6-dihydrothieno[2,3-d]thia[1]chromeno[4,3-b] pyrrole (VII) and their S,S-dioxides (VIII and IX, respectively).

TABLE 1. Thieno[2,3-d]thia[1]pyrano[4,3-b]pyrrole Derivatives (VI-IX)

Compound	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	N	S		C	H	N	S	
VI	206—206,5	55,4	5,4	5,3	23,2	$C_{13}H_{15}NO_2S_2$	55,5	5,4	5,0	22,8	81
VII	136—137	—	—	4,4	19,2	$C_{17}H_{15}NO_2S_2$	—	—	4,3	19,5	90
VIII	274,5—275	49,5	4,8	4,8	20,1	$C_{13}H_{15}NO_4S_2$	49,8	4,8	4,8	20,5	50
IX	287 (dec.)	—	—	4,1	17,9	$C_{17}H_{17}NO_4S_2$	—	—	3,9	17,6	72

*The compounds were recrystallized: VI from benzene, VIII from acetic acid, and VII and IX from alcohol.

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EXPERIMENTAL

2-Methyl-3-carbethoxy-4H,8H,5,6-dihydrothieno[2,3-d]thia[1]pyrano[4,3-b]pyrrole (VI). A mixture of 1 g (4 mmole) of hydrazine hydrochloride I, 0.53 g (4.5 mmole) of ketone II, and 5 ml of absolute alcohol was refluxed for 5 min, after which it was cooled, and the precipitate was removed by filtration and washed with water to give 1 g of pyrrole VI. To obtain VII, the reaction mixture was refluxed in absolute alcohol for 20 min. The condensation of hydrochloride I with ketones III and V was carried out in a 2% alcohol solution of hydrogen chloride in equimolar amounts; the solutions were refluxed for 1 h and 5 h, respectively. An increase in the concentration of the alcohol solution of hydrogen chloride led to resinification of the mixture. The data for VI-IX are presented in Table 1.

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PYRROLES FROM KETOXIMES AND ACETYLENE

8.*SYNTHESIS OF 4,5,6,7-TETRAHYDROINDOLE AND ITS 1-VINYL DERIVATIVE

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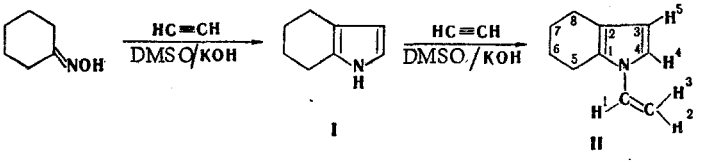
4,5,6,7-Tetrahydroindole or 1-vinyl-4,5,6,7-tetrahydroindole was obtained in 81 and 93% yields, respectively, by reaction of cyclohexanone oxime with acetylene at 90-140°C in the presence of alkali metal hydroxides or alkoxides in dimethyl sulfoxide (DMSO) or mixtures of DMSO with low-polarity or nonpolar solvents. The reaction is effective both in an autoclave (initial pressure 8-16 gage atm) and at atmospheric pressure.

In our previous communications [2, 3] we reported that 4,5,6,7-tetrahydroindole (I) and 1-vinyl-4,5,6,7-tetrahydroindole (II) were synthesized by the reaction of cyclohexanone oxime with acetylene:



I II

*See [1] for communication 7.

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