A STUDY OF THE BROMINATION OF o-XYLENE

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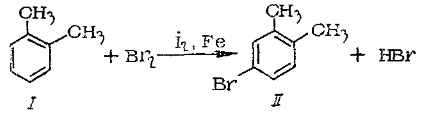
UDC 615.356:577.164.12].012.1.002.62

4-Bromo-o-xylene (II), which is an intermediate in the synthesis of vitamin B_2, is obtained by brominating o-xylene (I).



The process of brominating (I) has been studied fairly well [1-3]. In industry, it is performed by the gradual addition of bromine to (I) at a temperature of 15-27°C. Under these conditions, in spite of an excess of (I) (up to 10%), in addition to the main product the by-products 4,5-dibromo-o-xylene (III), 3,4-dibromo-o-xylene (IV), and, to a very small extent, ω-bromo-o-xylene (V) are formed. The bromination is carried out in the presence of catalytic amounts of iodine and iron. The technical product is purified by fractional distillation in vacuum. According to the literature [3], the rate of bromination increases considerably when the temperature is raised to 40°C. Under these conditions the rates both of the main and of the side reactions increase, but the selectivity of the process decreases.

In order to improve the technological process for obtaining (II) we have studied the bromination of (I) in the presence of water. By introducing a second (aqueous) phase into the process, we pursued the aim of avoiding a special system for trapping hydrogen bromide. At the same time, the aqueous solutions of hydrogen bromide, not mixing with (I) and with the reaction products, could have no fundamental influence on the direction and mechanism of bromination.

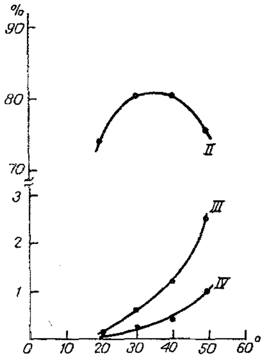


Fig. 1. Yield (in %) of bromination products (II, III, and IV) as a function of the temperature of the process. Time of addition of bromine 30 min; residence time 2 h.

On the other hand, it is known that hydrobromic acid dissolves bromine better than water does [4]. Consequently, with an increase in the concentration of hydrogen bromide in the aqueous phase the solubility of the bromine in it must increase. This could lead to some slowing down of the bromination process because of the fall in the concentration of the bromine in the organic phase. Furthermore, the presence of water imposed definite limitations in the choice of catalyst, which made necessary a study of the roles of its individual ingredients.

In order to find the optimum conditions for brominating (I) in the presence of water, we studied the dynamics of the conversion of (I) into (II), (III), and (IV) as functions of the intensity of stirring, the temperature, and the composition of the catalyst. The study was performed in comparison with the bromination of dry (I). In contrast to the investigations performed previously [2,3], bromination was performed at an equimolecular ratio of

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Leningrad Chemical and Pharmaceutical Institute. Translated from Khimiko-Farmatsevticheskii Zhurnal, Vol. 8, No. 1, pp. 31-34, January, 1974. Original article submitted October 23, 1972.

