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of Reliable Methods
for the Preparation
of Organic Compounds

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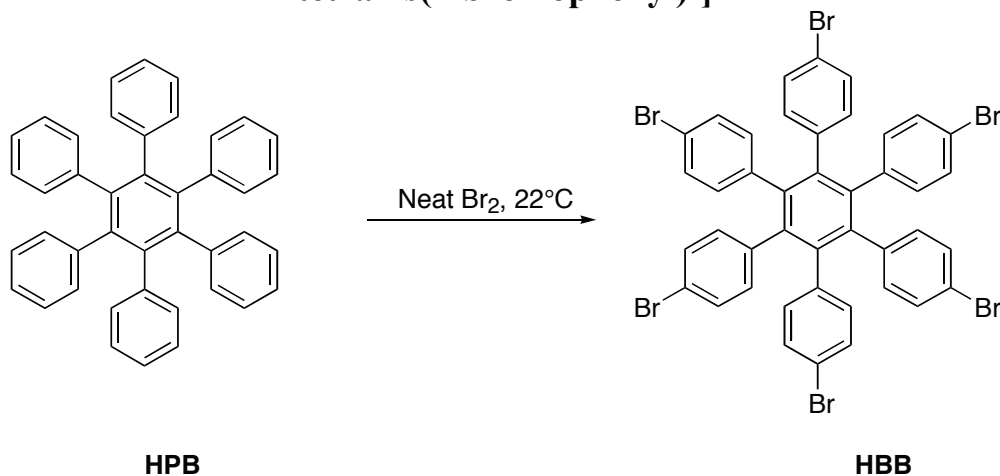
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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**PREPARATION OF
HEXAKIS(4-BROMOPHENYL)BENZENE (HBB)
[1,1':2',1''-Terphenyl, 4,4''-dibromo-3',4',5',6'-
tetrakis(4-bromophenyl)-]**



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Checked by Scott E. Denmark and Shinji Fujimori.

1. Procedure

A 500-mL, three-necked flask, equipped with a mechanical stirrer (fitted with an 11 cm Teflon paddle), a septum and an outlet adapter connected *via* rubber tubing to a pipette which is immersed in a 10% aqueous sodium hydroxide solution (250 mL) in a 500 mL Erlenmeyer flask is charged with 70 mL of bromine (1.37 mol) [Note 1]. The septum is replaced with a 250-mL powder addition funnel charged with 26.7 g (50 mmol) of hexaphenylbenzene (HPB) [Note 2]. The flask is placed in a water bath at ambient temperature to control the heat evolved from the reaction. To the slowly stirred bromine, hexaphenylbenzene is added slowly over 1 hour [Note 3]. The reaction starts immediately as judged by an evolution of gaseous hydrobromic acid [Note 4]. After the addition of hexaphenylbenzene is complete, the dark-orange slurry is stirred for an additional 20 min. [Note 5]

The bromine slurry of resulting product is carefully poured into 500 mL of pre-chilled (approx. -78 °C) ethanol in a 1-L Erlenmeyer flask with stirring by a magnetic stir bar [Note 6]. To the three-necked flask is added cold (-78 °C) ethanol (100 mL x 2) and the remaining precipitate is

transferred to the Erlenmeyer flask. The suspension of the product in ethanol is allowed to warm to room temperature over 2 h with stirring, and the suspension is filtered using a Büchner funnel. The pale yellow precipitate is washed with ethanol (50 mL), aqueous sodium bisulfite (5%, 100 mL), and ethanol (2 X 50 mL) successively. After being dried overnight *in vacuo* (0.5 mmHg) at room temperature to a constant weight, 47.8 g (96% yield) of *hexakis*(4-bromophenyl)benzene (HBB) is obtained with greater than >95% purity as judged by ¹H NMR spectroscopy.

The precipitated product is sufficiently pure for most purposes; however, it can be further purified by re-precipitation from tetrahydrofuran. Thus, 10 g of HBB was dissolved in refluxing tetrahydrofuran [Note 7] (350 mL) in a beaker. Upon slow evaporation at room temperature, the solution yields a colorless (microcrystalline) precipitate (9.4 g) of *hexakis*(4-bromophenyl)benzene (HBB). [Note 8] [Note 9].

