CHLORINATION OF 4,4-DICHLOROCHROMENES WITH SULFURYL CHLORIDE

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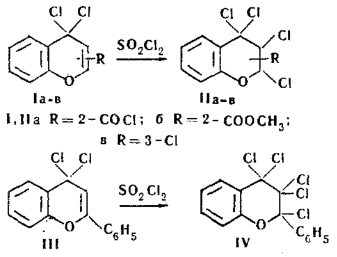
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, pp. 1133–1134, 1968

UDC 547.814.1:542.944.1:543.422.4

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).



Ia-в IIa-в

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

III IV

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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5 May 1967

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

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, p. 1134, 1968

UDC 547.841+547.811

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 con-