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SYNTHESIS OF VINYL AND ETHYL ETHERS OF 4- β -HYDROXYETHYL-1,4-PERHYDRO-THIAZINE 1,1-DIOXIDE

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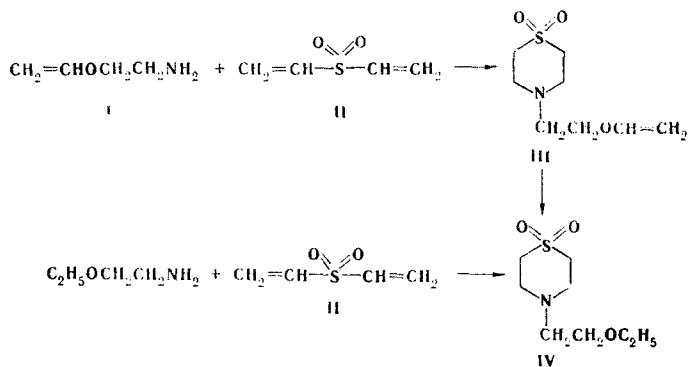
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Derivatives of 1,4-perhydrothiazine 1,1-dioxide that contain an ether group were synthesized by the reaction of vinyl and ethyl ethers of monoethanolamine with divinyl sulfone in methanol.

It is known that one of the methods for the synthesis of derivatives of 1,4-thiazine 1-oxide and 1,4-thiazine 1,1-dioxide is the reaction of primary amines with divinyl sulfoxide and divinyl sulfone [1-4]. A 1,4-thiazine 1,1-dioxide with an ester group was obtained by the reaction of glycine ethyl ester with divinyl sulfone [5]. N-Vinyloxy(alkoxy)alkyl-substituted 1,4-thiazine 1,1-dioxides have not yet been described in the literature.

In order to synthesize a 1,4-perhydrothiazine 1,1-dioxide derivative that contains a vinyl ether fragment we studied the reaction of monoethanolamine vinyl ether (I) with di-vinyl sulfone (II).

Vinyl ether I was subjected to reaction with an equimolar amount of sulfone II in methanol (with cooling) with subsequent brief refluxing of the reaction mixture. Heterocyclization occurs under these conditions, and 4- β -hydroxyethyl-1,4-perhydrothiazine 1,1-dioxide vinyl ether (III) is formed in 82% yield. The corresponding 4- β -hydroxyethyl-1,4-perhydrothiazine 1,1-dioxide ethyl ether (IV) was obtained by the reaction of monoethanolamine ethyl ether with sulfone II.



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Compounds III and IV are readily distillable (*in vacuo*) oily liquids that are quite soluble in many organic solvents. In the IR spectra of III and IV bands due to symmetrical and asymmetrical vibrations of the <SO_2 group of the thiazine oxide ring are found at 1130-1140 and 1335-1340 cm^{-1} [6]. The bands at 1625 and 3130 cm^{-1} are related to the absorption of a vinyl group, while the band at 1200 cm^{-1} is related to the absorption of a C—O—C= group. The observed shift of the absorption band of the ether bond to the long-wave region is apparently due to $\text{p-}\pi$ conjugation in the oxyvinyl group [7]. The structures of the compounds obtained were also confirmed by the PMR spectra and by catalytic hydrogenation of III, which leads to IV.

EXPERIMENTAL

The IR spectra of liquid films of the compounds were recorded with UR-20 and Specord 75 IR spectrometers. The PMR spectra of solutions in CDCl_3 were recorded with a Tesla BS-487 C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. Divinyl sulfone produced by Fluka AG (Switzerland) was used in this research. Vinyl ether I and monoethanolamine ethyl ether were obtained by the methods in [8] and [9], respectively.

4- β -Vinyloxyethyl-1,4-perhydrothiazine 1,1-Dioxide (III). A solution of 7.08 g (60 mmole) of sulfone II in 15 ml of methanol was added with stirring at -10°C to a solution of 5.22 g (60 mmole) of vinyl ether I in 15 ml of dry methanol (the sulfone solution was added in such a way that the temperature of the reaction mixture did not rise above $+10^\circ\text{C}$). The mixture was then refluxed for 1 h, after which the solvent was removed with a rotary evaporator, and the residue was distilled *in vacuo* to give 10.09 g (82%) of III with bp 128-130°C, n_D^{20} 1.5090, and d_4^{20} 1.2204. IR spectrum: 1200 (C—O—C=); 1625, 3130 (C=CH₂);

1130, 1310-1340 cm^{-1} (O=S=O). PMR spectrum: 2.5-3.1 [10H, m, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{S}$], 3.7 (2H, m, OCH₂), 3.9 (1H, d), 4.1 (1H, d), and 6.3 ppm (1H, q) ($J_{\text{ac}} = 14$, $J_{\text{bc}} = 7$, and $J_{\text{ab}} = -1.8$ Hz). Found: C 46.7; H 7.1; N 7.0; S 15.2%. $\text{C}_8\text{H}_{15}\text{NO}_3\text{S}$. Calculated: C 46.8; H 7.3; N 6.8; S 15.6%.

