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Synthesis of Functional Derivatives of 1,2-Bisbenzylbenzene

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We have been interested in the syntheses of functional derivatives of dibenzoylbenzenes and dibenzylbenzenes, since they are of considerable utility in organic synthesis, particularly as synthetic intermediates in the synthesis of new carbonyl host molecule. In recent communication[1] we reported general synthetic routes for the derivatives of dibenzoylbenzenes in which functional groups are introduced to every position of benzoyl group. In the present investigation, we wish to provide practical syntheses of 1,2-bis(2-functionalbenzyl)benzenes that are derivatives of 1,2-bisbenzylbenzene in which functional groups are introduced at ortho positions of each benzyl moieties. Some of them are symmetrical 1,2-bisbenzylbenzenes which have same functional groups on each ortho position of benzyl groups, as shown in structure I, and the others are unsymmetrical ones possessing different functional groups on each ortho position of benzyl groups, as shown in structure II.

The symmetrical 1,2-bisbenzylbenzenes I_{a-f}(Table 1) could be synthesized by the cross-coupling of aryl Grignard reagent, prepared from 2-functionalbromobenzene(**1**), with α,α'-dihalo-*o*-xylene(**2**) in the presence of copper(I) salt catalyst (Scheme 1). Without copper(I) salt the coupling reaction

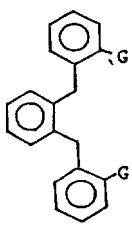
Table 1. Symmetrical 1,2-Bis(2-functionalbenzyl)benzenes I_{a-f}

Products (G)	Reactants	General procedure	yield[a] (%)	m.p.[b] (°C)	MS *m/e*(M$^+$)	IR[c] ν(cm^{-1})	NMR($CDCl_3$, TMS)[d] δ(ppm)
Ia (CH_3)	1a, 2	1	95	65-66	286	3060,3020,2980 2910,1600,1490	7.3-6.8(m, 12H$_{arom.}$) 3.8(s, 4H, benzylic) 2.25(s, 6H, CH_3)
Ib (OCH_3)	1b, 2	1	94	112-113	318	3060,2960,2840 1600,1587,1490 1460,1440,1160 1105	7.2-6.7(m, 12H$_{arom.}$) 3.95(s, 4H, benzylic) 3.75(s, 6H, OCH_3)
Ic (CH_2OH)	1c[e], 2	1	80	115-117	318	3600-3100(broad) 3060,3920,2920 1600,1580,1490 1450,1430	7.5-6.8(m, 12H$_{arom.}$) 4.5(s, 4H, CH_2O) 4.0(s, 4H, $ArCH_2Ar$) 2.2(s, 2H, OH)
Id (Id) (CHO)	1d[e], 2 (Ic)	1 (2)	50 (82)	106-107	314	3060,3010,2830 2730,1700,1600 1575,1490,1450	10.0(s, 2H, CHO) 8.0-6.7(m, 12H$_{arom.}$) 4.35(s, 4H, benzylic)
Ie (OH)	Ib	2	75	108-109	290	3430-3300(broad) 3060,3030,2920 1600,1585,1490 1455,1200,1160	7.2-6.5(m, 12H$_{arom.}$) 5.3(s, 2H, OH) 3.9(s, 4H, benzylic)
If (CH_2Br)	Ic	2	76	118-119	446 444 442	3055,3010,2920 2850,1600,1490 1448	7.5-6.8(m, 12H$_{arom.}$) 4.5(s, 4H, CH_2Br) 4.2(s, 4H, benzylic)

[a]Isolated yield based on α,α'-dibromo-*o*-xylene(**2**). [b]Melting point were not corrected. [c]IR spectra were recorded with Perkin-Elmer Model 782 spectrometer. [d]NMR spectra were recorded on Bruker AC80 FT NMR spectrometer. [e]Protected Ic and Id as THP ether and cyclic acetal respectively.

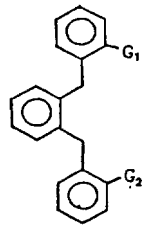
Table 2. Unsymmetrical 1,2-Bis(2-functionalbenzyl)benzenes II_{a-f}

