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SYNTHESIS OF 1-ETHOXY-2-ARYLACETYLENES FROM 1-ETHOXY-2-IODOACETYLENE AND ARYLCOPPER(I) COMPOUNDS*.

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Some years ago Oliver and Walton found that a wide range of arylcopper(I) reagents were capable of coupling with iodoethynyl(trimethyl)silane to give arylethynyl(trimethyl)silanes in moderate to good yields (29-61%)[1]. More recently [2] , Normant et al. showed that vinylic organocopper(I) species gave a similar reaction with other 1-halogeno-1-alkynes.

We now report a novel synthesis of 1-ethoxy-2-arylacetylenes (3) based on the interaction of 1-ethoxy-2-iodoacetylene (1)[3] and arylcopper(I) reagents (2) in a mixture of tetrahydrofuran (THF) and dimethylformamide (DMF) or hexamethyl-phosphoric triamide (HMPT). Without these co-solvents products 3 can be obtained too , but the conversion is less smooth.

$$\underset{(1)}{\mathrm{EtO\text{-}C{\equiv}C\text{-}I}} \quad + \quad \underset{(2)}{\mathrm{Ar\text{-}Cu.MgBr_2}} \quad \xrightarrow[\text{or THF-HMPT}]{\text{THF-DMF}} \quad \underset{(3)}{\mathrm{EtO\text{-}C{\equiv}C\text{-}Ar}}$$

Representative examples are summarized in the Table.

Hitherto only the preparation of some 1-alkoxy-2-phenylacetylenes has been reported in the literature , starting from bromoethoxystyrenes [4] , 2-chloro-2-fluorostyrene [5] or 1-chloro-2-phenylacetylene [6] , but the yields obtained were often low and difficulties were encountered with the purification of the acetylenic ethers in a number of cases. In our opinion the presented route to 3 ,which is complementary to the Stephens Castro coupling[7] between an aryliodide and a cuprous alkynylide , is an attractive alternative to the other methods mentioned.

The procedure for the conversion of (1) into (3) is as follows : To a stirred suspension of (2,0.050 mol) in THF-DMF or in THF-HMPT (5:1 (v/v) , 200 ml) the iodoacetylene (1,0.050 mol) was added at -40°C and the temperature of the reaction mixture was slowly raised (one hour) to + 20°C. Subsequently , the reaction mixture was poured into a saturated aqueous solution of NH_4Cl (200 ml) containing NaCN (3g). The product was isolated by extraction with diethyl ether (3 x 100 ml). After washing the combined extracts with water and drying over $MgSO_4$ the solvent was evaporated *in vacuo* and the residue purified as indicated in the Table.

Table Reaction of (1) with arylcopper(I)compounds (2)[a] to give the 1-alkynyl ethers (3)

Aryl in (2)	% yield of (3)[b]	Physical constants of (3)[c]	
		B.p.(°C/torr)	n_D^{20}
C_6H_5	60	53-55 / 0.01	1.5410
4-Me-C_6H_4	55	77-79 / 0.01	1.5470
4-MeO-C_6H_4	53	d	1.5571
2,4,6-Me_3-C_6H_2	32	d	1.5369

a) The arylcopper reagents were prepared by stirring Ar-MgBr (0.050 mol) with copper(I) bromide (0.050 mol) during 30 minutes in THF (180 ml) at 0°C.

b) Yields refer to purified products.

c) All compounds(3) showed an absorption at 2260 cm^{-1} in the IR-spectrum.The ^1H NMR data were consistent with the proposed structure.

d) Destillation caused a strong decomposition. Purification was carried out by column-chromatography [SiO_2 , pentane / CH_2Cl_2 : 85 / 15 (v/v)]

The starting ether (1)[3] was obtained in high yield (90%) by converting ethoxyacetylene (0.010 mol) with methyl lithium (0.010 mol , prepared from methyl iodide and lithium) into the corresponding lithium alkynylide , using diethyl ether as a solvent (200 ml) , followed by addition of iodine (0.010 mol) at - 50°C .

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