Tetrahedron Letters, Vol.22, No.39, pp 3873 - 3874, 1981
Printed in Great Britain

0040-4039/81/393873-02$02.00/0

FACILE SYNTHESIS OF p-CHLOROMETHYLATED STYRENE BY ELIMINATION REACTION OF p-(2-BROMOETHYL)BENZYLCHLORIDE USING POTASSIUM HYDROXIDE AS A BASE UNDER PHASE TRANSFER CATALYSIS

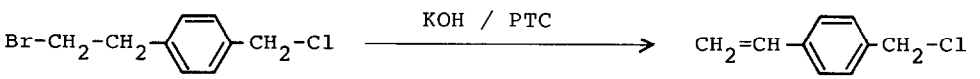
Tadatomi Nishikubo*, Takashi Iizawa, Kazuo Kobayashi, and Makoto Okawara#

Laboratory of Polymer Chemistry, Kanagawa University, Kanagawa-ku, Yokohama 221
#Research Laboratory of Resource Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama, 227 Japan

Summary: Phase transfer catalyzed elimination reactions of p-(2-bromoethyl)-benzylchloride with potassium hydroxide gave p-chloromethylated styrene in high yield.

The chloromethylated polystyrene is one of the important reactive polymers and has been used as polymeric supports for the solid phase peptide syntheses[1], polymeric catalysts[2], polymeric reagents[3], and biologically active polymers[4]. Tanimoto et al[5] reported the simple synthesis of p-chloromethylated styrene (CMS) by the reaction of p-(2-bromoethyl)benzylchloride (BEBC) with potassium tert-butoxide. Arshady et al[6,7] also reported interesting methods for the syntheses of CMS, however, these methods consisted of five or six step reactions to obtain the CMS and the yields obtained from these processes were not so good. Recently, phase transfer catalysis has found utility in many organic reactions[8], and these simple, mild and economical methods are very important for the syntheses of functional monomers and their polymers.

This communication reports on the successful facile synthesis of CMS from the reaction of BEBC with potassium hydroxide in the presence of phase transfer catalyst (PTC).



In a two phase reaction system consisting of an organic layer and a solid base, the reaction of BEBC with potassium hydroxide in tert-butanol proceeded with yield of 48% in the absence of a PTC and 32% of the charged BEBC was recovered. Whereas, the same reaction proceeded with high yield such as 73 and 64% under the same reaction condition when tetrabutylammonium bromide (TBAB) or 18-crown-6 (CR) was added as a PTC, respectively. Although the

reaction of neat BEBC with potassium hydroxide proceeded with high yield in the presence of TBAB as a PTC for the short reaction time such as 4 hr, the yield of CMS became low and the yield of oligomeric by-product increased by increasing the reaction time. In the two phase reaction system consisting of an organic layer and a water layer, CMS did not obtain with high yield and much amount of the charged BEBC recovered in the presence of TBAB as a PTC.

Table I. The reaction conditions and results

No	Solvent (50 ml)	Catalyst (0.01 mol)	Time (hr)	Yield of CMS (%)	Recovered of BEBC (%)
1	tert-butanol	None	24	48.2	31.9
2	tert-butanol	TBAB	24	73.1[9)]	7.4
3	tert-butanol	CR	24	63.6	12.9
4	benzene/water[a)]	TBAB	24	46.6	48.8
5	benzene/water	TBAB	24	37.9	-
6	None	TBAB	4	77.4	-
7	None	TBAB	24	66.7	-
8	None	TBAB	48	36.7	-

The reaction was carried out with 0.1 mol of BEBC and 0.012 mol of potassium hydroxide at 30°C.
a) 50% aqueous solution of potassium hydroxide.

From these results, it can be concluded that the phase transfer catalysis is a useful method for the facile synthesis of CMS by the reaction of BEBC with potassium hydroxide.

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9. Although, the yield of the obtained CMS was 73%, the yield from liquid chlomatograpy was about 90%.

(Received in Japan 13 June 1981)