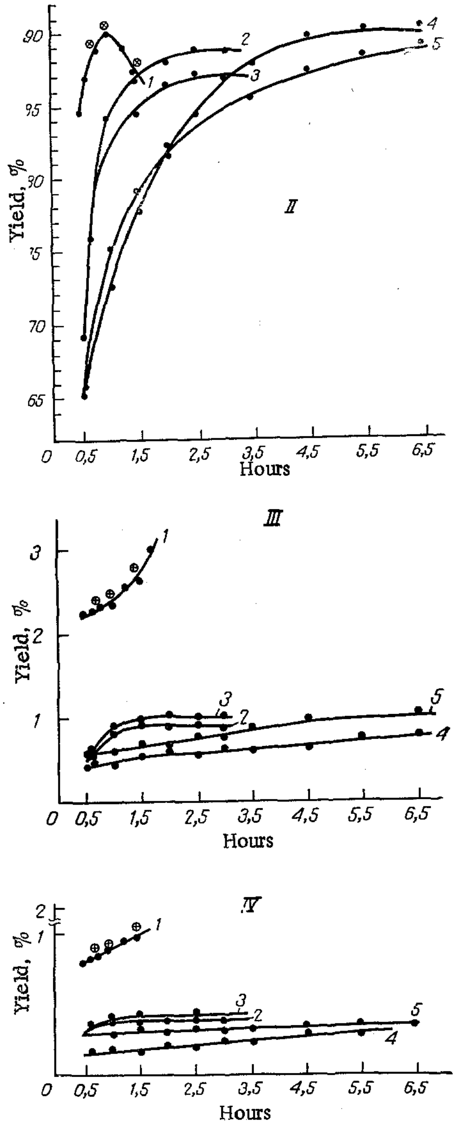

Fig. 2. Dynamics of the formation of (II), (III), and (IV) in the bromination of (I) in the absence and in the presence of water as a function of the composition of the catalyst. 1) Dry (I), Fe + I_2 (the ⊕ symbols denote experiments with iron alone); 2) dry (I) without a catalyst; 3) dry (I), I_2; 4) in the presence of water, without a catalyst; 5) in the presence of water, I_2. Time of addition of the bromine 30 min; temperature of bromination 30°C.

bromine and (I). The weight ratio of water and (I) ensuring the complete absorption of the hydrogen bromide was found experimentally to be 1.5 :1.

The experiments showed that the intensity of stirring has a fundamental influence on the yield of the main product and the by-products both in the bromination of dry (I) and in the presence of water, but the influence of stirring was smaller in the bromination of dry (I) because of the occurrence of the process in a single phase. The experiments were performed at 30°C. The results are given in Table 1.

In the bromination of (I) in the presence of water, iron was not used as catalyst because of the high solubility of ferric bromide in water.

In view of the results obtained, all the experiments in the study of the other factors were performed in flasks of the same size at a rate of stirring of 220-250 rpm.

The study of the bromination of (I) in the presence of water at various temperatures showed that raising the temperature leads to an increase in the rate of formation of (II) but to an even greater increase in the rate of dibromination (Fig. 1).

As in the case of the bromination of dry (I) [3], the temperature range from 30 to 40°C is the optimum. At 50°C, ω-bromo-o-xylene (about 2.5%) appears in the reaction mixture. The experiments were performed in the presence of catalytic amounts of iodine, which is used in the industrial production of (II).

There is information in the literature [5] according to which the bromination of polyalkylbenzenes does not require the presence of a catalyst. To determine the roles of the ingredients of the complex industrial catalyst, we investigated the bromination of (I) (dry and in the presence of water) as a function of the composition of the catalyst. It was established that the bromination of dry (I) takes place at practically the same rate in the presence of iodine and without it, but this rate is lower than in the presence of iodine and iron or of iron alone (Fig. 2, curves 1, 2, and 3). At the same time, the amounts of dibromides formed are similar (see Fig. 2, curves 2 and 3). A catalytic action of iodine in the bromination of dry (I) that is equal to

TABLE 1. Influence of the Intensity of Stirring on the Composition of the Products of the Bromination of (I)

Conditions of bromination	Stirring rate rpm	Comp. of reaction mixture after bromination, %				Notes
		I	II	III	IV	
Absence of water	0 65—80 220—250	3,6 3,3 3,2	89,7 92,4 93,0	5,2 3,5 2,8	1,7 1,3 1,3	Bromination performed in the presence of catalytic amts. of iodine and iron
Presence of water	0 65—80 110—250	13,7 12,3 8,5	73,7 79,9 90,1	9,8 5,4 1,5	3,9 2,2 0,3	Bromination performed in the presence of catalytic amts. of iodine

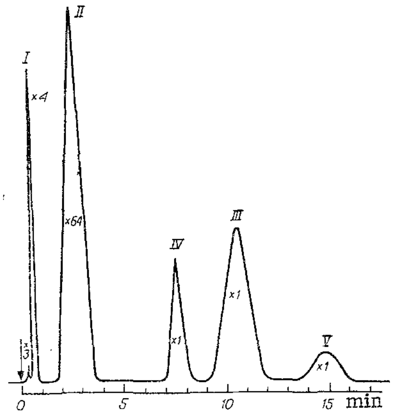

Fig. 3. Chromatogram of technical (II). X represents an unidentified product [sic].

the combined action of iodine and iron begins to appear only when it is used in an amount 10 times exceeding that used in industry. The amount of dibromides formed under these conditions is the same as in bromination without a catalyst. The increase in the rate of bromination that we observed on using a larger amount of iodine agrees well with literature information on the bromination of other aromatic compounds in the nucleus [5,6]. The results obtained show that the active part of the composite industrial catalyst leading to an increase in the rates of mono- and dibromination is the iron (see Fig. 2, curve 1). Elimination of the catalyst evidently permits an increase in the yield of the main product and a stabilization of the degree of conversion of (I) into dibromides at a level of 1.2-1.5%, with some slowing down of the bromination process.

