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THE REACTIONS OF ALKYLCOPPER COMPOUNDS WITH CUPROUS ACETYLIDES

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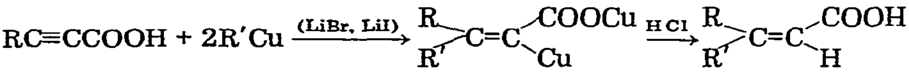
Summary

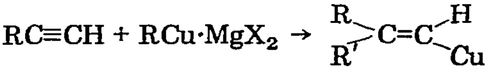
Alkylcopper compounds RCu react with salt-free cuprous acetylides $R'C\equiv CCu$ to give disubstituted acetylenes, $R'C\equiv CR$, the products of unsymmetrical coupling. Conjugated acetylenic acids react with methylcopper in the absence of salts to give similar products resulting from decarboxylation followed by coupling.

Introduction

Alkyl and aryl copper compounds in the presence of lithium salts have been shown recently to give *cis* addition to acetylenic esters [1,2] or acids [3] (eqn. 1). A similar reaction [4] was also shown to proceed with compounds containing an isolated terminal triple bond in the presence of complexing agents such as magnesium halides (eqn. 2).



$$RC\equiv CCOOH + 2R'Cu \xrightarrow{(LiBr,\ LiI)} \begin{matrix}R\\R'\end{matrix}\!\!>C=C<\!\!\begin{matrix}COOCu\\Cu\end{matrix} \xrightarrow{HCl} \begin{matrix}R\\R'\end{matrix}\!\!>C=C<\!\!\begin{matrix}COOH\\H\end{matrix} \qquad (1)$$



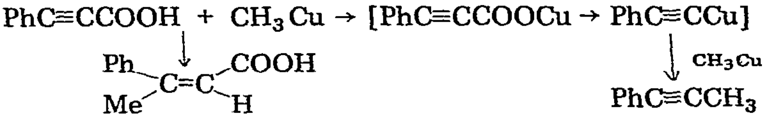
$$RC\equiv CH + RCu{\cdot}MgX_2 \rightarrow \begin{matrix}R\\R'\end{matrix}\!\!>C=C<\!\!\begin{matrix}H\\Cu\end{matrix} \qquad (2)$$

It was reported [5,6] that alkylcopper compounds do not undergo addition to conjugated ketones in the absence of salts. We have therefore examined the influence on the reaction between methylcopper with phenylpropiolic acid of removing the dissolved lithium salts (formed during the preparation of methylcopper).

Results and discussion

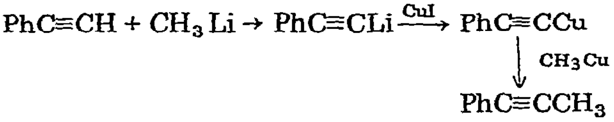
Only a small amount of the product shown in eqn. (1) was obtained when the reaction was carried out in the absence of salts; the main product (70%

yield) was 1-phenyl-1-propyne (I) (eqn. 3). Metallic copper and carbon dioxide were also formed. An excess (3 moles) of methylcopper was used in this reaction. When less than one mole of methylcopper was used, the products after protonolysis were unchanged acid together with phenylacetylene. Addition of lithium bromide to an excess of salt-free methylcopper regenerated its ability to add to the triple bond, and reaction (1) was again observed. This observation agrees with that of House [5] for addition to conjugated ketones, though not with the results of Riviere [6].


(11%) (I) (70%)

(3)

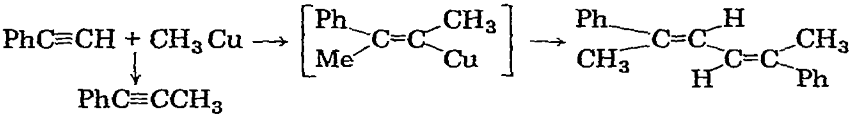
Since cuprous phenylacetylide was assumed to be an intermediate in the coupling reaction (reaction 3), we prepared it in the absence of salts and treated it with salt-free methylcopper. The expected 1-phenyl-1-propyne (I) was formed in good yield (eqn. 4).



$$\mathrm{PhC{\equiv}CH + CH_3Li \rightarrow PhC{\equiv}CLi \xrightarrow{CuI} PhC{\equiv}CCu \xrightarrow{CH_3Cu} PhC{\equiv}CCH_3} \qquad (4)$$

(I)
(75%)

Phenylacetylene itself under the same conditions gave in addition to 1-phenyl-1-propyne (65%) a 10% yield of a dimer (II) formed by the addition of the copper compound to the triple bond and subsequent dimerisation [4] (eqn. 5).


