

ON PHENYLCOPPER

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(Received October 2nd, 1965)

Phenylcopper was first reported¹ by Reich in 1923 as an impure product obtained in 60% yield from phenylmagnesium bromide and cuprous iodide in ether: later, Gilman and Straley² obtained a yield of 86% in a similar reaction. Formation of phenylcopper (not isolated) from phenyllithium³ and from tetraphenyllead⁴ has also been claimed. Reports^{5,6} that it is formed by the thermal decomposition of phenyldiazonium borofluoride in the presence of metallic copper have been questioned⁷.

It seems that the only σ -bonded organocopper compound which has been studied⁸ in some detail is the thermally unstable methylcopper CH_3Cu . Phenylcopper must be considered as poorly characterized and even the reactions reported to give it require further study.

The aim of the present work is to reexamine the reactions said to give phenylcopper, to determine the nature of the main product, and to report on the preparation and isolation of phenylcopper from phenyllithium.

Our experiences suggest that the nature of the products, expected to be phenylcopper, are strongly dependent on the method adopted and on reaction conditions. Different complexes can be obtained, both from phenylmagnesiumbromide and from phenyllithium when treated with copper salts. On the other hand, tetraphenyllead is not suited for the preparation of phenylcopper from cuprous halides as the reaction takes place only at temperatures at which the phenylcopper is not stable. Almost pure phenylcopper, $\text{C}_6\text{H}_5\text{Cu}$, was obtained by treating phenyllithium with a slight excess of cuprous bromide suspended in ethyl ether, but when even a slight excess of phenyllithium was used the complex $(\text{C}_6\text{H}_5\text{Cu})_4\text{C}_6\text{H}_5\text{Li} \cdot 3.5(\text{C}_2\text{H}_5)_2\text{O}$ (I) was obtained. A metallorganic compound free from Grignard reagent could not be obtained from the reaction of phenylmagnesium bromide with cuprous bromide; when the solvent used was THF, the complexes, $(\text{CuBr})_{2-3}(\text{C}_6\text{H}_5)_2\text{Mg} \cdot n\text{THF}$ (II) and $(\text{C}_6\text{H}_5)_2\text{Cu} \cdot (\text{C}_6\text{H}_5)_2\text{Mg} \cdot n\text{THF}$ (III) were isolated using equimolar amounts or an excess of Grignard reagent respectively. It must be emphasized that both the Grignard reagent and phenyllithium must be used shortly after their preparation, for even when decomposition is carefully prevented, a slow interaction of these reagents and the solvents apparently takes place and the course of the formation reaction of copper-organic complexes is no longer reproducible.

Phenylcopper is thermally much more stable than methylcopper⁸ or ethylcopper⁹, but it is highly reactive and almost as difficult to manipulate. It can be kept undecomposed for some days under nitrogen or in a vacuum.

As was observed for the methylcopper, phenylcopper strongly retains ethyl ether even after many hours under a good vacuum (0.012 mm).

Phenylcopper reacts with mercuric bromide yielding phenylmercury bromide almost quantitatively.

The complexes (I) and (II) are extremely reactive towards moisture. The former is inflammable in air, the latter reacts rapidly in air yielding yellow to black colored products. Both are slowly decomposed at room temperature under nitrogen even in a vacuum.

Complex (III) is more slowly decomposed in inert atmosphere but reacts rapidly in air (sometimes with flame) yielding a deliquescent violet solid.

IR SPECTRUM OF PHENYLCOPPER

The IR absorption frequencies of solid phenylcopper reported in Table I are assigned by comparison with the assignment of the spectra of C_6H_5X ($X = Cl, Br, I$). The frequencies of triphenylaluminium are also reported¹⁰.

Almost all the absorption bands can be easily assigned being in a narrow range near the frequencies and of similar intensities ratios as the vibration of the C_6H_5 group.

