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Preliminary communication

Improved synthesis of pentabromophenylmagnesium bromide and 1,2,4,5-tetrabromophenylbis(magnesium bromide)

CHARLES F. SMITH, GEORGE J. MOORE, and CHRIST TAMBORSKI
Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433 (U.S.A.)

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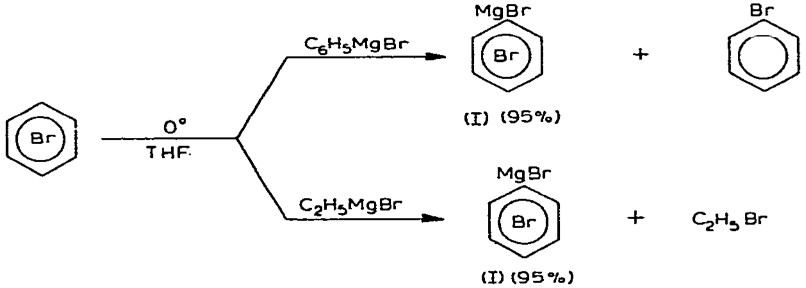
In earlier work, Durand and co-workers[1] studied the reaction between hexabromobenzene* and methyl- and phenylmagnesium bromide. The only products obtained upon hydrolysis, and in very low yields, were hexamethyl- and 1,2,4,5-tetraphenylbenzene[2] respectively. Much later, Berry and Wakefield[3] reported the reaction between hexabromobenzene and magnesium in tetrahydrofuran (THF), utilizing 1,2-dibromoethane as the entrainer. After hydrolysis of the reaction mixture, pentabromobenzene was obtained in 25% yield. The same reaction using diethyl ether as solvent yielded pentabromobenzene in less than 5%.

We wish to report an improved synthesis of pentabromophenylmagnesium bromide (I) through the reaction between hexabromobenzene and ethyl- or phenylmagnesium bromide in tetrahydrofuran (1). Pentabromophenylmagnesium bromide (I) was generated by the dropwise addition of phenylmagnesium bromide (or ethylmagnesium bromide) to a cooled (0°)THF slurry of hexabromobenzene. As Grignard reagent I formed, the slurry cleared. After 4 h of vigorous stirring at 0° (1 h for ethylmagnesium bromide), hydrolysis of an aliquot sample and subsequent GLC analysis indicated pentabromobenzene (95%) as the major product (Table 1). Concentration of



(1)

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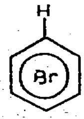
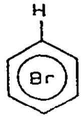
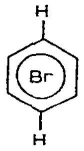
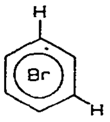
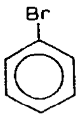
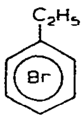
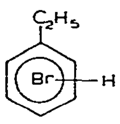
*  represents C_6Br_6; substituents other than Br are indicated e.g.  = C_6Br_5H

TABLE 1

REACTIONS OF HEXABROMOBENZENE WITH GRIGNARD REAGENTS (1/1)

RMgX	Solvent	Temp (°C)	Time (h)	Products (after hydrolysis); Yield (%)					
									
C_6H_5MgBr	THF	0	4	95	< 1	< 1	94		
C_6H_5MgBr	THF	0	48	82	< 1	2	94		
C_6H_5MgBr	Et_2O	25	2	[a]	[a]	[a]	8		
C_6H_5MgBr	Et_2O	35	23	20	1	< 1	34		
C_2H_5MgBr	THF	0	1	95	1	< 1			
C_2H_5MgBr	THF	0	48	48 (100)[b]	< 1 (1)[b]	< 1 (1)[b]		— (42)[b]	— (15)[b]
C_2H_5MgBr	Et_2O	0	4	68	7				
C_2H_5MgBr	Et_2O	0	24	61	6	1			

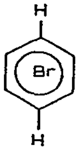
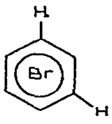
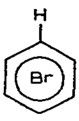
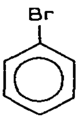
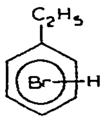
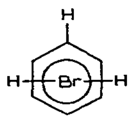
[a] Because the reaction mixture was nonhomogeneous, the extent of Grignard exchange was monitored by the formation of bromobenzene. [b] GLC ratio of area under each peak, with 100 being assigned to peak with largest area, absolute yields of the ethylated products were not determined.

this solution to a solid, followed by recrystallization from ethanol gave pentabromobenzene as a white powder, m.p. 160–161° (lit.[4] m.p. 159–160°); mass spectral analysis gave parent ion peak m/e 468, $C_6{}^{79}Br_5H$ calcd.: m/e 468. Also found present, by GLC–mass spectral analysis, were trace amounts (< 1%) of 1,2,4,5-tetrabromobenzene, m.p. 177.5–179° (lit.[5] m.p. 182°) and 1,2,3,5-tetrabromobenzene, m.p. 93–95° (lit.[6] m.p. 98°).

