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REACTIONS OF (POLYHALOARYL)COPPER COMPOUNDS WITH ARYL, ALKYL AND ALLYL HALIDES

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SUMMARY

(Polyhaloaryl)copper complexes in solution were reacted with some aryl and alkyl iodides and allyl halides to give the coupled products. The composition of some isolated complexes is reported.

INTRODUCTION

The isolation of (pentafluorophenyl)copper[1] and recent studies on solutions of this reagent or its complex[2] have shown that, as expected, the copper compound possesses high thermal stability. Increased stabilities have been noticed for many other pentafluorophenyl derivatives of metals and metalloids[†] over their hydrocarbon analogs. Our present interest is to describe some reactions of (polyhaloaryl)copper compounds, such as (pentafluorophenyl)copper, (pentachlorophenyl)copper, and (2,3,5,6-tetrachloro-4-pyridyl)copper, which have high thermal stability, with aryl and alkyl iodides in solution at elevated temperatures. A previous communication[4] dealt with the preparation of bis(polyhaloaryl)acetylenes from the copper compounds, also at elevated temperatures.

RESULTS AND DISCUSSION

The (polyhaloaryl)copper compounds were prepared by the three methods, designated A, B and C, previously described[5]: method A, addition of a copper(I) halide to a (polyhaloaryl)lithium compound; method B, addition of a copper(I) halide to a polyhaloaryl-Grignard reagent; and method C, addition of a polyhaloarene to lithium dimethylcopper. Copper compounds prepared by all methods react with iodoarenes to give the respective biaryls in good yields. A study of the reaction of phenylcopper with iodoarenes[6] in pyridine, quinoline, and DMF has demonstrated that both halogen–metal exchange and coupling occur, and that the reaction is markedly affected by the solvent. No products arising from halogen–metal exchange reactions

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have been isolated in the reaction of (polyhaloaryl)copper compounds with iodobenzene or other iodoarenes.

The reaction of the copper complexes with iodobenzene has been studied in greater detail with (pentafluorophenyl)copper or its complex prepared by method A. The yield of 2,3,4,5,6-pentafluorobiphenyl, (I), is dependent on the reaction conditions as follows. None of (I) was formed in ether/hexane solvent within 24 h at the ambient temperature. However, heating the residue left by evaporation of the solvent, at 100° for 44 h gave a 57% yield of (I), identical to that obtained by phenylation of hexafluorobenzene[7]. In dioxane at 100°, formation of (I) was complete in 36 h with a theoretical deficiency of iodobenzene or 24 h with excess iodobenzene. With 2,2,4,4-tetramethyltetrahydrofuran as solvent the reaction with excess iodobenzene at 110° was complete within 18 h. (Pentafluorophenyl)copper and bromobenzene gave only a trace of (I). The reaction of (pentafluorophenyl)copper with iodobenzene[1,2] was reported to be very slow in refluxing THF[2]. Other biphenyls were also prepared.

Generally, method A gave the highest yields, although in the preparation of (2,3,5,6-tetrachloro-4-pyridyl)copper by method A the instability of the lithium compound[8] may result in lower product yields in subsequent reactions.

Although the reaction of (polyhaloaryl)copper complexes with iodoarenes appears to be a useful preparation of unsymmetrical biaryls, the method has no advantages in the preparation of alkyl-substituted polyhaloarenes. We have prepared n-butylpentafluorobenzene, bis(pentafluorophenyl)methane, and 4-ethyltetrachloropyridine via the respective copper compound, but superior methods of preparation are reported[8-10] for all of these compounds. No apparent reaction occurred between (pentafluorophenyl)copper and n-butyl bromide.

The (polyhaloaryl)copper compounds, like phenylcopper[11], react exothermally with allyl halides: the observed order of decreasing reactivity of organic halides towards the copper compounds is allyl $\gg$ aryl $>$ alkyl.

Allylpentafluorobenzene, previously prepared from allylmagnesium bromide and hexafluorobenzene[12], was prepared in 68% and 60% yields from (pentafluorophenyl)copper and allyl bromide and allyl chloride, respectively. Similar reactions with (pentachlorophenyl)copper gave allylpentachlorobenzene in 76% and 72% yields, respectively. (2,3,5,6-Tetrachloro-4-pyridyl)magnesium chloride and the corresponding copper compound also coupled easily with allyl bromide. However, both coupling and halogen–metal exchange reactions occurred between allyl bromide and (2,3,5,6-tetrachloro-4-pyridyl)lithium or (pentachlorophenyl)lithium. In the latter reaction the products were bromopentachlorobenzene (31.6%) and allylpentachlorobenzene (31.7%); the product ratio may be quite fortuitous.

