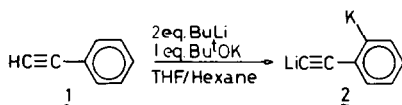


SYNTHESIS OF *o*-HALOGENOPHENYLACETYLENES VIA THE DIANION OF PHENYLACETYLENE (1)

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Abstract: The *o*-halogenophenylacetylenes *o*-iodophenylacetylene, *o*-bromophenylacetylene and *o*-chlorophenylacetylene can be prepared by regiospecific reaction of iodine, bromine, and hexachloroethane respectively with the dianion of phenylacetylene.

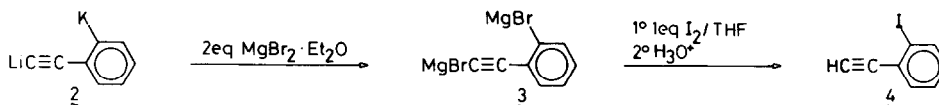
In the course of our investigations on dimetallations of unsaturated compounds (2,3) we discovered that phenylacetylene can easily be dimetallated using two equivalents of butyllithium and one equivalent of potassium *t*-butoxide (4). We assume that the potassium atom is introduced



in the ring. We showed that the aromatic ring was metallated exclusively at the *ortho*-position relative to the acetylide function. We also found that with one eq. of an alkylhalide

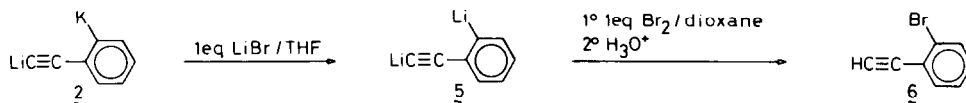
or one eq. of dimethyl disulphide regiospecific functionalization of the *ortho*-position occurred.

As *o*-halogenophenylacetylenes have been prepared by multistep synthesis (5-10) we wondered whether these potentially useful compounds could be obtained more easily from the dimetallated phenylacetylene 2. The first attempt to prepare *o*-iodophenylacetylene 4 by adding a solution of one eq. of iodine in tetrahydrofuran (THF) at  $-60^{\circ}\text{C}$  to 2 gave the desired product in very poor yields. Reasoning that this failure could be due to reaction of the initially formed 4 with the strongly basic 2 (dehydrohalogenation with aryne formation) we decided to transform 2 into the kinetically less basic *di*-Grignard derivative 3.

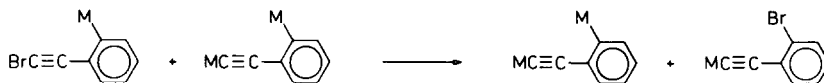


This conversion could be easily brought about by adding two eq. of  $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$  to 2. Reaction of 3 with one eq. of iodine dissolved in THF at  $-60^{\circ}\text{C}$  followed by increasing the temperature to  $+30^{\circ}\text{C}$  and the usual work-up gave pure 4, bp  $67^{\circ}/0.05\text{mm Hg}$ ,  $n_{\text{D}}^{20} = 1.6405$  in 71% yield (11).

A similar reaction of 3 with one eq. of bromine in dioxane did give the desired *o*-bromophenylacetylene 6 but contaminated with 15-20% of *Br-C≡C-Ph*, which must be the result of a competitive attack of the acetylide function on bromine. The pure product 6 was obtained by adding at  $-60^{\circ}\text{C}$  one eq. of bromine in dioxane to the *di*-lithio compound 5, the latter being prepared by adding a solution of one eq. of anhydrous LiBr in THF to 2.

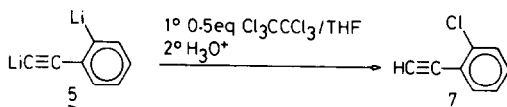


This better result may be explained by assuming that the halogen-metal exchange



is faster when  $M = \text{Li}$  than in the case of  $M = \text{MgBr}$ . A procedure, similar to that used for the preparation of **4**, afforded **6**, bp  $44^\circ/0.05\text{mm Hg}$ ,  $n_{\text{D}}^{20} = 1.5965$  in 59% yield (11).

Our attempt to prepare *o*-chlorophenylacetylene **7** by reaction of the *di-lithio* compound **5**



with *N*-chlorosuccinimid gave a mixture which contained as main component phenylacetylene **1** and also in minor amount **7**. However, reaction of **5** with *half* an eq. of hexachloro-

ethane dissolved in THF, followed by raising the temperature to  $+30^\circ\text{C}$  and the usual work-up gave **7**, bp  $75^\circ/20\text{mm Hg}$ ,  $n_{\text{D}}^{20} = 1.5613$  in 59% yield (11).

#### ACKNOWLEDGEMENT

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#### References and Notes

- 1) This communication can be considered as part III of Regiospecific Functionalisation of Unsaturated Compounds via their *dilithio* Derivatives.
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- 11) The structures of the compounds obtained were in accordance with spectroscopic data ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR and MS data). Their purity as determined by glc analysis was at least 97%.

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