A route to 4,4'-bis(benzocyclobutene) based on homocoupling catalysed by manganese or iron salts

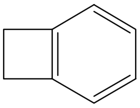
Zhiqiang Feng, Bin Xu, Hui Cang and Jintang Wang*

College of Sciences, Nanjing University of Technology, Nanjing 210009, P.R. China

An efficient and practical preparation of 4,4'-bis(benzocyclobutene) has been developed by the room temperature homocoupling of 4-bromobenzocyclobutene with magnesium and an iron or manganese catalyst.

Keywords: benzocyclobutene, Grignard reagents, homocoupling

Benzocyclobutene (BCB, **1**) and 4-bromobenzocyclobutene (4-BrBCB, **2**) are very useful starting materials for organic synthesis[1] and for the microelectronics industry because of their low dielectric constant, low dispersion factor, low moisture absorption, high thermal and chemical stability and ease of processing.[2] Also, homopolymers and copolymers of aryl bridged bis(benzocyclobutene) monomers (bisBCB) show excellent properties.[3] In general, these monomers have been prepared by Suzuki cross-coupling, which is one of the most efficient methods for carbon–carbon bond formation in biaryls[4] and can provide high yields (80–90%).[5] However, effective Suzuki coupling reactions require phosphine or amine palladium complexes as catalysts or high temperatures. Suzuki coupling reactions can occur without ligands or (and) at room temperature[6] but still require palladium dichloride as the catalyst and aryl boronic acids or esters which are expensive on a large scale.


1

Recently, the homocoupling of bromide compounds was successfully performed in one pot by a combination of metallic magnesium and a catalytic amount of iron salts. Various aromatic and alkyl bromides underwent the homocoupling smoothly, affording the corresponding symmetrical hydrocarbons in moderate to excellent yields.[7] Herein, we describe a simple, efficient and practical synthesis of the bisBCB monomer (**3**) in one pot from 4-BrBCB by iron- or manganese-catalysed homocoupling at room temperature (Scheme 1).

We investigated this model reaction using 2 molar equivalents of Mg in the presence of iron catalysts such as $Fe(acac)_3$, $FeCl_3$, or $Fe(DBM)_3$ (DMBH = $PhCOCH_2COPh$) with THF as solvent under a N_2 atmosphere when 4,4'-bis(benzocyclobutene) **3** was obtained in high yield (about 95%). The results are reported in Table 1.

Thus 2% and 5% of iron trichloride catalysis gave the bis(benzocyclobutene) in 79% and 82% isolated yields, respectively (Table 1, entries 1 and 2), and $Fe(acac)_3$ and $Fe(DBM)_3$ gave higher yields than $FeCl_3$ (Table 1, entries 3 to 6).

Table 1 $FeCl_3$, $Fe(acac)_3$ or $Fe(DBM)_3$ catalysed homocoupling of 4-BrBCB[a]

Entry	Moles% catalyst	Time/min	Yield/%[b]
1	2%$FeCl_3$	30	79
2	5%$FeCl_3$	30	82
3	2%$Fe(acac)_3$[c]	30	90
4	5%$Fe(acac)_3$[c]	30	96
5	2%$Fe(DBM)_3$[d]	60	89
6	5%$Fe(DBM)_3$[d]	60	91

[a]Reaction conditions: 4-BrBCB (**2**), 1 mmol; catalyst see the Table; Mg turnings, 2 mmol; anhydrous THF, 4 ml; stirring; room temperature.
[b]Isolated yield based on 4-BrBCB.
[c]acac = acetylacetonyl; [d]DBMH = dibenzoylmethane.

Table 2 The effect of manganese, vanadium, or titanium salts on the homocoupling of 4-BrBCB[a]

Entry	Moles% catalyst	Time/min	Yield/%[b]
1	5%$MnCl_2$	45	79
2	2%$TiCl_4$	30	60
3	5% $TiCl_4$	30	56
4	2%$VO(acac)_2$[c]	30	75
5	2%$VO(acac)_2$[c]	30	68
6	5%VCl_3	30	63
7	2% VCl_3	30	62

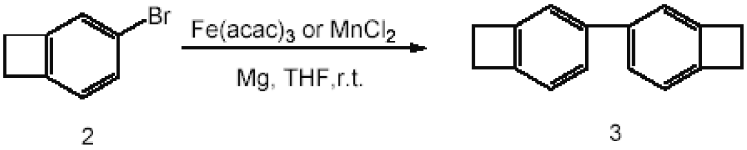
[a]Reaction conditions: 4-BrBCB (**2**), 1 mmol; catalyst: see the Table; Mg turnings, 2 mmol; anhydrous THF, 4 ml; stirring; room temperature.
[b]Isolated yield based on 4-BrBCB.
[c]acac = acetylacetonyl.

