

Synthesis of diphenylacetylenes containing donor and acceptor substituents with 4'-formyl-4-methoxydiphenylacetylene as an example

C. H. González-Rojas^{a,b*}, Yu. F. Oprunenko^c, and R. G. E. Morales^a

^aDepartment of Chemistry, University of Chile,
Santiago, Chile.

Fax: 8 (56 2) 239 2755. E-mail: chgonzal@uchile.cl

^bDepartment of Chemistry, Metropolitan Technological University, Santiago, Chile.

^cDepartment of Chemistry, Moscow State University,
Leninskie Gory, 119992 Moscow, Russian Federation.

Fax: +7 (095) 939 2677. E-mail: oprunenko@nmr.chem.msu.su

A method for the synthesis of diphenylacetylenes containing donor and acceptor groups in aryl substituents was proposed. 4'-Formyl-4-methoxydiphenylacetylene was synthesized as an example.

Key words: copper acetylenides, diphenylacetylenes, organocopper compounds.

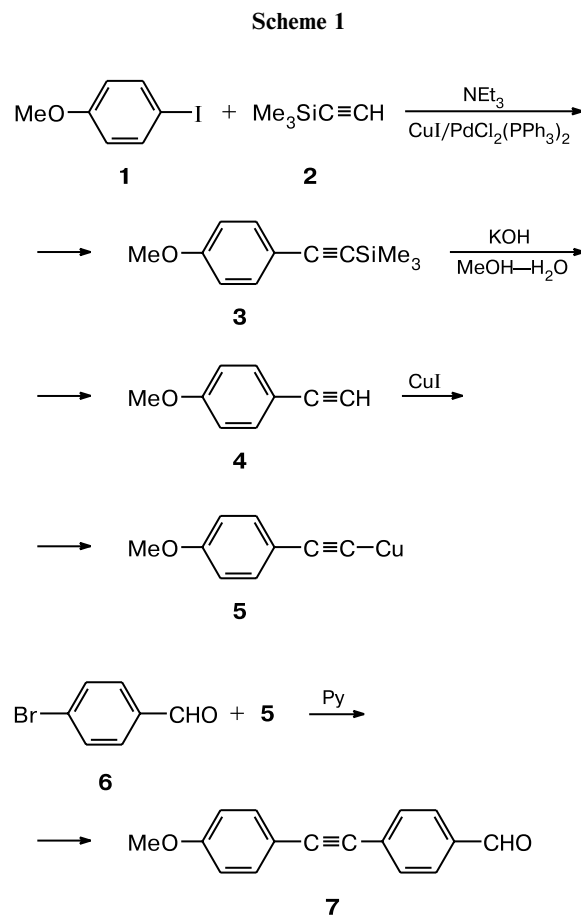
Diphenylacetylenes with a donor group in one phenyl substituent and an acceptor group in the other are of considerable practical interest because the electronic properties of these compounds in the excited state¹ allow them to be used for creating molecular photodiodes and devices with nonlinear optical properties.^{2,3}

Some diphenylacetylenes containing donor (NH₂, NHMe, NMe₂, and SMe) and acceptor (CN, COMe, CO₂Me, SO₂Me, and NO₂) substituents were synthesized by direct condensations of the corresponding phenylacetylenes and aryl halides.^{4,5}

The possibility of applying the promising optoelectronic properties of compounds of this class can be studied with 4'-formyl-4-methoxydiphenylacetylene as a model. This compound can be synthesized from inexpensive and accessible reagents, which makes it most promising for industrial use. However, we failed to obtain this compound in a satisfactory yield according to the published method. For this reason, we applied the Castro—Sladkov reaction,^{6,7} which consists of the introduction of an aryl substituent into an arylacetylene molecule *via* copper acetylenide.

Results and Discussion

The synthesis of the target compound is shown in Scheme 1. Condensation of *p*-iodoanisole (**1**) containing a donor methoxy group with trimethylsilylacetylene (**2**) in Et₃N in the presence of CuI and PdCl₂(PPh₃)₂ affords the known *p*-methoxyphenyl(trimethylsilyl)acetylene (**3**). Hydrolytic elimination of the trimethylsilyl group in an alkaline medium gives *p*-methoxyphenylacetylene (**4**), which is easily converted into copper acetylenide **5** in



high yield. The latter reacts with *p*-bromobenzaldehyde (**6**) in pyridine to give the target 4'-formyl-4-methoxydiphenylacetylene (**7**).

The above sequence of reactions opens a route to diarylacetylenes containing a donor group in one aryl ring and an acceptor group in the other.

Experimental

All reactions were carried out under nitrogen. Commercial reagents (*p*-iodoanisole and dichlorobis(triphenylphosphine)palladium(II) (Aldrich), CuI (Merck), and ammonia (Baker)) were used as purchased. Triethylamine (Riedel de Haën) was distilled over CaCl₂ and kept in an inert atmosphere. Raman spectra were recorded on a Perkin-Elmer 200 FT-IR instrument. Far IR spectra were recorded on a Bruker FT-IR spectrometer (polyethylene pellets). IR spectra were recorded in the liquid phase (NaCl cuvettes). ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-300 spectrometer (300 MHz) with (CD₃)₂CO as the internal standard. Signals in the NMR spectra were not assigned by special techniques. UV spectra were recorded on a Perkin-Elmer Lambda 11 spectrometer in 10-mm quartz cells in EtOH. Thin-layer chromatography (TLC) was performed on silica gel plates (250 μm). Mass spectra were recorded on a TRIO 1000 Fisons instrument (EI, 70 eV). All the compounds obtained were described earlier.

