REACTION OF COPPER ACETYLIDES WITH HALOGEN DERIVATIVES

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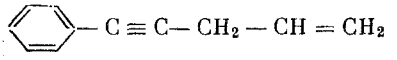
We have found that the reaction of copper acetylides with halogen derivatives under certain conditions leads to the formation of substituted acetylenes with yields of 20-70%. Thus, on boiling in dimethylformamide for 8-16 h, copper acetylides react with aryl iodides and their derivatives in accordance with the general scheme

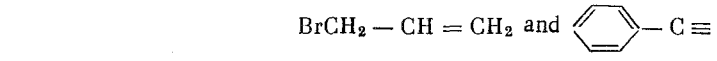
$$R-C\equiv C-Cu+IR'\rightarrow R-C\equiv C-R'+CuI.$$

Compounds with various functional groups—nitro, hydroxy, amino, etc.—may be used in the reaction. The table gives information on the production of a number of compounds.

The reaction of allyl bromide with copper acetylides under similar conditions is accelerated by the presence of catalytic amounts of powdered copper. The reaction takes 10-15 min. Thus, the compound



has been obtained from

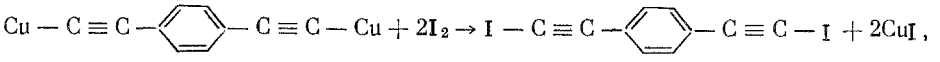


b.p. 72-73° (3 mm), n_D^{25} 1.5580. Literature data [3]: b.p. 107-108° (22 mm), n_D^{25} 1.5574. In the same way, $CH_2=CH-CH_2-C\equiv C-CH_2OH$ has been obtained from $BrCH_2-CH=CH_2$ and $Cu-C\equiv C-CH_2OH$, b.p. 53° (4 mm). Literature data [4]: b.p. 72.6-73.7° (10 mm).

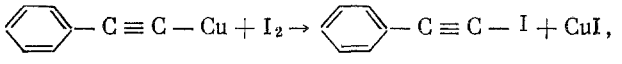
In order to obtain compounds containing conjugated triple bonds, polyacetylenes have been synthesized by the interaction of the corresponding acetylides with iodine in ether at room temperature (yields 50-70%)

$$CH_2=CH-CH_2-C\equiv C-CH_2OH- \text{ and } BrCH_2-CH=CH_2 \text{ and } Cu-C\equiv C-CH_2OH,$$

m.p. 180° (decomp.), unreported

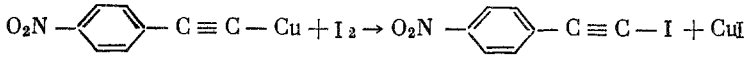


b.p. 107° (7 mm). Literature data [5]: b.p. 117° (15 mm).

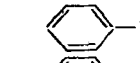
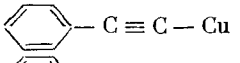
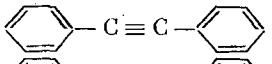
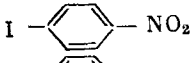
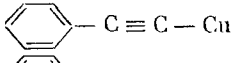
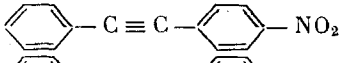
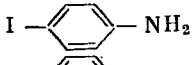
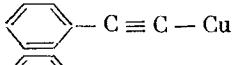
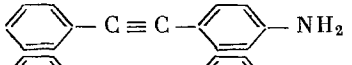
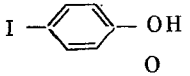
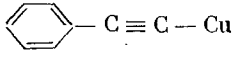
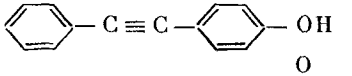
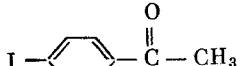
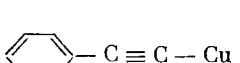
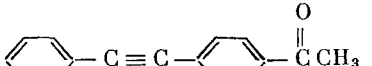
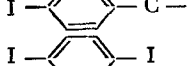
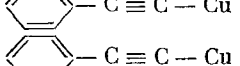
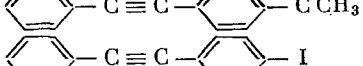
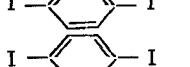
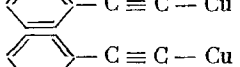
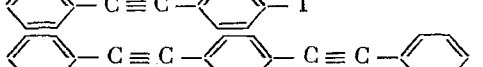


m.p. 196-199° (decomp.), unreported.

Copper acetylides may also react with certain halogen derivatives without a solvent. Thus, copper phenylacetylide and an excess of PCl_3 formed a white precipitate. The precipitate was washed with ether, treated with water or alcohol, and dissolved in pyridine. With water, the pyridine solution gave the phosphine



m.p. 90-91°. Literature data: m.p. 91° [6]. Silver acetylides, and also copper p-nitrophenylacetylide react explosively with PCl_3.

Starting materials		Product obtained	Characteristics of the reaction product, literature reference
Aryl iodide	Acetylide		
			M.p. 62-63° (identified chromatographically)
			M.p. 119-122°. Literature data: m.p. 98° [1], m.p. 202-203° [2]
			M.p. 126-128°. Literature data: m.p. 126-127° [2]
			M.p. 125-127°, unreported
			M.p. 98-99°, unreported, M.p. of the 2,4-dinitrophenylhydrazone, 194-200° (decomp.)
			M.p. 101-102°, unreported
			M.p. 180-183°

Bifunctional compounds form polymers. Thus, polymers were obtained from the acetylide of diethynylbenzene and methylene iodide, from p-iodophenylacetylide, the acetylide of propargyl bromide, etc. The structure and properties of the polymers obtained are now being studied.

SUMMARY

1. The following compounds have been synthesized by the reaction of copper acetylides with aryl iodides in dimethylformamide: tolane, 4-nitrotolane, 4-aminotolane, 4-hydroxytolane, 4-acetyltolane, 4-iodotolane, and others.

2. The reaction of copper acetylides with allyl bromide in dimethylformamide has given allylphenylacetylene and allylpropargyl alcohol.

3. The action of iodine on copper acetylides has given 4,4'-di-(iodoethynyl)-benzene, iodophenylacetylene, and iodo-4-nitrophenylacetylene.

4. Triphenylethynylphosphine has been obtained from phosphorus trichloride and copper phenylacetylide.

5. Polymers have been obtained from bifunctional compounds.

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