Similar reactions carried out in diethyl ether gave Grignard reagent I in lower yield, particularly when phenylmagnesium bromide was employed. It was later found that a 100% excess of ethylmagnesium bromide gave Grignard reagent I in 91% yield (Table 2).

TABLE 2

REACTIONS OF HEXABROMOBENZENE WITH GRIGNARD REAGENTS (1/2)

2 RMgX	Solvent	Temp (°C)	Time (h)	Products (after hydrolysis); Yield (%)					
									
C_2H_5MgBr	THF	0	0.75	51		25			
C_2H_5MgBr	THF	0	24	8 (51)[a]	1	10 (78)[a]		— (100)[a]	— (23)[a]
C_2H_5MgBr	Et_2O	25	1	7		91			
C_2H_5MgBr	Et_2O	25	23	19		80			
C_6H_5MgBr	THF	0	4	2	1	96	52		
C_6H_5MgBr	THF	25	48	2	3	17	64		

[a] GLC ratio of area under each peak, with 100 being assigned to peak with largest area.

However, the formation of the di-Grignard reagent II, although it occurs only to a small degree (7%), limits the utility of this method in diethyl ether.

When using stoichiometric amounts of reactants, the lower yield of Grignard reagent I in diethyl ether (*vs.* THF) can be attributed to two factors. Firstly, THF is a better solvating agent than diethyl ether in the formation of Grignard reagents, and secondly, in diethyl ether the insolubility of hexabromobenzene as well as the Grignard reagent I formed, causes the exchange to proceed in a partially heterogeneous system, resulting in a lower rate of exchange.

Pentabromophenylmagnesium bromide (I) is less stable at 0° than pentafluoro-[7] and pentachlorophenylmagnesium bromide[8]. Decomposition is much faster for C_6Br_5MgBr in the presence of ethyl bromide (*vs.* bromobenzene). with the formation of ethylated products being the major path of decomposition (Table 1).

Refluxing C_6Br_5MgBr in THF further promoted an intermolecular metal-halogen exchange reaction resulting in the formation of hexabromobenzene and 1,2,4,5-tetrabromophenylbis(magnesium bromide) (II). Two other products were isolated and partially characterized. Through mass spectral analysis, the following formulas were determined: $C_{10}H_6Br_4O$ and $C_{10}H_8Br_4O$. NMR analyses of these samples, which were separated by preparative TLC (silica gel), indicated the products to be the result of the reaction between C_6Br_5MgBr and the solvent THF. Further studies to elucidate their structure are in progress.

In recent publications Strand[9] and Delorme[10] concluded from electron diffraction and IR measurements that hexabromobenzene is nonplanar with the bromide atoms lying alternately above and below the nucleus. In considering the formation of the di-Grignard reagent, in terms of steric relief only, the most favored isomer would be the 1,2,4,5-tetrabromophenylbis(magnesium bromide) (II). This argument agrees well with the data presented in Table 2. Although in all cases the di-Grignard reagent is formed in low yield (3–51%), the results indicated that the di-Grignard reagent II is favored over 1,2,3,5-tetrabromophenylbis(magnesium bromide); no 1,2,3,4-tetrabromophenylbis(magnesium bromide) was detected. The most favorable conditions for the formation of the di-Grignard reagent II are those utilizing ethylmagnesium bromide in THF. Yields of 1,2,4,5-tetrabromobenzene as high as 51% have been obtained thus far. The di-Grignard reagent (II) prepared in this manner is much less stable than C_6Br_5MgBr prepared under similar conditions, with formation of ethylated products being the major path of decomposition (see Tables 1 and 2).

Attempted synthesis of the di-Grignard reagent via phenylmagnesium bromide gave only trace amounts of 1,2,4,5- and 1,2,3,5-tetrabromophenylbis(magnesium bromide). The major product of this reaction was C_6Br_5MgBr obtained in 96% yield.

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