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Submerged electric arc between graphite electrodes: a one-pot tool for the synthesis of long-chain polyynes in solution

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Abstract—Polyynes, a class of molecules described by the general formula $H–(C\equiv C)_mH$ (where *m* is an integer) can be synthesized using an electric arc between graphite electrodes submerged in an organic solvent such as methanol, *n*-hexane, *n*-dodecane, decahydronaphthalene or acetonitrile. When the electric arc is used in acetonitrile at −40 °C, polyyne chains of up to 18 carbon atoms ($m = 9$) have been produced together with monocyanopolyyne as by-product. The polyynes can be reduced to ene–ynes by shaking a hexane solution of them with Zn/HCl.

Polyynes are widely diffuse in nature and characterized by the presence of several carbon–carbon triple bonds.[1] More than one thousand naturally occurring polyynes are known.[1] Some are biologically active and some have antibiotic and/or antitumoral activity.[1] The simplest polyynes, carbon chains connected by a sequence of single and triple bonds, are described by the general formula:

$$H–(C\equiv C)_mH \quad \text{(where } m \text{ is an integer).}$$

Specific polyynes have been synthesized generally by complex multi-step coupling reactions[2] in low yields. The difficulty of synthesis has hindered research on the chemistry, properties and applications of these molecules. Mixtures of polyynes can be produced by the acid hydrolysis of oxidized dicopper acetylide or diacetylide[3] or by a dehalogenation and dehydrohalogenation reaction of chlorinated paraffins,[4] the latter reaction tending to give more ene–ynes than pure polyynes.

In this letter we present a one-pot method for the synthesis of mixtures of polyynes and cyanopolyynes in solution. Carbon chains of up to 18 carbon atoms are detectable through this process, which could provide compounds of interest in the context of the mechanism of fullerene,[5] polycyclic aromatic and soot formation.[6,7] Polyynes are also thought to be carriers of certain spectral features of the interstellar medium, while cyanopolyynes have been identified in molecular clouds using radioastronomy.[8]

The arc discharge between carbon electrodes is one of the preferred methods for the bulk production of fullerenes[9] and also of carbon nanotubes.[10] For their synthesis, the AC or DC arc discharge is usually performed in the gas phase under reduced pressure in the presence of a quenching gas, for example, He.[8,9] Usually very high currents are employed ranging from 50 to 100 A. For the synthesis of polyynes at room temperature two graphite electrodes submerged into the solvent and arranged in a 'V' geometry and electric current at 5–10 A[11] were used. The identification of the products was made by HPLC analysis using a diode-array detector and a C-8 column.[11,12] It has been found[11,12] that the formation of polyynes depends exclusively upon the vaporization of carbon from the graphite electrodes and is independent of the nature of the solvent, although in certain cases the solvent may interact and give by-products (e.g., polyynes end capped with adventitious groups and not with hydrogen). The polyynes produced from the submerged electric arc are essentially hydrogen terminated, because they react promptly with Ilosvay's reagent (CuI, aq ammonia and hydroxylamine) giving copper acetylides, which are insoluble and brown coloured with metallic lustre in some cases. Furthermore,

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the FT-IR spectra of the polyyne solutions show a sharp peak at 3312 cm^{-1}, which is due to the terminal triple bond –C≡C–H stretch proving that the polyynes are hydrogen capped.[11,12] HPLC analysis of the polyynes produced by the electric arc in CH_3CN at room temperature has permitted the unequivocal identification of all the polyynes series from $m = 4$ to $m = 8$, hence carbon chains from 8 to 16 atoms[11,12] and also the lower members of the series.[12]