TABLE I
IR SPECTRA AND ASSIGNMENTS

		C_6H_5Br	C_6H_5I	$(C_6H_5)_3Al$	C_6H_5Cu
ν_{17}	B_1	1637	1631		
ν_4	A_1	1580	1575	1575	1586
ν_{18}	B_1	1580	1575		
ν_5	A_1	1477	1473	1478	1470
ν_{19}	B_1	1443	1439	1416	1416
		1379	1397	1377	1384
		1351	1370	1338	1364
		1320	1326		
		1299	1302	1294	1303
ν_{20}	B_1	1266	1259	1248	
ν_7	A_1	1174	1176	1183	1162
ν_{21}	B_1	1159	1157	1167	1126
				1155	
ν_{22}	B_1	1068	1058	1082	1055
ν_8	A_1	1068	1063	1085	1036
ν_8	A_1	1019	1015	1047	1017-1020
ν_9	A_1	999	998	993	985-990
ν_{23}	B_2	987	987		
ν_{12}	A_2	962	961	942	935
ν_{26}	B_2	903	903	918	906-912
ν_{13}	A_2	831	833	857	861, 843
ν_{27}	B_2	735	729	753	722-725
				739	
ν_{24}	B_2	683	684	688	696
				676	
ν_{10}	A_1	672	654	715	672
				707	
ν_{29}	B_2	457	443		467
ν_{11}	A_1	315	268 ^a		300-287
ν_{24}	B_1	253 ^a	220 ^a		225-208
ν_{30}	B_2	180 ^a	167 ^a		157

^a Raman.

The substituent-sensitive frequencies ω_x , δ_x , γ_x , Γ_x (for the symbols see ref. 11) are also identified in the range, or slightly lower than that of bromo- and iodobenzene frequencies as would be expected from the mass of the Cu atom, intermediate between those of Br and I atoms, and from the expected lower force constant of the Cu-C bond.

The two characteristic vibrations of the phenyl group, the out-of-plane (umbrella) C-H deformation ω_{27} (γ_{CH}) and the out-of-plane ring vibration ω_{28} (Γ) are assigned to the bands at 725 and 696 cm^{-1} , respectively. The former falls very near to the frequency calculated (730 cm^{-1}) assuming a linear relationship with the reduced mass of the Cu-C atoms, as suggested by Margoshes and Fassel¹².

The far infrared absorption frequencies are only slightly lower than those of iodobenzene, likely owing to the lower force constant of the Cu-C bond.

EXPERIMENTAL

Reaction and manipulations on the sensitive compounds and at low temperature were carried out in an atmosphere of dry oxygen-free nitrogen; the reaction vessels were thoroughly dried and all reagents and solvents were made rigorously anhydrous. Grignard reagents in ethyl ether or in THF and phenyllithium in ether were freshly prepared before every reaction and titrated by conventional acidimetric methods. Lithium, magnesium, copper and bromine were determined by conventional titrimetric methods. Phenyl groups were determined by hydrolysis of the compounds in heptane suspension, followed by distillation and quantitative spectrophotometric analysis of the benzene in the distillate.

The IR spectra of phenylcopper (as nujol mull, hostafion mull, and KBr pellets) were registered using Perkin-Elmer Mod. 13 C and Beckman IR 11 spectrophotometers.

Phenylcopper

Cuprous bromide (1 g, 6.98 mmole) was suspended in diethyl ether (40 ml) and treated dropwise at 0° with 6.7 ml of a clear solution (~ 1 M) of phenyllithium under magnetic stirring. As the ratio Li/Cu (= *R*) was increased up to 0.5, the colour of the cuprous bromide changed from white to yellow and brownish red; then the solid phase dissolved and a clear brownish-red solution was obtained. The addition of phenyllithium was stopped when *R* ~ 0.9. An almost white precipitate formed after some time: the liquid phase was greenish and gave a negative Gilman test. The precipitate was washed ten times with 30 ml of anhydrous ether, several times with THF and dried in a vacuum to leave an almost white powder (yield 90%, based on phenyllithium). (Found: C, 51.48; H, 3.99; Cu, 43.79. $\text{C}_6\text{H}_5\text{Cu}$ calcd.: C, 51.24; H, 3.58; Cu, 45.18%.) The differences between calculated and found figures can be accounted for almost exactly by assuming that 3% of ethyl ether was retained in the product.

The hydrolysis of another sample yielded: Cu, 44.54; C_6H_5 , 53.66%; $\text{C}_6\text{H}_5/\text{Cu} = 0.99$ (calcd. Cu, 45.19; C_6H_5 , 54.82; $\text{C}_6\text{H}_5/\text{Cu} = 1.00$).

Phenylcopper (0.692 g) was suspended in THF and treated at 0° with a solution of 1.6 g of mercuric bromide in THF at 0°. From the filtered reaction solution 1.35 g (94%) of a white crystalline precipitate of phenyl mercuric bromide was obtained.

* When the reaction was performed at -50° a black product with metallic lustre was obtained which was not further examined.

The complex $(C_6H_5Cu)_4C_6H_5Li \cdot n(C_2H_5)_2O$.