4-Methoxyphenyl(trimethylsilyl)acetylene (3). A mixture of CuI (362 mg, 1.89 mmol) and PdCl₂(PPh₃)₂ (434 mg) was added to a solution of *p*-iodoanisole **1** (6.03 g, 26.92 mmol) in dry Et₃N (60 mL) in a Schlenk vessel. The solution was stirred for 1 h while purified N₂ was passed through. Trimethylsilylacetylene (**2**) (3.51 g, 35.73 mmol) was added, and the reaction mixture was stirred for 24 h. The precipitate was filtered off and the solvent was removed *in vacuo*. Chromatography of the oily red-brown residue in hexane—toluene (2 : 1) gave 4-methoxyphenyl(trimethylsilyl)acetylene (**3**) (5.10 g, 72%) as an oil, *R*_f 0.60. IR, ν/cm⁻¹: 2955, 2912, 2879 (OCH₃); 2154 (C≡C); 1606, 1508, 1463 (benzene ring); 1250 (C_{arom}—O); 1031 (OCH₃) and 731 (≡C—Si). ¹H NMR, δ: 7.30 (d, 2 H, H(2), H(6)); 6.80 (d, 2 H, H(3), H(5)); 3.70 (s, 3 H, MeO); 0.26 (s, 9 H, Me₃Si). ¹³C NMR, δ: 160.17 (C(4)); 134.17 (C(2), C(6)); 116.06 (C(1)); 114.89 (C(3), C(5)); 107.59 (Ar—C≡); 89.75 (≡C—Si); 55.66 (MeO); 5.05 (Me₃Si). UV, λ_{max} = 259 nm (logε = 4.48).

4-Methoxyphenylacetylene (4). Compound **3** (5.1 g, 25 mmol) was treated with 2 M KOH (40 mL) in MeOH (100 mL). The solution was filtered, the filtrate was diluted with water, and the product was extracted with ether (3×200 mL). The extract was dried with anhydrous Na₂SO₄ and the ether was removed *in vacuo*. Chromatography of the oily orange-red residue in hexane—toluene (2 : 1) gave compound **4** (3.17 g, 96%) as a yellow oil, *R*_f 0.54. IR, ν/cm⁻¹: 3288 (≡C—H); 2955, 2912, 2879 (OCH₃); 2106 (C≡C); 1606, 1507, 1464 (benzene ring), 1250 (C_{arom}—O) and 1031 (O—CH₃). ¹H NMR, δ: 7.30 (d, 2 H, H(2), H(6)); 6.80 (d, 2 H, H(3), H(5)); 3.36 (s, 1 H, ≡C—H); 3.74 (s, 3 H, MeO). ¹³C NMR, δ: 160.96 (C(4)); 133.39 (C(2), C(6)); 115.19 (C(1)); 114.88 (C(3), C(5)); 84.25 (Ar—C≡); 77.34 (≡C—H); 55.66 (MeO). UV, λ_{max} = 250 nm (logε = 4.31).

Copper 4-methoxyphenylacetylenide (5). A solution of CuI (1.74 g, 17.57 mmol) in saturated aqueous ammonia (150 mL) was stirred for 1 h in a Schlenk vessel under purified N₂. Then, hydroxylamine hydrochloride (1.35 mg, 19.42 mmol) was added as a reducing agent to prevent possible oxidation of Cu(I). The resulting mixture was added under N₂ to a solution of

4-methoxyphenylacetylene **4** (1.52 g, 11.50 mmol) in 50 mL of ethanol that had preliminarily been stirred for 1 h. The reaction mixture was stirred at ~20 °C for 10 h. The greenish yellow precipitate that formed was filtered off and successively washed with water, ethanol, and diethyl ether. The bright yellow product was dried in a desiccator at 20 °C (1 Torr) for 4 h to give copper 4-methoxyphenylacetylenide (**5**) (1.94 g, 86%). IR, ν/cm⁻¹: 2960, 2918 (OCH₃); 1600, 1494 (benzene ring); 1248 (C_{arom}—O); 1029 (OCH₃). Far IR, ν/cm⁻¹: 315 (C≡C—Cu). MS: [M]⁺_{calc} = 194.69, [M]⁺_{exp} = 194.

4'-Formyl-4-methoxydiphenylacetylene (7). Copper 4-methoxyphenylacetylenide (**5**) (110 mg, 0.56 mmol) was added in a flow of nitrogen to a stirred solution of *p*-bromobenzaldehyde (**6**) (172 mg, 0.93 mmol) in dry pyridine (80 mL). The reaction mixture was stirred for 24 h at 115 °C, turning rose amber, and cooled. The pyridine was removed as an azeotropic mixture with benzene and ethanol. Chromatography of the oily product in light petroleum—ethyl acetate (7 : 1) gave 4'-formyl-4-methoxydiphenylacetylene (**7**) (22 mg, 16%) as pale yellow needles, *R*_f 0.42; m.p. 133 °C. IR, ν/cm⁻¹: 2929, 2853 (OCH₃); 2214 (C≡C); 1692 (C=O); 1599, 1505, 1461 (benzene ring); 1252 (C_{arom}—O) and 1026 (OCH₃). ¹H NMR, δ: 10.10 (s, 1 H, —CHO); 8.10 (d, 2 H, H(3'), H(5')); 7.90 (d, 2 H, H(2'), H(6')); 7.60 (d, 2 H, H(2), H(6)); 7.10 (d, 2 H, H(3), H(5)); 4.00 (s, 3 H, MeO). ¹³C NMR, δ: 192.08 (C=O); 161.68, 136.69, 134.82, 134.15, 132.64, 130.72, 115.31, 114.35 (C_{arom}); 89.97, 73.51 (C≡C); 55.82 (MeO). UV, λ_{max} = 321 nm (logε = 4.53). MS: [M]⁺_{calc} = 236.26, [M]⁺_{exp} = 236.

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