β-DERIVATIVES OF FURAN

I. Direct Bromination of Furfural in the β-Position

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It has been shown in many cases [1, 2] that electrophilic substitution in the furan ring takes place in a free α-position, regardless of the nature of the substituents present.

In accordance with this, in the bromination of furfural in dichloroethane 5-bromofurfural is obtained in good yields [3], and as we have shown by gas-liquid chromatography no other bromination products are formed.

In the bromination of furfural in the presence of aluminum chloride with an excess of bromine, we isolated three products: 4, 5-dibromofurfural (58%), 4-bromofurfural (28%), and 5-bromofurfural (14%). The percentages of the products were evaluated by gas-liquid chromatography in comparison with chromatograms of pure samples.

The 4-bromofurfural was isolated from the mixture and was oxidized to 4-bromofuran-2-carboxylic acid, which was identical with the acid obtained by a published method [4]. A mixture showed no depression of the melting point.

Apparently the complex formed by furfural with aluminum chloride enhances the electron-accepting properties of the aldehyde group and changes its orienting capacity. A similar substitution in position 4 has been described previously in the alkylation of furfural with isopropyl chloride in the presence of aluminum chloride [5].

4-Bromofurfural. With water cooling and stirring, 48 g of freshly distilled furfural was added to 120 g of aluminum chloride. The complex so obtained was treated with 38 ml of bromine. On the following day the mixture was poured onto ice, the oil was separated off, the aqueous layer was extracted with ether, and after the ether had been driven off the residue was distilled with steam. Vacuum distillation then yielded 7 g of a product with bp 71–75° C (10 mm) and 48 g of a product with bp 95–98° C (10 mm).

The first fraction was heated with 50 ml of a 5% solution of sodium sulfide for 1 hr. After steam distillation of the dark mixture so formed, 4 g of 4-bromofurfural with mp 28–29° C was obtained.

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THE SYNTHESIS OF COUMARINS AND BENZOFURANS DEUTERATED IN THE HETEROCYCLIC RING

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Unsubstituted coumarin and benzofuran containing deuterium in the heterocyclic ring have not been described in the literature. Nevertheless, these types of deuterium derivatives may be interesting subjects for spectroscopic investigations.

We have synthesized [4-D] coumarin (I) and [3-D] coumarin (II) with good yields by the reduction of 1 g of 4-chloro- and 3-bromocoumarins respectively, with zinc dust in solution in a mixture of 15 ml of C_2H_5OD and 15 ml of D_2O (95 and 99% enrichment, respectively). The substances were purified by recrystallization from petroleum ether with the addition of benzene, mp of I 69.1–70° C, mp of II 69–69.5° C. The absence of impurities in the initial halogenocoumarins was established by thin-layer chromatography on Al_2O_3. In the PMR spectrum (60 MHz, the chemical shifts, δ, ppm, are given relative to HMDS) of I in $CDCl_3$ solution there is no signal of $C_{(4)}H$ in the 7.7 ppm region, but at 6.3 ppm there is a singlet signal of the $C_{(3)}H$ proton with an intensity of 1 H. In the spectrum of II at 7.7 ppm there is a singlet signal of the $C_{(4)}H$ proton, and in the 6.3 ppm region the intensity of the signal is less than 0.05 H. It is known that for deuterated coumarin in $CDCl_3$ the $C_{(3)}H$ and $C_{(4)}H$ signals appear in the form of a doublet with chemical shifts of 6.42 and 7.72 ppm, respectively [1].

[2-D] Benzofuran (III) was obtained by the decarboxylation of benzofuran-2-carboxylic acid: 3.24 g of this acid in 30 ml of anhydrous quinoline and 4 ml of D_2O was heated to the boil, the water and part of the quinoline were distilled off, another 4 ml of D_2O was added, the operation was repeated, 2.5 g of copper powder was added, and the mixture was heated at ~190° C for 45 min, after which a III was isolated in the usual way in a yield of 42%, bp 168–169° C (762 mm). In the PMR spectrum of III in CCl_4 a singlet signal at 6.75 ppm corresponds to the $C_{(3)}H$ proton, while in nondeuterated benzofuran this proton is split into a doublet with $J \approx 3$ Hz (the signal of the $C_{(2)}H$ proton overlaps the C_6H_4 signals).

The method for the synthesis of I and II that has been described is also convenient for the production of [3, 4-D_2] coumarin from the