CHLORINATION OF 4,4-DICHLOROCHROMENES WITH SULFURYL CHLORIDE

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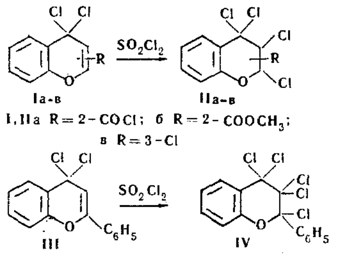
There is no information in the literature on the reactions of 4,4-dichlorochromenes with electrophilic reagents, while their reaction with nucleophilic reagents has been studied fairly widely (see, for example, [1]).

We have investigated the action of sulfuryl chloride on 4,4-dichlorochromenes substituted in the pyran ring. The course of the reaction depends on the nature of the substituent. However, the addition of a molecule of chlorine to the multiple bond of the pyran ring of the dichlorochromene (I) takes place with the formation of the corresponding polychlorochromane (II) or, as in the case of 4,4-dichloroflavene (III), simultaneously with the addition there is the replacement of the hydrogen in position 3 by chlorine with the formation of 2,3,3,4,4-pentachloroflavane (IV).



I, IIa R = 2-COCl; б R = 2-$COOCH_3$; в R = 3-Cl

The structure of the polychlorochromanes agrees with the data of the IR spectra and the NQR spectra and is confirmed by some of their reactions. The product of the chlorination of Ic, i.e., 2,3,3,4,4-pentachlorochromane (IIc) is converted on treatment with water (without isolation in the pure state) into 3,3,4,4-tetrachloro-2-hydroxychromane, which exists in the tautomeric form of 2,2,3,3-tetrachloro-3-(o-hydroxyphenyl)propionaldehyde (V) (in the IR spectrum, ν_{C-O} 1726 cm^{-1}). Under the same conditions, the tetrachloride **IIa** undergoes hydrolysis and cleavage with the elimination of carbon monoxide, giving, probably, 2,3,3-trichloro-3-(o-hydroxyphenyl)-propionic acid (VI), yield 83%, and a small amount of the known 3,4-dichlorocoumarin. In contrast to this, with methanol **IIa** forms **IIb**.

When **III** was boiled with an excess of sulfuryl chloride for 1 hr 30 min, after the sulfuryl chloride had been distilled off, the yield of IV was 66%, mp 143–144° C (from a mixture of benzene and petroleum ether). Found, %, C 47.17, 47.41; H 2.61, 2.67; Cl 46.12, 46.01. Calculated for $C_{15}H_9Cl_5O$, %: C 47.10; H 2.38; Cl 46.39.

Similarly (boiling for 3 hr), 2,3,4,4-tetrachloro-2-methoxycarbonylchromane (IIb) was obtained with a yield of 74%, mp 113.5–114° C (from ethanol). Found, %: C 39.92, 39.75; H 2.30, 2.40; Cl 42.66, 42.69. Calculated for $C_{11}H_8Cl_4O_3$, %: C 40.03; H 2.46; Cl 42.96. IR spectrum: $\nu_{C=O}$ 1752 cm^{-1}.

Sulfuryl chloride was boiled with **IIc** [2] (7 hr), the excess of the reagent was distilled off, aqueous dioxane (1 : 3) was added to the residue, after 7 days the solution was diluted with water and extracted with benzene, the extract was evaporated, and the residue was distilled in vacuum. The yield of V was 64%, mp 115–117° C (1 mm), n_D^{22} 1.5968. Found, %: C 37.93, 37.92; H 2.01, 1.96; Cl 49.49, 49.15. Calculated for $C_9H_6Cl_4O_2$, %: C 37.54; H 2.08; Cl 49.23.

Substance **VI**, mp 139° C (decomp.) is soluble in aqueous $NaHCO_3$ solution. Found, %: C 40.25, 40.15; H 2.98, 2.84; Cl 39.37, 39.25. Calculated for $C_9H_7Cl_3O_3$, %: C 40.11; H 2.62; Cl 39.47.

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SYNTHESIS OF 2-IODOMETHYL DERIVATIVES OF 1,4-DIOXANE AND TETRAHYDROPYRAN

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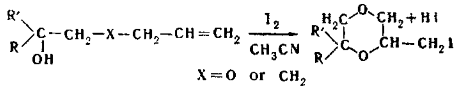
The known methods for synthesizing 2-iodomethyl derivatives of 1,4-dioxane and tetrahydropyran are characterized by a certain complexity [1,2]. We have considerably simplified the method of obtaining these compounds. The essence of the proposed method consists in that the starting material, which contains a double bond and a hydroxy group, is cyclized under the action of iodine in acetonitrile in accordance with the following scheme:



The reaction takes place by stirring a solution of iodine in acetonitrile with the appropriate compound at room temperature for 2–3 days. In the case of 1,4-dioxane derivatives, the reaction mixture may be boiled, which shortens the reaction time to 7–8 hr. By this method, we have obtained 2-iodomethyl-1,4-dioxane and 6-hydroxymethyl-2-iodomethyl-1,4-dioxane, the constants of which agree with those given previously [1, 3]. The structure of 2-iodomethyl-6,6-dimethyltetrahydropyran [bp 89° C (7 mm), n_D^{20} 1.5115, d_4^{20} 1.4867] has been confirmed by analyses and the IR spectrum.

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SYNTHESIS OF COMPOUNDS CONTAINING A NEW BIHETEROCYCLIC SYSTEM (s-TRIAZOLO [3,4-b]-s-TETRAZINE)

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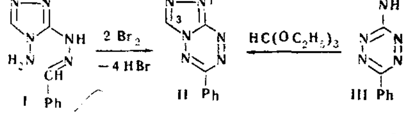
To study the fine structure and color of s-tetrazine, we have synthesized s-tetrazine with a fused s-triazole ring. First 4-amino-3-benzylidenehydrazino-1,2,4-triazole (I) [1] was brominated in chloroform at room temperature (1 mole of bromine per mole of I). The dibromide obtained (Found, %: Br 44.64. Calculated for $C_9H_6N_6 \cdot 2HBr$, %: Br 44.40), without further purification, was heated in chlorobenzene for 2 hr and the precipitate was filtered off. After the evaporation of the filtrate, 6-phenyl-s-triazolo[3,4-b]-s-tetrazine (II) was obtained. Yield 12%, small yellow plates, mp 229–230° C (a mixture of dimethylformamide and benzene). λ_{max} 264 nm (log ε 4.32), 338 (3.65), 460 (2.64) in ethanol. Found, %: C 55.03; H 3.08; N 42.56. Calculated for $C_9H_6N_6$, %: C 54.54, H 3.05; N 42.41.



The structure of II was shown by independent synthesis. 3-Hydrazino-6-phenyl-s-tetrazine (III) [2] (crimson red needles), mp 178° C (decomp.) (from ethanol), λ_{max} 305 (4.57), 410 (3.13), 530 (log ε 2.62) (in ethanol) was heated with an excess of orthoformic ester for 3 hr. The II was filtered off and recrystallized, mp 229–230° C. Yield 54%. Identical with that described above in respect to its spectra in the UV, visible, and infrared regions.

In spite of the difficulty of obtaining the initial hydrazine and its derivatives, the synthetic route III→II proved to be more suitable for obtaining compounds of the new biheterocyclic system with an aryl substituent in position 6. The route I→II may find use for the production of compounds II with substituents in position 3.

Attention is attracted by the considerable hypsochromic shift of the spectrum on passing from III to II which is apparently due to the fact that because of ring fusion the π-electronic system of tetrazine, which is distinguished by a high equivalence of the limiting structures, is disturbed.

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