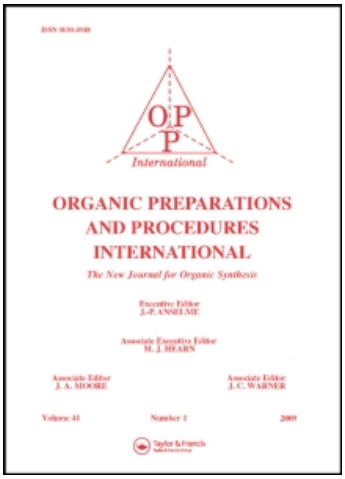

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CONVENIENT SYNTHESIS OF 2-PHENETHYL ALCOHOL BY HYDROLYSIS OF 2-BROMOETHYLBENZENE UNDER PHASE TRANSFER CONDITIONS

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CONVENIENT SYNTHESIS OF 2-PHENETHYL ALCOHOL BY HYDROLYSIS OF 2-BROMOETHYLBENZENE UNDER PHASE TRANSFER CONDITIONS†

Submitted by (08/18/92)

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The flowery odor of 2-phenethyl alcohol gives it a significant commercial value in the synthetic perfumes industry. However, traces of impurities have undesirable effects on the alcohol's rosy odor, rendering it unsuitable as a perfume grade alcohol. Most commercial preparations of 2-phenethyl alcohol involve the Friedel-Crafts reaction of benzene and ethylene oxide[1]. This method suffers from the disadvantage of producing bibenzyl and ethylene oxide polymers as by-products which necessitates further purification of the alcohol in order to achieve a fragrance grade product. Furthermore, this process has an overall selectivity of only about 66% and requires a large excess of $AlCl_3$ over ethylene oxide in order to obtain significant yields of 2-phenethyl alcohol. Moreover, benzene, ethylene oxide and aluminum chloride cause environmental problems. Another commercially feasible method for the production of 2-phenethyl alcohol is based on the hydrogenation of styrene oxide[1]. Limitations of this method include that the cost of the epoxide and the further purification necessary to meet perfume grade specifications. We report here a new process

for the preparation of a perfume grade 2-phenethyl alcohol from a mixture of 2-bromoethylbenzene (2-BEB) containing up to 10 mol% of 1-bromoethylbenzene (1-BEB)[2] under solid-liquid phase transfer catalysis (PTC) conditions.

This process is based on our finding of the clean elimination reaction of 1-BEB to yield styrene, with the simultaneous substitution of 2-BEB to form the corresponding formate ester. This formate ester is directly hydrolyzed in the reaction mixture to yield perfume grade 2-phenethyl alcohol.

EXPERIMENTAL SECTION

2-Bromoethylbenzene, 1-bromoethylbenzene, sodium formate, *n*-tetrabutylammonium bromide (TBAB), Aliquat 336, and sodium hydroxide were purchased from Aldrich or Fluka AG. Gas-Chromatography (GC) was performed on a 5% phenyl methyl silicone 25 m x 0.31 mm capillary column, installed in a Hewlett-Packard 5790 gas chromatograph with FID detector. Column temperature was programmed from 80° to 250° at 10°/min. The carrier gas was N_2 at a flow rate of 2 mL/min.

Preparation of 2-Phenethyl Alcohol from a Mixture of 2-BEB and 1-BEB.- A 250 mL round-bottomed flask equipped with mechanical stirrer and reflux condenser heated by a thermostatic oil bath, was charged with a mixture consisting of 2-BEB (92.5 g, 0.5 mol) and 1-BEB (3.0 g, 0.016 mol), sodium formate (68 g, 1 mol), and TBAB (8 g, 0.024 mol). The flask was stirred (800 rpm) at 155° for 3 hrs, then an aqueous 50% (w/w) sodium hydroxide solution was slowly added with stirring for 30 min. The organic phase was separated and dried over $MgSO_4$. Fractional distillation of the residue gave styrene, bp. 80°/40 mmHg, lit.[3] bp. 33.6°/10 mmHg, and 55.8 g (91%) of 2-phenethyl alcohol (99.8% pure), bp. 105°/15 mmHg, lit.[3] bp. 97.4°/10 mmHg, halogen free (Beilstein test).[4]

Preparation of 2-Phenethyl Alcohol from 2-BEB.- A mixture of 2-bromoethylbenzene (185 g, 1 mol), sodium formate (102 g, 1.5 mol), and Aliquat 336 (11.48 g, 0.0366 mol) in a 500 mL round-bottomed flask equipped as in the previous experiment, was stirred at 155° for 3 hrs. After cooling, aqueous 50% (w/w) sodium hydroxide solution (80 g, 1 mol) was slowly added with stirring for 30 min. The organic phase was separated and dried with $MgSO_4$ and fractionally distilled. Styrene was distilled off at 80°/40 mmHg and then 2-phenethyl alcohol at 105°/15 mmHg to yield 110.8 g (91%) of 99.8% pure 2-phenethyl alcohol, halogen free (Beilstein test).

Purification of a Mixture of 2-BEB and 1-BEB.- A 50 mL round-bottomed flask with a side-arm for sampling, equipped with mechanical stirrer and reflux condenser heated by a thermostatic oil bath, was charged with 2-bromoethylbenzene (13.7 g, 74 mmol), 1-bromoethylbenzene (1.52 g, 8.2 mmol), sodium formate (1.394 g, 20.5 mmol) and 540 mg of 1-methylnaphthalene (internal standard) at 155°. A quantitative conversion of 1-bromoethylbenzene was achieved after 2 hrs and the product distribution was 95% styrene and 5% 1-phenethyl formate; the 2-BEB was recovered unchanged. The GC analysis was performed under the conditions described above. Retention times were as follows:

styrene, 1.02 min; 1-phenethyl formate, 3.87 min; 1-bromoethyl benzene, 4.83 min; 2-bromoethyl-benzene, 6.35 min; 1-methylnaphthalene, 9.19 min.

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† Dedicated to Professor E. V. Dehmlow on the occassion of his 60th birthday.

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IMPROVEMENT OF THE VILSMEIER-HAACK REACTION

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During the course of a study of the asymmetric alkylation and deracemization of α-amino acids supported on a chiral polymer,[1] we required compound **2** in order to prepare one of the monomeric precursors. It has been reported[2] that treatment of N-methylformanilide (**1**) with a mixture of $POCl_3$ and PCl_5, gives *p*-N-methylaminobenzaldehyde (**2**) in 33% yield. However, when the literature conditions were used, the yields were erratic ranging from 15-30%. Moreover, purification of the product is somewhat difficult on account of the numerous by-products. We therefore undertook a study of the experimental conditions of the Vilsmeier-Haack reaction,[3] such as dilution with a solvent, the use of various halogenated reagents, the relative quantities of reagents, the reverse addition of reagents, etc.