When $TiCl_4$, VCl_3 or $VO(acac)_2$ was used instead of the iron catalyst, the desired product was obtained in moderate yield but with $MnCl_2$ the yield was excellent. The results are reported in Table 2.

It is concluded that combinations of $Fe(acac)_3$, $Fe(DMB)_3$ or $MnCl_2$ with Mg are the preferred systems to catalyse the homocoupling of 4BrBCB in THF. These systems have the advantage that, unlike $FeCl_3$, they are not moisture sensitive.

Experimental

THF was freshly distilled from sodium/benzophenone. Melting points were taken on a micro-apparatus (uncorrected). ^1H NMR spectra were recorded on an Avance Bruker-500 instrument and chemical shifts in ppm are reported with TMS as the internal standard. Mass spectra



Scheme 1

---

* Correspondent. E-mail: wjt@njut.edu.cn

were measured on a Finnigan MAT4510 instrument. IR spectra were obtained with a Perkin-Elmer 16 PC FT-IR spectrophotometer.

General procedure for the synthesis of **3**: To a 10 ml flame-dried two-necked roundbottom flask containing a suspension of 2 mmol (48 mg) of magnesium turnings and the manganese- or iron-catalyst in 4 ml of anhydrous THF, was added 1 mmol 4-BrBCB under an atmosphere of nitrogen. The mixture was stirred at room temperature for the time indicated in Tables 1 and 2. The product was isolated by chromatography through silica gel (300~400 mesh) with hexane as eluent to give the pure homocoupling product 4,4'-bis(benzocyclobutene) (**3**).

4,4'-Bis(benzocyclobutene) (**3**): M.p. 62–63 °C (Lit.[2] 62 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.21 (s, 8 H, CH_2CH_2), 7.09 (d, 2 H, *J* = 7.6 Hz, ArH), 7.21 (s, 2H, ArH), 7.35 (dd, 2H, *J* = 7.6, and 1.4 Hz, ArH). MS (*m/z*,%): 206 (M + , 100). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.8; H, 6.7%.

We thank the Education Ministry of China and the Analysis Centre of Nanjing University of Technology.

Received 20 April 2008; accepted 24 June 2008
Paper 08/5223 doi: 10.3184/030823408X347639

References

1 A.K. Sadana, R.K. Saini and W.E. Billups, *Chem. Rev.*, 2003, **103**, 1539.
2 G. Mehta and S. Kotha, *Tetrahedron*, 2001, **57**, 625.
3 R.A. Kirchhoff and K.J. Bruza, *Prog. Polym. Sci.*, 1993, **18**, 85.
4 M.F. Farona, *Prog. Polym. Sci.*, 1996, **21**, 505.
5 L.S. Corley and P.K. Wong, U.S. Patent 5157105, 1992.
6 L.S. Corley, U.S. Patent 5032451, 1991.
7 L.S. Corley, U.S. Patent 4973636, 1990.
8 H.Y. Toride, H.A. Yokohama and T.I. Yokohama *et al.*, U.S. Patent 5388328, 1995.
9 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
10 J. Hassan, M. Sevignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, 2002, **102,** 1359.
11 J.X. Yang, K.Y. Ma and F.H. Zhu, *J. Chem. Res.*, 2005, 184.
12 E.M. Campi, W.R. Jackson, S.M. Marcuccio and C.G.M. Naeslund, *J. Chem. Soc., Chem. Commun.*, 1994, 2395.
13 F.E. Goodson, T.I. Wallow and B.M. Novak, *Org. Synth.*, 1997, **75**, 61.
14 Y. Li, X.M. Hong, D.M. Collard and M.A. El-Sayed, *Org. Lett.*,2000, **2**, 2385.
15 A.F. Littke, C.Y. Dai and G.C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 4020.
16 D.W. Old, J.P. Wolfe and S.L. Buchwald, *J. Am. Chem. Soc.*, 1998, **120**, 9722.
17 D. Zim, A.S. Gruber, G. Ebeling, J. Dupont and A.L. Monteiro, *Org. Lett.*, 2000, **2**, 2881.
18 J.C. Anderson, H. Namli and C.A. Roberts, *Tetrahedron*, 1997, **53**, 15123.
19 X.L. Xu and D.P. Cheng, *J. Org. Chem*, 2006, **71**, 6637.