2. Notes

1. Bromine was obtained from Aldrich Chemical Co. was used as received.

2. Hexaphenylbenzene (HPB) was obtained following the *Organic Syntheses* procedure (Fieser, L. F. *Org. Synth.*, **1973**, 46, 44; *CV* 5, 604). Commercially available HPB (Aldrich Chemical Co.) can also be used.

3. The reaction is carried out without added solvent and thus for a thorough mixing of reagents an excess of bromine is required for a complete conversion of HPB to HBB. It is critical to maintain the reaction mixture as a slurry for complete conversion.

4. Gaseous HBr was trapped in an aqueous solution of sodium hydroxide.

5. At this point the HBr evolution completely ceases.

6. The slurry should be poured into cold ethanol (-78 °C) to prevent an exothermic reaction between excess bromine and ethanol.

7. Tetrahydrofuran (Optima grade) was obtained from Fischer Inc. and was used as received.

8. The spectral data for analytically pure HBB: mp 358-359 °C; ¹H NMR (CDCl₃) δ: 6.61 (d, *J* = 8.5 Hz, 12 H), 7.06 (d, *J* = 8.6 Hz, 12 H); ¹³C

NMR (CDCl₃) δ : 120.3, 130.5, 132.6, 138.4, 139.6. Anal. Calcd for C₄₂H₂₄Br₆: C, 50.04; H, 2.40; Br, 47.56. Found: C, 49.92; H, 2.27.

9. Crystallization can be performed in refrigerator (-15 °C) over 3 days to provide larger size crystals.

Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

The hexaphenylbenzene core is being extensively investigated as a platform for the preparation of nanometer-size macromolecules and supramolecular assemblies owing to their importance as materials that can be used as molecular devices such as sensors, switches, ferromagnets, and other electronic and optoelectronic devices.²⁻⁵ As we recently demonstrated, the elaboration of the hexaphenylbenzene core can be readily achieved using HBB for the preparation of a hexacation-radical salt⁶ for use as a (multi)electron-transfer catalyst in a variety of organic and organometallic transformations.⁷ The hexaphenylbenzene core is also being utilized for the preparation of well-defined graphite-like structures by Müllen and others and the progress in the area has been reviewed in two recent *Chemical Review* articles.^{8,9}

There is one reported procedure for the preparation of HBB, which utilizes the Diels-Alder approach using *tetrakis*(4-bromophenyl)cyclopentadienone and *bis*(4-bromophenyl)acetylene (also known as 4,4'-dibromotolan) as the starting materials.¹⁰ Both of these starting materials are prepared *via* multi-step syntheses. We have also discovered that trimerization of 4,4'-dibromotolan using *bis*(acetonitrile)palladium dichloride affords HBB in fair yield.¹¹

A similar bromination procedure (as described above for the preparation of HBB) can be employed for the preparation of *tetrakis*(4-bromophenyl)methane using tetraphenylmethane and bromine.⁶

The method described here for the preparation of HBB is essentially a detailed description of our recently published procedure⁶ using

hexaphenylbenzene and neat bromine. It is believed that the ready availability of HBB from hexaphenylbenzene will facilitate the synthesis of a variety of materials, which were otherwise not readily accessible.¹²

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Appendix

Chemical Abstracts Nomenclature (Registry Number)

Hexaphenylbenzene: 1,1':2',1''-Terphenyl, 3',4',5',6'-tetraphenyl-; (992-04-1)
hexakis(4-Bromophenyl)benzene: 1,1':2',1''-Terphenyl, 4,4''-dibromo-
3',4',5',6'-tetrakis(4-bromophenyl)-; (19057-50-2)
Sodium bisulfite: Sulfurous acid, monosodium salt; (7631-90-5)
Bromine; (7726-95-6)

Hexakis(4-bromophenyl)benzene (HBB)

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 17 2004	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~ dpwr		18
data/u400/fujimori-	dof		0
/HNMR-2709-SF-XV-1-	dm	nnn	
6-X1.fid	dmm	c	
ACQUISITION		dmf	
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dmm2	c
tof	0	dmf2	200
nt	1	dseq2	
ct	1	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.0	werr	
wp	5500.7	wexp	
vs	55	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	423.03		
rfl	5133.8		
rfp	3630.5		
th	24		
ins	12.000		
ai	ph		