The longest polyyne chain detected by arcing at room temperature in acetonitrile (and also in other solvents) consisted of 16 carbon atoms[11,12] ($m = 8$). In order to produce polyynes with chains having $m > 8$, we have arced acetonitrile at −40 °C and detected[13] a polyyne having a chain of 18 carbon atoms ($m = 9$). The results of the HPLC analysis[14] are summarized in Table 1. The polyynes were identified from their characteristic electronic absorption spectra and by comparison with published spectra.[2,15] Table 1 shows the band pattern of each individual polyyne detected compared with the pattern taken from the literature: the agreement is excellent. From Table 1, it can be observed that together with the hydrogen-capped polyynes, another series of molecular species was detected, which possessed intermediate retention times with respect to normal polyynes. For example, between the polyynes $H–(C≡C)_5–H$ and $H–(C≡C)_6–H$, which have retention times of 2.13 and 2.83 min, a smaller peak in the HPLC chromatogram was observed at 2.41 min. A similar situation occurred regularly in all the chromatographic analyses (see Table 1). The spectra of these species are essentially similar to those of the 'normal' polyynes but regularly shifted in the band position in an intermediate fashion between the preceding and the following hydrogen-capped polyyne. This fact can be appreciated in Table 1, where the most intense absorption band of each polyyne spectrum is reported in bold. From the electronic absorption spectra, the retention time and due to the fact that these intermediate species have been detected only by arcing acetonitrile (and not by arcing methanol or *n*-hexane), these species have been assigned as monocyanopolyynes. Thus, for instance the species having the retention time of 2.41 min is $H–(C≡C)_5–C≡N$. The FT-IR of the crude reaction mixture[13] shows acetylenic stretching bands at 2201 and 2160 cm^{-1} and also a nitrile band at 2247 cm^{-1}. Table 1 also reports both the retention time of $H–(C≡C)_9–H$, a polyyne with 18 carbon atoms, and its UV spectrum, which is in good agreement with literature data. This polyyne with $m = 9$ was never detected when acetonitrile was arced at room temperature but was obtained at −40 °C. Thus, it appears reasonable to assume that arcing graphite electrodes at much lower temperatures, in opportune liquid plasma conditions and liquid media should produce even longer chains.

The polyynes can be reduced in solution by treatment with Zn dust and HCl.[16] The reduction stops with the formation of ene–ynes. This conclusion can easily be rationalized by examining the changes in the UV spectrum introduced by the hydrogenation.[16] The spectrum of the crude reduced mixture[16] resembles that of several

Table 1. HPLC analysis of the polyynes formed from graphite arcing in acetonitrile at −40 °C

Number of carbon atoms		Retention time (min) Arcing @ −40 °C	Wavelengths (nm)														
4	Found, this work	1.034	**180**		215		234		242		275	290					
4	Literature (Refs. 2,15)					224	234		246								
6	Found, this work	1.421	**198**	**208**		228	235		247	260	275	290		295			
6	Literature (Refs. 2,15)			207					242	255	268	284		300			
7	Monocyanopolyyne	1.541	200	208	**218**	225											
8	Found, this work	1.647		200	218	**227**											
8	Literature (Ref. 2)				215	226											
9	Monocyanopolyyne	1.887			214	222	232	**240**		263	275						
10	Found, this work	2.127			218	227	239		**251**								
10	Literature (Ref. 2)					227	239		251								
11	Monocyanopolyyne	2.407				223	233	243	255	**268**	277	290		308			
12	Found, this work	2.834					237		248	260	**273**						
12	Literature (Ref. 2)					225	236		247	260	275						
13	Monocyanopolyyne	3.234					230	245	250	261	275	**288**		300	315	334	
14	Found, this work	3.954					237		253	268		280	**297**				
14	Literature (Ref. 2)						237		253	266		281	297				
15	Monocyanopolyyne	4.554							254	268	277		290	**308**	320	338	368
16	Found, this work	5.861							255	268		281	298		**318**		
16	Literature (Ref. 2)								255	268		281	298		318		
18	Found, this work	9.674								268		282	296		316	**333**	
18	Literature (Ref. 2)									267		287	296		313	332	

ene–ynes reported in literature[15b] and further arguments in favor of the ene–yne nature of the products can be inferred from the FT-IR spectra by the ethylenic stretching band at 3119 cm^{-1}, by the shift of the residual acetylenic triple bonds stretching at 2260 cm^{-1} due to the change in conjugation and by the development of an allenic band at 1957 cm^{-1}.

The submerged electric arc technique not only permits the one-pot and economic synthesis of long-chain polyynes but also permits the use of these products as cheap intermediates for the synthesis of other interesting molecules. For instance, the simple reduction of polyynes yields ene–ynes, which are another class of molecule of extreme importance for their antibiotic and antitumour activity.[1]

The easy availability of polyyne solutions has permitted us to explore some properties of these molecules. Surprisingly, diluted polyyne solutions in methanol, *n*-hexane and decahydronaphthalene are stable for more than a week if left in air or diffuse daylight.[11,12] The polyynes are easily photolysed by UV radiation in solution.[12] We have shown that, by using selected monochromatic radiation, it is possible to run selective photolysis of certain polyynes in the crude mixture whilst preserving others.[12] This may have some future practical applications.

