BRIEF COMMUNICATIONS

NEW METHOD FOR PREPARATION OF 2-BROMOTHIOPHENE

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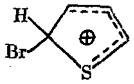
UDC 542.91:547.732:546.14

2-Bromothiophene is one of the important starting compounds for obtaining either mono- or polyfunctional compounds of the thiophene series [1]. Despite the simplicity of this compound, its preparation is associated with certain difficulties. They are caused primarily by the high reactivity of the two α-H atoms of thiophene, due to which the direct bromination with molecular bromine in various media gives, together with 2-bromothiophene, also commensurate amounts of 2,5-dibromothiophene. In view of this a number of methods was proposed, which limited the formation of this byproduct. For this purpose in [2] dioxane dibromide was used as the brominating agent, and in [3] it was proposed to use thallium triacetate during bromination with molecular bromine. A high yield of 2-bromothiophene is achieved in the latter case, but the formation of 2,5-dibromothiophene is not eliminated completely.

Previously one of us had studied the bromination of dithienylmethane [4] and methylthiophene [5] with potassium bromate and potassium bromide using a two-phase water–benzene system containing HCl, and in this way we obtained 5-bromo-2-methylthiopene in 74% yield. Our attempted use of this method to obtain 2-bromothiophene proved unsuccessful, since 2-chlorothiophene was formed along with the desired product. The formation of the latter was unexpected, since unused KBr remained in the mixture. To avoid the formation of 2-chlorothiophene, we replaced the HCl by HBr. The need of using KBr disappeared here. However, the formation of the dibromo derivative could not be avoided even under these conditions. In view of this it seemed expedient to replace the nonaqueous phase, for example the benzene by ether. The reaction was run with the addition of potassium bromate solution to the two-phase system; here the dibromide was not detected even in the first experiment when the reaction product was distilled. The product was mainly 2-bromothiophene; its yield after a double distillation exceeded 60%. The absence of 2,5-dibromothiophene as impurity was confirmed by the GLC method, where the data indicated that it was present only in the still residue in an amount not exceeding 2-3%.

In our opinion, the effect of replacing the benzene by ether is based on blocking one of the α positions of the thiophene ring, due to the formation of the σ complex. Complexes of this type were discussed previously [6] as intermediates when thiophene is brominated in a solvent. For the case discussed by us such a complex can be formed by attack of a Br$^+$ particle on the α position:



As a result, due to the formation of the σ complex, only one of the α-H atoms of thiophene remains unsubstituted. This σ complex, being a quite strong base, probably cleaves a portion when treated with ether, which in the final analysis leads to the formation of 2-bromothiophene. However, such a sharp difference in the ratio of the end reaction products when benzene is replaced by ether requires additional study.

The use of excess HBr does not give a quantitative yield of 2-bromothiophene. This is apparently explained by the fact that the bromine is also consumed in oxidizing the ether. The ability of bromine in acid medium at room temperature to oxidize ethers to carboxylic acids, bromocarboxylic acids, aldehydes, and ketones is mentioned in [7]. In addition, as was shown in [6], Br$_2$ in strongly acid medium can combine with Br$^-$ anion to form the Br$_3^-$ particle, which is incapable of electrophilic attack.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2388-2389, October, 1982. Original article submitted January 5, 1982.

0568-5230/82/3110-2104$07.50

EXPERIMENTAL

The GLC was run on an LKhM-8MD instrument, using a 110 × 0.3 cm stainless-steel column packed with 3% Dexsil-300 deposited on 80-100 mesh Chromosorb W, a katharometer as the detector, helium as the carrier gas, and a flow rate of 30 ml/min; the mass spectrum was taken on a Varian MAT CH-6 spectrometer.

2-Bromothiophene. Into a flask, fitted with a stirrer, thermometer, and a dropping funnel, was charged a solution of 33.6 g of distilled thiophene in 200 ml of ether, which was cooled to 5°C, and 200 ml of 40% HBr solution was added in portions, not permitting the temperature to exceed 10-12°. Then, with vigorous stirring, a solution of 22.3 g of $KBrO_3$ in 400 ml of water was added dropwise in 1.5 h, maintaining the temperature below 10°. After adding the solution the reaction mass was kept for 2 h at ~20°, and then the organic layer was separated, the aqueous layer was extracted with 50 ml of ether, and the organic layer and extract were combined, washed with 10% NaOH solution until the aqueous alkaline solution remained colorless, then with water, dried over $MgSO_4$, and the ether was evaporated. Distillation of the residue gave a fraction with bp 145-156°, and its redistillation gave 37.75 g (60.4%) of 2-bromothiophene, bp 150-153°, n_D^{25} 1.5864; from [8], bp 150-152°, n_D^{25} 1.5866. Mass spectrum: 162 and 164 (M^+).

CONCLUSIONS

The reaction of $KBrO_3$ with thiophene in the presence of HBr in a two-phase water-ether system permits obtaining 2-bromothiophene, not contaminated with 2,5-dibromothiophene, in high yield.

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