(II)

(5)

The yield of the dimer was raised to 35% in the presence of lithium bromide and iodide. However, methylcopper does not add to the triple bond of copper phenylacetylide, and reaction (4) can be carried out with greater convenience in the presence of salts; none of the dimer is formed.

The coupling reaction (4) is not limited to arylacetylides. 1-Tetradecyne was converted into the cuprous salt via the lithium acetylide and treated with methylcopper to give a reasonable yield (35%) of 2-pentadecyne together with a 35% yield of recovered starting material.

Salt-free butylcopper was a much less efficient reagent than methylcopper. Its reaction with phenylpropiolic acid gave only a low yield of the coupled product. This is apparently due to the low stability of butylcopper

TABLE 1
ARYLMETHYLACETYLENES $X{-}C_6H_4C{\equiv}C{-}CH_3$ (eqn. 3)

X	Yield (%) of $X{-}C_6H_4C{\equiv}C{-}CH_3$	IR ν(cm^{-1})	NMR[a] δ (ppm)	B.p. [°C(mmHg)]
p-CH_3	55	2220, 2260	2.17(s)	120 (25)
p-Cl	55	2220, 2260	1.88(s)	125 (25)
m-Cl	50	2230	1.93(s)	110 (20)
m-F	45	2230	1.96(s)	[b]

[a] This column contains the chemical shifts of the propargylic protons relative to TMS, with CCl_4 as solvent. [b] Separated by GLC column SE-30, on Chromosorb W, 2m, at 120°.

relative to methylcopper, which results in greater decomposition, e.g. by β -elimination [7], and less coupling.

Arylpropiolic acids are relatively easily accessible [8], more so than arylacetylenes, and are thus good starting materials for arylmethylacetylenes. A number of the latter were prepared by reaction (3) in fair yield from the appropriate arylpropiolic acids (see Table 1). This reaction therefore seems to be of practical usefulness.

Other coupling reactions between organocopper compounds are known [9,10]. The Glaser reaction [9] is an oxidative dimerisation of alkynylcopper compounds that yields conjugated diynes. Vinylic [11] and benzylic [12] copper compounds are known to dimerise thermally. These reactions, however, yield symmetrical products. The reaction we are reporting is remarkable in that no symmetrical diynes are produced, and also for the fact that it proceeds between two solids and nevertheless affords good yields of the unsymmetrical coupling product.

Experimental

NMR spectra (60MHz) were recorded on a Varian T60 machine in CCl_4 solutions, with TMS as internal standard. IR spectra were recorded on a PE457 spectrophotometer.

Phenylpropiolic acid [8], *p*-methyl- [13], *p*-chloro- [14], *m*-chloro- [15] and *m*-fluoro-phenylpropiolic acids [16] were prepared by standard methods. Phenylacetylene and 1-tetradecyne were supplied by Farchan. Copper iodide was from B.D.H.

All copper reactions were performed under anhydrous conditions under nitrogen, with magnetic stirring. Ether was distilled from $LiAlH_4$. Liquids were distilled using a Büchi ball-oven. B.p.'s are average oven temperatures.

*Salt-free methylcopper**

Methyllithium solution was prepared in ether from lithium and methyl bromide. Methylcopper was prepared [17] by stirring this solution with a 5% excess of cuprous iodide at 0°. Salts were removed at 0° by sucking off the supernatant ether from the heavy yellow precipitate with a syringe. Three successive portions of ether were then added, and removed with a syringe.

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* Dry methylcopper is a powerful contact explosive and the ethereal slurry must not be separated and washed by suction filtration.