Products (G_1, G_2)	Reactants	General procedure	yield (%)	m.p. (°C)	MS *m/e*(M^+)	IR ν(cm^{-1})	NMR($CDCl_3$, TMS) δ (ppm)
IIa (Br, CH_3)	6, 1a	3	74	54.5–55.5	350 352	3060,3020,2905 1600,1565,1495 1460,1440,740	7.8–6.8(m, $12H_{arom.}$) 4.2(s, 2H, benzylic) 3.95(s, 2H, benzylic) 2.2(s, 3H, CH_3)
IIb (Br, OCH_3)	6, 1b	3	97	oil	366 368	3065,3025,2940 1600,1590,1495 1440,1110,1030	7.8–6.8(m, $12H_{arom.}$) 4.2(s, 2H, benzylic) 4.1(s, 2H, benzylic) 3.8(s, 3H, OCH_3)
IIc (Br, CH_2OH)	6, 1c	3	71	86.5–87.5	348 350 (M^+-H_2O)	3500–3120(broad) 3060,3020,2910 2860,1600,1565 1455,1045	7.6–6.7(m, $12H_{arom.}$) 4.5(d, 2H, CH_2O) 4.05(s, 2H, $ArCH_2ArCH_2OH$) 3.95(s, 2H, $ArCH_2ArBr$) 1.60(s, 1H, OH)
IId (Br, CHO)	IIc	2	91	oil	366 364	3070,3020,2960 2860,2740,1700 1600,1575,1490 1440	10.1(s, 1H, CHO) 8.0–6.8(m, $12H_{arom.}$) 4.35(s, 2H, $ArCH_2ArCHO$) 4.02(s, 2H, $ArCH_2ArBr$)
IIe (Br, OH)	IIb	2	90	oil	352 354	3600–3300(broad) 3060,3030,2955 1600,1565,1490 1455,1010,750	7.9–6.8(m, $12H_{arom.}$) 4.82(s, 1H, OH) 4.2(s, 2H, benzylic) 4.05(s, 2H, benzylic)
IIf (Br, CH_2Br)	IIc	2	95	oil(r.t.)	432 430 428	3060,3030,2930 1600,1495,1455	7.60–6.85(m, $12H_{arom.}$) 4.33(s, 2H, CH_2Br) 4.05(s, 4H, $ArCH_2Ar$)



I_{a-f}

a: G=CH_3
b: G=OCH_3
c: G=CH_2OH
d: G=CHO
e: G=OH
f: G=CH_2Br

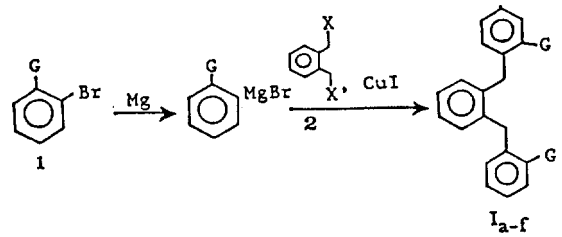


II_{a-f}

a: G_1=Br, G_2=CH_3
b: G_1=Br, G_2=OCH_3
c: G_1=Br, G_2=CH_2OH
d: G_1=Br, G_2=CHO
e: G_1=Br, G_2=OH
f: G_1=Br, G_2=CH_2Br

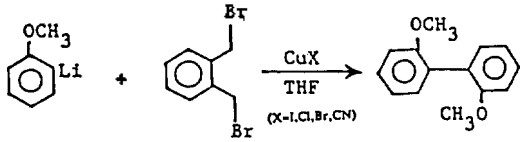
did not proceed well. In this reaction, α,α'-dibromo-*o*-xylene gave always much better yield (85–100%) of coupling product than α,α'-dichloro-*o*-xylene (20–30%).

In the cross-coupling reaction[2-11] between organometallics and benzylic halide, aryllithium could not take the place of arylmagnesium halide. It has been observed that the reaction of aryllithium with benzylic halide in the presence of copper (I) salt catalyst did not result in the formation of coupling product, but in the dimerization of aryllithium to give biaryl. The reaction of 2-lithioanisole, for example, with α,α'-dibromo-*o*-xylene in the presence of copper(I) salt afforded exclussively 2,2'-bianisole.



a: G=CH_3, b: G=OCH_3, c: G=CH_2OH
d: G=CHO, e: G=OH, f: G=CH_2Br

Scheme 1

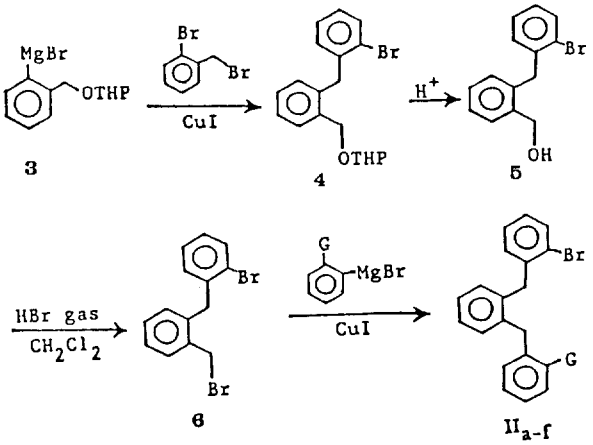


In this work, dimerization[12-14] of aryllithium to biaryl was requently observed by simple addition of copper(I) salt to a THF solution of aryllithium even in the low temperature (−78 °C), and in the absence of benzylic halide.

