Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

REACTIONS OF AN ALKENYLCOPPER REAGENT WITH IODOARENES

MARTIN NILSSON AND ROBERT WAHREN
Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70 (Sweden)

(Received December 31st, 1968)

Several organocopper reactions leading to the formation of new carbon–carbon bonds have been described in recent years, including preparations and reactions of alkyl-, alkynyl- and various arylcopper compounds[1–8]. One type of reaction (1) "dimerisation", leads to the formation of a new symmetrical carbon–carbon bond, generally with elimination of elemental copper[9]. The other type is the reaction (2) of an organocopper compound with an organic halide and generally leads to unsymmetrical compounds. This reaction seems to be favoured by coordinating solvents such as pyridine, and in some cases it is accompanied by copper–halogen exchange.

$$2\,RCu \rightarrow R\text{–}R + 2\,Cu \qquad (1)$$

$$RCu + R'I \rightarrow R\text{–}R' + CuI \qquad (2)$$

Alkenylcopper compounds have been studied less. Whitesides and Casey[10] have shown that propenyl- and 2-butenylcopper dimerise with retention of configuration around the carbon–carbon double bond. Kauffmann and Sahm[11] dimerised several vinylcopper compounds in tetrahydrofuran with high yields (compare ref. 11b).

The present investigation was undertaken in order to find out whether alkenylcopper reagents might also react with iodoarenes to form alkenylarenes. (2-Methylpropenyl)copper was chosen as a model substance to avoid complications due to acetylene formation.

For the preparation of a (2-methylpropenyl)copper reagent, 2-methylpropenyllithium (0.05 mole) in ether was reacted with copper(I) iodide (0.025 mole) at −60° to −40° under argon to give a light yellow suspension, the colour of which changed to reddish brown when the temperature was raised to −40°. When pyridine was added to complex the organocopper reagent, the suspension took on a light green colour; this darkened to deep green at room temperature, at which a homogeneous solution was obtained. Samples withdrawn and hydrolysed with dilute hydrochloric acid at this stage gave 2-methylpropene and a little 2,5-dimethyl-2,4-hexadiene. *p*-Iodoanisole (0.01 mole) was added and the reaction allowed to proceed at 35° until no 2-methylpropene was observed after hydrolysis (about 12 h).

The yield of *p*-(2-methylpropenyl)anisole is 65% (based on *p*-iodoanisole). The principal by-products are 4,4′-dimethoxybiphenyl (11%) and 2,5-dimethyl-2,4-hexadiene (3% based on the total amount of 2-methylpropenyl bromide).

The most favourable proportions were found to be two moles of (2-methylpropenyl)lithium to one mole of copper(I) iodide and our reagent may therefore be lithium bis(2-methylpropenyl)cuprate(I) analogous to the lithium dimethylcuprate(I) used, for instance, by House *et al.*[1]. With a molar ratio of 1/1 only about 6% *p*-(2-methylpropenyl)anisole was obtained.

A preliminary experiment on the reaction of lithium bis(2-methylpropenyl)-cuprate(I) with the highly reactive methyl *o*-iodobenzoate gave little or no unsymmetrical coupling, but a 25% yield of dimethyl diphenate and 7% of dimethylhexadiene.

The pyridine seems to be important for the unsymmetrical coupling. Without pyridine, lithium bis(2-methylpropenyl)cuprate(I) gives 22% dimethylhexadiene and about 5% *p*-(2-methylpropenyl)anisole.

At present nothing is known about the degree of aggregation of (2-methylpropenyl)copper. The essentially homogeneous solutions obtained after addition of pyridine or quinoline may contain low-molecular complexes. Tributylphosphine complexes of butenylcopper have been prepared but no details were published[10].

The formation of 4,4′-dimethoxybiphenyl may proceed via a metal–halogen exchange. This would be in accordance with the reactions of phenylcopper with iodoarenes described in ref. 4. So far, however, 2-methylpropenyl iodide has not been observed in the reaction mixture.

The present results show that alkenylcopper reagents can react with iodoarenes to produce alkenylarenes. To achieve this reaction, however, both a complexing solvent like pyridine and proportions corresponding to lithium dialkenylcuprate(I) seem to be desirable.

EXPERIMENTAL

All reactions involving organometallic compounds were performed under an inert atmosphere and anhydrous conditions.

2-Methylpropenyl bromide was prepared from 2-methylpropene according to Braude and Timmons[13] and was fractionated using a Nester–Faust spinning band column.

2-Methylpropenyllithium

2-Methylpropenyl bromide (0.05 mole) reacted with sliced lithium wire (0.5 mole) in 125 ml ether at 0° for 3 h. Small samples were withdrawn at intervals during the reaction and hydrolyzed in a mixture of isopropyl ether and dilute hydrochloric acid and analyzed by gas chromatography. The mixture was also tested for R–Li by colour test[12]. This reaction is crucial and generally calls for mechanical deformation of the lithium pieces in the initial stage.

(2-Methylpropenyl)copper reagents

The solution containing 2-methylpropenyllithium was added over a period of 0.5 h to a stirred suspension of copper(I) iodide (0.025 mole) in 50 ml ether at −60° to −40°. The mixture was then tested for R–Li with a negative result[12]. At −40°, pyridine (0.5 mole) was added to stabilise the organocopper reagent.

p-(2-Methylpropenyl)anisole

p-Iodoanisole (0.01 mole) was added to the organocopper solution and the mixture was stirred at 35° for about 12 h. The reaction was followed by withdrawing small samples, hydrolyzing and analyzing them using gas chromatography. The cooled reaction mixture was diluted with ether and filtered to remove the copper(I) iodide–pyridine complex. The solution was extracted with dilute acid to remove pyridine, dried, and evaporated to give a mixture of mainly *p*-(2-methylpropenyl)-anisole (65%), *p*-iodoanisole (8%), 4,4′-dimethoxybiphenyl (11%) and 2,5-dimethyl-2,4-hexadiene (3%).

Chromatography on silica gel gave 2,5-dimethyl-2,4-hexadiene identified by NMR and UV reference spectra and 4,4′-dimethoxybiphenyl identified by melting point, IR and comparison with an authentic sample.

p-Iodoanisole and *p*-(2-methylpropenyl)anisole were separated by preparative gas chromatography using a $\frac{3}{8}$″20′ 20% SE-30 column and identified by NMR, IR and comparison with authentic samples.

The NMR spectrum was recorded using a Varian HA-100 MHz instrument. The spectrum (solvent $CDCl_3$) shows two methyl doublets about 3.5 Hz apart at $\tau = 8.1$ due to the different chemical shifts of the methyl groups. Double resonance[14] showed that the coupling constant with the alkenic proton is 1.4 Hz.

ACKNOWLEDGEMENTS

This work has been supported by the Swedish Board of Technical Development. Most of the spectra were recorded by Gurli Hammarberg. The English has been checked by Patrick Hort.

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