From preparations of (pentafluorophenyl)copper by methods A and C there were isolated analogous complexes, (II) and (III) respectively, containing the pentafluorophenyl moiety, lithium iodide, and solvent molecules. The splendid work of Costa *et al.*[13] has shown that many complexes of phenylcopper are formed, one having a similar constitution to the complexes (II) and (III). In the preparation and isolation of the complex (II) it was found that the copper complex could be prepared using only 50% of the theoretical quantity of copper(I) iodide. The isolated complexes did not have the thermal stability of pure (pentafluorophenyl)copper[1] and decomposed completely within several months on storage at the ambient temperature in an atmosphere of nitrogen.

Other polyhalocopper compounds have been prepared by these general procedures. Of particular interest are trichloro-2-thienylcopper and 3,4-dichloro-2,5-dicopper-thiophene, formed from the corresponding RMgX and RLi compounds in good yields.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Ethereal solvents were dried over sodium and, excepting ether, further dried by distillation from sodium benzophenone ketyl. n-Butyllithium in hexane and methyllithium in ether were from the Foote Mineral Co. Copper(I) iodide was either prepared[14] or purchased from Alfa Inorganic Chemicals. Copper(I) chloride was prepared by purification[15] of commercial samples. GLC analyses were carried out with an F and M Model 500 Gas Chromatograph using a 36″ × ¼″ column packed with DC silicone oil 710 on Chromosorb W (1/20). All temperatures are uncorrected.

(Polyhaloaryl)copper compounds

The copper complexes were prepared as previously described[5], using (pentafluorophenyl)lithium[12], (pentachlorophenyl)lithium[16], (2,3,5,6-tetrachloro-4-pyridyl)lithium[8], and the analogous Grignard reagents[17–19].

The formation of organocopper complexes is indicated by comparison of the stability and reactivity of the (polyhaloaryl)copper compounds with the lithium compounds and Grignard reagents as mentioned elsewhere[1,2,5] and herein.

Isolation of (pentafluorophenyl)copper complexes

To the filtered (pentafluorophenyl)copper reagent, prepared by method A from C_6F_5H (0.05 mole), in ether/hexane, was added dioxane (20 ml). The voluminous white solid which precipitated was filtered off, washed with ether and dried at 25°/1 mm, to give a free flowing solid (35.8 g), Analysis of the solid by titrimetric procedures indicated the structure may be $\{Li[(C_6F_5)_2Cu]\cdot MI\cdot 3.5\,C_4H_8O_2\}$, (II), (where M is copper and lithium). [Found: Cu (total), 8.58; I, 16.88; Li (as RLi), 0.79 (II). Calcd.: (M: Cu/Li = 0.18) Cu (as RCu), 7.43; Cu (total), 8.58; I, 14.83; Li (as RLi), 0.81%.] The solid (II) (10.8 g) and iodobenzene (26.45 g, 0.13 mole) were heated at 100° for 44 h. The products were iodobenzene (16.40 g, 62% recovery) and 2,3,4,5,6-pentafluorobiphenyl, (I), (2.80 g, 46.5%), m.p. 112–112.5°, identical to a sample prepared by phenylation of hexafluorobenzene, m.p. 112–113° [cited[7]: 111–112°].

The UV spectrum of (I) showed a single absorption at λ 236 mμ, ε_{max} 12800 (cyclohexane), different from that cited[7].

The solid (II) (3.5 g), was heated under reduced pressure in a sublimation apparatus. Decafluorobiphenyl (0.25 g) was obtained at 75°/30 mm, and an unidentified white solid (0.30 g) at 190°/30 mm. The residue reacted vigorously with a few drops of hydrochloric acid but no tractable compounds have been obtained.

To a similar preparation of (pentafluorophenyl)copper by method A, after filtration, was added dry pyridine (20 ml). A yellow solid (8.6 g) precipitated, analysis of which indicated that it contained only metal iodides and pyridine, and not the pentafluorophenyl moiety. Addition of dioxane to the filtrate failed to precipitate a copper compound. There was obtained, subsequent to the addition of acetyl chloride and the usual work-up, 2,3,4,5,6-pentafluoroacetophenone (5.75 g, 55%)[20].

Dioxane was also added to the filtered (pentafluorophenyl)copper compound obtained from pentafluorobenzene (16.80 g, 0.10 mole) and lithium dimethylcopper (0.05 mole) in ether at −10°. A voluminous white solid precipitated and was shown to be a (pentafluorophenyl)copper compound. Analysis by conventional titrimetric means indicated that the compound may be $\{Li[(C_6F_5)_2Cu]\cdot LiI\cdot 8.5\ C_4H_8O_2\}$, (III). [Found: Cu, 5.10; I, 9.92; Li (as RLi), 0.54. (III) calcd.: Cu, 4.94; I, 9.86; Li (as RLi), 0.54%.] The lithium iodide arises from formation of the lithium dimethylcopper.