$$ArLi + CuI \longrightarrow Ar\text{-}Ar$$

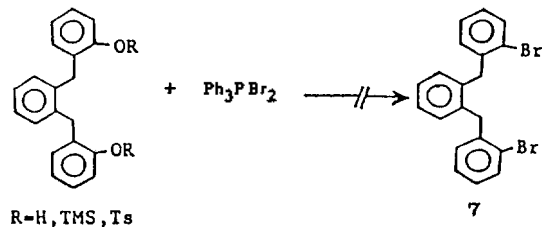
Since the formation of lithium diaryl cuprate[15], Ar_2CuLi, has not been fully investigated to data, the cross-coupling of aryllithium with benzylic halides is not recommendable.

The synthesis of unsymmetrical 1,2-bisbenzylbenzene II_{a-f}(Table 2) could be carried out by the procedure shown in Scheme 2. In spite of the other possible methods, this is known to be a most convient and economical synthetic procedure, because each step gave fairly good yield of product. Moreover, the coupling product **4**, a THP ether, was not neccessary to separate, and the crude product was deprotected directly to corresponding benzylic alcohol **5** which could easily be separated by column chromatography, and then converted to corresponding benzylic bromide **6**, in good yield, by treating **5** with HBr gas in dichloromethane solution.



Scheme 2

The functional groups in I and II may be converted to another ones to furnish another functional derivatives of 1,2-bisbenzylbenzenes we need. However we could not obtained the dibromo derivative, 1,2-bis(2-bromobenzyl)benzene, by this method. We tried, so many times, the conversion of the phenolic hydroxy group of Ie into bromine to prepared the dibromo derivative: Treatment of Ie, or the trimethylsilyl ether and tosylate ester, with triphenylphosphine dibromide, $Ph_3P{\cdot}Br_2$, in drastic condition (250–300 °) did not afford the dibromide.



Since the dibromo derivative **7** is very important synthetic intermediate for macrocyclic carbonyl crwon compound, the synthesis of **7** remained as a problem to be solved. It must be prepared by another synthetic procedure, and the investigation is beeing continued.

General Procedure 1: ***Symmetrical 1,2—bisbenzylbenzenes*** **(I_{a-f}).** For the Grignard reaction, the hydroxy group of 1c was protected previously by the reaction of dihydropyran in dichloromethane in the presence of PPTS or TsOH at room temperature, to give 80–90% yield of the THP ether. The formyl group of 1d was also protected by refluxing with ethylene glycol in benzene in the presence of PPTS or TsOH, and removing water formed using Dean Stark trap, to afford 80–85% of the ethylene acetal.

A Grignard reagent was prepared by adding, dropwise with stirring, a solution of 25 mmoles of 2-functionalbromobenzene(**1**) in THF (20 m*l*) to magnesium turnings(1g) under nitrogen, followed by refluxing for 4 hr. The Grignard reagent was added slowly by cannulation, with stirring at −30 °C, to a solution of 10 mmoles (2.64g) of α,α′-dibromo-*o*-xylene(**2**) in THF(20 m*l*) to which catalytic amount of cuprous iodide (0.5g) was added previously. The mixture was allowed to warm to room temperature and stirred overnight. To this reaction mixture was added aqueous ammonium chloride, filtered off CuI, evaporated the solvent(THF), extracted with ether, washed with dilute ammonium hydroxide and water successively, and evaporated the solvent to give crude coupling product. The chromatography and recrystallization afforded the symmetrical 1,2-bisbenzylbenzene (Table 1). If the coupling product contained protection group, it was deprotected, followed by chromatography and recrystallization. The THP ether was deprotected by heating, under gentle reflux, with PPTS or TsOH in ethanol for 5 hr, to give corresponding alcohol. The cyclic acetal was deprotected by stirring with PPTS or TsOH in acetone for 5 hr, to afford corresponding aldehyde.

General Procedure 2: ***Functional group interconversion.*** The ether linkage of methyl aryl ether was cleaved by refluxing the methoxy compound with a mixture of HBr–AcOH (1:1, *v/v*) for 5 hr to give about 80% yield of corresponding phenol. The benzylic alcohol could be converted to corresponding arylic aldehyde in 90% yield by oxidizing with PDC in dichloromethane for 4 hr. On the other hand, the benzylic alcohol could also be converted to corresponding benzylic bromide in 80–90% yield by bubbling dry HBr gas for 2 hr to a cold solution of the benzylic alcohol in dichloromethane.

General Procedure 3: ***Unsymmetrical 1,2—bisbenzylbenzenes*** **(II_{a-f}).** For all Grignard reactions, hydroxy group in benzylic alcohol and formyl group in aryl aldehyde were protected as THP ether and ethylene acetal respectively, as described in General procedure **1**.