Despite the polyyne solutions being air-stable, they are reactive with ozone,[12] as expected, and undergo easily the addition of bromine.[12]

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13. A 100 mL three-necked Pyrex round-bottomed flask was filled with 70 mL of acetonitrile (HPLC grade, Fluka). Two graphite electrodes (99.999% purity, Aldrich), having a diameter of 3 mm and length of 15 mm, were inserted into rubber stopcocks. The stopcocks with the electrodes were inserted into two adjacent necks of the flask so that the electrodes were submerged into the solvent and arranged in a 'V' geometry, in contact with each other. The third neck of the flask was equipped with a thermometer and used for sampling the solution. A DC electric arc was ignited between the two electrodes at about 15 V and a current of 10 A. For the generation of the polyynes the electrodes were kept in contact under the solvent and moved up and down slightly in order to generate a very bright light. The power supply maintained the current at 10 A while the tension was changing 15 ± 10 V due to the movement of the electrodes. CAUTION: THE ELECTRODES MUST BE ELECTRICALLY ISOLATED EXTERNALLY TO AVOID ELECTRIC SHOCK. During arcing the flask was kept suspended (but not immersed) inside a Dewar flask half filled with a mixture of acetone and solid CO_2. In this way the temperature of acetonitrile inside the flask was maintained at −40 °C. After 1 min of arcing it was possible to record the crude UV–vis spectrum of the polyyne mixture formed in acetonitrile: 228, 236, 249, 259, 273, 294, 314 nm. The FT-IR of the crude mixture showed $\nu_{-C\equiv C-H} = 3312\,\mathrm{cm}^{-1}$ (hexane); $\nu_{-CN} = 2247\,\mathrm{cm}^{-1}$ (KBr, sh); $\nu_{-C\equiv C-} = 2201\,\mathrm{cm}^{-1}$ (KBr) and $\nu_{-C\equiv C-} = 2160\,\mathrm{cm}^{-1}$ (KBr).
14. The crude acetonitrile solution containing the polyynes was filtered through a polyvinylidene fluoride (PVDF) Acrodisc membrane having a pore size of 0.45 μm. From 5 to 10 μL of the filtered solution was injected into a 4.6 × 150 mm column (Zorbax Eclipse XDB-C8) connected to an HPLC from Agilent Technologies model 1100. A mobile phase of CH_3CN/H_2O 80/20 v/v was used under isocratic conditions at a flow rate of 1.5 mL/min and a pressure of 151 bar. The eluted polyynes were detected by a diode-array detector and identified from their characteristic UV spectra.
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16. Graphite electrodes were arced at room temperature and 10 A in 70 mL of *n*-hexane until the polyyne absorption band at 226 nm reached a value of absorbance $A = 2.5$ units (about 3–4 min arcing). The crude polyyne solution in hexane had a UV spectrum as follows: 207,

217, 226, 239, 251, 262, 275, 296, 313 nm. FT-IR of the crude mixture: $\nu_{-C\equiv C-H} = 3312\,\mathrm{cm}^{-1}$ (hexane), $\nu_{-C\equiv C-} = 2190\,\mathrm{cm}^{-1}$ (KBr) and $\nu_{-C\equiv C-} = 2096\,^{-1}$ (KBr). The hexane solution was transferred to a conical flask and 16 g of Zn dust (Fluka) was added. Distilled water (50 mL) and concd HCl (150 mL) were then added and the mixture was hand shaken vigorously for 5 min. A sample of the hexane solution was taken to record the UV spectrum of the reduced polyynes. Further prolonged contact and shaking with Zn/HCl did not induce any further changes in the spectrum. Crude ene–yne mixture UV spectrum (hexane): 211(sh), 217, 225(sh), 236, 246, 255, 265, 277, 287, 301, 317, 333 nm. FT-IR of the crude ene–yne mixture: $\nu_{-HC=CH-} = 3119\,\mathrm{cm}^{-1}$ (KBr), $\boldsymbol{\nu}_{-C\equiv C-} = 2260\,\mathrm{cm}^{-1}$ (KBr), $\boldsymbol{\nu}_{-C=C=C-} = 1957\,\mathrm{cm}^{-1}$ (KBr); Other bands: 1380, 684, 667, 653 and 616 cm^{-1}.