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NOTE

REACTIONS OF SOME PERHALOARENES WITH METALS AND METAL HALIDES

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The preparation of (pentafluorophenyl)magnesium chloride has recently been described[1]. This reagent was one of several[2] we have used for the preparation of (pentafluorophenyl)copper or its complex, and corresponding reactions were employed for the preparation of (pentachlorophenyl)copper and (tetrachloro-4-pyridyl)-copper. Prior to our work, (pentafluorophenyl)copper was prepared by others[3].

We now report that (pentafluorophenyl)copper may be prepared by stirring together a mixture of magnesium, copper(I) halide, and chloropentafluorobenzene in THF. The reaction has been run at a number of temperatures between −30°, and +66°. The copper compound was characterised by reaction with acid chlorides to form ketones, or with tribromoethylene to form decafluorotolan. In all cases, the chloropentafluorobenzene (0.10 mole), magnesium (0.11 g-atom) and copper(I) halide (0.12 mole) were stirred at room temperature in THF (120 ml) until the onset of reaction was indicated by a darkening of the mixture. The reactants were then rapidly cooled to the desired reaction temperature, and stirred until GLC indicated that the concentration of the chloropentafluorobenzene had fallen to 1% or less of its initial value. The slight excess of magnesium and copper halide were desirable because of the direct reaction between them. When the consumption of chloropentafluorobenzene was complete, the derivating agent was added, stirred for 3 h at reaction temperature, and allowed to reach room temperature before customary work-up in the case of ketone preparations, or refluxed for 48 h in the case of the decafluorotolan preparation.

Some advantages of the procedure are greater convenience and reduction of time. Once the reaction has started, no further attention, other than occasional temperature checks, is needed until the copper compound is to be used. The most convenient conditions compatible with reasonable yields, are a bath temperature of −10°–0°, and three h stirring. Using copper(I) chloride, this gives yields of ketones similar to, or slightly higher than those previously obtained when a copper halide was added to the pre-formed Grignard reagent. The yields can be increased somewhat by using copper(I) iodide, and also by running the reaction at −30° for 6 h.

A rather poor yield of bis(pentafluorophenyl)mercury was obtained from the mercury(II) chloride reaction with magnesium and chloropentafluorobenzene; metallic mercury was also formed. This could result from reaction of magnesium with

TABLE 1

DETAILS OF REACTIONS

Perhaloarene (0.1 mole)	Metal (g-atom)	Metal halide (mole)	Induction time (min)	Temp. (°C)	Time (h)	Derivatizing agent (mole)	Product (yield) (%)	Yield by previous procedures (%)
C_6F_5Cl	Mg (0.11)	CuCl (0.12)	10	−5±5	3	C_6H_5COCl (0.11)	$C_6F_5COC_6H_5$ (77)	
C_6F_5Cl	Mg (0.11)	CuCl (0.12)	15	−5±5	3	CH_3COCl (0.11)	$C_6F_5COCH_3$ (72)	64[a,4]
C_6F_5Cl	Mg (0.11)	CuI (0.12)	15	−5±5	3	CH_3COCl (0.15)	$C_6F_5COCH_3$ (82)	69.5[b,1]
C_6F_5Cl	Mg (0.11)	CuI (0.12)	10	−5±5	3	$(\text{-}CH_2COCl)_2$ (0.045)	$(C_6F_5COCH_2\text{-})_2$ (71)	72[b,4]
C_6F_5Cl	Mg (0.11)	CuCl (0.12)	15	26	2	CH_3COCl (0.15)	$C_6F_5COCH_3$ (68)	
C_6F_5Cl	Mg (0.11)	CuCl (0.12)	10	Spontaneous reflux[c]	1.3	CH_3COCl (0.15)	$C_6F_5COCH_3$ (48)	4.3[d]
C_6F_5Cl	Mg (0.11)	CuCl (0.12)	10	−30±10	8	CH_3COCl (0.15)	$C_6F_5COCH_3$ (81)	
C_6F_5Cl	Mg (0.11)	CuCl (0.12)	15	−5±5	3	$CBr_2{=}CHBr$ (0.033)	$C_6F_5C{\equiv}CC_6F_5$ (43)	45[b,4]
C_6F_5Cl	Mg (0.11)	$HgCl_2$ (0.06)	5	0	8		$(C_6F_5)_2Hg$ (28)	73[e,5]; 84[b,1]
C_6F_6	Mg (0.20)	CuCl (0.27)		0	12	CH_3COCl (0.15)	$C_6F_5COCH_3$ (3)	3–5% from $C_6F_6+LiMe_2Cu$[4]
C_6F_6	Li (0.40)	CuCl (0.30)		−15±15	8	CH_3COCl (0.15)	$C_6F_5COCH_3$ (5.5)	

[a] From $C_6F_5Li+CuCl$, followed by derivatization. [b] From addition of the metal halide to the preformed Grignard reagent followed by derivatization where necessary. [c] 66°, Some cooling necessary, cooled to 0° before adding CH_3COCl. [d] CuCl added after C_6F_5Cl/Mg reaction subsided (20 min) stirred for 1 h, cooled to 0°, and derivatized. [e] From 2 $C_6F_5MgBr+HgCl_2$, in ether.

the mercury chloride or with the bis(pentafluorophenyl)mercury[4]. In the reactions with hexafluorobenzene, in which the products were derivatized with acetyl chloride, very poor yields of pentafluoroacetophenone were obtained. The results are summarized in Table 1. The identity of all products was established by comparison of GLC retention times. IR spectra, and m.p.'s with authentic samples.

As an indication of the reduction in time, mention might be made here of one experiment along such lines. Two and one-half hours were found to be adequate for the preparation of the pentafluorophenylcopper complex at 0°; then the reaction was worked up one-half hour after the rapid dropwise addition of acetyl chloride. The *total* time of reaction was thus three h, and the yield of 2',3',4',5',6'-pentafluoroacetophenone was essentially that obtained previously by the longer two-step procedure.

We are also reporting our finding of two patents[6] which were inadvertently omitted from the references on the preparation of (pentfluorophenyl)magnesium chloride[1].

The study is being extended to include other combinations of metals and metalloids together with various halides. Incidental to the C_6F_6 experiments it appears that C_6F_5MgI may be reasonably stable.

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REFERENCES

1 A. E. Jukes and H. Gilman, *J. Organometal. Chem.*, 17 (1969) 145.
2 S. S. Dua, A. E. Jukes and H. Gilman, *J. Organometal. Chem.*, 12 (1968) P24; A. E. Jukes, S. S. Dua and H. Gilman, *J. Organometal. Chem.*, 12 (1968) P44.
3 A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, 90 (1968) 2186; R. J. DePasquale and C. Tamborski, *J. Organometal. Chem.*, 15 (1968) 494.
4 A. E. Jukes, A. F. Webb and H. Gilman, unpublished studies.
5 R. D. Chambers, G. E. Coates, J. G. Livingstone and W. K. R. Musgrave, *J. Chem. Soc. (C)*, (1962) 4367.
6 E. I. DuPont deNemours and Co., *Brit. pat.* 1,026,035 [*Chem. Abstr.*, 64 (1966) 19307g]; Imperial Chemical Industries, Ltd., *Fr. pat.* 1,410,590 [*Chem. Abstr.*, 64 (1966) 11133c]; see also, N. Ishikawa and S. Hayashi, *J. Chem. Soc., Jap.*, 89 (1968) 1131.