4- β -Ethoxyethyl-1,4-perhydrothiazine 1,1-Dioxide (IV). A) This compound was obtained by a method similar to that used to prepare III. The reaction of 3.56 g (40 mmole) of monoethanolamine ethyl ether and 4.72 g (40 mmole) of sulfone II gave 6.62 g (80%) of 4- β -ethoxyethyl-1,4-perhydrothiazine 1,1-dioxide (IV) with bp 132-134°C (2 hPa), n_D^{20} 1.4908, and d_4^{20} 1.1775. IR spectrum: 1140 (C—O—C); 1130, 1310-1335 cm^{-1} (O=S=O). PMR spectrum: 1.1 (3H, t, CH₃), 2.5-2.8 (2H, m, CH_2N), 3.0 [8H, m, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{S}$], and 3.2-3.6 ppm (4H, m, CH_2OCH_2). Found: C 46.0; H 7.9; N 6.5; S 15.1%. $\text{C}_8\text{H}_{17}\text{NO}_3\text{S}$. Calculated: C 46.4; H 8.2; N 6.8; S 15.5%.

B) The hydrogenation of 4.1 g (20 mmole) of vinyl ether III in 30 ml of ethanol in the presence of 1.0 g of Raney nickel was carried out in a catalytic hydrogenation flask up to the point of complete saturation. The catalyst was then removed by filtration, the solvent was removed with a rotary evaporator, and the residue was distilled *in vacuo* to give 3.06 g (74%) of IV, the IR and PMR spectral data for which were in agreement with the data for the sample obtained by method A.

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SYNTHESIS OF NEW CONDENSED HETEROCYCLES BY THE FISCHER METHOD

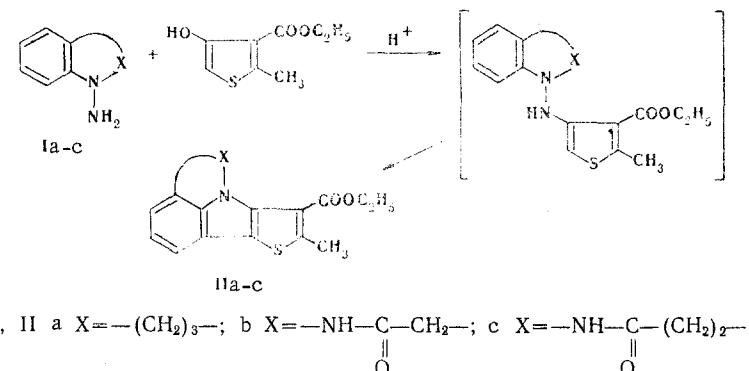
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Derivatives of thienoindolopyridine, thienoindolopyrazine, and thienoindolodiazepine derivatives were obtained by Fischer condensation of 2-methyl-3-carbethoxy-4-hydroxythiophene with 1-amino derivatives of tetrahydroquinoline, tetrahydroquinoxaline, and dihydro[1,5]benzodiazepin-4-one. Derivatives of indoloindolopyridine and indoloindolodiazepine were obtained in the reaction of N-acetylindoxyl with 1-amino derivatives of tetrahydroquinoline and dihydro[1,5]benzodiazepin-4-one under similar conditions.

The Fischer method, which is the most nearly universal method for the synthesis of diverse derivatives of indole, has found application for the preparation of condensed heterocycles [1, 2]. The method has made it possible to also obtain thieno[3,2-b]indole derivatives by condensation of 2-methyl-3-carbethoxy-4-hydroxythiophene with phenylhydrazine [3]. This is an unusual example of the Fischer reaction. The hydroxythiophene derivative exists in the hydroxy form, and its reaction with phenylhydrazine probably leads to a thienyl-phenylhydrazine derivative, which then undergoes a rearrangement similar to the o-benzidine rearrangement [4].

Further developments in research dealing with the synthesis of new condensed heterocycles are presented in the present paper. Derivatives of thieno[3',2'-2,3]indolo[1,7a,7-ab]pyridine (IIa), thieno[3',2'-2,3]indolo[1,7a,7-ab]pyrazine (IIb), and thieno[3',2'-2,3]indolo[1,7a,7-ab]diazepine (IIC) were obtained in the reaction of 1-amino derivatives of tetrahydroquinoline, tetrahydroquinoxalin-3-one, and dihydro[1,5]benzodiazepin-4-one with 2-methyl-3-carbethoxy-4-hydroxythiophene.



The reaction of 1-amino-1,2,3,4-tetrahydroquinoline (Ia), which was obtained by the method described in [5], with 2-methyl-3-carbethoxy-4-hydroxythiophene was carried out in acetic acid in the presence of concentrated hydrochloric acid at 70–80°C; the product was IIa. In other cases 1-amino-3-keto-1,2,3,4-tetrahydroquinoxaline (Ib) and 1-amino-2,3-dihydro[1,5]benzodiazepin-4-one (Ic), which were obtained by reduction of the corresponding nitroso derivatives [6, 7] with zinc in acetic acid, were subjected, without isolation from the reaction solution, to condensation with 2-methyl-3-carbethoxy-4-hydroxythiophene. As a result, we obtained IIb, c. Concentrated hydrochloric acid was also used as the catalyst.

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