Cuprous bromide (0.5 g, 3.49 mmole) was suspended in anhydrous ether (20 ml) and treated as before, dropwise but not too slowly, with a clear solution of ($\sim 1 M$) phenyllithium in ether. The same phenomena as before were observed. Time was not allowed for precipitation of phenylcopper, but addition of phenyllithium was continued until $R = 1.25-1.5$: a crystalline pale yellow precipitate was gradually formed. The product sparingly soluble in ether but soluble in THF, was washed 20 times with ether and dried in a good vacuum. A substantial amount of ether was always retained. (Found: Cu, 28.45; Li, 0.788; C_6H_5 , 42.15; Cu/ C_6H_5 , 0.798; Li/Cu, 0.255. $C_{44}H_{60}Cu_4LiO_{3.5}$ calcd.: Cu, 28.05; Li, 0.766; C_6H_5 , 42.54%. Cu/ C_6H_5 , 0.8; Li/Cu, 0.25.)

When an excess of phenyllithium was used (starting from $R \sim 2$) a clear yellow solution was obtained. The soluble complex is now under study*.

The complex $(CuBr)_{2.5}(C_6H_5)_2Mg \cdot nTHF$

Cuprous bromide (0.5 g, 3.49 mmole) was suspended in THF (30 ml) and treated at 0° dropwise under efficient stirring with 3.3 ml of a THF solution of the Grignard reagent from bromobenzene (1.08 M). After the addition the solution gradually became brownish yellow and later a voluminous yellow precipitate formed. Both the solution and the solid gave a negative Gilman test. The precipitate was washed 15 times with THF and dried in a vacuum to a pale yellow powder. (Found: Cu, 20.32; Mg, 3.18; Br, 25.44; C_6H_5 , 20.49. $C_{52}H_{76}Br_5Cu_5Mg_2O_7$ calcd.: Cu, 20.18; Mg, 3.08; Br, 25.31; C_6H_5 , 19.46%.)

The complex $(C_6H_5Cu)_2(C_6H_5)_2Mg(nTHF)$

Cuprous bromide (0.5 g, 3.49 mmole) was treated as before with 6.6 ml of a THF solution of the Grignard reagent from bromobenzene (1.08 M). The yellow precipitate formed at Grignard/Cu ratios from 0.5 to 1 gradually became discoloured giving a light violet solid and a deep purple solution. The precipitation was complete when the solution is allowed to stand for sometimes after the ratio $R = 2$ was reached. Both the solution and the solid product gave a negative Gilman test. The precipitate was washed with THF and dried to an almost white powder, $Cu_2Mg(C_6H_5)_4 \cdot 6THF$. (Found: Cu, 14.99; Mg, 2.35; C_6H_5 , 35.03; Cu/ C_6H_5 , 0.50. $C_{48}H_{68}Cu_2MgO_6$ calcd.: Cu, 14.24; Mg, 2.72; C_6H_5 , 34.56%.)

The analysis of the product from a different run was consistent with its containing only 4 molecules of THF.

ACKNOWLEDGEMENT

We thank the Ethyl Co., which in part supported this work, and the National Research Council (C.N.R.).

* Note added in proof: From a filtered solution $R = 1.9$ two products were isolated: (I) $C_6H_5Cu \cdot C_6H_5Li \cdot n(C_2H_5)_2O$, white crystals, which precipitated after some days at room temperature. Dried, they yielded a yellow powder, inflammable in air. Found: Cu, 24.99; Li, 2.72; C_6H_5 , 60.64. $C_{12}H_{10}CuLi \cdot 0.4 Ae$; calcd.: Cu, 24.78; Li, 2.50; C_6H_5 , 60.35. (II) $C_6H_5Cu \cdot C_6H_5Li \cdot n LiBr \cdot m C_4H_8O_2$, voluminous white powder precipitated by dioxan. Stable for weeks at room temperature, but extremely reactive towards air and moisture. Found: C, 39.44; H, 5.01; Br, 29.61; Cu, 7.25; Li, 0.79. $C_{12}H_{10}CuLi \cdot 3.25 LiBr \cdot 4.2 diox.$; calcd.: C, 39.96; H, 5.72; Br, 29.96; Cu, 7.38; Li, 0.79.

SUMMARY

The reactions which are reported to give phenylcopper from Grignard reagent and from phenyllithium have been examined. The nature of products is strongly dependent on the method adopted and on reaction conditions and different complexes can be obtained. Reaction conditions for obtaining almost pure phenylcopper are pointed out. The IR spectrum of phenylcopper is reported and assigned.

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J. Organometal. Chem., 5 (1966) 568-572