

## Synthesis of Monobrominated Anilines *via* Bromination–Isomerization

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Direct bromination of aniline and its 2- and 4-methyl derivatives and subsequent isomerization of the mono-, di- and tri-bromoanilines formed gives 4-bromoaniline (4-bromo-2-methylaniline and 2-bromo-4-methylaniline) in high yield.

**Table 1** The change in the isomeric composition during heating

Conditions of isomerization	Starting aniline (mol %) <sup>a</sup>				
	Aniline	2-Bromo-	4-Bromo-	2,4-Dibromo-	2,4,6-Tribromo-
After bromination, 0°C	66	7	10	10	5
110°C, 1 h	54	8	25	9	—
128°C, 1 h	52	6	38	5	—
135–140°C, 1 h	52	2	43	3	—
135–140°C, 2 h	50	<1	48	<1	—

<sup>a</sup> All products were identified by comparison of retention time in GC with authentic specimen and by MS.

Direct bromination of aniline with bromine gives a mixture of mono-, di- and tri-bromoanilines.<sup>1</sup> Selective *para*-bromination of aniline proceeds only in reactions with brominating agents milder than bromine.<sup>2</sup> It is known that brominated anilines undergo isomerization, but such isomerization leads to a mixture of isomers.<sup>3</sup> We have shown that heating the isomeric mixture obtained by the bromination of aniline with a deficiency of bromine in the presence of HBr leads to oriented isomerization and affords 4-bromoaniline with high yield and purity.†

† *General method:* 0.55 mol of HBr (48%) was added to 1 mol of aniline followed by 0.5 mol of bromine at 0°C. The mass was heated, water and excess HBr were distilled off and the wet solid salts were heated for 2 h at 135–140°C. Isomerization of the bromoanilines took place during the heating (Table 1). After addition of NaOH to the reaction mass, followed by distillation, 4-bromoaniline was obtained with 87% yield (on bromine consumed) or 83% on aniline (based on recovered starting material) and 98.5% purity.

The same procedure was used for the bromination–isomerization of 2- and 4-methylanilines. 4-Bromo-2-methylaniline and 2-bromo-4-methylaniline were obtained with *ca.* 90% yields, based on the recovered toluidines.

### References

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