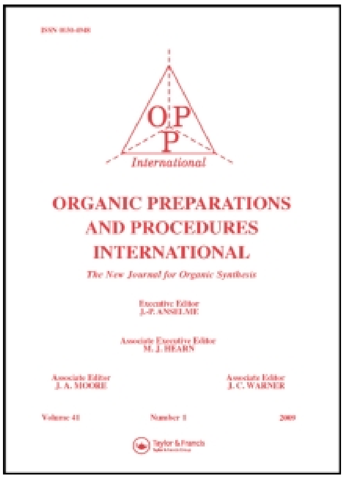

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2,4-DI-*t*-BUTYLBROMOBENZENE BY SILVER ION-ASSISTED BROMINATION OF 1,3-DI-*t*-BUTYLBENZENE

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OPPI BRIEFS

2,4-DI-*t*-BUTYLBROMOBENZENE
BY SILVER ION-ASSISTED BROMINATION OF 1,3-DI-*t*-BUTYLBENZENE

Submitted by
(02/01/91)

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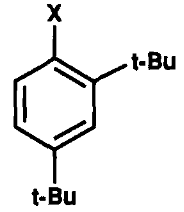
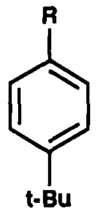
In the course of studies on the synthesis of sterically congested bibenzyls,[1] we required the title compound, 2,4-di-*t*-butylbromobenzene (**1a**). A review of the literature indicated that this substance has not been previously reported. This did not appear surprising in view of the relative inaccessibility of the most obvious starting material, 1,3-di-*t*-butylbenzene (**1b**),[2] and the ease with which dealkylation and skeletal rearrangement occur with **1b** and other *t*-butylbenzenes.[2-5] Our initial attempt at the synthesis of **1a** involved reaction of commercially available 2,4-di-*t*-butylphenol (**1c**) with triphenylphosphine dibromide.[6] This reaction, however, afforded 4-*t*-butylbromobenzene (**2a**) in good yield. This reaction probably proceeds by dealkylation of **1c** to afford 4-*t*-butylphenol, a reaction which has precedent,[7] followed by conversion of the latter to **2a**. We then treated 1,4-di-*t*-butylbenzene (**2b**) with a mixture of $AlCl_3$ and Br_2. We hoped to effect *in situ* rearrangement of **2b** to **1b**, followed by bromination of the latter, to afford **1a** in a reaction akin to the formation of 2,4-di-*t*-butylacetophenone as the major product when **2b** is subjected to Friedel-Crafts acetylation conditions.[4] However, this reaction afforded a complex mixture, which gc-mass spectrometry showed to consist of at least thirty-six components of general structure $C_6(t\text{-}Bu)_xBr_yCl_zH_{6-x-y-z}$, where x, y and z range from 0 to 3. These substances are apparently formed from **2b** by a series of dealkylation, alkylation, and rearrangement processes, together with attack on the arene nucleus by electrophilic bromine and/or chlorine.



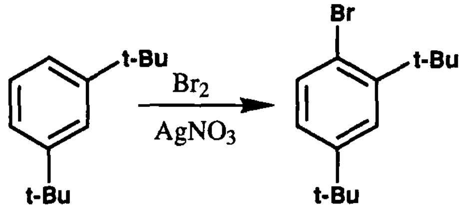
1

a) X = Br
b) X = H
c) X = OH



2

a) R = Br
b) R = t-Bu



1b **1a**

We then turned our attention to the direct conversion of **1b** to **1a**.[3,4] The high cost of commercially available **1b** prompted us to devise a convenient synthesis of **1b**. Treatment of **2b** with $AlCl_3$ in CS_2 afforded a mixture of **1b**, **2b**, *t*-butylbenzene, and 1,3,5-tri-*t*-butylbenzene in which the ratio of **1b** of **2b** is slightly greater than unity,[3,4] and from which **1b** could be isolated in pure form by careful fractional distillation (the yield of **1b** could be enhanced by re-equilibration of the distillation residue). It was clear that successful subsequent conversion of **1b** to **1a** would require activation of the bromine molecule by a reagent which is a sufficiently weak Lewis acid not to initiate rearrangement or dealkylation of **1b**. A combination of silver nitrate and bromine has been shown to brominate **3** without rearrangement,[8] and proved equally successful in converting **1b** to **1a** in 93% (purified) yield. This reaction is notable in that the sensitive 1,3-di-*t*-butylbenzene system is halogenated without rearrangement, dealkylation, or formation of the sterically more favorable 5-bromo-1,3-di-*t*-butylbenzene.[4,5]

