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Abstract

Full Text

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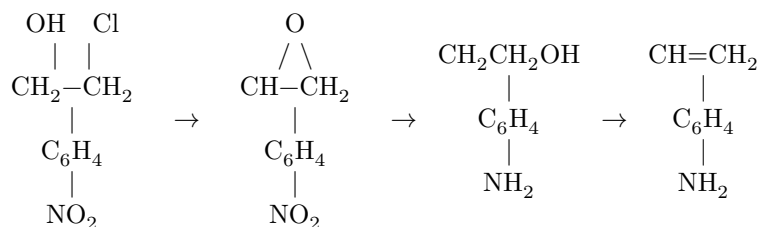
CATALYTIC SYNTHESIS OF PARA-AMINOSTYRENE

Para-aminostyrene (PAS) is an interesting intermediate not only in polymer chemistry, but also in organic synthesis. On the basis of aminostyrene, its polymers and copolymers, low-basicity anionites, selective cationites, polyazo dyes, and other products are obtained (1-4). In addition, polyaminostyrene is used as an intermediate for various polymer-analogous transformations (replacement of the amino group by an oxy group, by halides, etc.) (5). However, the lack of accessible methods for synthesizing *p*-aminostyrene limits the possibility of its still broader application.

The existing few methods for obtaining *p*-aminostyrene are multistage and, as a rule, give a low yield of the final product. Thus, in the dehydration of *p*-aminophenylcarbinol over Al_2O_3 at 250° , the yield of *p*-aminostyrene is 20% of theoretical (6).

The most widespread method for obtaining *p*-aminostyrene is the dehydration of β -(*p*-aminophenyl)ethyl alcohol. The yield in this case is 45-55% (7-10).

Sinyavskii, Turbina, and Romankevich (11) developed a method for obtaining *p*-aminostyrene from *p*-nitrophenylchloromethylcarbinol according to the scheme:



They succeeded in increasing the yield of the last stage to 84%. However, the overall yield of *p*-aminostyrene, taking all stages into account, is also rather low in this case.

Thus, the development of a convenient method for obtaining *p*-aminostyrene is of considerable interest. In this connection, the most promising is the synthesis of *p*-aminostyrene by catalytic dehydration of *p*-aminoethylbenzene, which in turn can be readily obtained either by direct alkylation of aniline with ethyl alcohol in the presence of zinc chloride (12), or by nitration of ethylbenzene and subsequent reduction of *p*-nitroethylbenzene (13).

We have carried out a study of the dehydration of *p*-aminoethylbenzene (PAEB) over a mixed oxide catalyst (14). The reaction was carried out at a temperature of 560–640° and with dilution by steam, carbon dioxide, and nitrogen. *p*-Aminoethylbenzene was fed into the reaction zone at a rate of 0.5–1.0 l per 1 l of catalyst per hour. The diluent was used in a ratio of 1 : 1–1 : 4 by weight.

Experimental Part

The starting *n*-aminoethylbenzene was obtained by us by nitrating ethylbenzene, isolating *n*-nitroethylbenzene from the mixture of isomers by rectification, and reducing it to *n*-aminoethylbenzene. For final purification from the impurity of the *o*-isomer, aminoethylbenzene was converted into the sulfate, which was recrystallized from water to a constant melting temperature (239°). Decomposition of the pure sulfate gave individual *n*-aminoethylbenzene with b.p. 95–96°/10 mm Hg, n_D^{20} 1.5558, d_4^{20} 0.96875. Lit. ⁽¹⁵⁾: b.p. 217.22°, n_D^{20} 1.55475, d_4^{20} 0.06875.

Procedure for Carrying Out the Experiments

Dehydration was carried out in a flow apparatus with 10 ml of catalyst. After each experiment the catalyst was regenerated with a steam-air mixture for 20–30 min. The activity of the catalyst was monitored from the results of dehydration of *n*-aminoethylbenzene under standard conditions. To ensure complete recovery, the residues of the reaction products after each experiment were washed out of the reactor with water. The aqueous catalyzates were saturated with potash and the organic layer was separated. The composition of the *n*-aminoethylbenzene dehydration products obtained in this way was determined by gas-liquid chromatography. In addition, the water content in each catalyzate was determined by the carbide method ⁽¹⁶⁾, its weight being subtracted from the total weight of the organic portion of the catalyzate obtained by salting out.

