SYNTHESIS AND REACTIONS OF β-SUBSTITUTED FURANS

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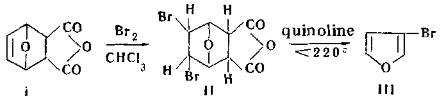
3-Bromofuran has been obtained in good yield by the reaction of 4,5-dibromo-3,6-endoxohexahydrophthalic anhydride with quinoline at 210–220° C. It has been shown that the reaction of 3-bromofuran with acetic anhydride in the presence of perchloric acid forms 2-acetyl-3-bromofuran.

β-Halofurans are difficult to obtain and have been little studied. The methods of preparing them described in the literature [1–3] are laborious and give low yields. The search for a better route to the synthesis of β-halo-substituted furans is of interest in connection with the possibility of converting them via the lithium derivatives [4] into β-substituted furans difficult to obtain by other methods.

We have developed a convenient method for the preparation of β-bromofuran (III) with a yield of up to 80% by the thermal decomposition of 4,5-dibromo-3,6-endoxohexahydrophthalic anhydride (II) in the presence of quinoline in accordance with the following scheme:



The compound III synthesized in this way was identical with the β-bromofuran obtained by the decarboxylation of 4-bromofuran-2-craboxylic acid.

On acetylation of II, in analogy with the case of α-bromofuran [5], an oily acetylbromofuran with bp 222° C, λ_{max} 265 nm (log ε 4.32) was obtained. The semicarbazone (SC) had mp 219–220° C. In the literature only 2-acetyl-4-bromofuran [1] with mp 69.5–70° C (mp of the SC 189–190° C, giving 4-bromopyromucic acid on oxidation [1]) and 2-acetyl-5-bromofuran with mp 95–96° C, λ_{max} 262 nm (log ε 4.21) (mp of the SC 204° C, oxidation gives 5-bromopyromucic acid) have been described.

The oxidation of the acetyl-β-furan that we obtained did not give these acids. Thus, in accordance with the orientation rule, the acetylation of β-bromofuran forms 2-acetyl-3-bromofuran (IV); In contrast to 2-acetyl-5-bromofuran [6], IV does not give a dye on being heated with sodium polysulfide.

EXPERIMENTAL

4,5-Dibromo-3,6-endoxohexahydrophthalic anhydride (II). A 16.6 g amount of the finely ground adduct [7,8] was shaken with 50 ml of chloroform and, with ice water cooling, 16 g of bromine in 50 ml of chloroform was added in small portions. The adduct dissolved and then the bromine derivative precipitated. The mixture was left to stand for an hour and was then filtered. Yield 26.2 g (78%). Mp 159° C (from chloroform).

β-Bromofuran (III). a) A mixture of 127.8 g of the freshly-prepared dibromide II and 25 ml of quinoline was slowly heated to 210–220° C (increasing the temperature further leads to spontaneous resinification). First the III distilled off and then the quinoline. The distillate was treated with 10% HCl solution to remove the quinoline, washed with water, dried with anhydrous $CaCl_2$, and distilled. Yield 45.1 g (78%). Bp 102–103° C (745 mm); n_D^{20} 1.4962; d_4^{20} 1.6605.

b) A mixture of 10 g of 4-bromo-2-furancarboxylic acid [9], 2 g of copper powder, and 15 ml of quinoline was slowly heated to 220° C. The III that distilled off was treated in a similar manner to the preceding method. Bp 102° C; n_D^{20} 1.4969; d_4^{20} 1.6608. For α-bromofuran: bp 101–102° C (752 mm); n_D^{20} 1.4980; d_4^{20} 1.6500 [10].

2-Acetyl-3-bromofuran (IV). Ten grams of III was treated with 30 ml of acetic anhydride and a drop of 60% $HClO_4$ and the mixture was left to stand for 30 min. Then 50 ml of water was added and it was distilled with steam. The oil that distilled over was separated off, the aqueous solution was extracted with ether, the ethereal extract was washed with sodium carbonate solution and with water, the ether was driven off, and the residue was distilled. Yield 12.8 g (74%); bp 222° C; n_D^{20} 1.5489; d_4^{20} 1.6240. Found, %: C 37.72; H 2.65. Calculated for $C_6H_5BrO_2$, %: C 38.12; H 2.67.

The semicarbazone precipitated directly when saturated methanolic solutions of starting materials were mixed in equimolecular amounts. Mp 219–220° C (decomp., from ethanol). Found, %: N 18.17. Calculated for $C_7H_8BrN_3O_2$, %: N 17.08.

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