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The Prins Reaction of Styrene in the Presence of Cation-exchange Resin

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The application of ion-exchange resin to the Prins reaction has been investigated by several workers. The reactions of styrene, methyl styrene[1] and propyrene[2] were carried out with KU-2 cation-exchange resin, which gave the corresponding 1,3-dioxanes in good yields. However, in any case, no detailed study from the viewpoint of a solid acid catalyst has been reported on a Prins reaction in the presence of ion-exchange resin. Because the active site of a solid catalyst is the surface of the resin, the reactivity of the ion-exchange resin is largely dependent upon a crosslinkage which is determined by the content of divinylbenzene(DVB), and the crosslinkage makes a micropore in the state of swelling. The ion-exchange resin with a higher DVB content has smaller micropores. Besides the micropores, the ion-exchange resin polymerized with a macroreticular reagent has macropores. Thus, the reaction of styrene with formaldehyde in the presence of various types of ion-exchange resins was carried out, and the relation of the reactivity and the crosslinkage was investigated. The ion-exchange resins used were Diaion SK 1B, SK 104, the Diaion PK series, and Amberlite XE 284, all of which are strongly acidic cation-exchange resins and WK 10, and WK 11, which are weakly acidic cation-exchange resins.

When the SK series was used, the crosslinkage was dependent upon the yield of 4-phenyl-1,3-dioxane. The crosslinkage of SK 104 is 4%, and that of SK 1B is 8%. The crosslinkage in the PK series varies from 4%(PK 208) to 14%(PK 228). It is interesting that the yield of 4-phenyl-1,3-dioxane is highest with the crosslinkage of 10% among the other PK series. It may be found from this result that the size of the micropores is related to the reactivity. As the size of the pores of the resins becomes larger, the yield of 4-phenyl-1,3-dioxane increases. However, the micropore sizes of No. 8, 9, and 10 in Table 1 are so large that swelling occurs and it is difficult to separate the product because of its adsorption by resin. Also, the macropore has an important effect upon the yield; the porous type of 10% crosslinkage is most effective. However, the highly porous types (HPK, XE 284) prepared from higher contents of DVB are not so excellent as the PK series. The highly porous ion-exchange resin adsorbs the start-

TABLE 1. PRINS REACTION OF STYRENE WITH ION EXCHANGE RESIN

No	Ion exchange resin	Reaction condition		Yield	
		Temp (°C)	Time (hr)	g	%
1	SK 104	50—53	27	20.2	41.2
2	SK 104	50—53	10	11.0	22.4
3	SK 104	50—53	10	11.0	22.4
4	SK 104	50—53	10	12.5	25.5
5	SK 104	25	10	3.0	6.1
6	SK 1B	50—53	18	9.0	18.0
7	SK 1B	25	10	2.3	4.6
8	PK 208	55	10	5.2	10.6
9	PK 212	55	10	25.0	51.0
10	PK 216	55	10	20.0	40.8
11	PK 220	55	10	34.5	70.4
12	PK 220	30	10	3.5	6.4
13	PK 224	55	10	19.0	38.8
14	PK 228	55	10	11.2	22.9
15	HPK	55	10	11.0	22.4
16	XE 284	55	3	12.0	24.5
17	WK 10	50—53	13	trace	
18	WK 11	50—53	13	trace	

1) V. I. Isagnlyants and M. G. Safarov, *Zh. Prikl. Khim.*, **39**, 1148 (1966); *Chem. Abstr.*, **65**, 5455; V. I. Isagnlyants, M. G. Safarov and D. I. Rakahncakulov, *Zh. Prikl. Khim.*, **40**, 1160 (1967); *Chem. Abstr.*, **67**, 108609.

2) B. N. Bolylev, E. P. Tepenitsya, and M. I. Farberov, *Neftekhimia*, **9**, 71 (1969); *Chem. Abstr.*, **70**, 115083.

ing materials and products, so filtration is troublesome. It may safely said that the highly porous ion-exchange resin is a good adsorbent, but is unsuitable for the catalyst of the Prins reaction. That is, XE 284 gave a considerable yield in 3 hr, but this resin was gradually wrecked by the reaction. Therefore, it is difficult to carry out the reaction further, and a repeated reaction with XE 284 is impossible.

In No. 2, 3, and 4 in Table 1, reactions with the same catalyst were repeated. The results show that this catalyst was sufficiently used without regeneration.

To examine the effect of the temperature, the reaction was carried out with PK 220 at 30°C. In the case of PK 220, the yield was 6.4%. When SK 1B and SK 104 were used as the catalysts, the same results were obtained. These results show that the reaction is dependent upon the temperature.

Swelling is a very important factor in a porous-type ion-exchange resin. Therefore the reactions were investigated in various solvents. As the solvents, dimethylsulfoxide, methylene chloride, dioxane, and methanol were used, and paraformaldehyde was employed instead of formalin. In dimethylsulfoxide, a small amount of 4-phenyl-1,3-dioxane was obtained. However, in the other solvent, 4-phenyl-1,3-dioxane was not obtained but an unidentified product was obtained besides recovered styrene. A further investigation of the reaction in nonaqueous solvents is now in progress.

When the reaction is carried out with ion-exchange resin as the solid acid catalyst insted of sulfulic acid, phospholic acid, acetic acid or Lewis acid, it is easy to separate the product and the catalyst, and styrene and formalin are made to flow from the top of the column, packed with resin, and 4-phenyl-1,3-dioxane is obtained at the bottom of the column. It is possible to recycle the unreacted material after the separation in order to raise the yield and the efficiency.

Experimental

The ion-exchange resin (100 m*l*) was immersed into 250 m*l* of 50% H_2SO_4 for 8 hr at room temperature, and then filtered and washed with water until the washings were found by litumus paper to be no longer acid.[3] The treated ion-exchange resin, 35 g of styrene, and 100 m*l* of formalin (37%) were mixed in a 300 m*l*, three-necked, round-bottom flask for a given time at an appropriate temperature. After the reaction, the mixture was poured into 300 m*l* of water and the resin was filtered off. The filtrate was extracted with ether. The ether solution was distilled, and the unreacted styrene was obtained at 42°C and 20 Torr. The product was distilled at 90—95°C and 3 Torr. This compound was identified as 4-phenyl-1,3-dioxane by comparison with the IR spectrum of an authentic sample. The results are shown in Table 1. In these reactions, the unreacted styrene was recovered quantitatively.

The SK series are the strongly acidic sulfonic-acid-type cation-exchange resins, and the WK series are the weakly acidic carboxylictype cation-exchange resins. The PK series are the porous ion-exchange resins, which are of the sulfonic-acid type. The HPK and XE 284 are highly porous ion-exchange resins.

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3) "Diaion Ion-exchange Resin Manual (I)" revised ed., Mitsubishi Chemical Industries, Ltd. (1970).