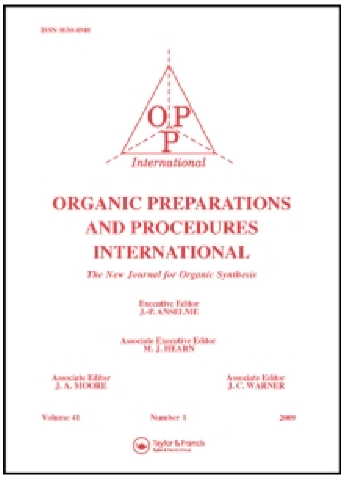

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SYNTHESIS OF 2-BROMOSTYRENE

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OPPI BRIEFS

(By J.-P. Anselme, Editor)

SYNTHESIS OF 2-BROMOSTYRENE

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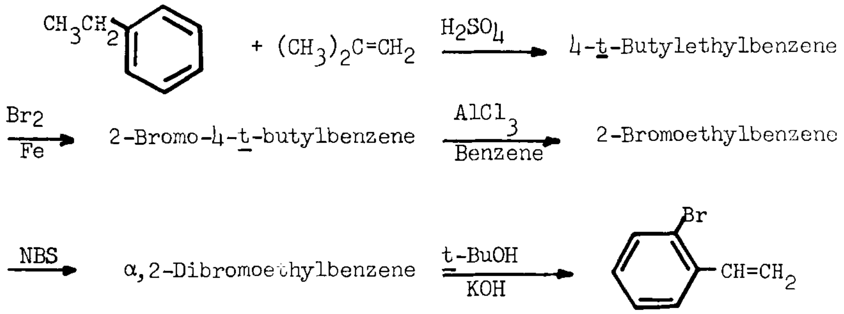
A less expensive route, more suitable for the large-scale synthesis of 2-bromostyrene (a fire retardant)[1,2] has been developed as shown in the scheme below.



EXPERIMENTAL

4-t-Butylethylbenzene.- Ethylbenzene (137.8 g., 1.3 mole) and 62.4 g. (0.65 mole) of concentrated H_2SO_4 were mixed at -6°. Then 73 g. (1.3 mole) of isobutene were introduced into the stirred mixture at such a rate as to keep the temperature at -6°. After the addition was completed, (∿ 2 hrs.), the acid phase was separated and the organic layer was poured into cold 1N NaOH solution. The organic layer was separated, washed with cold water, dried over $MgSO_4$ and distilled under reduced pressure. The fraction collected at 205-210°/700 mm Hg was a mixture of 4- and 3-*t*-butylethylbenzene, in the ratio of 95/5 respectively. The overall yield was 191 g. (91%).

2-Bromo-4-t-butylethylbenzene.- A solution of 191 g. (1.18 mole) of the above *t*-butylethylbenzene 100 ml of carbon tetrachloride was placed in a 3-neck round flask equipped with a magnetic stirrer, dropping funnel and a reflux condenser. After the addition of 3.5 g. (0.065 mole) of iron powder, 190 g. (1.2 mole) of bromine in 150 ml CCl_4 were introduced through the dropping funnel at room temperature. After 4 hrs., the reaction mixture was poured into cold 1N NaOH solution. The organic layer was separated and washed with cold water, dried over $MgSO_4$ and distilled under reduced pressure 241 g. (85%) of 2-bromo-4-*t*-butylethylbenzene, bp. 77°/0.5 mm Hg.

2-Bromoethylbenzene.- To a solution of 241 g. (1 mole) of 2-bromo-4-*t*-butylbenzene in 390 g. (5 mole) of benzene cooled to 0°, was added 2 g. (0.015 mole) of solid $AlCl_3$ and the mixture was stirred at 0°. After 1 hr., the reaction mixture was poured into cold 1N NaOH solution. The organic layer was separated, washed with cold water and dried over $MgSO_4$. Excess benzene was distilled at atmospheric pressure. An equimolar (0.92 mole) mixture of 2-bromoethylbenzene (170 g., G.C. determination) and *t*-butylbenzene (123 g., G.C. determination) was collected at 70-85°/18 mm Hg. The overall yield of 2-bromoethylbenzene in the mixture was 92%.