The compounds (II) and (III) possessed similar IR spectra (as nujol mulls) and showed the presence of the pentafluorophenyl moiety and dioxane, but not ether. Precautions were taken to prevent hydrolysis during mulling.

Reaction of (polyhaloaryl)copper compounds with iodobenzene (Table 1)

To the copper compound, prepared by method A, B or C using copper(I) iodide, was added iodobenzene, and the solvent (ether or THF) distilled off. The residue was heated at 100° (steam bath) for periods up to 44 h or, alternatively, a high b.p. ether such as dioxane or 2,2,4,4-tetramethyltetrahydrofuran (b.p. 121°) was added and the mixture heated. The reaction was monitored by GLC. After addition of aqueous ammonia and ammonium chloride and extraction with ether 2,3,4,5,6-pentafluorobiphenyl, (I), was obtained as a white solid from petroleum ether (b.p. 60–70°), m.p. 111–113°, identical to a sample kindly supplied by Dr. R. Stephens [cited[7]: m.p. 111–112°]. A pure sample had m.p. 113°.

2,3,4,5,6-Pentachlorobiphenyl was crystallized from petroleum ether (b.p. 60–70°) as white needles, m.p. 122–123°. (Found: C, 44.25; H, 1.88. $C_{12}H_5Cl_5$ calcd.: C, 44.15; H, 1.54%.)

TABLE 1

REACTIONS OF (POLYHALOARYL)COPPER COMPOUNDS WITH IODOBENZENE AT 100°

Copper compound[a]	Scale[b]	Method[c]	C_6H_5I (mole)	Solvent	Time (h)	Products (yields) (%)
C_6F_5Cu	0.05	A[d]	0.05		44	$C_6F_5C_6H_5$ (59.5)[e] C_6H_5I (18) Intractable oil (5.03 g)[f]
C_6F_5Cu	0.05	A	0.088		46	$C_6F_5C_6H_5$ (67)
C_6F_5Cu	0.05	A[d]	0.0375	Dioxane	36[h]	$C_6F_5C_6H_5$ (58.5)[e]
C_6F_5Cu	0.05	A[d]	0.103	Dioxane	24[h]	$C_6F_5C_6H_5$ (44)
C_6F_5Cu	0.05	A	0.103	TM-THF[g]	18[h,j]	$C_6F_5C_6H_5$ (65)
C_6F_5Cu	0.05	B	0.100	TM-THF	24	$C_6F_5C_6H_5$ (27.5)
C_6F_5Cu	0.10	C[d]	0.2	TM-THF	30	$C_6F_5C_6H_5$ (46.5)
C_6Cl_5Cu[k]	0.025	A	0.025		30	$C_6Cl_5C_6H_5$ (55)
C_6Cl_5Cu	0.10	B	0.20		30	$C_6Cl_5C_6H_5$ (30)
C_5Cl_4NCu-4	0.04	A	0.04		30	4-$(C_6H_5)C_5Cl_4N$ (36) 4-HC_5Cl_4N (19)
C_5Cl_4NCu-4	0.04	B	0.04		30	4-$(C_6H_5)C_5Cl_4N$ (55.5)

[a] No structures are to be implied from the notation for the copper compounds. [b] Scale is based on the quantity of the polyhaloarene used to prepare the organometallic compound. [c] The copper compound was prepared in THF/hexane unless otherwise specified, using copper(I) iodide. [d] In ether/hexane. [e] On the iodobenzene consumed. [f] An intractable oil was isolated in varying quantities in all runs. [g] 2,2,4,4-Tetramethyltetrahydrofuran (b.p. 121°). [h] Monitored by GLC. [j] At 110° (oil bath). [k] From C_6Cl_6.

4-Phenyltetrachloropyridine, m.p. 140–141°, was crystallized from petroleum ether (b.p. 60–70°). (Found: C, 45.15; H, 1.84. $C_{11}H_5Cl_4N$ calcd.; C, 45.09; H, 1.72%.)

To (pentafluorophenyl)lithium (from 0.05 mole C_6F_5H) in THF at −70° was added copper(I) iodide (4.75 g, 0.025 mole). After 16 h the mixture was warmed to room temperature, iodobenzene (21.7 g) added, the solvents evaporated, and the residue heated on a steam bath for 40 h. Subsequent to the usual work-up there was obtained compound (I) (8.09 g, 66%), m.p. 112–113°. Using 0.005 mole of copper(I) iodide, (I) was obtained in only 5% yield.

