## SYNTHESIS OF POLYCHLORINATED 2,5-DIHYDRO-2-FURANONES FROM MALEIC ANHYDRIDE

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The reaction of maleic anhydride with phosphorus pentachloride, which leads to polychlorinated 2,5dihydro-2-furanones, was studied. The structures of the compounds obtained were proved by means of spectral methods.

A great deal of attention has recently been directed to new convenient methods for obtaining chemical compounds that have a number of reactive functional groups and atoms. In particular, these include polychlorinated 2,5-dihydro-2-furanones, which are starting compounds for obtaining diphenyl esters of maleic and dichloromaleic acids that display biological activity [1]. The literature does not contain detailed data on obtaining polychlorinated 2,5-dihydrofuranones, and no detailed proof for the structures of the substances obtained is available. The meager amount of information available pertains only to the synthesis [2-5] and study [6] of some properties of 3,4,5,5-tetrachloro-2,5-dihydro-2-furanone, which, moreover, was obtained from almost inaccessible compounds.

We have studied the reaction of maleic anhydride (I) with phosphorus pentachloride (II), which leads to various polychlorinated 2,5-dihydro-2-furanones (III-V):



The results of the reaction depend primarily on three parameters: the molar ratio of the starting compounds (I:II) and the reaction temperature and time. By varying these parameters one can obtain a given chlorine-containing 2,5-dihydro-2-furanone (see Table 1). The yield of an individual product or mixture of these products depends to the greatest extent on the I:II ratio.

To confirm the chemical structures of the compounds obtained we used data from their IR (III, IV), <sup>1</sup>H NMR (III, IV), and <sup>13</sup>C NMR (IV, V) spectra, as well as from their <sup>35</sup>Cl NQR (V) and mass (III-V) spectra.

The mass spectra of V contain a specific group of molecular-ion peaks with m/z 220, 222, 224, and 226, as well as a weak signal of an ion with m/z 228. The distribution of the intensities of the peaks here is characteristic for ions that contain four chlorine atoms, and, in complete conformity with the additivity rule, the intensity of the isotope peak with mass number M + 2 exceeds the intensities of the peaks of ions that contain only the principal <sup>35</sup>Cl isotope [7]. The molecular ions of III are characterized by three peaks with mass numbers 152, 154, and 156, the ratio of the intensities of which is 100:65:11. In the case of IV the presence of three chlorine atoms is responsible for the appearance in the mass spectrum of four ions with m/z 186, 188, 190, and 192; the first two peaks have approximately the same maximum intensity, while the ion peak with m/z 192 can be detected only with maximum amplification.

The IR spectra of chloro derivatives III-V contain characteristic absorption bands at 1195-1255 cm<sup>-1</sup> that are related to stretching vibrations of an oxide group; the band at 1740-1790 cm<sup>-1</sup> corresponds to vibrations of a carbonyl group, while the bands at 1620-1640 cm<sup>-1</sup> are related to stretching vibrations of a C=C bond, the presence of which is also confirmed by the PMR spectra (signals with chemical shifts (CS) of 6.97 and 7.59 ppm for III and IV, respectively).

The presence in the <sup>13</sup>C NMR spectra of tetrachloro derivative V and trichloro derivative IV of signals of four carbon atoms (158.5, 151.6, 123.9, 104.4 and 160.5, 137.8, 114.9, 104.4 ppm, respectively), in contrast to the two signals in the spectrum of anhydride I, confirms their unsymmetrical character [8]. The presence and positions of the chlorine

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Com- pound	Empirical formula	bp, °C (1.01 kPa)	Reaction conditions			
			I:II molar ratio	<i>T</i> , ℃	time, h	Yield,
III IV V	C₄H₂Cl₂O₂ C₄HCl₃O₂ C₄Cl₄O₂	151 155 .169 174 191 193	1:1,08 1:2,34 1:3,45	128 136 153	10,6 8,8 12,8	97 41 98

TABLE 1. Characteristics of III-V and Conditions Used to Obtain Them

atoms in V are confirmed by the <sup>35</sup>Cl NQR spectrum (30.42, 30.54, 36.32, 37.54 MHz), which is in good agreement with the data in [9].

## EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer. The PMR spectra were obtained with a BS-487 spectrometer (80 MHz, hexamethyldisiloxane (HMDS) as the internal standard). The <sup>13</sup>C NMR spectra were recorded with an FT-80 spectrometer (20.1 MHz, tetramethylsilane (TMS) as the internal standard). The <sup>35</sup>Cl NQR spectrum was obtained with a UC-3 pulse spectrometer at 77°K. The mass spectra were recorded with an MKh-1303 spectrometer.

Chromatographic analysis was carried out with an LKhM-8 MD chromatograph with a column (2.5 mm by 3 mm) packed with SE-30; the vaporizer temperature was 150°C, the column temperature was 120°C, the detector temperature was 150°C, and the carrier gas (helium) flow rate was 5 liters/h.

The results of elementary analysis of III-V for C, H, and Cl were in agreement with the calculated values.

Synthesis of Polychlorinated 2,5-Dihydro-2-furanones III-V. The reaction was carried out at atmospheric pressure in a batch-operated reactor equipped with a high-speed stirrer, a reflux condenser, and a thermometer. The reactor was charged with the necessary amounts of reactants I and II, after which the mixture was heated with constant stirring to the necessary reaction temperature, and stirring was continued until anhydride I vanished (according to GLC data). The mixture was then distilled in vacuo to give III-V, the purity of which (97-99%) was established by means of GLC.

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