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STABLE ARYLCOPPER COMPOUNDS CONTAINING METHOXY, DIMETHYLAMINO, DIPHENYLPHOSPHINO OR DIMETHYLSULFAMOYL GROUPS AT THE ARYL NUCLEUS*

G.van Koten, A.J.Leusink and J.G.Noltes
Organisch Chemisch Instituut TNO, Utrecht, The Netherlands

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In a previous communication we described the synthesis of a new type of stable arylcopper compounds containing 2-(dimethylamino)methyl and 2-methoxymethyl substituents, which derive their stability most probably from copper-hetero atom coordinative bonding[1].

In the present paper we report on the synthesis and properties of arylcopper compounds containing methoxy, dimethylamino, diphenylphosphino and dimethylsulfamoyl groups at the aryl nucleus. The introduction of these hetero atom-containing substituents results in a considerable thermal stabilization of the copper-carbon bond. Moreover, unlike the recently reported perhalogenated arylcoppers[2], these new compounds are only slowly attacked by water and oxygen. Also in this case the observed stabilization of the copper-carbon bond is probably connected with copper-hetero atom coordinative bonding. However, inductive and mesomeric effects may also be important because in the present compounds the hetero atom of the substituent is directly bound to the aryl nucleus. The importance of electronic effects is reflected in the largely different thermal stability of 2-cuprio- and 4-cuprio-N,N-dimethylaniline (decomposition above 100°) as compared with 3-cuprio-N,N-dimethylaniline (decomposition below 0°).

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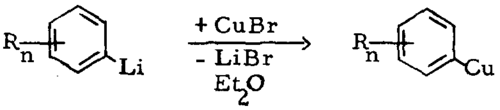
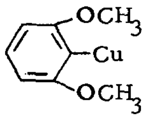
*Part II in the series "Organocopper Chemistry"; for Part I see ref. 1.

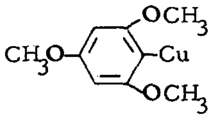
The compounds described in this communication have been prepared by the reaction of cuprous bromide with organolithium compounds:



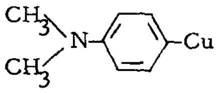
The following solid organocopper compounds [decomposition temperatures (°C) in a nitrogen atmosphere are given in brackets] have been isolated in 40-90% yield:



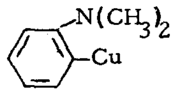
(I) (185-186)



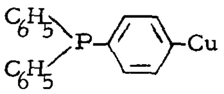
(II) (198-202)



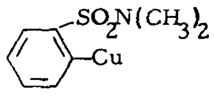
(III) (> 100)



(IV) (140)



(V) (> 110)



(VI) (> 150)

The identity of these new compounds* has been established by elemental analysis, by IR and NMR spectroscopy, and by degradation with D_2O.

Compounds (I)-(VI) are thermally more stable than phenylcopper which decomposes slowly at 25° and fast at 80°. Moreover, all compounds except (III) are rather stable against air and moisture; degradation of (I), (IV) and (V) with D_2O proceeds very slowly.

These organocopper compounds react readily with metal salts to give complexes with well-defined stoichiometries and form the expected coupling products with acyl and allyl halides, e.g.:

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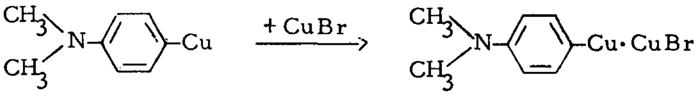
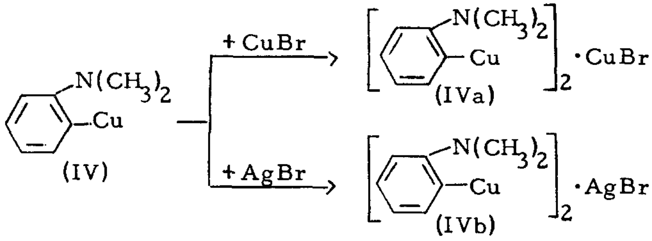
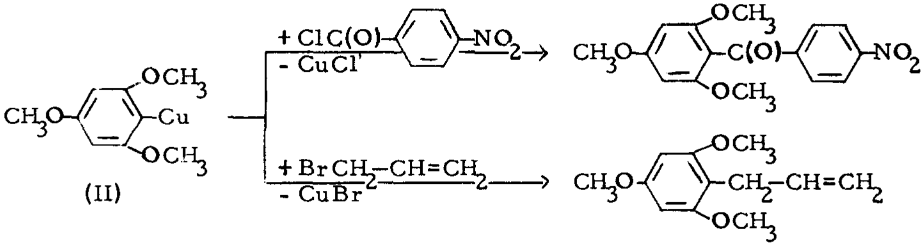
*Recently Nillson et al.[3] reported on 2-cuprio-1,3-dimethoxybenzene (I) and 2-argentio-1,3-dimethoxybenzene, which were described as "unexpectedly stable compounds".



(III) (IIIa) (90%)



(IV) (IVa) (71%) (IVb) (77%)



(II) (75%) (75%)

The organocopper-metal halide complexes (IIIa), (IVa) (dimeric in benzene), and (IVb) decompose at about 175°, 200° and 185°, respectively. It thus appears that complexation of (IV) with metal halides increases the thermal stability of the copper-carbon relation. Complex (IIIa) is much more stable against air and water than the free organocopper(III), which decomposed very rapidly in contact with air.

These studies are being continued. An X-ray structure investigation of some of the compounds will be undertaken.

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