Dehydrogenation of *n*-Aminoethylbenzene

As can be seen from the data in Table 1, dehydration of *n*-aminoethylbenzene proceeds with satisfactory yields of *n*-aminostyrene. When CO_2 and N_2 are used as diluents in a weight ratio of 1 : 1—1 : 2, the yield of *n*-aminostyrene is 45–47% of theory.

Table 1

Catalytic dehydrogenation of *n*-aminoethylbenzene over a mixed oxide catalyst

Temp., °C	Space ve- loc- ity of PAEÉB feed, l per l l cat- a- lyst	Diluent	Weight ratio PAEÉB — dilu- ent	Catalyst yield, wt. %	PAEÉB charged	PAEÉB cal- culated	PAS yield, cu- lated	PAEÉB cal- culated	n- Bulidim	Amiline	Dehydrogenation prod- ucts
560	0,5	H ₂ O	1 : 2	92,14	24,4	63,00	26,15	70,23	0,86	1,24	1,52
560	1,0	H ₂ O	1 : 2	95,64	21,05	80,00	20,93	76,77	0,55	0,90	1,45
580	0,5	H ₂ O	1 : 2	90,50	22,73	64,28	24,62	71,39	1,41	1,34	1,24
580	1,0	H ₂ O	1 : 2	93,40	21,69	70,00	22,85	73,52	0,66	0,90	2,07
600	0,5	H ₂ O	1 : 2	93,80	29,47	72,25	30,5	63,55	2,23	2,47	1,55
600	1,0	H ₂ O	1 : 2	90,90	26,52	66,70	28,68	67,27	1,53	2,00	1,52
620	0,5	CO ₂	1 : 0,5	82,41	41,20	66,33	49,93	28,45	11,06	7,84	2,72
620	0,5	CO ₂	1 : 1	81,16	47,60	59,74	58,94	22,88	8,66	6,61	2,91
620	0,5	H ₂ O	1 : 1	83,87	27,00	52,24	31,65	57,44	5,10	4,03	1,78
620	0,5	H ₂ O	1 : 2	86,55	35,10	62,54	39,92	50,03	3,95	4,25	1,85
620	0,5	CO ₂	1 : 2	75,00	45,34	56,00	60,38	23,54	7,34	6,67	2,07
620	0,5	N ₂	1 : 2	85,50	47,00	63,58	55,02	28,91	7,82	6,03	2,22
620	0,5	H ₂ O	1 : 3	82,41	30,37	52,00	36,62	49,41	5,53	6,42	2,02
620	0,5	H ₂ O	1 : 4	83,43	25,68	50,00	30,36	57,75	3,78	4,90	3,21
620	0,5	CO ₂	1 : 4	74,10	43,48	58,50	58,44	32,60	4,24	3,13	1,59
620	1,0	H ₂ O	1 : 2	88,62	29,05	60,52	32,31	61,03	2,46	2,76	1,44
640	1,0	H ₂ O	1 : 2	86,33	32,00	59,60	36,45	53,60	3,91	4,65	1,39

Cleavage of the amino group proceeds to an insignificant extent. The degree of dealkylation of the ethyl group does not exceed that observed during dehydrogenation, under these conditions, of other alkylaromatic compounds; however, under different conditions it varies. Dealkylation is most appreciable when CO₂ and N₂ are used as diluents; when steam is used, it is noticeably reduced.

The degree of dilution has a substantial effect on the dehydrogenation of *p*-aminoethylbenzene. When steam was used, it was found that the optimum dilution is a weight ratio of 1 : 2.

Gas-liquid chromatography of catalysts for the dehydrogenation of *p*-aminoethylbenzene

Chromatography of the products of dehydrogenation of *p*-aminoethylbenzene was carried out on a KhL-4 chromatograph, using as the stationary liquid phase a copolymer of ethylene oxide and tetrahydrofuran synthesized by us (found, %: C 61.78, H 10.22, which corresponds to the presence in the copolymer of 40% dimethylene- and 60% tetramethylene oxide units), deposited on NaCl crystals (grain diameter 0.25–0.5 mm) in an amount of 0.4%. Beforehand, 1% KOH was deposited on the NaCl. The column length was 2 m. The carrier gas—helium—was passed at a rate of 50 ml/min. The separation was carried out at 150°.

