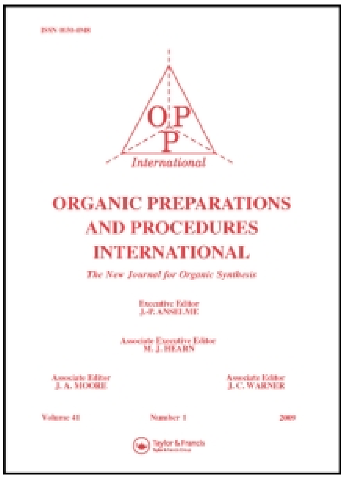

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10a. A CONVENIENT SYNTHESIS OF 3,5-DI-(*t*-BUTYL)BROMOBENZENE FROM BENZENE

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10a.A CONVENIENT SYNTHESIS OF 3,5-DI-(*t*-BUTYL)BROMOBENZENE FROM BENZENE

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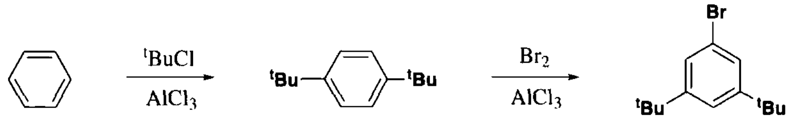
3,5-Di-*t*-butylbromobenzene (**2**) is a versatile reagent with a simple structure but difficult to synthesize.[1-3] As a part of another investigation, we needed **2**. A survey of its synthesis shows that four main routes have been reported, namely by a) bromination of 1,3,5-tri-*t*-butylbenzene (**1**) in the presence of iron (65-71% yield),[4,5] b) bromination of 1,3,5-tri-*t*-butylbenzene (**1**) in the presence of AgClO$_4$ (21% yield),[6] c) bromination of 3,5-di-*t*-butylphenol with bromine-triphenylphosphine at 130° (59% yield),[7] and d) from 3,5-di-*t*-butylbenzoic acid *via* degradation, diazotization, and bromine substitution (15% yield).[8] Method **a** is most frequently used.[1-3,5,9] All these methods require expensive, not readily available reagents. Furthermore, they are cumbersome and the yields of **2** are low except in method **a** when a large amount of iron is employed and by method **c** when stoichiometric amount of triphenylphosphine is used.[4] We report herein a new method for the synthesis of **2** from benzene, employing common and inexpensive reagents by in a one-pot procedure.



3 **2**

The reaction was performed in the presence of a catalytic amount of AlCl$_3$. 1,4-Di-*t*-butylbenzene (**3**), which could be isolated as an intermediate, was identified by its melting point and spectra. Compound **3** was treated with bromine *in situ* to afford **2**. Even though the mechanism is unclear, we believe that an isomerization must occur, as it is necessary in the formation of **2**. Preliminary experiments revealed that **3** may be isomerized to 1,3-di-*t*-butylbenzene (**4**) with AlCl$_3$ as the catalyst.[10] However, this is unsuitable for the preparation of **4** in large scale because of the low conversion and the difficulty of separating of **3** and **4** by distillation.[3] A strong Lewis acid such as AlCl$_3$ is necessary for one-pot synthesis of **2**. 2,5-Di-*t*-butylbromobenzene was obtained when iron was used as a catalyst instead of AlCl$_3$.

EXPERIMENTAL SECTION

Melting point was determined using a Yazawa BY-1 micro melting point apparatus, and is not corrected. NMR spectra were recorded in CDCl$_3$ on a BRUKER DRX-400 spectrometer. Chemical shifts were given in ppm relative to TMS as internal standard.

3,5-Di-(*t*-butyl)bromobenzene.- To a stirred suspension of 0.9 g (6.74 mmol) of $AlCl_3$ in 7.8 g (0.100 mol) of benzene, a solution of 18.5 g (0.200 mol) of *t*-butyl chloride in 20 mL of CCl_4 or 1,2-dichloroethane was added at 5° in 1 hr. Stirring was continued for another 20 min. Bromine (16.1 g, 0.101 mol) in 10 mL of CCl_4 or 1,2-dichloroethane was added slowly to the stirred mixture. After evolution of hydrogen bromide had ceased, the mixture was treated successively with ice-water (100 mL) and 50 mL aqueous solution of 2N NaOH, and dried over Na_2SO_4. After evaporation of the solvent, the liquid residue was heated with 2.0 g of solid NaOH at 95° for 4 hrs to neutralize the hydrogen bromide generated. After addition of 20 mL of water, the two phases were separated. The aqueous phase was extracted with carbon tetrachloride (3 x 10 mL) and the combined organic phase was dried over anhydrous sodium bicarbonate, filtered and distilled. After removal of the solvent, compound **2** was obtained by vacuum distillation (114-120°/3mm). Pure compound **2** (13.1 g, 49%), mp. 65.5-66°, *lit.*[4] mp. 63-64°, was obtained after recrystallization from petroleum ether; ^1H NMR (400 MHz, $CDCl_3$): δ 7.325 (s, 3H), 1.300 (s, 18H); ^{13}C NMR: δ 152.952, 125.219, 122.219, 121.030, 34.982, 31.291. *lit.*[9] ^1H NMR: δ 7.33 (s, 3H),1.28 (s,18H);[3] ^{13}C NMR: δ 152.95, 125.73, 122.18, 121.05, 34.98, 31.28.

Compound **3** could be isolated by general method if the reaction was stopped before bromine was added.

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