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Synthesis of mono- and diarylacetylenes

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Abstract

Arylacetylenes have been synthesized by C–C coupling of lithium acetylide with aryl bromide in the presence of a palladium(0) catalyst.

Introduction

The synthesis of certain mono- and diarylacetylenes has attracted much attention from many chemists, because of the importance of such compounds as intermediates in the synthesis of biologically-active substituted olefins [1]. Some of the methods reported for the synthesis of mono- and diarylacetylenes have disadvantages such as lack of generality [2,3], low yields, or limitations on the native of the groups attached to the aromatic rings [2,3].

We described here a general method for preparing mono- and diarylacetylenes in fair to good yields.

Discussion

A one-pot method for preparing both mono- and diarylacetylenes has been developed involving C–C coupling of a lithium acetylide with an aryl bromide in the presence of 0.05 molar equivalents of tetrakis(triphenylphosphine) palladium as catalyst (Table 1). The success of this reaction can be associated with the known ability of the palladium catalyst to undergo oxidative addition with a variety of organic halides [4,5].

Treatment of ethynyltrimethylsilane with methyllithium followed by treatment of the product with an aryl bromide in the presence of the Pd^0 catalyst gives arylethynyltrimethylsilanes in reasonable yield. The trimethylsilyl group can then be quantitatively removed by treatment with base [6] to give the desired monoarylacetylene. This terminal acetylene can then be treated with methyllithium, and this followed by treatment with aryl bromide in the presence of the Pd^0 catalyst to

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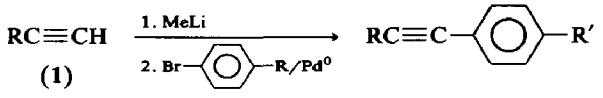
Table 1

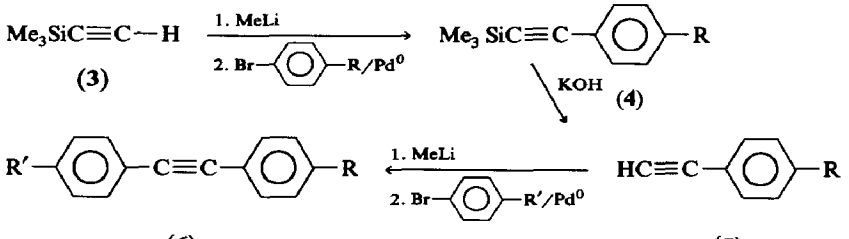


(2)

R	R′	%yield of 2	Molecular ion in MS; m/z		^{1}H NMR; δ ($CDCl_3$, TMS)
			calc.	found	
C_6H_5	H	75	[a]	[a]	7.40 (m)
C_6H_5	$OCH_2CH_2NMe_2$	52	265.1468	265.1454	2.32(s), 2.70(t), 4.01(t) and 7.35 (m)
C_6H_5	OCH_3	55	208.0889	208.0877	3.75(s) and 7.35 (m)
C_6H_5	CH_3	53	192.0940	192.0939	2.34(s) and 7.3 (m)
$CH_3CH_2CH_2CH_2$	OCH_3	48	188.1202	188.1208	0.80(t), 1.35(m), 2.05(t), 3.75(s) and 7.25 (m)
$CH_3CH_2CH_2CH_2$	$OCH_2CH_2NMe_2$	45	245.1781	245.1778	0.8(t), 1.35(m), 2.05(t), 2.32(s), 2.70(t), 4.01(t), and 7.35 (m)
CH_3	CH_3	50	130.0783	130.0772	1.65(s), 2.35(s) and 7.40 (m)
CH_3	$OCH_2CH_2NEt_2$	48	231.1624	231.1634	1.05(t), 1.65(s), 2.53(t), 2.73(t), 3.99(t) and 7.35 (m)

[a] Comparison with an anthentic sample gave superimposable spectra and a single peak in GLC upon co-injection by (OV1 on glass column).

Table 2



(6) (5)

R	Yield of 4, %	Yield of 5, %	R′	Yield of 6, %	Molecular ion in MS; m/z		^{1}H NMR, δ ($CDCl_3$, TMS)
					calc.	found	
H	65	95	H	68	[a]	[a]	7.40 (m)
CH_3	55	96	CH_3	58	206.1096	206.1081	2.35(s) and 7.35 (m)
OCH_3	52	95	CH_3	60	222.1045	222.1030	2.35(s), 3.75(s), and 7.35 (m)
$OCH_2CH_2NMe_2$	48	90	OCH_3	48	279.1624	279.1632	2.23(s), 2.70(t), 3.75(s), 4.01(t) and 7.35 (m)

[a] See Table 1.

give the corresponding diarylacetylene in reasonable yield (Table 2). This method appears to provide a more promising route to arylacetylenes than with the previously used methods [2,3]. Both the mono- and diarylacetylenes prepared can be used in the synthesis of biologically-active substituted olefins [7,8,9].

Experimental

Reactions were carried out with magnetic stirring under nitrogen in oven-dried (160 °C) glassware. Tetrahydrofuran and diethyl ether solvents were distilled over sodium benzophenone.

The formation of the products listed in Tables 1 and 2 was monitored by the disappearance of the ≡C-H band at 3300 cm^{-1} in the IR spectrum and by the disappearance of the peak for the starting material peak in GLC and the appearance of a new single peak with higher retention time (OV1 on glass column), and their identities confirmed by ^1H NMR spectroscopy and high resolution mass spectroscopy. (see Tables 1 and 2.)

General procedure

To 8 mmol of terminal alkyne in 16 ml of anhydrous ether, 8.5 mmol of 1 *M* methyllithium in hexane was added dropwise at −78 °C during 1 h. The mixture was allowed to warm to room temperature and then 8.5 mmol of 1 *M* anhydrous zinc chloride in dry tetrahydrofuran was added. The mixture was stirred at room temperature for 1 h, then treated with a mixture of 8 mmol of aryl bromide and 0.4 mmol (0.05 equiv) of tetrakis(triphenylphosphine)palladium in 20 ml of dry tetrahydrofuran. The resulting mixture was refluxed for 24 h and then treated with water.

The usual work-up and evaporation of solvent gave the crude product, which was chromatographed on silica gel. Elution with hexane–dichloromethane gave the desired alkyne.

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