As can be seen from Fig. 1, under the conditions described above a fairly complete separation occurs of all components of the mixture formed during the dehydrogenation of *p*-aminoethylbenzene. The products of deamination and subsequent transformation (ethylbenzene, styrene, toluene, benzene) under the conditions of analysis give one peak on the chromatogram; therefore, in each experiment their total amount was determined. However, all these components were identified by chromatography of the catalysts at a lower temperature. The presence in the dehydrogenation catalyst of the readily polymerizing *p*-aminostyrene raised concerns about its possible thermal polymerization under the chromatographic conditions. Therefore, to confirm the correctness of the quantitative evaluation of the composition of the organic part of the catalyst, we chromatographed an artificial mixture consisting of aniline, *p*-toluidine, *p*-aminoethylbenzene, and *p*-aminostyrene.

Fig. 1. Chromatogram of the catalyst for the dehydrogenation of *p*-aminoethylbenzene.

1—water, 2—deamination products, 3—aniline, 4—*p*-toluidine, 5—*p*-aminoethylbenzene, 6—*p*-aminostyrene.

Table 2

Chromatographic analysis of an artificial mixture

Component of the mixture	Taken	Determined from the chromatogram
Aniline	5.68	6.55
Paratoluidine	5.05	5.82
Paraaminoethylbenzene	52.39	51.16
Paraaminostyrene	36.87	36.47

As can be seen from the data in Table 2, during chromatography of the artificial mixture, within the limits of the determination error, good agreement was obtained for the contents of the mixture components.

Isolation of *p*-aminostyrene from the catalyst of the dehydrogenation of *p*-aminoethylbenzene

To isolate *p*-aminostyrene, 100 g of catalyst (composition: water —1.02%, deamination products —1.22%, aniline —5.6%, *p*-toluidine —4.15%, *p*-aminoethylbenzene —53.78%, *p*-aminostyrene —34.23%) was subjected to vacuum rectification in a stream of nitrogen, in the presence of

Table 3

Rectification of the catalyst of the dehydrogenation of *p*-aminoethylbenzene

Fraction	B.p., °C/14 mm Hg	Weight of fraction, g	aniline	<i>p</i> - toluidine	PAEB	PAS
I	73-101	10.82	32.6	22.1	41.3	4.0
II	101-103	48.72	—	3.0	85.7	11.3
III	103-114	9.05	—	—	52.9	47.1
IV	114-117	21.30	—	—	5.0	95.0
Bottom residue	—	6.0	—	—	—	—

4 g of zinc dust with a spruce dephlegmator 20 cm long. The results of the distillation are given in Table 3.

Thus, *p*-aminostyrene can be isolated rather readily in pure form from the mixture of products of the dehydrogenation of *p*-aminoethylbenzene.

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References

1. A. Skogseid, Norw. Pat., No. 73344, 1948; Chem. Abstr., **42**, 7791 (1948).
2. A. B. Davankov, E. V. Zambrovskaya, *Vysokomolek. soed.*, **9**, 1382 (1960).

3. M. Ya. Romankevich, V. G. Sinyavskii, N. P. Tsygankova, *Ukr. khim. zhurn.*, **9**, 1096 (1962).
4. V. G. Sinyavskii, A. I. Turbina, Author' s Certificate No. 797357, 1962.
5. G. Mancke, S. Singer, *Makromol. Chem.*, **37**, 119 (1960).
6. D. T. Mowry, M. Renoll, W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).
7. P. P. Shorygin, I. V. Shorygina, *ZhOKh*, **9**, 845 (1939).
8. M. Martynoff, *Bull. Soc. Chim.*, **22**, 374 (1955).
9. M. M. Koton, Yu. V. Mitin, F. S. Florinskii, *ZhOKh*, **25**, 1469 (1955).
10. J. Petit, R. Lumbroso, *C. R.*, **248**, 1541 (1959).
11. V. G. Sinyavskii, A. I. Turbina, M. Ya. Romankevich, *Dokl. AN USSR*, No. 12, 1622 (1962).
12. G. Benz, *Ber.*, **15**, 1646 (1882).
13. P. M. Kochergin, *ZhOKh*, **27**, 3204 (1957).
14. A. A. Balandin, N. I. Shuikin et al., *ZhPKh*, **32**, 2566 (1959).
15. R. R. Dreisbach, R. A. Martin, *Ind. and Eng. Chem.*, **41**, 2875 (1949).
16. A. P. Groshev, *Technical Analysis*, Moscow, 1958, p. 389.

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