EXPERIMENTAL SECTION

1,3-Di-*t*-butylbenzene (**1b**).- 1,4-Di-*t*-butylbenzene (**2b**) (100 g, 0.53 mol) and $AlCl_3$ (13.86 g. 0.1 mol) were combined in 100 ml of CS_2, together with two drops of water as a promoter.[4] The reaction was monitored by gas chromatography over a period of several hours, to the point where the proportion of **1b** exceeded that of **2b**. The mixture was then quenched with dilute acid and extracted with ether. The organic extracts were then dried over sodium sulfate and the solvents removed by rotary evaporation. Careful distillation of the resulting mixture through a vacuum-jacketed helix-packed distillation column afforded an initial fraction, bp 71°/40 mm, consisting of *t*-butylbenzene, followed by a second fraction, 28.3 g, bp 116°/33 mm, lit.[2] 105-107°/13 mm which was to be found to be **1b** (>99.7% purity by gas chromatography). The residue, consisting of **1b**, **2b** and 1,3,5-tri-*t*-butylbenzene, was treated with *t*-butyl chloride and aluminum chloride to produce a mixture which could be distilled to produce an additional quantity of **1b**. (This recycling procedure may also be used to obtain **1b** from the supernatant liquid from the synthesis[9] of **2b**).

2,4-Di-*t*-butylbromobenzene (**1a**).- A solution of $AgNO_3$ (25.24 g, 0.15 mol) and **1b** (28.27 g, 0.15 mol)[2] in 50 ml of acetic acid was heated to 70°. Bromine (23.74 g, 0.15 mol) was added dropwise with stirring over 2 hrs, and the reaction was stirred an additional 2 hrs. Silver bromide was removed by filtration and washed with acetic acid. The filtrate was poured into 350 ml of acetic acid and extracted with CH_2Cl_2. The CH_2Cl_2 extracts were then washed with sodium bisulfite, dried over sodium sulfate, and evaporated to afford 39.09 g (98%) of a deep orange liquid, which was distilled *in vacuo* to afford 37.0 g (93%) of 2,4-di-*t*-butylbromobenzene (**1a**) as a pale yellow liquid, bp 113-115°/2.5 mm; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 9 H), 1.54 (s, 9 H), 7.5 (d, J = 8.8 Hz, 1 H), 7.48 (d, J = 2.4 Hz. 1 H), 7.06 (dd, J = 2.4 and 8.8 Hz, 1 H). Upon standing in the refrigerator, this material solidified, mp. 21-22°.

Anal. Calcd for $C_{14}H_{21}Br$: C, 62.46; H, 7.86. Found: C, 62.73; H, 7.83

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REDUCTION CLEAVAGE OF AROMATIC CYCLIC ACETALS WITH ZIRCONIUM CHLORIDE-LITHIUM ALUMINUM HYDRIDE

Submitted by
(07/26090)

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The reductive cleavage of acetals and ketals to ethers or glycol monoethers in a synthetically useful process and a number of efficient reagents have been uncovered to effect such transformations, these include $LiAlH_4$-Lewis acid, Me_3SiH-Me_3SiOTf, Et_3SiH-acids, DIBAL, B_2H_6, H_2BCl, $NaBH_3CN$-HCl, $NaBH_4$-CF_3COOH, $Zn(BH_4)_2$-Me_3SiCl, Li-NH_3 and H_2-catalysts.[1] In addition, Ishihara and Kotsuki have applied such methodology to natural products syntheses.[2,3]