Oxidative transformations of phenylacetylene in a Ph_3MF_2 (M = Bi, Sb)—CuCl system

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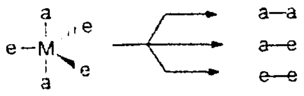
The composition of products of the reaction of phenylacetylene with Ph_3BiF_2 and Ph_3SbF_2 in the presence of CuCl is considerably affected by the amount of the promoter. When the molar ratio phenylacetylene : CuCl is 1 : 1, the major product is diphenylacetylene; a decrease in amount of CuCl to 10 mol. % results in an increase in the yield of tolan to 60%.

Key words: acetylenes, diacetylenes; hypervalent compounds, bismuth(v), antimony (v).

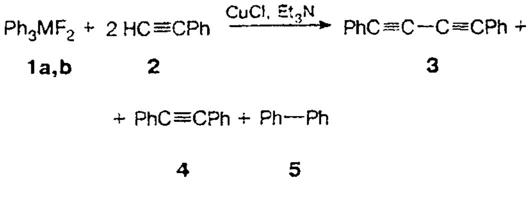
Oxidative coupling of substituents at hypervalent atoms of non-metals is intensely studied as a method for the synthesis of organic compounds of the desired structure.[1–3] Hypervalent Sb and Bi compounds has a trigonal bipyramid (TBP)[4] structure and, in principle, substituents can undergo three types of oxidative coupling.



However, there are no reliable data concerning the preference of either a—a- or a—e-coupling,[5] and the possibility of e—e-coupling have not been considered at all.

In this work, we made an attempt to determine the predominant direction of coupling of substituents in TBP structures.

In the studies of the reactions of Ph_3BiF_2 (**1a**) and Ph_3SbF_2 (**1b**) with phenylacetylene (**2**) in the presence of CuCl and Et_3N, we found that the composition of the reaction mixtures (and, therefore, the direction of the coupling) depends substantially on the amount of CuCl used as the promoter (the ratio **1a,b** : **2** was 1 : 2 in all cases).



$$\underset{\textbf{1a,b}}{Ph_3MF_2} + \underset{\textbf{2}}{2\,HC{\equiv}CPh} \xrightarrow{CuCl,\ Et_3N} \underset{\textbf{3}}{PhC{\equiv}C{-}C{\equiv}CPh} + \underset{\textbf{4}}{PhC{\equiv}CPh} + \underset{\textbf{5}}{Ph{-}Ph}$$

M = Bi (**a**), Sb (**b**)

When the molar ratio **2** : CuCl was 1 : 1 for both difluorides (**1a** and **1b**), diphenylacetylene (**3**) was the major product of the reaction (Table 1). The change in the ratio **2** : CuCl to 1.0 : 0.5 results in the formation of almost equal amounts of diphenylacetylene (**3**) and tolan (**4**). In the case of difluoride **1a**, when the amount of CuCl is further decreased (1.0 : 0.1), diphenyldiacetylene was not formed at all, and tolan **4** becomes the predominant product. In this case a considerable amount of biphenyl (**5**) appears, which is explained by the thermal instability of difluoride **1a** under the reaction conditions.[6] For difluoride **1b**, we also observed a decrease in the **3** : **4** ratio, when the amount of CuCl was changed, but in this case the decrease is less pronounced.

The results obtained can be rationalized as follows. At the first stage, intermediate cuprous acetylenide PhC≡C—Cu is formed,[7] which alkynylates difluorides **1a,b** to give either pentaorganyl compound **A** or tetraorganyl compound **B** (depending on the amount of CuCl). The most electronegative substituents F and C≡C—Ph in compound **B** are in apical positions.

Table 1. The effect of the amount of CuCl on the ratio of the reaction products

Starting difluoride	**2** : CuCl (mol/mol)	Yield of the reaction products (%)			Total yield (%)
		3	**4**	**5**	
Ph_3BiF_2 (**1a**)	1 : 1	100	Traces	Traces	81
	1.0 : 0.5	50	50	—	60
	1.0 : 0.1	—	60	40	50
Ph_3SbF_2 (**1b**)	1 : 1	100	Traces	—	83
	1.0 : 0.1	79	21	—	93

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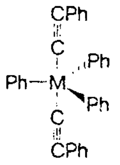
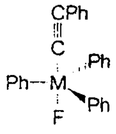


A



B

At the equimolar ratio of 2 and CuCl, compound A is probably formed. On heating, it is decomposed following the pattern of reductive elimination of a—a-substituents to give diphenyldiacetylene **3**, as was suggested earlier.[5] When CuCl is deficient, the formation of compound **B** predominates. Owing to coupling of substituents from a—e positions (probably, because of the strength of the M—F bond), it gives mainly tolan **4**.

Experimental

The reaction mixtures were analyzed on a Chrom-5 chromatograph fitted with a flame-ionization detector and a column (3.5 m) with OV-1. Diphenyldiacetylene **3**, used as the standard and for calibration, was synthesized by the literature procedure,[8] difluorides **1a** and **1b** were obtained using the procedures reported earlier.[9,10] Commercial samples of tolan **4** and biphenyl (**5**) were used. Bi- and Sb-containing products were not isolated nor analyzed.

Reaction of phenylacetylene with Ph_3MF_2. General procedure. Triethylamine ($9.3 \cdot 10^{-4}$ mol) was added to a suspension of CuCl ($6.2 \cdot 10^{-4}$ mol) in 5 mL of a solvent (benzene, toluene) under argon; the resulting mixture was stirred for 10 min, and phenylacetylene ($6.2 \cdot 10^{-4}$ mol) and either difluoride **1a** or difluoride **1b** ($3.1 \cdot 10^{-4}$) were added in succession. The mixture was refluxed for 5 to 6 h under argon and analyzed by GLC. The reactions with other **2** : CuCl ratios were carried out similarly.

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Synthesis of bromine- and iodine-containing perhaloisothiazoles

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A method was developed for the synthesis of bromine- and iodine-containing perhaloisothiazoles by bromination and iodination of 3-bromoisothiazole prepared from the available 3-hydroxyisothiazole.

Key words: isothiazole; 3-bromoisothiazole, bromination, iodination; polyhaloisothiazoles.

It is known that perchloroisothiazole can be used as a chemical means for plant protection[1] and as an intermediate for the synthesis of bactericides, fungicides, and dyes.[1–3] Preparation of bactericides based on perbromoisothiazole[2] is mentioned in the patent literature; however, we were not able to find an experimental proce-

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