STUDY OF A BY-PRODUCT IN THE PREPARATION OF p-NITRO-α-METHOXYSTYRENE

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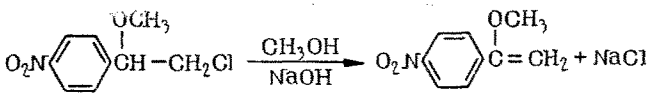
p-Nitro-α-methoxystyrene (I), an intermediate in the preparation of synthomycin and of chloromycetin, is obtained by dehydrochlorination of the methyl ether of the chlorhydrin of p-nitrostyrene (II) by heating it at 45-50° for 3 h in a 12-13% solution of sodium hydroxide in methanol; then the reaction mixture is heated to 65-66° and the insoluble precipitate is filtered off:

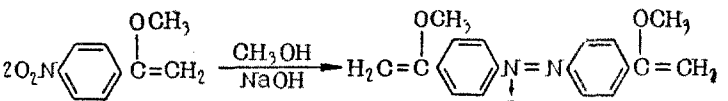


II I

Under these reaction conditions it was observed that, in certain cases, compound I contained a by-product III, whose presence reduced the melting point and the yield of product I.

The structure of the by-product was investigated by us.

Under the dehydrochlorination conditions described above it is possible to form a series of products by polymerization of p-nitro-α-methoxystyrene, (I) or to reduce its nitro group, in the methanol-alkaline medium, to the azoxy compound [2-4]:



I III

Heating pure p-nitro-α-methoxystyrene in 13% solution of sodium hydroxide in methanol and subsequent work-up of the reaction mixture yielded a lemon-yellow colored compound with melting point 132-133°. Elementary analysis of this compound was consistent with its being the azoxy compound of methoxystyrene (III). Its IR spectrum showed no bands for the nitro group. Analysis for the double bond, by the iodometric method, gave a result which was 98.44% of that calculated for the azoxy compound of methoxystyrene.

The effect of changes in the principal reaction parameters on the quality of p-nitro-α-methoxystyrene, I, was examined; it was shown that increased temperature and alkaline concentration, and also a lengthening of the reaction time significantly reduced the melting point of the final product, I, by increasing the contamination with product III.

To establish the dependence of the melting point of I on the percent of III present, a study of the melting points of different mixtures was conducted. The mixtures were prepared by mechanical mixing of the pure components in various proportions (see Fig. 1). From Fig. 1 it is seen that a concentration of the by-product, III, of about 30% reduces the melting point of I to 73°.

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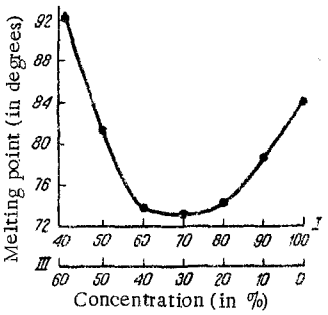

Fig. 1. Diagram showing the relationship between the melting point of a mixture of p-nitro-α-methoxystyrene (I) and the azoxy compound of methoxystyrene (III) and the amounts of the components.

EXPERIMENTAL

Preparation of the Azoxy Derivative of Methoxystyrene (III). To 400 ml of a 13% methanolic alkali solution was added 80 g of I, and the mixture was boiled for 10 h; the precipitate was filtered, and washed free of sodium chloride with water. There was obtained 16.6 g (21.7%) of III, with mp 124-126°. After washing with methanol, double recrystallization from benzene with activated charcoal yielded lemon-yellow colored crystals with mp 132-133°, which had good solubility in acetone and benzene and poor solubility in polar solvents and in water. Found, %: C 69.45; H 5.87; N 9.06. $C_{18}H_{18}N_2O_3$. Calculated, %: C 69.66; H 5.84; N 9.02.

CONCLUSIONS

It was shown that the by-product in the preparation of p-nitro-α-methoxystyrene is the azoxy derivative of methoxystyrene. The effect of changes in the principal reaction parameters on the quality of the p-nitro-α-methoxystyrene was examined.

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