249. *Mixed Laterally-halogenated Toluenes.*

By L. S. Heble, D. R. Nadkarni, and T. S. Wheeler.

The preparation of *benzylidene chloridebromide*, *benzodichloridebromide*, and *benzochloridedibromide* is described. Chlorine and bromine can each displace the other from the toluene side chain under suitable conditions.

Bromination of benzyl chloride at 100° gives benzyl bromide, *benzylidene chloridebromide*, and benzylidene bromide; benzylidene chloride with bromine at 120—140° yields *benzodichloridebromide* and *benzochloridedibromide*. Bromination of benzyl bromide at 135° gives benzylidene bromide and eventually at 160° benzotribromide; the former product, though long known, does not appear previously to have been prepared by the direct action of bromine, and the latter has been obtained by heating carbon tetrabromide with benzyl or benzylidene bromide (Hunter and Edgar, *J. Amer. Chem. Soc.*, 1932, **54**, 2028).

Chlorination of benzyl bromide at 110° gives benzylidene chloridebromide; at 150—160° benzodichloridebromide and benzotrichloride are obtained. It will be observed that chlorine and bromine can each displace the other from the toluene side chain under suitable conditions.

Control of fractionation subsequent to halogenation is facilitated by the observation that anhydrous formic acid reacts on heating with di- and tri-ω-halogenated toluenes to give, respectively, benzaldehyde and benzoic acid, hydrogen halide and carbon monoxide being evolved. This reaction can be used as the basis of a convenient method for the estimation of side-chain halogen in simple aromatic compounds [Gavankar, Heble, and Wheeler, *J. Univ. Bombay*, 1937, **6** (2), 112].

Experimental.

Side-chain halogen was estimated by the method described by Gavankar, Heble, and Wheeler (*loc. cit.*), and total halogen by the Carius method.

Bromination of Benzyl Chloride.—Bromine (250 g.) was slowly added to the halide (200 g.), which was heated under reflux in a round flask at 100°; initially reaction was vigorous. When bromine fumes had disappeared, heating was continued under water-pump vacuum to remove hydrogen bromide, and the liquid was then repeatedly fractionated at 2—3 mm. Fractionation was facilitated by approximate density determinations, by observation of whether heating with formic acid gave benzaldehyde or not, and by qualitative tests for chlorine and bromine. There were finally isolated: benzyl bromide (Found: side-chain halogen, 46·5; total halogen, 47·1. Calc.: side-chain and total halogen, 46·8%); *benzylidene chloridebromide*, b. p. 92—95°/2—3 mm. (Found: side-chain halogen, 55·9; total halogen, 56·3. C_7H_6ClBr requires side-chain and total halogen, 56·2%); and benzylidene bromide (Found: side-chain halogen, 63·5. Calc.: 64·0%). The last two compounds gave benzaldehyde (phenylhydrazone confirmation) on being boiled with formic acid. Benzylidene chloridebromide is colourless when pure, but rapidly clouds when exposed to air. It irritates the skin, has a pungent smell and is lachrymatory.

Bromination of Benzylidene Chloride.—The chloride (100 g.) when treated with bromine (100 g.) at 120—140° gave *benzodichloridebromide*, b. p. 88—94°/1 mm. (Found: side-chain halogen, 62·7; total halogen, 62·3. $C_7H_5Cl_2Br$ requires side-chain and total halogen, 62·9%), and *benzochloridedibromide*, b. p. 98—103°/1 mm. (Found: side-chain halogen, 68·5; total halogen, 68·5, 68·9. $C_7H_5ClBr_2$ requires side-chain and total halogen, 68·7%). Both compounds possess a pungent smell and fume when exposed to air; they give benzoic acid with formic acid.

Bromination of Benzyl Bromide.—Benzyl bromide (85 g.) was slowly treated with bromine

(80 g.) at 135°. After the mixture had been heated under reflux for 6 hours, samples gave benzaldehyde with formic acid and yielded benzylidene bromide on fractionation. A further quantity of bromine (80 g.) was added, and after the mixture had been heated at 160° for six hours, a sample gave benzoic acid with formic acid. The fraction of b. p. 130—140°/2—3 mm. solidified, and after crystallisation from light petroleum had m. p. 60° (Hunter and Edgar, *loc. cit.*, give 56—57°) [Found : side-chain halogen, 72·9, 72·6; total halogen, 73·3; *M* (cryoscopic in benzene), 328, 336. Calc. for $C_7H_5Br_3$: side-chain and total halogen, 73·0%; *M*, 329].

Chlorination of Benzyl Bromide at 110°.—Bromine fumes were evolved on passing chlorine into the bromide; after 4 hours the liquid was fractionated, and benzylidene chloridebromide (properties described above) was isolated (Found : side-chain halogen, 55·9%). When chlorination was performed at 150° for 7 hours, the liquid still gave benzaldehyde with formic acid. After chlorination had been continued for a further 4 hours at 160°, a sample gave benzoic acid with formic acid. Fractionation then yielded benzotrichloride (Found : side-chain halogen, 54·0. Calc. : 54·5%) (confirmed by b. p., by formation of benzoic acid with formic acid, by qualitative absence of bromine, and by density) and benzodichloridebromide (Found : total halogen, 63·1%).

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ROYAL INSTITUTE OF SCIENCE, BOMBAY. [*Received, June 28th,* 1938].