It follows from a comparison of curves 2, 3, 4, and 5 (see Fig. 2) that the rate of bromination of (I) in the presence of water, as in the case of the bromination of dry (I), does not depend on the presence of iodine but falls considerably. The fall in the rate of bromination of (I) in the presence of water, especially at the end of the process (see Fig. 2, curves 2-5), is connected with the decrease in the concentration of bromine in the organic phase as a result of its partial passage from the organic phase into the aqueous phase with an increase in the concentration of hydrogen bromide in the latter. Under these conditions, as is well known, polyhalide compounds of the type of $HBr[Br_2]$, the stability of which is determined by the temperature of the reaction mixture, are formed in an aqueous solution of hydrogen bromide [7].

The experimental results show that when bromination is performed in the presence of water at 30°C without a catalyst, a degree of conversion of (I) into (II) of 78% is achieved in $1\frac{1}{2}$ h and 90% in 6 h, while in the bromination of dry (I) an 89% conversion of (I) into (II) is achieved in 3 h when the process is performed at the same temperature (see Fig. 2, curves 2 and 4).

We have established that it is possible considerably to increase the rate of bromination in the presence of water if, after the mixture has been held at 30°C for $1\frac{1}{2}$ h, the temperature is raised to 50°C. Under these conditions, the degree of conversion of (I) into (II) amounts to 90% after $3\frac{1}{2}$ h with no reduction in the quality of the product obtained (the total degree of conversion of (I) into (III) and (IV) is 1.2-1.5%). Attention is also attracted by the fact that in all the experiments which we performed the bulk of the dibromides of (I) (80%) was formed in the first $1\frac{1}{2}$ h of the process.

On the basis of the results obtained, the best conditions for brominating (I) in the presence of water may be considered to be a molar ratio of (I) and bromine of 1 : 1, a weight ratio of (I) and water of 1 : 1.5, the addition of bromine after 30 min, and a holding time of 1 h at 30°C with subsequent heating to 50°C and holding at this temperature for 2 h.

The technical (II) obtained under these conditions, after the removal of the aqueous layer and washing free from acid, was analyzed by gas-liquid chromatography (GLC) and found to contain 2.9% of (I), 95% of (II), and 2% (total) of (III) and (IV). As a result of the investigations performed, an industrial method for brominating (I) in the presence of water is proposed which enables the apparatus for the bromination stage to be simplified, the yield of technical (II) to be increased, and its quality to be improved. The possibility of bromination at an equimolecular ratio of (I) and bromine without a catalyst has been shown.

EXPERIMENTAL

Analysis of the Technical 4-Bromo-o-xylene (II) by the GLC Method. The investigations were carried out on a Tsvet-5 chromatograph in the thermostat of which a standard thermal conductivity detector was set up. The bridge current was 220 mA. Fluorinated plastic column, 100 × 0.3 cm containing 10% of poly(ethylene adipate) on Chromaton N-Aw-HMDS (0.25-0.315 mm). The temperature of the column thermostat was 170°C, of the thermostat of the detectors 180°C, and of the evaporator 200°C. The carrier gas was helium and the rate of flow 100 ml/min.

The components of the mixture were identified by the method of tests. To determine the amounts of the components the method of normalizing the areas with calibration factors was used. The calibration factors were refined with the aid of a gas-density detector and had the following values: for (I), 0.7; for (II), 1; for (III), 1.3; for (IV), 1.4; and for (V), 1.6.

The errors in the determination did not exceed ± 2% rel. for (I) and (II) and ± 10% rel. for (III), (IV), and (V).

A chromatogram of technical (II) is shown in Fig. 3.

4-Bromo-o-xylene (II). With stirring (220-250 rpm), 80 g of bromine was added over 30 min to a mixture of 53 g of (I) and 80 ml of water in a black flask at a temperature of the reaction mixture of 30°C. After the addition of the bromine, the mixture was kept at 30°C for 1 h and was then heated to 50°C and was kept at this temperature for 2 h. After this period, the reaction mixture was cooled to 25°C and, after settling, the aqueous layer was separated off. The technical product was washed with a small amount of a 1-2% aqueous solution of ammonia and was analyzed by the GLC method. The yield amounted to 87.4 g of a product containing 2.9% of (I), 95% of (II), and 2% (total) of (III) and (IV), sp. gr. 1.3-1.33. The yield of (II) was 90% calculated on the (I) charged. The experiments were performed with technical bromine according to GOST 4109-64 and with "pure" o-xylene according to MRTU [Interrepublican Technical Specification] 6-09-3837-67.

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