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PRELIMINARY COMMUNICATION

POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS XXVIII*. BIS(POLYHALOARYL)ACETYLENES VIA ORGANOCOPPER COMPOUNDS

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We have recently made available perhalogenated aryldimethyl silanes of the general formula $RSiMe_2H$, wherein the R group is pentafluorophenyl, pentachlorophenyl, 2,3,5,6-tetrachloropyridyl and related types[2]. With these in hand the way was opened for an extension of studies on the preparation of organosilicon compounds and congeners by the addition of $RSiMe_2H$ to bis(polyhaloaryl)acetylenes, $RC{\equiv}CR$, in which the R groups are those just indicated. Bis(pentafluorophenyl)acetylene and other polyfluoroarylacetylenes have been prepared by a variety of procedures[3]. Bis(pentachlorophenyl)-acetylene has undoubtedly been prepared before[4] but not completely identified.

Our $RC{\equiv}CR$ compounds have been prepared by novel procedures, which may be methods of choice because of their convenience, and which give yields as high as 87%. The reactions involve polyhaloarylcopper compounds or their complexes and polyhaloethylenes or polyhaloethanes. The polyhaloarylcopper compounds were pentafluorophenylcopper, pentachlorophenylcopper, and 2,3,5,6-tetrachloropyridylcopper, which were prepared by the following general procedures: (1) addition of copper(I) halides to polyhaloaryl-metallic compounds[5,6,7], and (2) addition of a hydrogen or iodine-containing polyhaloaromatic compounds to lithium dimethylcopper[7,8]. The bis(acetylenes) were formed by reaction of the organocopper compounds or their complexes with the following: pentabromoethane, 1,1,2,2-tetrabromoethane, 1,1,2,2-tetrachloroethane, tetrabromoethylene, tribromoethylene, or trichloroethylene. Only a very small amount of bis(pentafluorophenyl)acetylene has been isolated from the reaction of pentafluorophenylcopper with tetrachloroethylene, even in the presence of a free-radical initiator such as benzoyl peroxide.

Studies are in progress to determine the nature of the intermediates, some of which are formed by halogen–metal and hydrogen–metal exchanges. In this connection it is interesting to note that the non-halogenated phenylcopper gives no tolan when treated with tribromoethylene. This may fit in with generalizations evolving from studies[9] concerned with the relative reactivities of phenyl- and polyhaloaryl-metallic compounds of magnesium, of lithium, and of copper. In these expanding studies, only a low yield of

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[*] For part XXVII see ref.1.

TABLE 1

PHYSICAL PROPERTIES OF SOME DIARYLACETYLENES

Compound	M.p. (°C)	IR[a] (cm^{-1})	UV[b] [λ_{max} mμ(log ε)]
$C_6H_5C{\equiv}CC_6H_5$	63		264 (4.37), 272 (4.38), 280 (4.51), 289 (4.36) and 297 (4.45)
$C_6F_5C{\equiv}CC_6F_5$	123	1472, 1507 and 1528 (C_6F_5)[c]	252i (4.11), 264 (4.33), 269s (4.34), 278 (4.48), 284i (4.32) and 296 (4.38)[d]
$C_6Cl_5C{\equiv}CC_6Cl_5$	359	1266, 1342 and 1415 (C_6Cl_5)	295i (2.76), 302 (2.80), 314 (2.96), 320i (2.88) and 336 (2.95)
4-C_5Cl_4N—C≡C—C_5Cl_4N-4	326	1206, 1247 and 1316 (C_5Cl_4N)	286s (4.01), 296 (4.05) and 317 (3.78)

[a] Fluorolube and nujol mulls. Due to their symmetrical structures, no absorptions characteristic of an acetylenic linkage were observed. [b] In THF. i = inflexion, s = shoulder. [c] cited ref. 3*b* 1506 and 1527 cm^{-1}. [d] For the UV spectrum of this compound, see also refs. 3*b* and 3*d*.

bis(pentachlorophenyl)acetylene was obtained from the reaction between pentachlorophenylmagnesium chloride and tetrabromoethylene in the presence of cobalt chloride[3b,10].

The applicability of organocopper or of pseudo-organocopper compounds, such as those of silicon and related metalloids and metals appears to be widely comprehensive. For example, the complex formed from Ph_3SiLi and copper iodide reacts with acetyl chloride to give a 74% yield of triphenylsilyl methyl ketone[11]. This is in agreement with the generalizations on the relative reactivities of organic copper compounds[7]

Some physical properties of bis(polyhaloaryl)acetylenes and of tolan are shown in Table 1.

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