1-Phenyl-1-propyne (I) from phenylpropiolic acid

Salt-free methylcopper prepared from cuprous iodide (8.0 g) and MeLi solution (20 ml, 2 *M*) was stirred with ether (30 ml). A solution of phenylpropiolic acid (1.46 g, 10 mmol) in ether (5 ml) was injected via a rubber septum. The mixture was stirred at room temperature overnight and then decomposed by the addition of ice and dilute HCl. It was filtered through Celite filter-aid in order to remove the black precipitate of metallic copper. The residue was washed well with methylene chloride and the combined filtrates were extracted with sodium carbonate solution. (Acidification of this extract precipitated 180 mg (11%) of *cis*-β-methylcinnamic acid [3].) The organic layer was dried ($MgSO_4$), evaporated and distilled to yield 1-phenyl-1-propyne (0.81 g, 70%), which was identified by comparison with a commercial sample.

In a similar manner, a number of arylmethylacetylenes were prepared from the appropriate substituted phenylpropiolic acids (see Table 1).

1-(*p*-Methylphenyl)-1-propyne: Found: C, 92.1; H, 8.0. $C_{10}H_{10}$ calcd.: C, 92.3; H, 7.7%. 1-(*p*-Chlorophenyl)-1-propyne: Mass spectrum: M^+ 150, 152. Found: Cl, 22.6. C_9H_7Cl calcd.: Cl, 23.6%. 1-(*m*-Chlorophenyl)-1-propyne: Found: C, 71.5: H, 4.4; Cl, 23.3. C_9H_7Cl calcd.: C, 71.8; H, 4.6; Cl, 23.6%. 1-(*m*-Fluorophenyl)-1-propyne: Found: C, 80.3; H, 5.1. C_9H_7F calcd.: C, 80.6; H, 5.2%.

1-Phenyl-1-propyne (I) from phenylacetylene

Phenylacetylene (357 mg, 3.5 mmol) in ether (10 ml) was treated with methyllithium solution (1.75 ml, 2 *M*) at 0°. Copper iodide (0.7 g, 3.7 mmol) was immediately added against a stream of nitrogen and the mixture stirred at room temperature to give a yellow slurry. This was transferred using a syringe (16-gauge needle) to a suspension of 10 mmoles of methylcopper (not salt-free) in ether (20 ml). The mixture was stirred overnight at room temperature, during which time it became black. It was then treated with ice and dilute HCl, filtered and the residue washed with methylene chloride. The combined filtrate was treated as above to yield 1-phenyl-1-propyne (0.30 g, 75%).

cis, cis-2,5-Diphenyl-2,4-hexadiene(II)

A suspension of methylcopper (10 mmol, not salt-free) in ether (25 ml) was prepared at 0°. Phenylacetylene (255 mg, 2.5 mmol) was injected and the mixture was stirred at room temperature for 4 hours. Treatment with ice and dilute HCl, followed by extraction into methylene chloride and evaporation gave a semi-crystalline residue. This was crystallised from acetone to yield (II) (102 mg, 35%), m.p. 134 - 136°. Recrystallisation raised the m.p. to 136 - 137.5°. UV (EtOH), λ max, (ε): 316 nm (3.0×10^4); mass spectrum: M^+ 234; NMR (δ ppm) 10H (7.3, m), 2H (6.75, s), 6H (2.15, s). (Found: C, 91.4; H, 7.9. $C_{18}H_{18}$ calcd.: C, 92.3; H, 7.7%.)

2-Pentadecyne

The reaction was repeated using 1-tetradecyne (680 mg, 3.5 mmol). The reaction mixture was treated as above (without extraction with sodium carbonate solution) and subjected to preparative TLC (elution with hexane). Starting material (240 mg) was recovered together with 2-pentadecyne (250 mg, 35%). NMR (δ ppm) 2H (1.95, m), 3H (1.55, s), 20H (1.15, (br)s), 3H (0.80, m). (Found: C, 86.1; H, 13.4. $C_{15}H_{28}$ calcd.: C, 86.4; H, 13.6%.)

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