α,2-Dibromoethylbenzene.- The above mixture was heated to reflux with 178 g. (1 mole) of N-bromosuccinimide in 300 ml CCl_4 in the presence of

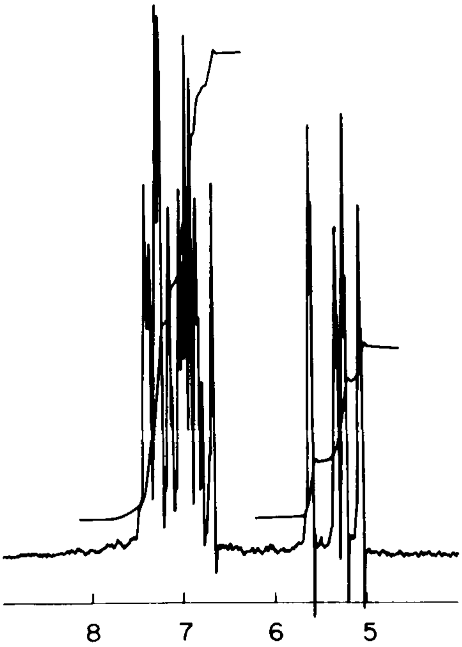
100 mg dibenzoylperoxide. At the end of the reaction, the succinimide was filtered and the CCl_4 solution was washed with a dilute NaOH solution and with water, and dried over $MgSO_4$. The solvent was removed by evaporation, and 230 g. (95%) of α,2-dibromoethylbenzene was collected at 85°/2 mm Hg.

2-Bromostyrene.-

a. Thermal dehydrobromination.- I (66 g., 0.25 mole) was heated to 150° at 65 mm Hg in a distillation apparatus; 2-bromostyrene (27 g., 60% yield) was distilled together with HBr.

b. Dehydrobromination with organic base.- A mixture of 129 g. (1 mole) of diisopropylethylamine and 66 g. (0.25 mole) of I was heated to 140° for 1 hr. The amine was extracted with dilute acid; the organic layer was washed with sodium bicarbonate solution and with water, then dried over $MgSO_4$. Distillation yielded 27 g. (60%) of 2-bromostyrene which was collected at 50°/2 mm Hg.

c. Dehydrobromination with an inorganic base.- A mixture of 132 g. (0.5 mole) of I and 62 g. (1.1 mole) of powdered KOH were heated to reflux in 300 ml of t-butanol with vigorous stirring for 1 hr. Quantitative G.C. determination showed a 94% conversion of I into 2-bromostyrene. The t-butanol, KBr and excess KOH were removed by the extraction with 300 ml water. The organic layer was dried over $MgSO_4$.



Distillation afforded 80 g. (86%) of 2-bromostyrene were collected at 50°C/2 mm Hg.

The figure shows the proton nmr spectrum of 2-bromostyrene in CCl_4. The chemical shifts are in δ ppm downfield from an external TMS. The two β protons appear as two sets of doublets between 5 and 5.7 ppm. The chemical shifts and the coupling constants are in agreement with those described by Gurudata et al.

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NEW 5-SUBSTITUTED-2-FURALDEHYDES

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The preparation of ten new 5-(substituted)-2-furaldehydes (Table I) are reported. 5-Aryl-2-furaldehydes (Compounds I & II, Table I) were prepared by reacting a diazotized solution of the corresponding aromatic amine with furfural and cupric chloride (Meerwein's arylation) according to the published procedure.[1] 5-Aryloxy-2-furaldehydes (Compounds III-VI) were obtained by the reaction of 5-bromo-2-furaldehyde with the corre-