The Grignard reagent, prepared from 30 mmoles(8.1g) of THF ether of 2-bromobenzyl alcohol(1c) and magnesium turnings(1g) in THF, was added, dropwise with stirring at 0 °C, to a solution of 20 mmoles(5g) of 2-bromobenzyl bromide in THF where copper(I) iodide(10 mole %) was suspended. The mixture was stirred at room temperature for 10 hr. After normal hydrolytic work-up, the crude coupling product, a THP ether **4**, was deprotected by stirring in ethanol with TsOH for 6 hr under gentle reflux, to give a colorless crystal (m.p. 86–87 °C) of 2-(2-bromobenzyl)benzyl alcohol (**5**). The benzylic alcohol **5** was dissolved in CH_2Cl_2 and dry HBr gas was bubbled for saturation, to give colorless liquid of 2-(2-bromobenzyl)benzyl bromide(**6**) with the overal yield of 92% based on the 2-bromobenzyl bromide. The reaction of Grignard of 2-functionalbromobenzene(**1**) with the benzylic bromide **6** in the presence of copper(I) iodide(10 mole %) afforded the coupling product, the unsymmetrical 1,2-bisbenzylbenzene (Table 2), which was purified by chromatography.

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Reactions of Molybdenum Atoms with various Conjugated Dienes

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Tris(η^4-butadiene)molybdenum **1** was first obtained by Skell *et al.*[1] by cocondensation of the metal atoms with 1,3-butadiene. The structure of **1** has an *s-cis* conformation and **1** adopts a trigonal prismatic rather than a octahedral geometry about the metal atom.[2,3] And yet the bond lengths of the terminal and internal C-C bonds in **1** are not clearly defined. We are interested in π-complexes and have synthesized some stable π-complexes, tris(isoprene)molybdenum **2** and tris (2,3-dimethyl-1,3-butadiene)molybdenum **3**, by cocondensation method.

We would like to report the effect of methyl substituents of diene ligand and the structures of these π-complexes. Analytical and spectroscopic data for **1**, **2**, and **3** are listed in Table 1. **1** forms yellow plates and **3** yellow needles. **1** decomposes after a week in air. **3** is the most stable among the three compounds. **3** is stable over 3 months in air and then decomposes slowly. However, **2** is a greenish yellow liquid at room temperature and turns a dark green sticky solid after a few days in air.

Yields and spectroscopic properties of **1**, **2**, and **3** indicate that methyl groups at carbon 2 or 3 position in 1,3-butadiene affect the formation of these π-complexes. Since electron donating ability of the diene ligand increases with methyl substituents, we can expect the stability and yield increase in the order of **1** ~ **2** < **3**. Yields of **1**, **2**, and **3**, based amount of molybdenum vaporized are 20–40, 30–40, and 60–70 percentages, respectively. The i.r. spectra of **1**, **2**, and **3** suggest that there are strong π-bonding between Mo atom and diene ligand and methyl substituents affect the strength of π-bonding. The UV-Vis. spectra of **1**, **2**, and **3** show broad absorption bands, due to *d-d* transition in the complexes. In these *d-d* transition bands, the red shifts occurred with methyl substituents indicate that the delocalization of electron increases with the methyl substituent. The methyl substituent effect is also observed in ^{1}H nmr spectra of these π-complexes. In-

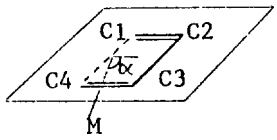

Table 1. Analytical and Spectroscopic Data

Compound and analysis[a](%)	I.R.[b](cm^{-1}) $\nu_{C=C}$ $\nu_{=CH}$	UV-Vis.[c](nm) λ_{max}	^{1}H nmr[d] data δ(ppm)
1, $(C_4H_6)_3Mo$	1490w, 3050m	314	4.58(m,6H), 1.56(qut,6H)
C, –; H, –			0.45(dd,6H)
2, $(C_5H_8)_3Mo$	1510m, 3040m	322	4.30(m,2H), 1.68(m,9H)
C, 60.09(60.00);			1.57(m,2H), 1.32(m,2H)
H, 8.11(8.10)			0.37(m,2H), –0.29(m,2H)
3, $(C_6H_{10})_3Mo$	1513m, 3040m	330	1.58(s,18H), 1.27(d,6H)
C, 63.51(63.15);			–0.47(d,6H)
H, 8.82(8.83)			

[a]Calculated values are given in parentheses. [b]Spectra recorded for KBr disks or KBr windows. Intensity; w = week, m = medium. [c]Measured in *n*-hexane at room temperature. [d]Chemical shifts referenced to residual solvent in toluene-d_8 at room temperature. Multiplicity; s = singlet, d = doublet, dd = double doublet, qut = quintet, m = multiplet.