Reaction of polyhaloarylcopper compounds with a miscellany of aryl, alkyl and allyl halides (Table 2)

All reactions with aryl and alkyl halides were performed under similar conditions as those with iodobenzene and are summarized in Table 2. Reactions with allyl halides were at the ambient temperature (ca. 25°).

TABLE 2

REACTIONS OF (POLYHALOARYL)COPPER COMPOUNDS WITH A MISCELLANY OF ARYL, ALKYL AND ALLYL HALIDES

Copper compound[a] (Scale[b])	Method[c]	Reactant (mole)	Solvent	Time (h)	Temp. (°C)	Products (%)
C_6F_5Cu (0.05)	A	n-BuI (0.05)		36	100	n-BuC_6F_5 (23)
C_6F_5Cu (0.05)	A[d]	CH_2I_2 (0.0125)	Dioxane	5 days	100	$(C_6F_5)_2CH_2$ (70)
C_6F_5Cu (0.05)	A	C_6H_5Br (0.10)		72	100	Intractable oil
C_6F_5Cu (0.05)	A	o-$MeOC_6H_4I$ (0.05)		44	100	o-$MeOC_6H_4C_5F_5$ (60)[e] o-$MeOC_6H_4I$ (21)
C_6F_5Cu (0.05)	A	Allyl Br (0.05)	THF	12	25	$C_6F_5CH_2CH{=}CH_2$ (68)
C_6F_5Cu (0.05)	A	Allyl Cl (0.06)	THF	12	25	$C_6F_5CH_2CH{=}CH_2$ (60)
C_6Cl_5Cu (0.05)	A	Allyl Br (0.06)	THF	6	25	$C_6Cl_5CH_2CH{=}CH_2$ (76)
C_6Cl_5Cu (0.05)	A	Allyl Cl	THF	12	25	$C_6Cl_5CH_2CH{=}CH_2$ (72)
C_5Cl_4NCu-4 (0.03)	A	Allyl Br (0.03)	THF	6	25	$C_5Cl_4N(CH_2CH{=}CH_2)$-4 (58.5)
C_5Cl_4NCu-4 (0.03)	B	Allyl Br (0.03)	THF	6	25	$C_5Cl_4N(CH_2CH{=}CH_2)$-4 (72)
C_5Cl_4NCu-4 (0.04)	B	EtO_2CCH_2Br (0.03)	THF	10	66	$(C_5Cl_4N\text{-}4)_2$

[a–k] See Table 1.

The physical properties of the products as isolated were: bis(pentafluorophenyl)methane, m.p. 58–60° (from ethanol) (cited[10]: 63–64°, corr.) with an identical IR spectrum to that reported for an authentic sample[10]; 2,3,4,5,6-pentafluoro-2′-methoxybiphenyl, m.p. 46.5° (cited[21]: 46–47.5°); n-butylpentafluorobenzene, b.p.

80–82°/35 mm, n_D^{20} 1.4220 (cited[9]: b.p. 84–86°/35 mm, n_D^{20} 1.4210), identical to a sample prepared by the reported procedure; 4-ethyltetrachloropyridine, m.p. 75–76°, identical to a sample prepared in this laboratory[8]; allylpentachlorobenzene, m.p. 59–60°, ν_{max} 1638 cm^{-1} (C=C), identical to a sample prepared in this laboratory[22]; allylpentafluorobenzene, b.p., 148–150°, n_D^{25} 1.4272 (cited[12]: 150°, n_D^{25} 1.4264), identical to an authentic sample (Pierce Chemical Co.); 4-allyltetrachloropyridine, b.p. 100–101°/0.2 mm, ν_{max} 1637 cm^{-1} (C=C)[19].

(Pentachlorophenyl)lithium and allyl bromide

To (pentachlorophenyl)lithium, prepared from hexachlorobenzene (14.24 g, 0.05 mole) in THF at −70°, was added allyl bromide (7.3 g, 0.06 mole) and the mixture stirred for 12 h at −70°. Work-up in the usual manner afforded a solid, sparingly soluble in petroleum ether (b.p. 60–70°), which was identified as bromopentachlorobenzene (5.20 g, 31.6%), m.p. 235–236°, identical to a sample kindly supplied by Dr. C. Tamborski. The residue was distilled under reduced pressure to give allylpentachlorobenzene (4.60 g, 31.7%), m.p. 59–60°, identical to a sample prepared in this laboratory[22].

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